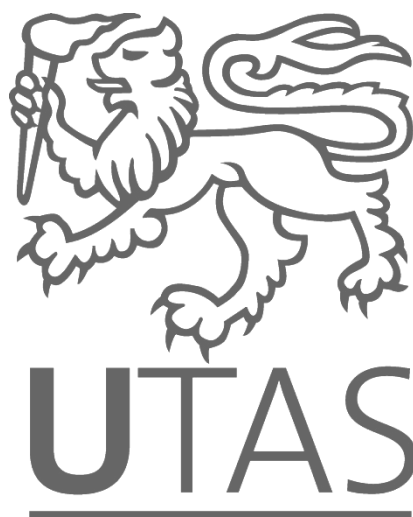


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**CHEMICALLY MODIFIED COTTON LINTERS:  
PREPARATIONS AND  
PAPERMAKING PROPERTIES**

**BY**

**LOUISE ANN TITCOMBE, B.Sc.(Hons.)  
CHEMISTRY DEPARTMENT**

**Submitted in fulfilment of the requirement  
for the degree of Doctor of Philosophy**

**University of Tasmania (July, 1992)**

*In memory of*  
*Gran (A. Joyce Blackwell)*  
*and*  
*my companion, Nimrod*

This thesis contains no material which has been accepted for the award of any other higher degree or graduate diploma in any tertiary institution and that, to the best of my knowledge and belief, the thesis contains no material previously published or written by another person except when due reference is made in the text of the thesis.

*Louise Titcombe*

Louise A. Titcombe



## ABSTRACT

Cotton linters are a relatively economic fibre source for the pulp and paper industry. However, their use is limited by poor interfibre bonding and low tensile and burst strength. This thesis describes efforts to improve the papermaking properties of Australian cotton linters via selected modifications of the cellulose backbone.

The reactions involved in cellulose modifications included substitution and addition reactions, introduction of an aldehyde functionality, Michael-type addition reactions and double derivatizations. Modifications also included blends of anionic and cationic derivatives. Reported methods were improved or modified and new derivatives prepared in each of the above reaction categories. In addition some cellulose derivatives previously prepared for other applications were investigated for their papermaking properties.

Using a new small scale method of pulp evaluation, approximately forty cellulose derivatives showed interfibre bonding improvements of 20% or more; possible reasons for these improvements are discussed. An improved method of sample preparation of cellulose derivatives for Fourier transform infrared spectroscopic studies was developed. Several previously unreported spectra of cellulose derivatives using solid state  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy techniques were also obtained.

Initially, several known cellulose modifications reported to improve papermaking properties were assessed. Carboxymethyl, hydroxyethyl and cyanoethyl celluloses were prepared, with only hydroxyethyl cellulose showing any bonding improvements.

6-Aldehyde cellulose and 2,3-dialdehyde cellulose were prepared, and the latter showed a 25% improvement in bonding properties over unmodified linters. The oxime and semicarbazone derivatives of the dialdehyde, whilst improving the

interfibre bonding, adversely affected the tensile strength. Cotton linters were reacted with Girard's Reagents P and T (a new derivative) but pulps inferior to unmodified cotton linters resulted. Halogen derivatives of cellulose were prepared via several routes. Cationization of linters with 3-chloro-2-hydroxypropyl-trimethylammonium chloride gave 30% improvement in interfibre bonding.

Cotton linters were reacted with a range of compounds in Michael-type addition reactions. Cyanoethylation of linters with acrylonitrile did not improve the interfibre bonding properties of linters despite modifications to the reaction procedures. Treatment of linters with the more hydrophilic analogue, acrylamide, gave improvements in interfibre bonding and tensile index of nearly 40%. In a study of other acrylamido derivatives, either the papermaking properties were poor or no reaction occurred. However, the reaction of *N*-(3-aminopropyl)methacrylamide with linters yielded a previously unreported derivative. The Michael reaction of several dicarboxylic acids, e.g. maleic acid, with linters showed some potential.

The double derivatives, amidoethyl hydroxyethyl cellulose and cationized amidoethyl cellulose, gave notable improvements in interfibre bonding.

Promising bonding improvements of up to 85% were achieved using new blends of anionic cellulose derivatives (the ethers of maleic and itaconic acids) with cationic cellulose. Significant increases in tensile strength were also obtained for blends of carboxymethyl cellulose and cationic cellulose.

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## GLOSSARY AND ABBREVIATIONS

Cellulose and Cotton Linters - The terms cellulose and cotton linters are often used interchangeably throughout this thesis, as cooked and bleached cotton linters consist of almost entirely cellulose (99%). Generally, syntheses are referred to as derivatives of cellulose and papermaking properties are discussed in terms of modified cotton linters, as distinct from modifications to other sources of cellulose, such as wood pulp, cotton, dissolving pulp, and bamboo.

Conformability - This is the ability of pulp fibres to be formed, matted and compressed into a uniform paper sheet and also reflects their flexibility.

Consistency - This term is used to express as a percentage the mass of fibres in water (synonymous with solids content).

Fibrillation - This refers to the separation of fibrils and is caused by beating which disrupts the bonds between adjacent microfibrillar layers of the cellulosic fibre. This effectively increases the surface area of the fibre and hence, the area available for fibre-fibre bonding.

Fines - These are very short fibres and fragments, which are usually generated during beating.

Formation - Refers to the ability of pulp to form a uniform sheet during papermaking.

Interfibre Bonding - This refers to the fibre-to-fibre bonds that develop during sheet formation which impart strength properties to the paper sheet. The level of interfibre bonding depends upon the effective contact area between adjacent fibres and the fibre elasticity.

Z-Direction tensile index, tensile index, zero span tensile index, beating, freeness, bulk, bending resistance, tensile energy absorption, scattering coefficient, opacity, burst and tear index - These papermaking terms and tests are defined and discussed in Section 4.1.2.

CP/MAS - Cross-polarization magic angle spinning.

CSF 250 - Canadian standard freeness at 250 mL. This is a measure of the drainage properties of a pulp (see Section 4.1.2).

DS - Degree of Substitution: The average number of substituent groups per hydroxyl group in the anhydroglucopyranose unit (maximum DS is 3).

FTIR - Fourier transform infrared spectroscopy.

NMR - Nuclear magnetic resonance spectroscopy.

o.d. - Oven dry, i.e. moisture free mass of pulp.

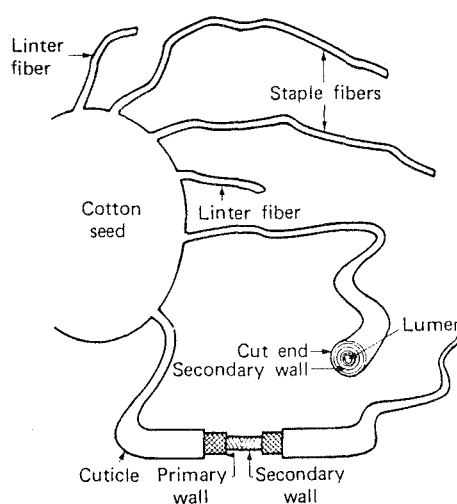
# CHAPTER 1:

## INTRODUCTION

### 1.1 GENERAL INTRODUCTION

Cotton linters are defined as the short fuzz fibres remaining on the cotton seed after the ginning process. As received in the paper mill, cotton linters consist of staple lint fibres, short immature lint fibres and fuzz fibres or linters<sup>1-3</sup> (Fig. 1.1).

**Figure 1.1:** Cotton Seed Showing Linters and Staple Fibres<sup>1</sup>



In Australia, cotton linters are a byproduct of the cotton seed oil industry. The cotton industry is expanding at a rate of 20 - 30% per annum and hence greater quantities of cotton linters are available. Linters constitute a relatively economic feedstock for the pulp and paper industry. As a papermaking fibre, linters pulp offers good durability, high bulk, high brightness and good formation.<sup>2</sup> Incorporation of cotton into fine writing paper results in paper with increased permanence and durability, which is well suited to use in archival papers. However, linters are thick-walled, have a relatively short fibre length and low bonded area

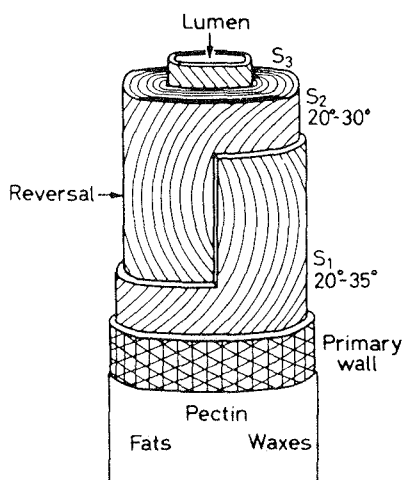
compared with staple lint fibres. This leads to low conformability (flexibility), poor tensile and burst strength, and poor bending stiffness because of poor interfibre bonding. Chemical modification of fibres for papermaking aims to ameliorate these problems by improving the interfibre bonding properties.

The use of cotton linters in blends with imported kraft pulp and recycled fibre at the Shoalhaven Mill of Associated Pulp and Paper Mills (APPM) is limited to about 20% of the papermaking blend because of their poor bonding properties. Chemical modification of the linters is desirable so that more of this feedstock may be incorporated into paper blends without adversely affecting the sheet strength and other papermaking properties. Increasing utilization of the renewable cotton linters resource for the production of paper and other chemical derivatives is especially pertinent in view of the currently expanding Australian cotton industry.

### **1.1.1 Morphology and Structure**

The structure of the cotton fibre is very complex.<sup>4</sup> It consists of a cuticle, primary wall, secondary wall and lumen (Fig. 1.2). These layers are composed of microfibrils, which in turn consist of elementary fibrils.<sup>1,5</sup>

**Figure 1.2: Morphological Structure of the Cotton Fibre<sup>5</sup>**



The outer wall or cuticle contains waxes, fats and pectins. Similarly, the primary wall, which is usually removed during pulping,<sup>6</sup> contains waxes and pectins, but consists mostly of cellulose in the form of microfibrils. The secondary wall has a thin outer layer  $S_1$ , and an inner layer  $S_2$ , which accounts for 95% of the dry weight of the fibre and may be up to 5  $\mu\text{m}$  thick. The microfibrils of the  $S_2$  layer spiral at 20-30° relative to the fibre axis with frequent reversals of pitch, in contrast to the microfibrils of the primary wall which are randomly arranged. The lumen, which forms a channel in the centre of the fibre, also has a lumen wall known as the  $S_3$  layer. Cotton linters have the same morphology as staple lint fibres but are typically twice the thickness of staple lint fibres (32  $\mu\text{m}$ ) and have a smaller lumen.<sup>1,6</sup>

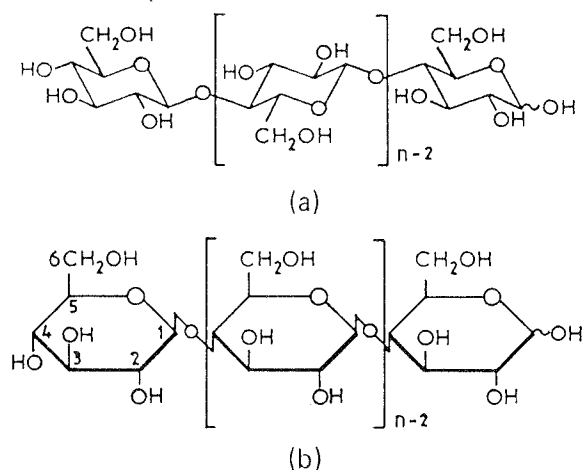
Microfibrils are composed of parallel cellulose chains, with contiguous molecules being held together by hydrogen bonding and van der Waals forces; they form concentric sheets and are 10-40 nm in width. Elementary fibrils are a smaller group of aggregated molecules (3-6 nm wide) and are thought to be highly crystalline.<sup>1</sup> Some debate continues over the definition and correct usage of these terms.<sup>1,7</sup>

The primary wall is effectively a semipermeable barrier which allows the diffusion of small molecules such as sugars, hormones and amino acids into the cell. This significantly restricts the accessibility of reagents used in chemical modifications to the functional groups in cellulose and to different parts of the fibre, as discussed later. In strong swelling solutions, the primary wall eventually ruptures as the inner layers or fibrils swell, leaving intact bands of the primary wall which constrict the swollen inner layers.<sup>5</sup>

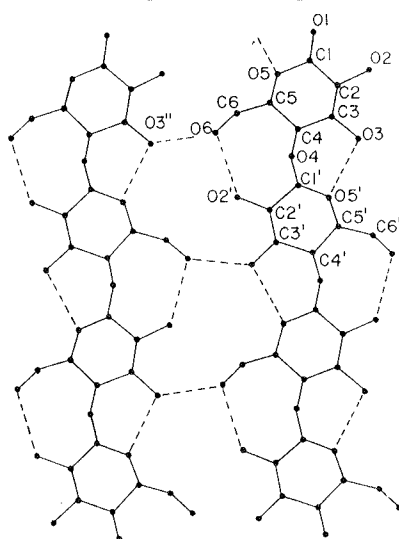
Cellulose, which accounts for 95% of the composition of raw cotton linters, is the most ubiquitous renewable natural resource available. It was first identified as the major component in the cell walls of most plants by Payen<sup>8</sup> in 1838 and is a polymeric carbohydrate, based on D-anhydroglucopyranose units joined by  $\beta$ -1,4-glycosidic bonds (Fig. 1.3). The  $\beta$ -1,4 linkages impart a stiff, ribbon-like

nature to the molecule, the surface of which is relatively hydrophobic because of the preponderance of carbon-hydrogen bonds. However, the protruding hydrophilic hydroxyl groups lead to extensive inter- and intra-molecular hydrogen bonding with up to five hydrogen bonds per glucose unit<sup>5</sup> (Fig. 1.4).

**Figure 1.3: Alternative Representations of Cellulose**



**Figure 1.4: Hydrogen Bonding in Cellulose<sup>5</sup>**



In terms of chemical reactivity, the key features of the cellulose molecule are the primary and two secondary hydroxyl groups and the glycosidic bond. The glycosidic bond is not readily cleaved except by hydrolysis, alcoholysis or by the action of some concentrated or anhydrous acids. The primary and secondary hydroxyl groups undergo reactions typical of alcohols and may be readily oxidized, etherified or esterified. The above factors account for many of the chemical and physical properties associated with cellulose.<sup>5</sup>

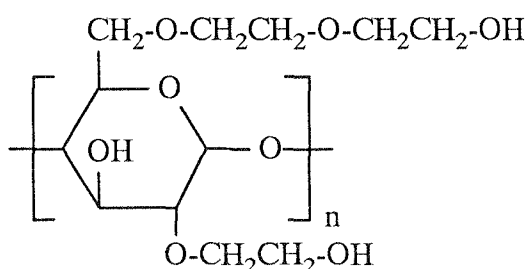
### 1.1.2 Previous Studies on Improving the Papermaking Properties of Pulps by Chemical Modification

Cellulose and cotton derivatives have been studied extensively in carbohydrate chemistry, polymer chemistry and the textile industry. Cellulose has been modified for use in such diverse products as soft-serve ice-cream, hydraulic cements, rayon and membranes in artificial kidneys.<sup>9-11</sup>

Modification of cellulose, with respect to the paper industry has also received a great deal of attention. Some of the more promising methods reported in the literature are discussed in the following paragraphs.

Hydroxyethylation of cellulose has been studied extensively and is regarded as one of the best methods for improving the strength properties of linters and wood pulp.<sup>12-16</sup> Hydroxyethylation is achieved by reaction of the pulp, previously steeped in aqueous sodium hydroxide, with either ethylene oxide or 2-chloroethanol.<sup>17</sup> Swelling in sodium hydroxide allows penetration of reagents into the fibre, and reaction may occur at any or all of the hydroxyl groups, together with further side-chain polymerization (Fig. 1.5). Higher degrees of substitution on the pulp result in better pulp properties. However, improved pulp properties must be balanced against decreased opacity and tear.<sup>18</sup> Strength increases in hydroxyethylated paper may be attributed mainly to increases in fibre-fibre bonding via changes in specific bonding strength.<sup>19</sup>

**Figure 1.5:** Hydroxyethyl Cellulose (possible substitution)



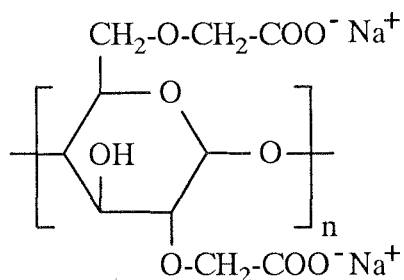


Several studies reported that greater benefits were obtained by modifying raw linters, in preference to cooked and bleached linters.<sup>12,13</sup> In addition, blending of unmodified with modified linters produced stronger sheets than those produced from an equivalent batch of uniformly treated linters.<sup>12,14,18</sup>

Hydroxypropylation of linters pulp also improves pulp strength, although not as significantly as hydroxyethylation.<sup>20</sup> Hydroxypropyl cellulose is obtained by the reaction of alkali-steeped pulp with propylene oxide.

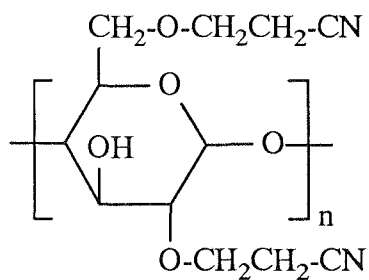
Carboxymethylation of linters is achieved by reaction of the pulp with chloroacetic acid and then with sodium hydroxide<sup>21</sup> (Fig. 1.6). Pulp strength is greatest at low substitution levels and if non-aqueous solvents such as isopropanol, methanol or dimethyl sulfoxide are used in the preparation.<sup>20,22,23</sup>

**Figure 1.6:** Carboxymethyl Cellulose (possible substitution)



Improved pulp strength properties have been achieved by reaction of pulp in an alkaline slurry with acrylonitrile, i.e. cyanoethylation<sup>14,20</sup> (Fig. 1.7). This is a reversible Michael-type addition reaction (hereafter referred to as a Michael addition reaction) and proceeds via the alkali-catalyzed addition of an activated vinyl group to cellulose.<sup>10</sup> Another Michael addition derivative, obtained by reaction of linters with acrylamide in aqueous alkali, has been reported to significantly improve pulp strength properties.<sup>14,23</sup>

**Figure 1.7:** Cyanoethyl Cellulose (possible substitution)



## 1.2 PROPOSED RESEARCH PROJECT

### 1.2.1 Aims and Proposed Solution

The general aim of this project was to improve the poor bonding properties of Australian cotton linters using new or improved chemical modifications. Reference to the literature indicated that the introduction of hydrophilic groups into the fibres provided the most promising method for interfibre bonding enhancement.<sup>12,20</sup> By increasing the affinity of the fibres for water, greater flexibility and deformation resulted, which led to increased hydrogen bonding during drying and hence, improved sheet strength.<sup>20</sup> The development of interfibre bonds in papermaking and the significance of increased hydrophilicity are discussed further in Chapter 4.

Thus, in choosing potential research alternatives, increasing the hydrophilic nature of the fibres was considered to be most important. These interactions may supplement other attractive forces, such as van der Waals forces and polar or ionic interactions. Covalent bond formation may also offer significant improvements in sheet strength.

### 1.2.2 Synthetic Work

The most promising methods noted in the literature for modifying cellulose were attempted and evaluated using Australian cotton linters, e.g. hydroxyethylation,

carboxymethylation and cyanoethylation. These evaluations provided a baseline to assess other novel modifications. In addition, the preparation of previously reported cellulose derivatives allowed characterization methods to be developed and refined.

A range of modifications to cellulose was attempted initially, unconstrained by applicability to industry and economic viability. The most promising of these was studied further in the search for a feasible method of improving the bonding properties of cotton linters.

Cellulose derivatives were investigated according to three key areas, viz. the introduction and modification of an aldehyde functionality, substitution and addition reactions, and Michael addition reactions. These derivatizations were all based on reactions of the primary and secondary hydroxyl groups of the anhydroglucose unit.

Investigation of the most promising reported cellulose derivatives, e.g. hydroxyethyl and carboxymethyl cellulose, led to a more general study of substitution and addition reactions of cellulose. The derivatives prepared included cellulose mesylate and other non-ethers (halo-deoxy celluloses), which were prepared for assessment of their papermaking potential, but more importantly as possible intermediates to other cellulose derivatives.

Similarly, the introduction of an aldehyde functionality was justified because of the potential for further derivatization. Conversion of the aldehyde derivative to imines, such as the oxime or semicarbazone derivative, offered potential improvements to the hydrophilic nature of the fibres.

The favourable papermaking properties of acrylonitrile and acrylamide derivatives of cellulose prompted a detailed study of the reactions of various vinyl monomers with cellulose in Michael addition reactions. It was anticipated that correlations between structure and papermaking properties would become apparent for the series

of unsaturated carbonyl reagents investigated. For example, structure-property relationships were expected for the series: acrylamide, methacrylamide and *N*-(3-aminopropyl)methacrylamide.

### 1.2.3 Assumptions and Limitations

It was necessary to make several assumptions in this study. Firstly, it was assumed that improvements obtained in the laboratory were transferable to the mill situation. Secondly, in order to reduce the variables in structure-property assessments, investigations were restricted to improving the papermaking properties of cotton linters only. It was tentatively assumed that similar improvements could be achieved when modified linters were blended with kraft pulp and recycled fibres on the papermachine.

A prerequisite for the chemical modification of papermaking fibres is that they remain fibrous after modification. This necessitates heterogeneous reaction conditions, as discussed in the following paragraphs. Relatively low substitution levels are dictated not only by heterogeneous reaction conditions, but also by the need to retain a fibrous product. At high substitution levels, the fibres may become soluble (e.g. hydroxyethyl cellulose) and excessive disruption of the fibre morphology may occur, which restricts the formation of interfibre bonds. In addition, low level substitution is more viable in the paper industry because of cost factors.

Because of the vast amount of research devoted to cellulose, it was necessary in this project to restrict the areas of study and hence, the following areas were *excluded*. Esterification of cellulose, e.g. cellulose acetate and cellulose xanthate, was considered not to show much promise in terms of papermaking properties.<sup>12</sup> Although acetylation of pulps at low degrees of substitution has been reported to improve papermaking properties, it was thought to act as a beater additive by

causing increased swelling and hydration, i.e. acetylation improved the hydrogen bonding capacity by swelling the fibres sufficiently such that newly exposed hydroxyl groups were available for hydration. At higher substitutions the hydrophobic nature of the acetyl groups predominated.<sup>12,24,25</sup> In a much later study, Heikal and Ibrahim<sup>26</sup> concluded that improved paper properties were due to structural effects of the fibre rather than to the presence of the acetyl groups.

The preparation, properties and applications of cellulose graft copolymers have been studied extensively. Significant increases in tensile, burst and tear strengths were reported with grafts of acrylonitrile, acrylamide and similar monomers but grafting levels up to 200% were used.<sup>27</sup> However, it is generally acknowledged that significant bonding improvements are not readily obtained with grafted cellulose derivatives.<sup>12</sup> Grafting of celluloses currently seems more applicable to specialty papers and textiles than for imparting bonding improvements to papermaking fibres.<sup>28</sup> Whilst it is possible to tailor-make derivatives to a certain extent by varying the monomers used, relatively high levels of substitution are often obtained. Cellulose grafting has not yielded large scale industrial applications in the paper industry or elsewhere.<sup>28,29</sup> Hence, grafted celluloses were not investigated in this study.

For the purposes of this project, low level chemical modification of the fibres was also considered preferable to the investigation of commercially available additives. Wet-end additives are retained on the fibre by colloidal interactions, such as adsorption, coagulation or by other physical means.<sup>30</sup> It was proposed by Harpman and co-workers<sup>20</sup> that additives generally accelerate beating of a pulp, whereas chemical modification was equivalent to substituting the fibres by a superior type of fibre.

As mentioned, a major limitation in this project was the need to use heterogeneous reaction conditions and to maintain the integrity of the cellulose fibres. Inherent

complications of heterogeneous cellulose modifications are unfavourable reaction kinetics, low level substitution and non-uniform substitution. The complex architecture of the cotton fibre also creates problems with reactivity and accessibility of reagents, which depend in part on the system of pores and voids, especially in crystalline regions. Accessibility is dictated as much by the reagent size and reaction conditions as by the physical structure of cellulose.<sup>31</sup> Surface cellulose chains are more accessible than others and some regions of each polymer chain may be more exposed to reagents than others. A study of the relative availability of the three hydroxyl groups showed that the C-2 hydroxyl group was the most available on accessible surfaces, suggesting a lower participation in hydrogen bonding, whereas the C-6 and C-3 hydroxyl groups were thought to be involved in higher levels of hydrogen bonding and hence were not as accessible.<sup>32</sup>

Consideration also needed to be given to the differing reactivities of the primary and secondary hydroxyl groups of each anhydroglucopyranose unit. Limited information was available to assist with the prediction of site reactivity toward differing reagents. In general, the primary alcohol on C-6 would be the most reactive site in the glucose ring but the acidity of the C-2 hydroxyl group is greater and hence, this may be the preferred site for etherification reactions; esterification often occurs preferentially at the C-6 hydroxyl group, with negligible substitution at the C-2 and C-3 positions.<sup>5</sup> If steric hindrance is a consideration, substitution at the C-6 site may predominate.<sup>33</sup> Hence, the relative reactivity of the hydroxyl groups varies, and substitution may occur at any of the hydroxyl groups in any combination.<sup>5</sup>

#### **1.2.4 Characterization Methods**

The characterization of cellulose derivatives was complicated by the morphology, crystallinity and insolubility of cellulose. The methods developed to characterize these derivatives were required to provide information on both the degree of

substitution and, if possible, the position of substitution. Evaluation of the pulp properties of modified linters was also crucial to the success of this project. As McCormick and Callais,<sup>34</sup> who studied solvent systems for homogeneous derivatization of cellulose, comment on heterogeneous preparations, "characterization of the starting material (cellulose) and the product derivatives is tedious if not impossible in many cases."

Methods used in this study to characterize modified celluloses included infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), pulp evaluation procedures and elemental analysis, where applicable. As the project progressed extensive use was made of pulp evaluations and elemental analyses for nitrogen-containing derivatives. This change in emphasis was due in part to the low substitution levels obtained which could not be detected using spectroscopic techniques.

Some development of the above characterization techniques was necessary. Various methods of FTIR analysis and sample preparation were assessed, but the substitution levels of cellulose derivatives were often below the detection limits of FTIR spectroscopy. Similarly, solid and solution state NMR spectroscopic techniques, whilst potentially very useful, had limitations (see Chapter 3). Due to the cost of chemicals and the physical constraints on large scale reactions, a small scale method of evaluating modified cotton linters was developed which allowed for the ranking of modified pulps based on a key papermaking property.

### **1.2.5 Summary of Project Objectives**

In successfully achieving the goals of this project, the interplay of several themes, namely the preparation of new derivatives, the specificity of substitution and the papermaking properties needed to be addressed. In summary the objectives of this research were:

- To prepare known derivatives using Australian cotton linters and assess their papermaking potential.
- To develop suitable methods of characterization for chemically modified linters.
- To develop a small scale method of pulp evaluation.
- To attempt the preparation of novel cellulose modifications, and assess their papermaking potential, unconstrained by economic feasibility and applicability to the paper industry.
- To prepare cellulose derivatives which are economically viable in an industrial situation.
- To investigate promising modifications further and scale up these modifications.
- To correlate structure and papermaking properties and propose reasons for the observed bonding improvements.

For ease of presentation and clarity, this thesis is divided according to synthetic work, spectroscopic characterization and a discussion of the papermaking properties of selected derivatives. This is in keeping with the fundamental aims of the project and the emphasis on the papermaking properties of modified Australian cotton linters. This was preferable to division according to reaction type (e.g. aldehyde functionality, substitution and addition, Micheal addition) followed by a discussion of the spectroscopic and papermaking properties of each derivative.



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## CHAPTER 2 :

# PREPARATION OF CELLULOSE DERIVATIVES

Preparations of cellulose derivatives are discussed according to the three main areas of investigation, i.e. the introduction of an aldehyde functionality, substitution and addition reactions with cellulose and Michael addition reactions. This is followed by a discussion of the double derivatives and anionic-cationic blends of cellulose derivatives prepared using techniques developed in the above three areas. Detailed descriptions of the preparations of cellulose derivatives are given in the experimental section (Section 2.7). The characterization of these derivatives is discussed in Chapters 3 and 4.

Unique numbers have been assigned for each experiment, e.g. S95, S324 in this study. These are used consistently throughout the thesis to allow cross-referencing between the discussion of the preparations, the experimental section, spectroscopic characterization and pulp evaluation results. The reaction number and corresponding substitution level are often reported in parentheses, for example '(S36, 0.15% N)'.

### 2.1 SOURCES OF CELLULOSE

Although raw cotton linters are known to show greater bonding improvements upon modification,<sup>1</sup> cooked and bleached cotton linters from APPM's Shoalhaven Mill, NSW, were used in most cellulose modifications. Details of the cooking and bleaching processes are provided in the experimental section of this chapter (Section 2.7.1).

In the early stages of the project, several different sources of cellulose were used, which were found to be unsuitable for various reasons. Initially raw cotton linters, as received from the Shoalhaven mill, were used in modifications, but problems were encountered with reaction reproducibility. In addition, the modified raw cotton linters could not be evaluated using industry standard methods because of excessive grit and uneven fibre distribution in the handsheets. To overcome these difficulties, the development of a small scale cooking method would have been necessary to enable modified linters to be evaluated. However, time constraints and other project priorities precluded this.

Alternatively, a considerable quantity of cooked and bleached cotton was available from ICI Australia (Deer Park, Melbourne). The use of this cotton in modifications overcame or avoided the limitations of raw linters. The fibre source was of higher purity and not as prone to seasonal variation as raw linters. However, after several preparations this starting material also proved unsuitable because the fibres were too long and could not be satisfactorily dispersed or beaten. The resulting handsheets could not be evaluated because of this flocculation. Cellobiose was also used in some preparations to model the more complex cellulose system.

## **2.2 INTRODUCTION OF AN ALDEHYDE FUNCTIONALITY**

### **2.2.1 Oxidation of Cellulose**

An aldehyde functionality is relatively reactive and the oxidation of cellulose to the aldehyde derivative would allow a range of other derivatives to be prepared. In particular, functional group conversion to oximes and semicarbazones was of interest.

Extensive research has been performed into the oxidation of cellulose.<sup>2-7</sup> This interest in the oxidation and partial oxidation of cellulose arose in part from efforts to minimize damage to textile fibres and pulps during industrial processing.<sup>2</sup> Other studies have been concerned with the investigation of bleaching and aging processes of cellulose.<sup>3,8</sup>

The oxidation of cellulose is particularly complex<sup>7</sup> as the oxidation may occur at the glycosidic linkage or in any combination of the three alcohol groups. The primary and secondary alcohol groups have different reactivities, while the alcohol groups may also be oxidized to either an aldehyde or acid group. This is further complicated by the accessibility of the oxidizing agent to the cellulose fibre itself.

Most oxidizing agents are unspecific in their action on cellulose. Hence, several types of oxidation usually occur simultaneously, yielding an array of products. Commonly used oxidizing agents include ozone, dinitrogen tetroxide, sodium hypochlorite, chlorine dioxide, chromic acid and periodate.<sup>2,4,9</sup> Only periodate and, to a limited extent, dinitrogen tetroxide demonstrate any specificity towards cellulose oxidation. Periodate treatment generates aldehydic groups, whereas dinitrogen tetroxide yields predominantly carboxyl groups.<sup>2</sup> Hence, of the array of oxidizing agents available, only periodate allows for the selective oxidation of cellulose to aldehydo cellulose. Studies with this reagent are discussed in detail in Section 2.2.4.

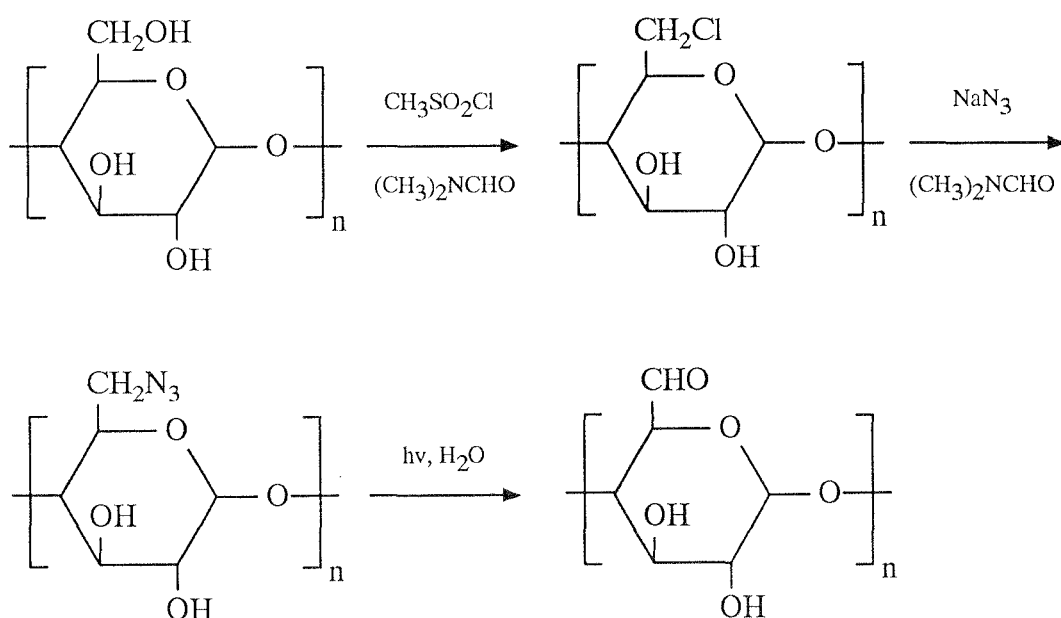
Routes to specific oxidation products are available however, using indirect methods. Kondo, Ishizu and Nakano<sup>10</sup> prepared aldehydo celluloses from allylated methyl, ethyl and tri-*O*-allyl celluloses by ozonization and reduction with dimethyl sulfide. Their spectroscopic studies revealed a preponderance of free aldehyde groups. Whilst their work reported selective oxidation to yield aldehydo cellulose, the site of oxidation was unspecific, i.e. oxidation may occur at the C-2, C-3 and C-6 positions. In addition, their derivatives were highly substituted and non-fibrous.

In contrast, Horton, Leutzow and Theander<sup>11</sup> cite the preparation of 6-aldehydo celluloses from cotton linters, filter paper, cellophane and regenerated cellulose. Hence, this preparation offered potential for use in this study as a means of selectively preparing aldehydo cellulose for conversion to the oxime and semicarbazone derivatives.

### 2.2.2 Photolytic Oxidation to Yield 6-Aldehydo Cellulose

6-Aldehydo cellulose was prepared by Horton, Luetzow and Theander<sup>11</sup> in their study of the oxidative degradation of cellulose during bleaching and aging processes. The selective oxidation of cellulose to yield unsubstituted 6-aldehydo cellulose was achieved by photolysis of 6-azido-6-deoxy cellulose. The cellulose was initially reacted with methanesulfonyl chloride in *N,N*-dimethylformamide, yielding 6-chloro-6-deoxy cellulose. The chloro derivative was then converted to the azide by reaction with sodium azide in *N,N*-dimethylformamide. The preparation of the chloro- and azido-cellulose derivatives is discussed in greater detail in Section 2.3.3. Photolysis of 6-azido-6-deoxy cellulose and mild hydrolysis of the resulting imine yielded the desired 6-aldehydo cellulose (Scheme 2.1).

**Scheme 2.1 :** Preparation of 6-Aldehydo Cellulose



In this study, difficulties arose reproducing Horton's<sup>11</sup> photolytic oxidation of cellulose. Based on FTIR spectroscopic evidence and elemental analysis results, the chloro- and azido-celluloses were successfully synthesized but the photolytic conversion failed, as indicated by functional group analysis. Photolysis conditions were varied in an attempt to affect conversion, but these were also unsuccessful. The nitrogen content decreased after photolysis (3.16% to 1.68% nitrogen, respectively), however this was not attributed to the formation of the corresponding aldehyde.

Another attempt was made to prepare 6-aldehydo cellulose following discussions with Theander.<sup>12</sup> Extra attention was devoted to grinding the 6-azido-6-deoxy cellulose and to dispersion during photolysis. In addition, cotton linters cooked and bleached at Shoalhaven were used in this latter trial, whereas the first trial involved much longer fibres from ICI Australia. This photolysis was successful and the presence of 6-aldehydo cellulose was confirmed by the preparation of the oxime and semicarbazone derivatives.<sup>13</sup>

Hence, with care, 6-aldehydo cellulose was successfully prepared by photolysis, but the resulting product was severely degraded and no longer fibrous. Luetzow and Theander<sup>8</sup> commented that the introduction of an aldehyde weakens the cellulose structure, possibly accelerating colour formation and depolymerization. Three- and four-step syntheses are not economically feasible in the paper industry and hence, the preparation was impractical, even if attempts were made to minimize degradation.

### **2.2.3 Alternative Routes to an Aldehyde Functionality**

Due to problems with the oxidative photolysis method, feasible alternative routes to aldehydo cellulose derivatives were sought. Possible methods included the oxidation of 6-chloro-6-deoxy cellulose with dimethylaminopyridine *N*-oxide



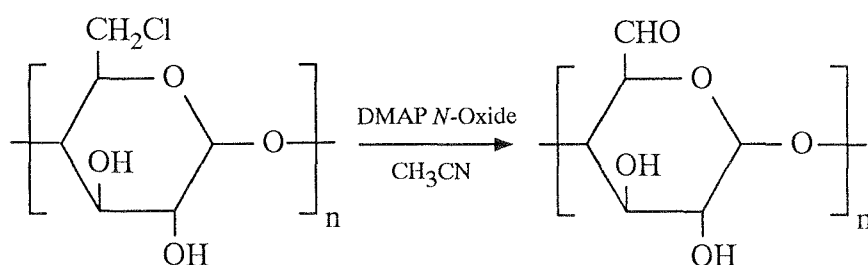
(DMAP *N*-oxide), catalytic oxidation of cellulose with tris(triphenylphosphine)-ruthenium(II) chloride,  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ , and oxidation with a tetramethyloxopiperidinium salt (TEMPO). The introduction of an aldehyde functionality via the reaction of cellulose with acrolein was also investigated (see Section 2.4.2).

#### Attempted Preparation of 6-Aldehydo Cellulose using 4-Dimethylaminopyridine *N*-Oxide

4-Dimethylaminopyridine *N*-oxide (DMAP *N*-oxide) has been reported as a suitable oxidizing agent for the conversion of alkyl halides to the corresponding aldehyde or ketone.<sup>14</sup> The *N*-oxide derivative of dimethylaminopyridine was obtained by oxidation with *m*-chloroperbenzoic acid in benzene, using the method of Pentimalli.<sup>15</sup>

The oxidation of alkyl halides with this reagent proceeds in two steps: salt formation and deprotonation with elimination of DMAP. The DMAP *N*-oxide was thus refluxed with 6-chloro-6-deoxy cellulose (Section 2.3.3) in acetonitrile and the base, 1,8-diazabicyclo(5.4.0)undec-7-ene, was then added to effect deprotonation (Scheme 2.2). Infrared spectral analysis failed to show the desired aldehyde absorbance, although elemental analysis determinations revealed a decrease in the chloride content from 3.8% to 1.3%. Hence, it is possible that the reaction was partially successful but the level of aldehydo cellulose synthesized was below the detection limits of FTIR analysis.

**Scheme 2.2 :** Attempted Oxidation of 6-Chloro-6-deoxy Cellulose using 4-Dimethylaminopyridine *N*-Oxide

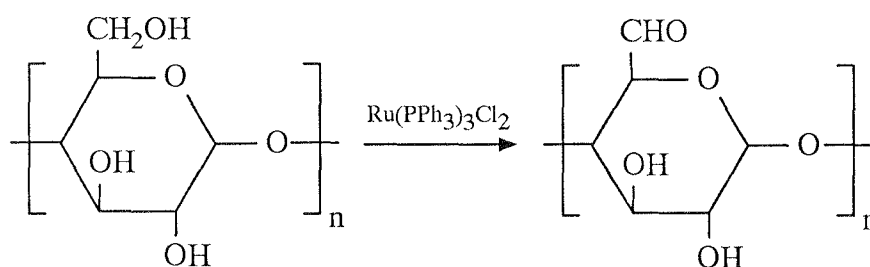


Attempted Oxidation of Cellulose and Cellobiose with  
Tris(triphenylphosphine)ruthenium(II) Chloride

Tris(triphenylphosphine)ruthenium(II) chloride,  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ , was reported to be a useful catalyst for the oxidation of relatively simple aliphatic and aromatic primary alcohols in the presence of secondary alcohols.<sup>16</sup> The complex  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  was prepared in this study from ruthenium trichloride by reaction with triphenylphosphine.<sup>17</sup>

The oxidation of cellulose using  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ , first attempted by reacting the ruthenium catalyst with linters in benzene (Scheme 2.3), was unsuccessful according to infrared spectroscopic studies. Cellobiose was then used on several occasions with the same catalyst to model the cellulose system but spectroscopic evidence again suggested that no oxidation had occurred. This oxidizing agent may have been too mild and the cellulosic system too complex to affect sufficient oxidation levels to be detected by routine spectroscopy.

**Scheme 2.3 :** Attempted Oxidation of Cellulose with  
Tris(triphenylphosphine)ruthenium(II) Chloride



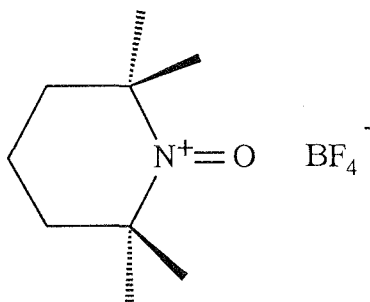
Attempted Oxidation with a Tetramethyloxopiperidinium Salt

Selective oxidation of alcohols is possible using oxoammonium salts, derived from the 2,2,6,6-tetramethylpiperidinoxy radical (TEMPO). In a study of the electrooxidation of alcohols to aldehydes and ketones using TEMPO salts, Semmelhack, Chou and Cortes<sup>18</sup> reported good selectivity towards primary alcohols,

in the presence of secondary alcohols, with no tendency for further oxidation to the acid. Hunter, Barton and Motherwell<sup>19</sup> extended the investigation of the selectivity of oxidation with TEMPO salts towards a range of substances including phenols, amines, sulfides and olefins.

In the current study, the tetrafluoroborate salt of TEMPO (Fig. 2.1) was reacted on two occasions with cellobiose in acetonitrile, but the white solid recovered from the solution was confirmed by spectroscopic evidence to be unmodified cellobiose. The failure of the TEMPO oxidations may be attributable to partial decomposition of the TEMPO-BF<sub>4</sub> salt, as the TEMPO-Cl salt is moisture and light sensitive.<sup>19</sup> Alternatively, a different solvent system (e.g. acetic anhydride, t-butanol or dichloromethane at - 80°C) may have proven more suitable.

**Figure 2.1:** 2,2,6,6-Tetramethyl-1-oxopiperidinium Tetrafluoroborate



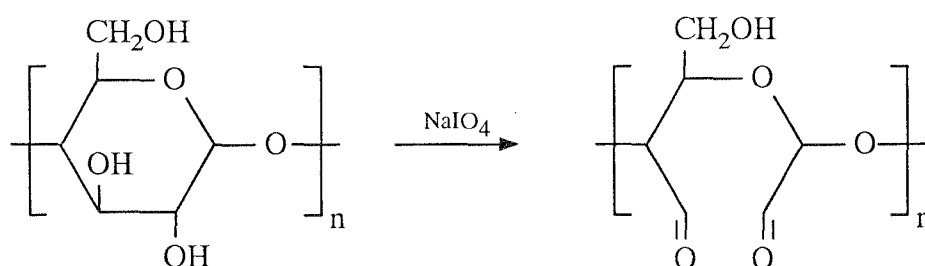
#### **2.2.4 Preparation of 2,3-Dialdehydo Cellulose and Derivatives**

In contrast to other attempts to obtain aldehydo celluloses, the oxidation of cellulose with sodium periodate is facile and selective, giving 2,3-dialdehydo cellulose, which retains its fibrous nature at low and moderate oxidation levels.

The oxidation of cellulose with sodium metaperiodate to yield 2,3-dialdehydo cellulose or oxy cellulose has been studied extensively.<sup>2,3</sup> Moreover, the characterization and optimization of reaction conditions for the preparation of 2,3-dialdehydo cellulose has received considerable attention.<sup>4,20</sup>

Periodate oxidation is one of the few types of selective oxidation available for cellulose.<sup>2</sup> It was first performed by Jackson and Hudson,<sup>21</sup> who proposed that the reaction was of the Malaprade type, i.e. selective cleavage of the (C-2)-(C-3) bond of the glucopyranose ring (Scheme 2.4). It has been noted, however, that it is important to exclude light during the oxidation to prevent the formation of side-products.<sup>2,4</sup>

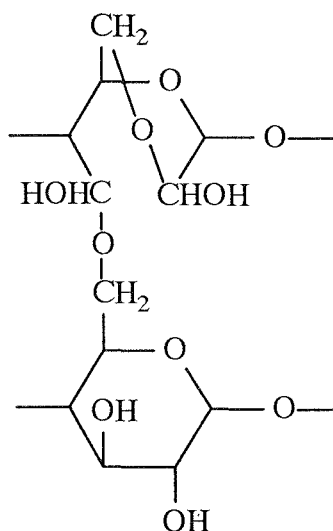
**Scheme 2.4 :** Preparation of 2,3-Dialdehydo Cellulose



Periodate ions are reputedly able to penetrate and react with the whole cellulose fibre but generally, periodate oxidation does not take place uniformly on the cellulose fibre at a reasonable rate; accessible regions are oxidized then allowing subsequent oxidation in the crystalline regions to occur.<sup>2,20,22</sup>

Treatment of cellulose with periodate was reported to improve the strength and papermaking properties of pulps in both the wet and dry states.<sup>2,3,23</sup> Studies by Zeronian, Hudson and Peters<sup>24</sup> ascertained that the maximum wet strength of periodate oxidized pulps occurred at 0.17 atoms of added oxygen per glucose unit. Higgins and McKenzie<sup>25</sup> determined that the maximum strength for air-dry paper occurred at 0.2 atoms of oxygen per glucose unit.

The mechanism of strength improvement is discussed in detail in Section 4.4.1. However, the strength improvements were generally attributed to increased hydrogen bonding as a result of the formation of hemiacetal and hemialdal linkages (Fig. 2.2).<sup>2,3,24</sup>

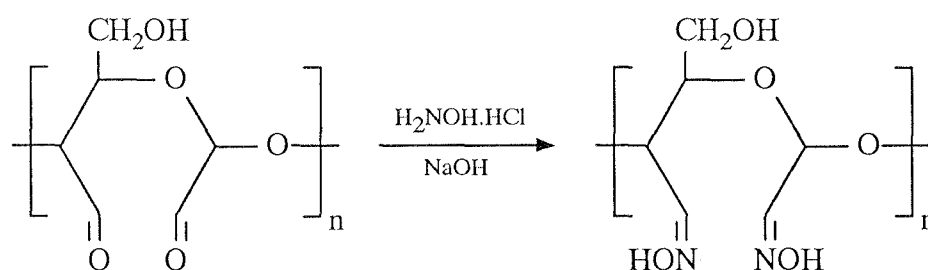
**Figure 2.2 : Hemiacetal Form of 2,3-Dialdehydo Cellulose**

In this study, 2,3-dialdehydo cellulose was prepared with reference to several publications.<sup>4,20,24,25</sup> Australian cotton linters were oxidized using aqueous sodium periodate and oxidation times were varied to obtain the maximum papermaking improvement; this occurred after four hours oxidation (Copper number 7.1).

#### Preparation of 2,3-Cellulose Oxime, Semicarbazone, and Thiosemicarbazone

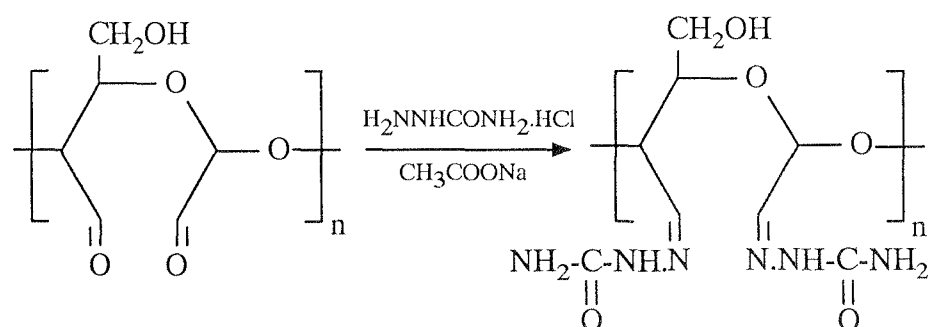
The oxime derivative of 2,3-dialdehydo cellulose was first prepared by Rogovin and co-workers in 1960.<sup>26</sup> The oxime was then converted to other derivatives, such as the amine<sup>26</sup> and the nitrile.<sup>27</sup> The chelating properties of 2,3-cellulose thiosemicarbazone and the oxime were investigated as part of a study by Japanese workers.<sup>28</sup> The papermaking properties of these dialdehyde derivatives have not been reported previously.

2,3-Cellulose oxime, semicarbazone and thiosemicarbazone were prepared using standard methods for the preparation of oximes and semicarbazones.<sup>13</sup> 2,3-Dialdehydo cellulose was reacted with hydroxylamine hydrochloride in the presence of sodium hydroxide, readily yielding the oxime derivative (Scheme 2.5).

**Scheme 2.5 : Preparation of 2,3-Cellulose Oxime**

Efforts were then directed towards optimizing the papermaking properties of the oxime. In a series of fourteen experiments, changes were made to reaction conditions that included using sodium acetate in preference to sodium hydroxide to reduce fibre damage as dialdehyde cellulose is unstable towards alkali,<sup>2,20</sup> adjusting the pH and significantly reducing the substitution levels. Overall, these efforts did not improve the papermaking properties of oxime derivatives significantly, relative to unmodified linters.

The semicarbazone and thiosemicarbazone derivatives of 2,3-dialdehyde cellulose were prepared by reacting semicarbazide hydrochloride and thiosemicarbazide hydrochloride ( $\text{H}_2\text{NNHCSNH}_2 \cdot \text{HCl}$ ), respectively with periodate-oxidized linters (Scheme 2.6). In a series of experiments, the substitution levels of semicarbazone and thiosemicarbazone were significantly reduced to optimize the papermaking properties. However, properties were only improved for 2,3-cellulose thiosemicarbazone.

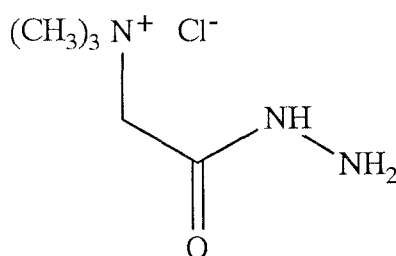
**Scheme 2.6 : Preparation of 2,3-Cellulose Semicarbazone**

### Reaction of Girard's Reagent T and Girard's Reagent P with 2,3-Dialdehyde Cellulose

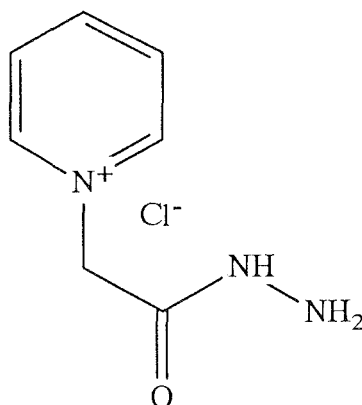
Girard's Reagents react with aldehydes and ketones and were used commonly to isolate keto-based steroids, and to separate carbonyl components from mixtures of essential oils.<sup>29</sup>

Girard's Reagent T, (carboxymethyl)trimethylammonium chloride hydrazide (Fig. 2.3), was reacted with 2,3-dialdehyde cellulose and sodium acetate, using the methods described to prepare the oxime and semicarbazone derivatives. The reaction of Girard's Reagent T with 2,3-dialdehyde cellulose yielded a previously unreported derivative. The success of the initial reactions was confirmed by elemental analysis (S158, 0.93% N; S174, 0.97% N). In a later trial, the substitution level was lowered in an effort to improve the papermaking properties (see Chapter 4) (S188, 0.37% N).

**Figure 2.3 : Structure of Girard's Reagent T**



The reaction of Girard's Reagent P, [1-(carboxymethyl)pyridinium chloride hydrazide] (Fig. 2.4), with periodate treated paper was reported by Jermyn and Thomas<sup>30</sup> for use in paper electrophoresis. Substitutions ranged from 0.03 to 0.06% nitrogen. However, they did not report the papermaking properties of this derivative.

**Figure 2.4 :** Structure of Girard's Reagent P

In this study, Girard's Reagent P was reacted successfully with 2,3-dialdehyde cellulose. A ten fold increase in the substitution level was obtained in this study (S229, 0.64% N) over Jermyn and Thomas's work.<sup>30</sup>

#### Concluding Remarks

Studies of 2,3-dialdehyde cellulose initially showed considerable promise in terms of both papermaking properties and scope for the formation of novel cellulose derivatives. Despite the preparation of a new derivative and the reporting for the first time of the papermaking properties of several other derivatives, the results obtained for dialdehyde derivatives did not meet expectations. The interfibre bonding improvements were not as good as anticipated, being achieved usually in the formation of the dialdehyde derivative and not in subsequent derivatizations (see Sections 4.3.1 and 4.4.1).

The scope for new work was also limited by the preparation of numerous dialdehyde cellulose derivatives by Maekawa and co-workers<sup>31-34</sup> and hence, studies of dialdehyde cellulose derivatives were not pursued further.



## **2.3      SUBSTITUTION AND ADDITION REACTIONS WITH** **CELLULOSE AND DERIVATIVES**

Carboxymethyl, hydroxyethyl and hydroxypropyl celluloses were prepared for several reasons in this study. In combination, these derivatives provide a reference point to compare the papermaking properties of these known derivatives with the papermaking properties of other cellulose derivatives. According to the literature, carboxymethylation and hydroxyethylation impart the greatest bonding improvements to cotton linters at low degrees of substitution.<sup>35</sup> The above three derivatives are also prepared on an industrial scale.

### **2.3.1      Preparation of Carboxymethyl, Hydroxyethyl and Hydroxypropyl** **Celluloses**

#### **Preparation of Carboxymethyl Cellulose**

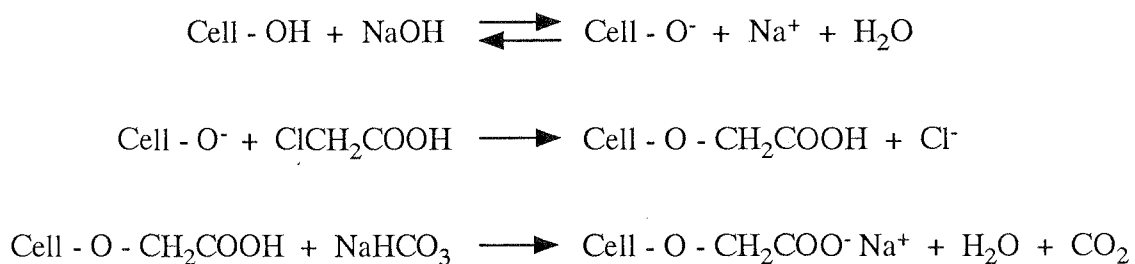
Carboxymethyl cellulose is the most widely used cellulose ether.<sup>36</sup> A procedure describing the carboxymethylation of cellulose was first patented in 1918.<sup>37</sup> The preparation, optimization, reaction mechanism, substituent distribution, characterization, applications and spectroscopic study of carboxymethyl cellulose have been investigated extensively since then.<sup>38</sup>

Carboxymethyl cellulose and its sodium salt are widely used in a variety of applications. It is used extensively as a thickener and binder in paints, detergents, cosmetics, pharmaceuticals and the food industry, principally because of its excellent rheological properties. It also finds use as a superabsorbent, a sizing agent, and in ion exchangers.<sup>38-42</sup>

The synthesis of carboxymethylated celluloses with different degrees of substitution from different cellulose sources, such as cotton and pulp, to produce industrial grade

and pure grade derivatives has also received considerable attention. Carboxymethyl cellulose is commonly prepared by reaction of alkali cellulose with chloroacetic acid or sodium chloroacetate in an aqueous or alcoholic solvent. The reaction mechanism has been reported to be intermediate between  $S_N1$  and  $S_N2$  and hence, the choice of solvent is significant with branched-chain alcohols being preferred.<sup>42</sup> This nucleophilic substitution reaction is shown in Scheme 2.7. As shown below, cellulose is abbreviated as Cell-OH, where it is assumed that substitution may occur at any or all of the primary and secondary hydroxyl groups, i.e. C-6, C-3 and C-2, in any combination.

**Scheme 2.7 : Preparation of Carboxymethyl Cellulose**



Several NMR spectroscopic studies on carboxymethyl celluloses have shown that the substituent distribution decreases in the order C-2 > C-6 >> C-3.<sup>43-46</sup> The numerical values obtained for the relative rate constants, i.e. the reactivity of the three hydroxyl groups toward carboxymethylation, reported in these studies were concordant, with a ratio of approximately 2.0:1.0:1.5.<sup>44-46</sup>

Initially, relatively highly substituted carboxymethyl celluloses were prepared and thereafter, only those methods relating to the preparation of carboxymethyl cellulose for papermaking were considered.<sup>47,48</sup> The sodium salt of carboxymethyl cellulose was reported to have far superior papermaking properties than the free acid.<sup>49</sup> Previous studies reporting the papermaking improvements achieved by carboxymethylation are discussed in Section 4.3.2.

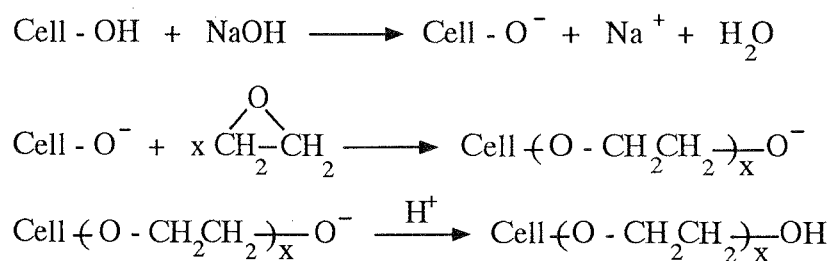
Preparations using the method of Green,<sup>47</sup> which were characterized spectroscopically (see Section 3.3), gave non-fibrous products and hence, their papermaking properties could not be evaluated. Linters were then carboxymethylated using a modification of the method reported by Ward, Murray and Thomas.<sup>48</sup> They performed a more detailed study of the carboxymethylation of cotton linters using a range of reaction conditions and obtained some significant papermaking improvements. The trial reported by them to give the highest folding endurance and breaking length (degree of substitution, DS 0.036) was performed numerous times in this work, for use in blends with cationized celluloses (Section 2.5.2). This involved pre-drying the linters with methanol and benzene, and performing the reaction in dimethylsulfoxide. The substitution levels typically obtained (8 meq/100g, DS 0.013) were much lower than those reported by Ward and co-workers.<sup>48</sup>

#### Preparation of Hydroxyethyl Cellulose

As for carboxymethyl cellulose, considerable attention has been devoted to the study of hydroxyethyl cellulose, which also finds use in thickeners and stabilizing agents. However, hydroxyethyl cellulose is not used as a food additive, and has limited use in cosmetics and pharmaceuticals.<sup>41,42</sup>

Hydroxyethyl cellulose is prepared by reacting alkali cellulose with ethylene oxide or 2-chloroethanol, usually in an organic solvent such as acetone or isopropanol.<sup>36</sup> In the case of ethylene oxide, the hydroxyethyl cellulose is produced by an S<sub>N</sub>2 displacement reaction in which a new reactive site is generated at the end of the epoxide-derived side chain and thus side-chain polymerization often occurs (Scheme 2.8).<sup>38</sup> Possible byproducts include ethylene glycol and polyethylene oxide.<sup>42</sup>

**Scheme 2.8 : Preparation of Hydroxyethyl Cellulose**



Numerous studies have addressed the relative reaction rates and preferred position of substitution of hydroxyethyl celluloses.<sup>38</sup> Reuben and Casti<sup>50</sup> ascertained, in their <sup>13</sup>C NMR study of hydrolyzed hydroxyethyl celluloses, that the alkoxide side-chain was by far the most reactive, followed by the C-6, C-2 and C-3 hydroxyl groups, respectively. However, in other earlier <sup>13</sup>C NMR studies, the C-2 and side-chain hydroxyl groups were found to be the most reactive, followed by the C-6 hydroxyl with very limited substitution reported at the C-3 hydroxyl group.<sup>43,51</sup> These apparent discrepancies were partly explained by the fact that the relative reaction rates were found to be dependent on the sodium hydroxide concentration, i.e. at high concentrations C-6 substitution predominated.<sup>38,52</sup>

Previous studies relating to the papermaking improvements obtained with hydroxyethylated celluloses are discussed in Section 4.4.1.

In the current study, linters were hydroxyethylated using several reported methods.<sup>53-55,58</sup> As part of a preliminary study to assess reported cellulose modifications, the method of Ward, Morak, Murray and Thomas<sup>53</sup> was used to yield a highly substituted hydroxyethyl cellulose, which was characterized spectroscopically (Section 3.3). The papermaking properties of this hydroxyethyl cellulose could not be evaluated successfully because of swelling of the fibres.

Several hydroxyethylations were then performed using a later method described by Ward and co-workers.<sup>54</sup> The method chosen was reported by them to give the best papermaking properties, having the highest breaking length, zero span breaking length and stretch values of the series studied (molar substitution 0.22). The 30% sodium hydroxide solutions used by Ward and co-workers<sup>54</sup> made filtration extremely difficult and caused excessive swelling with Australian cotton linters. Hence, lower concentrations were found to be more suitable. Substitution levels approximately half those obtained by Ward *et al.*<sup>54</sup> were obtained in this study, which may be partly attributable to the lower concentrations of sodium hydroxide used.

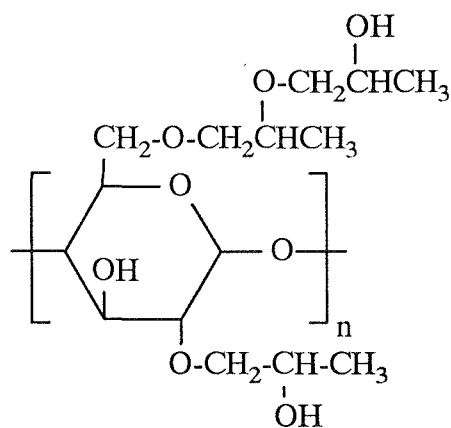
Further preparations were performed according to a method reported by Harpman, Reid and Turner,<sup>55</sup> which gave significant improvements in key papermaking properties of the derivatized product. However, substitution levels were again well below the reported values. 2-Chloroethanol was used in these trials in preference to ethylene oxide because it is less hazardous<sup>56</sup> and less volatile under ambient conditions.<sup>57</sup> According to previous studies,<sup>54</sup> there was no discernable effect upon the hydroxyethylated linters or their papermaking properties in using 2-chloroethanol or ethylene oxide. Other minor variations were undertaken in an attempt to replicate the bonding improvements obtained by both Harpman, Ward and their co-workers.<sup>53-55</sup> Also, no significant improvement in paper quality was obtained using derivatized linters with a low DS prepared by a modification of Klug's procedure.<sup>58</sup>

The substitution levels obtained by hydroxyethylating Australian cotton linters ranged from a DS of 0.05 to 0.11 (1.45% to 3.00% hydroxyethyl groups) and generally, were below the levels reported by Ward, Harpman and co-workers,<sup>53-55</sup> reflecting the lower reactivity of these linters towards hydroxyethylation. The effect of these lower substitution levels on the papermaking properties are discussed in Section 4.4.1.

### Preparation of Hydroxypropyl Cellulose

Hydroxypropyl cellulose is more hydrophobic than hydroxyethyl cellulose because of the methyl group on the side chain (Fig. 2.5), which imparts to it quite different properties from those of the hydroxyethyl analogue, such as good solubility in polar organic solvents and limited solubility in water. Nonetheless the uses of hydroxypropyl cellulose are many and diverse, including the formation of liquid crystalline solutions.<sup>36,38</sup>

**Figure 2.5 :** Representation of Hydroxypropyl Cellulose



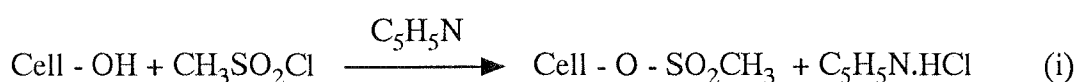
Hydroxypropyl cellulose is prepared in a manner similar to hydroxyethyl cellulose, using propylene oxide in place of ethylene oxide (see Scheme 2.8). Side-chain polymerization is again a unique feature of this S<sub>N</sub>2 displacement reaction between cellulose and the epoxide.<sup>36,38</sup> The C-2 and C-6 hydroxyl groups were found, by <sup>13</sup>C NMR spectral studies of a highly substituted hydroxypropyl cellulose, to be equally and more readily substituted than the C-3 hydroxyl group.<sup>59</sup>

In this study, linters were hydroxypropylated using modifications of methods reported by Harpman and co-workers,<sup>55</sup> and by modifications to the method reported by Klug<sup>58</sup> for the preparation of hydroxyethyl cellulose. Although different preparative methods were used, with some variation in substitution levels being obtained, papermaking properties were not changed favourably relative to unmodified linters.

### 2.3.2 Preparation of Cellulose Mesylate

Methanesulfonates (mesylates) are particularly good leaving groups, and although esters were generally not used in this study, the preparation of mesylates was pursued because they provided a convenient pathway to more inaccessible cellulose derivatives. The mesylate readily undergoes nucleophilic displacement to produce halo, amino, phenolic and thiocyanato derivatives.<sup>60-62</sup> Cellulose mesylate was used in this study to prepare fluoro-deoxy cellulose and cyano-deoxy cellulose (Section 2.3.3).

Cellulose may be esterified with methanesulfonyl chloride in anhydrous pyridine, as shown in equation (i).<sup>62</sup> Cellulose mesylate was synthesized according to methods reported by Pacsu<sup>62</sup> and Wolfrom, Sowden and Metcalf<sup>63</sup> for heterogenous mesylation, with substitutions of 11.4 to 15.8% sulfur. This was similar to the level obtained by Pacsu<sup>62</sup> but lower than the substitution of 17.9% sulfur obtained by Wolfrom, Sowden and Metcalf<sup>63</sup> and is possibly attributable to side-reactions such as chlorination and pyridinium salt formation.<sup>62</sup>



Sawatari, Naito and Suzuki<sup>64</sup> prepared cellulose mesylates with substitutions from 0.6 to 22% mesylate and found that maximum handsheet strength occurred at 1% substitution.

The mesylate derivative was prepared for use as an intermediate in the synthesis of fluoro-deoxy cellulose. After the success of initial fluorination reactions, attention was directed towards evaluating and optimizing the papermaking properties of the fluoro-derivative, which in turn meant improving the properties of the precursor, cellulose mesylate.

Pulp evaluation studies of the cellulose mesylates revealed that the fibres were severely damaged and overall, their papermaking properties were very poor. In view of the poor pulp evaluation results for mesylates and the studies by Sawatari and co-workers,<sup>64,65</sup> efforts were directed towards improving the papermaking properties by reducing both the substitution levels and the severity of the reaction conditions. Key modifications were the omission of the treatment with sodium hydroxide and significant reductions in the ratio of cellulose to methanesulfonyl chloride used. These modifications did result in some papermaking property improvements relative to initial mesylations, but interfibre bonding strengths were still slightly below those of unmodified linters.

### **2.3.3 Preparation and Reactions of Deoxy Cellulose Derivatives**

6-Chloro-6-deoxy cellulose and 6-azido-6-deoxy cellulose were originally prepared as precursors for the preparation of 6-aldehydo cellulose as discussed previously (Section 2.2.2). Because of their ease of preparation and the potential of the chloro-deoxy derivative as a good leaving group, the chloro- and azido-deoxy derivatives of cellulose were used as intermediates for the preparation of other cellulose derivatives.

In particular, halo derivatives of cellulose are of interest because they can be prepared with pre-specified properties, and their flame retardancy and biological activity were of interest.<sup>60</sup> Some halogen derivatives are noted for immobilizing enzymes, inhibiting acid and enzyme hydrolysis, as absorbents and for their ion exchange capacity.<sup>60</sup> Papermaking properties of halogen derivatives have not been assessed. The amino and cyano derivatives, which may be prepared from these precursors, offered potentially interesting papermaking properties; the cyano derivative itself could also have served as a precursor for further transformations.

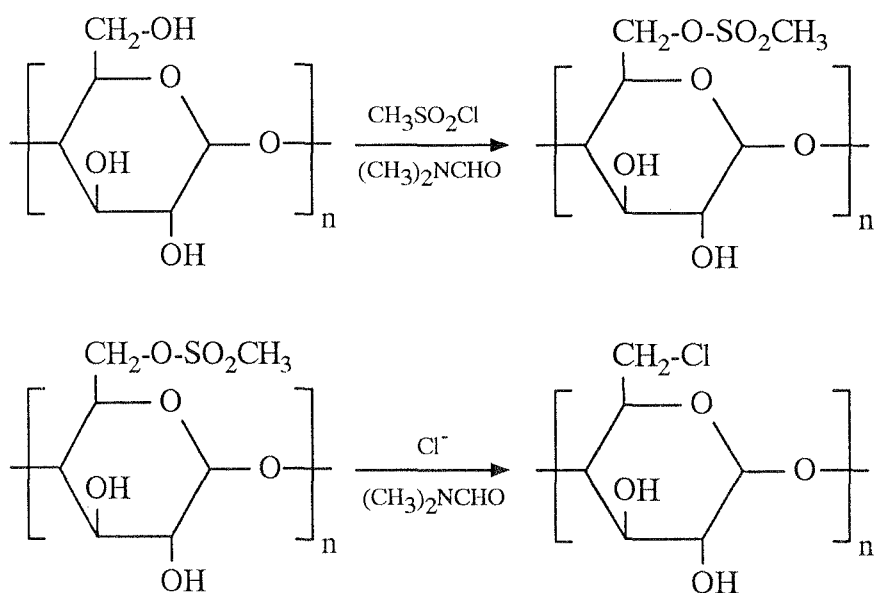


### Preparation of 6-Chloro-6-deoxy Cellulose

Chloro-deoxy cellulose was first prepared by reacting cellulose with thionyl chloride in pyridine.<sup>66</sup> This reaction was studied more exhaustively by Boehm<sup>67</sup> in 1958, who noted extensive degradation during chlorination. Polyakov and Rogovin<sup>68</sup> used *N,N*-dimethylformamide in their reaction of cotton linters with thionyl chloride and obtained a less degraded, fibrous product. *N,N*-Dimethylformamide facilitated the chlorination by forming reactive intermediates. Degradation was minimized by removing liberated hydrogen chloride from the system as the dimethyl chloroforminium salt.<sup>68,69</sup> However, other side-products were produced.<sup>68</sup>

Horton, Luetzow and Theander<sup>11</sup> were the first to selectively introduce chlorine at the C-6 position. This was achieved without the need to protect the secondary hydroxyl groups at C-2 and C-3. Previous studies had yielded non-specific chloro-deoxy celluloses.<sup>66-69</sup> Theander and co-workers<sup>11</sup> prepared 6-chloro-6-deoxy cellulose by reacting cellulose with methanesulfonyl chloride in *N,N*-dimethylformamide (Scheme 2.9). Formyl groups on the chlorinated cellulose were removed by steeping the chloro derivative in aqueous sodium carbonate.

**Scheme 2.9 :** Preparation of 6-Chloro-6-deoxy Cellulose  
using Methanesulfonyl Chloride



The method of Theander *et al.*<sup>11</sup> was used in this work, and heating times and temperatures were varied as in their study. Substitution levels similar to Theander's preparations<sup>11</sup> were obtained, ranging from 2.62 to 6.90% chlorine. No attempts were made to minimize degradation and hence, considerable degradation of the cellulose upon chlorination was noted in some preparations.

#### Preparation of 6-Azido-6-deoxy Cellulose

6-Azido-6-deoxy cellulose (Scheme 2.1) was prepared by heating 6-chloro-6-deoxy cellulose with sodium azide in *N,N*-dimethylformamide for three days.<sup>11</sup> Theander and co-workers<sup>11</sup> noted some depolymerization with *N,N*-dimethylformamide, recommending the use of water or dimethyl sulfoxide as solvents to minimize degradation. *N,N*-Dimethylformamide was used initially because the only trial reported by Theander *et al.*<sup>11</sup> with linters used *N,N*-dimethylformamide as a solvent. Thereafter, assessment of the other two solvents used by Theander *et al.*<sup>11</sup> was not justified because of the degradation already evident in the preparation of the precursor, 6-chloro-6-deoxy cellulose.

#### Preparation of 6-Iodo-6-deoxy Cellulose

6-Iodo-6-deoxy cellulose is the most reactive of the halo-deoxy celluloses towards nucleophilic attack and should provide a better leaving group than the chloro derivative.<sup>70</sup> In particular, iodo-deoxy cellulose was prepared for conversion to cyano-deoxy cellulose.

Iodo derivatives of cellulose have been prepared by numerous workers. Iodo-cellulose nitrates were prepared using sodium iodide as part of a study to determine the distribution of nitrate groups.<sup>71</sup> Similarly, Gardner and Purves<sup>72</sup> converted cellulose tosylate to the iodo form to determine the distribution of acetyl groups in cellulose acetate. This study was continued by Malm, Tanghe and

Laird.<sup>73</sup> Ishii<sup>70</sup> cited the facile conversion of 6-chloro-6-deoxy cellulose to 6-iodo-6-deoxy cellulose in both the homogeneous and heterogeneous states, metathesis being affected with sodium iodide in 2,5-hexanedione.

Trials with cotton linters for the preparation of 6-iodo-6-deoxy cellulose were based on Ishii's method.<sup>70</sup> However, *N,N*-dimethylformamide was used as the solvent and reaction times were doubled. Substitution levels were significantly less in this study, viz. 0.46% iodine compared with typically 25% iodine reported by Ishii.<sup>70</sup> This was due to the use of 6-chloro-6-deoxy celluloses with substitution levels one third those used in Ishii's study and, by the residual chloride present in the reaction product, incomplete conversion of the chloro derivative to iodo-deoxy cellulose. Two later attempts at iodination were unsuccessful.

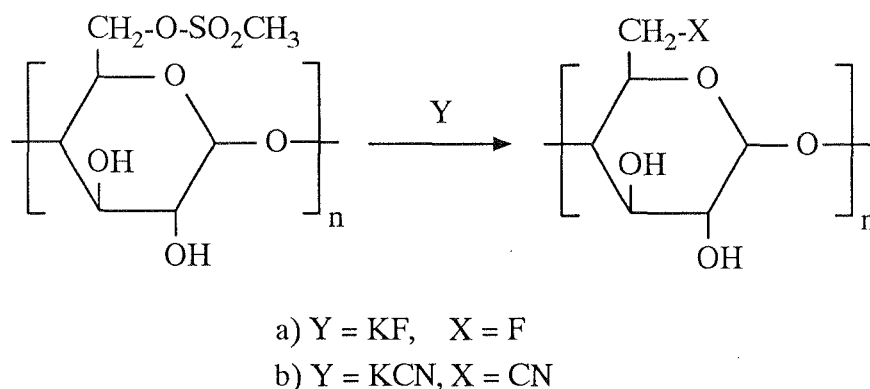
#### Preparation of Fluoro-deoxy Cellulose

Organo-fluorine derivatives often have interesting properties, and fluorination of biologically active compounds, for example, frequently leads to enhanced activity.<sup>74</sup> Investigation of the papermaking properties of fluoro-cellulose derivatives, however, has received little attention.

Fluoro-deoxy cellulose has been prepared by numerous researchers using a variety of fluorinating agents.<sup>60</sup> Cellulose mesylate has been reacted with aqueous sodium fluoride yielding a low substitution product.<sup>75</sup> Several hydroxyl and carboxyl containing polymers were fluorinated with sulphur tetrafluoride in the gaseous phase and very high substitutions were achieved with, in the case of cellulose, one third of the hydroxyl groups being fluorinated.<sup>76</sup> The fluoro-cellulose was found to be incombustible. In later studies, Gorbunov and co-workers<sup>77,78</sup> obtained fluoro-deoxy cellulose with up to 50% substitution of the hydroxyl groups. However, significant degradation occurred, especially if the hydrofluoric acid byproduct was not completely removed.

In this study, fluoro-deoxy cellulose was prepared by reacting cellulose mesylate with sodium or potassium fluoride in diethylene glycol<sup>75,79</sup> (Scheme 2.10a). Substitutions of nominally 0.9% fluoride were obtained, but a high sulfur content remained.

**Scheme 2.10 :** Preparation of 6-Fluoro- and 6-Cyano-6-deoxy Celluloses from Cellulose Mesylate



Fluoro-deoxy celluloses were anticipated to have interesting papermaking properties, due in part to the similarity between the fluoro and the hydroxyl groups in terms of hydrogen bonding capacity and high electronegativity. Hence, the papermaking properties of the precursor, cellulose mesylate, were optimized (Section 2.3.2) to obtain maximum benefit from fluorination. However, conversion to the fluoride with these improved mesylates was not attempted because of severe degradation often noted upon fluorination, which meant that pulp evaluation was impractical. Moreover, fluorination often resulted in a non-fibrous product.

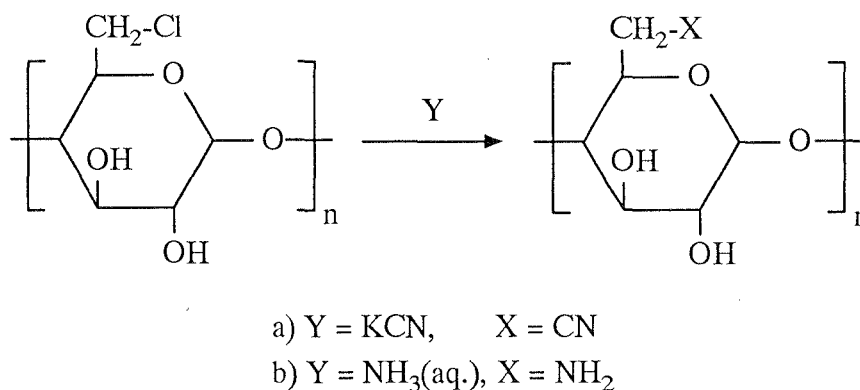
#### Preparations of 6-Cyano-6-deoxy Cellulose

Cyano-deoxy cellulose was first prepared by reaction of chloro-deoxy cellulose with potassium cyanide in *N,N*-dimethylformamide or methanol.<sup>68</sup>

Three precursors were investigated for conversion to 6-cyano-6-deoxy cellulose by reaction with potassium or sodium cyanide: cellulose mesylate (Scheme 2.10b), and chloro- (Scheme 2.11a) and iodo-deoxy celluloses. According to elemental analysis,

these three routes were successful. Routine NMR and FTIR spectroscopy could not be used to confirm substitution because of the low substitution levels obtained (typically 0.5% N). The highest substitution (1.0% N) was obtained by reaction of 6-chloro-6-deoxy cellulose with potassium cyanide in acetonitrile. Although all products were quite degraded, less degradation was evident using acetonitrile than *N,N*-dimethylformamide as a solvent. Thorough washing was complicated by the severely degraded nature of the products, making filtration times extremely long.

**Scheme 2.11** : Preparation of 6-Cyano- and 6-Amino-6-deoxy Celluloses from 6-Chloro-6-deoxy Cellulose



#### Attempted Preparation of 6-Amino-6-deoxy Cellulose

The different synthetic routes to 6-amino-6-deoxy cellulose investigated were firstly, reduction of the corresponding azide derivative with stannous chloride and secondly, reaction of 6-chloro-6-deoxy cellulose with aqueous ammonia (Scheme 2.11b).

An azide group is commonly used in organic synthesis as a means of introducing an amino group. Maiti, Singh and Micetich<sup>80</sup> reduced a range of azides to the corresponding amines using stannous chloride in methanol. However, the reduction of 6-azido-6-deoxy cellulose did not appear to proceed, as the appropriate amine absorbances were not observed in the infrared spectra of the reaction product.

Reaction of 6-chloro-6-deoxy cellulose with aqueous ammonia also failed to give 6-amino-6-deoxy cellulose, although Polyakov and Rogovin<sup>68</sup> obtained the amino cellulose in this way with notable substitutions being obtained only at elevated temperatures in a non-quantitative experiment.

These preparations may have been unsuccessful because of poor dispersion of the azido-deoxy cellulose and of the chloro-deoxy cellulose, both of which were very degraded and no longer fibrous.

#### **2.3.4 Preparation of Cationized Celluloses**

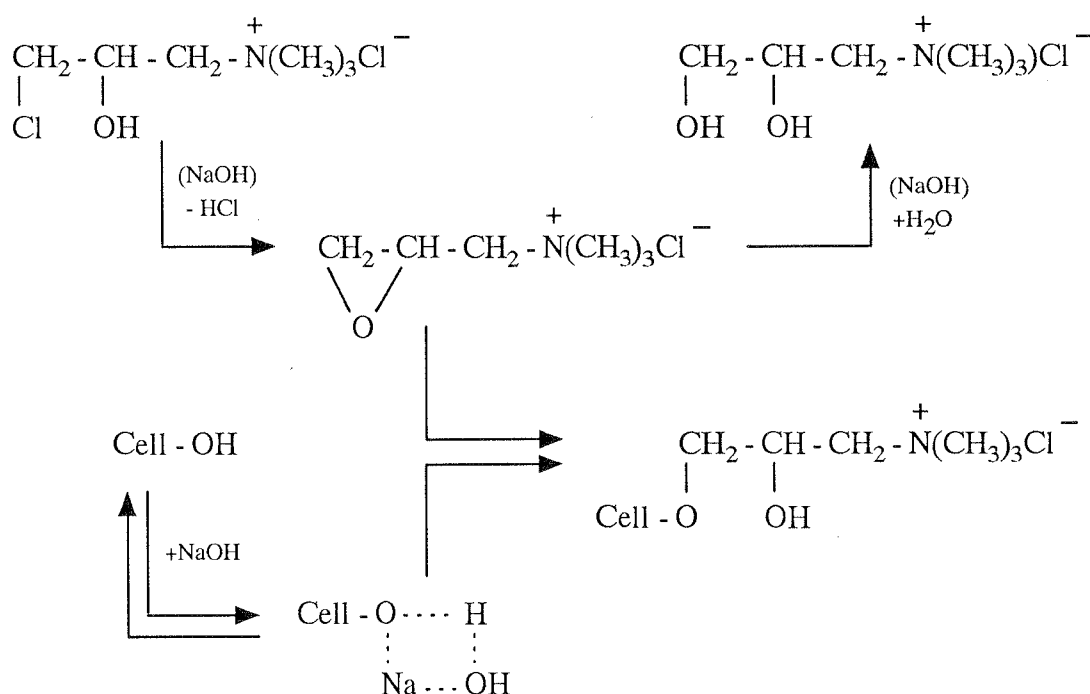
The introduction of cationic groups to the cellulose backbone was expected to benefit papermaking properties because cooked and bleached pulp contains anionic groups and hence, favourable electrostatic interactions were anticipated.

The effect of cationization of cellulose on various papermaking and related properties has been investigated in numerous studies. Schempp, Kaufer and Krause<sup>81,82</sup> studied the optimization of substitution levels and reaction kinetics of spruce pulp cationized with (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHMAC), but did not evaluate the papermaking properties of their derivatives. Improved dyeability and retention of some pigments have also been reported upon cationization.<sup>83,84</sup> Antal, Paszner and Micko<sup>85</sup> reported significant changes in papermaking properties for cationized softwood organosolv pulps, while Simkovic and co-workers<sup>86</sup> investigated the effects of cationization on the properties of ligno-cellulosic materials.

Of the various cationizing reagents available,<sup>83,84</sup> only CHMAC was used in trials with cotton linters as this was most frequently reported in the cationization of pulps and is more hydrophilic than longer chain aliphatic quaternary ammonium groups. The cationizing agent is converted to the more reactive epoxide in the presence of

sodium hydroxide. Similarly, the cellulose hydroxyl groups are converted to the corresponding alkoxide in the presence of base. As shown in Scheme 2.12, the epoxide formed in situ then reacts with the alkoxide groups of cellulose via a base-catalyzed  $S_N2$  reaction and forms the ether, cationized cellulose.<sup>81,85,87</sup> Hydrolysis of the epoxide, to give the corresponding glycol, has also been reported to occur.<sup>81,82</sup>

**Scheme 2.12 :** Preparation of Cationized Cellulose using (3-Chloro-2-hydroxypropyl)trimethylammonium Chloride



Reaction of the linters with CHMAC, after the method of Schempp, Kaufer and Krause,<sup>81,82</sup> was unsuccessful, but cationization was achieved using a modification of Antal, Paszner and Micko's method.<sup>85</sup> An initial trial gave a pulp with promising papermaking properties, but the bonding improvements could not be reproduced in later preparations.

The preparation of more highly substituted cationic celluloses was of interest mainly because of their application in anionic-cationic cellulose blends. Attempts to increase the substitution levels of cationized linters were successful provided

stoichiometric quantities of sodium hydroxide were used. A trial performed at elevated temperature, using much shorter reaction times, gave a similar substitution level to that performed using standard conditions, but the papermaking properties were not as adversely affected.

## 2.4      MICHAEL ADDITION REACTIONS WITH CELLULOSE

### 2.4.1    Introduction

Michael addition reactions with cellulose were investigated with the aim of introducing in a facile fashion a variety of functional groups using relatively mild reaction conditions and commercially available reagents.

Further impetus for this investigation arose from the improved papermaking properties reported for Michael addition derivatives of cellulose, such as cyanoethyl and amidoethyl cellulose,<sup>35</sup> as discussed in the following sections.

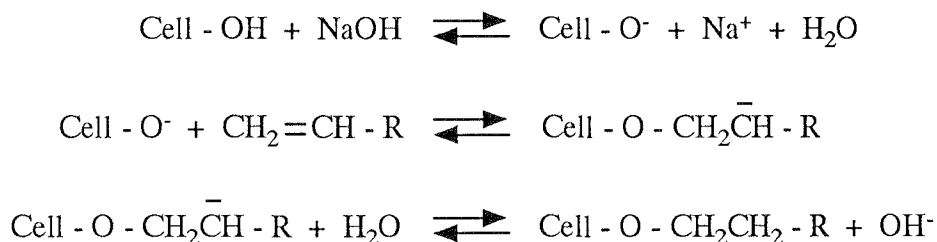
#### Mechanism of Michael Addition Reactions

In their investigation of the reactions of acrylonitrile, Bruson and Riener<sup>88</sup> found that acrylonitrile, by virtue of the electron withdrawing nitrile group, will react with primary and secondary alcohols in the presence of a basic catalyst yielding cyanoethyl ethers. Similarly, the hydroxyl groups in cellulose react with acrylonitrile in a Michael-type reaction.

Michael addition is the base-catalyzed 1,4-nucleophilic addition of a carbanion to  $\alpha,\beta$ -unsaturated carbonyl compounds or, more widely, to an activated double bond. Other nucleophiles can also add in the same fashion, and the reaction with cellulose under alkaline conditions is such an example (Scheme 2.13).



**Scheme 2.13 : Reaction Mechanism for Michael Addition Reactions  
with Cellulose (R = CN, CONH<sub>2</sub>, CHO etc.)**

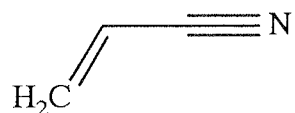


The electron attracting group that is conjugated with a double bond activates the double bond towards nucleophilic attack at the  $\alpha$ -carbon. The basic catalyst abstracts a proton from cellulose producing an alkoxide ion or carbanion, which acts as a nucleophilic reagent attacking the conjugated system. The stabilized carbanion produced then reacts with water to yield the final product and regenerate the alkoxide ion.<sup>38,87,89</sup>

**2.4.2 Reactions of Acrylonitrile, Acrylamide and their Derivatives  
with Cellulose**

**Preparation of Cyanoethyl Cellulose**

The reaction of acrylonitrile (Fig. 2.6) with cellulose giving cyanoethyl cellulose was one of the earlier cellulose ethers to be investigated. First patented in 1938, it received considerable attention thereafter and was commercially produced in the 1950s.<sup>38,89</sup> The uses of cyanoethyl cellulose vary greatly with the substitution levels.<sup>90</sup> Low DS cyanoethyl celluloses are resistant to mould and microbial attack.<sup>89</sup> Cyanoethylated pulps have a high dielectric constant and thermal stability, hence their use as insulating papers.<sup>35</sup> At higher substitutions, cyanoethyl cellulose is soluble in organic solvents.<sup>38</sup>

**Figure 2.6 :** Structure of Acrylonitrile

Numerous side reactions may occur in the preparation of cyanoethyl cellulose, principally because of the presence of sodium hydroxide, the most significant being the formation of 2-cyanoethyl ether.<sup>89</sup> The use of high temperatures or high concentrations of sodium hydroxide should be avoided as this may lead to the formation of carboxyethyl cellulose by hydrolysis of the nitrile.<sup>35,89,91</sup> A recent <sup>13</sup>C NMR study<sup>92</sup> has shown that the preferred site for cyanoethylation of the hydroxyl groups decreases in the order C-6 > C-2 > C-3.

Improvements in folding endurance and tensile strength of cyanoethylated pulps were observed by Ward, Swenson, Wink and Greisinger.<sup>93</sup> Cyanoethyl cellulose has been shown to have superior burst, tear and fold strength properties to unmodified cotton linters at low degrees of substitution (DS 0.06),<sup>55</sup> as discussed further in Chapter 4.

Despite the hydrophobic nature of the nitrile, investigation of the cyanoethylation of cotton linters was justified in view of the reported strength improvements. Cyanoethylation was also used as a baseline for comparison with other modified celluloses.

In this study, cellulose was cyanoethylated using modifications of several reported methods. Highly substituted cyanoethyl celluloses were prepared by refluxing linters in a bath of acrylonitrile.<sup>94</sup> Some of these experiments were unsuccessful for no apparent reason. Also some variation was caused in early trials (pre S49) by the use of different sources of cellulose (raw linters and cooked and bleached linters from ICI). Preparation of cyanoethyl celluloses using Compton's method<sup>94</sup> to yield

a degree of substitution of nominally 0.25 with different sources of cellulose also resulted in some variation in substitution levels. Efforts were then directed towards reducing the detrimental effects of pretreatment upon the fibres, thereby aiming to improve the papermaking properties. Moreover, sodium hydroxide concentrations, steeping times and substitution levels were reduced, with corresponding improvements noted in papermaking properties.

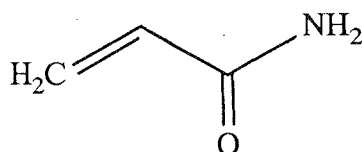
A modification of the method reported by Harpman, Reid and Turner<sup>55</sup> was used to prepare low DS cyanoethyl cellulose. Substitution levels of about 0.1% nitrogen were obtained, which was one fifth the substitution reported by Harpman and co-workers.<sup>55</sup> Increasing the reaction time increased the substitution level, whereas increasing the reaction temperature did not appear to have any effect on the substitution level. Compton<sup>90</sup> cited that both reaction time and temperature were significant variables in cyanoethylation reactions. However, his comments pertain to relatively high substitution levels that were approaching full substitution in the amorphous regions of the cellulose structure (3.65% N); in this study, much lower substitutions were under investigation. A one-off trial using aqueous ammonium hydroxide to swell the fibres did not alter the substitution level or improve the papermaking properties.

Finally, linters were cyanoethylated by adapting the method reported by Frick, Reeves and Guthrie<sup>95</sup> in their study of the reactions of a range of activated olefinic compounds with cellulose. This allowed the substitution levels and papermaking properties of cyanoethylated linters to be compared with other Michael addition derivatives. The reaction conditions used were similar to those reported by Compton (see early attempts at cyanoethylation and Section 2.7.4) and resulted in substitution levels in the range 0.78 to 1.70% nitrogen.

### Preparation of Amidoethyl Cellulose

The considerable previous research and papermaking improvements reported for cyanoethyl cellulose led to the investigation of the reaction between the more hydrophilic analogue, acrylamide (Fig. 2.7) and cotton linters. The papermaking potential of carbamoylethyl or amidoethyl cellulose was confirmed by several studies.<sup>53,96</sup>

**Figure 2.7:** Structure of Acrylamide



The reaction of acrylamide with cellulose proceeds much less readily than the analogous acrylonitrile reaction, yielding lower substitution levels.<sup>89,96</sup> The relative reactivities of the hydroxyl groups, determined by chromatography of the hydrolyzates, was found to be in the order C-6 > C-2 > C-3.<sup>97</sup>

Initially amidoethyl cellulose was prepared by a modification of the method reported by Ward, Morak, Murray and Thomas<sup>53</sup> with similar substitution levels being obtained. The quantities of reagents were then varied to assess the effect on both substitution level and papermaking properties. Significantly reducing the amounts of acrylamide and sodium hydroxide used in amidoethylations resulted in corresponding decreases in substitution levels but did not improve the papermaking properties. Doubling the reaction consistency appeared to have no effect on substitution levels. The substitution levels obtained by treatment of cellulose with acrylamide were found to be quite reproducible.

Increasing reaction times resulted in only a slight increase in substitution levels and did not adversely effect the papermaking properties, but the filtration times were

extremely long. These results are in contrast to the study by El-Shinnawy and El-Kalubi,<sup>96</sup> who found that the nitrogen contents of their amidoethylated wood pulps decreased sharply with impregnation times greater than 45 minutes.

Frick, Reeves and Guthrie<sup>98</sup> investigated the factors influencing the preparation of amidoethyl cellulose and the properties of the resulting amidoethylated fabric. They obtained relatively high substitution levels (2.22% nitrogen) using extremely high concentrations of aqueous acrylamide (up to 48%) and very short reaction times. Frick *et al.*,<sup>98</sup> who were interested only in the textile properties of these treated fabrics, dried their samples prior to oven-curing (i.e. heat treatment). However, in this study it was not possible to dry the samples first because of the irreversible, detrimental effect drying has on the papermaking properties of pulp.<sup>99</sup>

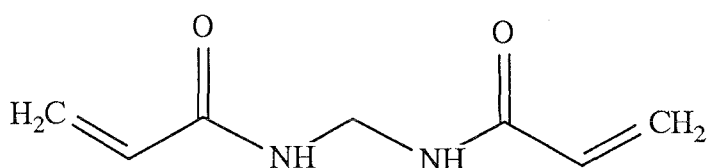
With reference to the work of Frick, Reeves and Guthrie<sup>98</sup>, and El-Shinnawy and El-Kalubi,<sup>96</sup> shorter reaction times were then used and the effects on substitution levels and papermaking properties were assessed. These trials using shorter reaction times gave substitution levels similar to those obtained by El-Shinnawy and El-Kalubi.<sup>96</sup> However, Australian cotton linters gave much lower substitution levels than those reported by Frick *et al.*,<sup>98</sup> when comparing trials using similar reaction conditions. This may reflect the different heat treatment used, and the different reactivity and crystallinity of cotton linters, compared with the peroxide bleached cotton sheeting used by Frick and co-workers.<sup>98</sup>

Michael addition reactions are facilitated reputedly by the presence of amines or amides.<sup>87</sup> Hence, in two trials *N,N*-dimethylformamide was used as a solvent, with some aqueous sodium hydroxide still being required because of the low solubility of the base in *N,N*-dimethylformamide. The use of this solvent system appeared to offer no advantage in the preparation of amidoethyl celluloses.

### Reaction of *N,N*-Methylenebisacrylamide with Cellulose

In an extension of the work with acrylamide, the reaction of *N,N*-methylenebisacrylamide (MBA) (Fig. 2.8) with cellulose was studied. MBA has the capacity to crosslink cellulose chains and hence, fibres via the vinyl functionality. The two secondary amide groups offer greater potential for hydrogen bonding than the analogous acrylamide derivative. While steric hindrance may limit the possible bonding advantages that exist, it was considered that an MBA-cellulose derivative may have useful papermaking properties.

**Figure 2.8:** Structure of *N,N*-Methylenebisacrylamide



The reaction of MBA with cellulose has been reported by numerous researchers. Frick, Reeves and Guthrie<sup>95</sup> in 1957 treated cotton fabric with MBA to assess potential applications in the textile industry. Because of MBA's tendency to crosslink, its ability to impart crease resistance when grafted to cotton fibres has been investigated.<sup>100</sup> In another study, cotton was impregnated with a mixture of MBA, phosphate salts and *N*-methoylacrylamide<sup>101,102</sup> and fabrics with improved abrasion resistance and strength were obtained. MBA has also been reported as a component of a graft polymerization additive in the preparation of absorbent pulps.<sup>103</sup>

Hence the grafting of MBA to cellulose and applications in the textile industry have received some attention. However, it appears the papermaking properties of MBA-cellulose derivatives have not been investigated previously.

The general methods used for Michael addition reactions with cellulose were modified for MBA because of its tendency to polymerize violently upon heating.

For most MBA trials, lower concentration aqueous MBA solutions were used and samples were not heat-treated. In the eleven trials conducted using low levels of MBA, substitutions ranged from 0.05 to 0.18% nitrogen. The longest reaction time gave the highest substitutions (S134, 0.18% N), but an initial pulp evaluation assessment indicated that MBA substitution had lowered the interfibre bonding.

Hence, reaction conditions were modified in an attempt to improve the bonding properties of MBA-cellulose derivatives, i.e. shorter reaction times were used in various combinations with increased temperatures and higher sodium hydroxide concentrations. These changes to the reaction conditions effectively reduced the fibre damage and maintained interfibre bonding at approximately the level of unmodified cotton linters.

In later trials, the amounts of MBA used were increased to those more typical of Michael addition reactions and the sample was heat-treated. An experiment based on the work of Frick *et al.*<sup>95</sup> yielded a more highly substituted derivative than previous MBA modifications (0.61% N), but did not improve the papermaking properties of the cellulose derivative (see Section 4.3.4). Extending the reaction time at elevated temperatures significantly increased the substitution levels (up to 4.14% N), but this was detrimental to the papermaking properties.

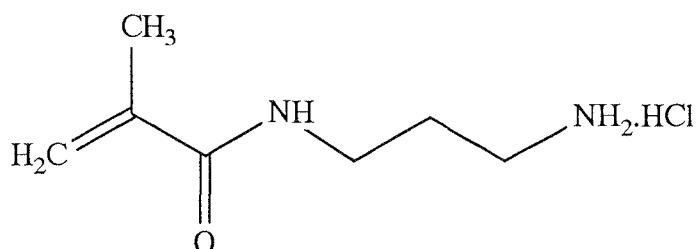
#### Reaction of *N*-(3-Aminopropyl)methacrylamide Hydrochloride with Cellulose

Treatment of cellulose with *N*-(3-aminopropyl)methacrylamide hydrochloride (APMA) in sodium hydroxide yielded a previously unreported derivative.

The preparation of APMA, shown in Figure 2.9, was first reported in 1978 by Owers<sup>104</sup> with a view to possible applications in photographic coatings, affinity chromatography and ion exchange. It has received scant attention since with only two subsequent reported studies.<sup>105,106</sup> APMA was of interest in this study because

of the availability of the amino group for further hydrogen bonding with the cellulose hydroxyl groups.

**Figure 2.9:** Structure of *N*-(3-Aminopropyl)methacrylamide Hydrochloride



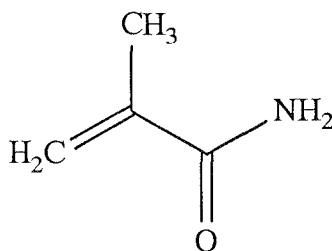
The preparation of the APMA-cellulose derivative was based on preparations involving the analogous acrylamide derivative. In two small scale experiments to assess the feasibility and reproducibility of this reaction, derivatives containing 0.80% and 0.67% nitrogen were obtained (S252 and S285, respectively).

Due to the high cost of APMA, the quantity used in larger scale trials was halved. This lowered the substitution level (S301, 0.27% N) and a corresponding improvement in papermaking properties was noted. In a final trial, milder reaction conditions were used in an attempt to further improve the papermaking properties, but elemental analysis revealed the conditions chosen were too mild and that no detectable substitution took place.

#### Reaction of Methacrylamide and Methacrylonitrile with Cellulose

The success of reactions of *N*-(3-aminopropyl)methacrylamide with cellulose prompted investigation of methacrylamide (Fig. 2.10). From the reactions of acrylamide, methacrylamide and *N*-(3-aminopropyl)methacrylamide with cellulose, it was possible to comment on the structure-property relationships of this series, as discussed in Chapter 4.

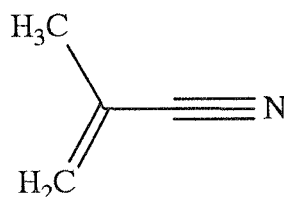


**Figure 2.10 : Structure of Methacrylamide**

Methacrylamide was reacted with cellulose by Franklin, Madasci and Rowland<sup>107</sup> as part of a study to improve the properties of cotton fabrics by polymerization and crosslinking.

Of the seven trials with methacrylamide, only three gave detectable levels of nitrogen after reaction with cotton linters using standard Michael addition reaction procedures (S304, 0.12% N; S320, 0.08% N; S375, 0.09% N). Significant differences in the ease of reaction were noted for acrylamide and its methyl analogue.

Lukanoff, Zielski and Philipp<sup>108</sup> reported that methacrylonitrile (Fig. 2.11) was much less reactive towards cellulose than acrylonitrile, reflecting the effect of alkyl substitution on the polarizability of double bonds. This study confirms the findings of Lukanoff and co-workers,<sup>108</sup> as the reaction of methacrylonitrile with cotton linters was successful according to elemental analysis for only one trial (S332, 0.17% N) and two other similar attempts were unsuccessful (S303 and S333, N <0.1%).

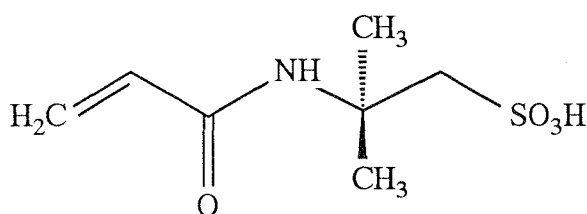
**Figure 2.11 : Structure of Methacrylonitrile**

Hence, it appears that methylation of acrylamide and acrylonitrile significantly lowers the reactivity of these reagents towards Michael addition by electronic effects. The facility of reactions with *N*-(3-aminopropyl)methacrylamide eliminates steric effects as a significant factor in the decreased reactivity of the methylated derivatives.

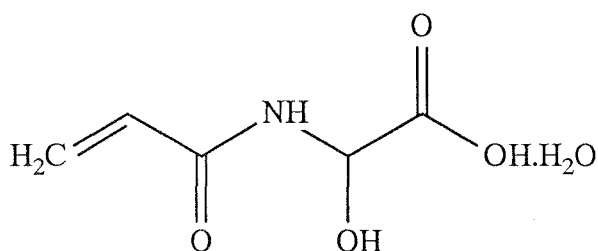
Attempted Reactions of 2-Acrylamido-2-methyl-1-propanesulfonic Acid and 2-Acrylamidoglycolic Acid Monohydrate with Cellulose

The ease of acrylamide reactions and their potential papermaking improvements prompted the investigation of other commercially available acrylamido- derivatives, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and 2-acrylamidoglycolic acid monohydrate (AGA), shown in Figures 2.12 and 2.13, respectively. They would have considerable potential for hydrogen bonding and other dipole-dipole interactions, and it was thought they may also be useful in blends of anionic-cationic cellulose derivatives.

**Figure 2.12:** Structure of 2-Acrylamido-2-methyl-1-propanesulfonic Acid



**Figure 2.13:** Structure of 2-Acrylamidoglycolic Acid Monohydrate



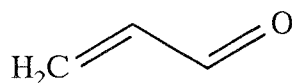
The propanesulfonic acid derivative has been used with cellulose in several grafting studies. Fanta, Burr and Doane<sup>109</sup> grafted softwood pulps with AMPSA and investigated the oil absorbing properties of the resulting graft pulp. Other AMPSA-cellulose grafts, prepared for textile applications, showed improved dyeability,<sup>110</sup> antistatic properties<sup>111</sup> and crease and flame resistance.<sup>112</sup> Several of these studies also reported improved hydrophilicity.<sup>110,111</sup> The glycolic acid derivative has received very little attention in the literature and has not been reacted with cellulose.

In most attempts in this study, low concentration solutions of AGA and AMPSA were used and the acid converted to the sodium salt after reaction with the linters. These attempts were unsuccessful and thereafter, minor variations were made to the above procedure but still without success. Two trials gave detectable quantities of nitrogen (0.05%) however, this was most likely due to the presence of some unreacted starting material. Attempts using higher concentration solutions of the acrylamido derivatives also proved unsuccessful. These reactions may have been unsuccessful because of steric hindrance factors.

#### Attempted Reaction of Acrolein with Cellulose

Acrolein has been used as a cross-linking agent for cellulosic materials in an analogous fashion to formaldehyde, producing crease-resistant, permanent-press fabrics.<sup>113</sup> Some debate has arisen as to the mode of addition to cellulose, i.e. addition may occur at either or both the aldehyde and vinyl groups<sup>114</sup> (see Fig. 2.14). Addition at the vinyl site in acrolein was desired in this instance. The aldehyde product thus obtained was then to be converted to the oxime and semicarbazone.

**Figure 2.14 :** Structure of Acrolein



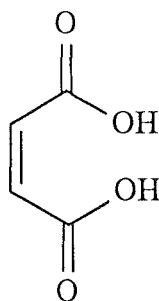
In this study, the method used for the attempted synthesis of the acrolein-cellulose derivative was based on the synthesis of the analogous acrylamide derivative, but was unsuccessful. An alternative route to the desired cellulose derivative may be to synthesize the oxime and semicarbazone derivatives directly from acrolein and then react these derivatives with cellulose, but this was not investigated further.

### **2.4.3 Reactions of Maleic and Itaconic Acids, and Related Derivatives with Cellulose**

#### **Reaction of Maleic Acid with Cellulose**

Maleic acid is a readily available, economical and water-soluble reagent (Fig. 2.15). Reaction of this diprotic acid with cellulose offers possibilities for both hydrogen bonding and for further derivatization to mono- and diamides.

**Figure 2.15:** Structure of Maleic Acid



Frick, Reeves and Guthrie<sup>95</sup> reacted the disodium salt of maleic acid with cotton to assess the fabric and dyeing characteristics of the Michael adduct. Using an aqueous solution of disodium maleate (20.4%) with sodium hydroxide they obtained a derivative with a substitution level of 22.6 meq/100g, which dyed readily with methylene blue, before and after boiling in a 5% sodium hydroxide solution. Hence, they were confident that a stable ether linkage, and not an ester, had formed as a result of a Michael addition reaction.

Other studies of cellulose with maleic and maleamic acid salts were also aimed at altering fabric properties, not papermaking properties. Franklin, Madasci and Rowland<sup>115</sup> used maleic acid salts as coreactant catalysts for creasable durable-press fabrics. Maleic acid derivatives have also been reacted with cellulose acetate in grafting studies, but this involved the formation of ester linkages.<sup>116</sup>

In this present study, maleic acid and sodium hydroxide were reacted initially with cellulose using standard methods, yielding a pulp with significant improvements in interfibre bonding. It appeared in the first trial (S222) that the maleic acid did not dissolve completely. According to reported solubilities of maleic acid in water,<sup>117</sup> the precipitate was not maleic acid, but the mono- or disodium salt of maleic acid. The experiment was repeated and the presence of the precipitate was noted again, irrespective of the sequence of addition of the reagents (S244, S273, S274). Frick, Reeves and Guthrie<sup>95</sup> used the disodium salt of maleic acid in all their 'maleic acid' trials. Hence, in trial S293, the maleic acid was neutralized with a stoichiometric amount of sodium hydroxide and the insoluble sodium salt that formed dissolved as more sodium hydroxide was added. The resulting disodium maleate was then combined with linters in aqueous sodium hydroxide and the experiment continued as usual.

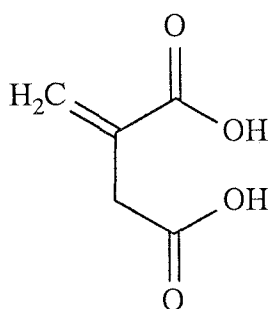
In a series of thirteen experiments, reaction times, maleic acid concentrations and the use of disodium maleate were varied in attempts to replicate the success of the first experiment. Considerable variation in substitution levels was noted, ranging from 3.62 to 12.86 meq/100g, which was considerably lower than those obtained by Frick and co-workers (*ca.* 24 meq/100g).<sup>95</sup> Increasing the reaction time at elevated temperature, as used in numerous other Michael addition preparations, may increase the substitution level to the range obtained by Frick and co-workers.<sup>95</sup>

The sodium salt of carboxymethyl cellulose is widely recognized as having superior papermaking properties to those of the acid form.<sup>49</sup> Hence, in one trial, the maleic acid-cellulose derivative was converted to the sodium salt by steeping in a saturated sodium bicarbonate solution, but papermaking properties were not improved (see Section 4.3.3).

#### Reaction of Itaconic Acid with Cellulose

Itaconic acid (Fig. 2.17) is a diprotic acid, having a similar capacity for hydrogen bonding as maleic acid.

**Figure 2.17:** Structure of Itaconic Acid



Frick, Reeves and Guthrie<sup>95</sup> noted altered dyeing properties for cotton fabric treated with itaconic acid. Their study found that trimethylbenzylammonium hydroxide was a suitable catalyst, whereas trials with sodium hydroxide were largely unsuccessful. They noted that some reaction occurred with cellulose but did not report the substitution levels obtained.<sup>95</sup>

Franklin, Madasci and Rowland<sup>107</sup> reacted itaconic acid with cotton fabric. However, this was as part of a grafting study in which an ester linkage was formed with one of the carboxyl groups. In another grafting study, Dimov, Semkova, Dimitrov and Terlemezyan<sup>118</sup> investigated the grafting of itaconic acid and acrylamide onto cellulose fibres and determined the ion exchange capacity of these grafted celluloses. Very little attention has been devoted to investigating the papermaking properties of the ether derivative of itaconic acid and cellulose.

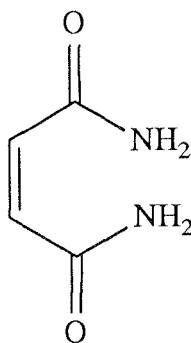
The basic catalyst benzyltrimethylammonium hydroxide was used in the first two trials of the reaction between itaconic acid with cotton linters (S256 and S257). As this appeared to offer no advantage, sodium hydroxide was used thereafter. In remaining trials, the effects of heat treating the linters as a slurry or filter pad, doubling the consistency and doubling the concentration of itaconic acid on substitution levels and papermaking properties were assessed. Substitution levels ranged from 5.13 to 13.37 meq/100g, similar to the levels obtained with maleic acid.

#### Reactions of Related Derivatives with Cellulose

A fumaric acid-cellulose derivative was also prepared using standard procedures, which gave a substitution of 13.16 meq/100g and was used as a baseline for comparison with the fumaric acid-cellulose derivative used in the blends.

Numerous attempts were made to react maleic diamide (Fig. 2.16), prepared from dimethylmaleate and aqueous ammonia using reported methods,<sup>119</sup> with cellulose. However, according to elemental analysis results, these attempts were unsuccessful; the reasons for this are not clear.

**Figure 2.16:** Structure of Maleic Diamide



Attempts to prepare cellulose derivatives of other maleic acid derivatives, including maleic hydrazide, maleimide and citraconic acid (methylmaleic acid), were either unsuccessful or did not improve the papermaking properties.

## **2.5      DOUBLE DERIVATIVES AND BLENDS OF ANIONIC AND CATIONIC CELLULOSE DERIVATIVES**

### **2.5.1    Preparation of Double Derivatives of Cellulose**

A diverse range of cellulose ethers have been reported that contain two different derivatives substituted onto the cellulose, i.e. double derivatives. These include commercially available derivatives such as carboxymethyl hydroxyethyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose and cationized hydroxyethyl cellulose.<sup>38,39,120</sup>

This very active area of research has yielded some novel combinations of cellulose derivatives with interesting properties. Mays<sup>121</sup> investigated the suitability of cyanoethyl hydroxypropyl cellulose at high substitution levels for use in liquid crystals. Sato, Nambu and Endo<sup>122</sup> incorporated a viologen moiety into hydroxypropyl cellulose and investigated the redox behaviour of this new derivative. They prepared the viologen derivative from tosylated hydroxypropyl cellulose because hydroxypropyl cellulose is more reactive and has better solubility than cellulose and hence, allowed for the preparation of a highly tosylated cellulose derivative. In an extension of the photolytic preparation of 6-aldehydo cellulose reported by Horton, Luetzow and Theander,<sup>11</sup> Petrus and Petrusova<sup>123</sup> prepared azido hydroxypropyl cellulose, from the corresponding chloro derivative, and by photolysis and acid hydrolysis obtained formyl hydroxyethyl cellulose. Russian workers<sup>124</sup> investigated the fibre spinning properties of cyanoethyl hydroxyethyl celluloses and noted that hydroxyethyl cellulose was more reactive towards acrylonitrile than cellulose. In another study, cyanoethylated hydroxyethyl cellulose was found to be a thermoplastic material with excellent insulating properties.<sup>125</sup> The analogous amidoethylated hydroxyethyl cellulose has also been prepared.<sup>126</sup>



Cationizing reagents have been used for primary and secondary derivatizations in the preparation of a range of double derivatives of cellulose. Using cationized cellulose as an internal catalyst, Rowland and Brannan<sup>127</sup> reacted numerous vinyl compounds, such as acrylonitrile, acrylamide, *N,N*-methylenebisacrylamide, and methacrylonitrile, with cationized cotton fabrics. In secondary derivatizations, a German patent described the cationization of hydroxyethyl, methyl hydroxyethyl and carboxymethyl celluloses.<sup>128</sup> The use of cationized hydroxyethyl cellulose, prepared in a one-pot reaction, as a paint remover has also been described.<sup>129</sup> In a much later study, cationized hydroxyethyl cellulose was blended with anionic derivatives, as discussed in Section 2.5.2.<sup>130,131</sup>

In double derivatizations, substitution may occur on the functional group of the primary derivative, on the cellulose backbone or a combination of both; the preferred site of substitution and hence, relative reactivity of each reagent may also differ significantly for each derivatization. Most of the above-mentioned derivatives were prepared at high substitution levels and substitution was assumed to occur predominately on the primary derivative, not on the cellulose backbone.

In a comprehensive study by Kamide, Okajima, Matsui and Ohnishi,<sup>132</sup> the synthesis, position and level of substitution, and clotting ability towards blood and coagulating ability towards plasma of amidoethyl carboxyethyl cellulose was investigated. Under the conditions chosen, carboxyethyl substitution predominated and substitution at (C-2)-(C-3) was favoured over C-6 substitution. This derivative is strictly not a double derivative but two derivatives or functional groups obtained from the one reagent, acrylonitrile. This significantly lessens the likelihood of substitution on the primary reagent and conversely, increases the probability that both groups are attached directly to the cellulose backbone. Hence, very little information is available on the position of substitution in double derivatives of cellulose, with the exception of some common mixed ethers, such as methyl hydroxypropyl and amidoethyl carboxyethyl cellulose.<sup>38,132</sup>

The positions of substitution for the double derivatives prepared in this study have not been determined because of the complexity of this task. This problem is exacerbated by the difficulty of developing suitable methods to analyze the range of derivatives prepared and by the low substitution levels obtained in this work. Knowledge of this positional information may have assisted in explaining the observed changes in papermaking properties.

Double derivatives were prepared in this study using typical methods developed for each derivative, as described in the appropriate sections. As far as is known, the following double derivatives of cellulose have not been reported elsewhere: carboxymethylation of cationized cellulose, cationized amidoethyl cellulose, cationized maleic acid-cellulose derivative, maleic acid-treated cationized cellulose, maleic acid-hydroxyethylated cellulose and *N,N*-methylenebisacrylamide-treated hydroxyethyl cellulose.

A distinction should be made between the physical blending of anionic and cationic cellulose derivatives and double derivatives of cellulose that contain anionic and cationic groups substituted onto the one batch of pulp in two derivatizations. Hence, some double derivatives, such as maleic acid-treated cationized cellulose and carboxymethylated cationized cellulose, were prepared to allow the papermaking properties of these derivatives to be compared with the properties of handsheets prepared from physical blending of anionic and cationic cellulose derivatives. The papermaking properties obtained for double derivatives and blends were markedly different (see Sections 4.3.4 and 4.4.2).

Epoxides are capable of reacting with carboxylic acids, alcohols and amides.<sup>87</sup> Hence, amidoethyl cellulose and maleic acid-treated cellulose were reacted with the cationizing reagent. These reactions were performed in two separate stages and not as one-pot reactions, because the epoxide-based cationizing agent reacts more readily with acids, i.e. unsubstituted maleic acid, than alcohols. Because of this

preferential reactivity and steric hindrance,<sup>87</sup> substitution in these derivatives was more likely on the carboxylic acid and amide groups of the primary derivative than on the hydroxyl groups of the cellulose backbone. The cationized amidoethyl cellulose, which showed promising papermaking properties, was prepared several times with quite different substitution levels being obtained (0.12 to 0.82% N).

In the converse, cationized cellulose was treated with maleic acid and, in another experiment, the carboxymethylated cationized cellulose derivative was prepared. For these derivatives, substitution on the cellulose backbone was anticipated, instead of reaction with the quaternary ammonium groups.

Two attempts were made to prepare maleic acid-treated amidoethyl cellulose. However, no nitrogen was detected in the fibres, which indicated probable hydrolysis of the amide and not the absence of substitution by either Michael addition reagent; the derivative was not characterized further.

Several Michael addition reagents were reacted with hydroxyethyl cellulose. The acrylamide derivative of hydroxyethyl cellulose was prepared several times using progressively milder conditions to yield, finally, an amidoethylated hydroxyethyl cellulose that could be evaluated; improvements in papermaking properties were obtained for this derivative. Similarly, maleic acid and *N,N*-methylene-bisacrylamide were reacted with hydroxyethylated cellulose using the milder reaction conditions used for acrylamide treatments. Substitution of these Michael reagents was assumed to occur on the hydroxyethyl groups, in preference to the cellulose backbone, because of the reputedly greater reactivity of hydroxyalkyl celluloses towards derivatization.

### **2.5.2 Blends of Anionic and Cationic Cellulose Derivatives**

The potential of cellulose and its derivatives for anionic-cationic interaction has

been long recognized in their ion exchange capacity and thereafter, use in ion exchangers, the dyeing of textiles and as dialysis membranes.<sup>133,134</sup> The combination of anionic and cationic cellulose derivatives was expected to impart significant papermaking improvements via electrostatic interactions, complementing the improvements obtained for most cellulose derivatives at low degrees of substitution via secondary valence forces.<sup>55</sup>

Previous studies reporting the papermaking improvements obtained with blends of anionic-cationic cellulose derivatives are discussed in Section 4.4.3. The derivatives investigated included amine donor groups and a range of acceptor groups, such as carboxylic acid, nitrile, hydroxyl and sulfonic acid groups, that were grafted onto the pulp.<sup>135</sup> Other studies addressed the electron-donor-acceptor interaction between the acceptor, cellulose tripropionate, and various plasticizers, which acted as donor groups, with a view to improving the thermoplastic processing properties of cellulosic systems.<sup>136</sup>

Anionic-cationic cellulose derivatives and graft copolymers were also found to have excellent blood compatibility in haemodialysis membranes.<sup>130,137</sup> In a series of papers, Japanese workers<sup>130,131,137,138</sup> investigated the effects of combining relatively highly substituted cationic components, cationized cellulose and cationized hydroxyethyl cellulose, with anionic carboxymethyl cellulose and cellulose sulfate.

In this study, cationized cellulose was blended with the following anionic derivatives: carboxymethyl cellulose, and maleic, itaconic and fumaric acid derivatives of cellulose. Whilst blends of carboxymethyl and cationic cellulose have been reported by Frolov and co-workers,<sup>135</sup> blending of cationic cellulose with the three diprotic acids, maleic, itaconic and fumaric acids, has not been reported previously. These derivatives were prepared using procedures discussed and described elsewhere (Sections 2.3, 2.4 and 2.7). Minor modifications to these

procedures were performed to assess the effect on papermaking properties, viz. carboxymethylated cellulose was blended with a more highly cationized cellulose derivative and quantities of maleic acid used were halved in most blend preparations, relative to maleic acid-cellulose preparations. In other trials, several attempts were made to replicate the outstanding improvements noted for an early maleic acid-cationic cellulose blend (S324/S323) and all blends, except the fumaric acid-cationic cellulose blend, were scaled up to the 125 g oven dry (o.d.) scale for full pulp evaluation testing.

### **2.5.3 Concluding Remarks**

Considerable scope exists for further work in the area of double derivatives and blends. Moreover, determination of the position of substitution, the preparation of new double derivatives by reaction of other Michael addition reagents with hydroxyalkyl celluloses, and the blending of anionic double derivatives with cationic double derivatives of cellulose (e.g. cationized hydroxyethyl cellulose with maleic acid-treated hydroxyethyl cellulose) are key areas worthy of further investigation.

## **2.6 SUMMARY AND CONCLUSIONS**

6-Aldehydo cellulose was successfully prepared using reported methods but extensive degradation occurred. Alternative routes to selectively oxidize cellulose to 6-aldehydo cellulose were unsuccessful.

In contrast, oxidation with sodium periodate to yield 2,3-dialdehydo cellulose was facile and gave limited papermaking improvements. A range of cellulose derivatives were obtained from the dialdehydo cellulose, amongst these was the previously unreported Girard's Reagent T-cellulose derivative. Reaction conditions

and substitution levels of the dialdehyde cellulose derivatives were varied to assess the effects of these changes on papermaking properties.

The derivatives, carboxymethyl, hydroxyethyl and hydroxypropyl celluloses, prepared using several reported methods, provided a baseline for comparison with other derivatives. Generally, substitution levels obtained in this study were below the levels obtained in other studies.

Cellulose mesylate was prepared for use as a synthetic intermediate and the preparative method was modified in a series of experiments to optimize the papermaking properties of the mesylate.

Numerous deoxy cellulose derivatives were prepared, including chloro-, azido-, iodo-, fluoro- and cyano-deoxy celluloses. Some of these derivatives were prepared from cellulose mesylate and several others were prepared from 6-chloro-6-deoxy cellulose, originally prepared as a precursor in the synthesis of 6-aldehyde cellulose. These deoxy cellulose derivatives, while offering potentially interesting papermaking properties, were too degraded to undergo pulp evaluation testing.

Cationized cellulose was prepared numerous times, with more highly cationized derivatives being prepared principally for use in blends.

Considerable emphasis was placed on Michael addition reactions of a range of vinyl derivatives with cellulose. Cyanoethyl and amidoethyl celluloses were prepared using previously reported methods which were modified extensively. Studies of these derivatives led to an investigation of related compounds, including the preparation of the *N,N*-methylenebisacrylamide, methacrylonitrile and methacrylamide-cellulose derivatives, and the new *N*-(3-aminopropyl)-methacrylamide-cellulose derivative. Attempts to react 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-acrylamidoglycolic acid and acrolein with cellulose were

unsuccessful. The maleic and itaconic acid derivatives of cellulose were also prepared, with the reaction conditions for the maleic acid derivative being varied in efforts to replicate initial papermaking improvements. Experimental conditions for most Michael addition reactions were varied extensively in attempts to optimize their papermaking properties.

Studies of double derivatives of cellulose and blends of anionic-cationic cellulose derivatives yielded some novel combinations of derivatives. Most of the double derivatives were prepared using cationized or hydroxyethylated cellulose, as either the primary or secondary derivative, usually in combination with a Michael addition reagent or the corresponding Michael-cellulose derivative. Blends of the diprotic maleic, fumaric and itaconic acid derivatives with cationic cellulose have not been reported previously and also gave significant papermaking gains.

This study of modified cotton linters has led to the synthesis of several new derivatives, the preparation of numerous cellulose derivatives using modifications of reported methods and some previously reported derivatives were prepared for evaluation of their papermaking properties.

## **2.7      EXPERIMENTAL**

### **2.7.1    General Methods**

#### **Cotton Linters**

Second cut Australian cotton linters were used in almost all cellulose modifications. The other sources of cellulose, raw cotton linters from APPM's Shoalhaven Mill in NSW, and first cut cooked and bleached cotton from ICI Australia Pty. Ltd., were used as received; no further processing details were available from ICI.

The second cut linters were cooked with sodium hydroxide (10% on o.d. linters) in a Pandia digester at 800 kPa and 175°C, bleached using chlorine, followed by hypochlorite, and then refined. Cooking conditions changed to 570 kPa and 155°C in July 1989. Hence, trial S275 and thereafter, were performed on linters cooked using these new conditions. Samples were taken from the final stage of the cotton linters processing plant (T10), just prior to blending with other fibres on the paper machine.

The linters thus received from Shoalhaven were pressed to a moisture content of approximately 2.48 g/g o.d.. The pressed cakes were crumbed in a refiner but this tended to cause clumping of the fibres. A mechanical crumber was then used to process most batches of linters. The moisture content of the crumbed pulp was determined and the samples were then frozen in pre-weighed lots.

Prior to use in modifications, linters were thawed and soaked overnight in distilled water (20 g o.d. in 300 mL water) and then dispersed by mixing in a domestic blender (5 to 10 sec). After modification, the pulps were refrozen before undergoing pulp evaluation testing. Samples not submitted for pulp evaluation were air-dried.

Modified linters were filtered by forming a filter pad from the fibres (the filtrate was returned to the pad) in preference to using filter papers, which often resulted in lengthy filtering times. To isolate some degraded or alkali treated samples, coarse glass filter papers or centrifugation was used. Generally, mechanical stirrers were required to achieve proper mixing, magnetic stirrers being inadequate given the consistency of most reaction mixtures. A significant number of modifications were performed in heat-sealed polyethylene bags to minimize exposure to air.

Because of the nature of the starting material, it was not considered relevant to measure yields for cellulose modifications. Little physical loss of cellulose occurred in the preparations.



### Solvent Exchange Technique:

It was necessary in some preparations, such as carboxymethylations and mesylations, to remove the water present in cellulose by displacement with an organic solvent, which prevents collapse and preserves the capillary structure of the fibres as required for evaluation of their papermaking properties. A solvent exchange technique reported by Green<sup>139</sup> was used in which the water was first displaced by an alcohol and then a hydrocarbon as follows: a filter cake of linters was steeped and stirred in alcohol in an open beaker, filtered, washed with alcohol and this process was then repeated. The linters were then steeped in the second solvent, usually the one used in the preparation itself, filtered, washed and processed, as for the alcohol displacement.

### Solvents and Reagents

Solvents were used as received except for those that required purification, all of which were purified according to one of the methods cited by Perrin, Armarego and Perrin.<sup>140</sup> Chloroform was purified by washing with water, drying with calcium chloride, refluxing and distilling from phosphorus pentoxide, and was stored in the dark. Dichloromethane was pre-dried with calcium chloride, distilled from phosphorus pentoxide and stored over 4A molecular sieves. Pyridine was dried by refluxing with solid sodium hydroxide, fractionally distilled over sodium hydroxide and stored over 4A molecular sieves. Acrolein was fractionally distilled under nitrogen, dried with anhydrous calcium sulfate, distilled under vacuum and stabilized with pyrocatechol.<sup>140</sup>

Liquid ammonia was distilled and recondensed as needed by passing gaseous ammonia through a stainless steel coil cooled in a dewar of dry ice and acetone (-77°C).

### Analyses

Elemental analyses were performed by Amdel Ltd. (Melbourne, Australia), but mostly by the Canadian Microanalytical Service Ltd. (Vancouver, Canada). Although it is conventional to report microanalyses to one decimal place, to avoid introducing further error into such low level determinations, in this study, they were reported to two decimal places (uncertainty 0.03% nitrogen).

Carboxyl contents of carboxymethyl cellulose, and cellulose derivatives of maleic, itaconic and fumaric acids were determined using the TAPPI Standard Test Method T237 om-83, scaled down by a factor of 10.

Copper numbers of 2,3-dialdehydo cellulose were determined using the TAPPI Standard Test Method T430 om-83. Unmodified cooked and bleached cotton linters gave a Copper number of 1.0.

Hydroxyethyl and hydroxypropyl contents were determined using the Standard Test Method ASTM D3876-79 (Reapproved 1985) and the method described by Hodges, Kester, Wiederrich and Grover.<sup>141</sup>

### Equipment

Cotton linters were crumbed using a Sprout-Waldron refiner and a Veeder-Root mechanical crumber (Model KC 1359).

Crumbed linters were dispersed in water using a National Super Blender (Model N/10186/MX-100PN) or a Sunbeam Solid State Blender (Model PB-B) on the maximum setting.

Reaction mixtures (20 g o.d. scale and above) were usually stirred using a Sunbeam Mixmaster (Model MX-AB, setting 1) or a Janke and Kunkel Ika-Werk stirrer (RW20 S5) fitted with a Sunbeam Mixmaster beater to effect adequate agitation.

Photolysis reactions were performed using an immersion-well photoreactor with an internal light source (Hanovia 450 W medium pressure mercury arc lamp) and glass filter sleeves (pyrex transmission > 300 nm; corex transmission > 250 nm; vycor transmission > 210 nm).

Samples were ground using a domestic coffee grinder (Kambrook Model V/79353/CG7).

Linters were ultrasonicated in a Branson ultrasonic cleaner (Bransonic 12, 50-60 Hz, 80 W).

## **2.7.2 Preparations of Aldehyde Derivatives of Cellulose (Section 2.2)**

### **Preparations in Section 2.2.2**

#### **Preparation of 6-Aldehydo Cellulose by Photolysis**

6-Aldehydo cellulose was prepared by a modification of the procedure reported by Horton, Luetzow and Theander.<sup>11</sup> The preparation of the precursors, 6-chloro-6-deoxy cellulose and 6-azido-6-deoxy cellulose are described in Section 2.6.3. All photolysis reactions were performed under argon and the reaction mixtures were stirred using a magnetic stirrer.

6-Azido-6-deoxy cellulose (S7, 6.4 g, 3.16% N) was soaked in 4:1 2-methoxyethanol:benzene (400 mL) overnight and ultrasonicated for 30 min in an

attempt to disperse the azide derivative. This slurry was then photolyzed for 5 h with stirring using a pyrex filter. The product was washed with ethanol, hydrolyzed with 2% acetic acid (4 h), washed with water and air-dried. An infrared spectrum indicated that the azide was still present and hence the photolysis was repeated as above using corex and vycor glass filters, but these attempts were also unsuccessful.

In another attempt using a portion of 6-azido-6-deoxy cellulose (S7, 3.16% N) that had not been photolyzed, the photolysis was performed without a pyrex filter (i.e. quartz, transmission > 190 nm) and using only 2-methoxyethanol as the solvent. Elemental analysis results before and after photolysis showed a decrease in the amount of nitrogen present (3.16% to 1.68% N respectively), but a test for aldehydes using 2,4-dinitrophenylhydrazine was negative.<sup>13</sup>

In a final attempt, the azide derivative (4 g, S62, 2.49% N) was ground in a coffee grinder and then dispersed in a 4:1 mixture of 2-methoxyethanol:benzene (150 mL). The azide was photolyzed for 6 h with vigorous stirring using a vycor filter and a reduction in the intensity of the azide absorbance in the infrared spectrum was noted. The product was then photolyzed for a further 4 h, hydrolyzed and isolated as before. The amount of nitrogen present decreased from 2.49 to 0.37% nitrogen; the preparation of the oxime and semicarbazone derivatives, as described below, confirmed the presence of 6-aldehydo cellulose.

#### Preparation of 6-Deoxy Cellulose Oxime and 6-Deoxy Cellulose Semicarbazone

The oxime and semicarbazone derivatives of 6-aldehydo cellulose were prepared using the procedures described later in this section for 2,3-cellulose oxime and semicarbazone.<sup>13</sup>

6-Aldehydo cellulose (S62, 0.64 g air-dry (a.d.)) was combined with hydroxylamine hydrochloride (0.68 g, 10 mmol) in water (20 mL). The solution was adjusted to pH

10-12 (1 M sodium hydroxide), heated and stirred (45 min), allowed to cool, neutralized with hydrochloric acid (5%), filtered and washed with water (S89(i), 0.82% N).

6-Aldehydo cellulose (S62, 0.62 g a.d.) was combined with a solution of semicarbazide hydrochloride (0.68 g, 6 mmol) and sodium acetate (0.97 g, 10 mmol) in aqueous ethanol (10 mL:7 mL). The mixture was stirred and heated (2 h), filtered and washed with water yielding a product containing 2.06% nitrogen (S89(ii)).

### Preparations in Section 2.2.3

#### Preparation of 4-Dimethylaminopyridine *N*-Oxide

4-Dimethylaminopyridine *N*-oxide was prepared using a modification of the method reported by Pentimalli.<sup>15</sup>

4-Dimethylaminopyridine (2.0 g, 16 mmol) was dissolved in benzene (25 mL) and *m*-chloroperbenzoic acid (5.6 g, 33 mmol) added gradually with stirring. After stirring for 40 h, a saturated solution of sodium carbonate (2 mL) was added and stirring continued for 30 min. The solution was dried with anhydrous sodium sulfate, filtered and dried. The residue was dissolved in dichloromethane, evaporated in vacuo, and washed with diethyl ether, yielding a pale yellow hygroscopic<sup>14</sup> product (S32), which was used immediately.

#### Attempted Preparation of 6-Aldehydo Cellulose using 4-Dimethylaminopyridine *N*-Oxide

This preparation was performed with reference to the method reported by Mukaiyama, Inanaga and Yamaguchi.<sup>14</sup>

In a 100 mL round-bottom flask fitted with a reflux condenser, 4-dimethylaminopyridine *N*-oxide (S32, 2.8 g, wet with diethyl ether) was combined with 6-chloro-6-deoxy cellulose (S26, 3.8% Cl, 0.96 g a.d.) in acetonitrile (35 mL). The mixture was stirred at reflux for 24 h, 1,8-diazabicyclo[5.4.0]undec-7-ene (4 mL) was added and refluxing continued for a further 18 h. The dark brown product was filtered, washed with hot distilled water and air-dried (S43, 0.84 g o.d., 1.07% Cl), but according to infrared spectroscopy the oxidation was unsuccessful.

#### Synthesis of Tris(triphenylphosphine)ruthenium(II) Chloride

Tris(triphenylphosphine)ruthenium(II) chloride was prepared using a modification of the method reported by Hallman, Stephenson and Wilkinson.<sup>17</sup>

Ruthenium trichloride (1.0 g, 4.8 mmol) was suspended in methanol (250 mL) under nitrogen in a 500 mL three-neck round-bottom flask fitted with a magnetic stirrer and a double surface condenser. The black solution was refluxed for 5 min and triphenylphosphine (7.6 g, 28.9 mmol) was added to the cooled solution and it was again refluxed under nitrogen for 3 h. A brown/black precipitate was isolated from the hot solution by filtering through a sinter under nitrogen, it was then washed with degassed diethyl ether and dried under vacuum. The derivative was obtained in 71% yield (S12, 3.26 g) and had a melting point of 133°C (lit. m.p.<sup>17</sup> 132-134°C).

#### Attempted Oxidation of Cellulose with Tris(triphenylphosphine)ruthenium(II) Chloride

Cellulose was reacted with tris(triphenylphosphine)ruthenium(II) chloride using an adaptation of the method reported by Oshima and co-workers.<sup>16</sup>

Cotton linters (0.05 g o.d.) were ultrasonicated (30 min) in benzene (5 mL) and then combined with tris(triphenylphosphine)ruthenium(II) chloride (0.29 g, 0.3 mmol).

More benzene was added (5 mL) and the slurry stirred with a magnetic stirrer for 4 h. The linters were filtered, washed with benzene and diethyl ether, and air-dried (S16). A standard test<sup>13</sup> for the presence of aldehydes using 2,4-dinitrophenylhydrazine was negative and an aldehyde absorbance was not present in the infrared spectrum.

Several oxidations were also attempted using cellobiose instead of cellulose but these were unsuccessful according to infrared spectroscopy.

#### Attempted Oxidations of Cellobiose using 2,2,6,6-Tetramethyloxopiperidinium Tetrafluoroborate (TEMPO)

Attempts were made to oxidize cellobiose with TEMPO, using a modification of the procedure reported by Hunter, Barton and Motherwell.<sup>19</sup>

In two trials, cellobiose (0.14 g, 0.41 mmol) was combined with TEMPO (0.10 g, 0.40 mmol) in acetonitrile (10 mL) in a 50 mL round-bottom flask. The yellow slurry was stirred for 24 h, filtered on a sinter and washed with acetonitrile. The air-dried white product (S34, 0.10 g; S42, 0.13 g) was confirmed by infrared spectroscopy and melting point determination to be unreacted cellobiose (m.p. of white product 223°C; lit. m.p.<sup>57</sup> of cellobiose 225°C).

#### Preparations in Section 2.2.4

##### Preparation of 2,3-Dialdehydo Cellulose

2,3-Dialdehydo cellulose was prepared with reference to several methods.<sup>4,20,24,25</sup>

In a typical procedure, cotton linters (20 g o.d.) were mixed with an aqueous solution of sodium periodate (1 L, 0.05 M) in an Erlenmeyer flask and steeped for 4

h, excluding light to avoid the formation of byproducts. The dialdehyde cellulose was then filtered and washed with water (2 L), giving a Copper number of 7.1.

In initial trials, the oxidation level was varied according to reaction times, viz.: 1-6, 8, and 24 h. The reaction was repeated a further 18 times, using a 4 h oxidation time for conversion to other cellulose derivatives. Several of these trials were conducted at the 125 g o.d. scale.

#### Preparation of 2,3-Cellulose Oxime

2,3-Cellulose oxime was prepared from 2,3-dialdehyde cellulose using an adaptation of the standard method for the preparation of oximes.<sup>13</sup>

2,3-Dialdehyde cellulose (19.49 g o.d.) was combined with an aqueous solution of hydroxylamine hydrochloride (19.45 g, 0.28 mol, 800 mL) and the pH adjusted to 10-12 using a sodium hydroxide solution (1 M). The slurry was heated at 60°C with stirring for 30 min. It was then cooled, neutralized with hydrochloric acid (5%), filtered and washed with water.

Initial trials showed that sodium hydroxide caused too much damage to the linters and sodium acetate was then used in preference. Hence, in a typical preparation, dialdehyde cellulose (20 g o.d.) was combined with an aqueous solution (600 mL) of hydroxylamine hydrochloride (20 g, 0.29 mol) and sodium acetate (35 g, 0.43 mol) in a sealed plastic bag and heated at 60°C for 2 h. The product was filtered and washed with water (2 L). In further experiments, quantities of reagents were progressively reduced to 0.05 g of hydroxylamine hydrochloride and 0.10 g sodium acetate to reduce substitution levels from 0.73% to 0.12% nitrogen (refer to Table 2.1 for details).



**Table 2.1:** Preparations of 2,3-Cellulose Oxime

Reaction Number	2,3-Dialdehyde Cellulose (g o.d.)	Ratio of $\text{CH}_3\text{COONa}$ : Hydroxylamine $\text{HCl}$ : $\text{H}_2\text{O}$ to Dialdehyde Cellulose (1)	Time (h)	Temp. ( $^{\circ}\text{C}$ )	Comments	Substitution (%N)	Z-Direction Tensile Index # (% Change)
S153	19.5	* : 1 : 40	1	60	pH 10-12, stirred	0.39	—
S164**	20	1.75 : 1 : 30	2	60	pH 5.5	0.73	+19
S175	20	1.75 : 1 : 30	2	60	As above	0.68	+11
S186	20	0.5 : 0.25 : 30	2	RT***	Decreased temp. and reagents	0.42	+12
S209	20	0.5 : 0.25 : 30	4	RT	Doubled time	0.59	+19
S210	20	0.1 : 0.05 : 30	4	RT	Decreased reagents	0.50	+23
S211	20	0.1 : 0.05 : 30	4	75	Increased temp.	0.55	+19
S237	20	0.05 : 0.025 : 30	4	RT	Halved reagents	0.44	+18
S238	20	0.1 : 0.05 : 30	1	RT	See S210, decreased time	0.37	+13
S239	20	0.05 : 0.025 : 30	1	RT	See S237, decreased time	0.32	+13
S268	20	0.025 : 0.0125 : 30	1	RT	Halved reagents	0.19	-18
S269	20	0.01 : 0.005 : 30	0.5	RT	Decreased reagents and time	0.16	-8
S270	20	0.005 : 0.0025 : 30	0.5	RT	Halved reagents	0.12	-13
S292	125	0.005 : 0.0025 : 30	0.5	RT	125 g o.d. scale	0.12	+9

\* Sodium hydroxide solution used(1 M).

\*\* Sealed bag used for S164 to S268.

\*\*\* Room temperature.

# Change relative to unmodified linters reference.

Indicates changes in interfibre bonding - see Section 4.1.2 for definition.

### Preparation of 2,3-Cellulose Semicarbazone

Cellulose semicarbazone was prepared from 2,3-dialdehyde cellulose using a standard method for the derivatization of aldehydes.<sup>13</sup>

A typical preparation involved combining 2,3-dialdehyde cellulose (20 g o.d.) with an aqueous solution (600 mL) of semicarbazide hydrochloride (1.03 g, 9.2 mmol) and sodium acetate (2.07 g, 25 mmol). The slurry was sealed in a plastic bag for 30 min and the product filtered and washed with water (1 L). The different reaction conditions used are summarized in Table 2.2.

**Table 2.2:** Preparations of 2,3-Cellulose Semicarbazone

Reaction Number	2,3-Dialdehyde Cellulose (g o.d.)	Ratio of CH <sub>3</sub> COONa: Semicarbazide: H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (%N)	Z-Direction Tensile Index (% Change)
S157	20	1.75 : 1 : 30	2	50	Stirred	1.85	+6
S173	20	1.75 : 1 : 30	2	50	*	1.98	NS***
S187	20	0.5 : 0.25 : 30	2	RT**	Reduced reagents and temp.	1.13	NS
S280	20	0.1 : 0.05 : 30	0.5	RT	Reduced reagents and temp.	0.83	-8
S281	20	0.01 : 0.005 : 30	0.5	RT	Reduced reagents ten-fold	0.23	NS

\* Sealed bag.

\*\* Room temperature.

\*\*\* Not significant (< 5% change).

### Preparation of 2,3-Cellulose Thiosemicarbazone

The preparation of 2,3-cellulose thiosemicarbazone was based on the analogous procedure, described for the preparation of 2,3-cellulose semicarbazone.

In an initial trial, an aqueous solution (600 mL) containing thiosemicarbazide (20.03 g, 220 mmol) and sodium acetate (35.4 g, 430 mmol) was combined with 2,3-dialdehydo cellulose (20 g o.d.) and heated in a sealed plastic bag at 60°C for 2 h. The reaction mixture was cooled, filtered and washed with water to afford the derivatized 2,3-dialdehydo cellulose (S223, 1.00% N, 0.76% S).

To reduce substitution levels, the quantities of thiosemicarbazide and sodium acetate were reduced (2.0 g and 4.13 g, respectively) and the mixture was not heated (S271, 0.42% N). In a similar preparation, quantities of thiosemicarbazide and sodium acetate were lowered further (0.13 g and 0.24 g respectively; S272, 0.24% N).

### Reactions of Girard's Reagent T with 2,3-Dialdehydo Cellulose

The reaction of Girard's Reagent T, (carboxymethyl)trimethylammonium chloride hydrazide, with 2,3-dialdehydo cellulose was based on the preparation of cellulose semicarbazone.

In a 1 L three-neck round-bottom flask fitted with a magnetic stirrer, Girard's Reagent T (21.78 g, 0.130 mol) and sodium acetate (35.17 g, 0.429 mol) were added to 2,3-dialdehydo cellulose (20 g o.d.) dispersed in ethanol:water (250 mL:350 mL). The mixture was stirred for 2 h and then heated at 60°C for 30 min. The resulting derivative was isolated by filtration and washed with water (1 L) (S158, 0.93% N, 0.27% Cl).

Essentially, the same procedure was used in another attempt except that no ethanol was used and the reaction was performed in a sealed plastic bag heated at 60°C for 2 h (S174, 0.97% N).

In an attempt to lower substitution levels, quantities of Girard's Reagent T and sodium acetate were reduced (5.46 g and 10.55 g respectively) and the reaction performed without heating (S188, 0.37% N).

#### Reaction of Girard's Reagent P with 2,3-Dialdehydo Cellulose

The preparation of the Girard's Reagent P, [1-(carboxymethyl)pyridinium chloride hydrazide]-cellulose derivative was based on the method used to prepare the other dialdehydo cellulose derivatives. An aqueous solution (600 mL) of Girard's Reagent P (10.38 g, 0.055 mol) and sodium acetate (17.59 g, 0.214 mol) was combined with 2,3-dialdehydo cellulose (20 g o.d.), sealed in a plastic bag and heated at 60°C for 2 h. The product was allowed to cool, filtered and washed with water (S229, 0.64% N).

### **2.7.3 Preparations of Substitution and Addition Derivatives of Cellulose** **(Section 2.3)**

#### **Preparations in Section 2.3.1**

##### Preparation of Carboxymethyl Cellulose

Carboxymethyl celluloses were prepared using modifications of several reported methods.<sup>47,48</sup>

A preliminary trial was performed using a procedure similar to that described by Green<sup>47</sup> to yield carboxymethyl cellulose with a DS of nominally 1.2. Air-dry raw linters (15 g) in isopropanol (400 mL) were stirred vigorously with a mechanical stirrer, during the addition of 30% aqueous sodium hydroxide (30 mL); stirring was continued for 1 h. Chloroacetic acid (18 g, 0.19 mol) was added gradually with stirring. The slurry was heated in a 1 L beaker covered with aluminium foil (3.5 h, 55°C), the excess liquor decanted, and 70% aqueous methanol added. The mixture was neutralized with acetic acid, drained and washed with 70% aqueous methanol and then methanol. A partially fibrous product and a viscous liquid were obtained, suggesting uneven substitution (S9). The water-solubility of the product indicates the DS was between 0.4 and 1.2.<sup>38</sup> The mixture was characterized by <sup>13</sup>C NMR spectroscopy (177 ppm - assigned as a carboxyl resonance).

This procedure was repeated with minor modifications, i.e. more linters were used (15 g o.d.), which required more isopropanol solvent (600 mL). The product (S17, 177 ppm - carboxyl resonance) readily dissolved in water, in agreement with the observation noted by Green.<sup>47</sup>

Linters were also carboxymethylated using a modification of the procedure reported by Ward, Murray and Thomas.<sup>48</sup> Cotton linters (20 g o.d.) were solvent exchanged with methanol and then benzene. The linters were treated with a solution of chloroacetic acid in dimethyl sulfoxide (4%, 320 mL) for 30 min. The slurry was filtered and the linters pad steeped in aqueous sodium hydroxide (1%, 320 mL) for 1 h to neutralize the excess acid. The product was filtered, washed with water, steeped in aqueous acetic acid (10%, 1 L), filtered, washed with water and converted to the sodium salt form by steeping in aqueous sodium bicarbonate (6%, 500 mL) overnight. The resulting sodium carboxymethyl cellulose was filtered and washed with water (S81, 2.14 meq/100g).

This procedure was repeated with minor variations, i.e. the carboxymethylation and neutralization steps were performed in sealed plastic bags to reduce degradation and reprotonation of the carboxymethyl cellulose was affected using 5% aqueous acetic acid, not 10% (S197, 7.28 meq/100g). Repetition of the procedure used in experiment S197, using 10% acetic acid solution for reprotonation, yielded a derivative with a substitution of 8.36 meq/100g (S235).

#### Preparation of Hydroxyethyl Cellulose

Cellulose was hydroxyethylated using modifications of several reported methods.<sup>53-55,58</sup>

Hydroxyethyl cellulose was first prepared using a modification of the procedure reported by Ward, Morak, Murray and Thomas.<sup>53</sup> Cotton linters (20 g o.d.) were combined with aqueous sodium hydroxide (22%, 250 mL) and mixed with a mechanical mixer (2 h). 2-Chloroethanol (100 g, 1.24 mol) was added with dichloromethane (800 mL) to the mixture, which was shaken and then left to stand (24 h). The spongy product was filtered, washed with water, neutralized in acetic acid (5%, 500 mL, 1 h), filtered, and washed with water (2 L). The product was characterized by <sup>13</sup>C NMR spectroscopy, but could not be made into handsheets for testing because of excessive swelling and hence, was not characterized further (S52).

Linters were also hydroxyethylated with reference to the work of Ward, Murray, Morak and Voelker.<sup>54</sup> In several unreported attempts using their procedure, the linters could not be filtered or isolated from the 30% aqueous sodium hydroxide solution used to swell the linters. Hence, cotton linters (20 g o.d.) were stirred with a mechanical stirrer (10 min) in a 10% aqueous sodium hydroxide solution (450 mL water). The swollen linters isolated by filtration (1 h), were then beaten with 2-chloroethanol (15.2 g, 0.19 mol) using a domestic mixer (1.5 h). To minimize

degradation, the mixer bowl was covered with a perspex disc and kept under nitrogen. The modified linters were neutralized with acetic acid (5%, 500 mL) filtered, and washed with water (2 L) (S191, 3.00% hydroxyethyl groups).

In a similar trial, a stronger sodium hydroxide solution was used (20%, 500 mL) and excess solution was removed by centrifugation (15 min), not filtration. The experiment was then continued according to the previous experiment, S191, giving a substitution of 1.82% hydroxyethyl groups (S195). The experiment was repeated again (2-chloroethanol, 15.7 g, 0.195 mol) using a 1 L reaction flask fitted with a mechanical stirrer. Mixing with this system was not as efficient as with the domestic mixer. A product with a substitution of 2.16% hydroxyethyl groups was obtained (S217).

The method reported by Klug<sup>58</sup> was also used as the basis for a low DS hydroxyethylation. The quantity of hydroxyethylating reagent was reduced to one quarter the amount cited and 2-chloroethanol was used instead of ethylene oxide. In a 2 L reaction flask, cotton linters (80 g o.d.), isopropanol (1270 mL) and aqueous sodium hydroxide (152 g of 15.8%) were combined with vigorous stirring. The slurry was stirred for 1 h in a nitrogen atmosphere. 2-Chloroethanol (10.82 g, 0.13 mol) was added and stirring continued for 1 h at ambient temperature. The slurry was then heated at 60°C for 1.5 h, cooled and filtered. The linters were redispersed in 70% aqueous methanol (1 L), neutralized with acetic acid, filtered and washed with 70% aqueous methanol (1 L) and water (2 L) (S316, 2.60% hydroxyethyl groups).

Further hydroxyethylations were performed with reference to a method reported by Harpman, Reid and Turner.<sup>55</sup> For ease of use, 2-chloroethanol was used in preference to ethylene oxide. Cotton linters (40 g o.d.) were steeped in a sodium hydroxide solution (10%, 400 mL) for 15 min and filtered. The filter cake was redispersed in isopropanol (400 mL) and 2-chloroethanol (4.2 g, 52 mmol), and

tumbled on a rotary evaporator (2 h) at ambient pressure, with heating at 60°C. Uneven colouration of the linters was noticed during the reaction, suggesting poor mixing. The slurry was filtered, steeped in aqueous acetic acid (pH 4), filtered and washed with water (2 L), (S261, 2.46% hydroxyethyl groups).

Experiment S261 was repeated at twice the scale and a 2 L reaction flask fitted with a mechanical stirrer was used to overcome the poor mixing of S261. Hydroxyethylated linters with a substitution of 1.45% were obtained (S318). Experiment S318 was then scaled up to 125 g o.d. cotton linters for use in double derivatizations yielding a product with a substitution of 1.97% hydroxyethyl groups (S396).

In a blank determination for use in pulp evaluation trials, experiment S318 was repeated without the addition of 2-chloroethanol (S390).

#### Preparation of Hydroxypropyl Cellulose

Hydroxypropyl cellulose was prepared using modifications of two reported methods. In an initial trial,<sup>55</sup> linters (40 g o.d.) were steeped in an aqueous sodium hydroxide solution (8%, 400 mL) for 15 min and filtered. The linters were transferred to a 1 L flask fitted to a rotary evaporator, propylene oxide (6.96 g, 0.120 mol) was distilled onto the linters, and the mixture tumbled for 8 h using a rotary evaporator at atmospheric pressure. The product was then redispersed in water, filtered and washed with water (S263, 1.04% hydroxypropyl groups).

The method by Klug<sup>58</sup> for the preparation of hydroxyethyl cellulose was used as the basis for another hydroxypropyl cellulose preparation, but propylene oxide was used at half the suggested molar quantity to lower the substitution level. Linters (80 g o.d.), washed with isopropanol, were combined with isopropanol (1270 mL) in a 2 L reaction flask fitted with a mechanical stirrer. Sodium hydroxide (152 g of 15.8%



solution) was added over 15 min and stirring continued for 1 h. Propylene oxide (15.65 g, 0.36 mol) was added and the slurry heated for 4 h at 60°C. The mixture was filtered, redispersed with aqueous methanol (1 L, 70%), neutralized with acetic acid, filtered, washed with aqueous methanol (1 L, 70%) and water (2 L), yielding a product with 3.08% hydroxypropyl groups (S265).

Hydroxypropyl cellulose was again prepared using a modification of Klug's method,<sup>58</sup> but the quantity of propylene oxide was doubled (31.4 g, 0.54 mol) and the mixture heated for only 2 h (S315, 1.20% hydroxypropyl groups).

Finally, the method described by Harpman, Reid and Turner<sup>55</sup> to prepare hydroxyethyl cellulose was used. Linters (80 g o.d.) were steeped in sodium hydroxide (800 mL, 10%) under nitrogen for 15 min and filtered. Propylene oxide (6.0 g, 0.103 mol) in isopropanol (790 mL) was added to the linters in a 2 L reaction flask. The slurry was heated at 50°C for 2 h under nitrogen. The product was filtered, neutralized with acetic acid and washed with water (S314, 1.03% hydroxypropyl groups).

### **Preparations in Section 2.3.2**

#### **Synthesis of Cellulose Mesylate**

Cellulose mesylate was synthesized using the method reported by Pacsu<sup>62</sup> and Wolfrom, Sowden and Metcalf.<sup>63</sup> Dry pyridine<sup>138</sup> was used in all trials.

In a typical preparation, linters (20 g o.d.) were steeped in aqueous sodium hydroxide (18%, 440 mL) for 1 h, filtered and washed with water. This was then solvent exchanged twice with dry pyridine. The filter cake was added to dry pyridine (500 mL) in a 1 L pear-shaped flask and cooled in an ice bath. Methanesulfonyl chloride (84.8 g, 0.74 mol) cooled in ice, was added by pipette to

the linters slurry, with vigorous shaking. The appearance of a salmon colour and later, a reddish-brown colour, indicated that the reaction was successful. The mixture was shaken for 48 h and the product isolated by filtration, washed with hot water (2 L), acetone and cold water (S70, 11.42% S).

Several alternative mesylation experiments were performed in an attempt to reduce the detrimental effect of this modification on the papermaking properties, i.e. the 1 h sodium hydroxide steep was omitted, reaction times were reduced to 24 h and lower amounts of methanesulfonyl chloride were used. A one-off trial using liquid ammonia as a solvent and stoichiometric quantities of pyridine was unsuccessful (S80, S < 0.5%). Details of these experiments are summarized in Table 2.3.

### **Preparations in Section 2.3.3**

#### **Synthesis of 6-Chloro-6-deoxy Cellulose**

6-Chloro-6-deoxy cellulose was prepared by reaction of cellulose with methanesulfonyl chloride,<sup>11</sup> and was used as an intermediate in several syntheses. The chloro-derivative of cellulose was prepared nine times with substitution levels ranging from 2.62 to 6.90% chloride.

In a typical preparation, cotton linters (10 g o.d.) were steeped in *N,N*-dimethylformamide for 2 h at 80°C, filtered and washed twice with fresh *N,N*-dimethylformamide. The filter cake was transferred to a 1 L three-neck round-bottom flask with methanesulfonyl chloride (75 mL) and *N,N*-dimethylformamide (750 mL). The slurry was heated at 95°C with a heating mantle for 48 h. The light brown coloured linters were filtered, washed with water, steeped for 4 h in aqueous sodium carbonate (400 mL, pH 9-10), filtered, washed and air-dried (5.13% Cl; 1.30% S).

**Table 2.3:** Preparation of Cellulose Mesylate Derivatives

Reaction Number	Cellulose (g o.d.)	NaOH Steep*	Mole Ratio of MeSO <sub>2</sub> Cl to Cellulose (1)	Dry Pyridine (mL)	Time (h)	Comments	Substitution (%S)	Z-Direction Tensile Index (% Change)
S50	10	220 mL, 1 h	6	250	48		0.46	—
S57	2.5	55 mL, 1 h	6	63	48	See S50, small scale	15.8	—
S63	10	220 mL, 1 h	6	250	48	Repeat of S50	0.89	—
S70	20	440 mL, 1 h	6	500	48	Repeat of S50, double scale	11.4	—
S80	10	150 mL Liq. NH <sub>3</sub>	6	50	1	Liq. NH <sub>3</sub> solvent	<0.5	-23
S86	20	—	6	450	24	Decreased time, no NaOH steep	7.34	-66
S103	2.6	—	1	63	24	See S86, 1:1 cotton : MeSO <sub>2</sub> Cl ratio	<0.1	—
S109	20	—	1	450	24	As above, 20 g o.d. scale	4.15	-13
S117	20	—	3	300	48	Increased time, 1:3 cotton : MeSO <sub>2</sub> Cl	6.53	-48
S125	20	—	0.5	450	24	2:1 Cotton : MeSO <sub>2</sub> Cl uneven substitution	< 0.3	—
S131	20	440 mL, 1 h	6	500	48	See S 57, 20 g o.d. scale	13.1	—

\* 18% Aqueous sodium hydroxide solution used

\*\* Molecular weight of cellulose approximated as 162 gmol<sup>-1</sup>

### Preparation of 6-Azido-6-deoxy Cellulose

This derivative was prepared from 6-chloro-6-deoxy cellulose according to the method reported by Horton, Luetzow and Theander.<sup>11</sup>

6-Chloro-6-deoxy cellulose (1.66 g o.d., S26, 3.8% Cl) was combined with sodium azide (3.38 g, 52 mmol) in *N,N*-dimethylformamide (160 mL). The slurry was heated using an oil bath (110°C) and stirred for 72 h. 6-Azido-6-deoxy cellulose was filtered from the solution and washed with water, giving a product with 3.7% nitrogen (S26). In another preparation with greater temperature variation, the azide derivative was prepared with 2.49% nitrogen (S62) from a chloro-derivative with 4.18% Cl (S62).

### Preparation of Iodo-deoxy Cellulose

Iodo-deoxy cellulose was prepared from the corresponding chloro- derivative for conversion to cyano-deoxy cellulose. The preparation was based on the method reported by Ishii.<sup>70</sup>

Chloro-deoxy cellulose (10.99 g, S62, 4.18% Cl) was combined with sodium iodide (5.18 g, 35 mmol) and *N,N*-dimethylformamide (100 mL) in a 250 mL round-bottom flask and refluxed for 18 h. The product was filtered and washed with water (S79, 0.46% I, 1.62% Cl).

Another two attempts were made to obtain the iodo- derivative with heating at 60°C and three-fold excesses of sodium iodide. However, both attempts were unsuccessful (S128, S130, I <0.1%).

### Synthesis of Fluoro-deoxy Cellulose

Fluoro-deoxy cellulose was prepared by reaction of cellulose mesylate with sodium or potassium fluoride.<sup>75,79</sup>

Three experiments were performed using sodium or potassium fluoride and diethylene glycol as the solvent. Cellulose mesylate (1.06 g, S70, 11.42% S) was combined with potassium fluoride (2.08 g, 36 mmol) and diethylene glycol (150 mL) in a 250 mL round-bottom flask fitted with a magnetic stirrer and reflux condenser. The mixture was refluxed for 18 h. The product was filtered from the solution and washed with water, ethanol and water (S94, 0.92% F, 5.44% S). This procedure was repeated and a product with 0.86% fluoride was obtained (S77). Using a ratio of 5:1 potassium fluoride to cellulose mesylate and only heating at 70°C for 6 h proved unsuccessful (S127, F <0.1%).

A trial using liquid ammonia as a solvent to prepare fluoro-deoxy cellulose was unsuccessful, according to elemental analysis (S90, F <0.1%).

### Synthesis of 6-Cyano-6-deoxy Cellulose

6-Cyano-6-deoxy cellulose was prepared from several precursors, viz. 6-chloro-6-deoxy cellulose, 6-iodo-6-deoxy cellulose and cellulose mesylate by reaction with potassium cyanide.

6-Chloro-6-deoxy cellulose (S26, 0.5 g o.d., 3.8% Cl) was reacted with aqueous potassium cyanide (0.2 g, 40 mL water) in a 100 mL round-bottom flask and stirred for 72 h. The product was filtered and washed with water (S30, 0.6% N). In a similar preparation using acetonitrile as a solvent and a reaction time of 6 h, higher substitutions were obtained (S39, 1.0% N, 3.5% Cl).

A method reported by Polyakov and Rogovin<sup>68</sup> was used as the basis for a further seven preparations. In these preparations *N,N*-dimethylformamide was used as a solvent and the mixture refluxed for 2 to 24 h. Substitution levels ranged from 0.07 to 0.14% nitrogen; chloride ranged from less than 0.1 to 4.04% remaining after reaction with cyanide.

6-Iodo-6-deoxy cellulose was used in two conversions to the cyano derivative. 6-Iodo-6-deoxy cellulose (S79, 0.70 g a.d., 0.46% I) was added to potassium cyanide (1.9 g, 29 mmol) in liquid ammonia (150 mL). The slurry was stirred until the liquid ammonia evaporated (20 min). The product was filtered, washed and dried (S87, 0.21% N, 0.37% I). In a second trial, 6-iodo-6-deoxy cellulose was heated with potassium cyanide in *N,N*-dimethylformamide as for previous trials (S100, 0.20% N, I < 0.1%).

The reaction of cellulose mesylate (S57, 1.0 g o.d., 15% S) with potassium cyanide (5.0 g, 77 mmol) in *N,N*-dimethylformamide (100 mL) at reflux for 24 h, yielded a product with 0.36% nitrogen (S65, S < 0.2%). In a similar experiment, 6-cyano-6-deoxy cellulose with 0.35% nitrogen (S76, S < 0.2%) was obtained from cellulose mesylate with 11.42% sulfur (S70). A third experiment was performed using reagents dried over silica gel and *N,N*-dimethylformamide dried over 4A molecular sieves, with refluxing for 2 h (S91, 0.32% N, 0.65% S). The preparation of cyano-deoxy cellulose from cellulose mesylate (S70, 2.2 g a.d., 11.42% S, 0.10% N) and potassium cyanide (6.33 g) in liquid ammonia (100 mL) was also attempted, giving a slight increase in nitrogen content (S83, 0.30% N, 10.02% S).

#### Attempted Preparation of 6-Amino-6-deoxy Cellulose

The preparation of 6-amino-6-deoxy cellulose was attempted using the method of Maiti, Singh and Micetich<sup>80</sup> for the reduction of azides to amines with stannous chloride.

6-Azido-6-deoxy cellulose (S26, 0.5 g, 3.7% N) was stirred with stannous chloride (1.37 g, 6.0 mmol) in methanol (10 mL) for 3 h. The derivative was isolated by filtration and washed with copious quantities of methanol (S29, 3.7% N). Infrared spectra indicated the nitrogen was present as the azide ( $\nu_{\text{N}_3}$  2116  $\text{cm}^{-1}$ ). A similar preparation using a longer reaction time was also unsuccessful (S95, 0.85% N).

An attempt to convert 6-chloro-6-deoxy cellulose to the amine by bubbling ammonia into the aqueous solution, followed by steeping in sodium bicarbonate was unsuccessful (S31, N <0.2%).

#### Treatment of Cellulose with Glyoxal

Glyoxal was reacted with cellulose using a reported method,<sup>142</sup> with some modifications. Four glyoxalation trials were performed, with one trial being on a small scale.

Linters (20 g o.d.) were combined with boric acid (2.0 g), glyoxal solution (30.7 g of 40% solution) and water (300 mL). The mixture was steeped for 4 h, filtered and washed with water. In another trial, the linters were stirred vigorously for 3 h, instead of steeping. Later trials followed the reported method<sup>140</sup> more closely, viz. after steeping, the linters were filtered, washed, and cured overnight at 110°C. The product was redispersed in hot water, filtered and washed with several lots of hot water. Because of the very poor papermaking properties of these modified linters, further characterization was not undertaken.

#### Treatments Involving Liquid Ammonia

Liquid ammonia was used as a solvent in several attempts to modify linters, but the papermaking properties of the linters were very poor in all cases and they were not characterized further.

Cellulose Carbamate: Linters (12 g o.d.) were combined with urea (20 g) dissolved in liquid ammonia (400 mL) and steeped overnight. The linters were isolated and washed with water. In the four trials conducted in this manner, elemental analysis results were <0.05%, <0.05%, 0.05% and 0.16% nitrogen (S96, S97, S105, S85).

In another trial, linters (20 g o.d.) were steeped in urea (75 g) and liquid ammonia (800 mL). After most of the ammonia had evaporated, the linters were oven-cured at 150°C for 30 min and washed (S142, 0.29% N).

Pyridine: Using the first method described for urea, three attempts were made to alter the crystallinity of linters by treating linters with pyridine in liquid ammonia (S84, 0.08% N; S98, N <0.05%; S107, N <0.05%).

#### **Preparations in Section 2.3.4**

##### Cationization of Cellulose

Cationization of cellulose was initially performed using the method of Schempp, Kaufer and Krause.<sup>81,82</sup> Cotton linters (20 g o.d.) were briefly shaken with aqueous sodium hydroxide (0.15 g in 445 mL H<sub>2</sub>O) and (3-chloro-2-hydroxypropyl)-trimethylammonium chloride (CHMAC) (2.90 g of a 60% solution) was then added. The mixture was shaken for 24 h, filtered and washed, but the reaction was unsuccessful according to elemental analysis (S124, N <0.05%).

The method of Antal, Paszner and Micko<sup>85</sup> was then used. In a typical preparation, linters (20 g o.d.), steeped in water (300 mL), were activated by vigorous stirring with sodium hydroxide (20 mL, 17.5% solution) for 20 min. CHMAC (20 mL) was added and the mixture heated in a water bath at 60°C for 2 h with stirring. The product was filtered, washed with 1% hydrochloric acid in ethanol (500 mL), washed with 80:20 ethanol:water (500 mL) and water (0.15% N).



An initial trial replicated Antal and co-workers'<sup>85</sup> attempts at high, medium and low level substitution (S126, 22.5 mL of 17.5% NaOH, 22.5 mL CHMAC, 0.22% N; 20 mL of each, 0.15% N; 17.5 mL of each, 0.13% N, respectively). The medium level substitution reaction was repeated numerous times, with consistencies ranging from 5.7% to 3% (i.e. 300 mL to 600 mL of water added) and substitution levels from 0.16 to 0.05% N, respectively (S139, S213).

Details of experiments aimed at increasing the substitution level of cationizations are given in Table 2.4.

**Table 2.4:** Cationization of Cellulose with  
(3-Chloro-2-hydroxypropyl)trimethylammonium Chloride  
(CHMAC)

Reaction Number	Cellulose (g o.d.)	Ratio of *NaOH: CHMAC:H <sub>2</sub> O (in mL) to Cellulose (g)	Time (h)	Temp. (°C)	Comments**	Substitution (%N)	Z-Direction Tensile Index (%Change)
S276	40	3 : 3 : 15	2	60	3x(CHMAC) 3x(NaOH)	0.38	***
S277	20	1 : 3 : 15	2	60	3x(CHMAC)	<0.1	—
S278	20	1 : 3 : 15	2	90	3x(CHMAC) Higher temp.	<0.1	—
S279	20	5 : 5 : 15	2	60	5x(CHMAC) 5x(NaOH)	0.47	***
S283	20	5 : 5 : 15	0.25	90	As above, higher temp. shorter time	0.43	-14

\* 17.5% aqueous solutions of NaOH and CHMAC used.

\*\* Relative to medium level substitution method.

\*\*\* Freeness values too low to extrapolate.

## **2.7.4 Preparations of Michael Addition Derivatives of Cellulose**

### **(Section 2.4)**

#### General Michael Addition Reaction Methods

Numerous Michael addition reactions were performed using the procedure described below, which was developed from reported methods.<sup>53,95,98</sup>

Cotton linters (20 g o.d.) were combined with sodium hydroxide (32 g) and the Michael addition reagent (160 g) in water (800 mL), i.e. in a ratio of 1:1.6:8:40, respectively. The slurry was stirred (15 min), sealed in a polyethylene bag and then heated in a water bath (2 h, 60°C). The slurry was then cooled and filtered, giving a filter cake that was heated in an oven (15 min, 145°C). The cake was redispersed in water, filtered, washed with water, redispersed, filtered and washed with more water. In some preparations, the reaction mixture was not filtered prior to heat treating (15 min, 145°C) and was heated as a slurry. In the tables used throughout this section, the reaction time refers to the temperature quoted in the same row of the table.

#### **Preparations in Section 2.4.2**

##### Preparation of Cyanoethyl Celluloses

Cotton linters were cyanoethylated in 24 trials using modifications of several reported methods.<sup>55,94,95</sup> The reference to each general method and the experimental conditions used are summarized in Tables 2.5 and 2.6.

##### Method A - Based on Compton's DS 1.0 Method:<sup>94</sup>

In a typical preparation, cotton linters (20 g o.d.) were steeped in aqueous sodium hydroxide (2%, 2 L) for 2 h, filtered and rinsed with water. The linters pad was then

combined with acrylonitrile (1.5 L) in a 3 L round-bottom flask fitted with a reflux condenser. The slurry was refluxed vigorously for 5 min, cooled, filtered, washed with water and steeped in aqueous acetic acid (5%, 2 L), filtered, washed with water and ethanol, redispersed with water, filtered, washed with diethyl ether and finally with water (S66, 4.96% N). Substitution levels using this method and modifications as in Table 2.6 ranged from 8.25% nitrogen (S5) to below detectable limits (S49, N <0.05%). The main variations performed included scaling up the preparation for pulp evaluation and the use of different sources of cotton linters (Table 2.5).

Trial S6 was based on Method A, with 6% aqueous sodium hydroxide being used and a longer steeping time (18 h) in an attempt to effect higher substitutions. According to elemental analysis, a product with 2.90% nitrogen was obtained.

Method B - Based on Compton's DS 0.25 Method:<sup>94</sup>

Raw cotton linters (20 g o.d.) were stirred with an aqueous solution of sodium hydroxide and urea (2% each, 200 mL) with cooling. Acrylonitrile (3.25 g, 0.5 mol) was added and stirring continued for 45 min. The slurry was then neutralized with aqueous acetic acid (10%, 35 mL), filtered and stirred vigorously during the addition of aqueous ethanol (50%, 500 mL). The filtered and washed cyanoethylated raw cotton linters contained 0.51% nitrogen (S22). Substitution levels of 0.15% nitrogen (S58) and 1.0% nitrogen (S37) were obtained for Shoalhaven cooked and bleached linters and cotton linters received from ICI, respectively (Table 2.5).

Method C - Based on Harpman, Reid and Turner's DS 0.06 Method:<sup>55</sup>

Experiments S18, S67, S71, S160, S182 and S184 were based on the low DS method reported by Harpman, Reid and Turner.<sup>55</sup> In a typical preparation, acrylonitrile (5.76 g, 0.11 mol) was added gradually to aqueous sodium hydroxide (6%, 370 mL) and cotton linters (20 g o.d.) at ambient temperature and the slurry stirred (2 h). The reaction was stopped by the addition of aqueous acetic acid (20%, 200 mL) to pH 5; stirring was continued for 1 h. The filtered and washed product contained 0.10%

**Table 2.5:** Preparation of Cyanoethyl Celluloses - Methods A and B\*

Reaction Number (Method)	Cellulose (g o.d.)	Ratio of NaOH : Acrylonitrile : H <sub>2</sub> O to Cellulose (1) **	Time (h)	Temp. (°C)	Comments	Substitution (%N)	Z-Direction Tensile Index (% Change)
S5 (A)	3.0 <sup>#</sup>	2 : 50 : 100	2 0.25	RT <sup>+</sup> 74	Small scale	8.25	—
S6 (A)	5.0 <sup>#</sup>	6 : 50 : 100	18 0.5	RT 74	6% NaOH	2.90	—
S40 (A)	30 <sup>#</sup>	3.3 : 27 : 167	2 0.25	RT 74	Lower consistency, large scale	6.1	—
S41 (A)	30 <sup>##</sup>	3.3 : 27 : 167	2 0.25	RT 74	As above, ICI cotton	3.7	—
S49 (A)	20	2 : 20 : 100	4 0.25	RT 74	See S5, large scale	<0.05	—
S51 (A)	20	5 : 40 : 250	4 0.25	RT 74	Lower consistency, increased NaOH	0.27	NS <sup>++</sup>
S53 (A)	20	2 : 40 : 100	4 0.25	RT 74	See S49	0.08	NS
S66 (A)	20	2 : 60 : 100	2 0.25	RT 74	As above, decreased time	4.96	-25
S69 (A)	20	1 : 20 : 50	0.25	RT	No NaOH steep, double consistency	1.39	NS
S22 (B)	20 <sup>#</sup>	0.2 : 0.16 : 10	0.5 0.5	0 RT	No NaOH steep, not pressed	0.07	—
S37 (B)	25 <sup>##</sup>	0.1 : 0.16 : 5	0.5 0.5	0 RT	Double consistency	1.0	—
S58 (B)	20	0.1 : 0.16 : 5	0.5 0.5	0 RT	As above	0.15	-8

\* Refer to text for details of Method and work-up procedures.

\*\* Bath of acrylonitrile used in Method A. Urea added at same ratio as NaOH in Method B.

+ Room temperature.

++ Not significant (< 5% change).

# Raw cotton linters from Shoalhaven Mill.

## Cotton from ICI Australia Pty. Ltd.

nitrogen (S67). Reaction conditions were varied to assess the effect of changes on substitution levels and papermaking properties (refer to Table 2.6).

#### Method D:

Cyanoethylations S249, S250 and S312 were adapted from a procedure reported by Frick *et al.*<sup>95</sup> for treating fabrics with acrylamide. Typical procedures are described in the general Michael addition reaction method and details are given in Table 2.6.

**Table 2.6: Preparation of Cyanoethyl Celluloses - Methods C and D<sup>+</sup>**

Reaction Number (Method)	Cellulose (g o.d.)	Ratio of NaOH : Acrylonitrile : H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (%N)	Z-Direction Tensile Index (% Change)
S18 (C)	20	1.2 : 0.3 : 20	2	RT <sup>++</sup>	Raw linters	0.31	-
S67 (C)	20	1.2 : 0.3 : 20	2	RT	As above	0.10	NS <sup>+++</sup>
S71 (C)	20	0.4 : 0.3 : 20	1	RT	Decreased NaOH and time	0.08	NS
S160 (C)	20	* : 0.3 : 20	1	RT	As above, NH <sub>4</sub> OH solution	0.11	NS
S182 (C)	20	0.4 : 0.3 : 20	2	60	See S71, sealed bag, heated	0.06	NS
S184 (C)	20	0.4 : 0.3 : 20	4	RT	See S182, no heating, increased time	0.40	NS
S249 (D)	20	1.6 : 8 : 40	0.25	145	20% Acetic acid steep	1.70	-
S250 (D)	20	S249 filtrate used	0.25	145	As above	0.78	-15
S298 (D)	125	1.6 : 2 : 40	0.5 0.25	RT 145	**Quarter acrylonitrile, unfilterable	-	-
S312 (D)	125	1.6 : 2 : 40	0.5 0.25	RT 145	**Quarter acrylonitrile	1.28	+15

+ Refer to text for description.

++ Room temperature.

+++ Not significant (< 5% change).

\* NH<sub>4</sub>OH solution used (25%).

\*\* Relative to general Michael addition reaction method.

### Preparation of Amidoethyl Cellulose

Amidoethyl cellulose was prepared using modifications of two reported methods.<sup>53,95</sup> A summary of the experimental conditions used in the eighteen trials are shown in Table 2.7.

The method of Ward, Morak, Murray and Thomas<sup>53</sup> essentially involved steeping the cellulose in an aqueous solution of sodium hydroxide (4%) and acrylamide (20%) for 4 h. The slurry was filtered and the filter cake heated in an oven at 115°C for 15 min. The product was then redispersed, filtered and washed with water (polyacrylamide, if any formed, is water-soluble and would be readily removed by washing with water).<sup>143</sup> The quantities of reagents and conditions were varied as shown in Table 2.7. Some experiments were conducted in a sealed plastic bag to enable higher consistencies to be used and to reduce fibre damage by excluding oxygen.

The procedure adopted by Frick, Reeves and Guthrie<sup>95</sup> was similar to Ward and co-workers,<sup>53</sup> except that reaction times were reduced to the oven-curing time, with virtually no steeping time.

### Reaction of *N,N*-Methylenebisacrylamide with Cellulose

*N,N*-Methylenebisacrylamide (MBA) was reacted with cellulose according to the procedure used for the analogous acrylamide derivative. In most trials, lower quantities of MBA were used, and the product was not oven-cured because of MBA's tendency to polymerize violently on heating. However in later trials, heating was applied and higher concentrations of MBA were used. Details of these different trials are given in Table 2.8.

**Table 2.7: Preparations of Amidoethyl Cellulose**

Reaction Number	Cellulose (g o.d.)	Ratio of NaOH : Acrylamide : H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (%N)	Z-Direction Tensile Index (% Change)
S10	3.13	1.6 : 8 : 40	4 8 min	RT* 115	Small scale	0.89	-
S55	20	1.6 : 8 : 40	4 8 min	RT 115	20 g o.d. scale	0.75	+33
S121	20	1.6 : 4 : 40	4 0.25	RT 115	Halved acrylamide	0.25	+11
S122	20	0.8 : 2 : 40	4 0.25	RT 115	1/2 NaOH, 1/4 acrylamide	0.09	NS**
S141	15	1.6 : 2 : 40	4 0.25	60 115	Extra heating, 1/4 acrylamide	0.19	-14
S162	20	0.8 : 2 : 20	4 0.25	RT 115	Double consistency <sup>+</sup>	0.26	+12
S200	125	0.48 : 1.2 : 12	4 0.25	RT 115	High consistency, 125 g o.d. scale	0.25	+26
S201	125	0.48 : 1.2 : 12	4 0.25	RT 115	As above	0.27	+20
S202	20	1.6 : 4 : 40	4 0.25	RT 115	See S121, filt. problems	0.38	+33
S203	20	1.6 : 4 : 40	4 0.25	RT 115	As above, filt. problems	0.34	+9
S226	40	1.6 : 4 : 40	4 0.25	RT 115	Double batch	0.51	+31
S230	20	1.6 : 4 : 40	24 0.25	RT 115	Increased time, filt. problems	0.58	+26
S233	20	1.6 : 4 : 40	8 0.25	RT 115	See S203, increased time, filt. problems	0.57	NS
S246	20	1.6 : 8 : 40	0.25 0.25	RT 145	Stirred <sup>++</sup>	0.23	-10
S247	20	1.6 : 8 : 40	0.25 0.25	RT 145	As above, <sup>++</sup> filter cake	0.46	+10
S313	125	1.6 : 4 : 40	0.5 0.25	RT 145	NaOH steep (0.5 h) <sup>++</sup>	0.67	+27
S342	20	1.6 : 8 : <sup>+++</sup>	2 0.25	60 180	DMF solvent, filter cake <sup>++</sup>	0.30	-9
S343	20	1.6 : 8 : <sup>+++</sup>	0.25 0.25	RT 180	See S342, <sup>++</sup> decreased time and temp.	0.15	-39

\* Room temperature.

\*\* Not significant (&lt;5% change).

+ Sealed bag used for S162 to S343.

++ Refer to text (based on method of Frick, Reeves and Guthrie).

+++ 50 : 50 *N,N*-Dimethylformamide : water used as a solvent (800 mL).

**Table 2.8: Preparations of *N,N*-Methylenebisacrylamide (MBA) Derivatives of Cellulose**

Reaction Number	Cellulose (g o.d.)	Ratio of NaOH : MBA : H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (%N)	Z-Direction Tensile Index (% Change)
S133	2.0	2 : 1 : 50	4	RT***	Slow filtering	0.07	-
S134	2.0	2 : 0.5 : 50	24	RT	Increased time, halved MBA	0.18	-
S148	20	2 : 0.5 : 50	24	RT	20 g o.d. scale	0.15	-25
S170	20	2 : 0.5 : 50	4	RT	Decreased time	0.06	NS****
S198	20	1.6 : 0.5 : 40	4	RT	Higher consistency*	<0.05	-
S199	20	1.6 : 0.5 : 40	4 0.25	RT 110	Heat treated, filter cake*	<0.05	-
S207	20	2 : 0.5 : 50	8	RT	See S170, doubled time	0.06	NS
S208	20	2 : 0.5 : 50	8	RT	As above**	0.05	+10
S224	20	1.6 : 0.5 : 40	4	60	See S198, increased temp.	0.09	-6
S225	20	1.6 : 1 : 40	4	RT	See S198, doubled MBA	0.12	-8
S227	20	1.6 : 0.5 : 40	4 0.25	60 110	See S224, heat treated	0.10	-8
S282	20	1.6 : 4 : 40	0.25 0.25	RT 145	Increased MBA eight- fold	0.61	-11
S295	20	1.6 : 4 : 40	0.5 2	RT 60	NaOH steep (0.25 h)*	4.14	-59
S371	20	1.6 : 4 : 40	0.25 2 0.25	RT 60 145	*	1.45	-50
S403	125	1.6 : 4 : 40	0.25 0.25	RT 145	See S282, large scale	0.12	NS

\* Experiments performed in sealed bags

\*\* Checking effect of using sealed bags

\*\*\* Room temperature

\*\*\*\* Not significant (< 5% change)



### Reaction of *N*-(3-Aminopropyl)methacrylamide Hydrochloride with Cellulose

The procedure for the preparation of the cellulose derivative of *N*-(3-aminopropyl)methacrylamide, APMA, was based on previous amidoethyl cellulose preparations.

In a small scale preparation under argon, cotton linters (1.25 g o.d.) were combined with an aqueous solution (50 mL) of sodium hydroxide (2.17 g) and APMA (10.22 g) in a 250 mL round-bottom flask, fitted with a magnetic stirrer. The slurry was heated using a hot water bath (60°C), stirred for 3 h, filtered, oven-cured (15 min, 145°C), redispersed, filtered, washed with water, methanol and water (S252, 0.80% N). On repetition, a product with a slightly lower substitution level was obtained (S285, 0.62% N).

In a trial using 20 g o.d. of cotton linters, a 1:10 APMA solution (80.4 g, 800 mL water) and sodium hydroxide (32.1 g) were stirred in a 2 L reaction flask and heated at 60°C for 2 h. The mixture became a reddish-brown colour after heating. The work-up procedure was the same as for previous APMA trials (S301, 0.27% N).

A final trial involving less severe reaction conditions was performed in which the linters (20 g o.d.) were steeped in a sodium hydroxide solution for 5 min (32 g, 800 mL water) and APMA (80 g) was added undissolved. The mixture was stirred for 15 min at ambient temperature and the same colour change noted. The same work-up procedure was used as in other APMA trials. According to elemental analysis results, this trial was unsuccessful (S374, N <0.1%).

### Reaction of Methacrylamide with Cellulose

Cotton linters (20 g o.d.) were steeped in an aqueous solution of sodium hydroxide (32 g, 800 mL water) for 15 min. Methacrylamide (80 g or 160 g) was added and

the mixture heated in a sealed bag (2 h, 60°C), filtered, oven-cured (15 min, 145°C) and washed with water, ethanol and water. These conditions were varied in an attempt to facilitate substitution (see Table 2.9).

**Table 2.9 : Reactions of Methacrylamide with Cellulose**

Reaction Number	Cellulose (g o.d.)	Ratio of NaOH : Methacrylamide : H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (%N)	Z-Direction Tensile Index (%Change)
S302	20	1.6 : 4 : 40	2 0.25	60 145	Sealed bag, filter cake	<0.1	-
S304	20	1.6 : 8 : 40	2 0.25	60 145	Double reagent	0.12	+15
S319	40	1.6 : 8 : 40	2 0.25	60 145	As above	<0.1	-
S320	20	1.6 : 4 : 40	4 0.25	60 145	Doubled reaction time, sealed bag	0.08	NS**
S340	20	1.6 : 8 : 40	2 0.25	60 145	See S304, slow filtering	<0.1	-
S341	20	1.6 : 8 : 40*	2 0.25	60 145	As above, EtOH solvent	<0.1	-
S375	20	1.6 : 8 : 40	18 0.25	60 145	Increased time, slow filtering	0.09	-13

\* 50 : 50 Ethanol : water used.

\*\* Not significant (< 5% change).

#### Reactions of Methacrylonitrile with Cellulose

The first trial with methacrylonitrile was performed using standard procedures (e.g. see S304 in Table 2.9), but was unsuccessful (S303, N <0.1%). Increasing the reaction time to 24 h, with heating for 18 h, yielded a product with 0.17% nitrogen (S332). This experiment was repeated using 50% aqueous ethanol as a solvent, but this was also unsuccessful (S333, N <0.1%).

Attempted Reaction of 2-Acrylamidoglycolic Acid Monohydrate and 2-Acrylamido-2-methyl-1-propanesulfonic Acid with Cellulose

The attempted preparation of these cellulose derivatives was based on reactions of acrylamide with cellulose, but much lower quantities were used in most trials.

In a typical preparation, cotton linters (20 g o.d.) were combined with an aqueous solution of sodium hydroxide (32 g, 800 mL water) in a 1 L Erlenmeyer flask. 2-Acrylamidoglycolic acid monohydrate (19.96 g, 0.122 mol) was added and the mixture heated for 3 h, with the flask wrapped in aluminium foil to exclude light. The amber-coloured mixture was filtered, washed with water, steeped in acetic acid (5%, 500 mL), filtered, washed, steeped in aqueous sodium bicarbonate (6%, 1 L) for 30 min, filtered and washed with water. According to elemental analysis results, no substitution took place (S156, N <0.05%).

Reaction conditions were varied in an attempt to effect substitution, as shown in Table 2.10. The presence of nitrogen in the second trial was attributed to the different washing technique used.

Trials with 2-acrylamido-2-methyl-1-propanesulfonic acid were performed using the procedures given in Table 2.10. According to elemental analyses, no nitrogen was detected in the fibres (S159, S190, S204, S384, S386, N <0.05%), except for the second trial and this was probably due to traces of unreacted starting material (S176, 0.05% N).

**Table 2.10:** Attempted Reaction of 2-Acrylamidoglycolic Acid Monohydrate (AGA) with Cellulose

Reaction Number	Cellulose (g o.d.)	Ratio of NaOH:AGA: H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp (°C)	Comments	Substitution (%N) *	Z-Direction Tensile Index (% Change)
S156	20	1.6 : 1 : 40	3	60	Neutralized,** Na salt form	<0.05	-
S177	20	2.4 : 1 : 40	3 0.25	60 115	Stronger NaOH; acid form	0.05	-
S189	20	1.8 : 0.75 : 32	3 0.25	60 115	Higher consistency, Na salt	<0.05	-
S205	20	2.4 : 1 : 40	3 0.25	60 115	Repeat of S177	<0.04	-
S383	1	1.6 : 8 : 40	24	60	Small scale, increased time and AGA conc.	<0.1	-
S385	20	1.6 : 8 : 40	2 0.25	60 145	General Michael addition reaction conditions	<0.1	-

\* Elemental analysis results as reported by Canadian Microanalytical Services.

\*\* See description in text for details.

#### Attempted Reaction of [3-(Methacrylamido)propyl]trimethylammonium Chloride with Cellulose

In a one-off trial, cotton linters (20 g o.d.) were combined with an aqueous solution of sodium hydroxide and [3-(methacrylamido)propyl]trimethylammonium chloride (32 g, 321 g of a 50% solution, respectively in a total of 800 mL of water), mixed thoroughly, sealed in a plastic bag, and heated at 60°C for 2 h. The resulting brown solution was cooled, filtered, oven-cured (15 min, 145°C), redispersed, filtered,

washed with water, redispersed, filtered and washed again. According to elemental analysis, no substitution took place (S395, N <0.1%).

#### Attempted Reaction of Acrolein with Cellulose

Two attempts were made to react acrolein with cellulose using the general Michael addition reaction method. Cotton linters (20 g o.d.) were combined with aqueous sodium hydroxide (32.3 g, 800 mL water) and stirred for 5 min. Acrolein (80 g) was added to the slurry and some effervescence noted, along with a colour change to yellow. The slurry was stirred (30 min), filtered and washed with water (1 L), ethanol (1 L) water, ethanol (1 L), diethyl ether (600 mL) and water; the pulp changed colour from orange to pale yellow upon washing (S406). In a similar trial, acrolein was added in two batches; the gas evolution and colour change noted in the previous preparation were not apparent (S409). However, a standard test<sup>13</sup> for the presence of aldehydes using 2,4-dinitrophenylhydrazine was negative for both trials.

#### Preparations in Section 2.4.3

##### Preparation of Maleic Acid Derivatives of Cellulose

Maleic acid derivatives of cellulose were prepared using a modification of the method reported by Frick, Reeves and Guthrie<sup>95</sup> and the methods used to prepare other Michael addition derivatives.

Details of experimental conditions are presented in Table 2.11. Conditions were varied to assess the effects of changing steeping times, the concentration of maleic acid, consistency, the use of disodium maleate, conversion to the sodium salt and oven-curing as a slurry or filter cake.

**Table 2.11: Preparation of Maleic Acid-Cellulose Derivatives**

Reaction Number	Cellulose (g o.d.)	Ratio of NaOH : Maleic Acid :H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (meq/100g)	Z-Direction Tensile Index (% Change)
S222	20	1.6 : 8 : 40	0.25	145	Slurry <sup>+</sup>	3.95	+36
S244	20	1.6 : 8 : 40	0.25	145	Combined NaOH and maleic acid	5.53	-10
S273	125	0.8 : 2 : 20	0.5	145	Double consistency, 125 g o.d. scale	10.18	-7
S274	125	0.8 : 2 : 40	0.25 0.5	RT* 145	As above, <sup>++</sup> filter cake	12.86	NS**
S293	125	1.6 : 8 : 40	0.5 0.25	RT 145	Na <sub>2</sub> maleate, 125 g o.d. scale, filter cake	8.97	NS
S294	20	1.6 : 8 : 40	0.25 0.25	RT 145	See S222 <sup>++</sup>	5.06	NS
S339	20	1.6 : 8 : 40	0.25 0.25	RT 145	See S222 <sup>++</sup>	11.90	NS
S349	20	1.6 : 4 : 40	0.25 0.25	RT 145	Halved maleic acid, <sup>++</sup> slurry	3.61	-27
S350	20	1.6 : 8 : 40	15 15	RT 145	Na salt form, <sup>++</sup> filter cake	-	-21
S351	20	1.6 : 8 : 40	2 0.25	60 145	Increased time and temp., <sup>+++</sup> sealed bag, filter cake	-	-18
S372	20	1.6 : 8 : 40	0.25	145	Zero steep time, slurry	-	+12
S373	20	1.6 : 8 : 40	0.25 0.25	RT 145	Maleic acid steep only, slurry	-	NS

\* Room temperature.

\*\* Not significant (&lt; 5% change).

+ Maleic acid added to NaOH-cellulose solution.

++ 15 min NaOH steep prior to addition of maleic acid.

+++ Standard Michael addition reaction conditions used.

### Preparation of Maleic Diamide

Maleic diamide was prepared using the method reported by Rinkes.<sup>119</sup> In a typical preparation, dimethyl maleate (26.2 g, 0.18 mol) and aqueous ammonia (78 mL, 25%) were cooled in an ice bath for several hours prior to reaction. The maleate and ammonia were combined in a 250 mL round-bottom flask, with stirring; the flask was covered with aluminium foil and cooled in an ice bath for 3 h. The white crystalline product was filtered, washed with methanol, dried in a vacuum oven and stored in the dark (S135, 10 g, 49% yield). The second crop of crystals was not isolated or purified in this trial. Elemental analysis results were as follows: found (calc for  $C_4H_6N_2O_2$ ), C 41.9 (42.0), H 5.4 (5.3), N 24.2 (24.5)%.  $^{13}C$  NMR chemical shifts in dimethyl sulfoxide- $d_6$ : 172 ppm,  $CONH_2$ ; 137 ppm  $C=C$ .

This preparation was repeated numerous times with yields up to 60% being obtained. Yields were improved by cooling the reagents in a freezer for several hours, in preference to using an ice bath. In most trials, a second crop of product was isolated and washed, but this frequently gave incorrect elemental analysis results.

### Attempted Reaction of Maleic Diamide with Cellulose

Attempts were made to react maleic diamide with cellulose in a series of experiments using different reaction conditions. According to elemental analysis all trials were unsuccessful (N <0.1%). In a small scale trial, cotton linters (2 g o.d.) were combined with aqueous sodium hydroxide (4%, 100 mL) and maleic diamide (S135, 2.0 g) in a 250 mL round-bottom flask and stirred for 2 h. The product was filtered and washed with water, ethanol and water (S136, N <0.05%). This procedure was repeated with heating at 80°C for 4 h but was again unsuccessful (S147, N <0.05%). In another trial, cotton linters (20 g o.d.) were solvent

exchanged with *N,N*-dimethylformamide, and then added to sodium hydroxide (32 g) and maleic diamide (S135, 5.1 g) in *N,N*-dimethylformamide (500 mL), sealed in a plastic bag and heated at 80°C for 4 h, cooled, filtered and washed with water (1 L) (S179, N <0.05%).

A final attempt using larger quantities of maleic diamide (S411 and S413, 80 g), as per the general Michael addition reaction method was unsuccessful (S416, N <0.1%).

#### Attempted Reaction of Maleimide with Cellulose

Cotton linters (0.6 g o.d.) were stirred with aqueous sodium hydroxide (1.0 g, 25 mL water) and maleimide (5.1 g) in a 150 mL round-bottom flask under argon and heated using a water bath (3 h, 60°C). The linters were filtered, oven-cured (15 min, 145°C), redispersed, filtered and washed with water, methanol and water. According to elemental analysis no substitution occurred (S251, N <0.06%).

#### Attempted Reaction of Maleic Hydrazide with Cellulose

Cotton linters (2.0 g o.d.) were combined with an aqueous solution of sodium hydroxide (2%, 100 mL) and maleic hydrazide (2.50 g, 22 mmol). The mixture was stirred for 4 h, filtered, steeped in acetic acid (250 mL, 5%), filtered, washed with water, ethanol and water. Based on elemental analysis results, no maleic hydrazide was substituted on the fibres (S110, N <0.05%).

#### Preparation of Itaconic Acid Derivatives of Cellulose

These preparations were also performed with reference to amidoethyl cellulose preparations, and Frick, Reeves and Guthrie.<sup>95</sup> Details are cited in Table 2.12. Benzyltrimethylammonium hydroxide<sup>95</sup> was used as a catalyst in the first trial of



itaconic acid with cellulose and higher consistencies were used because of the limited availability of this catalyst.

**Table 2.12:** Preparation of Itaconic Acid-Cellulose Derivatives

Reaction Number	Cellulose (g o.d.)	Ratio of NaOH: Itac. Acid:H <sub>2</sub> O to Cellulose (1)	Time (h)	Temp. (°C)	Comments	Substitution (meq/100g)	Z-Direction Tensile Index (% Change)
S256*	20	* : 4.5 : 30	0.25 0.25	RT** 145	Filter pad, high consistency	—	NS***
S326	20	1.6 : 4 : 40	0.25 0.25	RT 145	Oven cured as slurry	5.13	+15
S327	20	1.6 : 4 : 40	0.25 0.25	RT 145	Filter pad	7.91	+20
S367	125	1.6 : 4 : 40	0.25 0.25	RT 145	Large scale, 15min NaOH steep, stirred, filter pad	8.29	+9
S368	40	0.8 : 4 : 20	0.25 0.25	RT 145	Double consistency, 20min NaOH steep, filter pad	9.33	NS
S369	20	1.6 : 8 : 40	0.25 0.25	RT 145	Doubled reagent, NaOH steep	13.37	NS

\* Benzyltrimethylammonium hydroxide (36 g) used as a catalyst, in preference to sodium hydroxide in this trial.

\*\* Room temperature.

\*\*\* Not significant (< 5%).

#### Reactions of Fumaric, Acrylic, Methacrylic, Citraconic, Crotonic and *trans*-Cinnamic Acids with Cellulose

Fumaric, acrylic, methacrylic, citraconic (methylmaleic), crotonic and *trans*-cinnamic acids were reacted with linters in one-off trials using the general

Michael addition reaction method (using 20 g o.d. of cotton linters). Reactions with fumaric and *trans*-cinnamic acids were performed using a 50% ethanol:water mixture to improve solubility; ethanol was also used in the work-up procedure. Only the fumaric acid-cellulose derivative (S363), which showed any promise in bonding improvements, was characterized (carboxyl content 13.16 meq/100g).

### **2.7.5 Preparations of Double Derivatives and Blends of Cellulose** **(Section 2.5)**

#### **Preparations in Section 2.5.1**

##### **Carboxymethylation of Cationized Cellulose**

Cotton linters were cationized using the medium level substitution method (Section 2.6.3, 3.6% consistency, S212, 0.05% N) and then carboxymethylated using the procedure described for carboxymethylation S235 in Section 2.6.3. According to elemental analysis of the product, no nitrogen was present (S214, N <0.04%).

The above carboxymethylation procedure was repeated on two-thirds the scale of experiment S235 using, as the starting material, cationized linters prepared at 5.7% consistency (S231, 0.13% N). After carboxymethylation, a product containing 0.12% nitrogen and a carboxymethyl content of 8.72 meq/100g was obtained (S241).

##### **Preparation of Cationized Amidoethyl Cellulose**

The amidoethyl cellulose was prepared using the method described for S313 (Table 2.7) on the 20 g o.d. scale, and was reacted with (3-chloro-2-hydroxypropyl)-trimethylammonium chloride using standard cationization conditions (medium level substitution method in Section 2.7.3) to yield a product with 0.82% nitrogen (S348).

This was repeated twice yielding products with 0.12 and 0.31% nitrogen (S388 and S405, respectively).

### Secondary Derivatives of Hydroxyethyl Cellulose

The methods used to prepare the acrylamide, maleic acid and *N,N*-methylenebisacrylamide derivatives of hydroxyethyl cellulose are described in Table 2.13.

**Table 2.13:** Preparations of Double Derivatives of Hydroxyethyl Cellulose (HEC)

Reaction Number	Reagent Added onto HEC	Methods Used to Add Reagent	HEC <sup>+</sup> Used	Substitution (% N)	Substitution (% Hydroxyethyl Groups)	Comments	Z-Direction Tensile Index (% Change)
S262	Acrylamide	S230*	S261	1.31	2.40	Could not be filtered or washed properly	—
S336	Acrylamide	See S313,* treated for 2 h at 60°C	S318	0.81	1.30	As above, decreased time, heated	—
S410	Acrylamide	See S313, 20 g scale	S396	0.51	1.95	Decreased time and temp.	+43
S338	<i>N,N</i> -Methylenebisacrylamide	S282**	S318	0.31	1.49	As above	NS <sup>+++</sup>
S337	Maleic Acid	S349***	S318	4.61 <sup>++</sup>	1.49	As above, EtOH wash	NS

+ See preparations described in Section 2.6.3.

++ Carboxyl content (meq/100g).

+++ Not significant (< 5% change).

\* See Table 2.7.

\*\* See Table 2.8.

\*\*\* See Table 2.11.

The three hydroxyethylated celluloses used in these double derivatizations (S261, S318 and S396) were prepared using the method described for trial S261 in Section 2.6.2.

### Attempted Preparations of a Maleic Acid-Treated Amidoethyl Cellulose Derivative

In a one-pot reaction, cotton linters (20 g o.d.) were stirred with an aqueous sodium hydroxide solution (32 g in 600 mL) for 15 min, partially dissolved acrylamide (80 g in 100 mL water) was added with stirring, followed by the addition of a slurry of maleic acid (80 g in 100 mL water); the temperature of the slurry increased markedly. Stirring was continued for a further 15 min and the mixture filtered, oven-cured (15 min, 145°C), redispersed, filtered, washed with water (2 L), hot water (600 mL), redispersed, filtered and rewashed with water (1 L). According to elemental analysis no nitrogen was present on the fibres (S344, N <0.1%). A similar trial using twice the quantity of acrylamide was also unsuccessful (S370, N <0.1%). These derivatives were not characterized further in view of the failure of the amidoethylation.

### Cationized Maleic Acid-Cellulose Derivative

Cotton linters were treated with maleic acid using the method described for S349 in Table 2.11 (3.61 meq/100g) and then cationized as usual (S345, 0.21% N, 4.13 meq/100g). These reactions were performed separately to avoid preferential reaction of the cationizing reagent with maleic acid, instead of with the maleic acid-cellulose derivative.

### Maleic Acid-Treated Cationized Cellulose Derivative

In the converse of trial S345, linters were cationized first and then treated with maleic acid using the same methods (S347, 0.18% N, 3.95 meq/100g).

### Preparations in Section 2.5.2

Anionic and cationic cellulose derivatives prepared by separate reactions were physically combined in the ratios 80:20, 60:40, 40:60, and 20:80 based on oven-dry weights, prior to beating.

The cationized cellulose samples used in blends were prepared using the medium level substitution method described in Section 2.6.3. Reaction numbers and the substitution levels obtained for cationized celluloses are recorded in the appropriate table for each anionic derivative. For the carboxymethyl-cationic cellulose blend S317/S306, a high DS cationic cellulose was used, which was prepared according to S283 in Table 2.4.

### Preparation of Carboxymethyl Cellulose for Blends with Cationized Celluloses

Cotton linters were carboxymethylated for studies of blends with cationic cellulose using the procedure described for S235. Table 2.14 summarizes these experiments and any variations.

### Preparation of Maleic Acid-Cellulose Derivatives for Blends with Cationized Cellulose

These derivatives were prepared using the procedures described previously (see Table 2.11) with minor variations as detailed in Table 2.15.

**Table 2.14:** Preparations of Carboxymethyl Cellulose for Blends with Cationized Cellulose

Reaction Number	Comments	Substitution (meq/100g)	Blended with Cationized Cellulose	Substitution (%N)	Z-Direction Tensile Index** (% Change)
S220	Double batch, carboxymethylation 1h	9.10	S218 S219	0.05 0.06	+54
S234	Double batch	9.11	S232	0.14	+51
S317	Double batch, carboxymethylation 1h	10.9	S306*	0.47	+57
S380, S381	125 g o.d. scale " "	10.1 11.8	S376 S377	0.20 0.19	+40

\* Prepared according to S283 in Table 2.4.

\*\* The greatest % increase is shown for each set of blends.

#### Preparation of Itaconic Acid-Cellulose Derivatives for Blends with Cationized Cellulose

Itaconic acid-cellulose derivatives were prepared for blending studies using the methods described for S367 and S368 in Table 2.12. Other relevant details for these preparations are cited in Table 2.16.

#### Preparation of a Fumaric Acid-Cellulose Derivative for Blends with Cationized Cellulose

This fumaric acid-cellulose derivative was prepared using the procedure described for the fumaric acid derivative, S363 (13.2 meq/100g). The resulting derivative (S404, 12.8 meq/100g) was blended with a cationized cellulose derivative containing 0.16% nitrogen (S414).

**Table 2.15: Preparation of Maleic Acid-Cellulose Derivatives  
for Blends with Cationized Cellulose**

Reaction Number	Comments	Substitution (meq/100g)	Blended with Cationized Cellulose	Substitution (% N)	Z-Direction* Tensile Index (% Change)
S308	See S294,** but 40 g o.d. scale, 30 min NaOH steep, 30 min reaction	11.1	S307	0.24	+58
S324	See S308,** half maleic acid added, 5 min steep and reaction times	8.5	S323	0.21	+83
S358, S359***	See S324, 125 g o.d. scale 15 min steep, 30 min reaction times	12.9 12.2	S356, S357***	0.24 0.17	+32
S379	See S324, 80 g o.d. scale, 15 min steep, 5 min reaction times	10.1	S382	0.19	+28
S393, S394***	See S324, 125 g o.d. scale	12.2 14.9	S399, S400***	0.22 0.23	+32

\* The greatest % increase is shown for each set of blends.

\*\* Refer to Table 2.11.

\*\*\* S358 and S359 were combined and then blended with the combined cationized celluloses, S356 and S357. Similarly, S393 and S394 were combined and blended with combined S399 and S400.

**Table 2.16: Preparation of Itaconic Acid-Cellulose Derivatives  
for Blends with Cationized Celluloses**

Reaction Number	Comments	Substitution (meq/100g)	Blended with Cationized Cellulose	Substitution (%N)	Z-Direction** Tensile Index (% Change)
S321	See S368*, double consistency	7.2	S322	0.23	+80
S401, S402	See S367*, 125 g o.d. scale	11.6 12.0	S407, S408	0.19 0.22	+45

\* Refer to Table 2.12.

\*\* The greatest % increase is shown for each set of blends.

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## CHAPTER 3 :

# SPECTROSCOPIC CHARACTERIZATION OF CELLULOSE DERIVATIVES

### 3.1 INTRODUCTION

Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopic techniques offer considerable potential for the characterization of cellulose derivatives, and for providing information on both the level and position of substitution in modified celluloses.

Other characterization methods such as molecular weight determinations by size exclusion chromatography or viscosity measurements, and degree of crystallinity measurements, which are often used to compare unmodified celluloses, were not considered to provide relevant additional information. Analysis using these methods was also a potential source of complications because of the unknown effects of solvent interactions and dissolution on the range of cellulose derivatives prepared, the properties of which are largely unknown. Whilst these analyses may have provided internally consistent results for each derivative, they do not provide a good comparative method across all the derivatives prepared.<sup>1</sup>

In the following discussion only those derivatives that were highly substituted and showed spectral changes relative to unmodified linters are discussed. In addition, in a series of reactions to yield a range of substitution levels of the one cellulose derivative, generally only the spectra of the most highly substituted derivative is discussed. It is assumed that this is representative of the series.

### **3.2      FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDIES**

Infrared spectroscopy has been used extensively in structural studies of cellulose,<sup>2-6</sup> including crystallinity determinations,<sup>7</sup> and in the analysis of different plants<sup>8,9</sup> woods<sup>10</sup> and cellulose-synthetic fibre blends.<sup>12</sup> Derivatizations of cellulose have also been commonly monitored using this spectroscopic technique.<sup>11-14</sup> More recently, reactions of wood during pulping,<sup>15</sup> bleaching and aging processes,<sup>16-20</sup> and Kappa number determinations<sup>21-23</sup> have been reported using FTIR spectroscopy. Techniques used in these FTIR studies included second derivative<sup>21,22</sup> and difference spectra.<sup>15</sup>

#### **3.2.1      FTIR Methods Used to Characterize Cellulose Derivatives**

Various FTIR spectroscopic techniques were assessed in attempts to obtain useful information on cellulose derivatives. Initially, samples were ground using a Wiley mill and pressed into potassium bromide discs in a method similar to that reported in previous studies.<sup>26,27</sup> However, due to the small sample size, this proved to be impractical. Samples were then "fluffed" using a domestic coffee grinder and pressed into discs. Attenuated total reflectance and diffuse reflectance<sup>14,17,28</sup> techniques were also assessed. Attenuated total reflectance was only feasible on modified cotton linters made into handsheets and hence, was not applicable to smaller scale preparations.

For most of this study, cellulose derivatives were routinely characterized using an FTIR microscope attachment. This technique offered significant advantages in ease of sample preparation and appeared to give the same spectra as obtained using other methods. Cellulose samples were spread on a metal die and pressed to give translucent discs, suitable for spectroscopy (see Section 3.5 for details). An FTIR

spectrum of unmodified cotton linters, shown for comparison with modified celluloses (Fig. 3.1c), compares closely with reported spectra of celluloses and cotton.<sup>2,4,11</sup>

FTIR spectroscopy is a relatively new technique in the paper industry<sup>28</sup> and FTIR microscopy more so. FTIR microscopy has been reported in a study of pulp and paper samples and was used to analyze impurities and defects in paper samples.<sup>29</sup> Similarly, Sommer, Lang, Miller and Katon<sup>30</sup> investigated the applications of infrared microscopy to paper chemistry and characterized a range of pulps and paper products, including hardwood and softwood pulps, printing inks and additives used in selected paper products. Although using a different sample preparation technique to that used in this study, they also noted the minimal sample preparation required with infrared microscopy and hence, the corresponding reduction in overall analysis time. As far as is known, FTIR microscopy has not been used previously to characterize derivatives of cellulose.

Routine FTIR spectroscopy has detection limits of nominally 1% by weight, which severely restricted the usefulness of the technique as a characterization method in this project. Most derivatives were prepared with less than 1% substitution and moreover, those derivatives that showed significant papermaking improvements all had substitution levels below 1%.

### **3.2.2 Characterization of Aldehydo Celluloses and Derivatives**

#### **6-Aldehydo Cellulose**

Horton, Luetzow and Theander<sup>31</sup> reported that the spectra of 6-aldehydo cellulose showed no absorptions attributable to the free carbonyl in the 1800-1600 cm<sup>-1</sup> region<sup>32</sup> and suggested that the aldehyde functionality was present in the hemiacetal or hydrated form. Similarly in this study, no aldehyde absorptions were observed,

so the photolytic conversion of the azido- to aldehydo- group was monitored spectroscopically (FTIR) by the reduced intensity of the azide absorbance in the precursor.

### 2,3-Dialdehydo Cellulose

Nevell<sup>33</sup> commented that no aldehyde absorption was present in the infrared spectrum of 2,3-dialdehydo cellulose because the aldehyde groups were hydrated or present in the hemiacetal and hemialdal forms. In a detailed study of periodate-oxidized cellulose using infrared spectroscopy, Higgins and McKenzie<sup>34</sup> concluded that the intensity of the carbonyl stretching frequency varied with the moisture content of the sample, and in air-dry pulps the aldehyde band was absent.

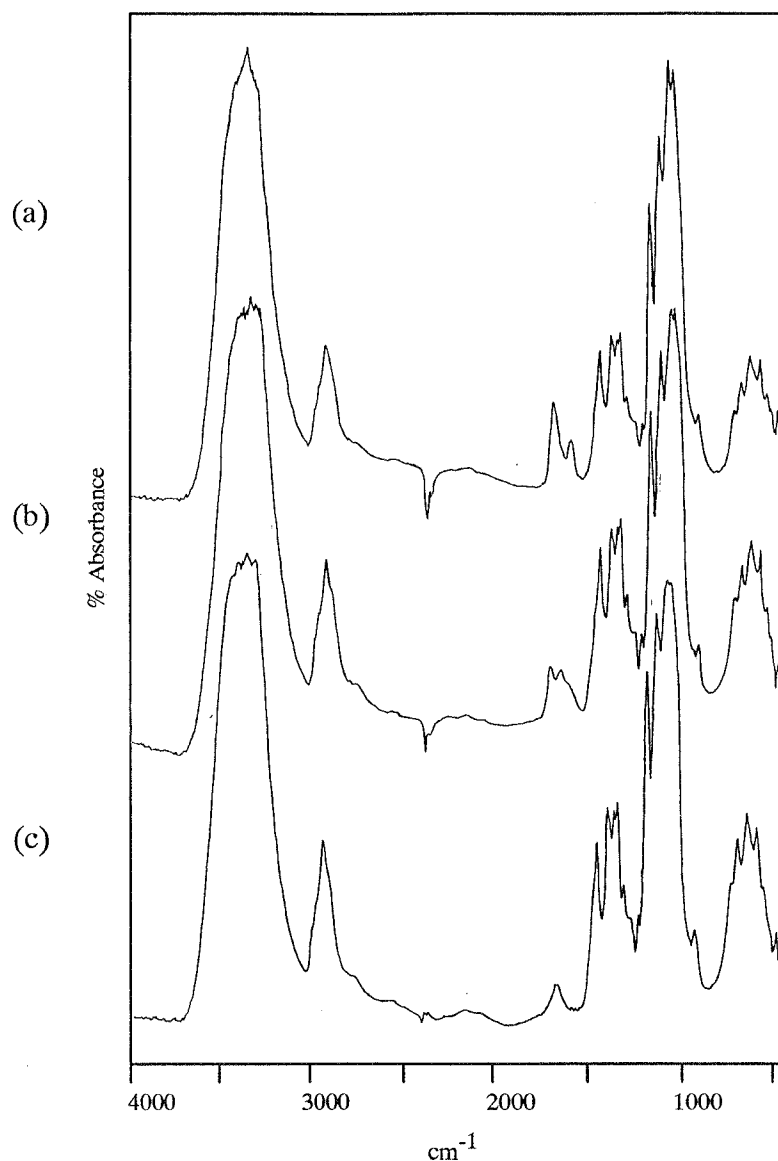
In this study, there were generally no visible changes in the spectra of cellulose upon oxidation with sodium periodate, with the exception of one sample. The dialdehyde sample S267, showed a weak absorption at  $1732\text{ cm}^{-1}$ , attributed to the carbonyl stretching frequency.

### 2,3-Cellulose Semicarbazone

The spectrum of 2,3-cellulose semicarbazone (S173, 1.98% N) showed the presence of two characteristic bands at  $1674$  and  $1586\text{ cm}^{-1}$  (Fig. 3.1a). These peaks may be attributed to C=N or C=O stretching, and N-H bending, respectively.<sup>32,35</sup> It was not possible to distinguish between the C=N stretching band and the C=O band in this spectrum. A difference spectrum obtained by subtracting the semicarbazone spectrum from that of unmodified linters, revealed the presence of the N-H stretching frequency of the semicarbazone at  $3348\text{ cm}^{-1}$ .



**Figure 3.1:** FTIR Spectra of (a) 2,3-Cellulose Semicarbazone  
 (b) Girard's Reagent T-Cellulose Derivative  
 (c) Unmodified Cotton Linters



### 2,3-Cellulose Thiosemicarbazone

Maekawa and Koshijima<sup>36</sup> prepared a range of highly substituted nitrogen-based derivatives of 2,3-dialdehyde cellulose (typically 10% nitrogen) that were characterized using infrared spectroscopy. They prepared 2,3-cellulose thiosemicarbazone and reported absorptions at 1600 and 1520 cm<sup>-1</sup> attributed to the N-H and " $=N-NH_2$ " groups, respectively. Their assignments appear to be incorrect and should be reversed; the absorption at 1600 cm<sup>-1</sup> was probably due to  $NH_2$

bending and the absorption at  $1520\text{ cm}^{-1}$  to N-H stretching adjacent to a C=S group,<sup>32</sup> with the C=N stretching being masked by the absorbed water band<sup>2,5</sup> at  $1640\text{ cm}^{-1}$ .

The most highly substituted thiosemicarbazone derivative of 2,3-dialdehyde cellulose (S223, 1.0% N) showed a broader peak than the precursor centred around  $1630\text{ cm}^{-1}$ , and a barely detectable peak at  $1520\text{ cm}^{-1}$ , concordant with reported spectra.<sup>36</sup>

#### Girard's Reagent T Derivative of 2,3-Dialdehyde Cellulose

Routine spectra of Girard's Reagent T derivatives of 2,3-dialdehyde cellulose showed numerous weak unassignable peaks between  $1500$  and  $1710\text{ cm}^{-1}$ . A difference spectrum obtained for one such derivative (S158, 0.93% N) showed distinct peaks at  $1693$ ,  $1626$ , and a shoulder at  $1593\text{ cm}^{-1}$ , assigned as C=O and C=N stretching, and N-H bending, respectively (Fig. 3.1b).

### **3.2.3 Characterization of Substitution and Addition Reaction Derivatives**

#### Carboxymethyl Cellulose

O'Connor and colleagues<sup>12,27</sup>, in their study of a range of cellulose derivatives, reported the infrared spectrum of carboxymethyl cellulose; the main feature being a broad band centred around  $1595\text{ cm}^{-1}$  assigned as the carboxylate ion.

Only one of the highly substituted, water-soluble carboxymethyl celluloses (S9), prepared early in this project, showed evidence of the carboxylate moiety with a characteristic carbonyl stretching frequency at  $1602\text{ cm}^{-1}$ .

### Cellulose Mesylate

Numerous infrared spectral studies have been made of cellulose mesylate. O'Connor, DuPre and McCall<sup>27</sup> reported prominent bands at 2941, 1370 and 1176  $\text{cm}^{-1}$ , due to the sulfonate group. In particular, the absorptions at 1370 and 1176  $\text{cm}^{-1}$  were assigned to asymmetric and symmetric stretching of the  $-\text{O}-\text{SO}_2-$  moiety, respectively.<sup>11,32,37</sup> The appearance of a peak at 827  $\text{cm}^{-1}$  due to C-O-S vibrations and a band at 3034  $\text{cm}^{-1}$  due to C-H stretching of the methyl group adjacent to the sulfonate group were also reported.<sup>11,12</sup>

In this study, mesylate peaks were noted at 3034, 2942, 1363, 1176 and 833  $\text{cm}^{-1}$  for this cellulose derivative.

### 6-Chloro-6-deoxy, 6-Azido-6-deoxy Cellulose and Related Derivatives

The presence of a C-Cl absorption in a spectrum of chloro-deoxy cellulose was barely detectable, with a shoulder at 755  $\text{cm}^{-1}$  being attributed to C-Cl stretching (S88, 6.90% Cl), in agreement with assignments made by Japanese workers<sup>38</sup> and expected absorptions from correlation charts.<sup>32</sup>

Infrared spectra of some of the 6-chloro-6-deoxy cellulose derivatives also showed absorptions at about 1730  $\text{cm}^{-1}$  due to a formyl group, as reported by Horton, Luetzow and Theander<sup>31</sup> (S59, S88). The formyl group was an artifact of chlorination with methanesulfonyl chloride in *N,N*-dimethylformamide and was removed by steeping the chlorinated cellulose in aqueous sodium carbonate.

Spectra of 6-azido-6-deoxy cellulose, prepared from the corresponding chloro derivative, showed a characteristic absorption at 2116  $\text{cm}^{-1}$ , assigned to the azide group<sup>32</sup> (S62, 2.49% N). However, Horton and co-workers<sup>31</sup> used a potassium

bromide matrix for their infrared determinations and reported an azide absorption for 6-azido-6-deoxy cellulose at  $2070\text{ cm}^{-1}$ .

The spectra of fluoro-deoxy cellulose (S77, 0.86% F) and cyano-deoxy celluloses, both prepared from cellulose mesylate, showed decreases in the intensity of the mesylate peaks, but did not reveal the presence of the corresponding fluoro and cyano derivatives, presumably because of the low substitution levels obtained. The C-F absorption occurs in the fingerprint region<sup>32</sup> and may be obscured by cellulose absorbances.

#### Cationization of Cellulose

By reference to the spectrum of a commercially cationized cellulose sample (DS 0.18), the only evidence obtained in this study for cationization of cellulose from routine FTIR spectra was the presence of a shoulder at about  $1480\text{ cm}^{-1}$ , due to C-H deformations of the methyl and methylene groups (S279, 0.47% N). This was confirmed by a difference spectrum of a derivative with a lower substitution level (S150, 0.16% N).

### **3.2.4 Characterization of Michael Addition Derivatives**

#### Cyanoethyl Cellulose

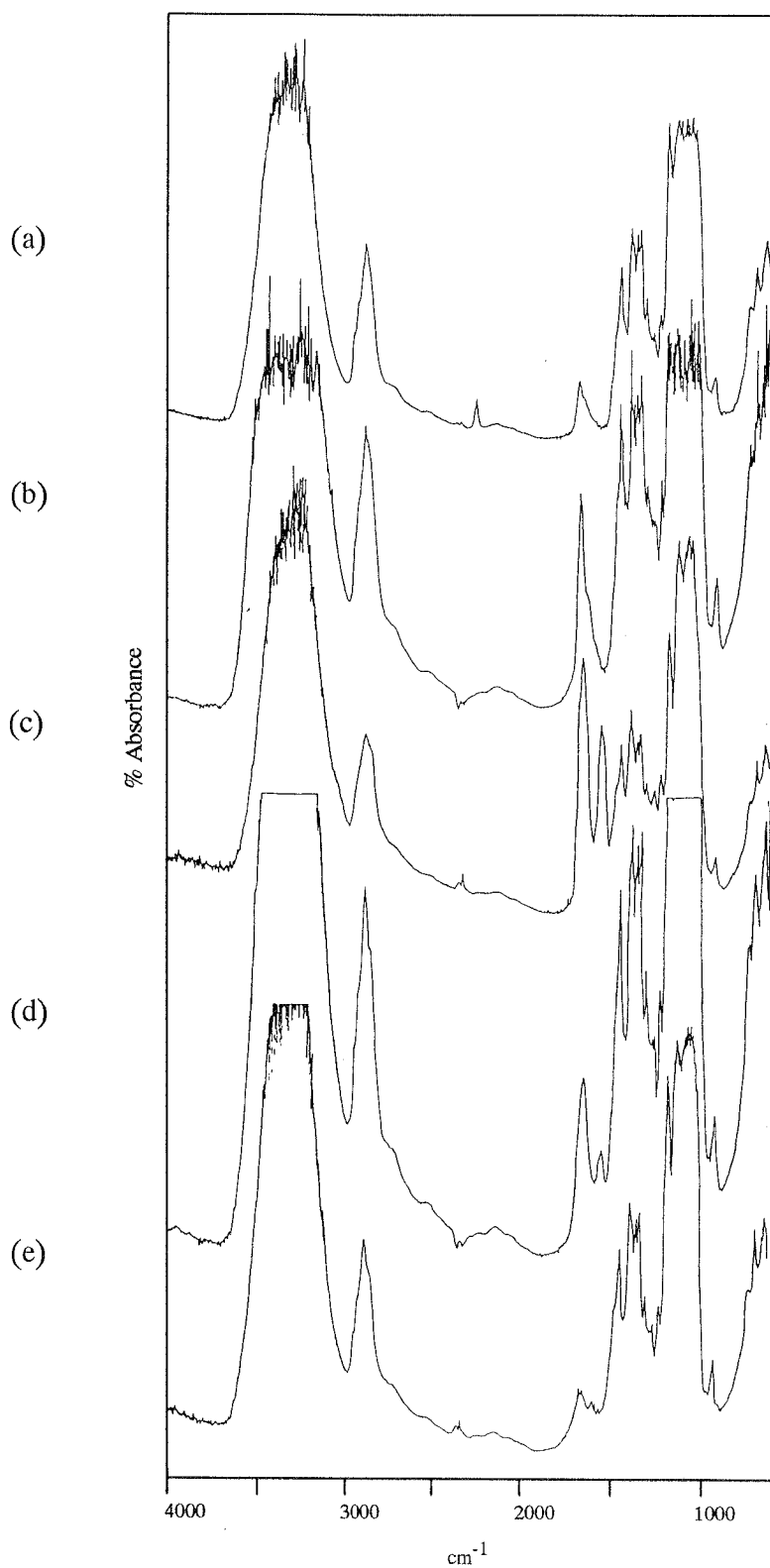
The success of cyanoethylation reactions at higher substitution levels was ascertained readily by the observation of the characteristic nitrile stretching frequency at  $2253\text{ cm}^{-1}$ ; this band could be detected in cyanoethyl cellulose derivatives containing as little as 0.75% nitrogen. These spectra were in agreement with the findings of other workers.<sup>11,12,27</sup> Interestingly, the spectrum of one cyanoethyl cellulose derivative (S69, 1.39% N) (Fig. 3.2a) also showed evidence of amidoethylation (C=O stretch at  $1663\text{ cm}^{-1}$ ), due to hydrolysis of the nitrile.<sup>39-41</sup>

**Figure 3.2:** FTIR Spectra of (a) Cyanoethyl Cellulose

(b) Amidoethyl Cellulose

(c) *N,N*-Methylenebisacrylamide-Cellulose Derivative(d) *N*-(3-Aminopropyl)methacrylamide-Cellulose  
Derivative

(e) Maleic Acid-Cellulose Derivative



### Amidoethyl Cellulose

Spectra of the amidoethyl celluloses clearly showed typical amide I absorbances at  $1667\text{ cm}^{-1}$  assigned to C=O stretching of a primary amide (Fig. 3.2b; S313, 0.67% N). The amide II band, due to N-H deformation, was obscured by other absorbances in this region. A difference spectrum revealed the N-H stretch of the amidoethyl cellulose at  $3340\text{ cm}^{-1}$ .

Amide I and II absorbances of acrylamide-treated celluloses were reported by O'Connor and colleagues<sup>11,12</sup> at  $1664$  and  $1563\text{ cm}^{-1}$ . The absorbance at  $1563\text{ cm}^{-1}$ , assigned as amide II, was at quite a low frequency for a primary amide absorbance and more likely corresponds to the carbonyl stretching frequency of a carboxylate ion, produced by hydrolysis of the amide in amidoethyl cellulose to give carboxyethyl cellulose.<sup>39-41</sup> This was confirmed in another study by O'Connor, DuPre and McCall,<sup>27</sup> in which they reported the carboxylate absorbance for cellulose carboxyethylated with acrylic acid ( $1563\text{ cm}^{-1}$ ).

In this study, the FTIR spectrum of a sample prepared using more severe reaction conditions than used in most amidoethylations (S141, 0.19% N) clearly showed two relatively strong bands at  $1667$  and  $1570\text{ cm}^{-1}$ , which were assigned as the carbonyl stretching frequencies of a primary amide (amide I) and a carboxylate ion, respectively.

### *N,N*-Methylenebisacrylamide-Cellulose Derivative

The spectra of *N,N*-methylenebisacrylamide treated linters clearly showed the amide I and II absorbances of a secondary amide at  $1649$  and  $1535\text{ cm}^{-1}$  (S295, 4.14% N), as shown in Figure 3.2c. Absorption bands of the unreacted acrylamide moiety, if present, were obscured by the strong absorptions of the derivatized moiety. Evidence exists for the presence of reacted and unreacted amide moieties in a

difference spectrum of the *N,N*-methylenebisacrylamide-cellulose derivative. The spectra were quite different to the spectra of the starting material *N,N*-methylenebisacrylamide, with a lowering in frequency upon reaction with cellulose for both amide I and II bands by 10 and 8  $\text{cm}^{-1}$ , respectively. No reported spectra of *N,N*-methylenebisacrylamide-cellulose derivatives were available for comparison.

#### *N*-(3-Aminopropyl)methacrylamide Hydrochloride (APMA) Treated Cellulose

The amide II absorbance at  $1531\text{ cm}^{-1}$  was evident in the spectra of this new acrylamido derivative (Fig. 3.2d) (S252, 0.8% N), which represents a shift of  $-10\text{ cm}^{-1}$  in the APMA absorbance upon derivatization with cellulose. The amide I absorbance coincides with the band at  $1640\text{ cm}^{-1}$ , corresponding to absorbed water.<sup>2,5</sup> No shoulder was evident for this strong carbonyl absorption near the absorbed water band and hence, it appears that a shift of  $17\text{ cm}^{-1}$  (from  $1657\text{ cm}^{-1}$  for amide I in APMA) has occurred upon reaction with cellulose.

As this was a new cellulose derivative, no other spectra were available for comparison. The spectral assignments were made based on comparisons with the acrylamide and *N,N*-methylenebisacrylamide-cellulose derivatives and the spectrum of APMA, as well as on data from correlation charts for secondary amides.<sup>32</sup>

#### Maleic and Itaconic Acid Derivatives of Cellulose

O'Connor and co-workers<sup>12,27</sup> reported the appearance of a broad band at  $1600\text{ cm}^{-1}$ , in a poorly resolved spectrum of a disodium maleate-cellulose derivative, and assigned this to the carbonyl stretching frequency of a carboxylate group. In the current study, the free acid of maleic acid was used and hence, carboxyl absorptions around  $1700\text{ cm}^{-1}$  were anticipated. However, only two derivatives clearly showed evidence of spectral changes (S274, 12.86 meq/100g; S394, 14.9 meq/100g, used in

blends), possessing a preponderance of absorptions in the 1700 to 1550  $\text{cm}^{-1}$  region (1695, 1680, 1667, 1632, 1620, 1580 and 1555  $\text{cm}^{-1}$ ) as shown in Figure 3.2e, whereas maleic acid had absorptions at 1707, 1638, 1589 and 1568  $\text{cm}^{-1}$  in this region.

Similarly, a carboxylate absorption was reported in the product of the reaction between itaconic acid and cellulose (1634  $\text{cm}^{-1}$ ),<sup>12</sup> but no such peak was evident in this study, presumably due to the low substitution levels.

### **3.2.5 Characterization of Double Derivatives**

O'Connor<sup>12</sup> cited examples by other workers in which the use of infrared spectroscopy was a useful tool to monitor replacement reactions and multiple modifications of cellulose. These usually involved replacement of reactive sulfonates, aminized celluloses and carboxymethylated celluloses.

Several double derivatives in this study showed changes in their infrared spectra upon modification. Spectra of amidoethyl hydroxyethyl cellulose (S262, 1.31% N; S336, 0.81% N) revealed that the product was contaminated with unreacted acrylamide, as noted in the preparations (Section 2.7.5), by the bands at 1670 and 1612  $\text{cm}^{-1}$ , assigned to amide I and C=C stretching frequencies. The band at 1570  $\text{cm}^{-1}$  indicated that hydrolysis of amidoethyl cellulose to the carboxylate ion had also occurred, which is water-soluble<sup>41</sup> and may explain the filtration problems encountered in these preparations. No evidence of hydroxyethylation was apparent in the FTIR spectrum (Fig. 3.3a).

The presence of *N,N*-methylenebisacrylamide on hydroxyethylated cellulose was confirmed by the FTIR spectrum of this double derivative (Fig. 3.3b; S338, 0.31% N), with absorptions of the secondary amide being noted at 1649 and 1535  $\text{cm}^{-1}$ , as reported in spectra of the *N,N*-methylenebisacrylamide-cellulose derivatives.

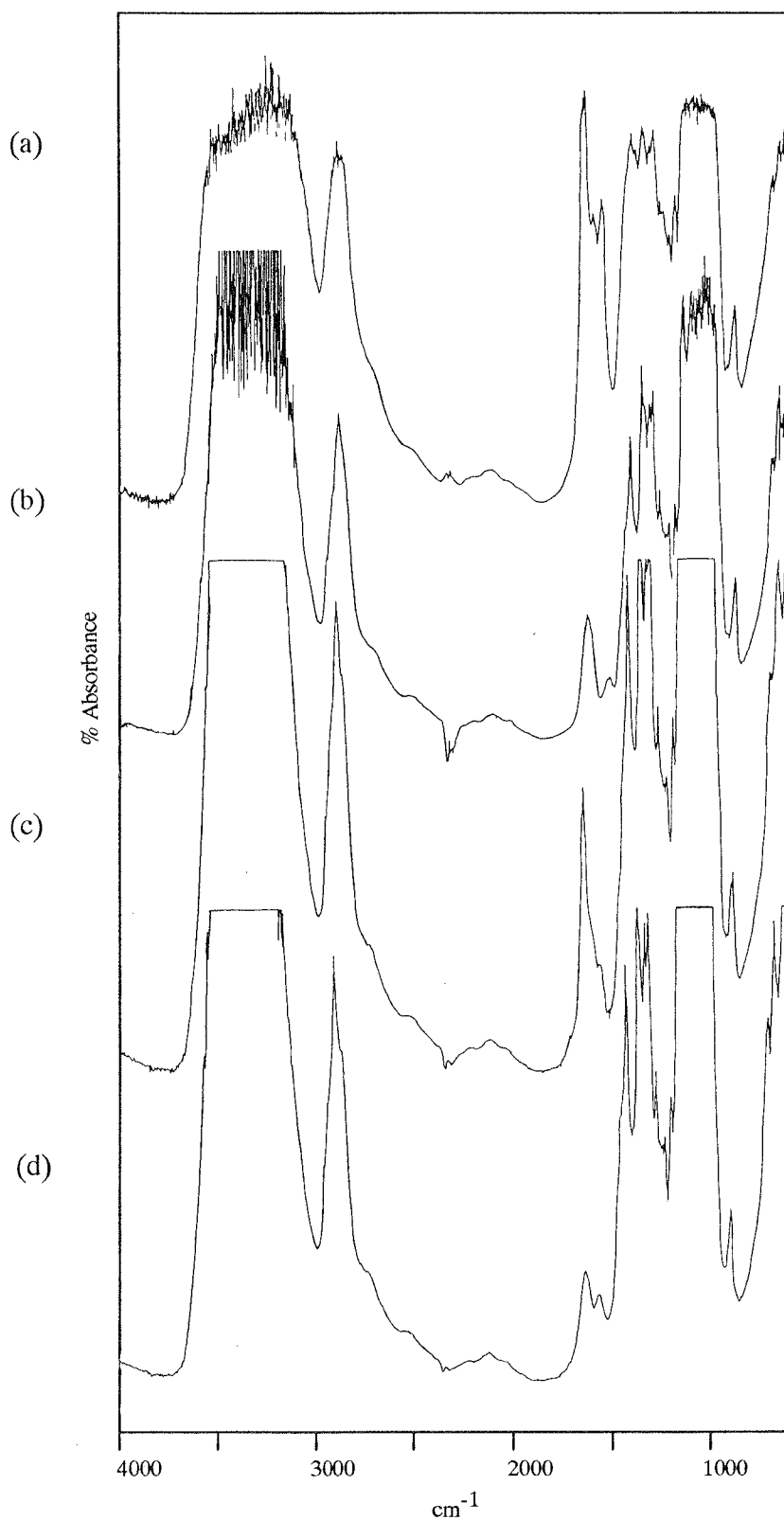


**Figure 3.3: FTIR Spectra of (a) Amidoethyl Hydroxyethyl Cellulose\***(b) *N,N*-Methylenebisacrylamide

Hydroxyethyl Cellulose

(c) Cationized Amidoethyl Cellulose

(d) Maleic Acid-treated Cationized Cellulose



\* Contaminated with unreacted acrylamide

The FTIR spectrum of cationized amidoethyl cellulose (S348, 0.82% N) showed an amide I absorbance at  $1667\text{ cm}^{-1}$  and an absorption at  $1574\text{ cm}^{-1}$  (Fig. 3.3c). This second band was assigned to the N-H stretch of a secondary amide (amide II), assuming the epoxide of the cationizing agent reacted with amidoethyl cellulose in preference to the hydroxyl groups of the cellulose backbone. Alternatively, it may be due to a carbonyl absorption and provide evidence of hydrolysis of the amide to the carboxylate ion in the cationization step.

The spectrum of maleic acid-treated cationized cellulose (S347, 0.18% N), showed a broad peak centred around  $1570\text{ cm}^{-1}$  (Fig. 3.3d), which was attributed to the maleic carboxylate moiety.

### **3.2.6 Concluding Remarks**

The use of FTIR microscopy significantly reduced the time required for sample preparation. This spectroscopic technique confirmed the successful preparation of numerous cellulose derivatives. Caution was needed in assigning absorbances of the spectra of these cellulose derivatives because most showed absorption changes in the vicinity of  $1640\text{ cm}^{-1}$ , which coincided with the stretching frequency of absorbed water.<sup>2,5</sup> Hence, some peaks may have been obscured by this absorbance and been undetected by routine FTIR spectroscopy.

Appropriate absorbances were noted for the semicarbazone, thiosemicarbazone and Girard's Reagent T derivatives of 2,3-dialdehyde cellulose. Mesylation of cellulose was readily ascertained by FTIR spectroscopy, this being facilitated by the higher substitution levels obtained for this derivative. Of the deoxy cellulose derivatives, the azide derivative was readily monitored by FTIR spectroscopy, but this was not the case for the chloro, fluoro and cyano derivatives. Limited spectroscopic evidence existed for the presence of cationized cellulose.

The formation of Michael adducts was confirmed by the FTIR spectra of these cellulose derivatives and, particularly, by the absence of ester absorptions. Moreover, spectra of cyanoethyl and amidoethyl celluloses revealed the appropriate absorbances, and in some cases, showed evidence of hydrolysis of the nitrile and amide groups. The spectra of the *N,N*-methylenebisacrylamide and *N*-(3-aminopropyl)methacrylamide cellulose derivatives showed a lowering in frequency of the amide absorptions upon reaction with cellulose.

The effects of the second derivatization step could be monitored by FTIR spectroscopy for some double derivatives, but generally this technique was of limited use because only one of the two derivatives was visible in the FTIR spectra.

Hence, FTIR spectroscopy provided useful information on the majority of derivatives at higher substitution levels and was applicable down to levels of 0.2% nitrogen for some strongly absorbing groups, such as carbonyl stretching modes in acrylamide derivatives. Difference spectra were also of assistance in some assignments. Although the low substitution levels used to improve the papermaking properties of cotton linters restricted the applications of FTIR spectroscopy in this project, it yielded information not available from other spectroscopic characterization methods at such low substitution levels.

### **3.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY STUDIES**

#### **3.3.1 Scope and Limitations of NMR Techniques**

NMR spectroscopy offers potential for qualitative and quantitative analysis of cellulose derivatives. Studies may be performed in solution or in the solid state and access to both multinuclear NMR and pulsed sequences offered further possibilities. However, inherent problems exist with the analysis of cellulose and its derivatives in either solution or the solid state.

There have been many reports on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of cellulose derivatives in solution. Some derivatives, such as carboxymethyl and hydroxyethyl celluloses, have received considerable attention in solution NMR studies (see Section 3.3.3). In most cases acid hydrolysed or partially degraded celluloses were used to affect dissolution and increase spectral resolution.<sup>42,43</sup> However, in this current study, acid hydrolysis of cellulose derivatives was avoided because of the uncertainty of the processes involved and the complexity of assigning the range of products obtained by hydrolysis, i.e. considerable development work was required for each derivative.

A variety of solvent systems are available for NMR studies of celluloses, including *N*-methylmorpholine-*N*-oxide with dimethyl sulfoxide.<sup>44-46</sup> Dissolving cellulose derivatives in this solvent system may cause the degradation of cellulose,<sup>47</sup> and is time consuming and costly. Hence, it was not suitable as a routine characterization tool, being better suited to detailed spectral assignment work.

Furthermore, the dissolution of cellulose derivatives for solution state NMR analysis may lead to chemical modification of the derivative caused by interaction with the solvent system, resulting in the decomposition or reversal of existing modifications, or cause the degradation of cellulose itself. This problem was compounded by the difficulty in ascertaining which, if any, of these effects has occurred. Because such a range of cellulose derivatives was being investigated in this study, and as alternative characterization methods were available, the use of solution NMR techniques was generally avoided for the reasons stated.

Characterization by solid state  $^{13}\text{C}$  NMR offered the advantages of requiring minimal sample preparation and avoiding the dissolution problems of cellulose with suitable solvent systems. The possibility of being able to determine the DS from the same spectrum was also an advantage. A significant disadvantage was the decreased resolution inherent in solid state NMR spectroscopy.

Qualitative studies of modified cellulose using  $^{13}\text{C}$  cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy were relatively straightforward, provided substitution levels were above about 2%. Quantitative analysis to determine the substitution level, however, was more complex. Despite the increased utilization of solid state NMR techniques with celluloses and advances in the interpretation of spectra of cotton and wood in recent years DS determinations have not become commonplace because of numerous complications. These complications include: (i) the low resolution of solid state NMR spectroscopy, despite CP/MAS which yields finer spectral details, (ii) integrations may not be relied upon if insufficient time is allowed for relaxation to occur between irradiations thus, requiring measurement of spin-lattice relaxation parameters ( $T_1$ ) which vary greatly for  $^{13}\text{C}$  nuclei, and (iii) the nuclear Overhauser enhancement effect is not the same for all nuclei.<sup>48-50</sup>

### **3.3.2 Solid State $^{13}\text{C}$ NMR Studies of Cellulose Derivatives**

Fundamental aspects of the structure and morphology of cellulose have been studied using solid state NMR spectroscopy.<sup>51-53</sup> The relaxation behaviour,  $T_1$ , of cellulose and wood components have been investigated in numerous studies and these have yielded information on intermolecular effects and secondary valence bonds, particularly the effects of different water contents on hydrogen bonding, in polymers such as cellulose.<sup>50,54-59</sup> A two-dimensional solid state NMR study of cellulose has also been reported.<sup>60</sup>

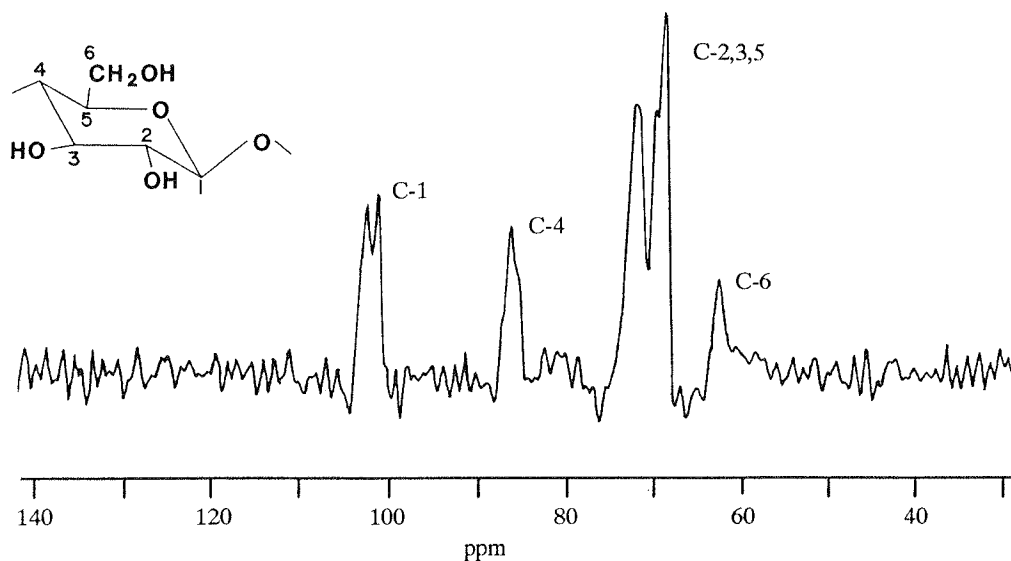
Quantitative studies using  $^{13}\text{C}$  CP/MAS NMR spectroscopy include the estimation of cellulose crystallinity<sup>61</sup> and the determination of the distribution of cellulose, hemicellulose and lignin in wood and pulp.<sup>49,62,63</sup> In another quantitative study, the relative ratios of components in cotton/polyester blends were ascertained using peak height ratios.<sup>64</sup> It should be noted that these quantitative studies were concerned with major changes in sample composition and the corresponding ratios of selected resonances in the NMR spectra.

Whilst the structure of cellulose has been studied extensively in the solid state using  $^{13}\text{C}$  CP/MAS NMR techniques, derivatized celluloses have received little attention. Several highly substituted silyl ethers and phenylacetoxo esters of cellulose<sup>65</sup> were studied using high power decoupling in conjunction with  $^{13}\text{C}$  CP/MAS NMR techniques and limited positional information was also obtained. Hoshino, Takai, Fukuda, Imura and Hayashi<sup>66</sup> studied numerous cellulose ethers and esters using solid state NMR techniques, some of which are considered in detail in the following discussion of the spectra of individual cellulose derivatives.

To date, solid state DS analysis of cellulose derivatives has been reported only for ethyl hydroxyethyl cellulose (EHEC), in an attempt to overcome the poor resolution caused by high viscosity EHEC solutions. Hjertberg, Zadorecki and Arwidsson<sup>67</sup> obtained DS values in agreement with gas chromatography analysis using  $^{13}\text{C}$  CP/MAS NMR. However, they reported difficulties and in a following paper reported the  $^{13}\text{C}$  NMR solution study of hydrolysates of EHEC.<sup>68</sup>

In this study, characterization of cellulose derivatives was achieved using CP/MAS and TOSS (total suppression of sidebands)<sup>69</sup> solid state  $^{13}\text{C}$  NMR techniques. The spectra thus obtained of unmodified cellulose (Fig. 3.4) agreed with those reported in the literature.<sup>54,70-73</sup>

**Figure 3.4:**  $^{13}\text{C}$  CP/MAS NMR Spectrum of Cotton Linters



### Carboxymethyl Celluloses

The solid state  $^{13}\text{C}$  NMR spectrum of carboxymethyl cellulose, first reported as part of this study,<sup>74</sup> showed the characteristic carboxyl resonance at 177 ppm (Fig. 3.5a). Comparison with the spectrum of a commercial sample of carboxymethyl cellulose further confirmed that the correct derivative had been prepared. Spectra were only obtained of early carboxymethylation derivatives prepared at relatively high substitution levels (e.g. S9, S17) and thereafter the reaction was presumed to proceed in the same manner, yielding carboxymethylated celluloses that were characterized by other methods.

In a later study, Hoshino and co-workers<sup>66</sup> reported a carboxyl resonance at 177 ppm for a carboxymethylated derivative with a DS of 1.35; other resonances were also the same as those reported previously.<sup>74</sup> Detailed assignments for the other resonances were more complex, with Hoshino *et al.*<sup>66</sup> assigning a resonance at 104 ppm to C-1, a shoulder at 81 ppm to C-2,3,4, a broad resonance at 74 ppm to C-5,6 and O-CH<sub>2</sub>, and C-6 at 62 ppm.

### Hydroxyethyl Cellulose

Hoshino and colleagues<sup>66</sup> were the first to report the solid state  $^{13}\text{C}$  NMR spectrum of hydroxyethylated cellulose (DS 2.55) in 1989. The resonances of the substituted hydroxyethyl group occurred in the same region as unsubstituted cellulose resonances, complicating the spectroscopic assignment of this derivative. Nonetheless, they assigned C-1 at 103 ppm, C-2,3,4 at 83 ppm, C-5,6 and O-CH<sub>2</sub> at 74 ppm, and CH<sub>2</sub>OH at 61 ppm. The spectrum was similar to that of some samples of unmodified cellulose except for the greater intensity of the peak at 74 ppm, due to the O-CH<sub>2</sub> groups in the side-chain.

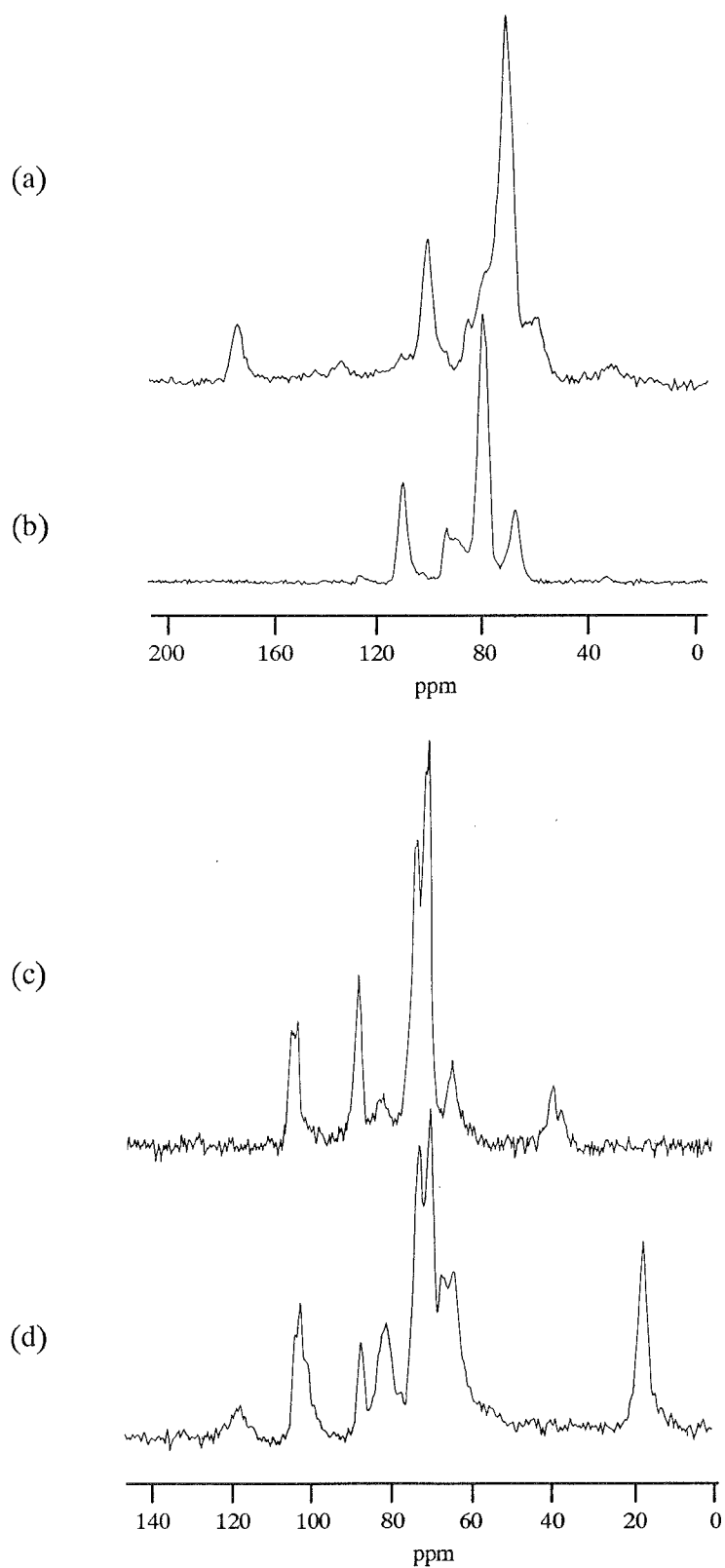
**Figure 3.5:**  $^{13}\text{C}$  CP/MAS NMR Spectrum of Cellulose Derivatives:

(a) Carboxymethyl Cellulose

(b) Hydroxyethyl Cellulose

(c) Cellulose Mesylate

(d) Cyanoethyl Cellulose





The solid state NMR spectra of hydroxyethyl celluloses obtained in this study were identical to those described by Hoshino and co-workers.<sup>66</sup> A typical spectrum of hydroxyethylated linters is shown in Figure 3.5b (S52).

### Cellulose Mesylate

Considerable attention has been devoted to the mesylation of cellulose and derivatives thereof. However, no literature reports could be found of the solution or solid state NMR spectra of cellulose mesylate prior to this present study.<sup>74</sup>

The solid state  $^{13}\text{C}$  NMR spectra of highly substituted cellulose mesylate derivatives clearly showed the presence of the methyl resonance of the mesylate group at about 39 ppm (Fig. 3.5c). This peak was evident down to a substitution level of 7.34% sulfur (S86). No spectra were obtained of derivatives prepared at intermediate substitution levels and those obtained at 1% and less (e.g. S63, 0.89% S) did not possess the  $\text{CH}_3\text{-SO}_2$  resonance.

Some mesylate spectra showed evidence of changes in crystallinity due to the severity of the reaction conditions used. Moreover, peak broadening of C-4 and C-6 and loss of resolution of C-1 and C-2,3,5 occurred. The appearance of peaks upfield of C-4 and C-6, which contributed to peak broadening, were attributed to non-crystalline cellulose.<sup>70,75</sup> The resonances of the substituted celluloses further complicated and broadened the resonances of these mesylates.

In the solution state  $^{13}\text{C}$  NMR spectra of the analogue, cellulose tosylate (DS 1), a downfield shift of C-6 and upfield shift of C-1 were reported upon tosylation.<sup>76,77</sup> However, the shifts expected upon mesylation of cellulose, especially the anticipated downfield shift of the C-6 resonance, were not clearly apparent in the NMR spectra of these mesylates and may have been masked by the C-2,3,5

resonance or the peak broadening that occurred with crystallinity changes, or a combination of both.

### Cyanoethyl Cellulose

Despite being one of the most studied cellulose derivatives, the NMR spectroscopic characterization of cyanoethyl cellulose has received scant attention. The solution state  $^{13}\text{C}$  NMR spectrum of cyanoethyl cellulose (DS 0.5) was first reported by Miyamoto and co-workers<sup>76</sup> in 1987. They cited the resonances of substituted C-1, C-2 and C-6, and the appearance of unspecified methylene resonances at 66 and 67 ppm. They did not report the chemical shift of the nitrile group, expected between 115 and 125 ppm.<sup>48</sup>

The solid state  $^{13}\text{C}$  NMR spectrum of cyanoethyl cellulose was first reported in this study.<sup>74</sup> Spectroscopic evidence for cyanoethylation was apparent for derivatives with 3.7% nitrogen (S41) and above. The characteristic nitrile resonance occurred at approximately 122 ppm and a new peak was evident at about 20 ppm, due to a  $\text{CH}_2$  group. Assignments for the rest of the spectra were more complex. At higher substitutions (see Fig. 3.5d; e.g. S5, 8.25% N), several other changes appeared in the spectra of this derivative: a resonance appeared slightly upfield of C-1 (100 ppm), and strong peaks between C-4 and the C-2,3,5 resonance (83 ppm) and downfield of C-6 (68 ppm) also appeared.

A later study by Japanese workers<sup>66</sup> of the  $^{13}\text{C}$  CP/MAS NMR spectrum of cyanoethyl cellulose (DS of 2.83) also cited the presence of a nitrile peak at 120 ppm and the  $\text{CH}_2$  group at 19 ppm. In addition, they reported an  $\text{O-CH}_2$  resonance at 68 ppm, downfield shifts of the C-2, C-3 and C-6 carbons and upfield shifts of C-1 and C-4, which resulted in a peak at 83 ppm assigned as C-2,3,4 and another at 74 ppm, attributed to C-5,6 resonances.

The spectrum of cyanoethyl cellulose observed by Hoshino *et al.*<sup>66</sup> differed from those obtained in this study in the 60-90 ppm region, reflecting the different substitution levels of the derivatives. In this work, the resonances of unsubstituted cellulose were clearly apparent, especially the C-6 resonance at 65 ppm which was not present in Hoshino and co-worker's<sup>66</sup> spectrum. Whilst the C-2,3,4 resonance (83 ppm) of substituted cyanoethyl cellulose was evident, the unsubstituted resonances were of similar intensity. The upfield shift of the C-5 and downfield shift of C-6 of the derivatized cellulose, reported by Hoshino *et al.*,<sup>66</sup> were masked by the unsubstituted C-2,3,5 resonances in this work. The O-CH<sub>2</sub> resonance at 68 ppm was also less intense in this work.

#### Chromium (III) Doping of Modified Celluloses

In a study aimed at rapidly determining the lignin contents of wood and pulp samples using <sup>13</sup>C CP/MAS NMR spectroscopy, Newman and Dunn<sup>78</sup> investigated the use of paramagnetic doping techniques to facilitate the acquisition of spectra. They studied the effects of treating wood and pulp samples with a series of transition metal salts and found that chromium (III) markedly facilitated relaxation in cross polarization experiments, i.e. T<sub>1</sub>'s were shortened and hence, accumulation times were greatly reduced.

The application of this doping technique to the low level substituted cellulose derivatives prepared in this project was assessed. The spectrum of an undoped sample of cyanoethyl cellulose (S40, 6.1% N) was compared with the spectrum of the same sample doped with chromium (III) to ensure that this technique did not adversely effect the derivative or the corresponding spectrum. Apart from a marked increase in the number of scans possible in a given time and the corresponding reduction in the signal to noise ratio, no other differences were apparent between the spectra of the doped and undoped samples. Numerous low level cellulose

derivatives were then doped with 0.1% by weight chromium (III) according to the procedure of Dunn, Newman and Hemmingson.<sup>79</sup> The spectra obtained of the derivatives were the same as the spectra of unmodified cellulose, despite in some cases the accumulation of 120,000 scans. Hence, the substitution levels of most cellulose derivatives were below the detection limits of  $^{13}\text{C}$  CP/MAS NMR spectroscopy even with the reported enhanced sensitivity achieved using chromium (III) doping.

### **3.3.3 $^{13}\text{C}$ NMR Solution Studies of Cellulose Derivatives**

Preliminary attempts were made to study cellulose derivatives using solution NMR techniques, despite the potential complications (see Section 3.3.1). This decision was in response to the resolution problems and detection limits imposed by solid state  $^{13}\text{C}$  CP/MAS NMR spectroscopy, as discussed previously.

Extensive NMR studies have been performed on a variety of cellulose derivatives, especially the water-soluble hydroxyethyl and carboxymethyl celluloses. Solution state NMR spectroscopy has been used to determine the substitution level in numerous cellulose derivatives and also the position of substitution or relative reactivities of the hydroxyl groups (see Section 2.3.1).

#### **Carboxymethyl Cellulose**

In their study of commercially important soluble cellulose ethers, Parfondry and Perlin<sup>42</sup> examined the  $^{13}\text{C}$  NMR spectrum of acid hydrolyzed carboxymethyl cellulose and observed strong deshielding of the  $^{13}\text{C}$  bearing alkoxyl groups upon carboxymethylation; hydroxyl group reactivities were also determined. Similarly, the acid hydrolyzed derivative of carboxymethyl cellulose was used by Ho and Klosiewicz<sup>80</sup> to determine the DS and distribution of substituents using solution  $^1\text{H}$  NMR techniques. This quantitative technique was refined later by Bach Tuyet,

Iiyama and Nakano,<sup>43</sup> who provided detailed assignments based on the spectra of carboxymethyl glucoses using a high resolution NMR spectrometer. Gronski and Hellmann<sup>81</sup> compared the substituent distribution and DS obtained by  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses of hydrolyzed carboxymethyl celluloses and obtained reasonable correlation between the two methods.

In this study, the  $^1\text{H}$  NMR spectra of carboxymethylated cotton linters hydrolyzed with deuterated sulfuric acid, according to a reported method,<sup>43</sup> yielded spectra comparable to those cited above.

More recent studies,<sup>82,83</sup> taking advantage of the availability of high resolution spectrometers, assigned the  $^{13}\text{C}$  NMR spectrum and determined the substituent distribution of intact carboxymethyl celluloses, with strong deshielding effects also being reported.

A  $^{13}\text{C}$  NMR spectrum of a dilute solution of carboxymethyl cellulose (S17) in deuterated dimethyl sulfoxide and deuterium oxide showed the unsubstituted cellulose resonances in the 105-65 ppm region and a carboxyl resonance at 180 ppm. The substitution level was too low to show the substituted hydroxyl groups in the NMR spectrum, but otherwise agreed with those reported in the literature.<sup>82,83</sup> This spectrum also compared favourably with spectra obtained of commercial samples of carboxymethyl cellulose.

#### Hydroxyethyl Cellulose

Clemett<sup>84</sup> determined the DS of several ethers and mixed ethers of cellulose, including hydroxyethyl cellulose (DS 1.8), using proton NMR techniques by hydrolysis of the derivatives. Parfondry and Perlin<sup>42</sup> reported the  $^{13}\text{C}$  spectrum of a partially degraded hydroxyethyl cellulose (DS 0.8) and determined the relative reactivities of the hydroxyl groups. They ascertained that partial decomposition or

hydrolysis was a prerequisite for successful analysis by NMR. A more detailed study of hydroxyethyl cellulose and model compounds swollen in deuterium oxide was presented by DeMember and co-workers<sup>85</sup> with quantitative analysis (DS and MS), position of substitution and detailed assignments being provided. As part of a study to develop a theoretical model to describe the kinetics and distribution of substituents upon hydroxyethylation, Reuben and Casti<sup>86</sup> hydrolyzed and reduced hydroxyethyl cellulose to obtain the D-glucitol derivatives, which were assigned by comparison with substituted hydroxyethyl-D-glucitols.

In this study, weak signals at 61.8, 71.1 and 73.3 ppm were noted in the  $^{13}\text{C}$  NMR spectrum of intact hydroxyethylated linters (S52) swollen in deuterium oxide<sup>85</sup> and deuterated dimethyl sulfoxide. These resonances were assigned as the more intense C-9, C-7 and C-8 resonances, respectively of the hydroxyethyl chain and agreed with those reported by DeMember and colleagues.<sup>85</sup> Further confirmation was obtained by comparison with spectra of commercial hydroxyethyl celluloses, with the lower substitution levels obtained in this study being apparent.

#### **3.3.4 Concluding Remarks**

Most cellulose derivatives had degrees of substitution below the detection limits of  $^{13}\text{C}$  CP/MAS NMR spectroscopy. In some instances, the NMR characterization of cellulose derivatives was straightforward, e.g. cyanoethyl and carboxymethyl celluloses. This was a combination of relatively high substitution levels and characteristic resonances free of unmodified cellulose resonances.

The NMR spectrum of cellulose mesylate had not been reported previously and the solid state  $^{13}\text{C}$  CP/MAS spectra of cellulose derivatives such as cyanoethyl and carboxymethyl celluloses had not been reported prior to the commencement of this project.

Solution state  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies of carboxymethylated and hydroxyethylated cotton linters agreed with previously reported spectra of these derivatives.

Although there was considerable scope for new work in the solid state NMR characterization of derivatives of aldehydo celluloses, substitution and addition derivatives, Michael adducts and double derivatives, the substitution levels, as required for papermaking, were generally too low to be detected. In addition, position of substitution and relative reactivity information was of interest for novel cellulose derivatives, but the use of NMR techniques was again precluded by the low substitution levels. Definitive information on the position of substitution in double derivatives, i.e. whether the second derivatization occurred on the primary derivative or on the cellulose backbone, may have assisted in reconciling the structural modification with the observed papermaking properties.

### **3.4**      **CONCLUSIONS**

FTIR and NMR were not as productive as anticipated, principally because of the low substitution levels involved. Hence, pulp evaluation, elemental analyses and conventional chemical analyses proved more useful in this project (Chapter 4 and Section 2.7, respectively). Nonetheless, spectroscopic characterization complemented elemental analysis results by confirming that substitution had indeed occurred.

### **3.5**      **EXPERIMENTAL**

Commercial samples of cellulose derivatives, hydroxyethyl cellulose (Natrosol) and cationized cellulose (PC Cel 1800 N), were obtained from Hercules Inc. (Rijswijk, Netherlands) and Degussa (Frankfurt), respectively and were used as received.

Infrared spectra were recorded on a Hitachi 270-30 spectrophotometer and on a Digilab FTS.20E FTIR spectrophotometer.

For the FTIR microscope work, air-dry samples of 1 mg of linters and modified linters were pressed at 1000 psi for 5 min and spectra run on the pressed fibre mat. Typically 64 scans were obtained, with a resolution of  $4\text{ cm}^{-1}$ , although up to 200 scans were obtained for some spectra.

NMR spectra were obtained using a Bruker AM 300 MHz spectrometer and an operating frequency of 75.5 MHz for  $^{13}\text{C}$  spectra. Samples for solid state analysis were ground in a mortar and pestle, and packed into zirconia sample holders.

Carboxymethyl and hydroxyethyl cellulose samples were prepared for solution NMR studies using reported methods.<sup>43,85</sup>

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## CHAPTER 4:

# EVALUATION OF THE PAPERMAKING PROPERTIES OF CHEMICALLY MODIFIED COTTON LINTERS

### 4.1    INTRODUCTION

Cotton linters pulp offers several advantages as a specialty papermaking fibre. These include excellent durability and permanence, high bulk, good formation, as well as its relatively economical cost, being a byproduct of the cotton industry. However, inherent disadvantages which exist in the use of linters pulp for papermaking include poor interfibre bonding and bonding properties, reflected in low Z-direction tensile,<sup>1a</sup> tensile and burst strengths, and low sheet stiffness. Cotton linters are used in pulp blends with imported kraft pulp and recycled fibre at the Shoalhaven Mill of APPM. Their use in papermaking blends is limited to about 20% because of poor bonding and hence poor strength and sheet stiffness properties.

The key objective of this project, to improve the interfibre bonding properties of linters pulp, may be achieved by chemical modification which increases the hydrophilicity of the fibres and also their electrostatic bonding interactions. Linters are thick-walled and have a small lumen, making them resistant to collapse during beating and drying. The fibrils obtained by beating linters are also stiff and resist flattening, restricting the relative bonded area developed during sheet formation and hindering the development of strength properties.<sup>1</sup> Furthermore, the surface of the linters fibres are creased and these ridges prevent close contact between fibres and reduce the surface area available for bond formation, whereas the ridges present on staple lint fibres are almost entirely removed during pulping.<sup>1</sup> Linters may be thought of as short rod-like fibres, compared with long tubular first-cut cotton fibres. Increasing the flexibility or conformability of the fibres is desirable, as a means of increasing the effective bonding area available during sheet formation.

Hence chemical modification was intended to increase interfibre bonding and improve the papermaking properties of linters pulp, so that the proportion of linters used in blends could be increased, without adversely affecting the sheet strength.

#### **4.1.1 The Development of Interfibre Bonds in Papermaking**

In papermaking, the processes of beating, pressing and drying aim to develop fibre-to-fibre bonds as a means of imparting strength to the fibre network. Beating and drying cause collapse of the fibres which effectively increases the surface area available for contact with other fibres and therefore, increases the relative bonded area.<sup>2</sup> The overall bonding and strength of a sheet is a combination of the fibre strength, the contact area available for bonding, the number of bonds, and also the strength of the bonds holding the fibres together.<sup>3</sup>

At the molecular level, a major factor in the formation of fibre-to-fibre bonds in paper is the presence of the cellulose hydroxyl groups which form hydrogen bonds with contiguous fibres and contribute significantly to the rigidity and strength of the sheet.<sup>4</sup>

The bonded area of a fibre is an important concept in understanding the behaviour of paper. Whilst hydrogen bonding dominates fibre interactions at the molecular level, at the macroscopic level interfibre bonding is controlled by fibre conformability and interfibre contact, which determine the bonded area. Beating produces fines, fibrillates fibres, increases flexibility and swelling, and decreases bulk. Hence, the beating process increases bonding by increasing both specific surface area and fibre flexibility, which improve the strength properties of the sheet.<sup>2</sup>

Cellulose is hygroscopic and water plays a crucial role in the development of interfibre bonds in the sheet network. Water molecules penetrate the amorphous

regions of the fibre during beating and cause lateral swelling of the cellulose fibre. The water in the swollen fibres then acts as a plasticizer and increases fibre conformability.<sup>2</sup>

In papermaking, water first drains from the large spaces between the fibres forming a mat. After the excess water is removed by drainage and pressing, the surface tension created as air replaces water in the voids between the fibres further compacts the sheet and draws the fibres into more intimate contact. As drying begins, water then escapes from the swollen fibre walls in the reversal of fibre swelling and the fibres shrink laterally; interfibre bonding starts when this intrafibre shrinkage commences. This process of water removal continues until only small gaps exist between fibres effectively forming capillaries. The removal of water from these capillaries under surface tension forces draws the fibres together allowing hydrogen bonds to form. It is largely the fibril surfaces, acting under surface tension, which are thought to merge and form bonds.<sup>3,5</sup>

The development of interfibre bonds during drying is complex and it is this final mechanism, which allows sufficiently intimate contact of the fibres to form hydrogen bonds, that is unresolved. An alternative mechanism to the Campbell effect, i.e. movement of fibrils under surface tension forces, has been proposed by McKenzie,<sup>6</sup> who considered the applicability of the diffusion theory of adhesion to the development of interfibre bonds. According to diffusion theory, adhesion between plasticized polymeric materials, e.g. cellulose swollen with water, will occur because of diffusion or intermingling of molecular segments at the air-water interface. The removal of a solvent allows the formation of intermolecular bonds and hence results in bond formation between adjacent surfaces.

In a paper sheet, the development of interfibre bonds proceeds via the following key steps. Initially, drainage compacts the wet sheet by surface tension forces. Wet pressing further consolidates this and the area available for interfibre bonding is

largely established at this stage. Thereafter, evaporation of the remaining water increases the effective contact area by drawing the readily mobile microfibrils towards fibre intersections. Similarly, fibrillar segments on adjacent fibres will assume lowest energy configurations relative to these microfibrils. The molecular rearrangement and intermingling continues as water is removed from the regions of fibre-fibre contact until the water bridges between cellulose hydroxyl groups are shortened sufficiently and superseded by hydrogen bonds between contiguous fibres as the plasticizer is removed.<sup>3,6</sup>

In the case of chemically modified pulps, Ward<sup>7</sup> proposed that the introduction of hydrophilic groups, by increasing the fibre's affinity for water, promoted penetration of water molecules into the fibre, causing swelling and solvation. At these localized points of substitution, increased mobility of molecular segments and increased fibre flexibility occurred which facilitated interfibre bond formation via increased conformability. Jurbergs<sup>1</sup> studied hydroxyethylated linters using an electron microscope and found that the swollen modified fibres fibrillated readily on beating. Moreover, regions of the hydroxyethylated pulp were able to draw the fibrils and fibres together as drying proceeded, reinforcing existing bonds and generating new bonds. In this way, the introduction of hydrophilic groups into cotton linters pulp improved flexibility and conformability, increased the effective bonding area and thus improved the strength properties.

The ability of cellulose fibres to develop and participate in interfibre bonding is controlled by fibre flexibility and by surface characteristics, especially the hydrophilic nature of the fibre surface. Hence, the importance of the chemical nature of the fibre surface to bonding cannot be overstated and exemplifies the great significance of investigating increased hydrophilicity as a means of increasing fibre conformability and thereby, interfibre bonding levels in this project.

#### **4.1.2 Definitions and Significance of Pulp Evaluation Tests**

The effects of chemical modifications on the papermaking properties of linters pulp were monitored using a selection of industry standard tests. These tests are mostly mechanical in nature and assess the ability of paper to resist deformation or, in some cases, to resist failure under stress. The key tests used were Z-direction tensile index, zero span tensile index, tensile index and bulk. In combination with other tests, it is possible to deduce the effect of modifications upon the fibres. A brief definition and description<sup>8-14</sup> of each test and its significance is given below.

Z-Direction Tensile Index - This test measures the tensile strength perpendicular to the plane of the sheet, i.e. the force required when applied perpendicularly to delaminate a standard sample of paper.

Z-Direction tensile strength indicates the internal bond strength and bonded area or extent of interfibre bonding in the paper sheet. Interfibre bonding is related to fibre conformability and flexibility, and reflects the cohesion of a sheet, i.e. the formation of strong fibre-to-fibre bonds, which is a combination of the bonding strength of individual fibres and also the effective contact area between adjacent fibres.<sup>15</sup> In this project, improvements in the interfibre bonding, as measured by increases in Z-direction tensile index, were paramount. The factors influencing this test are discussed further in Section 4.2.1 (pp. 177 and 180).

Tensile Index - This is the tensile force required to rupture a strip of paper under specified conditions. A sample is clamped between two jaws and the jaws are then moved apart until the sample ruptures under tension. It is usually expressed in terms of the width of the sample.

The tensile index is a complex parameter, being dependent on several factors, such as the individual fibre strength, individual fibre length and interfibre bonding or

bonding strength (tenacity with which fibres adhere to each other in a paper sheet). Tensile strength is increased, up to a limit, by increased beating, increasing the fibre length, increasing fibre strength, increasing the interfibre bonding and decreasing bulk.

In rupturing, the sample has undergone fibre straightening and stretch. Sheet failure is a combination of fibre breakage and bond failure, depending on their relative strength; in a well-bonded sheet, the fibres will tend to fail and similarly weak fibres will rupture before bonds fail.

Zero Span Tensile Index - This may be defined as the tensile force required to rupture a paper sample when the distance between the test clamps is effectively zero. It is used as a measure of individual fibre strength, in contrast to tensile strength which reflects the sheet strength. Zero span tensile index was used in this project as an indicator of fibre strength and hence, the extent of fibre damage upon chemical modification.<sup>13,14</sup>

Beating - Beating or refining is the mechanical treatment of fibres to develop or enhance their papermaking properties. Beating effects include crushing, cutting, collapsing and flexing of the fibres. This in turn decreases the bulk and the freeness (drainage) characteristics of the pulp.

Beating increases the hydration of the fibres and the relative surface area by fibrillation and delamination; these combined effects increase the flexibility and conformability of the fibres. Strength properties improve with beating to a maximum and decrease thereafter as fibre damage becomes significant.

Freeness - This is the most frequently used papermaking test and measures the drainage properties of pulp, i.e. the drainage of water through pulp as a pulp mat forms. In papermaking, freeness provides a qualitative measure of the

sheet-forming characteristics of a pulp. It is sensitive to the presence of fines and decreases with increased fibre beating.

Canadian standard freeness (CSF) was used in this study and is defined as the volume of water collected from the side orifice of a standard tester when dilute stock is drained through a perforated plate. Pulps used in APPM's paper mills are refined to freenesses in the range CSF 250 and hence, in this study, all work was interpolated at CSF 250.

Bulk - Bulk is the volume per unit mass of paper. It is measured as the thickness of a specified number of sheets, at a specified pressure, divided by the mass.

Bulk, which is inversely proportional to sheet density, is directly affected by beating. Bulky papers are generally more opaque and less strong than a dense paper of the same grammage. Cotton linters typically have high bulk. The development of papermaking strength properties are often plotted against bulk, reflecting the effect of beating levels on the pulp.

Bending Resistance or Stiffness - This property measures the bending force required to deflect a rectangular test piece of paper by a given amount according to standard procedures.

The factors which control sheet stiffness are the sheet thickness and Young's modulus (elastic modulus), i.e. the ability to withstand strain. Increasing either the bulk or the interfibre bonding will increase the bending resistance of a given test sheet provided the other is kept constant. Cotton linters are thick-walled and stiff but lack the fibre length to impart sheet stiffness. In cases of adequate interfibre bonding and fibre length, the sheet stiffness reflects the stiffness of the individual fibres. Conversely, the bending resistance may indicate changes in the plasticity and conformability of the fibres.

Scattering Coefficient - This is a measure of the ability of a sheet to scatter incident light.

The scattering coefficient is often used as an indicator of the level of bonding: at sites of fibre-to-fibre bonds light passes directly from one fibre to another without passing through air and so light is not scattered at these points. Hence, with increased interfibre bonding, the scattering coefficient decreases. Scattering is also dependent on surface area and increased scattering will occur by virtue of beating, but the decrease in scattering caused by increased interfibre bonding upon beating is usually much more significant.

Opacity - This is a measure of the ability of a test sample to obstruct the passage of light or conversely, to resist the transmission of light. As described for the scattering coefficient, increases in surface area increase the opacity, whereas improved interfibre bonding tend to reduce opacity.

Tensile Energy Absorption - Tensile energy absorption is a measure of the energy absorbed by a sample under tension before it ruptures. It may be obtained by integrating the area under the tensile-stretch, i.e. stress-strain curve.

Burst - This is the pressure required to rupture a sheet of paper when pressure is applied to one face of the sheet; the test is often performed by expanding a flexible diaphragm against a circular area of the test sheet.

Burst is largely determined by the tensile strength and extensibility or stretch of the paper. Despite being a widely used test, its usefulness is questionable and it is used more for historical reasons as a general indicator of strength and toughness (ability of a sample to absorb energy). Because of the strong correlation of burst with tensile strength, it was not considered to provide additional information and hence, was not included in the small scale pulp evaluation tests (Section 4.2).



Tear Index - This is the ability of a sheet to resist tearing and is measured as the energy required to tear a standard strip of paper under specified conditions.

Tear is predominately controlled by fibre length, fibre strength and interfibre bonding. Tear strength is dependent on the amount of work done to break fibres relative to the work required to pull the fibres from the paper sheet. It is more sensitive to changes in fibre strength than tensile index. The tear-tensile indices graph is a good indicator of fibre damage. Because tensile index is strongly influenced by interfibre bonding, the tear-tensile index graph gives an indication of changes in fibre strength by changes in tear index for a given tensile index.

## **4.2 DEVELOPMENT OF A SMALL SCALE PULP EVALUATION METHOD**

Full pulp evaluation in a PFI mill typically involves four different beating times and requires a total of 125 g o.d. pulp. A small scale method of pulp evaluation was desirable because of the cost of chemicals per modification and the physical constraints of large scale reactions (e.g. to modify 125 g o.d. pulp approximately 10 L of solvent were required).

A method was developed in collaboration with staff at APPM to evaluate 5 g o.d. samples of chemically modified linters. Typically three 5 g o.d. samples were evaluated using a small Waring blender (*sic*) and variable beating times, depending on freeness levels. Each 5 g sample yielded pulp for freeness, moisture determination and the preparation of three standard handsheets, which allowed Z-direction tensile index, tensile index, zero span tensile index, bulk, stiffness, optical properties, roughness, air permeance, stretch and tensile energy absorption to be measured. Details of the small scale method and the above pulp evaluation tests are given in Appendix 1.

The effects of beating in the small Waring blender were compared with pulp beaten in the PFI mill.<sup>16</sup> The small blender produced pulps having lower freeness, and higher tensile and Z-direction tensile strengths at a given bulk than those obtained from the PFI mill. Also at CSF 250, the Waring blender did not reduce the bulk, nor possibly the fibre length as much as the PFI mill; stretch was significantly higher for pulp beaten in the Waring blender.

#### **4.2.1 Assessment of the Reproducibility of the Cotton Linters Preparation, Handling and Pulp Evaluation System**

The reproducibility of the cotton linters handling and pulp evaluation system was assessed by performing pulp evaluations on six samples of unmodified cotton linters from one particular batch of linters from Shoalhaven; throughout the remainder of this thesis, each modified linters pulp was compared with unmodified linters taken from the corresponding batch of Shoalhaven linters. The pulp evaluation results obtained reflect the reproducibility of the whole system, which includes the heterogeneity of the Shoalhaven cooking and bleaching system and their sampling technique. When received at Burnie, the linters were pressed in batches, crumbed with a mechanical crumber, bagged in weighed amounts and frozen prior to use. Freezing of pulps is a commonly accepted storage method, but reported effects include contraction of the fibre walls, making the fibres less flexible, and the possibility of introducing permanent kinks.<sup>16a</sup> For use in modifications, the samples were thawed, soaked overnight in water and dispersed in a blender. Modified linters were then refrozen prior to pulp evaluation. Linters samples were evaluated using the small scale and standard pulp evaluation methods described in Appendix 1.

The summary data interpolated at CSF 250 allows for the comparison or ranking of pulps at a common degree of development. The property development graphs show the relationship between various parameters and may be used to ascertain the underlying cause of changes in pulp properties during processing.<sup>13</sup>

The summary data interpolated at CSF 250, shown in Table 4.1, are generally quite reproducible. The variation of the tensile index and opacity values were minimal and whilst the Z-direction tensile index and bending resistance parameters show some variability, they are within the normal error limits for these tests. Some readings for zero span tensile indices, bulk and scattering coefficients for these unmodified linters show a variability that would usually be considered significant (e.g. see bulk values for samples 2 and 5 in Table 4.1)

**Table 4.1 : Pulp Evaluation Data for Six Samples of Unmodified Cotton Linters from the Same Batch, at CSF 250.**

Unmodified Cotton Linters Sample	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity (%)	Beating Time (min)	Stretch (%)
1	350	18	66	41	2.42	48	80	0	3.5
2	345	18	63	45	2.50	50	82	0	3.7
3	390	18	59	38	2.38	48	81	0.2	3.8
4	370	18	60	41	2.35	47	82	0	4.1
5	390	17	61	41	2.33	46	81	0	4.1
6	395	18	58	38	2.34	46	82	0	3.9
$\bar{X}$	375	18	61	41	2.39	48	81	0	3.9
% Difference*	15	6	14	18	7	9	3	-	17

\* Percentage difference between highest and lowest values.

However, it should be emphasized that these results reflect the variability of the entire system, not just pulp evaluation procedures. Hence, the apparent variability may be a consequence of different pulp compositions (fibre lengths, and immature

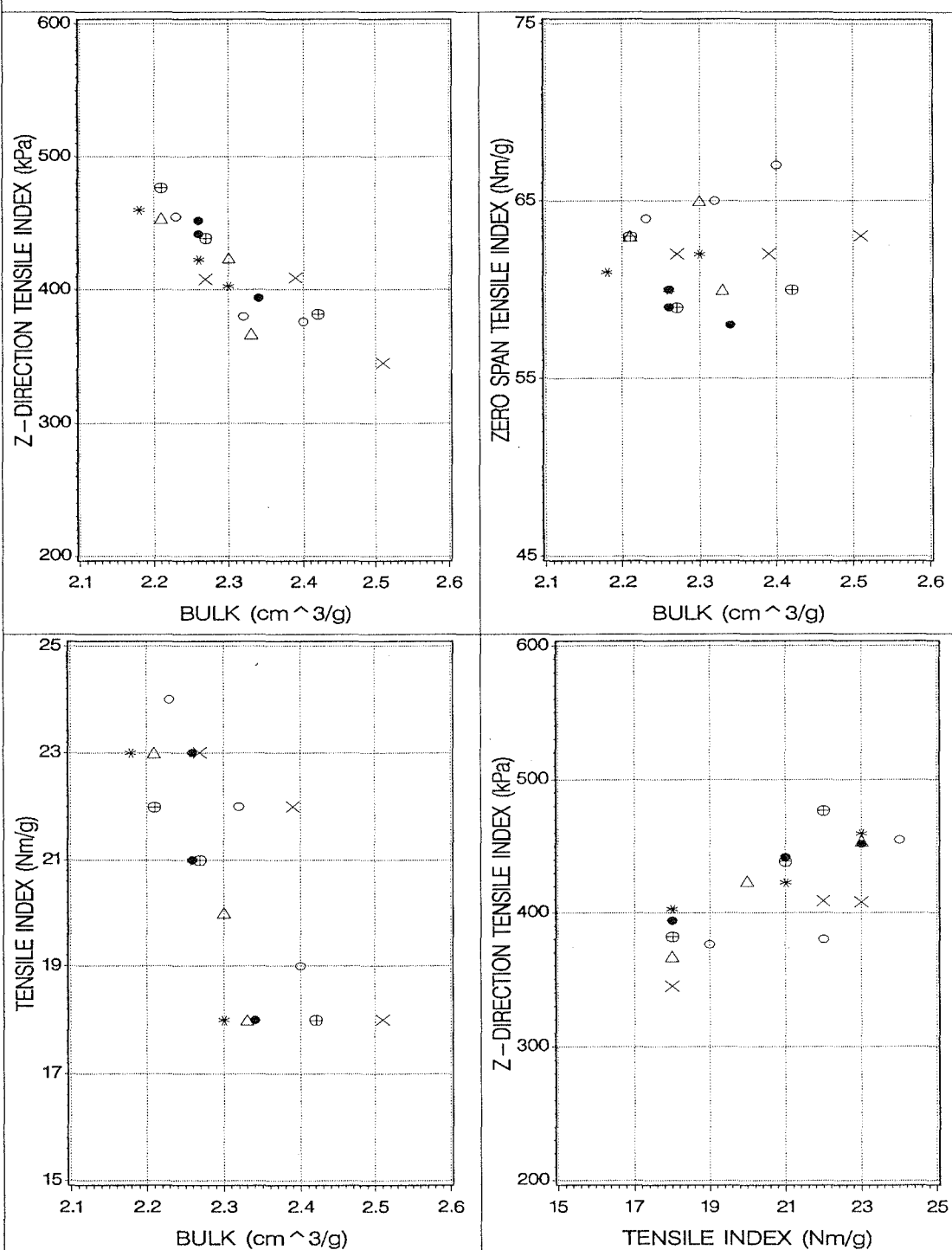
fibres to linters fibre ratio) and variable fines retention, especially in the filtration stage. In addition, this batch of linters exhibited low freenesses and hence, low beating times were used. All of the first sets were prepared using zero beating times, introducing further uncertainty into the results.

The graphs of the key papermaking properties of these six unmodified cotton linters samples are generally quite acceptable (Fig. 4.1). The most important graph, Z-direction tensile index versus bulk gave a narrow band of data points. The zero span tensile-bulk graph tends to converge and become more reproducible with beating. The variation in bulk apparent in these two graphs is exaggerated in the graph of tensile index against bulk, giving an impression of poor reproducibility. The plots of Z-direction tensile against tensile indices show clusters or envelopes of points around tensile strengths of 18, 21 and 23 Nm/g.

The 95% confidence limits and regression line graphs for the six samples of unmodified linters are shown in Figure 4.2. In the 95% confidence limit plot, the maximum variation in Z-direction tensile strength at a given bulk was slightly less than 20%. The variation of up to 30% apparent in the tensile index-bulk graph is due to the spread of bulk readings, not the tensile indices. The zero beating times, mentioned previously, with their concomitant uncertainty have contributed to the variation in the bulk readings; the spread of readings upon beating is quite acceptable. Tensile index readings typically have a variation of 5 to 10%. However, in this study, a higher percentage error than this was expected because of the low tensile strength of cotton linters (e.g. 15-25 Nm/g compared with pine and eucalypt Kraft pulps with tensile indices in the range 30-110 Nm/g<sup>13</sup>) and hence, any variation in the pulp evaluation system would result in a relatively high percentage error for tensile index readings.

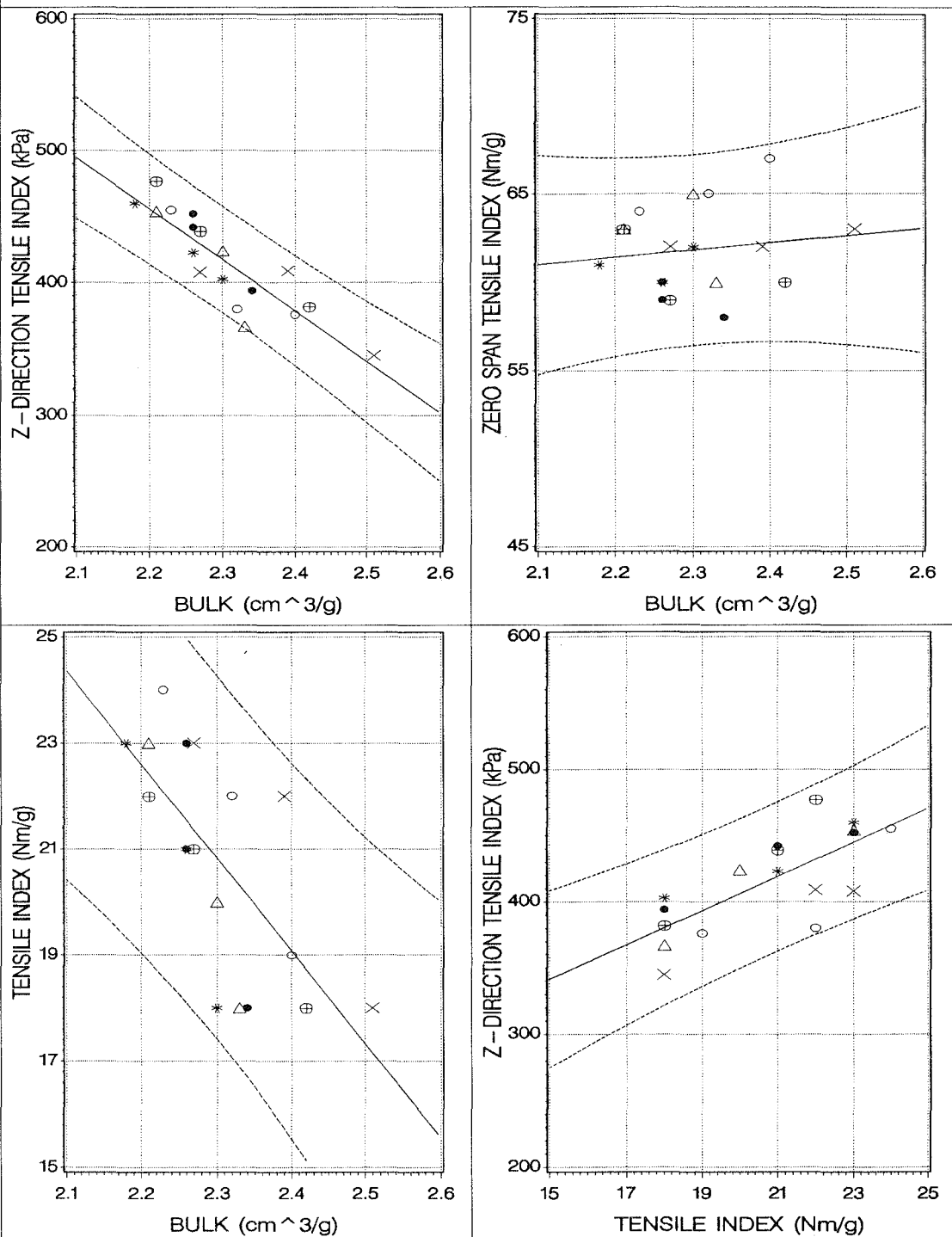
A crucial parameter in this project was the improvement of interfibre bonding as measured by changes in the Z-direction tensile index upon modification. The two

**Figure 4.1: Key Papermaking Properties of Unmodified Cotton Linters Showing Six Replications**



Six samples of cotton linters were evaluated from the same batch. Each replication is shown with a different symbol.

Figure 4.2: 95% Confidence Limits for Papermaking Properties of Unmodified Cotton Linters (N=6)



The solid line is the regression line through the combined points of six three-point replications. Each replication is shown with a different symbol.

main causes of variation in Z-direction tensile index readings arise from the intrinsic basis weight variation caused by the non-uniformity of paper and the presence of defects which coincide with the location of sheet failure. A commonly accepted error limit for Z-direction tensile index measurements is 15%<sup>17</sup> and allowing for the slightly larger variation noted in this system, a 20% change in Z-direction tensile strength was used as a selection criterion to rank the papermaking properties of modified cotton linters.

In summary, the reproducibility of the pulp evaluation system is quite good and within the error bounds expected of routine pulp evaluations. The procedures developed do not provide comprehensive evaluations but do allow for ranking of modified linters and estimation of strength properties relating the results to evaluations conducted on unmodified linters. Based on these rankings, the most promising chemical modifications may be scaled up and comprehensive pulp evaluations performed.

#### Limitations of the Small Scale Pulp Evaluation Method

The main disadvantage of the small scale evaluation method was that less handsheet material was available for testing and hence, fewer readings were taken of each parameter; only three beating points, not four, were obtained to monitor trends and interpret the development of key papermaking properties. A further consequence of using only three beating points for the evaluation of cellulose derivatives with such widely differing beating properties was the difficulty in choosing appropriate beating times for interpolation at CSF 250.

Another limitation of this small scale pulp evaluation method was the exclusion of some more traditional tests included in typical pulp evaluation regimes, namely burst and tear strengths, also because of the reduced quantity of handsheets available for testing.

### **4.3 EVALUATION OF THE PAPERMAKING PROPERTIES OF CELLULOSE DERIVATIVES**

Based on the assessment of the small scale pulp evaluation method, a 20% improvement in Z-direction tensile index over the unmodified cotton linters reference was used as a selection criterion to rank cellulose derivatives. Cellulose derivatives which gave improvements of 20% and above are discussed in Section 4.4 and PFI mill evaluations are discussed in Section 4.5. Those derivatives which gave less than 20% improvement in Z-direction tensile index are discussed in summary in the following sections. The interpolated data at CSF 250, showing key papermaking properties for these pulps and their unmodified reference, are presented in Appendix 2.

It should be noted that not all preparations described in Chapter 2 were evaluated for various reasons, which included visible and often extensive degradation, the small scale of some preparations and some anomalies in the pulp evaluation system.

#### **4.3.1 Properties of 2,3-Dialdehydo Celluloses and Derivatives**

##### **2,3-Dialdehydo Cellulose**

Cotton linters treated with sodium periodate for four hours generally gave bonding properties similar to or slightly better than unmodified cotton linters. However, they typically exhibited increased bulk (*ca.* 20%), which contributed to increases in stiffness and some loss of individual fibre strength. These property changes may be caused by fibre swelling due to improved hydration. Increased bulk was also present in the derivatives prepared from 2,3-dialdehydo cellulose.



### 2,3-Cellulose Oxime

The papermaking properties of 2,3-cellulose oxime have not been reported previously. Derivatization of 2,3-dialdehydo cellulose to the oxime generally gave papermaking properties similar to unmodified linters. At substitution levels of about 0.6% nitrogen, the increased Z-direction tensile indices and decreased scattering coefficients provide evidence of limited interfibre bonding improvements; some fibre damage was observed. At substitution levels of *ca.* 0.4% nitrogen, bonding properties were also slightly improved. Lowering the substitution level to 0.1 - 0.2% nitrogen was detrimental to bonding and strength properties, i.e. sheet stiffness was dependent on reaction time but the concomitant decrease in substitution level adversely affected other bonding properties (S237, S238 and S239). The lower substitution oximes produced fibres with a high bulk that were harder to beat. Decreased sheet stiffness, reduced tensile strength and increased scattering coefficient were also apparent.

### 2,3-Cellulose Semicarbazone

The papermaking properties of cellulose semicarbazones have not been assessed prior to this study.

Attempts to improve the papermaking properties of semicarbazone derivatives by reducing substitution levels were unsuccessful. An initial modification yielded a pulp with lower fibre strength and tensile strength than the unmodified reference. However, considering the high substitution level (S157, 1.85% N) the strength properties of this pulp were quite acceptable. Progressively reducing the substitution level restored the bonding properties to those of unmodified linters, despite evidence of fibre damage and a notable increase in bulk.

### 2,3-Cellulose Thiosemicarbazone

Although the thiosemicarbazone derivative of cellulose has been reported, its potential in papermaking had not been assessed previously. Despite relatively high substitution levels (S223, 1.0% N), the papermaking properties of the thiosemicarbazone derivative were similar to unmodified linters; some fibre damage was evident as a result of the sodium periodate oxidation, and the higher bulk increased optical properties slightly.

Lowering the substitution level had an adverse affect on papermaking properties. A marked increase in bulk (20%), decreases in bending resistance, tensile and fibre strength, and increased scattering coefficients were noted, but interfibre bonding appeared unaffected by this modification. In combination, these results indicated that marked swelling and weakening of the fibres had occurred.

### Girard's Reagent P and Girard's Reagent T Derivatives of Cellulose

The papermaking properties of these derivatives were found to be very poor. The Girard's Reagent T derivative of 2,3-dialdehydo cellulose is a new derivative and the ammonium moiety offered potential for interesting papermaking properties in blends with anionic cellulose derivatives. However, extensive fibre damage occurred on reaction, which halved tensile strength, and decreased sheet stiffness and interfibre bonding; bulk and scattering were reduced, opacity increased, and the fibres lost their elasticity. These effects seem to be largely a result of the extreme loss of fibre strength. Reducing the substitution level did not rectify this situation. In view of these results, assessment of the papermaking properties of this derivative in blends with anionic cellulose derivatives was not justified.

Girard's Reagent P, being more hydrophobic than the trimethylammonium analogue, was not expected to offer potential in papermaking. Indeed, the papermaking properties of this derivative were extremely poor, with bulk and optical properties being significantly increased. These results may be explained by reference to the results of the Girard's Reagent T derivative. Despite extensive fibre damage, interfibre bonding properties for this derivative were only slightly worse than unmodified linters. In the case of the hydrophobic Girard's P reagent, interfibre bonding was down 59% at CSF 250. Hence, the hydrophobic nature of this derivative was responsible for the poor interfibre bonding, poor conformability and low bonded area, which led to the observed high bulk and optical properties. The hydrophilic Girard's Reagent T derivative may have partly counteracted the effects of fibre damage by almost maintaining the interfibre bonding component, and maintaining the bulk and optical properties at their more usual levels.

#### **4.3.2 Properties of Cellulose Derivatives Prepared by Substitution and Addition Reactions**

##### **Carboxymethyl Cellulose**

The papermaking properties of carboxymethylated cotton linters were similar to those of unmodified linters. The derivatives were generally easier to beat but showed evidence of limited fibre damage. In contrast, blends of carboxymethyl celluloses with cationic cellulose derivatives, gave very significant improvements in bonding and strength properties (see Section 4.4). In view of the reputed papermaking advantages of carboxymethyl celluloses, carboxymethyl and hydroxyethyl celluloses were both used as standard references for comparison of modified Australian cotton linters in this project.

Only a select number of carboxyethyl celluloses were considered and most were prepared using a similar procedure to that which gave the most significant papermaking improvements, as reported by Ward, Murray and Thomas.<sup>18</sup> The reaction conditions used to prepare cellulose derivatives and their corresponding papermaking properties were not optimized for Australian cotton linters.

Substitution levels were lower than those obtained by Ward and co-workers<sup>18</sup> using essentially the same method (DS 0.013 *cf.* 0.036). Although relatively low substitution levels were obtained in this work, a derivative prepared by Ward *et al.*<sup>18</sup> with a similar substitution level (DS 0.014) yielded notable increases in breaking length, folding endurance and zero span breaking length. In addition, Walecka<sup>19</sup> reported improvements in key strength properties (burst, tensile and zero span tensile strengths) for substitution levels between 0.006 and 0.062. Hence, the low substitution levels obtained with Australian cotton linters should not have precluded notable strength improvements.

Numerous factors may have contributed to the apparent lack of bonding and strength improvements evident in this study. The most significant consideration is that most studies report carboxymethylation of raw linters, followed by purification, which is known to give far superior improvements to carboxymethylation of purified linters, as used in this study. Reasons for the use of cooked and bleached linters are given in Section 2.1.

Walecka<sup>19</sup> obtained 50-60% increases in tensile strength and over 200% improvement in burst strength, at a given beating time, by carboxymethylation of rag stock. Talwar<sup>20</sup> reported a 15% increase in the relative bonded area. Ward, Murray and Thomas<sup>18</sup> obtained a 230% increase in breaking length over the control. However, it is difficult to assess the improvements obtained and directly compare other results with those obtained in this study, because their results were not cited at a standard freeness or refining level.

Another difficulty in comparing these modifications with others is that key work on the carboxymethylation of papermaking fibres was performed in the period 1956 to about 1969. Hence, some standard pulp evaluation tests used to report improvements then (folding endurance and burst) are not used or favoured today, and tests such as Z-direction tensile index were not commonly available. In addition, by using the small scale pulp evaluation method as a screening procedure in this study, two commonly used tests, burst and tear strength, were not available for comparison with previous work.

A very significant difference exists in the beating times used to develop linters pulp strength. Beating times of one to three hours were often used by Walecka,<sup>19</sup> Harpman<sup>21</sup> and Ward<sup>18</sup> and their co-workers, whereas in this study, beating times one order of magnitude lower were typically used. In addition, they used Jokro and Valley beaters which may have contributed to the longer beating times. A Valley beater was not used in this work, despite being found to be best suited to Australian linters,<sup>16</sup> because a much larger pulp charge was required than with a PFI mill (300 g o.d. cf. 125 g o.d.). However, a PFI mill also simulates modern mill refining better than a Valley beater.

Harpman, Reid and Turner<sup>21</sup> used purified cotton linters that had received no prior mechanical treatment or beating. Walecka<sup>19</sup> used bleached rag stock because of its high degree of polymerization but beat the fibres prior to modification. Ward, Murray and Thomas<sup>18</sup> used chemical cotton, a grade of second-cut cotton linters, which presumably was cooked and bleached prior to carboxymethylation; no mention was made of prior beating. In this present work, the second-cut cotton linters used were pre-cut, cooked, bleached and beaten prior to modification and were from the final stage of the linters processing plant, immediately prior to use on the papermachine. Hence, it may not have been possible to develop strength properties and realize the benefit of modifications, before detrimental beating effects became significant.

### Hydroxyethyl Cellulose

Evaluation S318, which gave a noteworthy improvement in Z-direction tensile, is discussed in Section 4.4.

Hydroxyethylation of cellulose is considered as a benchmark for modifications and is one of the most exhaustively studied cellulose derivatives. However, papermaking properties of hydroxyethylated linters were not as high as anticipated on the basis of previous results reported in the literature.

An initial pulp evaluation of hydroxyethylated linters gave results similar to unmodified linters, with some loss of fibre strength and sheet stiffness (S191). Increasing the concentration of the sodium hydroxide used to swell the fibres resulted in a pulp that was very resistant to beating and gave high freeness values that could not be extrapolated reliably to CSF 250. Repetition of this experiment, but with increased beating times to allow interpolation at CSF 250, revealed slight improvements in interfibre bonding confirmed by decreased scattering and increased sheet stiffness, which were negated by the considerable fibre damage that occurred. The pulp was much harder to beat than the unmodified reference and the bulk was increased significantly. In combination these factors are indicative of fibre swelling and extensive hydration. Investigation of other hydroxyethylation methods produced a pulp similar to unmodified linters (S261), and another that was resistant to beating (S316). Although not interpolated at CSF 250, extremely poor bonding properties were expected, but without the anticipated decrease in individual fibre strength.

Scaling up the procedure that yielded a derivative with a 22% increase in Z-direction tensile strength (S318) gave pulp that did not show an overall improvement in papermaking properties and was possibly worse than unmodified linters (S396).

This result was probably due to changes in the derivatized cellulose caused by the use of different equipment, stirring techniques and filtering times in the large scale reaction.

Pulp evaluation results for a blank run using hydroxyethylation conditions, but without the addition of the hydroxyethylating reagent (S390), clearly showed significant fibre damage and loss of strength properties in the pretreatment, which hydroxyethylation had to overcome.

### Hydroxypropyl Cellulose

Harpman, Reid and Turner<sup>22</sup> obtained strength improvements for hydroxypropylated linters. Whilst they found that hydroxypropylation of cooked and bleached linters improved the papermaking properties compared with the control linters, far superior properties were obtained by hydroxypropylation of raw cotton linters. The gains achieved by hydroxypropylation are commonly acknowledged as not being as significant as for hydroxyethylation,<sup>23</sup> because of the more hydrophobic nature of the former derivative.

In a preliminary investigation to assess the potential of several hydroxypropylations for papermaking, hydroxypropylation of cotton linters did not impart favourable strength properties to the linters pulp. Several modifications could not be interpolated at CSF 250 because the freenesses obtained were much higher than anticipated, which indicated that the hydroxypropyl celluloses were quite resistant to beating. Nonetheless, beating point data suggested poor bonding and strength properties (S263, S265 (i) and S314). By tripling the beating times, a usable evaluation was obtained which revealed that extensive fibre damage had occurred. This was confirmed by the low tensile strength (S265), although interfibre bonding was only slightly lowered.

It may be tentatively deduced from a further pulp evaluation, which required extrapolation to CSF 250, that hydroxypropylation did not cause fibre damage. However, the results suggested the fibres were bulky and less conformable than the unmodified linters. Their lower tensile strength and bending resistance may have been due to a decreased interfibre bonding component, reflecting a reduced bonded area. This was confirmed by an increase in the scattering coefficient (S315, +17%). Alternatively, these property changes may be attributed to fibre swelling.

### Cellulose Mesylate

The strength properties of handsheets prepared from mesylated pulps were investigated by Japanese workers.<sup>24,25</sup> Using X-ray photoelectron spectroscopy, Sawatari<sup>24</sup> also investigated the location of substituents on the fibre. Pulps were obtained with up to 22% mesylate substitution, using pulps in a permutoidal or swollen state. However, the maximum handsheet strength was obtained at only 1% mesylate. Mesylate substitution of only 0.6% was achieved under topochemical or "unswollen" conditions, with strength properties decreasing sharply with increasing mesylate content. Sawatari<sup>24,25</sup> concluded that the hydrophobic mesylate groups interfered with the hydrogen bonding ability of the hydroxyl groups and hence, hindered the development of sheet strength.

Mesylates were prepared in this study as useful intermediates in syntheses and not for their potential in papermaking. Poor papermaking properties were anticipated because the mesylate group is hydrophobic. Moreover, quite high substitution levels were obtained for most mesylations (e.g. S86, 7.34% S), further reducing the likelihood of bonding improvements. This was confirmed by initial pulp evaluations which demonstrated very poor papermaking properties, with interfibre bonding decreased to 34% of the value of unmodified linters. Attempts were made to improve the poor papermaking properties of cellulose mesylates for use in further derivatizations, i.e. it was hoped fluorodeoxy cellulose could be evaluated provided



the properties of the precursor, cellulose mesylate, were similar to unmodified cotton linters. By reducing the severity of the reaction conditions and the substitution level to 4.15% sulfur, a pulp with properties similar to unmodified cotton linters was obtained. A preparation that was intended to give a substitution of about 1% sulfur was unsuccessful ( $<0.3\%$  S), but again, papermaking properties very similar to unmodified cotton linters were obtained. Hence, if the pulp evaluation results of this trial may be given some credence, and treated as a blank trial, it may be tentatively deduced that the poor pulp properties of cellulose mesylates were due to the mesylate group itself and the substitution level, not the reaction conditions.

Overall, mesylation of cotton linters increased the bulk and sheet stiffness, which resulted in decreased conformability and decreased bonded area. In combination with the hydrophobic effects, this explained the observed decreases in strength and increased optical properties.

### Cationized Cellulose

Cationization of cotton linters using essentially the method of Antal, Paszner and Micko<sup>26</sup> produced quite different results to those reported in their study (see also Section 4.4.1). Their low and medium level preparations, with virtually the same substitution level (S126, 0.13 and 0.15% N, respectively), had markedly different papermaking properties. The medium substitution gave a Z-direction tensile strength increase of 30% over the unmodified reference with evidence of some fibre damage. However, the low substitution level trial was considerably worse in all properties, except tensile strength (Z-direction tensile reduced by 35%) and the high-level trial was similar to that using unmodified linters. Replications of the medium trial did not yield the same improvement in interfibre bonding (S139, 0.15% N, 0% change in Z-direction tensile index; S213, 0.05% N, 17% increase).

Significantly increasing the substitution level was not beneficial to the papermaking properties. By increasing both the amount of cationizing reagent and sodium hydroxide used, freenesses were too far below CSF 250 to interpolate, indicating poor drainage properties and hence extensive fibre damage and fines generation. Reducing exposure time to sodium hydroxide (S283, 0.43% N) gave a pulp that could be evaluated, but which demonstrated worse strength and optical properties than unmodified linters. Similarly, a trial at half the consistency of most trials gave papermaking properties slightly worse than the reference pulp (S352, 0.12% N, -18%).

A blank run for cationization experiments revealed some fibre damage and a minor reduction in strength properties (S334, -12%).

Hence, with the exception of one trial which yielded a 30% increase in Z-direction tensile strength (see Section 4.4.1) and could not be repeated, cationizations at moderate substitution levels (0.1% N) had little effect on the papermaking properties of cotton linters. At higher substitution levels (0.4% N), with concomitant exposure to greater quantities of sodium hydroxide, the strength properties were adversely affected.

### **4.3.3 Properties of Michael Addition Reaction Cellulose Derivatives**

#### **Blank for Michael Addition Reactions**

The pulp evaluation results for a blank experiment performed using standard conditions for the Michael addition reactions exhibited some fibre damage (zero span tensile index -27%) and possibly a slight decrease in Z-direction tensile and tensile strengths (-16 and -14%) compared to untreated linters. Hence, any improvement in papermaking properties for Michael adducts of cotton linters is

attributable to the substituent itself and not the combined effects of the reaction conditions, i.e. sodium hydroxide treatment and heat treatment.

### Cyanoethyl Cellulose

Cyanoethylated papers are widely used as insulating papers because of their thermal stability and dielectric properties.<sup>27</sup> However, cyanoethylated pulps were also reported to have superior strength properties to unmodified pulps at low substitution levels.<sup>21,27</sup> Harpman, Reid and Turner<sup>21</sup> reported improved burst, fold and tear strength for cyanoethylated cotton linters containing 0.56% nitrogen. Spadaro, Janssen, Vix and Simons<sup>28</sup> reported a maximum improvement in papermaking properties of cyanoethylated pulps in the range 1.55 to 1.85% nitrogen. However, they did not consider these improvements to be commercially significant.

In a much later study on wood pulp, El-Shinnawy and El-Kalyoubi<sup>29</sup> obtained improved breaking length, fold number and burst factor (nearly double) over the untreated pulp, with substitution levels in the range 0.2 to 0.9% nitrogen. The tear factor was generally not improved by cyanoethylation.

The thermal stability of cyanoethylated kraft and cotton linters pulps was investigated by Ward and co-workers.<sup>30</sup> They reported significant improvements in folding endurance, tensile strength, stretch and tensile energy absorption. The observed property improvements at low substitution levels were attributed to greater affinity for water, resulting in greater swelling during beating, increased bonding and hence, improvements in sheet strength. At higher substitutions, the water absorption capabilities were reduced by the hydrophobic properties of the cyanoethyl group.

It was found in the present study that cyanoethylation of cotton linters at low substitutions did not significantly affect the papermaking properties of the pulp. The

severity of reaction conditions was reduced by reference to blank trials for cyanoethylations. This optimization of the papermaking properties upon cyanoethylation, restored key properties to the level of unmodified linters. Hence, reducing the effects of pretreatment at low substitutions (0.1% N) resulted, possibly, in a slight increase in interfibre bonding, decrease in optical properties and decrease in individual fibre strength. Modifications at high substitutions (e.g. 1.39 and 4.9% N) resulted in progressively worse papermaking properties. Moreover, Z-direction tensile strength, tensile strength, sheet stiffness and fibre strength losses became significant. Worsening bonding properties were confirmed by a marked increase in scattering coefficient. These property losses at high substitution appear to be more a consequence of the reaction conditions than an effect of the cyanoethyl moiety.

A one-off trial using ammonium hydroxide as a swelling agent in a cyanoethylation appeared to have little effect on the pulp evaluation results of the cyanoethylated linters.

Cyanoethyl cellulose prepared using an adaptation of the method reported by Frick and co-workers,<sup>31</sup> which involved shorter reaction times and much greater acrylonitrile concentrations, resulted in higher substitution levels (*ca.* 1% N). However, interfibre bonding and fibre strength were lowered. These effects were not evident in the tensile index results.

The papermaking properties of cyanoethyl cellulose prepared at the 125 g o.d. scale, which gave significant improvements in tensile and burst strengths, are discussed in Section 4.5.

#### Amidoethyl Cellulose

Acrylamide treatments that gave significant bonding improvements or were performed at the 125 g o.d. scale are discussed in Sections 4.4 and 4.5, respectively.

Pulp evaluations of the remaining amidoethyl celluloses generally maintained interfibre bonding levels at those of unmodified linters and showed limited fibre damage. Lowering the substitution level (0.75% to 0.09% N) by significantly reducing the concentration of acrylamide used did not improve the pulp properties. Performing experiments in sealed bags to minimize alkaline degradation (see discussion overpage for the *N,N*-methylenebisacrylamide-cellulose derivative) and using higher consistencies caused minor, insignificant changes in pulp properties.

Increased reaction times did not appear to adversely affect the pulp properties. Discrepancies were apparent in the results of trial S233 compared with S230 and S226, which both showed significant bonding improvements (Section 4.4.1). Similar substitution levels were obtained in these three trials, but the properties of S233 were worse than those of S230, which had a much longer reaction time. The decreased optical properties and bulk of S233 suggested improved fibre conformability, but this did not translate into improved interfibre bonding.

Linters treated with acrylamide using the method of Frick and co-workers<sup>32</sup> did not improve the papermaking properties, although less fibre damage was evident. Bending resistance was also significantly lowered.

Two trials using *N,N*-dimethylformamide as a solvent produced the worst papermaking properties of all the acrylamide treatments. The lower substitution derivative of the two exhibited poor Z-direction tensile (-39%) and tensile strengths, with evidence of fibre damage. The bulk and optical properties were markedly increased. These property changes are probably a direct consequence of the presence of *N,N*-dimethylformamide itself. Decreased hydration and conformability caused by this relatively hydrophobic solvent would reduce fibre-to-fibre bonding and thus, effectively increase bulk.

### *N,N*-Methylenebisacrylamide Derivatives of Cellulose

Whilst the reaction of *N,N*-methylenebisacrylamide (MBA) with cellulose is known, the papermaking properties of the MBA-cellulose derivative have not been reported previously. The derivatization of cellulose with MBA did not impart favourable papermaking properties to cotton linters. In a series of experiments with substitutions ranging from 0.05 to 4.14% nitrogen, papermaking properties generally deteriorated with increasing substitution levels.

At substitution levels of about 0.1% nitrogen, properties of the MBA derivative were very similar to unmodified linters, despite a slight increase in bulk (S224, S225 and S227). Similarly, a derivative prepared using much higher concentrations of MBA was not significantly different to those produced in the above trials, except for evidence of limited fibre damage and increased bulk (S282, 1:4 parts cotton to MBA, 0.61% N).

Reactions performed using more typical conditions for Michael addition reactions, which resulted in much higher substitution levels, gave very poor papermaking properties. The resulting sheets were bulky, possessed very low strength and bonding properties, and showed extensive fibre damage, whereas optical properties were largely unaffected.

In trials to assess the effect of excluding oxygen, the use of sealed bags was found to be superior to atmospheric conditions because less fibre damage occurred and interfibre bonding levels were maintained or slightly better than unmodified linters. These results were expected because of reduced exposure to oxygen and hence, reduced alkaline degradation of the cellulose. The scattering coefficient was lowered and bending resistance increased, which indicate increased interfibre bonding.

Hence, substitution levels of about 0.1% nitrogen yielded the best pulp evaluation results for MBA-cellulose derivatives, but these were largely the same as unmodified linters. Modifications of the reaction conditions for this derivative reduced the fibre damage and marginally increased the interfibre bonding.

The anticipated improvement in papermaking properties for this derivative, due to its capacity to crosslink and potential for hydrogen bonding via the two amide groups, were not realized over a range of substitution levels. The papermaking properties of the MBA-cellulose derivative suggested that the effects of the vinyl group of the unreacted acrylamide moiety counteracted the advantages of the two amide functionalities, i.e. at high substitution levels the hydrophobic vinyl moiety negated the possible improvements resulting from hydrogen bonding available with the two secondary amide groups.

#### *N*-(3-Aminopropyl)methacrylamide-Cellulose Derivatives

A one-off assessment of the papermaking properties of this new derivative gave results very similar to unmodified linters, with the possibility of a slight improvement in interfibre bonding (17% increase). An attempt to decrease the substitution level and possibly further improve the papermaking gains was unsuccessful.

The *N*-(3-aminopropyl)methacrylamide derivative of cellulose was also prepared as part of a study to assess the effect on pulp properties of the series, acrylamide, methacrylamide and *N*-(3-aminopropyl)methacrylamide. However, the disparity in substitution levels obtained made it difficult to assess the effect of the different substituents on the papermaking properties. Although several amidoethyl cellulose derivatives at similar substitution levels gave slight bonding improvements, as did the *N*-(3-aminopropyl)methacrylamide derivative, optimum papermaking properties

for amidoethylated linters were generally obtained at higher substitution levels, thus hindering a direct comparison at equivalent substitution levels.

#### Methacrylonitrile and Methacrylamide Cellulose Derivatives

The methacrylonitrile-cellulose derivative (S332), whilst exhibiting similar properties to unmodified linters, showed evidence of slight fibre damage, an increase in bulk and worsening of optical and stiffness properties. Similarly, the three methacrylamide-cellulose derivatives either had no affect or a slight adverse affect on papermaking properties.

The methacrylamide derivative of cellulose could only be prepared at relatively low substitution levels (0.1% N), whereas the acrylamide derivatives of cellulose which showed the greatest interfibre bonding improvements typically contained 0.5% nitrogen. Hence, they cannot be compared meaningfully with acrylamide and *N*-(3-aminopropyl)methacrylamide in a study of the structure-property relationships of these substituents on papermaking properties. Both the methacrylonitrile and methacrylamide derivatives of cellulose are more hydrophobic than their unmethylated analogues, but this effect was not significant in the papermaking properties of the modified pulps. These results indicate that the methyl group of *N*-(3-aminopropyl)methacrylamide did not have a significant adverse affect on the properties of the cellulose derivative and that the amino groups of *N*-(3-aminopropyl)methacrylamide were most probably the dominant influence in terms of papermaking properties.

#### Maleic Acid-Cellulose Derivatives

The reaction of maleic acid with cellulose is known to alter the fabric properties of the fibre.<sup>31</sup> However, reports of the effect of this modification on the papermaking properties have not been forthcoming. It was anticipated the diprotic acid



functionality would promote hydrogen bonding and hence, improve hydrophilicity and conformability.

The first trial of maleic acid on cotton linters resulted in significant interfibre bonding improvements and is discussed in Section 4.4.1; PF1 mill evaluations are discussed in Section 4.5. A series of attempted replications of this experiment, including minor variations to this procedure, did not reproduce the observed bonding improvements. Derivatives prepared with similar substitution levels did not attain similar bonding improvements.

Numerous trials were performed on a batch of unmodified linters that had particularly low freeness values (S349 to S373, Appendix 2). The consequences of this were (i) the strength and bonding properties of this batch may not have developed sufficiently by beating and (ii) at zero beating times most freenesses were already below CSF 250 and hence, beating curves were extrapolated not interpolated, potentially introducing further errors. On more typical linters, these modified pulps may have shown papermaking improvements.

In the series of treatments of linters with maleic acid, there did not appear to be a systematic effect on the papermaking properties. In general, properties were similar to those of unmodified linters. Some trials showed changes in bending resistance, zero span tensile index or bulk, whilst other trials exhibited the opposite effect. These effects did not appear to correlate with substitution levels. A low substitution derivative obtained by halving the amount of maleic acid used had the worst pulp evaluation results of the maleic acid derivatives, with interfibre bonding, tensile index and fibre strength being lowered (S349, -27%, -19%, -16%, respectively). Conversion of the free acid derivative to the sodium salt (S350) gave virtually identical results to this previous trial, except for increased bulk. This was somewhat different to the improvement anticipated from studies of the sodium salt of carboxymethyl cellulose<sup>20</sup> (see Section 2.3.1).

### Itaconic Acid-Cellulose Derivatives

In general, the papermaking properties of itaconic acid-cellulose derivatives did not differ significantly from those of unmodified cotton linters. One trial (S327) gave a 20% increase in interfibre bonding and is discussed in Section 4.4.1.

The use of benzyltrimethylammonium chloride as a catalyst for Michael addition reactions offered no advantage to the bonding properties of these pulps. Similarly, oven-curing the reagents as a filter pad or as a slurry appeared to have little effect, with the slurry method offering possibly a slight improvement in interfibre bonding.

For the itaconic acid derivative with the lowest substitution level, most strength and optical properties increased slightly, except tensile strength which was constant (S326). Increasing the substitution level by doubling the concentration of the itaconic acid solution negated the slight positive effect of treatment with itaconic acid. Doubling the consistency of the reaction had, if anything, an adverse effect on most key properties. These last two trials were performed on the low freeness batch of cotton linters, discussed previously, and hence, their true papermaking potential may be masked by the poor properties of the unmodified reference.

### Reactions of Other $\alpha,\beta$ -Unsaturated Carbonyl Compounds with Cellulose

Selected Michael addition reagents were reacted with cotton linters in one-off trials to assess their papermaking potential. Borderline improvements in papermaking properties were obtained after reaction of linters with fumaric and methacrylic acids, but reactions with *trans*-cinnamic, crotonic and acrylic acids offered no advantage in papermaking properties compared to unmodified linters. These reactions were all performed on the low freeness batch of cotton linters and may not accurately represent the effects of these modifications on pulp properties.

The methacrylic acid derivative (S361) gave an 18% improvement in interfibre bonding with no affect on other properties.

Fumaric acid on linters slightly increased the interfibre bonding (18%), but without the corresponding decrease in optical properties. Tensile strength and sheet stiffness were also improved (+26% and +17% respectively). The minor decrease in bulk partly explains these improvements by suggesting increased hydrophilicity and conformability (see also Section 4.4.1).

#### **4.3.4 Properties of Double Derivatives and Blends**

Most of the blends of cationic-anionic cellulose derivatives exhibited marked improvements in papermaking properties and are discussed in Section 4.4.2. However, of the double derivatives prepared, only cationized amidoethyl cellulose (S348, S388) and amidoethyl hydroxyethyl cellulose (S410) showed improved papermaking properties (Section 4.4.2).

##### **Double Derivatives**

The reactions of acrylamide, maleic acid and *N,N*-methylenebisacrylamide with hydroxyethyl cellulose often proved detrimental to the papermaking properties of the hydroxyethylated linters. Initially, handsheets could not be formed from an amidoethylated hydroxyethyl cellulose (S336) because of excessive swelling, but a later trial using modified reaction conditions gave significant bonding improvements (S410, Section 4.4.2). The *N,N*-methylenebisacrylamide derivative possessed extremely poor bending resistance (-65%) and tensile strength with evidence of significant fibre damage. Interestingly, opacity was lowered, whilst bulk was increased and interfibre bonding was maintained. The maleic acid-treated hydroxyethyl cellulose derivative showed a 21% reduction in interfibre bonding, along with reductions in tensile strength, bulk and sheet stiffness.

Cationization of amidoethyl cellulose (S405, 0.31% N) adversely affected the bending resistance and optical properties; bonding properties were unaffected. Carboxymethylation of cationic linters (S241, 0.12% N, 8.72 meq/100g) reduced the interfibre bonding and scattering coefficient, but increased the sheet stiffness.

Cationization of the maleic acid-cellulose derivative had a detrimental affect on all key papermaking parameters. All bonding, strength and optical properties were lowered and bulk was increased. This modification was performed on the low freeness batch of linters discussed previously. Conversely, treatment of cationic cellulose with maleic acid did not have such an adverse affect on the pulp properties, with only minor changes to the tensile and Z-direction tensile indices.

Significant bonding improvements were anticipated with these derivatives because of the introduction of both an anionic and cationic functionality, as evidenced in the blends of these derivatives. The nominally 30% decrease in individual fibre strength for the double derivatizations is not much greater than for one step derivatizations. This suggests that the two step derivatization (e.g. by exposure to sodium hydroxide twice) was not causing excessive damage and hence, was not responsible for the poor bonding properties. The poor strength properties may be a consequence of the second reagent reacting with the first cellulose derivative and not the primary alcohol groups on the cellulose backbone, as discussed in Section 2.5.1. For example, in the cationization of the maleic acid-cellulose derivative, the epoxide group of the cationizing reagent would preferentially react with the acid moiety and not the hydroxyl groups of the cellulose chain. Hence, the favourable electrostatic forces created by positive and negative sites along the cellulose backbone would not exist. This may explain the poor performance of the cationized maleic acid-cellulose derivative, as discussed in the preceding paragraph.

### Blends of Anionic and Cationic Cellulose Derivatives

Of the blends evaluated only six did not exhibit 20% or greater improvement in interfibre bonding.

The maleic acid-cationic cellulose blend S379/S382 (80:20 ratio) showed signs of slight bonding improvements and limited loss of fibre strength and elasticity.

The fumaric acid-cationic cellulose blends (S414/S404) also showed signs of bonding improvements, with the 40:60 and 20:80 blends giving 19 and 18% improvements in interfibre bonding, respectively. They also demonstrated a marked increase in tensile energy absorption, suggesting greatly improved fibre elasticity and possibly conformability, which did not translate into significant bonding improvements. The unaffected scattering coefficient suggested the minor bonding improvements were due to an increase in their respective bond strength and not an increase in the number of fibre-to-fibre bonds.

The 40:60 and 20:80 ratios of a maleic acid-cationic cellulose blend prepared using a more concentrated maleic acid solution (S307/S308) went "through the hoop", in industry-accepted terminology, i.e. beating was so severe that the fibres did not form a mat during freeness testing and hence, a high and invalid CSF reading was obtained.

## **4.4 DISCUSSION OF THE MOST PROMISING MODIFIED CELLULOSES**

The most promising modified celluloses will be discussed according to two categories: (i) aldehydo, substitution and addition, and Michael addition cellulose derivatives and (ii) double derivatives and blends. These are discussed in ascending

order of improvement in Z-direction tensile index, and not according to reaction type as in previous sections. Approximately forty pulps showed greater than 20% improvement in Z-direction tensile index.

The property changes of these promising pulps relative to their unmodified reference are shown as percentage increases or decreases at CSF 250. For ease of discussion, the results for each blend set are grouped together, regardless of the percentage improvements in Z-direction tensile index obtained for the other ratios in the set.

#### **4.4.1 Promising Oxidized, Substitution and Addition, and Michael Addition Cellulose Derivatives**

##### **Itaconic Acid-Cellulose Derivative (S327)**

This derivative gave a 20% improvement in interfibre bonding at CSF 250 (see Table 4.2). Most other papermaking parameters were similar to unmodified linters, with the exception of an apparent slight increase in scattering coefficient and increased bending resistance.

Similarly, the graphs of the key papermaking properties of this derivative show relatively minor changes (Appendix 3, Fig. 1). The Z-direction tensile indices of the itaconic acid-cellulose derivative were higher than for cotton linters, but not significantly. No fibre damage occurred and the apparent increases in interfibre bonding and tensile strengths were not of great importance. The unmodified linters showed significant development of papermaking properties with beating, whereas the modified pulp did not respond greatly with beating, which may be a consequence of the very low beating times used.

**Table 4.2:** Most Promising Modified Celluloses<sup>a</sup> Prepared by Oxidation, Substitution and Addition, and Michael Addition Reactions

Cellulose Derivative (Number)	Z-Dir. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity (%)	Beating Time (min)	Stretch (%)	Substitution
Itaconic Acid (S327)	+20	NS <sup>b</sup>	(+7)	+19	NS	(+7)	(+7)	-50	+17	7.91 meq/100g
Fumaric Acid (S363)	+22	+20	-12	+20	NS	NS	NS	+225	+15	13.2 meq/100g
Hydroxyethyl (S318)	+22	-26	-23	-28	+8	NS	NS	+400	+12	1.45% hydroxyl
2,3-Dialdehydo (S325)	+22	NS	-26	+30	+24	+19	NS	+150	-26	Cu No. 7.5
2,3-Oxime (S210)	+23	-16	-28	(+6)	NS	-24	NS	+220	(-7)	0.50% N
2,3-Thiosemi. (S272) <sup>c</sup>	+25	+17	+12	-32	70	NS	NS	+395	-32	0.24% N
Cationized (S126)	+30	NS	-27	-9	NS	-25	NS	-80	+21	0.15% N
Amidoethyl (S230)	+26	+31	-18	-20	-9	-28	-10	-32	+39	0.58% N
Amidoethyl (S226)	+31	+38	-13	-51	NS	-28	-10	-38	+39	0.51% N
Amidoethyl (S202)	+33	(+8)	-16	-14	NS	-	-	-42	(+7)	0.38% N
Maleic Acid (S222)	+36	NS	(-6)	-29	NS	NS	NS	NS	+39	3.95 meq/100g

- a. Small scale pulp evaluation method used. Only modifications showing 20% or greater improvement in Z-direction tensile index relative to their unmodified linters reference are included. Property changes are shown as % increases or decreases relative to unmodified linters.
- b. Not significant change (5% or less). Bracketed values are probably not significant.
- c. Properties improved relative to 2,3-dialdehydo cellulose precursor.

### Fumaric Acid-Cellulose Derivative (S363)

This fumaric acid-cellulose derivative (S363, 13.16 meq/100g) gave a 22% improvement in Z-direction tensile index at CSF 250 (Table 4.2). A 17% increase in tensile strength was accompanied by minor fibre damage and an increase in bending resistance. The increase in tensile strength may reflect the minimal fibre damage and improved interfibre bonding that occurred upon modification.

Although showing signs of improvement, the papermaking properties of this derivative showed only minor changes to key properties (Appendix 3, Fig. 2).

### Hydroxyethyl Cellulose (S318)

The improvement in the papermaking properties of pulp by hydroxyethylation has been studied exhaustively. Ward<sup>27</sup> stated that all studies reported increased sheet strength properties, especially if high concentration alkali solutions were used that produced high swelling. Moreover, significant gains in breaking length, folding endurance and tear were obtained upon hydroxyethylation but with notable losses in opacity.

Harpman, Reid and Turner<sup>21</sup> obtained a hydroxyethylated pulp with 0.18 DS which had double the burst, 20 to 30% improvement in tear strength and up to 70 times the folding endurance of the reference pulp. They also reported no adverse effects on other papermaking properties. In another study<sup>22</sup> they obtained increases in burst of 220%, in tear of 150% and folding endurance was increased by 250 times upon hydroxyethylation; they also noted better formation.

Ward,<sup>33</sup> in one of his many studies, reported significant improvements obtained by blending an intractable hydroxyethylated pulp with unmodified pulp, in which the hydroxyethylated pulp functioned as a beater additive. In a more detailed study,



Ward and colleagues<sup>34</sup> found that blends of low DS hydroxyethyl celluloses and unmodified linters gave superior properties to the equivalent DS hydroxyethylated linters. Ward and co-workers<sup>35</sup> also noted the importance of using high alkali concentrations to promote swelling and increase reagent accessibility, thereby producing a derivatized cellulose that gave superior handsheet properties.

In a study by Spadaro, Janssen, Vix and Simons,<sup>28</sup> hydroxyethylated linters with degrees of substitution above 0.2 gave significant increases in folding endurance at much lower beating times than the control. Moreover, a folding endurance of 14,000 was obtained for a 0.34 DS sample (CSF 115) compared with only 500 folds for the unmodified pulp (CSF 220). Only slight improvements were noted for tear strength. Didwania<sup>36</sup> noted that individual fibre strength was decreased but fibre elasticity was improved.

Both Didwania<sup>36</sup> and Ward<sup>7,27</sup> proposed explanations for the strength improvements of hydroxyethylated linters. The introduction of hydrophilic groups as in hydroxyethylation, increases the affinity of the fibres for water and their swelling ability. This promotes greater flexibility of the wet fibres and better deformability and conformability during drying, which results in greater contact and hence, better bonding. Hydroxyethylation acts as a "built-in plasticizer" or beater additive.

Didwania<sup>36</sup> ascertained that the strength increases were due predominantly to fibre-to-fibre bonding with increased specific bonding strength, and not changes in individual fibre strength, fibre length distribution, or increased surface area available for bonding. According to Didwania,<sup>36</sup> hydroxyethylation promotes high density sheets via high shrinkage, high collapsing tendency and greater deformability.

Hydroxyethylation of cotton linters, in this work, gave an improvement in interfibre bonding for one trial only, S318 (1.45% hydroxyl groups, DS 0.05). At CSF 250, this pulp gave a 22% improvement in Z-direction tensile with loss of tensile

strength, fibre strength and bending resistance, and an increase in bulk (-26, -23, -28 and +8%, respectively). The freenesses of the modified pulp were also much higher than the unmodified pulp and hence, beating times at CSF 250 were much longer (Table 4.2).

The graphs showing the development of papermaking properties for this hydroxyethyl cellulose are shown in Appendix 3 (Fig. 3). The hydroxyethylated linters generally produced a higher Z-direction tensile strength at a given bulk than unmodified linters. The fibres were slightly bulkier than the reference pulp, at a given degree of beating, but show better refining response. Some fibre damage was evident by the reduction in zero span tensile index. The modified pulp has developed lower tensile strengths at slightly higher bulk. The plot of Z-direction tensile index versus tensile index, which is effectively a graph of interfibre bonding against network bonding, showed rapid gains in interfibre bonding at a given tensile strength compared with unmodified linters.

The overall effect of hydroxyethylation was to improve the interfibre bonding but not sufficiently to counteract the fibre damage that occurred and the concomitant effect on tensile strength. The decreased tensile strength also resulted in lower bending resistances. The interfibre bonding gains were obtained in conjunction with swelling of the fibres, resulting in a bulkier sheet. This suggests hydroxyethylation has improved hydration and plasticization which led to more flexible, conformable fibres and therefore lower bending resistances.

Whilst Spadaro and co-workers<sup>28</sup> demonstrated appreciable strength increases with a DS of 0.2 and above, Harpman and co-workers<sup>21</sup> obtained notable improvements with a DS of only 0.09. Hence, improvements were anticipated in this present study despite the low level of hydroxyethylation. The derivative with the lowest substitution level gave the best papermaking properties, but the difference in substitution levels alone does not appear sufficient to explain the observed variation

in papermaking properties (see Section 4.3.2 and Appendix 2), which more likely reflect the different reaction conditions used.

Numerous factors may explain the discrepancy between the improvements reported by most other workers and the relatively poor papermaking properties obtained in this study using Australian cotton linters. These include the fact that cooked and bleached linters were hydroxyethylated in this study, as opposed to raw linters. It is difficult to compare previous test results because of non-standard freenesses and different pulp evaluation tests used in these studies (e.g. reliance on fold endurance and burst strength). Only six trials were conducted as a preliminary investigation to assess the relative potential of other modifications compared with hydroxyethylations and to provide a benchmark. It appears considerable degradation may have been involved. Generally, much shorter beating times were used in this study, which may not have allowed for sufficient property development. In these early studies, a Valley beater or Jokro mill was used which partly accounts for the discrepancy in beating times, as discussed previously in the papermaking properties of carboxymethyl cellulose (Section 4.3.2).

In explaining the mechanism of bonding improvements, Ward<sup>27</sup> cited a previous study<sup>35</sup> in which the hydroxyethylated pulp was filtered and then neutralized, not vice-versa. The properties of the product thus obtained were only slightly better than unmodified linters. This further explains the poor performance of the linters used in this present study as the pulps were generally filtered and then acidified to displace the sodium. Ward<sup>27</sup> believed that by neutralization, significant quantities of soluble hydroxyethyl cellulose fines were precipitated onto the fibre. Hence, this fibre had a surface layer that acted as a beater additive, resulting in increased deformability by internal plasticization. Some or all of the above factors may account for the relatively poor and anomalous papermaking properties of hydroxyethylated Australian cotton linters.

### 2,3-Dialdehydo Celluloses

Whilst the oxidation of cellulose with sodium periodate has received considerable attention, the effect on papermaking properties has not been studied as extensively. In an early study by Schur and Levy,<sup>37</sup> it was found that the wet strength of oxidized pulps was increased but their dry strength was diminished. More detailed studies by Higgins and McKenzie<sup>38,39</sup> found that the strength properties depend upon the level of oxidation. They found that mild oxidation decreased the tensile strength and folding endurance. At higher levels of oxidation, the strength properties improved. However, the sheets were less extensible, brittle and had poor folding properties. Continued oxidation decreased the strength properties, until the cellulose was severely degraded and no longer fibrous. They proposed the initial decrease in strength properties was due to increased bulk caused by acid hydrolysis. As oxidation proceeded, the fibrous structure was disrupted and the crystallinity reduced. Further oxidation led to extensive degradation and loss of strength properties. Zeronian, Hudson and Peters<sup>40</sup> also obtained strength improvements which varied in magnitude according to the extent of oxidation. It is difficult to compare quantitatively the improvements observed by others with those in this study because of their reliance on tests such as tenacity and initial modulus, which are tests not used commonly in current pulp evaluation test regimes.

Oxidation of cellulose with sodium periodate generates 2,3-dialdehydo cellulose, but it is generally accepted that the carbonyl groups are present in the hemiacetal and hemialdal forms.<sup>38,40,41</sup> These may form intra- and interfibre covalent crosslinks, which account for the strength increases in the dry state. A detailed study by Zeronian and colleagues<sup>40</sup> confirmed that the air dry strength increases were due to covalent interfibre bonds rather than an increase in the number of secondary valence interfibre bonds, such as hydrogen bonding and van der Waals forces.

In this study, the dialdehydo cellulose that gave an interfibre bonding improvement of 22% did not show improvements in other papermaking properties at CSF 250 (Table 4.2). The tensile strength was unaffected, fibre damage was evident and a significant bulk increase was apparent. The increase in scattering coefficient noted for trial S325 is explained by the increased bulk, as is the increased bending resistance. These increases and the fibre damage suggest that oxidation with sodium periodate has resulted in increased hydration and hence, swelling of the fibres.

Plots of the papermaking properties of this dialdehydo cellulose showed convincingly that the most important change upon modification was the change in bulk (Appendix 3, Fig. 4), as illustrated by the Z-direction tensile index against bulk graph. The zero span tensile index was lowered markedly as a result of oxidation. The tensile index against bulk plot again showed clearly the increased bulk. At a given tensile strength, the Z-direction tensile index for each oxidized cellulose was higher than the unmodified reference.

### 2,3-Cellulose Oxime

Several cellulose oxime derivatives gave about 20% improvement in Z-direction tensile strength, but only trial S210 with a 23% increase satisfied the selection criteria as a promising modification (Table 4.2). Apart from the Z-direction tensile improvement mentioned, the oxime derivative did not, in general, impart favourable properties to the pulp. Slight decreases in tensile indices and bulk were noted and considerable fibre damage occurred. The scattering coefficient was significantly lower (-24%), which may have been due to bonding changes or, more likely, was a consequence of the unusually high scattering of the unmodified linters reference.

In the plots of the key papermaking properties of the oxime derivative and its unmodified reference (Appendix 3, Fig. 5), the minor bonding improvements at CSF 250 were no longer evident. The loss of individual fibre strength is quite apparent

and tensile strength is significantly worse than unmodified linters. The plot of Z-direction tensile index versus tensile index shows the oxime derivative develops the same interfibre bonding as unmodified linters but at lower tensile strengths. Overall it appeared that the interfibre bonding was improved, but not enough to compensate for the detrimental effects of periodate oxidation and hence, the nett result was reduced tensile strength.

### 2,3-Cellulose Thiosemicarbazone

The thiosemicarbazone derivative of 2,3-dialdehydo cellulose showed bonding improvements at CSF 250 relative to the dialdehyde precursor, but not relative to unmodified linters (see Table 4.2). Most 2,3-dialdehydo celluloses showed papermaking improvements, but this particular trial (S267), showed loss of interfibre bonding, tensile strength, fibre strength and bending resistance, and a significant bulk increase (-20, -29, -33, -44 and +33% respectively). Relative to the 2,3-dialdehydo cellulose reference (S267), the thiosemicarbazone derivative showed improved interfibre bonding, tensile strength and slightly less fibre damage. The bulk was lowered by 10% and the bending resistance by 32%. However, relative to unmodified linters, the thiosemicarbazone derivative showed no improvement in interfibre bonding, and loss of individual fibre strength which translated into lower tensile strength. The paper was very bulky (+20%) and extensive loss of sheet stiffness was apparent (-62%), reflecting the decreased tensile strength. The fibres were harder to beat and had much lower stretch and tensile energy absorption values.

The most obvious change shown by the graphs of these pulp evaluations is the significant increase in bulk for the two modified pulps (Appendix 3, Fig. 6). The apparent improvement of the thiosemicarbazone pulp over the dialdehydo cellulose may be a consequence of the reduction in bulk. Zero span tensile strengths of the thiosemicarbazone derivative were not significantly reduced upon modification,

relative to the 2,3-dialdehyde cellulose. The modified pulps were also noted to give lower tensile strengths at much higher bulk. The plot of Z-direction tensile against tensile indices confirmed that, whilst the thiosemicarbazone derivative gave better interfibre bonding than the 2,3-dialdehyde cellulose, the unmodified linters had better interfibre bonding at higher tensile strengths.

#### Cationization of Cellulose (S126)

The effect of cationization on various papermaking and related properties has been investigated by several workers. Antal, Paszner and Micko,<sup>26</sup> in their study of the cationization of unbleached softwood organosolv pulps, obtained significant decreases in sheet bulk and tear strength, with a slight improvement in tensile strength. They postulated the reduced bulk was due to improved fibre bonding, i.e. highly bonded sheets were formed with higher tensile strength as a result of improved conformability and fibre-to-fibre bonding, but only limited quantitative data was cited in their paper.

Due to the presence of anionic groups on the cellulose backbone, cationization of linters was expected to improve their papermaking properties via favourable electrostatic interactions.

In this study cotton linters cationized with (3-chloro-2-hydroxypropyl)-trimethylammonium chloride gave improvements in papermaking properties in only one trial, despite efforts to replicate this result. Cationization of linters improved the interfibre bonding, had no detectable affect on the tensile strength, and caused some fibre damage at CSF 250 (Table 4.2). The scattering coefficient was significantly reduced (-30%) and tensile energy absorption and stretch were improved. This modification appears to have increased the bonded area and made the fibres more flexible or elastic. The observed decrease in freeness suggested that cationization had the same effect as a beater additive.

The summary data at CSF 250, which again involve extrapolation because of the low freenesses, has misrepresented the data plotted in the pulp evaluation graphs for this derivative (Fig. 4.3). Cationization gave better interfibre bonding at slightly lower bulk than unmodified linters but the derivative did not improve greatly with beating. Fibre damage was evident and notable increases in tensile strength were apparent with a slight reduction in bulk. The Z-direction tensile index or interfibre bonding component of the cationized linters did not increase significantly with increased tensile strength, although the cationized linters showed both superior Z-direction tensile and tensile indices to the unmodified linters.

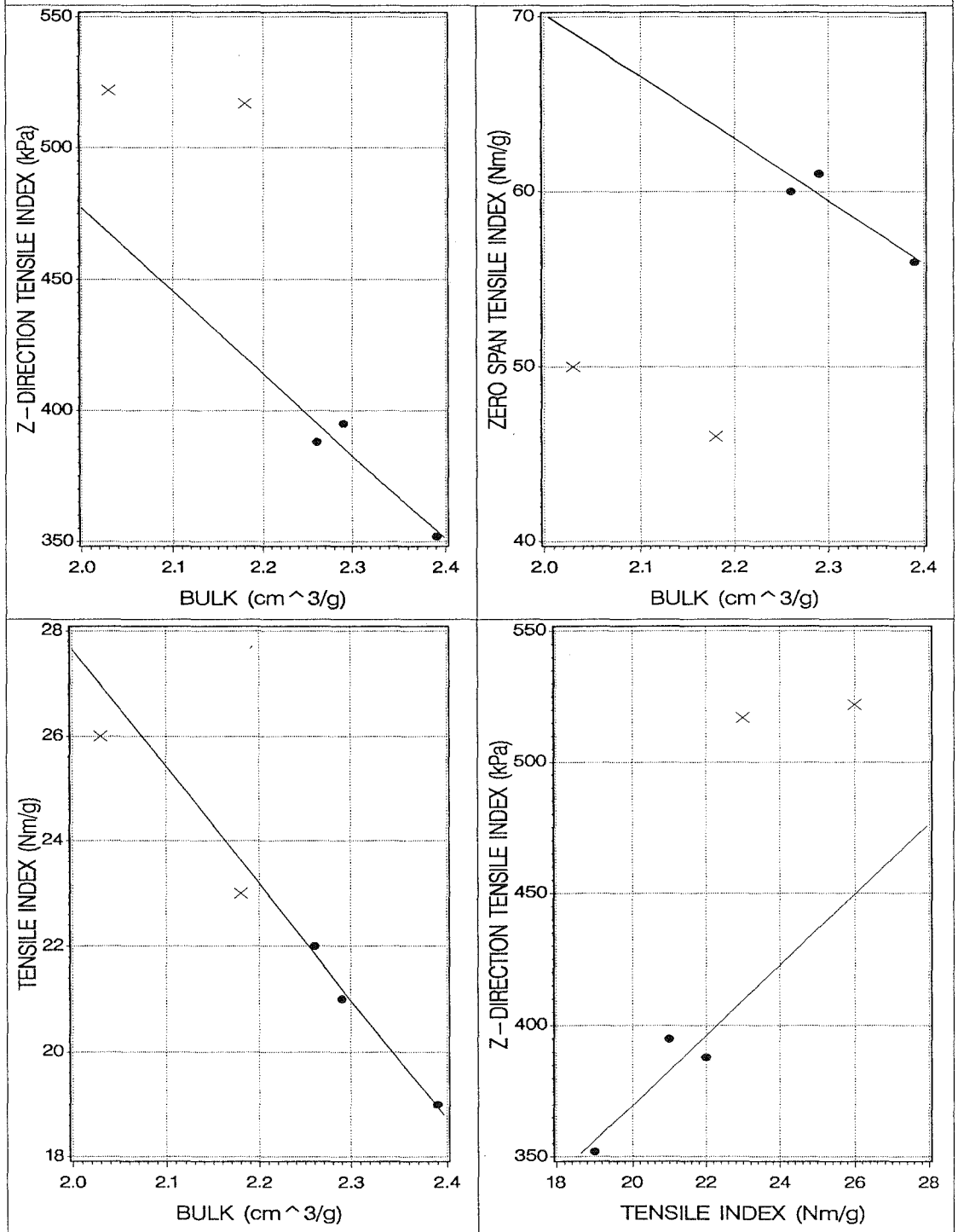
#### Amidoethyl Celluloses

The preparations and properties of acrylamide grafted pulps have been studied more widely than those from the Michael addition of acrylamide to cellulose. Frick, Reeves and Guthrie,<sup>32</sup> although investigating fabric properties of acrylamide treated cottons, report reduced Elmendorf tear strength. A preliminary trial by Ward and co-workers<sup>33</sup> yielded an amidoethyl cellulose with double the tensile strength, marked gains in folding endurance and superior zero span tensile strength. They attributed these enhanced strength properties to the introduction of the hydrophilic amide functionality. The improved water affinity resulted in increased fibre-to-fibre contact, increased conformability, and greater bonded area during drying.

El-Shinnawy and El-Kalubi<sup>42</sup> conducted a detailed study into the preparation and papermaking properties of acrylamide-treated wood pulp. They obtained significant increases in breaking length and burst strength, both being approximately doubled. Folding endurance, although higher, was not significantly improved by treatments with acrylamide. The water retention value was also generally lowered upon modification. El-Shinnawy and El-Kalubi<sup>42</sup> attributed this to the hydrophobic character of the introduced amidoethyl group, which contradicts the explanation proffered by Ward.<sup>33</sup>



**Figure 4.3: Key Papermaking Properties of Cationized Cellulose (S126) \***



Sample:

X X Cationized Cellulose

• • Unmodified Cotton Linters

\* Unmodified linters are generally represented by a dot and a solid line. Lines were omitted on modified linters for clarity. In certain cases, only two beating points were available because of insufficient sample for testing.

Amidoethyl cellulose was one of the few derivatives in this study to show notable tensile strength improvements at CSF 250 (S226 and S230). As shown in Table 4.2, the increase in Z-direction tensile index was about 30% for the three modifications (S202, S226 and S230). Evidence of minor fibre damage existed and sheet stiffness was lowered, especially for S226 (-51%). Optical properties were lowered perhaps reflecting improved fibre-to-fibre contact, but the bulk which was only reduced for trial S230 (-9%) did not confirm this.

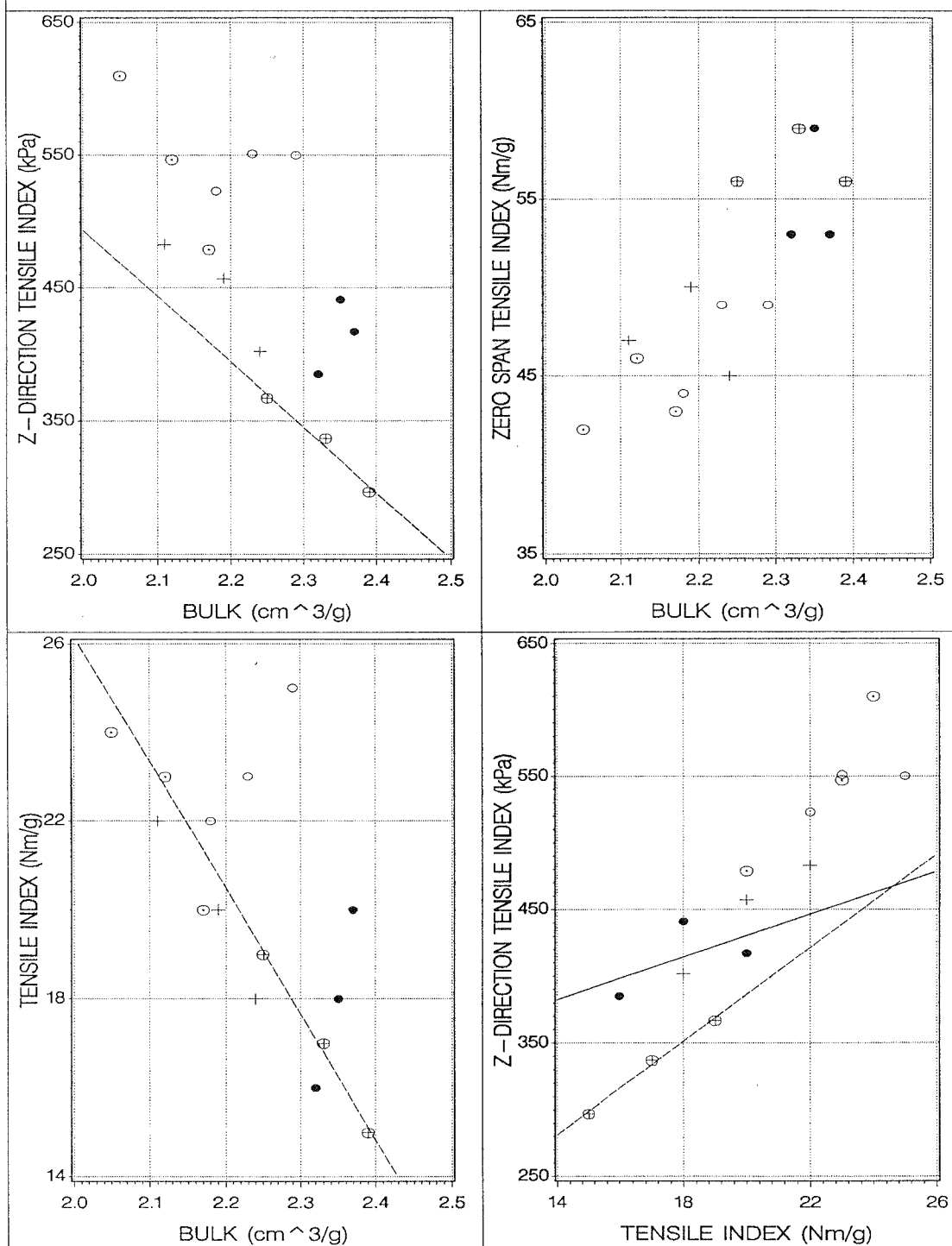
The strength improvements apparent at CSF 250 were not as obvious in the plots of the pulp evaluation data (Fig. 4.4). Relative to its unmodified reference (symbol '⊕'), modification S202 does not seem to be improved, whilst S226 and S230 show improved interfibre bonding with a corresponding reduction in bulk relative to their unmodified reference (symbol '●'). Amidoethyl celluloses S226 and S230, developed tensile strengths above those of unmodified linters. Similarly the amidoethyl cellulose pulps, S226 and S230, extend beyond the unmodified reference in the graph of Z-direction tensile index versus tensile index, with the slope reflecting the significant gains in interfibre bonding for a given bonding increase.

Hence, the minor bulk reduction and decrease in optical properties indicated increased hydrophilicity, conformability and increased bonded area. It appears that the effect of modification was not as severe as other modifications and that the Z-direction tensile improvements also translated to tensile strength improvements.

#### Maleic Acid-Cellulose Derivative (S222)

This particular maleic acid-cellulose derivative S222, was the only one to show improved interfibre bonding properties, despite numerous attempts to replicate this result. This trial gave a 36% increase in Z-direction tensile at CSF 250 and a decrease in bending resistance of 29% (see Table 4.2). By virtue of the hydrophilicity of the diprotic maleic acid residue, this derivative was expected to

**Figure 4.4: Key Papermaking Properties of Amidoethyl Celluloses (S202, S226, S230)**



Sample:

○ ○ S226 Amidoethyl Cellulose

○ ○ S230 " "

• • Unmodified Cotton Linters

+ + S202 Amidoethyl Cellulose

⊕ ⊕ Unmodified Linters

improve the papermaking properties of the pulp by improving its conformability and hence relative bonded area. Indeed, the observed changes in papermaking properties suggest that the fibres are more plastic and conformable.

The graphs of the main papermaking properties of this maleic acid-cellulose derivative are a guide only, largely because of the bulk values obtained for the three beating points (Fig. 4.5). Nonetheless, interfibre bonding is elevated at a slightly higher bulk and the interfibre bonding component increased markedly with increasing tensile strength; the interfibre bonding component of the unmodified reference increased only slightly with increasing tensile strength.

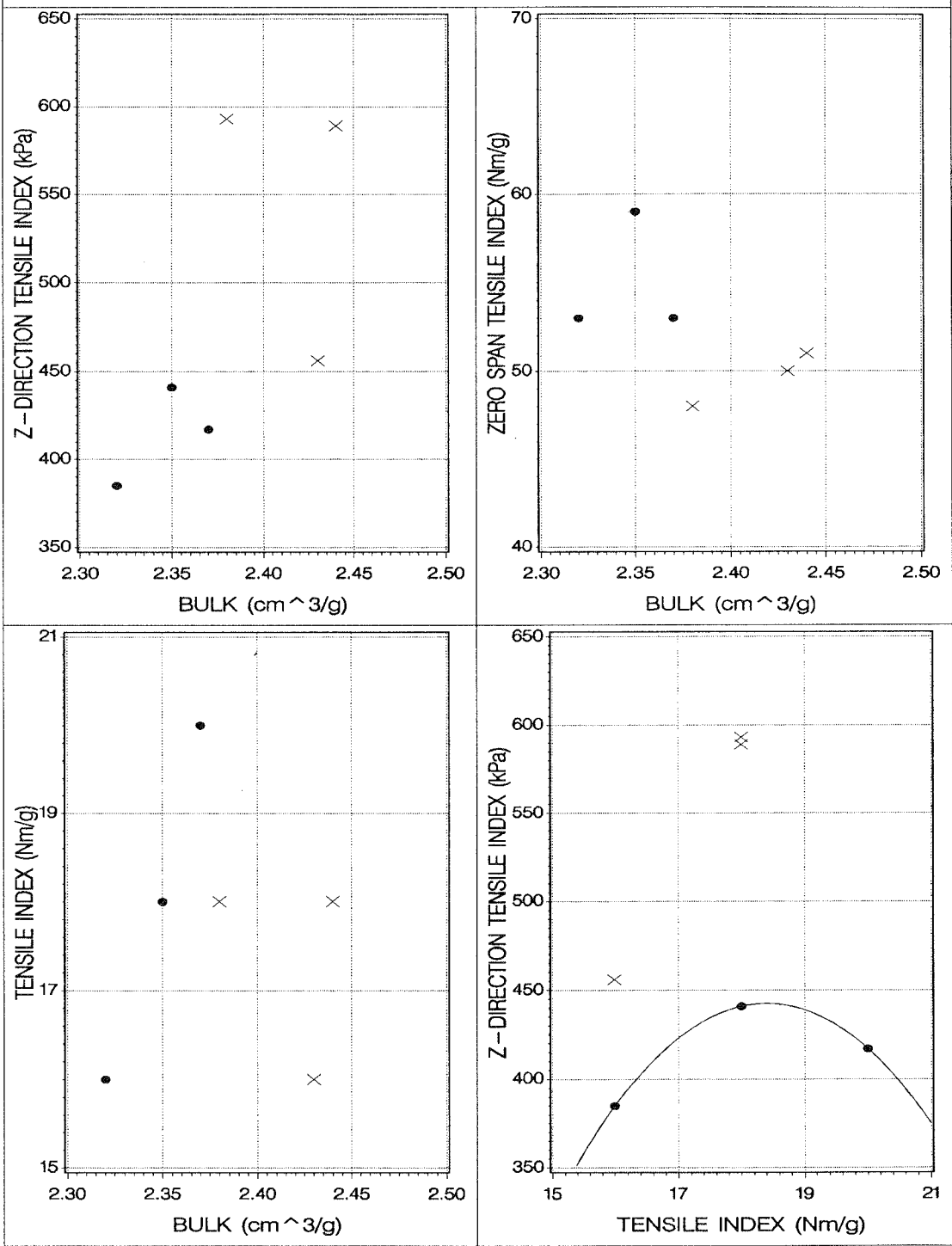
Of the single derivatives discussed in this section, it is significant that the derivative with the greatest increase in Z-direction tensile index was the maleic acid-cellulose derivative. This suggested that the dicarboxylic acid functionality was instrumental in improving interfibre bonding by virtue of its hydrophilicity. The itaconic and fumaric acid-cellulose derivatives did not exhibit such notable improvements. In the former case, this could be due to differences in structure affecting the geometry required for hydrogen bonding, and in the latter case, to different substitution levels.

#### **4.4.2 Promising Double Derivatives and Blends of Anionic-Cationic Cellulose Derivatives**

The papermaking properties of double derivatives of cellulose do not appear to have been reported previously. Hence, the papermaking improvements observed for the double derivatives, cationized amidoethyl cellulose and amidoethyl hydroxyethyl cellulose, are particularly significant.

The blending of anionic and cationic cellulose derivatives to improve their papermaking properties has been reported in studies by Frolov and co-workers.<sup>43,44</sup> Volovich, Frolov and Toporov<sup>43</sup> reported increased wet and dry bursting strength

Figure 4.5: Key Papermaking Properties of a Maleic Acid – Cellulose Derivative (S222)



Sample:  
x x Maleic Acid – Cellulose Derivative  
• • Unmodified Cotton Linters

with various combinations of amine donor groups and carboxylic acid, nitrile, hydroxyl, sulfonic acid and alkenyl acceptor groups grafted onto kraft pulp, but did not quantify the increases obtained or their effect on other papermaking properties.

Frolov<sup>44</sup> cited donor-acceptor groups as a means of regulating the mechanical properties of papermaking pulps and ascertained that donor-acceptor fibres impart electrostatic character to the interfibre bonds. As drying proceeds, the hydration layer reduces and this results in increased charge densities in the double electric layer and hence, strengthening of interfibre bonds.

#### Fumaric Acid-Cationic Cellulose Blends (S404/S414)

The most promising pulp of the fumaric acid-cationic cellulose blends was the 40:60 blend (S404, 12.8 meq/100g; S414, 0.16% N) with 25% improvement in interfibre bonding (Table 4.3A). The other blend ratios gave improvements in Z-direction tensile index of marginally less than 20%. This may be due to a combination of the low freenesses of the unmodified linters and steric effects of the fumaric acid. At CSF 250, the tensile strength of the blend was improved, zero span tensile was increased and bending resistance was lowered, with other properties being unaffected. The apparent increase in zero span tensile was within the error limits.

The graphical representation of the key pulp evaluation results for this blend are atypical (Appendix 3, Fig. 7). According to the Z-direction tensile against bulk graph, no significant improvement was apparent and the pulps tended to converge with beating. The blend showed a much greater response to refining and hence, lowering of bulk than the unmodified pulp. There was no conclusive evidence of fibre damage upon blending these two derivatives, but some inconsistency was apparent in the result as the zero span tensile index did not decrease with beating. The tensile index versus bulk plot of unmodified linters showed more typical behaviour, although the blend was unaffected by beating. The plot of Z-direction

**Table 4.3A: Most Promising Modified Celluloses<sup>a</sup> -  
Double Derivatives and Blends of Anionic and Cationic Celluloses**

Cellulose Derivative (Number)	Z-Dir. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity (%)	Beating Time (min)	Stretch (%)	Substitution
Fumaric Acid-Cationic <sup>b</sup> (S404/S414) 40:60	+25	+19	+9	-14	NS <sup>c</sup>	NS	NS	+77	+23	12.8 meq/100g 0.16% N
Cationized Amidoethyl (S348)	+31	+24	-28	-8	-12	-28	NS	+83	NS	0.82% N
Cationized Amidoethyl (S388)	+35	+15	-34	-14	(-6)	-34	-9	NS	-13	0.12% N
Amidoethyl Hydroxyethyl (S410)	+43	+19 <sup>d</sup>	-32	-23	-10	-20	-11	+680	-12	0.51% N 1.95% hydroxyl
Carboxymethyl- Cationic (S234/S232) <sup>b</sup> 20:80	+21	(+6)	-28	-27	NS	-15	NS	-44	(+6)	9.11 meq/100g 0.14% N
40:60	+31	(+6)	-24	-37	(-6)	-15	NS	-40	+10	
60:40	+39	+31	-28	NS	-11	NS	NS	+28	(+6)	
80:20	+51	+38	-20	-10	-8	NS	NS	+105	+16	
Carboxymethyl- Cationic (S220/SS218,S219) <sup>b</sup> 40:60	+54	+16	-11	NS	NS	-14	NS	+84	NS	9.10 meq/100g 0.06% N
60:40	+45	+21	-11	+31	NS	-10	NS	+110	-11	
80:20	+39	NS	(-8)	+25	NS	(-8)	NS	+120	NS	

- a. Small scale pulp evaluation method used. Only modifications showing 20% or greater improvement in Z-direction tensile index at CSF 250 relative to their unmodified linters reference are included. Property changes are shown as % increases or decreases relative to unmodified linters.
- b. These derivatives were blended as discussed in the text.
- c. Not significant change (5% or less). Bracketed values are probably not significant.
- d. Tensile index improved 36% relative to hydroxyethyl cellulose precursor.

tensile against tensile indices best depicted the blend as a cluster of points above the unmodified pulp, although the interfibre bonding gains were not significant.

#### Cationized Amidoethyl Cellulose

The pulp evaluation results for both cationized amidoethyl celluloses were similar, despite a relatively large difference in substitution levels (Table 4.3A; S348, 0.82% N; S388, 0.12%N). At CSF 250 both pulps have improved interfibre bonding and sheet strength, with loss of individual fibre strength and bending resistance. The reduced bulk and optical properties reflect increased conformability and fibre-to-fibre bonding.

The graphs depicting the key papermaking properties of these cationized amidoethyl celluloses clearly show the bulk reduction that occurred upon modification (Fig. 4.6). The improvement in interfibre bonding, loss of fibre strength and improved tensile strength with bulk reduction were also quite apparent. The improved tensile index and Z-direction tensile index of the modified linters have effectively offset them from their unmodified linters references. Furthermore, the cationized amidoethyl cellulose showed a marked increase in interfibre bonding with increased tensile strength.

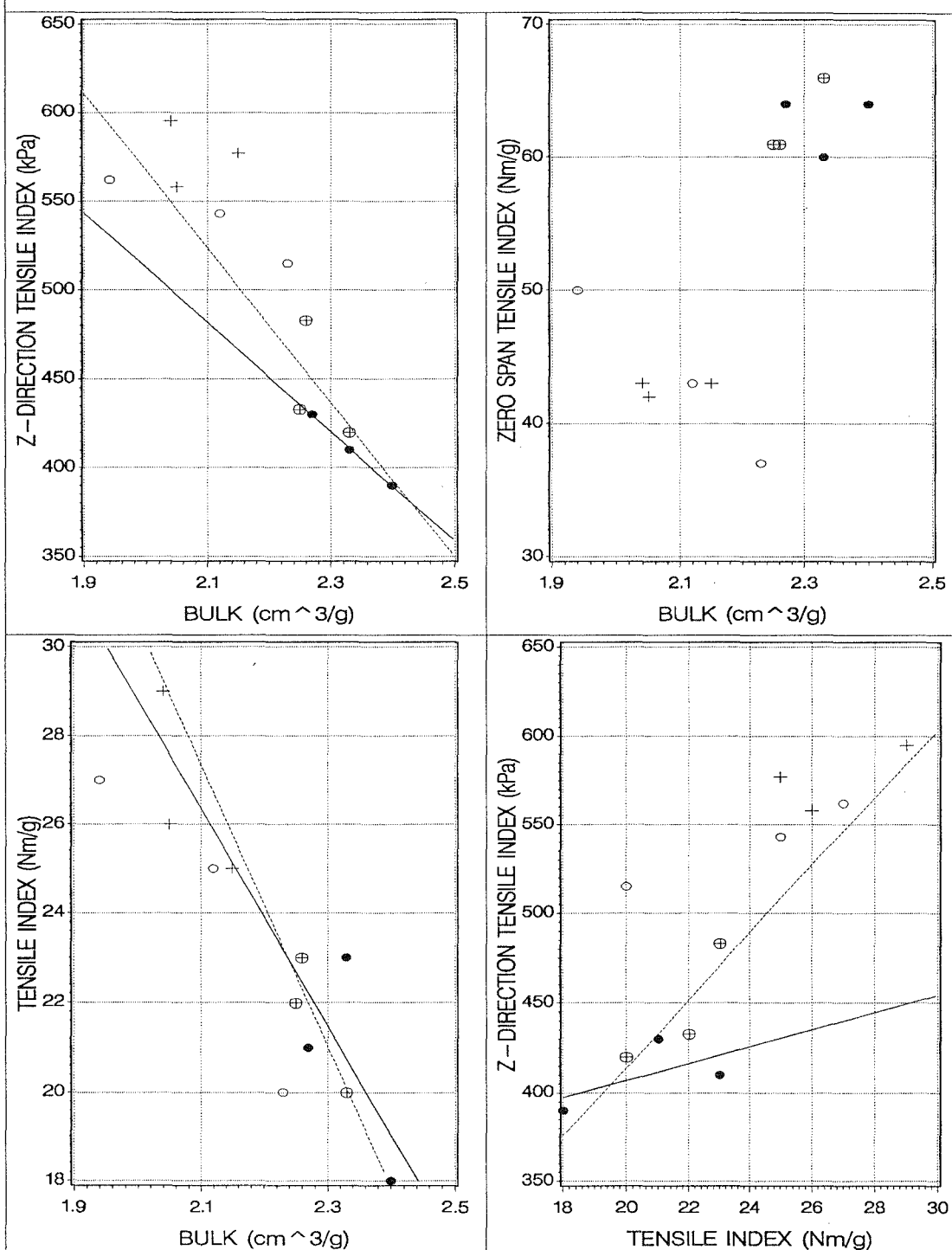
#### Amidoethyl Hydroxyethyl Cellulose (S410)

The unmodified cotton linters used as a reference for this pulp gave low freeness values on beating and hence, strength improvements for this cellulose derivative may be artificially lowered.

At CSF 250, the acrylamide treated hydroxyethyl cellulose gave a significant interfibre bonding improvement of 43% (Table 4.3A). The tensile strength of this double derivative improved 19% relative to the unmodified reference and 36%



Figure 4.6: Key Papermaking Properties of Cationized Amidoethyl Celluloses (S348, S388)



Sample:

- ○ S348 Cationized Amidoethyl Cellulose    + + S388  
 • • Unmodified Linters    ⊕ ⊕ Unmodified Linters

relative to the precursor, hydroxyethyl cellulose (S396, see Section 4.3.2). Fibre damage was evident and the bending resistance was lowered, but the reduced bulk and optical properties reflect the increased bonded area. The stretch and tensile energy absorption values of the modified pulp were noted to decrease for the third beating point. Most notably this modification significantly altered the freeness properties of the pulp from low to quite high initial values.

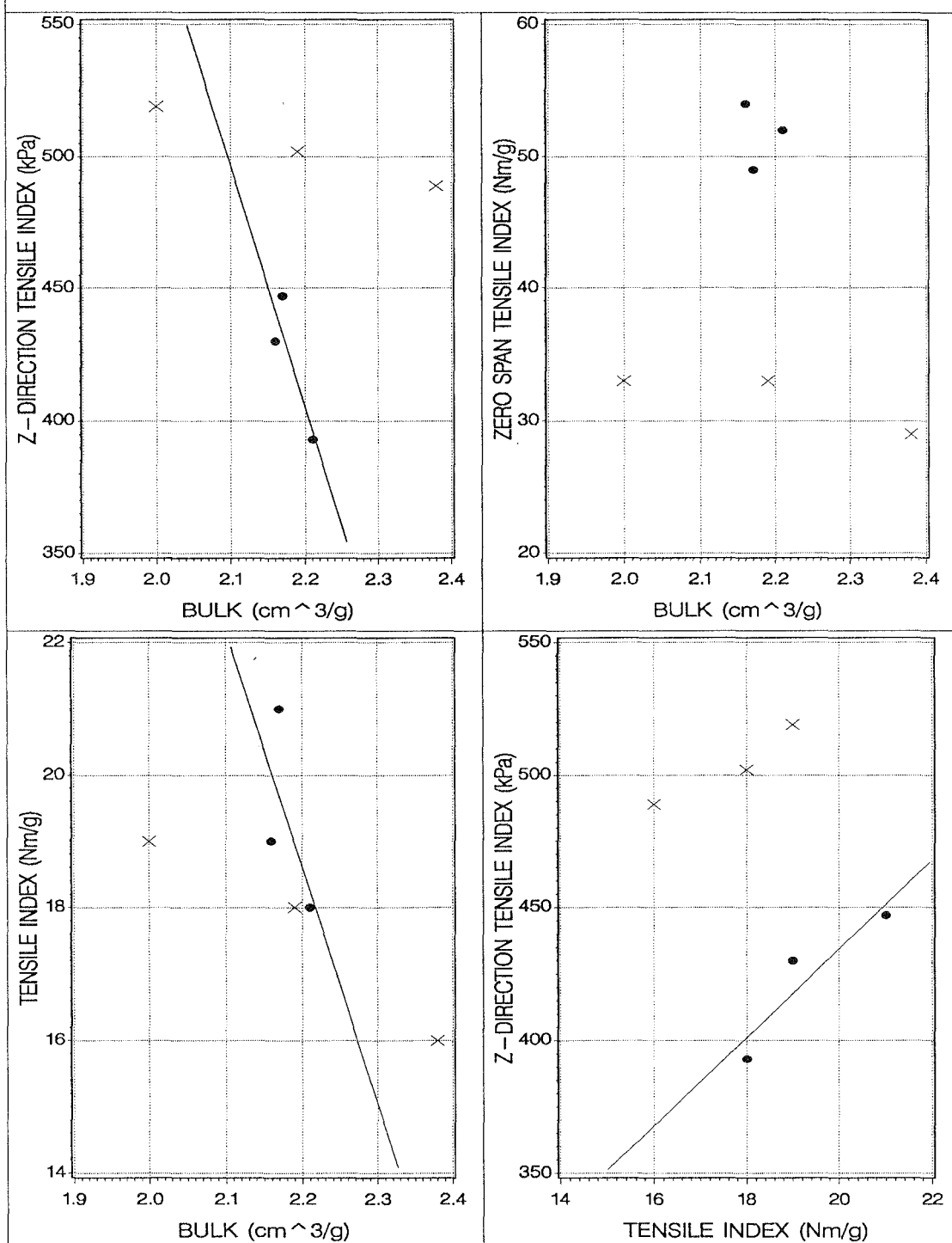
The papermaking property graphs for this derivative (Fig. 4.7) accentuate the different beating behaviours of the modified and unmodified pulps. Beating had little effect on the bulk of the unmodified pulp, but the modified pulp showed significant bulk reduction upon beating (-20%). In the tensile index versus bulk graph, the tensile strength of the unmodified linters was slightly higher than the modified pulp, which contradicted the apparent improvement at CSF 250. At a given tensile index, the Z-direction tensile index of the modified pulp showed limited improvement over the unmodified linters. The discrepancy between the apparent improvements at CSF 250 and the impression obtained from the four papermaking graphs was due to the low freenesses of the unmodified pulp and the extrapolation necessary to obtain values at CSF 250.

### Carboxymethyl-Cationic Cellulose Blends

#### Blend S234/S232

Pulp evaluation results for the unmodified cotton linters reference used with these blends were not typical and were used as a guide only. In this set of blends, the 80:20 carboxymethyl cellulose:cationic cellulose blend ratio gave the most significant bonding improvements, shown in Table 4.3A (S234, 9.11 meq/100g; S232, 0.14% N, respectively). The Z-direction tensile strength improvement of 51% is also accompanied by a tensile strength increase of 38%, which is one of the largest gains in tensile strength obtained in this study. The bonding improvements

Figure 4.7: Key Papermaking Properties of Amidoethyl Hydroxyethyl Cellulose (S410)



Sample:

x x Amidoethyl Hydroxyethyl Cellulose

• • Unmodified Cotton Linters

coincided with a significant reduction in bulk. Optical properties were maintained, with a slight reduction in bending resistance and individual fibre strength. This suggested that the 80:20 blend had reduced the bulk, resulting in enhanced conformability, flexibility and hence, increased bonded area.

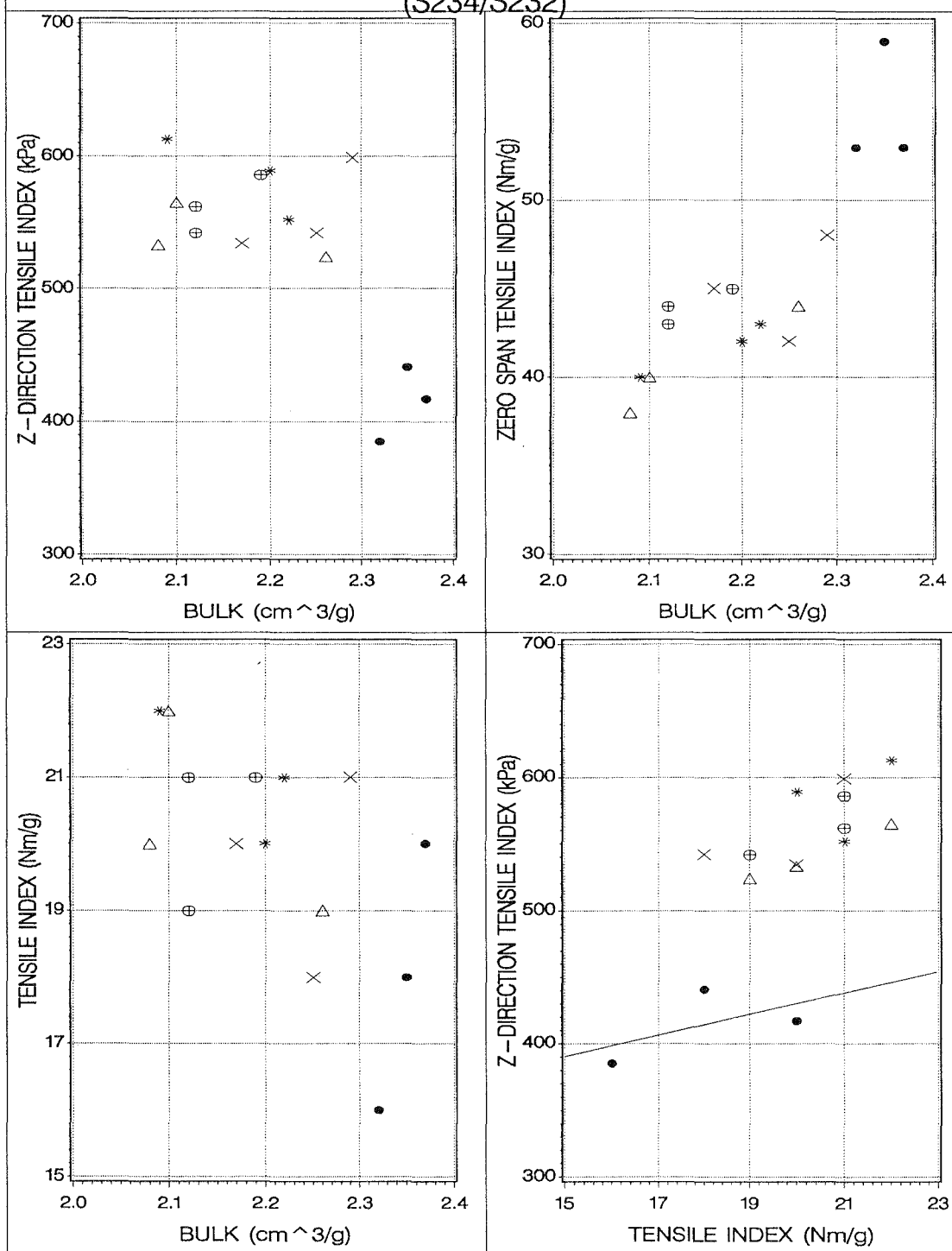
The 60:40 blend gave similar but less notable results to the 80:20 blend. The 40:60 blend, still with significant interfibre bonding improvements, did not however improve the tensile strength. Bending resistance was significantly reduced and optical properties were lowered. Finally, the 20:80 blend was similar to the 40:60 blend but with a smaller increase in Z-direction tensile index.

The blend containing mostly cationic cellulose was the least promising in terms of interfibre bonding or strength improvements. Freenesses were generally directly related to interfibre bonding gains, with low freeness blends resulting in poorer bonding than more typical freeness-value blends. This correlated well with interpolated beating times at CSF 250.

Graphs of the key papermaking properties for this set of carboxymethyl-cationic cellulose blends (Fig. 4.8) demonstrated clearly that a substantial bulk reduction occurred. This bulk reduction may reflect greater compressibility and conformability by virtue of the attractive electrostatic forces, i.e. bulk was decreased because of greater interfibre bonding caused by electrostatic interaction, or the interfibre bonding was increased because of reduced bulk caused by greater compressibility and conformability.

Data for this set of blends were not clearly ranked and appear more as a cluster of points. Beating appeared to have little effect on the Z-direction tensile index of these blends but significantly reduced the bulk. Significant gains in interfibre bonding were evident, and these blends showed evidence of greater fibre damage than other blends. The tensile index versus bulk graph, while giving erratic data

**Figure 4.8: Key Papermaking Properties of Carboxymethyl Cellulose and Cationic Cellulose Blends (S234/S232)**



points, shows the reduction in bulk. The significant gains in tensile strength reported at CSF 250 were not evident in the graph of this same data. This apparent anomaly reflects the variation in beating times and freenesses obtained in preparing handsheets of these blends and the unmodified linters.

#### Blend S220/S218,S219

The 40:60 blend of carboxymethyl cellulose and cationic cellulose (S220, 9.10 meq/100g; S218, 0.05% N; S219, 0.06% N) gave a 54% improvement in interfibre bonding at CSF 250, over the unmodified reference (Table 4.3A). An improvement in tensile strength was noted along with a decrease in scattering coefficient, reflecting increased bonded area, and a slight decrease in fibre strength. Hence, it appears the significant improvement in interfibre bonding was again contributing to increased tensile strength, with the gains counteracting the fibre damage that occurred.

A 45% improvement in Z-direction tensile was obtained for the 60:40 blend of these derivatives. Pulp evaluation results were similar to the 40:60 blend, except for the significant increase in bending resistance (+31%); the reason for this marked increase is not known. The 80:20 blend, which exhibits a 39% improvement in interfibre bonding, did not give the tensile strength improvement noted for the previous carboxymethyl cellulose-cationic cellulose blends. A significant improvement in bending resistance was still evident. The 20:80 blend did not show significant improvements in Z-direction tensile index and is discussed in Section 4.3.4. As observed with the maleic acid-cationic and itaconic acid-cationic cellulose blends, this blend ratio gave low freeness values at low beating times. The blend with 80% cationic cellulose again resulted in low freenesses. The trend to be noted from these blends is that the scattering coefficient decreased with increasing improvement in Z-direction tensile, suggesting increased fibre-to-fibre bonding and increased conformability.

The development of key papermaking properties of these carboxymethyl and cationic cellulose blends are shown in Figure 4.9. At a given bulk, significant gains in interfibre bonding have been achieved. The 40:60 blend, which gave the greatest improvement at CSF 250, did not respond greatly to beating, whereas the Z-direction tensile indices of the 60:40 and 80:20 blends increased significantly with beating.

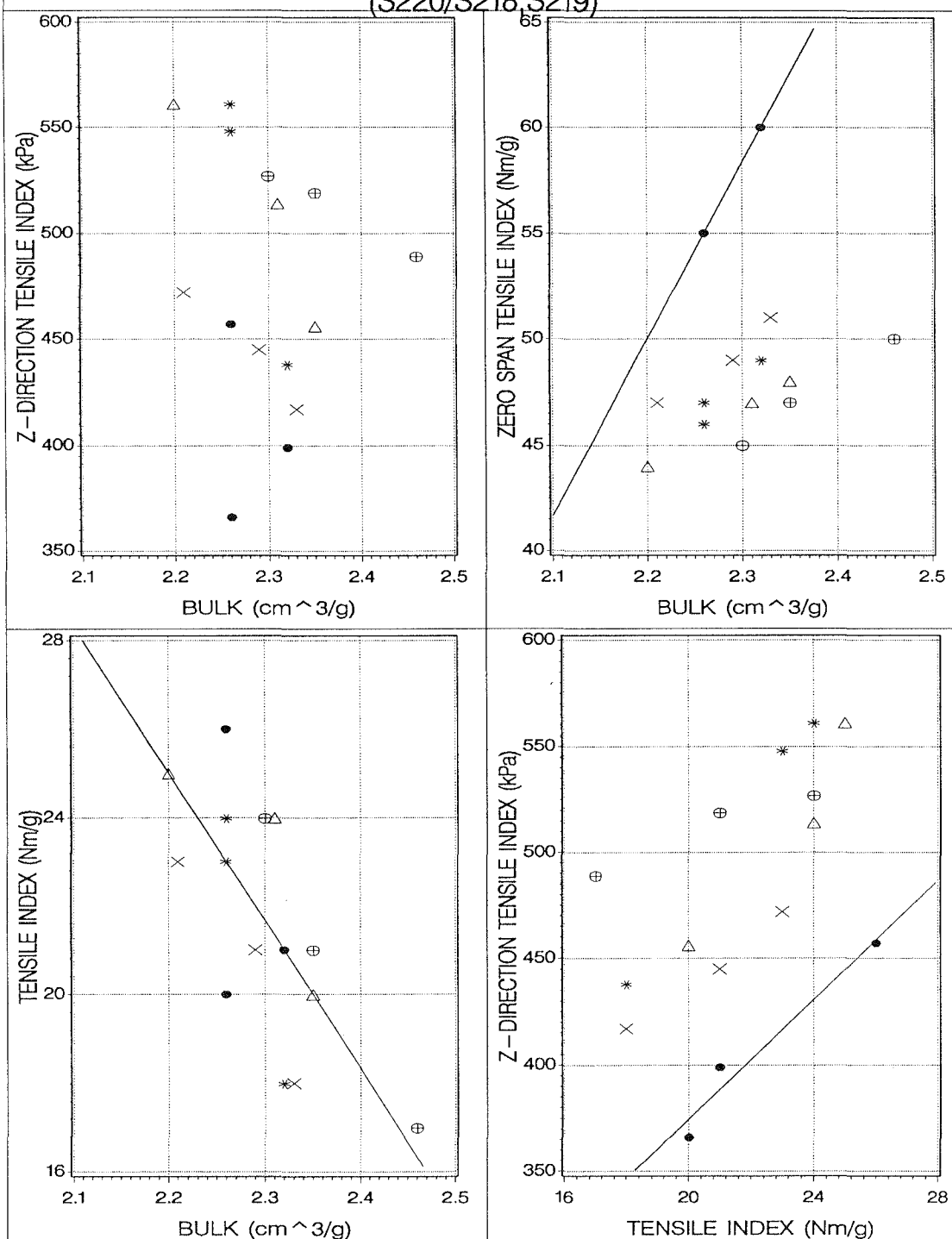
The blends showed evidence of some fibre damage with beating, compared with the unmodified reference. The zero span tensile index of each blend was ranked according to its Z-direction tensile strength at CSF 250, i.e. fibre strength decreased with increasing interfibre bonding improvements. From the tensile index versus bulk graph, tensile strength was not greatly improved by combining these derivatives in blends, but the development of interfibre bonding with increasing tensile strength was quite pronounced. The Z-direction tensile index of unmodified cotton linters increased sharply with increasing tensile strength, which indicates significant enhancement of the interfibre bonding component of tensile strength. The steeper slopes of the 60:40 and 80:20 blends suggest a significant interfibre bonding component in tensile strength improvements.

Overall, this set of carboxymethyl-cationic cellulose blends did not affect bulk, in contrast to other carboxymethyl, and maleic and itaconic acid-cationic cellulose blends which resulted in significant bulk reduction. Hence, the observed improvements were not due in part to bulk reduction as was the case with some other blends.

#### Blend S317/S306

These blends of carboxymethyl cellulose with cationic cellulose (Table 4.3B; S317, 10.9 meq/100g; S306, 0.47% N), whilst yielding significant improvements in interfibre bonding, had very low freenesses. Hence, the very short beating times

**Figure 4.9: Key Papermaking Properties of Carboxymethyl Cellulose and Cationic Cellulose Blends (S220/S218,S219)**



Sample:

- |     |                           |     |       |
|-----|---------------------------|-----|-------|
| X X | 20:80 CMC – Cat           | ⊕ ⊕ | 40:60 |
| Δ Δ | 60:40                     | * * | 80:20 |
| • • | Unmodified Cotton Linters |     |       |



**Table 4.3B: Most Promising Modified Celluloses<sup>a</sup> -  
Blends of Anionic and Cationic Cellulose Derivatives**

Cellulose Derivative (Number)	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity (%)	Beating Time (min)	Stretch (%)	Substitution
Carboxymethyl- Cationic (S317/S306) <sup>b</sup> 20:80	+57	+11	NS <sup>c</sup>	-43	NS	-23	-9	-100	NS	10.9 meq/100g 0.47% N
40:60	+57	NS	-12	-34	NS	-19	(-6)	-100	NS	
60:40	+50	NS	-16	-36	NS	-9	(-6)	-92	-12	
80:20	+22	NS	NS	-17	NS	NS	NS	-85	-10	
Itaconic Acid- Cationic (S321/S322) <sup>b</sup> 20:80	+22	NS	(-9)	-15	NS	+19	NS	-100	NS	7.15 meq/100g 0.23 % N
40:60	+55	+16	NS	NS	NS	NS	NS	-40	+12	
60:40	+80	+11	+15	-11	NS	NS	NS	+65	-33	
80:20	+68	+11	-12	NS	NS	NS	NS	+88	-21	
Maleic Acid- Cationic (S379/S382) <sup>b</sup> 40:60	+28	+20	-20	+14	(-6)	NS	NS	d	-22	10.1 meq/100g 0.19% N
60:40	+22	NS	-20	+14	-8	-15	NS	d	-28	
80:20	+23	+15	-20	+14	-8	NS	NS	d	(-7)	
(S308/S307) <sup>b</sup> 20:80	+58	NS	-19	-19	NS	-19	(-6)	-85	NS	11.1 meq/100g 0.24% N
40:60	+51	NS	-14	+23	NS	-16	NS	-75	-12	
(S324/S323) <sup>b</sup> 20:80	+49	NS	NS	-28	NS	-14	NS	-100	+26	8.51 meq/100g 0.21% N
40:60	+58	+11	NS	NS	NS	-12	NS	-63	NS	
60:40	+57	+16	NS	-15	NS	-12	NS	+10	(-7)	
80:20	+83	+26	NS	-32	-7	NS	NS	+230	+12	

a. Small scale pulp evaluation method used. Only modifications showing 20% or greater improvement in Z-direction tensile index relative to their unmodified reference at CSF 250 are included. Property changes are shown as % increases or decreases relative to unmodified linters.

b. These derivatives were blended as discussed in the text.

c. Not significant change (5% or less). Bracketed values are probably not significant.

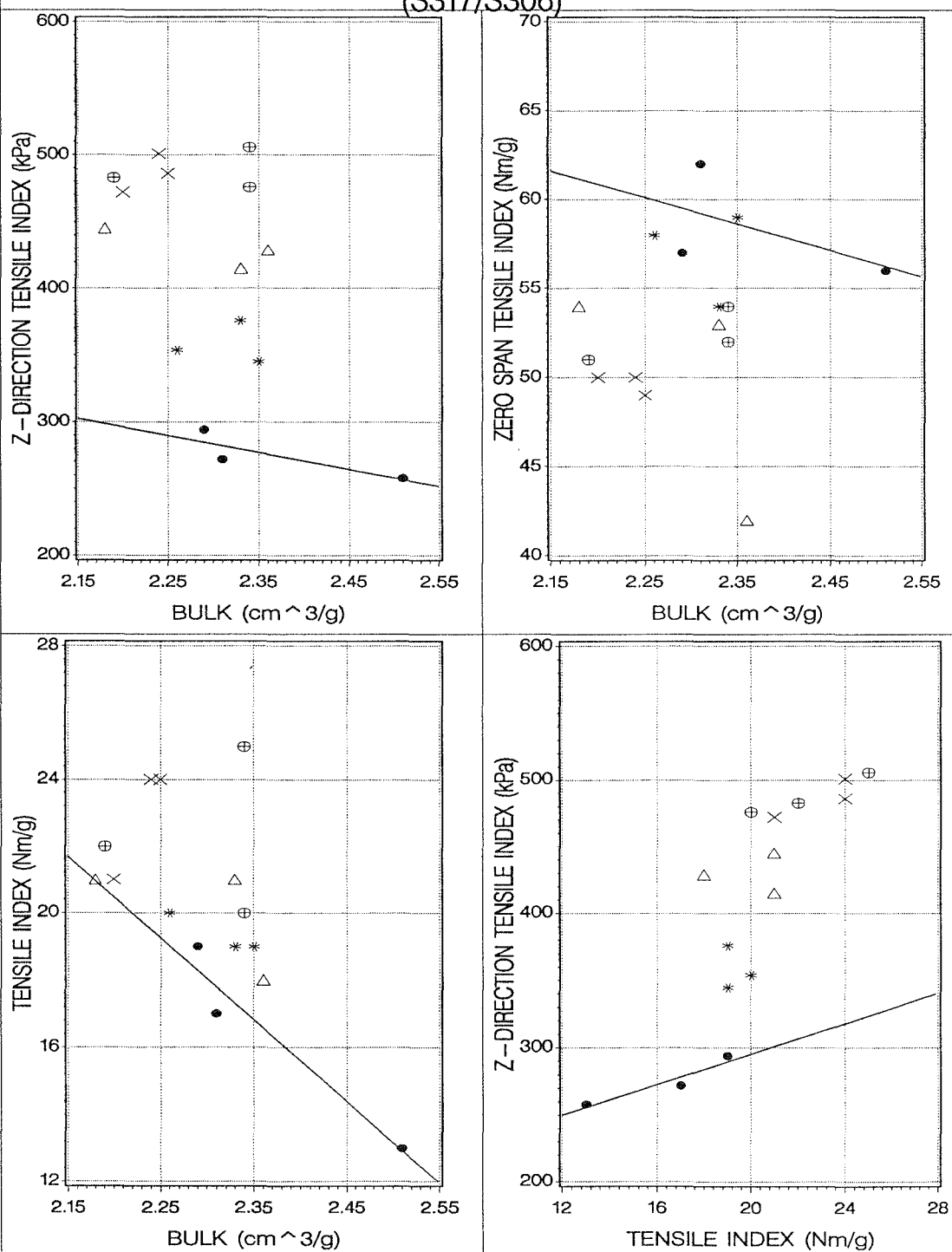
d. Low freeness pulp (zero beating time at CSF 250).

used may not have allowed properties to develop to their optimum levels and because it was necessary to extrapolate to CSF 250, these results may be less reliable.

The 20:80 blend of carboxymethyl-cationic cellulose with a 57% increase in Z-direction tensile at CSF 250, suffered some fibre damage, reduction in scattering coefficient and extensive reduction in bending resistance (-43%). The reduction in scattering may confirm the gains in interfibre bonding, assuming increased fibre-to-fibre bonding has occurred. The 40:60 blend with the same interfibre bonding improvement suffered a less notable decrease in optical properties and bending resistance, however the bulk was increased. For the 60:40 and 80:20 blends, the decreasing Z-direction tensile improvements correspond to a reduced effect on zero span tensile index, bending resistance, scattering coefficient and opacity. As interfibre bonding improved, the scattering coefficient decreased as expected for an increase in the effective bonded area. In contrast to the previous set of carboxymethyl-cationic cellulose blends (S220/S218, S219), two of which showed improved bending resistance, these blends had a significant adverse affect on the bending resistance. It is also noteworthy that the blend with the smallest Z-direction tensile improvement in this set was again the 80:20 blend.

According to the graphical representation of the pulp evaluation data for this blend, a slight bulk reduction has occurred upon blending (Fig. 4.10). The graph of Z-direction tensile against bulk has ranked the blends according to their blend ratios and interfibre bonding improvement. The 20:80 and 40:60 blends have very similar property development with bulk reduction, however the improvement in Z-direction tensile with beating was not as pronounced as with some previous sets of blends. The zero span tensile index versus bulk graph again ranked the blends inversely according to their Z-direction tensile improvement, but it is not clear why the best papermaking blends also have the lowest individual fibre strength properties. The blends have also produced gains in tensile index at a given bulk. In the plot of

Figure 4.10: Key Papermaking Properties of Carboxymethyl Cellulose and Cationic Cellulose Blends (S317/S306)



Sample:

$\times$   $\times$  20:80 CMC – Cat       $\oplus$   $\oplus$  40:60

$\triangle$   $\triangle$  60:40       $*$   $*$  80:20

$\bullet$   $\bullet$  Unmodified Cotton Linters

Z-direction tensile against tensile index the blends were ranked as before. They were also offset from the unmodified cotton linters having higher tensile strengths. With increasing tensile strength, the corresponding improvement in interfibre bonding was not as marked as for most other blends, and each blend appears to form a cluster of points, rather than show clear property development with beating.

Of the carboxymethyl-cationic cellulose blends the greatest improvement in Z-direction tensile index at CSF 250 was obtained for the high level cationization blend, S306/S317 at the 20:80 blend ratio. The 80:20 blend of S234/S232, with 51% improvement in interfibre bonding, gave the largest tensile strength improvement at CSF 250 of 38%.

#### Itaconic Acid-Cationic Cellulose Blend (S321/S322)

The 60:40 blend of itaconic acid-cellulose with cationic cellulose gave an 80% increase in Z-direction tensile at CSF 250 (Table 4.3B; S321, 7.15 meq/100g; S322, 0.23% N). In most other aspects the pulp was the same as unmodified linters, the exceptions being reduced stretch and bending resistance. The properties of the 80:20 blend with 68% increase in Z-direction tensile strength were otherwise similar to unmodified linters, but with evidence of slight fibre damage. The 40:60 blend gave a 55% increase in interfibre bonding and a 16% increase in tensile strength. The 20:80 blend with only 22% improvement in interfibre bonding showed no improvement in tensile strength, but a decrease in individual fibre strength, loss of bending resistance and a significant increase in scattering coefficient. Extremely low freenesses were obtained for this blend (CSF 213 at zero beating).

A trend observed from the pulp evaluation summary data was that stretch appeared to be inversely proportional to the Z-direction tensile improvements for this set of blends, as maximum bonding improvements were achieved with loss of fibre elasticity. This suggested that by blending the anionic and cationic derivatives

optimum use has been made of the fibre flexibility, and that blending has maximized the surface area available for interfibre bonding, i.e. the vast quantity of network bonds has reduced the sheet elasticity. This in turn indicated improved fibre conformability and hydration as expected from favourable interactions of the hydrophilic cationic and anionic groups attached to the cellulose backbone. Furthermore, the two carboxyl groups of the itaconic acid-cellulose derivative were expected to markedly improve the hydrogen bonding and electrostatic interactions between fibres to produce improved sheet properties.

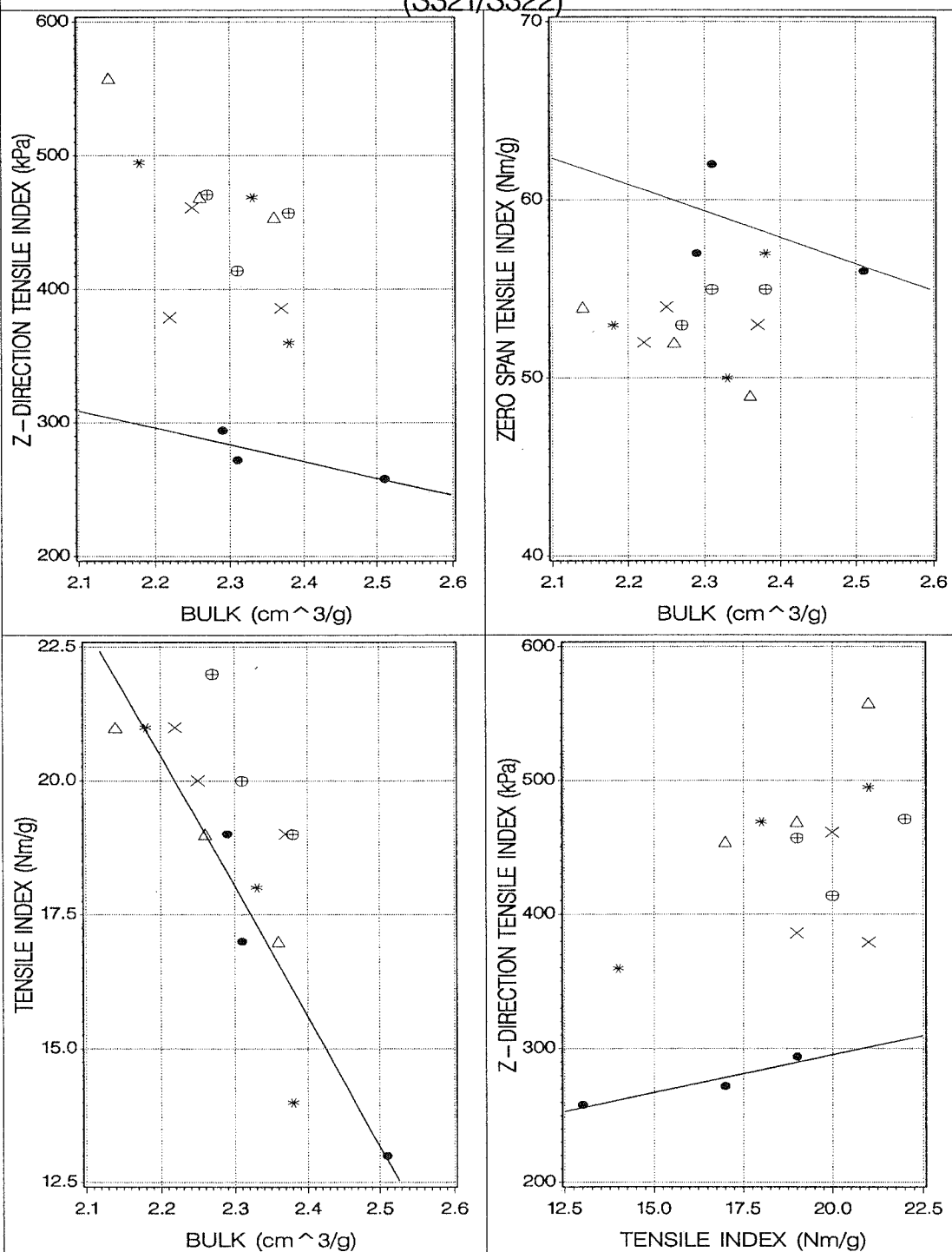
The changes in key papermaking properties with bulk for these itaconic acid-cationic cellulose blends (Fig. 4.11) were not as systematic as with the maleic acid-cationic cellulose blends discussed in the following paragraphs. Nonetheless, significant improvements in interfibre bonding were apparent. At a given bulk, limited fibre damage may have occurred and tensile strength was slightly improved. Significant gains in interfibre bonding were again evident from the graph of Z-direction tensile index against tensile index.

### Maleic Acid-Cellulose and Cationic Cellulose Blends

#### Blend S379/S382

The papermaking properties of the S379/S382 maleic acid-cationic cellulose blends were intended to replicate the results of trial S324/S323, discussed below. However, despite using the same reaction conditions only slight papermaking improvements were obtained for the S379/S382 blends (Table 4.3B). Differences in substitution levels do not explain the discrepancies in papermaking properties (S379, 10.11 meq/100g; S382, 0.19% N; S324, 8.51 meq/100g; S323, 0.21% N). A plausible explanation is that the relatively low freeness of the unmodified linters used in blend S379/S382 adversely affected its potential for significant improvement.

Figure 4.11: Key Papermaking Properties of  
Itaconic Acid – Cellulose and Cationic Cellulose Blends  
(S321/S322)



Sample:

X X 20:80 Itac – Cat      ⊕ ⊕ 40:60

Δ Δ 60:40

\* \* 80:20

• • Unmodified Cotton Linters

The greatest Z-direction tensile improvement of 28% was obtained for the 40:60 blend, with a corresponding 20% improvement in tensile strength and improved bending resistance (Table 4.3B). There was evidence of fibre damage and slight bulk reduction. The 80:20 and 60:40 blend ratios were similar to the 40:60 blend, but the 60:40 blend showed no improvement in tensile strength and the scattering coefficient was lowered by 15%.

The graphical representation of this pulp evaluation data did not reveal significant property enhancements (Appendix 3, Fig. 8). The blends showed reasonable property development with beating. Individual fibre strength was lowered and a slight reduction in bulk occurred for some of the blends. The Z-direction tensile against tensile indices graph indicated improved interfibre bonding at slightly higher tensile strengths, but these are not significant improvements.

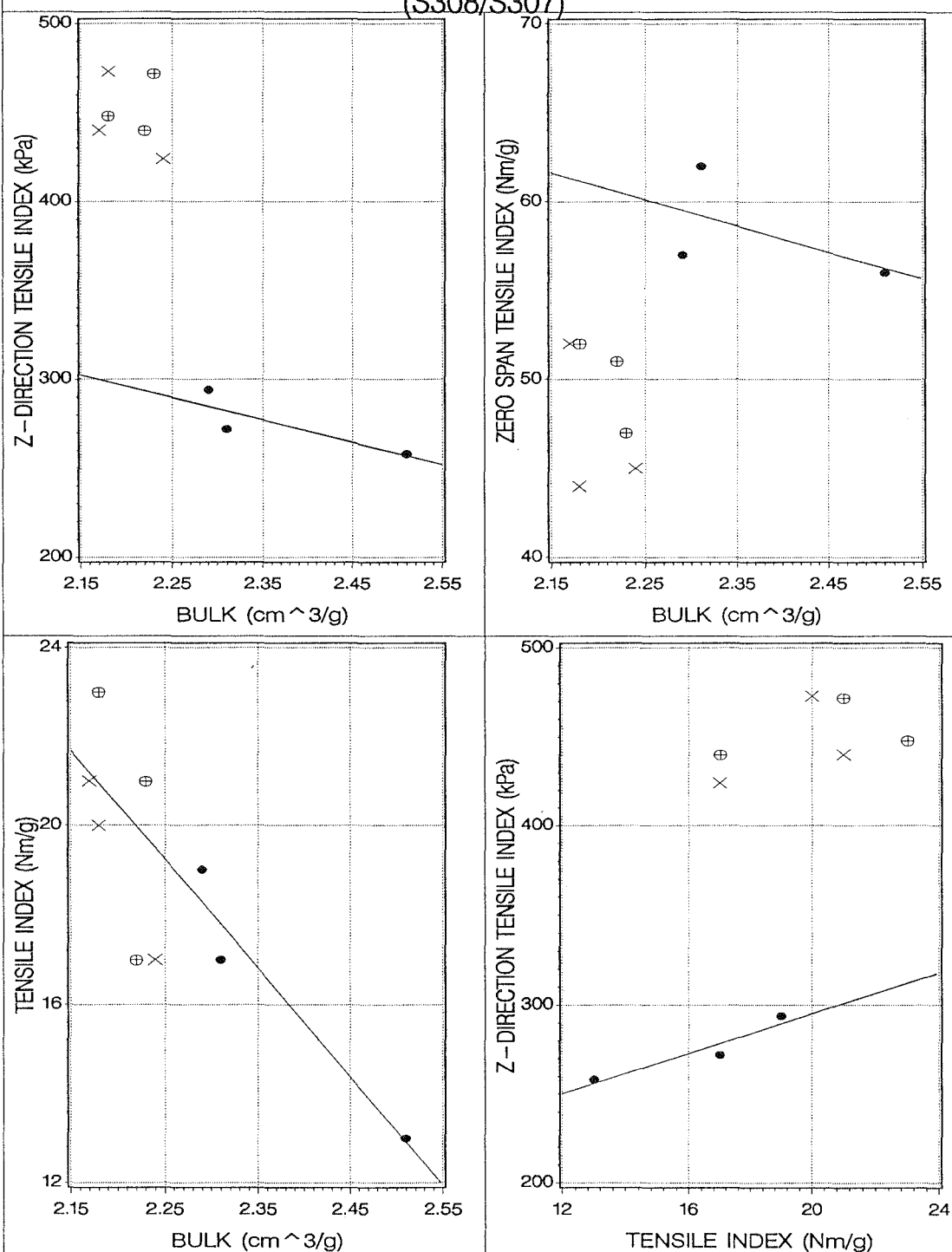
#### Blend S308/S307

The 20:80 and 40:60 blends of these maleic acid and cationic cellulose derivatives (Table 4.3B; S308, 11.07 meq/100g; S307, 0.24% N) show significant interfibre bonding improvements at CSF 250 of 58% and 51%, respectively. The other two blends "went through the hoop" and hence, could not be evaluated. The bonding improvements of the 20:80 blend were confirmed by the reduced optical properties and slightly reduced bulk. The tensile strength was not improved reflecting the fibre damage which had occurred. The 40:60 blend has a reduced scattering coefficient and increased bending resistance (+23%).

The Z-direction tensile versus bulk graphs of these two blends clearly show a cluster of data points at higher Z-direction tensile and lower bulk than unmodified linters, suggesting greater conformability upon blending (Fig. 4.12). Some fibre damage was evident and the blends appear to have developed slightly higher tensile

Figure 4.12: Key Papermaking Properties of Maleic Acid – Cellulose and Cationic Cellulose Blends

(S308/S307)



Sample:

X X 20:80 Mal – Cat      ⊕ ⊕ 40:60

• • Unmodified Cotton Linters



strengths, again at lower bulk than cotton linters. Significant interfibre bonding gains were apparent in the Z-direction tensile index versus tensile index graph.

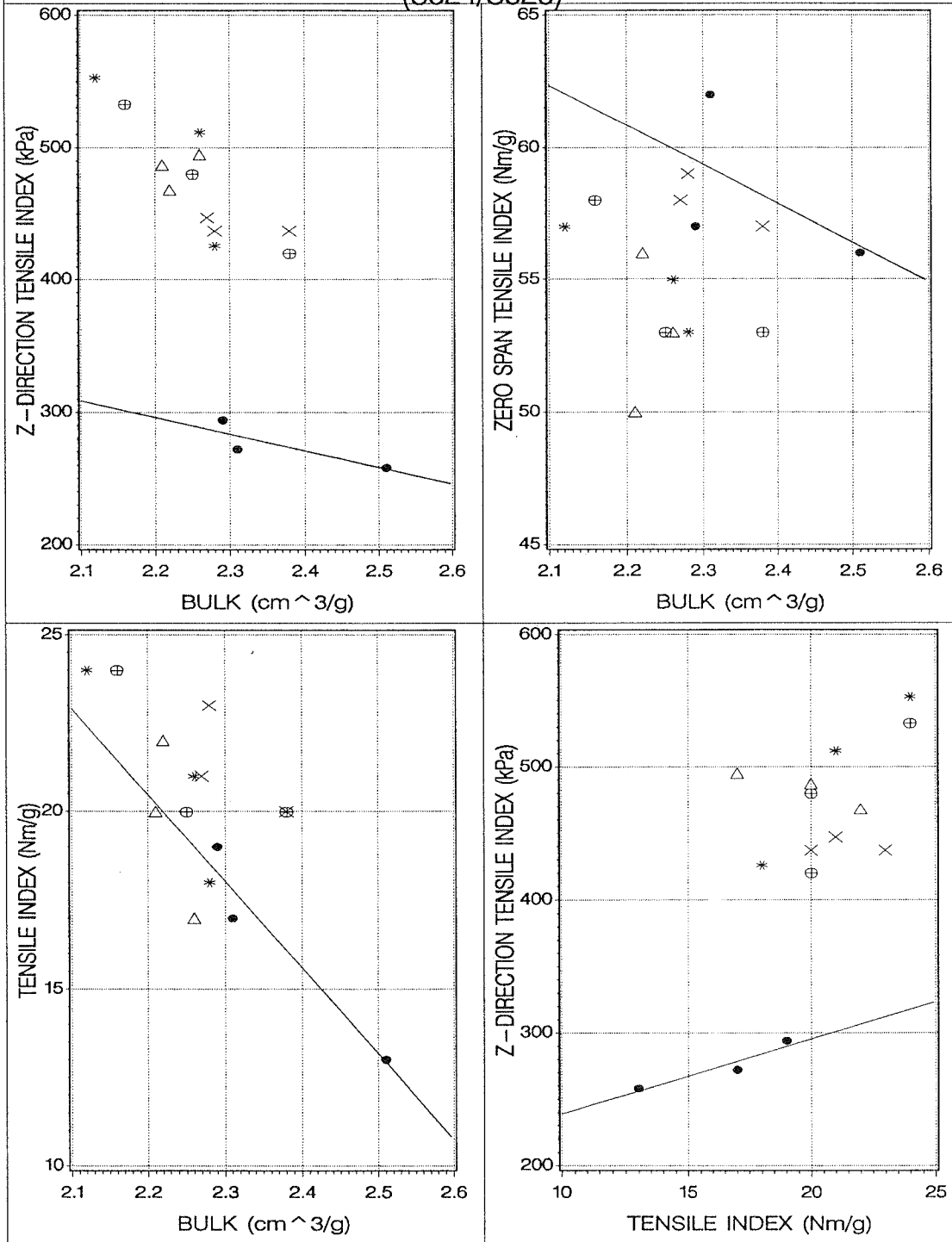
#### Blend S324/S323

The greatest improvement in interfibre bonding of 83% was realized for an 80:20 blend of a maleic acid-cellulose derivative and cationic cellulose (Table 4.3B; S324, 8.51 meq/100g; S323, 0.21% N). This blend showed improved tensile strength, with some loss of bending resistance and minor bulk reduction. No fibre damage was evident and other properties were unaffected.

The effect of different blend ratios is quite marked when comparing the CSF 250 interpolated values. The 60:40 blend, whilst similar to the 80:20 blend, did not have as pronounced an effect on the properties but did reduce optical properties. The 40:60 blend restored the bending resistance to that of the unmodified reference. Finally the 20:80 blend with 49% improvement in interfibre bonding has reduced optical properties and bending resistance, with increased bulk and stretch. The 20:80 blend possessed low freeness values and hence, these results should only be used as an indication of papermaking properties. The increase in tensile strength indicated that the increase in interfibre bonding compensated for the fibre damage that occurred upon modification.

The development of key papermaking properties of these blends are shown in Figure 4.13. The graph of Z-direction tensile index versus bulk clearly demonstrates the significant gains in interfibre bonding, for these maleic acid-cationic cellulose blends. Blending has effectively decreased the bulk which may reflect increased conformability and hence increased bonded area leading to the observed bonding improvements. However, the absence of any changes in optical properties suggests an increase in the strength of bonds due to electrostatic forces, rather than an increase in the number of fibre-to-fibre bonds.

Figure 4.13: Key Papermaking Properties of Maleic Acid – Cellulose and Cationic Cellulose Blends (S324/S323)



Sample:

- X X 20:80 Mal – Cat      ⊕ ⊕ 40:60
- Δ Δ 60:40                      \* \* 80:20
- • Unmodified Cotton Linters

The graph of zero span tensile index against bulk reveals that some fibre damage has occurred. The blend with minimum interfibre bonding improvements has suffered the least fibre damage. At a given bulk, the tensile strength of most of these blends were above that of the unmodified reference. The blends developed higher tensile strengths at lower bulk than the unmodified reference. With increasing tensile strength significant increases in interfibre bonding were apparent. The observed improvement in tensile strength is attributable to increases in the interfibre bonding component of this parameter.

#### **4.4.3 Concluding Remarks**

As anticipated the blends of anionic-cationic cellulose derivatives significantly improved the interfibre bonding properties of cotton linters. These improvements were much greater than the improvements noted for any of the anionic or cationic derivatives alone. It is proposed that blending increases the strength of bonds by electrostatic interactions during sheet formation. In addition, if not involved in electrostatic interactions, these hydrophilic groups may act individually to facilitate plasticization, increase conformability and thus, increase the contact area available for bonding interactions and the number of such interactions.

The marked increase in interfibre bonding for the carboxymethyl-cationic cellulose blends, as opposed to the properties noted for the carboxymethyl cellulose derivatives alone (less than 20% improvement in Z-direction tensile index), suggests that the dominant factor in improving the interfibre bonding is the strength of bonds formed via electrostatic attraction, with the improvements obtained by increased bonded area and number of bonds playing a lesser role.

Blends of maleic and itaconic acid-cellulose derivatives with cationic cellulose gave the greatest increases in Z-direction tensile indices possibly because they are

diprotic acids and offer additional opportunities for electrostatic interactions between the carboxylate groups and the cationic groups than the monoprotic carboxymethyl cellulose.

#### **4.5 DISCUSSION OF THE PAPERMAKING PROPERTIES OF CELLULOSE DERIVATIVES EVALUATED IN THE PFI MILL**

The results for PFI mill evaluations which gave less than 20% improvement in Z-direction tensile index are cited in Appendix 4. With the exception of one cyanoethyl cellulose, which gave large increases in tensile and burst strengths, only those PFI evaluations that gave notable interfibre bonding improvements are discussed in the following paragraphs.

##### Cyanoethyl Cellulose (S312)

Despite considerable fibre damage, this derivative showed the greatest increases in tensile and burst strengths of any derivative at CSF 250 (Table 4.4). The 55% increase in tensile strength and concomitant increase in burst strength of 71% does not coincide with a significant increase in interfibre bonding at CSF 250. The major changes to optical properties were possibly the combined result of reduced bulk and increased bonding. Also the stretch and tensile energy absorption values of the cyanoethylated pulp were much higher than for unmodified linters (+19 and *ca.* +85%, respectively).

The Z-direction tensile index versus bulk graph depicting these beating-point data showed the cyanoethyl cellulose developed superior interfibre bonding at a lower bulk than unmodified linters (Fig. 4.14) and that extensive fibre damage occurred. As expected from the interpolated data, the tensile strength of the cyanoethylated pulp was far superior to the reference pulp with a greater relative rate of

**Table 4.4:** PFI Mill Pulp Evaluations of a Range of Cellulose Derivatives at CSF 250<sup>a</sup>

Cellulose Derivative (Number)	Z-Dir. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity (%)	Burst Index	Tear Index	Beating Time (rev/g)	Stretch (%)	Substitution
Cyanoethyl (S312)	+15	+55	-41	NS <sup>c</sup>	-7	-46	-14	+71	NS	+100	+19	1.28% N
Amidoethyl (S313)	+27	+36	-22	+32	NS	-31	-8	+43	NS	+150	+19	0.67% N
Maleic Acid-Cationic (S358, S359/ S356,S357) <sup>b</sup> 60:40	+22	+14	-13	NS	NS	-11	NS	+18	NS	+29	-12	12.9 meq/100g 12.2 meq/100g 0.24% N
80:20	+32	+24	-13	+15	-10	(-7)	NS	+27	-11	+440	-17	0.17% N
(S393,S394/ S399, S400) <sup>b</sup> 60:40	+21	NS	-16	(-7)	NS	(-8)	NS	NS	NS	-38	-13	12.2 meq/100g 14.9 meq/100g 0.22% N
80:20	+32	+16	NS	NS	(-6)	(-8)	NS	NS	NS	+35	-25	0.23% N
Carboxymethyl-Cationic (S380, S381/ S376, S377) <sup>b</sup> 60:40	+28	+14	-10	+18	(-6)	-15 <sup>d</sup>	+9 <sup>d</sup>	+17	(-7)	+67	-12	10.1 meq/100g 11.8 meq/100g 0.20% N
80:20	+40	+29	NS	+18	-13	-11	NS	+33	-13	+660	-9	0.19% N
Itaconic Acid-Cationic (S401, S402/ S407, S408) <sup>b</sup> 40:60	+31	+16	NS	-12	NS	-10	NS	NS	+27	NS	-9	11.6 meq/100g 12.0 meq/100g
60:40	+45	+32	-9	-14	-11	NS	NS	+27	+12	+210	NS	0.19% N
80:20	+21	+16	NS	NS	-7	NS	NS	NS	(+6)	+62	-9	0.22% N

a. Only modifications showing 20% or greater improvement in Z-direction tensile index at CSF 250 relative to their unmodified linters reference are included.

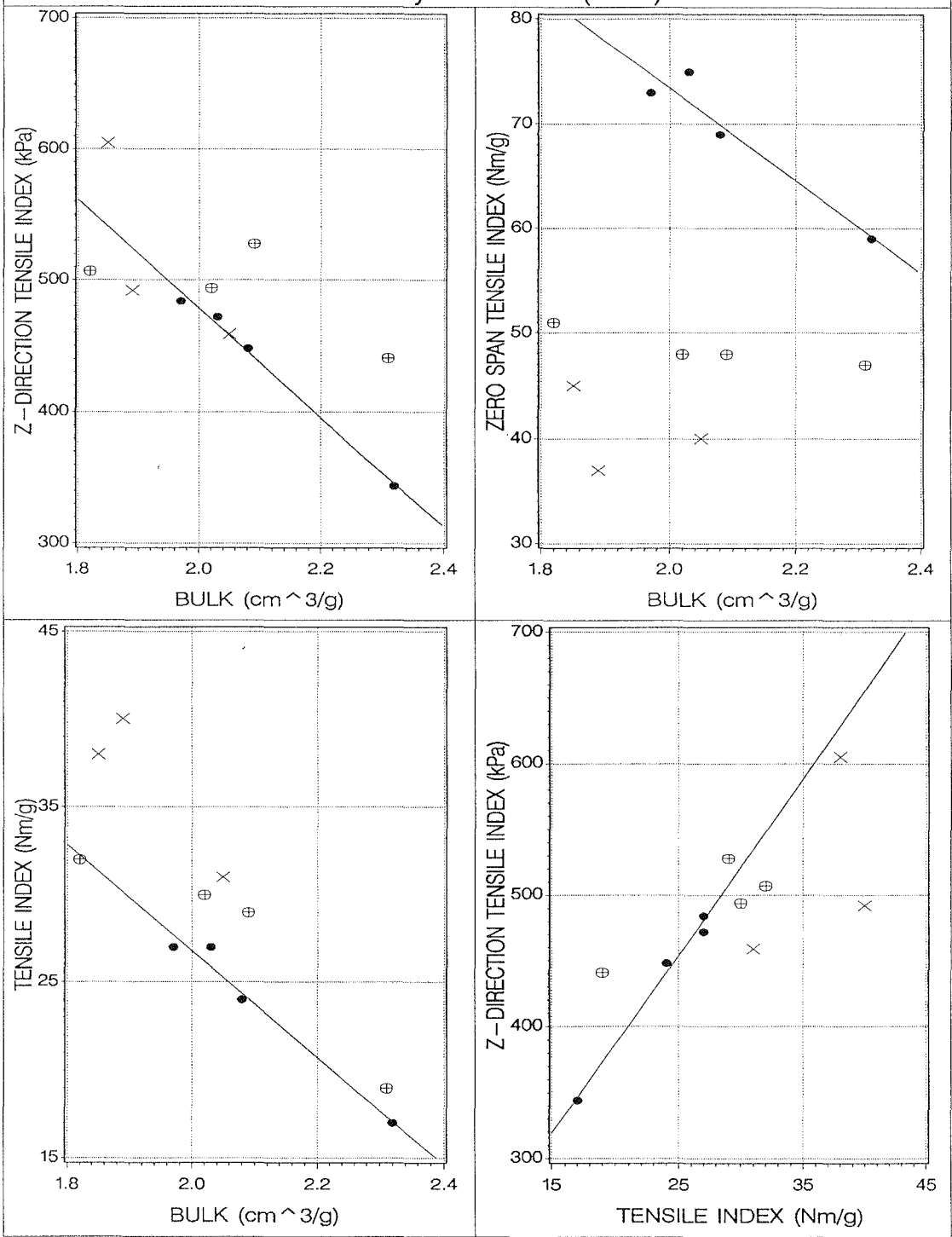
Property changes are shown as % increases or decreases relative to unmodified linters.

b. These derivatives were blended as discussed in the text.

c. Not significant change (5% or less). Bracketed values are probably not significant.

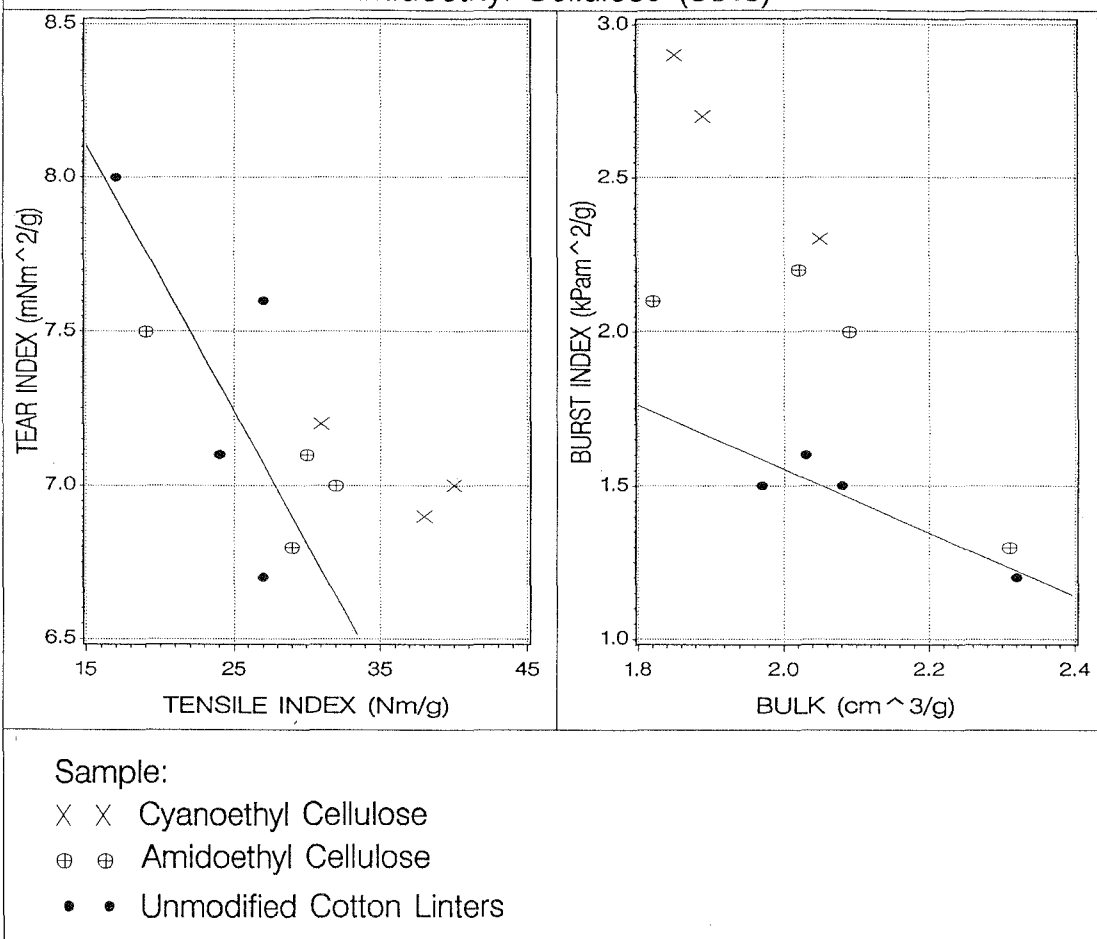
d. Optical properties may be affected by contaminated water.

Figure 4.14: Key Papermaking Properties of  
Cyanoethyl Cellulose (S312) and  
Amidoethyl Cellulose (S313)



Sample:  
 X X Cyanoethyl Cellulose  
 ⊕ ⊕ Amidoethyl Cellulose  
 • • Unmodified Cotton Linters

**Figure 4.14: Key Papermaking Properties of Cyanoethyl Cellulose (S312) and Amidoethyl Cellulose (S313)**



development. Similarly, the graph showing the rate of interfibre bonding with bonding development suggested that other factors apart from interfibre bonding increases were contributing to the tensile strength improvements. The modified pulp generally developed lower tear strengths, but at higher tensile strengths, than unmodified linters. Cyanoethylation greatly improved the burst at a given bulk. These results suggested that this cyanoethylation optimized the beating process by maximizing fibrillation with no loss of fibre length. The absence of interfibre bonding improvements probably reflect the hydrophobic effects of this derivative at this substitution level.

### Amidoethyl Cellulose (S313)

This amidoethyl cellulose yielded favourable improvements in several key properties at CSF 250. Improvements were noted for Z-direction tensile index, tensile index, bending resistance and burst index (Table 4.4). Light scattering confirmed these bonding improvements. Reasonable loss of individual fibre strength was evident. As for the cyanoethylated pulp, the stretch and tensile energy absorption were increased significantly indicating increased elasticity.

From the Z-direction tensile graph (Fig. 4.14), it was apparent that the acrylamide-treated linters did not develop higher interfibre bonding than the unmodified pulp. However, at low beating times there was a significant difference between the two pulps. The bulk was reduced, suggesting increased conformability upon modification. Higher tensile strengths were achieved, despite significant fibre damage. The Z-direction tensile index versus tensile index graph showed that the unmodified linters develop interfibre bonding more rapidly with increased tensile strength, but both the amidoethylated and untreated linters tended to converge around similar bonding levels. The burst-bulk graph reflects the tensile strength gains, with the burst being much higher at a given bulk.

### Maleic Acid-Cationic Cellulose Blends (S358,S359/S356,S357)

Blends of maleic acid-cellulose and cationic cellulose, intended to replicate the success of blends S324/S323 at the PFI mill scale, gave disappointing results. The greatest improvement in interfibre bonding at CSF 250 was 32%, compared with 83% for the small scale evaluation. The 32% increase was obtained for the 80:20 maleic acid-cellulose:cationic cellulose blend. Improvements were noted for tensile strength, bending resistance and burst index with minor losses of fibre strength, bulk and tear index. In combination these changes suggest that blending of these modifications has increased the hydrophilicity, conformability and hence, bonded



area. The 60:40 blend with 22% improvement in Z-direction tensile also produced minor increases in tensile and burst strengths with limited fibre damage and reduced scattering coefficient (Table 4.4).

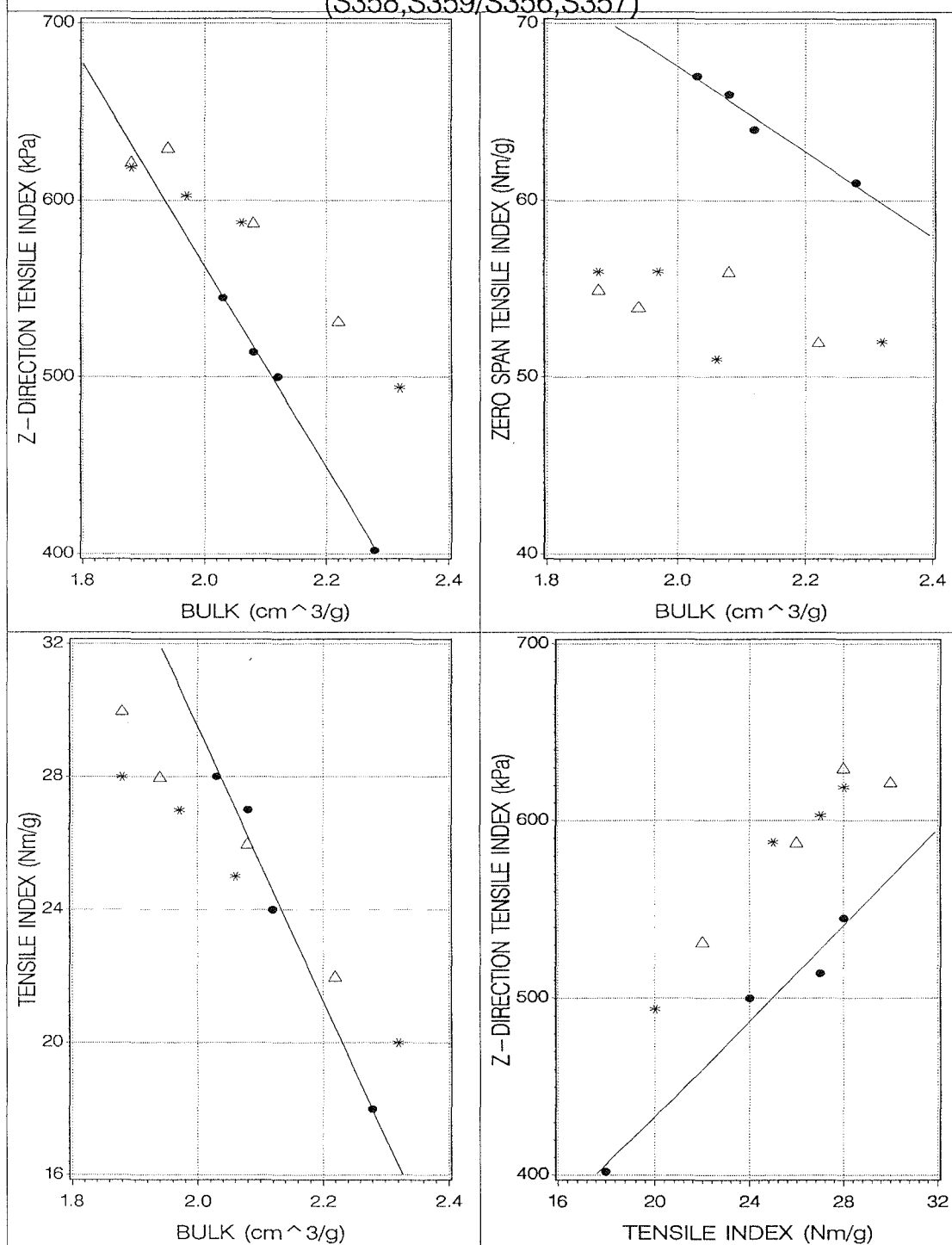
The graph of Z-direction tensile versus bulk revealed quite different relative rates of property development between the two blends and unmodified linters (Fig. 4.15). The blends developed higher interfibre bonding but at a lower bulk than unmodified linters. The blends did not give as marked an increase in Z-direction tensile with beating, i.e. unmodified linters responded to beating but blending allowed greater bulk reduction and hence, the observed bonding improvement. Some fibre damage occurred according to the zero span tensile versus bulk graph. However, the individual fibre strength of unmodified linters appeared to increase with beating, an anomalous finding.

After an initial beating, the blends generally showed the same tensile strengths as unmodified linters at lower bulk, again reflecting the better refining response of the blends. The Z-direction tensile versus tensile index graph showed that the modified and unmodified linters had the same rate of increase but that the modified linters had a greater interfibre bonding component than unmodified linters. The burst-bulk graph was similar to the tensile-bulk graph, showing similar burst values but at lower bulk than unmodified linters. The tear-tensile graph revealed marked differences. For the unmodified linters, the loss of tear strength with increasing tensile strength was minimal. However, for the two blends the tear strength decreased sharply with increasing sheet strength.

#### Maleic Acid-Cationic Cellulose Blends (S393,S394/S399,S400)

This maleic acid-cationic cellulose blend was also prepared in an attempt to replicate the best improvement of 83% (S323/S324 blend), at the PFI mill scale, as was blend S356-S359. They were replicated in part because of the low freeness

Figure 4.15: Key Papermaking Properties of Maleic Acid – Cellulose and Cationic Cellulose Blends (S358,S359/S356,S357)



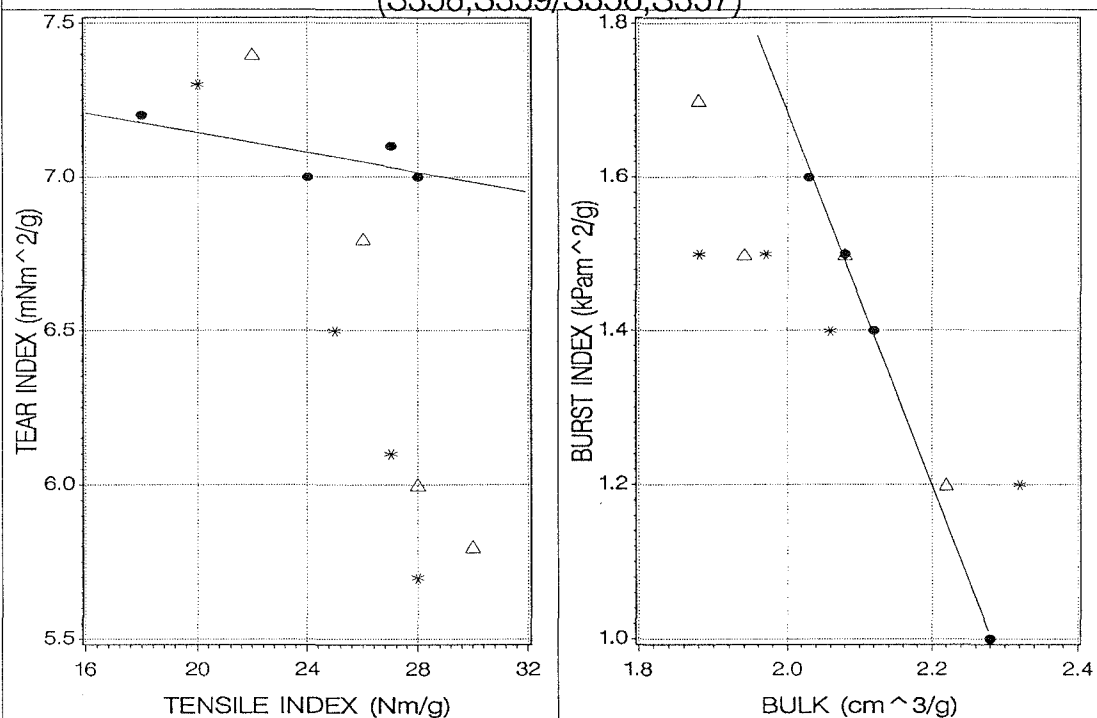
Sample:

△ △ 60:40 Mal – Cat

\* \* 80:20

• • Unmodified Cotton Linters

**Figure 4.15: Key Papermaking Properties of  
Maleic Acid – Cellulose and Cationic Cellulose Blends  
(S358,S359/S356,S357)**



Sample:

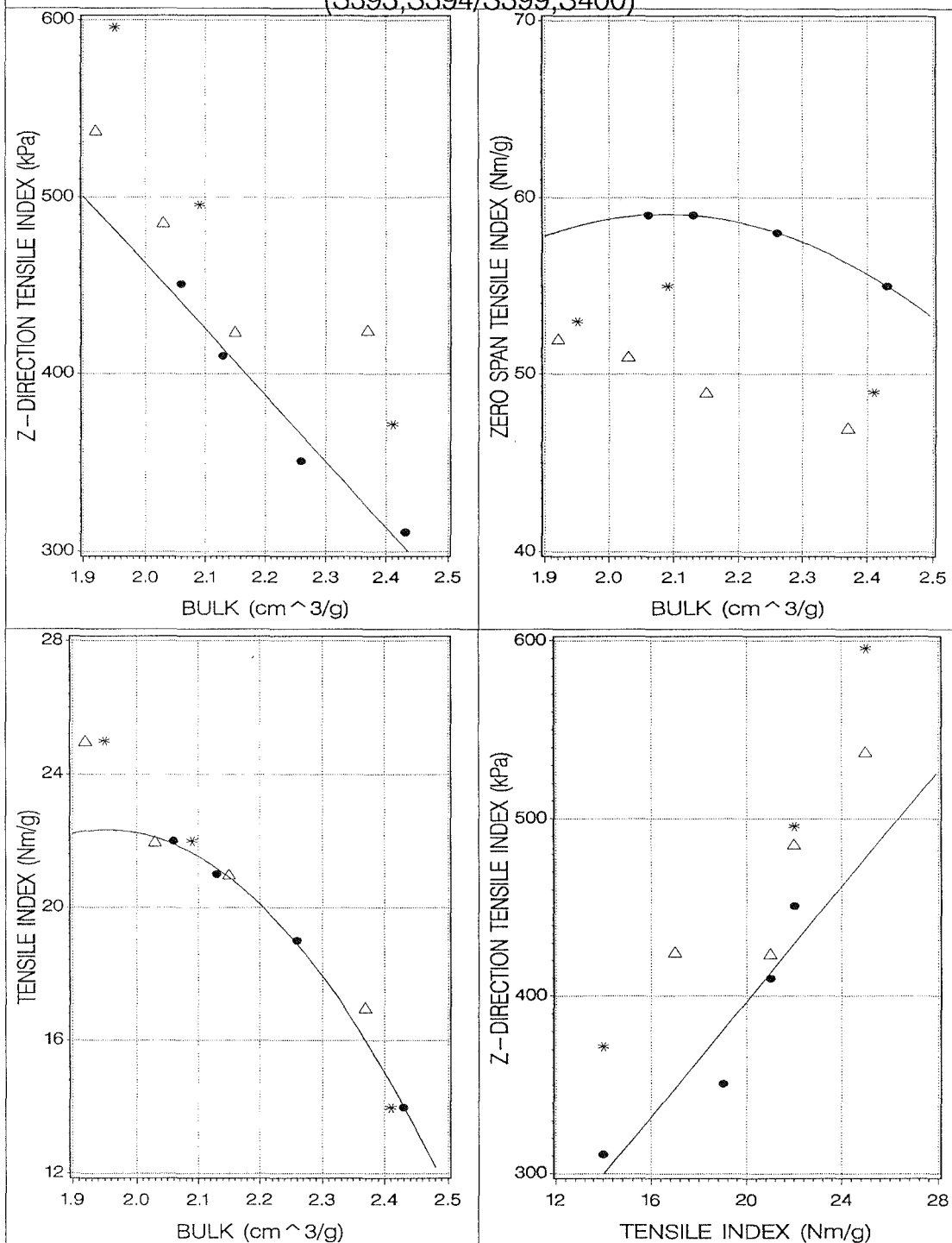
△ △ 60:40 Mal – Cat                      \* \* 80:20

• • Unmodified Cotton Linters

pulp used in modifications S356-S359. However, the desired improvement was not obtained and results similar to the previous low freeness PFI mill evaluation were obtained. The 80:20 blend gave a reasonable Z-direction improvement of 32% with a possible increase in tensile strength, decrease in scattering coefficient and some bulk reduction at CSF 250; other properties were unaffected. The decreased bulk may reflect increased conformability and hence, explain the bonding improvements. The 60:40 blend with 21% improvement in Z-direction tensile strength, showed loss of individual fibre strength and bending resistance at CSF 250.

The gains in interfibre bonding for these blends were quite apparent in the graph of Z-direction tensile versus bulk (Fig. 4.16). The blends developed higher levels of interfibre bonding at lower bulk. The zero beating point for the 60:40 blend

Figure 4.16: Key Papermaking Properties of  
Maleic Acid – Cellulose and Cationic Cellulose Blends  
(S393,S394/S399,S400)

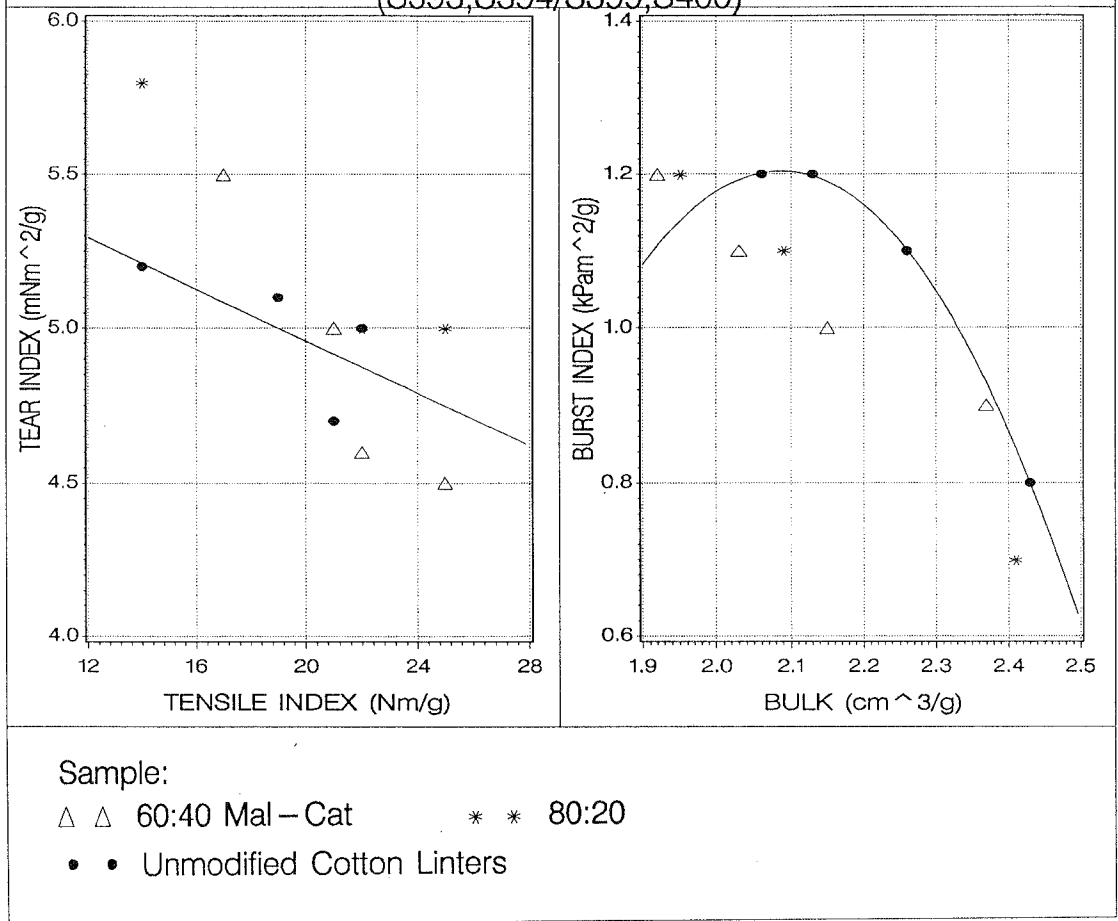


Sample:

△ △ 60:40 Mal – Cat      \* \* 80:20

• • Unmodified Cotton Linters

Figure 4.16: Key Papermaking Properties of Maleic Acid – Cellulose and Cationic Cellulose Blends (S393,S394/S399,S400)



appeared spurious and showed considerable bulk reduction. Although fibre damage occurred, this was not significant. The Z-direction tensile versus tensile graph highlighted the interfibre bonding improvements obtained at higher tensile strengths than for unmodified linters. Blending appeared to have maintained burst index but at lower bulk. The development of tensile strength reduced the tear strength more rapidly for the blends than for unmodified linters.

Carboxymethyl-Cationic Cellulose Blends (S380,S381/S376,S377)

This set of carboxymethyl and cationic cellulose blends prepared for PFI mill evaluation showed less significant papermaking improvements than the corresponding small scale modification. This may have been due to experimental

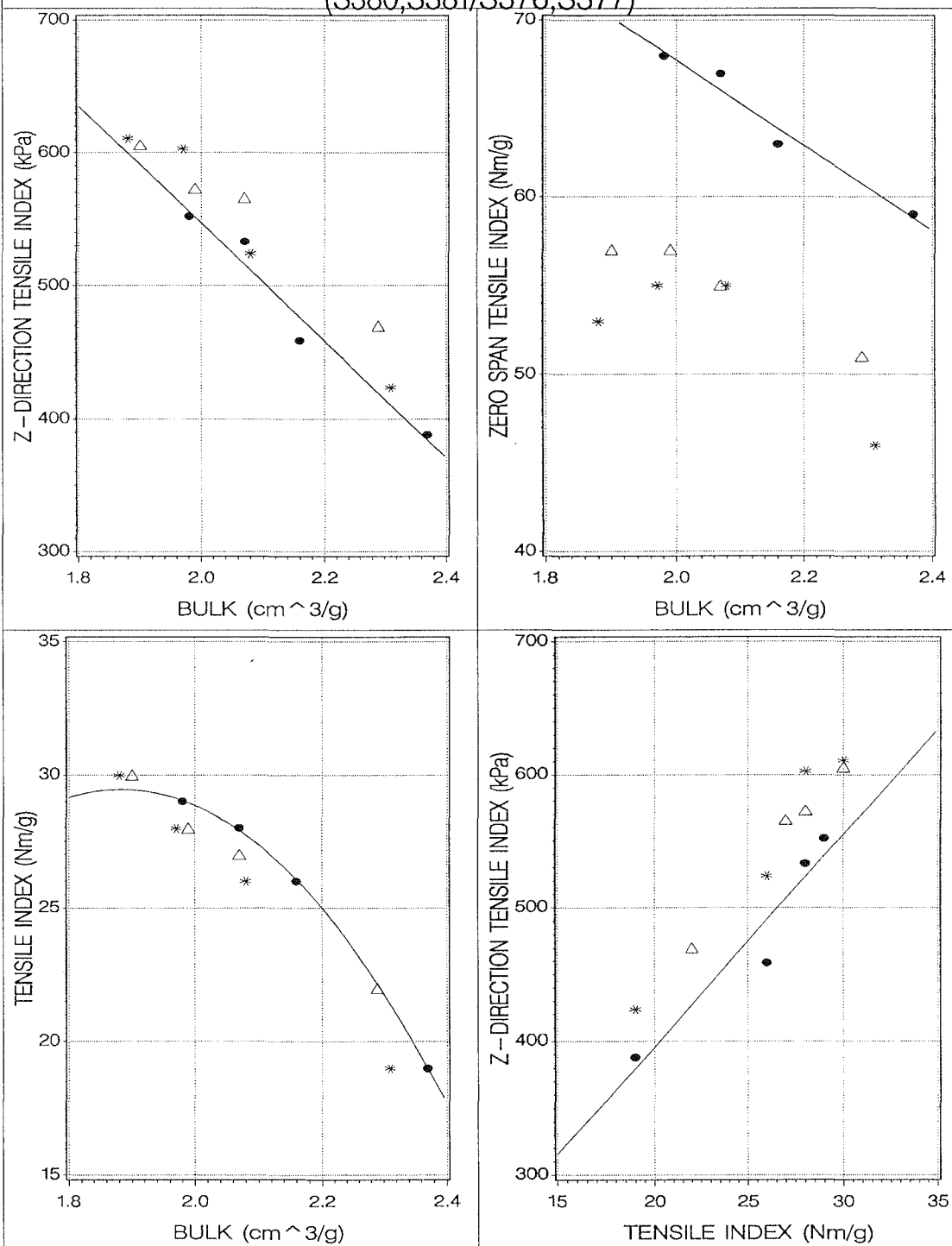
changes in scaling up, the low freenesses of the unmodified linters, the different refining response of the PFI mill and different substitution levels. However, the 80:20 blend still gave a 40% improvement in interfibre bonding and the 60:40 blend, 28% improvement at CSF 250 (Table 4.4). Other papermaking properties correlate directly with improved interfibre bonding, viz. tensile strength, burst and sheet stiffness were increased and bulk, scattering coefficient and tear index were decreased. There was no evidence of fibre damage. Hence at this blend ratio, the fibres are more conformable and have greater flexibility. Alternatively, all of the above changes may be explained simply by the effect of reduced bulk. The 60:40 blend showed similar trends to the 80:20 blend, but to a lesser extent, and there was evidence of limited fibre damage.

The graphs of the key papermaking properties of this set of blends gave quite a different impression to the CSF 250 data (Fig. 4.17). No significant gains were evident in interfibre bonding from the Z-direction tensile versus bulk graph. At a given bulk, individual fibre strength decreased upon blending. The graph showing the relative rates of development of Z-direction tensile and tensile indices suggested a slightly greater interfibre bonding at a given tensile strength. The tear-tensile graph showed that the tear strength of the blends decreased more rapidly with increasing tensile strength than for unmodified linters, which correlated with the lower zero span tensile indices.

#### Itaconic Acid-Cationic Cellulose Blends (S401,S402/S407,S408)

These itaconic acid-cationic cellulose blends were also prepared for comparison with blends of the 20 g o.d. scale which gave very promising bonding improvements, i.e. 80% increase in Z-direction tensile (blends S321/S322). However, at the PFI mill scale the maximum improvement obtained at CSF 250 was only 45% for the 60:40 blend. This blend also exhibited a marked increase in tensile strength, with possible increases in burst and tear strengths. Most other properties

Figure 4.17: Key Papermaking Properties of Carboxymethyl Cellulose and Cationic Cellulose Blends (S380,S381/S376,S377)



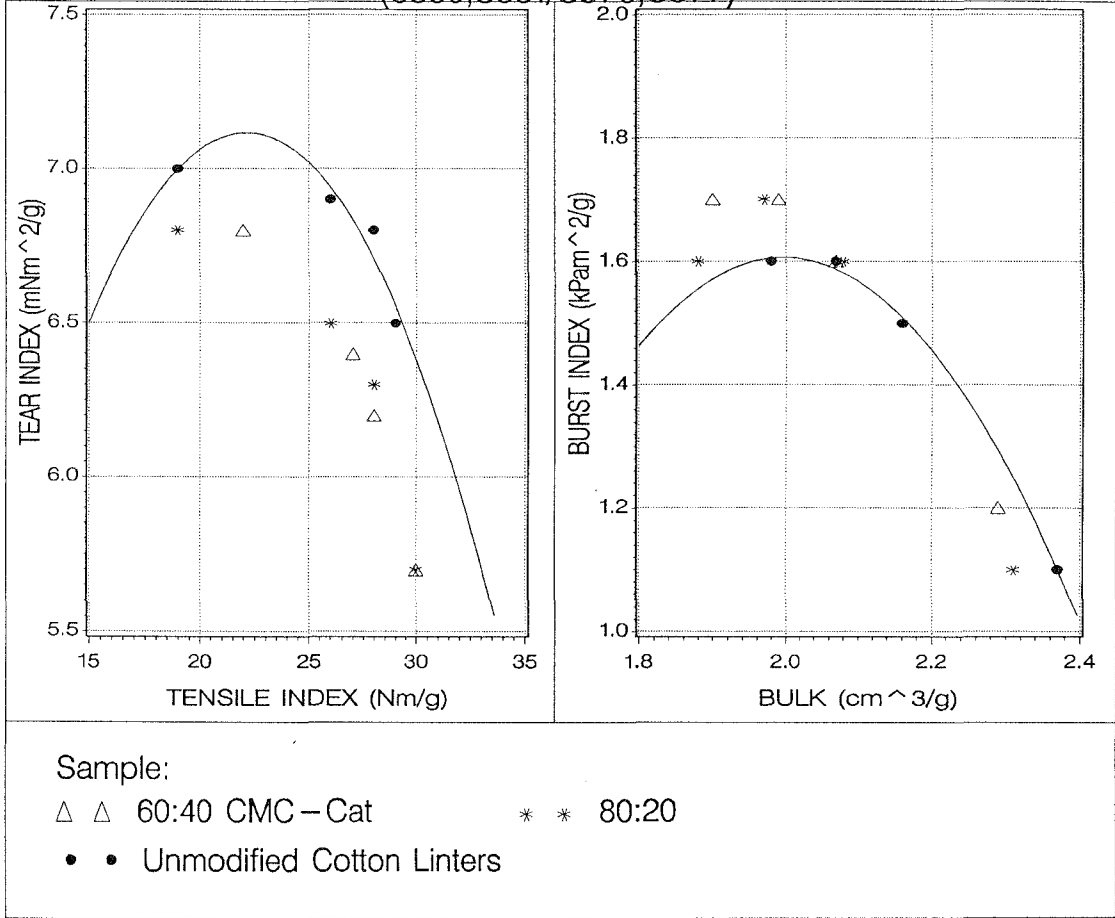
Sample:

△ △ 60:40 CMC – Cat

\* \* 80:20

• • Unmodified Cotton Linters

Figure 4.17: Key Papermaking Properties of Carboxymethyl Cellulose and Cationic Cellulose Blends (S380,S381/S376,S377)

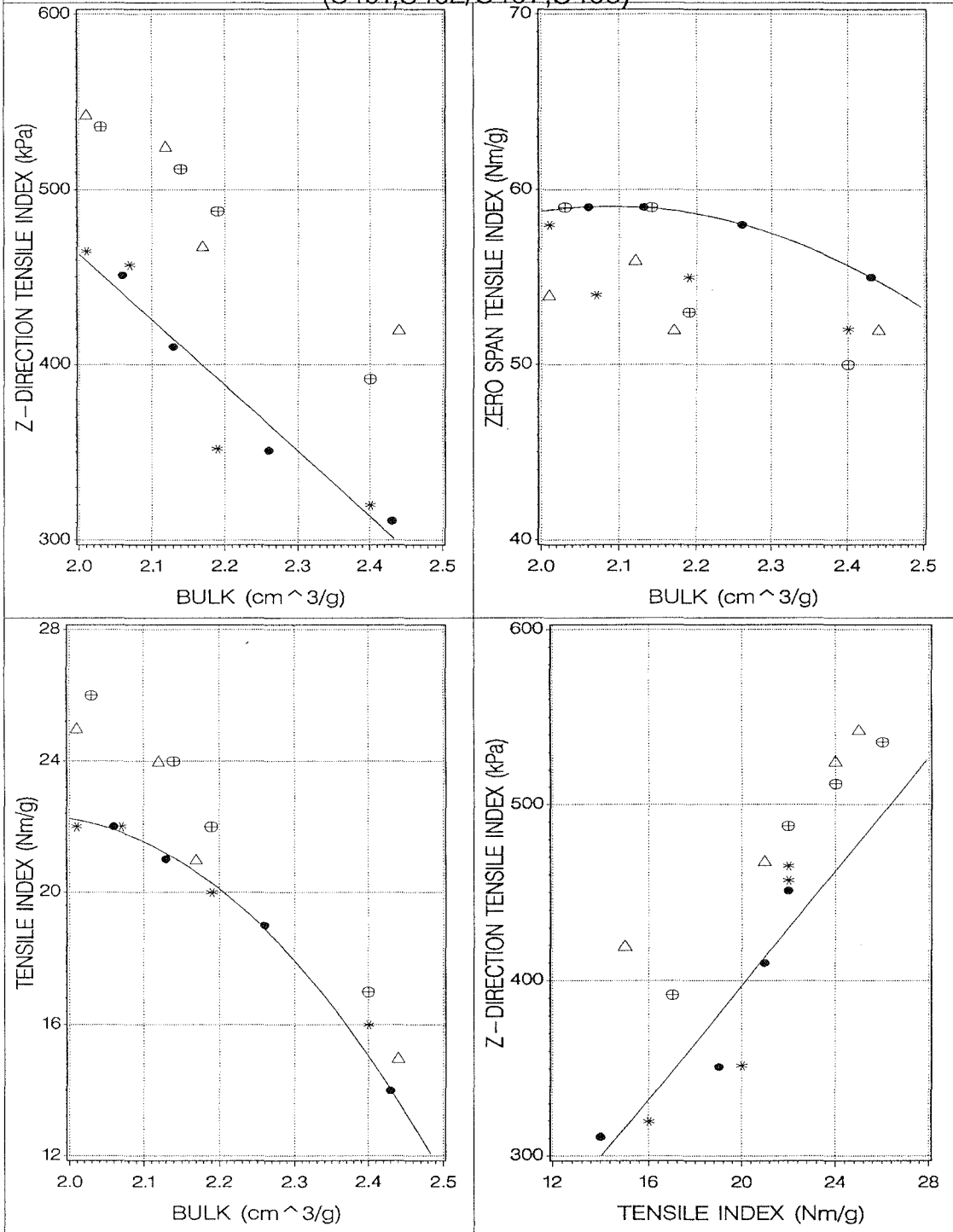


were lowered (Table 4.4). The 40:60 blend with 31% interfibre bonding improvement, gave an increase in tensile strength and a significant increase in tear strength (27%). No fibre damage was evident but some loss of bending resistance and scattering coefficient occurred upon blending. The 80:20 blend, whilst similar to unmodified linters, yielded slight improvements in Z-direction tensile and tensile indices.

According to the Z-direction tensile-bulk graph, the 40:60 and 60:40 blends show significant gains in interfibre bonding over unmodified linters without loss of bulk (Fig. 4.18). The 80:20 blend showed similar property development relative to unmodified linters. It is possible slight fibre damage has occurred for the blends. At a given bulk, the tensile strengths of the blends were also improved slightly. With

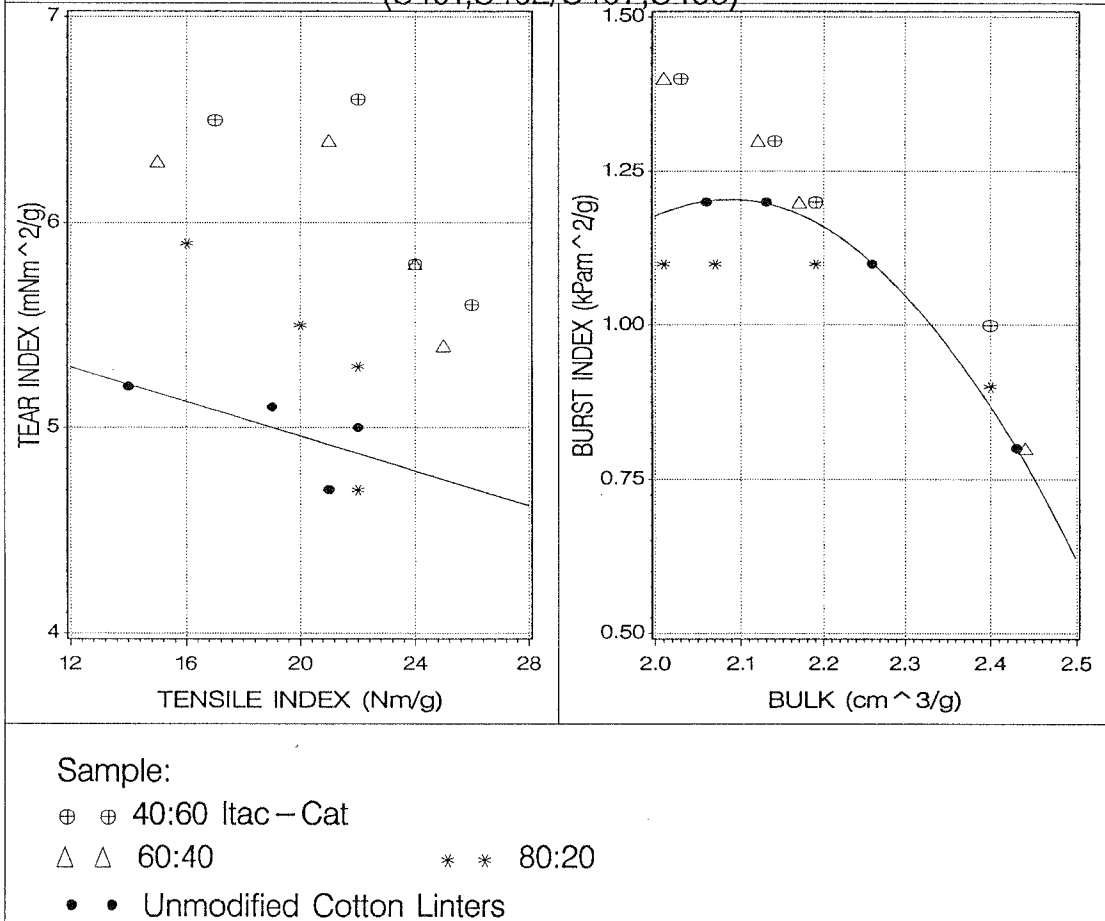


Figure 4.18: Key Papermaking Properties of  
Itaconic Acid – Cellulose and Cationic Cellulose Blends  
(S401,S402/S407,S408)



Sample:  
⊕ ⊕ 40:60 Itac – Cat  
△ △ 60:40                      \* \* 80:20  
• • Unmodified Cotton Linters

**Figure 4.18: Key Papermaking Properties of Itaconic Acid – Cellulose and Cationic Cellulose Blends (S401,S402/S407,S408)**



the exception of the 80:20 blend, blending these two derivatives has improved the interfibre bonding at higher tensile strengths than for unmodified linters. Minor improvements were noted for burst index at a given bulk. Finally the tear-tensile graph showed superior tear strengths to the reference pulp. This reflects the increased bonding without significant loss of fibre strength. The blends developed higher tear strengths which markedly reduced with increased bonding, whereas unmodified linters almost maintained their tear strength with increased bonding.

#### 4.6      SUMMARY

The development of the small scale pulp evaluation screening method allowed the papermaking properties of modified cotton linters to be assessed with significant savings in chemical costs, time and labour.

Of the several hundred modified linters samples evaluated about forty derivatives showed significant improvements. The papermaking properties of carboxymethyl and hydroxyethyl celluloses, accepted as standards for improving strength properties, did not yield the anticipated strength improvements. This was most probably due to the low substitution levels involved and the prior treatment given to Australian cotton linters. Some cationic, acrylamide and maleic acid derivatives of cellulose showed noteworthy improvements in Z-direction tensile index, with the acrylamide derivative showing marked improvements in tensile strength (*ca.* +35%).

Double derivatives and especially blends of anionic-cationic cellulose derivatives gave the most significant interfibre bonding improvements. The cationized amidoethyl cellulose and amidoethyl hydroxyethyl cellulose derivatives gave increases of between 31 and 43% in interfibre bonding. Although the groups introduced are hydrophilic, the papermaking improvements cannot be explained definitively without detailed information on the position of substitution.

Improvements in Z-direction tensile index of nominally 80% were obtained for blends of the diprotic maleic and itaconic acids with cationic cellulose. The carboxymethyl-cationic cellulose blends consistently gave improvements of 50-60% in Z-direction tensile strength. The above improvements were attributed to electrostatic interactions of the anionic and cationic groups on cellulose. Furthermore, the hydrophilic nature of these derivatives would facilitate plasticization, and increase conformability and interfibre bond formation during papermaking.

In general, the results obtained for pulps evaluated in the PFI mill were not as good as anticipated, with a maximum improvement in interfibre bonding of 45% being obtained for an itaconic acid-cationic cellulose blend. This apparent discrepancy was attributed to the development of lower Z-direction tensile and tensile strengths by the PFI mill and difficulties encountered in scaling up some experiments.

Further studies should address the relative contribution of changes in the contact area, number of bonds and their strength to the observed interfibre bonding improvements. Also colloidal titrations could be useful in ascertaining the ratios of anionic and cationic derivatives that give optimum results.

#### **4.7**      **EXPERIMENTAL**

##### Cotton Linters

Cooked and bleached cotton linters were used in most chemical modifications. Raw linters were not used in chemical modifications because of excessive grit and uneven fibre distribution present in the handsheets, making them unsuitable for pulp evaluation testing. All pulp evaluations were performed on never-dried linters, with most pulps being frozen prior to evaluation. Details of the processing and treatment of linters prior to pulp evaluation testing are given in Section 2.7.1.

##### Handsheet Preparation and Testing Procedures

Handsheets were prepared and tested in accordance with Australian Standard and Tappi Test methods in the NATA registered laboratories of Associated Pulp and Paper Mills. The test methods used are cited in Appendix 1.

### Procedure for Small Scale (20 g o.d.) Pulp Evaluation Method

This procedure was developed in conjunction with staff at APPM to allow small quantities of modified cotton linters to be evaluated. The test work was undertaken by staff at APPM using the above procedures.

In summary, three 5 g o.d. batches of cotton linters were beaten in a Waring blender for varying times to give three beating points (normal PFI mill evaluations required 20 g o.d. pulp for each of four beating points).

The detailed method for the preparation of a set of three handsheets for typically three beating points is given in Appendix 1.

### Equipment Used in Pulp Evaluation Test Procedures

The equipment used to evaluate the papermaking properties of cotton linters, in accordance with the standard testing procedures, is listed in Appendix 1.

Cotton linters were beaten using a Waring blender (small scale evaluations) and PFI mill (normal evaluations).

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## CHAPTER 5:

### CONCLUSIONS

This chapter summarizes the gains made towards improving the papermaking properties, especially the interfibre bonding, of cotton linters by chemical modification. In doing so, the range of cellulose derivatives prepared, their spectroscopic characterization and the assessment of their papermaking properties are discussed. The significance of these findings is discussed in relation to the original aims and objectives of the project.

The requirements for papermaking in this project, i.e. for a fibrous product at relatively low substitution levels, had repercussions in other aspects of the project. Namely, a fibrous product necessitated heterogeneous reaction conditions and concomitant low substitution levels, which constrained the synthetic methods used in Chapter 2. The low level substitution required to yield bonding improvements and minimize cost factors in the paper industry, in turn, complicated characterization methods and imposed limitations on the usefulness of spectroscopic techniques, restricting the new work possible in this area.

#### **5.1 SUMMARY OF FINDINGS**

##### **5.1.1 Preparation and Spectroscopic Characterization of Cellulose Derivatives**

The investigation of 2,3-dialdehyde celluloses led to the preparation of a new Girard's Reagent T-cellulose derivative. The product of the Michael addition reaction of *N*-(3-aminopropyl)methacrylamide hydrochloride with cellulose was also a previously unreported derivative.

Blends of the anionic cellulose derivatives of maleic, itaconic and fumaric acids, with cationic cellulose have not been reported elsewhere. The double derivatives: cationized amidoethyl cellulose, *N,N*-methylenebisacrylamide and maleic acid on hydroxyethyl cellulose, maleic acid-cationized cellulose and cationized maleic acid-cellulose were also new.

Synthetic methods leading to a number of cellulose derivatives were altered significantly from the reported methods. In particular, the procedures reported for the preparation of cellulose mesylate, cationized cellulose, hydroxyethyl cellulose, cyanoethyl cellulose, amidoethyl cellulose, *N,N*-methylenebisacrylamide-cellulose derivative, and maleic and itaconic acid-cellulose derivatives were modified in a series of reactions to assess the corresponding effects on papermaking properties.

Principally because of low substitution levels, the spectroscopic characterization of cellulose derivatives was not as useful as anticipated. However, some significant gains were made. A novel method of preparing samples of cellulose derivatives for FTIR microscope studies was developed. Using this technique the successful preparation of numerous cellulose derivatives was confirmed. While most spectra agreed with those reported in the literature, some reassignments were made to reported spectra. Assignments for previously unreported spectra, such as the *N,N*-methylenebisacrylamide and *N*-(3-aminopropyl)methylacrylamide cellulose derivatives, were made by reference to spectra of similar cellulose derivatives and to spectra of the corresponding Michael addition reagent. In addition, FTIR spectroscopy provided evidence of hydrolysis in some cyanoethylations and amidoethylations, and in the preparation of some double derivatives.

Despite the detection limits of solid state  $^{13}\text{C}$  NMR spectroscopy, spectra were obtained of more highly substituted cellulose derivatives. The  $^{13}\text{C}$  NMR spectrum of cellulose mesylate was obtained. Solid state NMR spectra of cyanoethyl and

carboxymethyl cellulose were also reported for the first time in this project. Spectra of unmodified cotton linters and hydroxyethyl cellulose were in agreement with previously reported spectra. Chromium doping of modified celluloses, while reducing accumulation times, did not improve the signal-to-noise ratio sufficiently, and the substitution levels of most cellulose derivatives were still below the detection limits of  $^{13}\text{C}$  solid state NMR spectroscopy. Solution NMR spectra of carboxymethyl cellulose and hydroxyethyl cellulose agreed with reported spectra.

### **5.1.2 Papermaking Properties of Modified Cotton Linters**

A small scale method of pulp evaluation was developed successfully and this allowed for ranking of the modified celluloses based on key papermaking properties. The reproducibility of this method and the pulp handling system were assessed and found to be acceptable, with an improvement in Z-direction tensile index of 20% or greater being used to rank modified pulps.

About forty modified celluloses showed interfibre bonding improvements of 20% or greater. A significant proportion of these were obtained for blends of anionic-cationic cellulose derivatives.

Some cellulose derivatives reputed to improve the papermaking properties of cotton could be reproduced and some could not. Carboxymethyl-cationic cellulose blends, amidoethyl cellulose and cationized cellulose gave reasonable interfibre bonding improvements. Hydroxyethylation of Australian cotton linters yielded only marginal improvements, contradicting some previous studies. Carboxymethylation and hydroxypropylation did not yield interfibre bonding improvements. This discrepancy was attributed to differences in the starting materials, i.e. pre-beaten cooked and bleached linters were used in modifications in this work. Low freeness batches of unmodified cotton linters also caused problems in reproducing the papermaking properties of some earlier promising modifications.

A number of cellulose derivatives previously prepared for other applications were assessed in this study for their potential in papermaking. These included 2,3-cellulose oxime, semicarbazone, thiosemicarbazone and Girard's Reagent T derivatives, 6-chloro-6-deoxy cellulose, *N,N*-methylenebisacrylamide, maleic acid and itaconic acid cellulose derivatives, amidoethyl hydroxyethyl cellulose and carboxymethylation of cationized cellulose. However, only the amidoethyl hydroxyethyl cellulose derivative gave significant interfibre bonding improvements (43%). The maleic acid-cellulose derivative, and oxime, semicarbazone and thiosemicarbazone derivatives of 2,3-dialdehyde cellulose also showed minor improvements in papermaking properties relative to unmodified linters.

Of the new derivatives and blends prepared, only maleic and itaconic acid-cellulose blends with cationized cellulose and cationized amidoethyl cellulose showed improvements in interfibre bonding relative to the reference pulp. Marginal improvements were noted for the fumaric acid-cationic cellulose blend. New derivatives such as the *N*-(3-aminopropyl)methacrylamide and the Girard's Reagent T-cellulose derivatives did not show improved papermaking properties.

Significant gains in Z-direction tensile index were achieved for a number of derivatives. Improvements of 83% and 80% in interfibre bonding were obtained for the previously unreported blends of maleic acid-cationic cellulose and itaconic acid-cationic cellulose derivatives, respectively, over unmodified cotton linters. These improvements were largely attributed to increased electrostatic interactions which resulted in increased conformability and reduced bulk. Most of the other blends, i.e. the best of each set, gave interfibre bonding improvements in the vicinity of 50%. The largest tensile strength improvement of 38% was obtained for a blend of carboxymethyl cellulose and cationic cellulose, at the 20 g o.d. scale.

Evaluation of the papermaking properties of blends on a large scale in the PFI mill gave lower interfibre bonding improvements than small scale trials, with an itaconic acid-cationic cellulose blend giving the greatest increase in Z-direction tensile index of 45%.

The PFI mill evaluation of cyanoethyl cellulose yielded the greatest increases in tensile and burst strengths of any modification in this study (55 and 71%, respectively). Similarly the amidoethylation on this scale gave significant bonding and sheet strength improvements.

## **5.2 RECOMMENDATIONS AND FUTURE WORK**

In view of the significant interfibre bonding improvements obtained in this study, pilot scale or mill trials are recommended. The most significant papermaking improvements were obtained consistently with blends of anionic cellulose derivatives (carboxymethyl, maleic acid and itaconic acid) and cationized cellulose. Whilst carboxymethyl cellulose is a well documented commercially produced derivative and may have a market in its own right in Australia, the synthesis involves the use of non-aqueous solvents and the highly toxic and corrosive reagent chloroacetic acid. Alternatively, maleic acid is a readily available, relatively non-toxic<sup>1,2</sup> and cheap reagent. It also has the added advantage of reacting with cellulose in an aqueous system. Itaconic acid is not as readily available as maleic acid. Cationized cellulose is prepared in an aqueous system using a commercially available cationizing reagent and should pose no particular problems in the mill situation. Hence of the derivatives offering significant papermaking improvements, the maleic acid-cationic cellulose blend appears the most feasible.

Considerable scope exists for future work to complement the findings of this study. A more extensive study of the papermaking properties of blends of other

anionic-cationic cellulose derivatives may prove beneficial. Scope also exists for further refinement and optimization of the reaction conditions for the preparation of the carboxymethyl and maleic acid-cellulose components of blends with cationized cellulose. The preparation of double derivatives of cellulose offers potential for a number of new derivatives with interesting properties, for example the blending of cationized hydroxyethyl cellulose with the maleic acid-cellulose derivative may have interesting papermaking properties. Moreover, reacting other Michael adducts with hydroxyethyl cellulose may yield new and useful derivatives.

More detailed spectroscopic studies of selected cellulose derivatives, especially  $^{13}\text{C}$  solution and 2D NMR studies, would be worthwhile. The preparation of some cellulose derivatives at high substitution levels, possibly using heterogeneous reaction conditions, would yield a range of previously unreported spectra, as the spectroscopic characterization of cellulose derivatives is limited.

Further spectroscopic work needs to be directed towards determining the position of substitution in new derivatives, cationized cellulose, maleic acid-cellulose derivatives and double derivatives such as cationized amidoethyl cellulose and amidoethyl hydroxyethyl cellulose.

In terms of papermaking, more detailed studies may provide information on the relative contribution of electrostatic interactions to the observed bonding improvements.

Finally, the preparation of some cellulose derivatives reported in this study at high substitution levels may possess entirely different properties and hence, find different applications and end-uses.

### 5.3      CONCLUDING REMARKS

In summary, the original aims and objectives of this project have been satisfied. Known cellulose derivatizations, assessed using Australian cotton linters, generally did not impart favourable papermaking properties to these linters. Suitable methods of characterization were developed for most chemically modified linters including a small scale method of pulp evaluation. Novel cellulose derivatives were prepared and their papermaking properties assessed, with blends of anionic-cationic cellulose derivatives giving major improvements in interfibre bonding. Selected modifications were also scaled up for full pulp evaluation. Cellulose derivatives feasible in a mill situation have been recommended and reasons for the observed bonding improvements proposed.

### 5.4      REFERENCES

- 1    Sax, N.I., and Lewis, R.J., Sr., 'Dangerous Properties of Industrial Materials' 7th. ed., Vol. III, p. 2155 (Van Nostrand Reinhold: New York 1989).
- 2    Budavari, S., Ed., 'The Merck Index' 11th. ed., p. 895 (Merck: New Jersey 1989).



## **APPENDICES**

## **APPENDIX 1: PULP EVALUATION TEST METHODS AND EQUIPMENT**

### **Pulp Evaluation Test Methods**

The following standard methods were used to evaluate the papermaking properties of cotton linters:

Forming of Handsheets for Physical Testing of Pulp	AS1301.203s-80
Freeness of Pulp	AS1301.206s-88
Determination of Stock Concentration	AS1301.207s-89
Physical Testing of Pulp Handsheets	AS1301.208s-89
Laboratory Processing of Pulp - PFI Mill Method	AS1301.209rp-89
Equipment for Preparation of Handsheets	AS1301.214s-89
Standard Atmosphere for Paper Testing	AS1301.415m-85
Determination of Temperature and Relative Humidity of Atmospheres	AS1301.416s-85
Internal Tearing Resistance of Paper	AS1301.400s-91
Bursting Strength of Paper	AS1301.403s-89
Bulking Thickness of Paper and Paperboard	AS1301.427s-88
Sheffield Air Permeance of Paper	AS1301.447s-91
Tensile Strength of Paper and Paperboard	AS1301.448s-91
Zero Span Tensile of Pulp and Paper	Tappi T231cm-85
Z-Direction Tensile of Pulp and Paper	Tappi T541OM-89

### **Procedure for Refining and Handsheet Preparation of 5 g o.d. Pulp Samples**

1. Stock Concentration and Moisture Content (g o.d. Pulp)
  - 1.1 A sample of pulp (0.3 to 0.5 g) was weighed, to three decimal places, onto a preweighed filter paper.

- 1.2 The filter paper was folded and dried on a hot plate to constant weight.
- 1.3 Pulp charge was calculated using the equation  $\frac{\text{a.d. wt pulp}}{\text{o.d. wt pulp}} \times 5 = 5 \text{ g o.d.}$ .

## 2. Beating

- 2.1 Pulp (5 g o.d. equivalent) was placed in a small blender (Sunbeam Model PB-B, liquefy speed) and made up to 500 mL total volume. The water contained in the pulp sample was included (e.g. 22 g = 5 g o.d. + 17 g water in pulp sample). A refining consistency equivalent to 10 gL<sup>-1</sup> was used.
- 2.2 The blender and stopwatch were started simultaneously and the pulp refined for the desired time. Note: Refining times varied considerably, e.g. 0 to 2 min, 10 to 60 min and above.

## 3. Sheet Making

- 3.1 A known amount of wash water was measured out (approximately 1 L but not greater than 1.17 L).
- 3.2 The contents of the blender were emptied into the stock divider and rinsed with wash water.
- 3.3 The pulp in the stock divider was further diluted to give a total volume of 1.67 L (consistency 3 gL<sup>-1</sup>) and air agitated at 25 kPa for 2 min.
- 3.4 Freeness was determined on a 1 L sample. The freeness was corrected for temperature and the freeness stock was then returned to the stock divider.
- 3.5 The pulp in the stock divider was further diluted by adding 2.83 L of water (total volume in stock divider 4.5 L).
- 3.6 This was air agitated for 2 min at 25 kPa.
- 3.7 One trial sheet was made using 1125 mL of stock and this was dried on a hot plate to constant weight. If the trial sheet weight was above 1.245 g, the stock was diluted according to the dilution table overpage. If the trial sheet was below 1.245 g, the weight was noted and no extra stock added during sheetmaking.
- 3.8 Three test handsheets were prepared as above.

3.9 Stock (43 mL) was used for Kajaani fibre length and fibre coarseness measurements.

3.10 Freeness pad weight correction: Trial sheet x 2.395 = freeness pad.

**Table A1.1:** Dilutions for Trial Sheets in the 5 g o.d. Pulp Evaluation Method

Trial Sheet (g)	Volume (mL)	Trial Sheet (g)	Volume (mL)	Trial Sheet (g)	Volume (mL)
1.246	2	1.256	29	1.266	56
1.247	4	1.257	31	1.267	59
1.248	7	1.258	34	1.268	61
1.249	10	1.259	37	1.269	64
1.250	13	1.260	40	1.270	67
1.251	15	1.261	42	1.271	69
1.252	18	1.262	45	1.272	72
1.253	21	1.263	48	1.273	75
1.254	23	1.264	50	1.274	77
1.255	26	1.265	53	1.275	80

#### 4. Property Testing

<u>4.1 Property</u>	<u>Replicates</u>
o.d. grammage*	3 o.d. bending resistance pieces
Thickness (bulk)	3 sheet thickness x 10 readings
Z-Direction Tensile Index	3, 1 reading per sheet
Zero Span Tensile Index	3, 1 reading per sheet
Tensile Index	6, 2 readings per sheet
Bending Resistance	3, 1 reading per sheet
Optical Properties	3, 1 reading per sheet
Stretch	6 obtained with tensile
Tensile Energy Absorption	6 obtained with tensile
Finish/Sheffield Roughness	3, 1 reading per sheet
Sheffield Air Permeance	3, 1 reading per sheet

\*o.d. grammage = bending resistance specimen (38 x 50) wt x 526.3 = o.d. gm<sup>2</sup>.

The above procedure was repeated from item 2. onwards, for each of the beating times (typically three).

### **Equipment Used in Pulp Evaluation Test Procedures**

The equipment listed below was used to evaluate the papermaking properties of cotton linters according to the cited standard testing procedures.

<u>Company and Model</u>	<u>Property Measured</u>
Digimike Thickness Tester	bulk
Instron High Wycombe	Z-direction tensile index
Lorentzen and Wettre Alwetron TH1	tensile index
Pulmac	zero span tensile index
Lorentzen and Wettre	bending resistance
Lorentzen and Wettre Burst Tester	burst index
Australian Optical Co.	tear index
Kajaani FS100 Fibre Length Analyser	fibre length
Technidyne Technibrite Micro TBIC	opacity, scattering and absorption coefficients
Sheffield Precisionnaire Air Permeance and Roughness Tester	air permeance
Sheffield Bendix Porosimeter	porosity

Cotton linters were beaten using a Waring blender (small scale evaluations) and PFI mill (normal evaluations).

## APPENDIX 2: PULP EVALUATION DATA AT CSF 250 (SECTION 4.3)

The following comments apply to all the tables in Appendix 2:

The ‘% Change’ represents the percentage increase or decrease in Z-direction tensile index at CSF 250 of the modified linters pulp relative to the unmodified linters reference. The abbreviation ‘NS’ is used to denote ‘not significant’, i.e. changes in Z-direction tensile index at CSF 250 of 5% or less. Bracketed values are the CSF 250 values for the unmodified linters reference.

Full beating point data is available on request from the author.

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)
2,3-Dialdehyde Cellulose										
S93(1 h)	+8	480(445)	18(20)	40(57)	37(44)	2.37(2.33)	-(-)	91(-)	6(5)	2.9(4.2)
S93(2 h)	+10	490(445)	17(20)	37(57)	37(44)	2.39(2.33)	46.5(-)	87(-)	7(5)	2.5(4.2)
S93(4 h)	+19	530(445)	18(20)	34(57)	38(44)	2.37(2.33)	-(-)	-(-)	9(5)	2.5(4.2)
S93(24 h)	+11	495(445)	19(20)	25(57)	39(44)	2.38(2.33)	44(-)	85(-)	20(5)	1.6(4.2)
S113(3 h)	NS	390(385)	17(21)	42(59)	48(44)	2.47(2.31)	46(44)	81(80)	15(15)	3.3(4.2)
S113(4 h)	NS	390(385)	18(21)	42(59)	48(44)	2.73(2.31)	48(44)	83(80)	17(15)	3.1(4.2)
S113(6 h)	NS	385(385)	18(21)	39(59)	40(44)	2.32(2.31)	40(44)	81(80)	19(15)	3.2(4.2)
S115(2 h)	+7	410(385)	19(21)	48(59)	43(44)	2.64(2.31)	47(44)	82(80)	13(15)	3.7(4.2)
S115(5 h)	+12	430(385)	18(21)	43(59)	46(44)	2.73(2.31)	47(44)	81(80)	17(15)	3.3(4.2)
S115(8 h)	NS	390(385)	15(21)	37(59)	56(44)	2.77(2.31)	45(44)	81(80)	35(15)	2.7(4.2)
S215	+10	380(345)	15(19)	35(53)	48(36)	2.95(2.31)	51(50)	81(81)	12(2.5)	2.5(4.4)
S275	-11	330(370)	17(20)	43(64)	47(44)	2.76(2.21)	44(40)	80(78)	6(1.5)	4(4.9)

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution (% N)
2,3-Cellulose Oxime											
S164	+18	400(340)	17(18)	38(59)	40(44)	2.36(2.30)	38(-)	80(-)	23(6)	3.1(4.8)	0.73
S175	+11	365(330)	16(17)	39(55)	35(44)	2.46(2.32)	40(-)	81(-)	21(6)	3.9(4.2)	0.68
S186	+12	370(330)	17(17)	60(55)	37(44)	2.27(2.32)	-(-)	-(-)	5.2(6)	4.5(-)	0.42
S209	+19	410(345)	19(19)	38(53)	39(36)	2.24(2.31)	39(50)	82(81)	4.2(2.5)	3.8(4.4)	0.59
S211	+19	410(345)	17(19)	35(53)	36(36)	2.28(2.31)	39(50)	81(81)	3.5(2.5)	3.8(4.4)	0.55
S237	+18	460(390)	19(16)	41(54)	37(49)	2.23(2.36)	43(46)	79(81)	3.9(2.5)	2.7(3.1)	0.40
S238	+13	440(390)	19(16)	39(54)	46(49)	2.19(2.36)	41(46)	80(81)	3.6(2.5)	3.3(3.1)	0.37
S239	+13	440(390)	19(16)	41(54)	49(49)	2.33(2.36)	44(46)	83(81)	3.9(2.5)	3.3(3.1)	0.32
S268	-17	330(400)	13(17)	33(39)	25(34)	2.61(2.29)	45(43)	77(79)	6(2.9)	3.1(3.1)	0.19
S269	-8	370(400)	14(17)	36(39)	25(34)	2.71(2.29)	45(43)	76(79)	6.7(2.9)	3.4(3.1)	0.16
S270	-13	350(400)	13(17)	33(39)	22(34)	2.81(2.29)	47(43)	77(79)	7.2(2.9)	2.4(3.1)	0.12
2,3-Cellulose Semicarbazone											
S157	+6	350(330)	16(21)	39(61)	36(45)	2.88(2.77)	42(46)	81(81)	9.8(9.4)	3.4(4.2)	1.85
S173	NS	330(330)	11(17)	38(55)	43(44)	2.57(2.32)	41(-)	79(-)	22(6)	3.7(4.2)	1.98
S187	NS	325(330)	17(17)	49(55)	47(44)	2.53(2.32)	-(-)	-(-)	24(6)	4.5(4.2)	1.13
S280	-8	340(370)	16(20)	46(64)	54(44)	2.54(2.21)	39(40)	79(78)	2.2(1.5)	3.9(4.9)	0.83
S281	NS	360(370)	17(20)	28(64)	52(44)	2.73(2.21)	43(40)	78(78)	2.3(1.5)	3.4(4.9)	0.23
2,3-Cellulose Thiosemicarbazone											
S223	+8	420(390)	16(16)	34(54)	42(49)	2.59(2.36)	48(46)	84(81)	2.7(2.5)	2.6(3.1)	1.00
S271	-15	340(400)	14(17)	30(39)	26(34)	2.73(2.29)	48(43)	79(79)	7.5(2.9)	2.4(3.1)	0.42
S272	NS	400(400)	14(17)	29(39)	13(34)	2.75(2.29)	46(43)	74(79)	11.5(2.9)	2.1(3.1)	0.24
Girard's Reagents T and P											
S158	-24	250(330)	11(21)	12(61)	33(45)	2.56(2.77)	42(46)	83(81)	8.8(9)	1.4(4.2)	0.93
S174	-23	255(330)	10(17)	11(55)	31(44)	2.55(2.32)	41(-)	86(-)	23(6)	1.6(4.2)	0.97
S188	-12	290(330)	11(17)	17(55)	38(44)	2.50(2.32)	-(-)	-(-)	21(6)	2.3(4.2)	0.37
S229	-59	160(390)	7(16)	18(54)	29(49)	3.27(2.36)	54(46)	93(81)	5.8(2.5)	2.4(3.1)	0.64

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution
Carboxymethyl Cellulose											
S81	-13	410(470)	18(20)	45(53)	45(44)	2.18(2.21)	44(45)	84(85)	3(5)	3.2(3.6)	2.14 *
S197	+12	370(330)	18(18)	47(57)	36(44)	2.30(2.31)	47(-)	81(-)	1.3(6)	4.1(4.5)	7.28 *
S235	-8	360(390)	14(16)	49(54)	45(49)	2.31(2.36)	42(46)	77(81)	1.9(2.5)	2.8(3.1)	8.36 *
Hydroxyethyl Cellulose											
S191	+9	360(330)	16(18)	48(57)	34(44)	2.28(2.31)	42(-)	79(-)	8.5(6)	3.5(4.5)	3.00%**
S217	+16	400(345)	17(19)	34(53)	43(36)	2.66(2.31)	37(50)	75(81)	48(2.2)	3.7(4.4)	2.16%**
S261	-10	370(410)	17(18)	50(42)	31(32)	2.30(2.27)	43(43)	79(79)	2.7(2.7)	3.6(3.5)	2.46%**
S316	Evaluated at CSF 400. No unmodified linters available as a reference.										
S396	+6	380(360)	14(16)	40(47)	37(44)	2.27(2.25)	41(39)	78(79)	9.6(1.3)	2.7(2.6)	1.97%**
S390***	-34	250(380)	10(18)	36(61)	27(41)	2.39(2.34)	59(47)	84(82)	3.3(0)	3.7(4.1)	_
Hydroxypropyl Cellulose											
S263	Evaluated at CSF 400. No unmodified linters available as a reference.										
S265	-15	340(400)	9(17)	17(39)	27(34)	2.54(2.29)	43(43)	79(79)	11(2.9)	2.8(3.1)	3.08%****
S314	Evaluated at CSF 400. No unmodified linters available as a reference.										
S315	-39	180(295)	10(19)	49(57)	30(47)	2.66(2.29)	51(43)	84(81)	15(1.6)	-(4.2)	1.20%****

\* meq/100g.

\*\* Hydroxyethyl groups.

\*\*\* Blank trial for hydroxyethyl and hydroxypropyl celluloses.

\*\*\*\* Hydroxypropyl groups.



Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution
Cellulose Mesylate											
S80*	-22	345(445)	12(20)	47(57)	27(44)	2.56(2.33)	-(-)	-(-)	14(5)	2.4(4.2)	<0.5% S
S86	-66	160(470)	9(20)	38(53)	30(44)	2.55(2.21)	82(45)	99(85)	24(5)	2.4(3.6)	7.34% S
S109	-13	330(380)	16(21)	52(61)	37(45)	2.35(2.25)	58(43)	90(80)	52(18)	3.5(4.3)	4.15% S
S117	-48	200(385)	13(21)	46(59)	42(44)	2.51(2.31)	63(44)	98(80)	26(15)	2.9(4.2)	6.53% S
S125	NS	400(385)	23(21)	60(59)	38(44)	2.23(2.31)	48(44)	83(80)	19(15)	4.1(4.2)	<0.3% S
Liquid Ammonia Treatments											
S105	-17	315(380)	15(21)	56(61)	41(45)	2.73(2.25)	49(43)	83(80)	61(18)	4.4(4.4)	0.05% N
S142	-30	270(385)	12(21)	48(59)	23(44)	2.84(2.31)	46(44)	78(80)	69(15)	3.2(4.2)	0.29% N
Treatments with Glyoxal											
S104	NS	375(380)	21(21)	59(61)	45(45)	2.23(2.25)	43(43)	81(80)	15(18)	3.6(4.4)	-
S106	-39	230(380)	12(21)	27(61)	39(45)	2.94(2.25)	54(43)	86(80)	73(18)	3.0(4.4)	-
S114	-42	225(385)	8(21)	13(59)	35(44)	2.75(2.31)	51(44)	85(80)	48(15)	2.0(4.2)	-
Cationized Cellulose											
S126low	-50	250(500)	19(21)	48(43)	24(40)	2.25(2.27)	35(33)	73(81)	3(3)	4.3(5.1)	0.13% N
S126high	NS	400(385)	19(21)	48(59)	39(44)	2.18(2.31)	33(44)	76(80)	3(15)	5.1(4.2)	0.22% N
S139	NS	380(385)	19(21)	53(59)	34(44)	2.39(2.31)	35(44)	78(80)	1(15)	3.9(4.2)	0.15% N
S213	+17	380(325)	17(31)	45(52)	38(36)	2.4(2.34)	46(51)	83(82)	3(2.2)	3.5(4.9)	0.05% N
S276	Freeness too low to extrapolate to CSF 250.										0.38% N
S279	Freeness too low to extrapolate to CSF 250.										0.47% N
S283	-13	320(370)	16(20)	44(64)	27(44)	2.48(2.21)	33(40)	76(78)	-(1.5)	4.9(4.9)	0.43% N
S352	-18	345(420)	16(21)	53(64)	49(48)	2.30(2.33)	39(46)	81(80)	-(0.6)	2.6(3.7)	0.15% N
S334**	-12	370(420)	17(21)	49(64)	41(48)	2.36(2.33)	42(46)	79(80)	0.3(0.6)	3.9(3.7)	<0.05% N

\* Using liquid ammonia as a solvent.

\*\* Blank trial for cationized celluloses.

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution (% N)
Blank for Michael Addition Reactions											
S335	-15	355(420)	18(21)	47(64)	43(48)	2.34(2.33)	44(46)	80(80)	0.5(0.6)	4.2(3.7)	_
Cyanoethyl Celluloses											
S58	-8	480(520)	15(22)	35(52)	31(43)	2.28(2.29)	41(44)	80(83)	1.3(13)	3.5(4.2)	0.15
S66	-25	360(480)	13(19)	29(45)	24(40)	2.19(2.24)	55(46)	90(88)	30(11)	2.8(3.5)	4.96
S67	NS	480(480)	18(19)	39(45)	42(40)	2.26(2.24)	42(46)	84(88)	6(11)	3.0(3.5)	0.10
S69	NS	480(480)	17(19)	31(45)	36(40)	2.14(2.24)	35(46)	81(88)	8(11)	3.3(3.5)	1.39
S71	+10	530(480)	17(19)	41(45)	35(40)	2.33(2.24)	41(46)	82(88)	3(11)	2.7(3.5)	0.08
S160	NS	330(330)	20(21)	59(61)	37(45)	2.45(2.77)	42(46)	80(81)	6(9)	4.1(4.2)	0.11
S182	NS	330(330)	16(17)	62(55)	55(44)	2.64(2.32)	40(-)	79(-)	18(6)	4.8(4.2)	0.05
S184	NS	345(330)	16(17)	52(55)	42(44)	2.46(2.32)	43(-)	81(-)	22(6)	4.8(4.2)	0.40
S250	-15	345(410)	19(18)	29(42)	28(33)	2.23(2.27)	42(43)	76(79)	1.3(2.7)	3.1(3.6)	0.78
Amidoethyl Celluloses											
S121	+12	430(385)	23(21)	57(59)	44(44)	2.29(2.31)	41(44)	79(80)	9(15)	4.7(4.2)	0.25
S122	NS	370(385)	22(21)	57(59)	48(44)	2.16(2.31)	39(44)	82(80)	9(15)	4.0(4.2)	0.09
S141	-14	330(385)	17(21)	55(59)	54(44)	3.13(2.31)	33(44)	74(80)	1.3(15)	4.6(4.2)	0.19
S162	+12	370(330)	21(21)	50(61)	41(45)	2.41(2.77)	39(46)	77(81)	8.5(9.4)	4.1(4.2)	0.26
S203	+9	360(330)	18(18)	50(57)	38(44)	2.27(2.31)	37(-)	76(-)	2.8(6)	4.4(4.5)	0.34
S233	NS	390(390)	19(16)	39(54)	43(49)	2.11(2.36)	33(46)	73(81)	2.1(2.5)	3.4(3.1)	0.57
S246	-10	370(410)	19(18)	37(42)	19(33)	2.37(2.27)	43(43)	81(79)	1.8(2.7)	2.9(3.6)	0.23
S247	+10	450(410)	16(18)	36(42)	22(33)	2.27(2.27)	39(43)	79(79)	2.0(2.7)	3.7(3.6)	0.46
S342	-10	380(420)	17(21)	44(64)	34(48)	2.51(2.33)	44(46)	81(80)	3.4(0.6)	4.4(3.7)	0.3
S343	-39	255(420)	15(21)	47(64)	37(48)	2.61(2.33)	49(46)	84(80)	3.3(0.6)	3.8(3.7)	0.15

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution
<i>N,N</i> -Methylenebisacrylamide-Cellulose Derivatives											
S148	-25	290(385)	17(21)	45(59)	40(44)	2.54(2.31)	43(44)	80(80)	12(15)	3.3(4.2)	0.15% N
S170	NS	335(330)	17(18)	52(59)	44(44)	2.52(2.30)	43(-)	82(-)	20(6)	4.1(4.8)	0.06% N
S207	NS	335(345)	16(19)	42(53)	43(36)	2.32(2.31)	43(50)	79(81)	2.4(2.5)	3.2(4.4)	0.06% N
S208	+10	380(345)	16(19)	50(53)	41(36)	2.33(2.31)	42(50)	79(81)	3.2(2.5)	3.9(4.4)	0.05% N
S224	NS	370(390)	17(16)	49(54)	46(49)	2.51(2.36)	44(46)	80(81)	2.9(2.5)	3.7(3.1)	0.09% N
S225	-8	360(390)	16(16)	49(54)	46(49)	2.56(2.36)	44(46)	78(81)	2.4(2.5)	3.4(3.1)	0.12% N
S227	-8	360(390)	17(16)	46(54)	39(49)	2.46(2.36)	44(46)	79(81)	3.2(2.5)	4.1(3.1)	0.10% N
S282	-11	330(370)	17(20)	52(64)	44(44)	2.47(2.21)	39(40)	77(78)	2(1.5)	3.7(4.9)	0.61% N
S295	-59	150(370)	7(20)	29(64)	14(44)	4.09(2.21)	42(40)	76(78)	9(1.5)	4.6(4.9)	4.14% N
S371	-50	190(380)	6(18)	33(61)	33(41)	2.56(2.34)	42(47)	79(82)	-(0)	2.4(4.1)	1.45% N
<i>N</i> -(3-Aminopropyl)methacrylamide-Cellulose Derivative											
S301	+18	350(295)	19(19)	43(57)	48(47)	2.34(2.29)	42(43)	82(81)	2.1(1.6)	3.9(4.2)	0.27% N
Methacrylamide-Cellulose Derivatives											
S304	+15	340(295)	18(19)	53(57)	41(47)	2.4(2.29)	38(43)	76(81)	3.3(2)	4.1(4.2)	0.12% N
S320	NS	310(295)	17(19)	55(57)	44(47)	2.39(2.29)	41(43)	79(81)	1.4(1.6)	4.3(4.2)	0.08% N
S375	-13	360(415)	16(20)	49(64)	40(43)	2.33(2.33)	39(47)	78(81)	-(0)	4.1(4.6)	0.09% N
Methacrylonitrile-Cellulose Derivative											
S332	NS	400(420)	19(21)	47(64)	44(48)	2.41(2.33)	39(46)	78(80)	0.3(0.6)	4.6(3.7)	0.17% N
Treatments with Acrolein											
S406	+11	400(360)	13(16)	34(47)	40(44)	-(2.25)	42(39)	84(79)	1.5(-)	2.2(2.6)	_
S409	NS	350(360)	14(16)	39(47)	33(44)	2.27(2.25)	39(39)	77(79)	1.5(-)	2.1(2.6)	_

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution (meq/100g)
Maleic Acid-Cellulose Derivatives											
S244	-10	370(410)	17(18)	51(42)	27(33)	2.34(2.27)	44(43)	83(79)	2.9(2.7)	3.6(3.6)	5.53
S294	NS	390(370)	21(20)	59(64)	50(44)	2.35(2.21)	44(40)	80(78)	2.2(1.5)	4.4(4.9)	5.06
S339	NS	410(420)	20(21)	56(64)	43(48)	2.36(2.33)	46(46)	81(80)	1(0.6)	4.9(3.7)	11.9
S349	-27	305(420)	17(21)	54(64)	53(48)	2.36(2.33)	46(46)	82(80)	0.3(0.6)	3.1(3.7)	3.61
S350	-21	330(420)	18(21)	54(64)	46(48)	2.44(2.33)	45(46)	80(80)	16(0.6)	4.5(3.7)	_
S351	-18	345(420)	18(21)	56(64)	44(48)	2.33(2.33)	45(46)	81(80)	0.3(0.6)	3.8(3.7)	_
S372	+12	425(380)	19(18)	58(61)	34(41)	2.35(2.34)	46(47)	80(82)	0(0)	4.4(4.1)	_
S373	NS	395(380)	19(18)	54(61)	47(41)	2.37(2.34)	42(47)	79(82)	0(0)	4.3(4.1)	_
Itaconic Acid-Cellulose Derivatives											
S256	NS	390(410)	16(18)	49(42)	31(32)	2.38(2.27)	44(43)	80(79)	2.6(2.7)	3.6(3.6)	_
S326	+16	340(295)	18(19)	62(47)	57(47)	2.29(2.36)	47(43)	84(81)	1(1.6)	4(4.2)	5.13
S368	NS	370(380)	16(18)	51(61)	34(41)	2.44(2.34)	43(47)	79(82)	-(0)	3.5(4.1)	9.33
S369	NS	365(380)	18(18)	56(61)	40(41)	2.31(2.34)	46(47)	80(82)	-(0)	3.6(4.1)	13.37
Fumaric Acid-Cellulose Derivative											
S362	+19	450(380)	22(18)	56(61)	48(41)	2.23(2.34)	47(47)	83(82)	0.6(0)	4.1(4.1)	_
Acrylic Acid Treatment											
S360	-6	355(380)	19(18)	55(61)	35(41)	2.43(2.34)	44(47)	77(82)	-(0)	4.3(4.1)	_
Methacrylic Acid Treatment											
S361	+19	450(380)	17(18)	57(61)	38(41)	2.33(2.34)	45(47)	81(82)	-(0)	3.8(4.1)	_
Citraconic Acid Treatment											
S305	-7	275(295)	17(19)	59(57)	39(47)	2.41(2.29)	41(43)	76(81)	1(2)	4.3(4.2)	_
Crotonic Acid Treatments											
S364	+7	405(380)	19(18)	53(61)	44(41)	2.3(2.34)	46(47)	81(82)	0.1(0)	4.1(4.1)	_
S398	NS	320(330)	17(17)	56(55)	39(42)	2.32(2.33)	40(42)	79(79)	3.5(1.2)	4.0(3.7)	_
<i>trans</i> -Cinnamic Acid Treatment											
S366	+7	405(380)	19(18)	53(61)	46(41)	2.36(2.34)	46(47)	82(82)	1.0(0)	4.1(4.1)	_

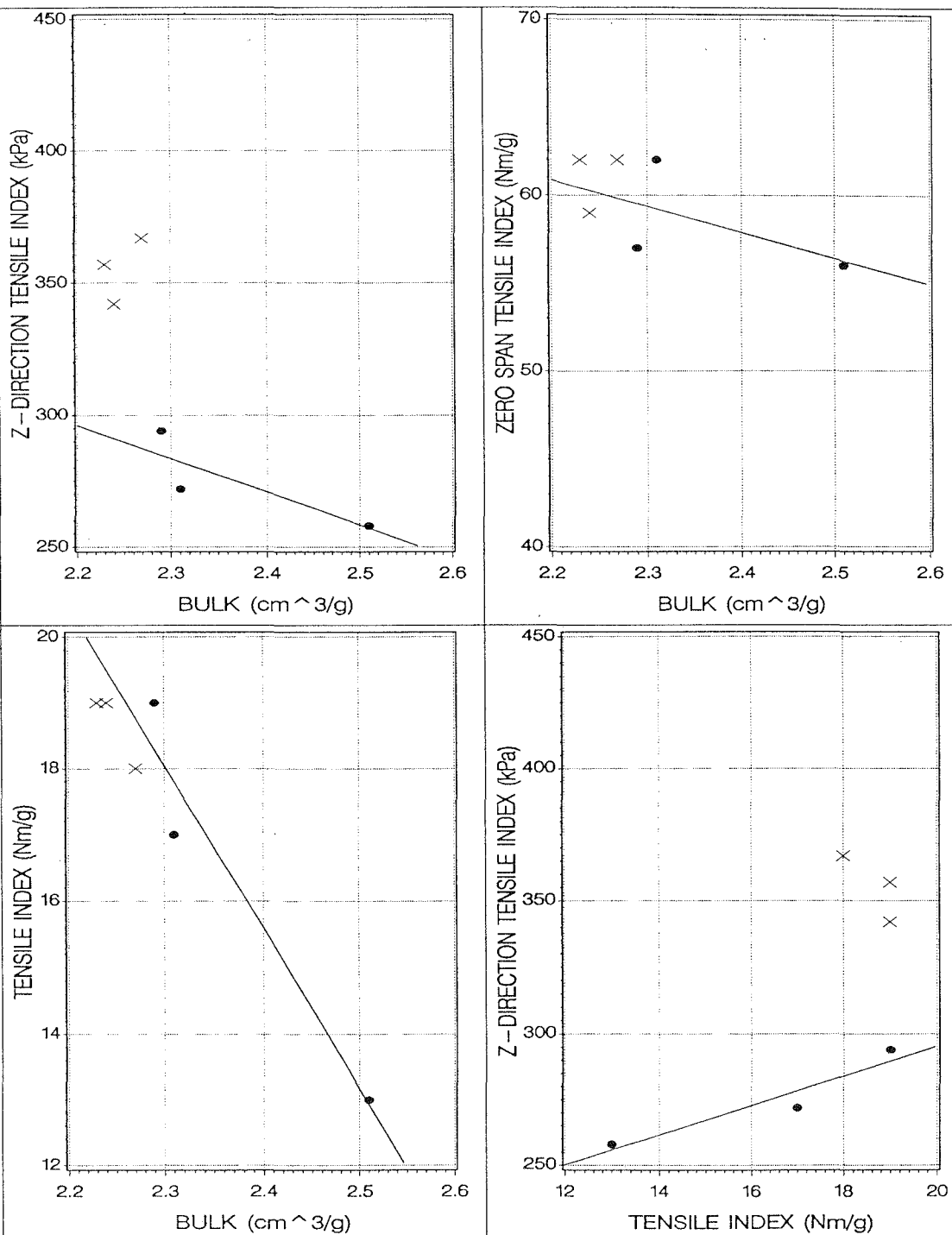
Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (cm <sup>3</sup> /g)	Bulk Scatt. Coeff.	Opacity	Beating (min)	Stretch (%)	Substitution
Carboxymethyl Cationized Cellulose									8.72 **
S241	-21	330(420)	16(16)	47(54)	42(36)	2.25(2.33)	38(45)	79(81)	2.2(2.6) 3.6(3.1) 0.12% N
Cationized Amidoethyl Cellulose									
S405	+15	380(330)	19(17)	47(55)	32(42)	2.34(2.33)	34(42)	75(79)	1.3(1.2) 3.9(3.7) 0.31% N
<i>N,N</i> -Methylenebisacrylamide on Hydroxyethyl Cellulose									0.31% N
S338	NS	410(420)	12(21)	37(64)	17(48)	2.6(2.33)	43(46)	74(80)	9(0.6) 4.3(3.7) 1.49%*
Maleic Acid on Hydroxyethyl Cellulose									4.6 **
S337	-21	330(420)	13(21)	44(64)	33(48)	1.59(2.33)	44(46)	79(80)	6.5(0.6) 4.0(3.7) 1.49%*
Cationized Maleic Acid-Cellulose Derivative									0.21% N
S345	-31	290(420)	16(21)	42(64)	30(48)	2.57(2.33)	36(46)	76(80)	-(0.6) 3.5(3.7) 4.13 **
Maleic Acid-Treated Cationized Cellulose Derivative									3.95 **
S347	-7	390(420)	9(21)	46(64)	41(48)	2.36(2.33)	36(46)	76(80)	-(0.6) 3.5(3.7) 0.18% N
Maleic Acid-Cationic Cellulose Blend									
S379/S382									10.1 **
20:80	+11	460(415)	17(20)	47(64)	41(43)	2.22(2.33)	37(47)	79(80)	-(0) 3.7(4.6) 0.19% N
Fumaric Acid-Cationic Cellulose Blend									
S404/S414									12.8 **
20:80	+10	395(360)	19(16)	43(47)	46(44)	2.34(2.25)	37(39)	78(79)	1.5(-) 3.5(2.6) 0.16% N
60:40	+19	430(360)	19(16)	47(47)	47(44)	2.17(2.25)	40(39)	82(79)	4(-) 3.0(2.6)
80:20	+18	425(360)	19(16)	48(47)	43(44)	2.24(2.25)	40(39)	82(79)	5.4(-) 4.3(2.6)

\* Hydroxyethyl groups.

\*\* meq/100g.

# APPENDIX 3: PULP EVALUATION GRAPHS (FIGURES 1-8, SECTION 4.4)

Figure 1: Key Papermaking Properties of Itaconic Acid – Cellulose Derivative (S327)

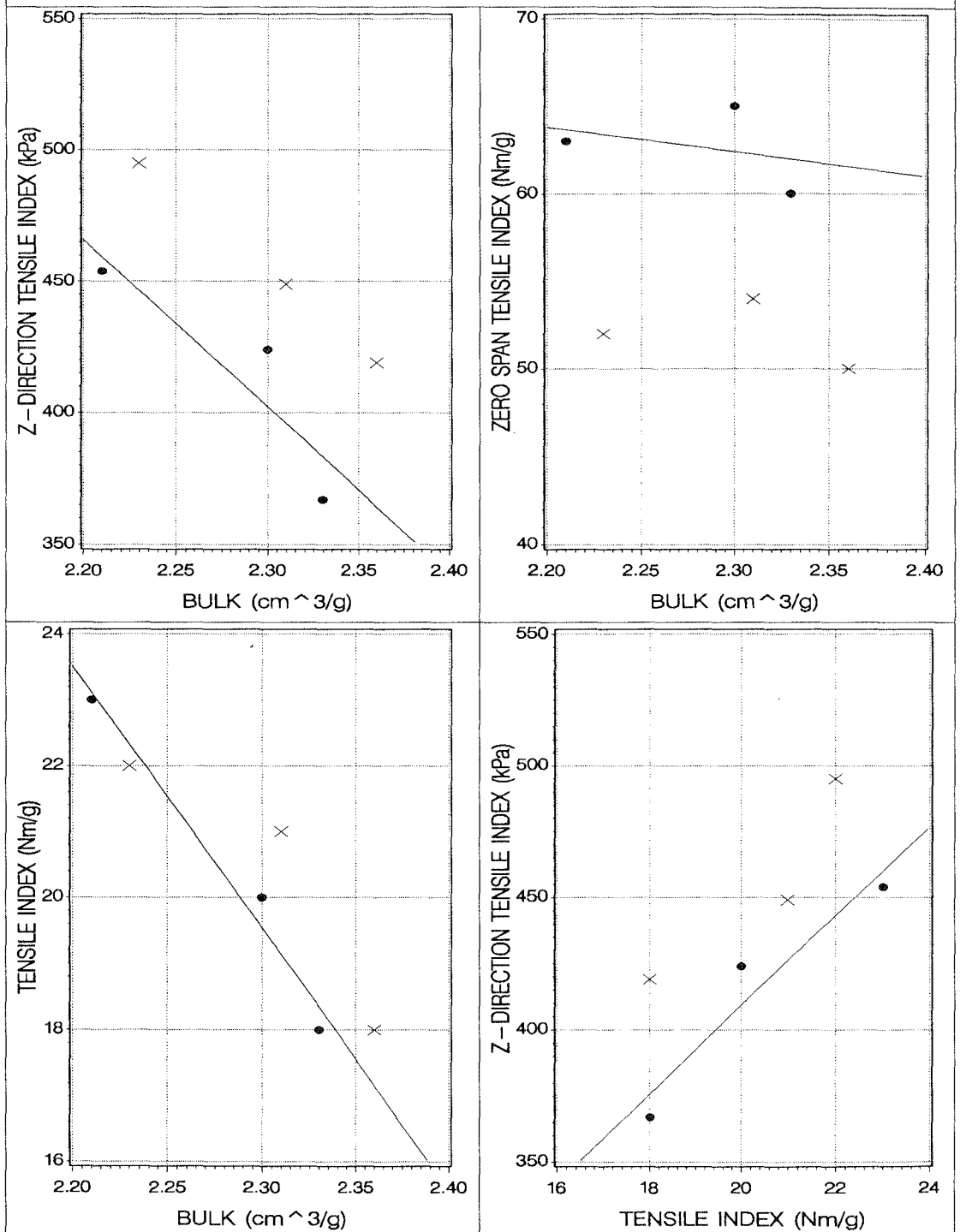


Sample:

X X Itaconic Acid – Cellulose Derivative

• • Unmodified Cotton Linters

Figure 2: Key Papermaking Properties of Fumaric Acid – Cellulose Derivative (S363)

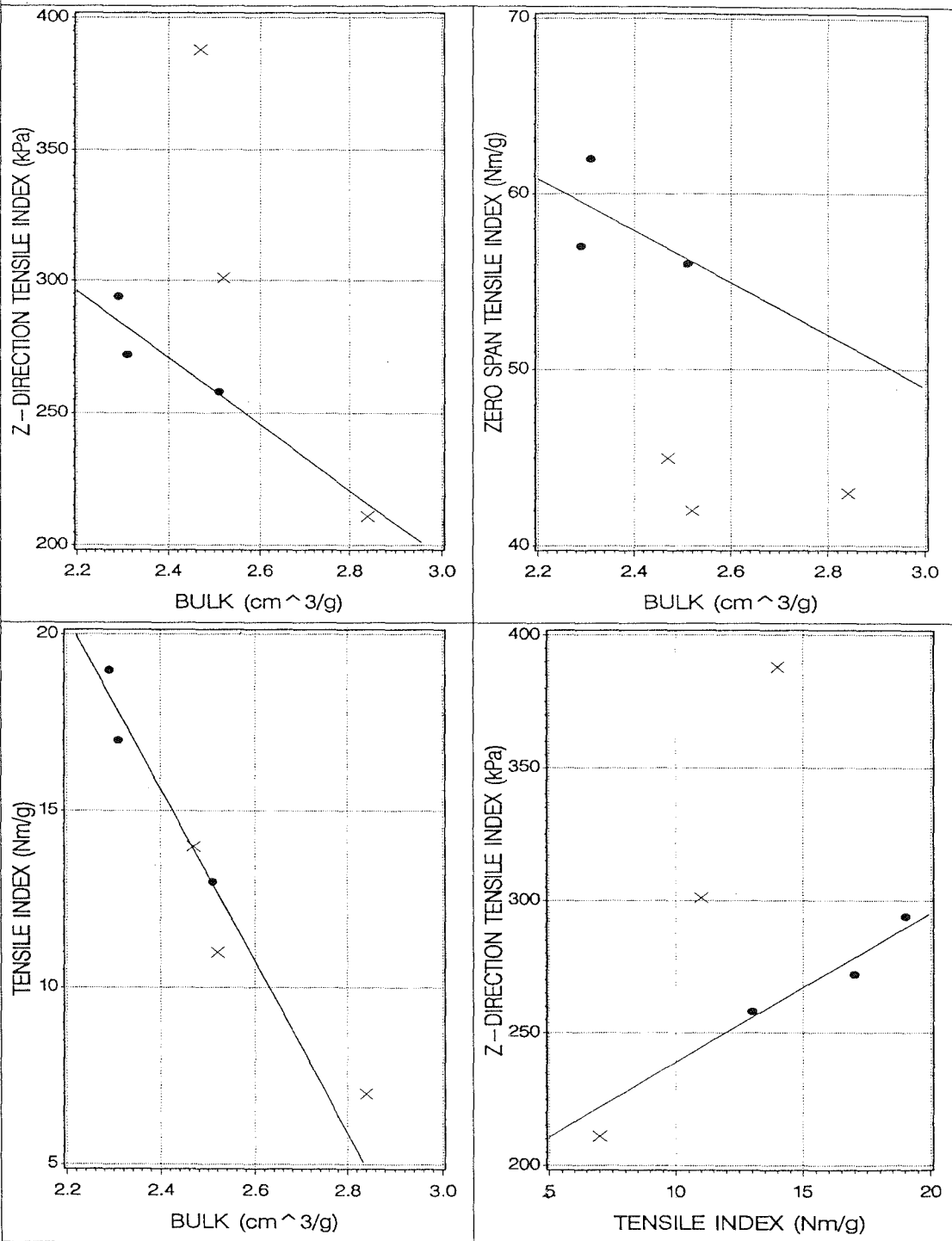


Sample:

X X Fumaric Acid – Cellulose Derivative

• • Unmodified Cotton Linters

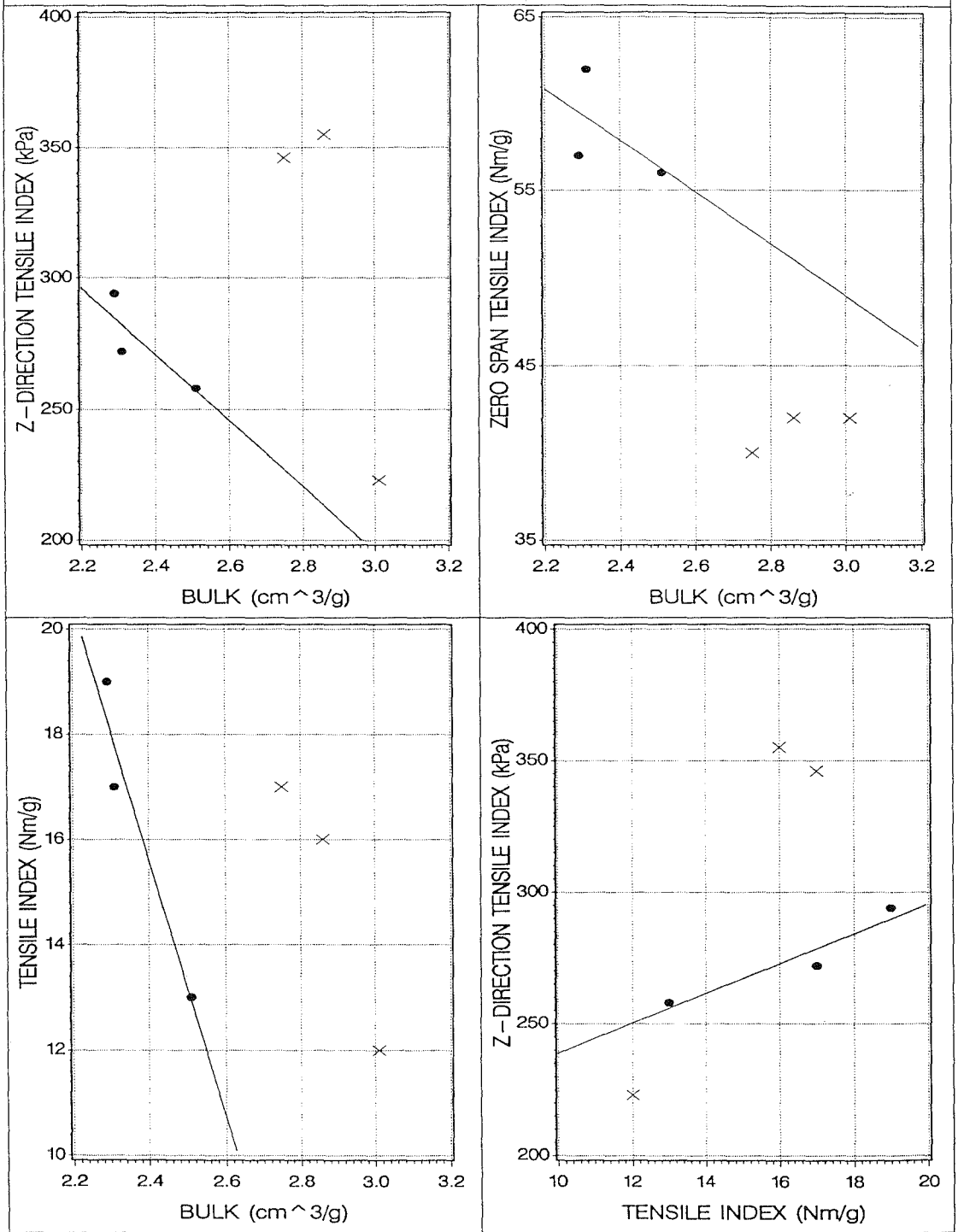
Figure 3: Key Papermaking Properties of Hydroxyethyl Cellulose (S318)



Sample:  
x x Hydroxyethyl Cellulose  
• • Unmodified Cotton Linters



Figure 4: Key Papermaking Properties of 2,3 – Dialdehydo Cellulose (S325)

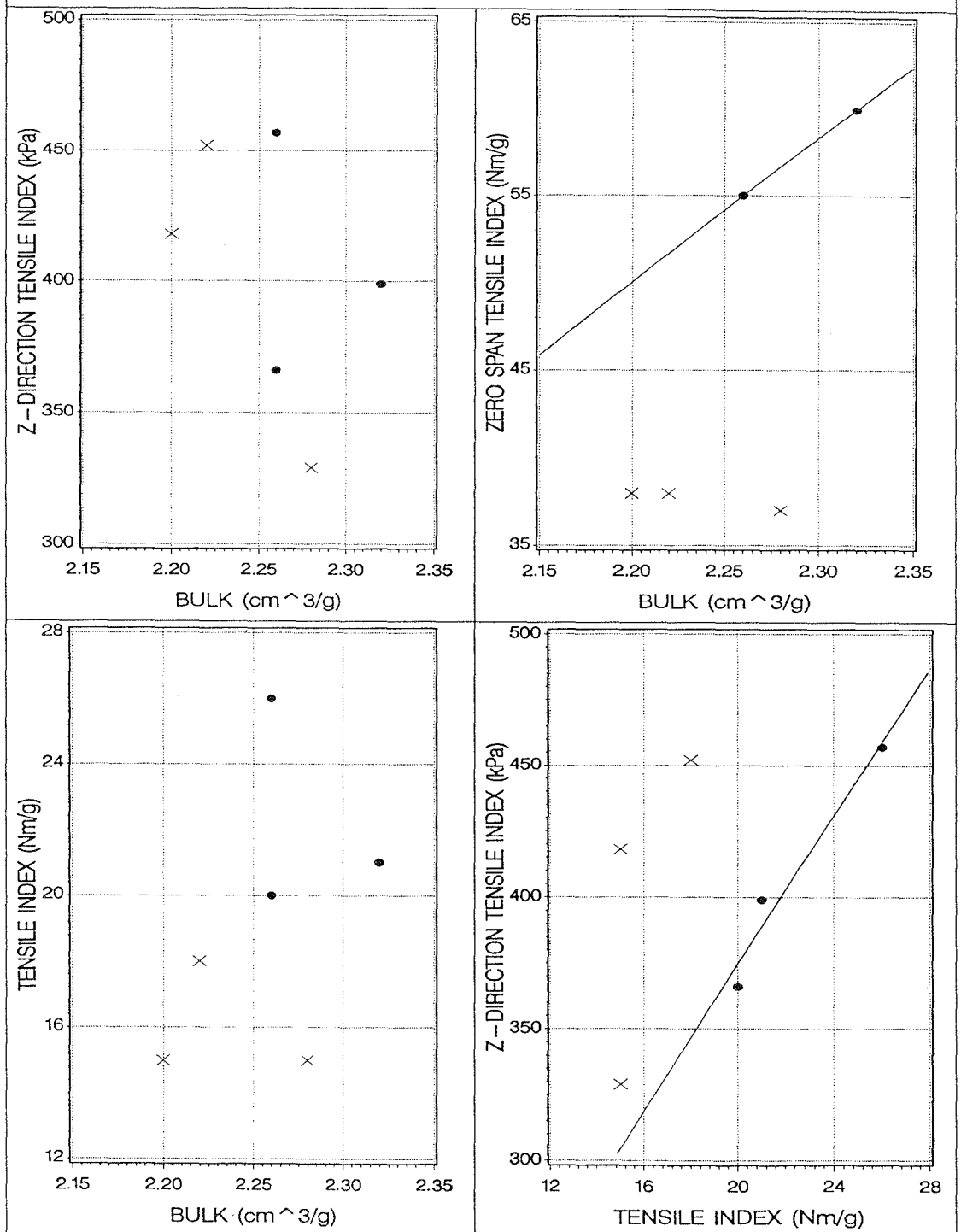


Sample:

× × 2,3 – Dialdehydo Cellulose

• • Unmodified Cotton Linters

Figure 5: Key Papermaking Properties of  
2,3 – Cellulose Oxime (S210)

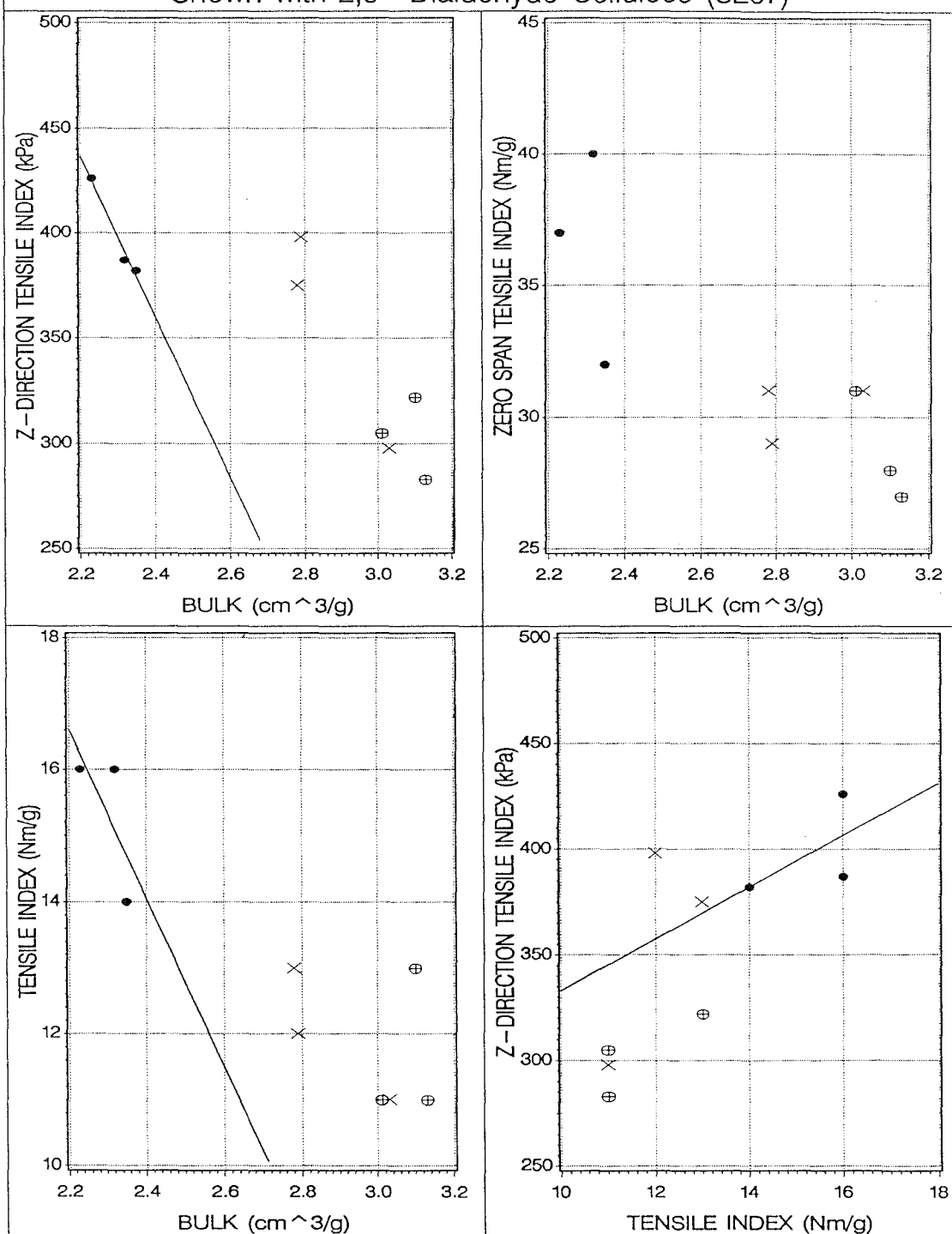


Sample:

× × 2,3 – Cellulose Oxime

• • Unmodified Cotton Linters

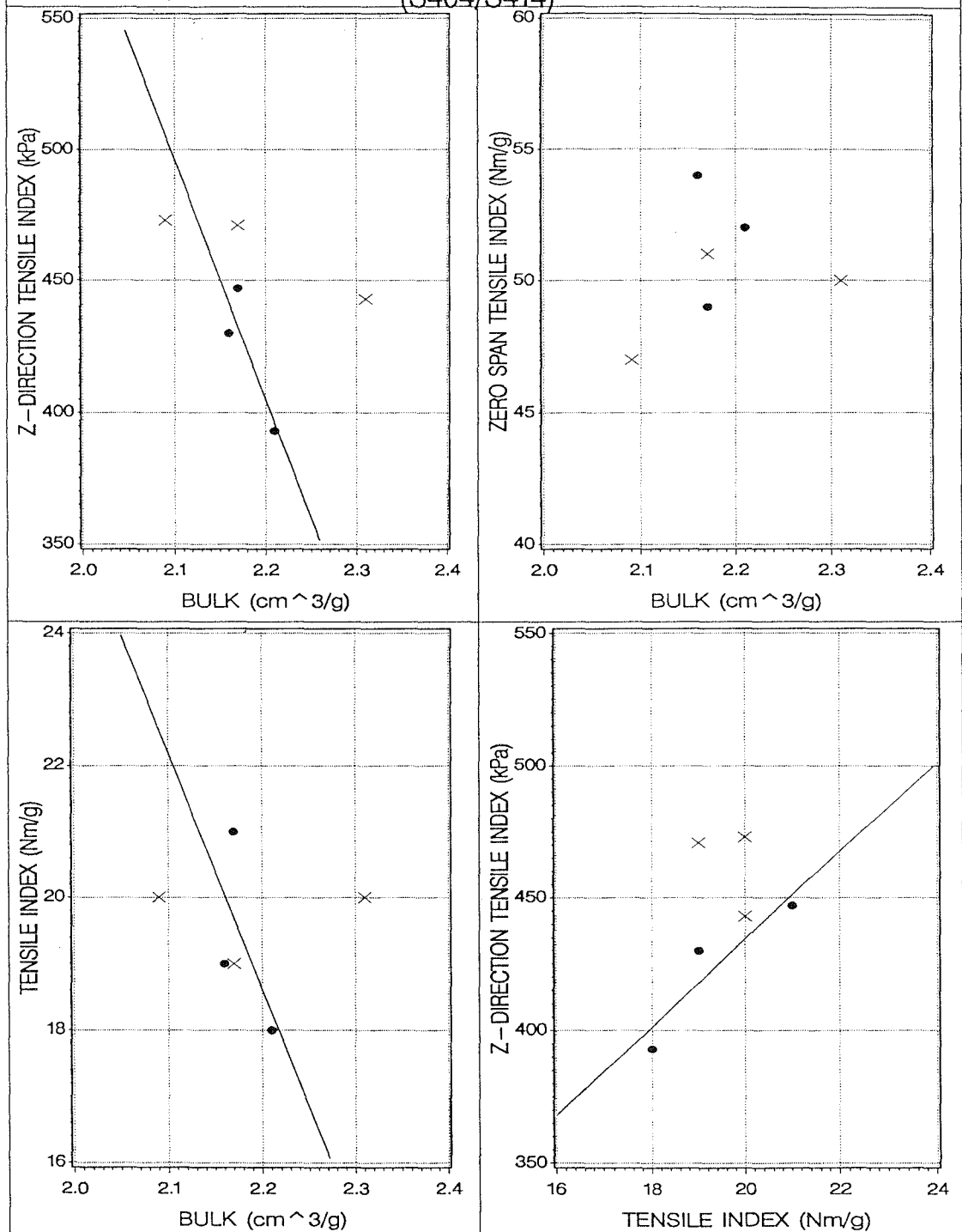
Figure 6: Key Papermaking Properties of  
2,3 – Cellulose Thiosemicarbazone (S272)  
Shown with 2,3 – Dialdehyde Cellulose (S267)



Sample:

- X X 2,3 – Cellulose Thiosemicarbazone
- ⊕ ⊕ 2,3 – Dialdehyde Cellulose
- • Unmodified Cotton Linters

Figure 7: Key Papermaking Properties of  
Fumaric Acid – Cellulose and Cationic Cellulose Blend  
(S404/S414)

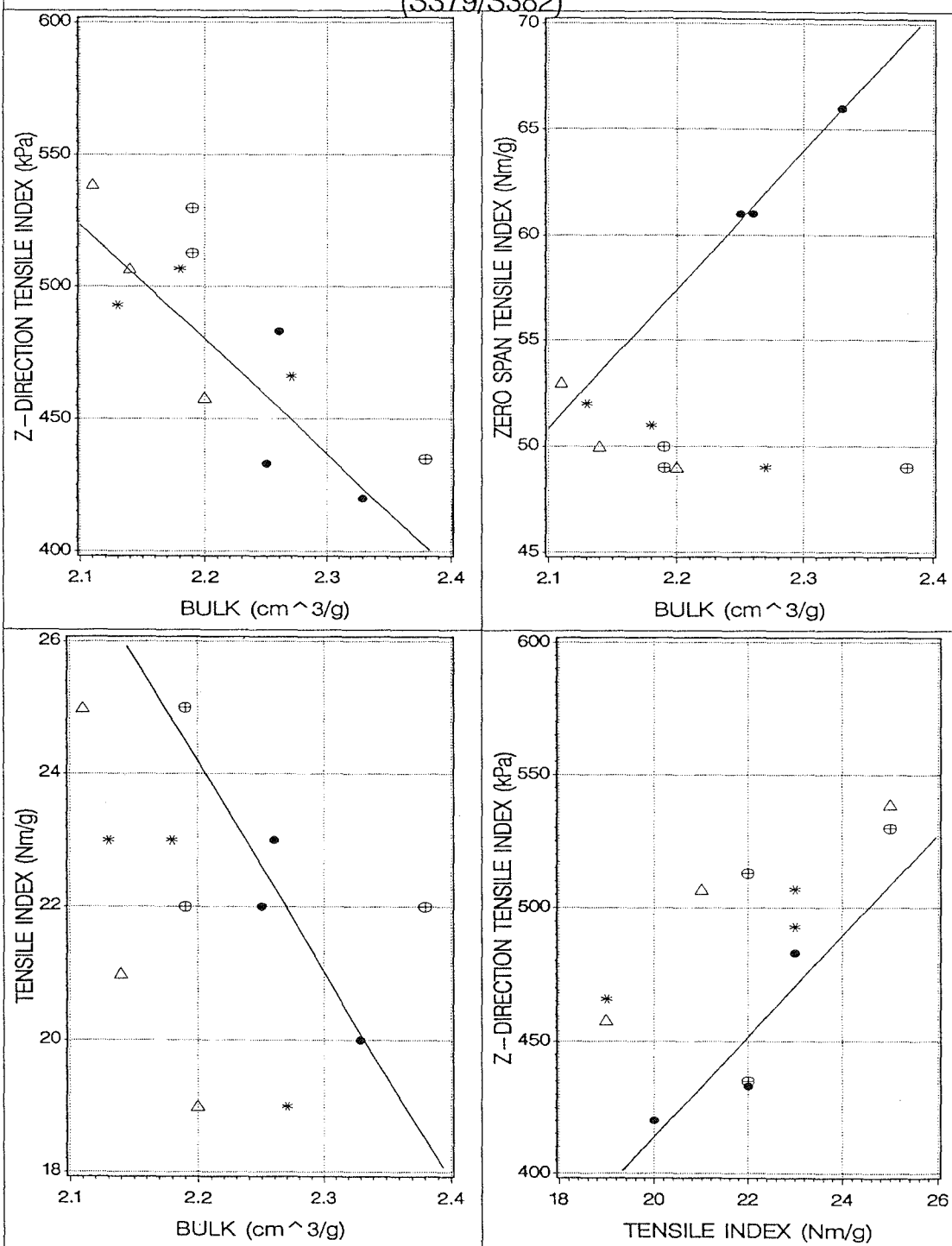


Sample:

X X 40:60 Fumaric Acid – Cellulose/Cationic Cellulose Blend

• • Unmodified Cotton Linters

Figure 8: Key Papermaking Properties of  
Maleic Acid – Cellulose and Cationic Cellulose Blends  
(S379/S382)



Sample:

⊕ ⊕ 40:60 Mal – Cat

△ △ 60:40

\* \* 80:20

• • Unmodified Cotton Linters

#### APPENDIX 4: PULP EVALUATION DATA AT CSF 250 FOR PFI MILL EVALUATIONS (SECTION 4.5)

Reaction Number	% Change	Z-Direct. Tensile Index (kPa)	Tensile Index (Nm/g)	Zero Span Tensile Index (Nm/g)	Bend. Resist. (mN)	Bulk (cm <sup>3</sup> /g)	Scatt. Coeff.	Opacity	Burst Index (kPam <sup>2</sup> /g)	Tear Index (mNm <sup>2</sup> /g)	Beating (rev/g)	Stretch (%)	Substitution
2,3-Dialdehyde Cellulose													
S297	+18	455(385)	21(26)	43(51)	46(46)	2.31(2.04)	41(40)	78(76)	1.2(1.6)	4.1(7.7)	60(70)	2.9(4.0)	-
2,3-Cellulose Oxime													
S292	+9	420(385)	18(26)	38(51)	40(46)	2.32(2.04)	40(40)	77(76)	1.1(1.6)	3.8(7.7)	60(70)	3.1(4.0)	0.12% N
N,N-Methylenebisacrylamide-Cellulose Derivative													
S403	NS	390(375)	19(19)	52(58)	44(42)	2.15(2.23)	37(40)	76(77)	1.0(1.1)	4.5(4.9)	74(29)	2.5(3.2)	0.12% N
Maleic Acid-Cellulose Derivatives													
S273	-7	410(440)	16(21)	41(52)	33(39)	2.21(2.17)	41(41)	78(78)	0.7(1.0)	3.7(5.4)	30(26)	2.4(2.6)	10.2*
S274	NS	440(440)	18(21)	54(52)	42(39)	2.14(2.17)	40(41)	78(78)	1.1(1.0)	5.4(5.4)	30(26)	2.9(2.6)	12.9*
S293	+7	410(385)	24(26)	55(51)	43(46)	2.07(2.04)	39(40)	77(76)	1.4(1.6)	7.1(7.7)	40(70)	3.9(4.0)	8.97*
Itaconic Acid-Cellulose Derivative													
S367	+9	435(400)	18(21)	53(59)	38(39)	2.33(2.32)	46(46)	79(80)	1.0(1.2)	6.3(7.1)	5(9)	4.3(4.3)	8.29*
Carboxymethyl-Cationic Cellulose Blend (S380, S381/S376, S377)													
20:80	+8	430(400)	21(21)	47(59)	39(39)	2.33(2.32)	38(46)	78(80)	1.9(1.2)	7.2(7.1)	-(9)	4.4(4.3)	10.1, 11.8*
40:60	+9	435(400)	21(21)	52(59)	39(39)	2.36(2.32)	38(46)	87(80)	1.3(1.2)	6.8(7.1)	1(9)	4.2(4.3)	0.20, 0.19% N
Maleic Acid-Cationic Cellulose Blends (S358, S359/S356, S357)													
20:80	NS	455(450)	19(21)	48(62)	38(41)	2.36(2.23)	41(44)	79(78)	1.1(1.1)	7.6(7.1)	-(7)	4.1(4.1)	12.9, 12.2*
40:60	+19	535(450)	22(21)	49(62)	44(41)	2.26(2.23)	39(44)	77(78)	1.2(1.1)	6.9(7.1)	0(7)	3.9(4.1)	0.24, 0.17% N
(S393, S394/S399, S400)													
20:80	+9	410(375)	16(19)	43(58)	34(42)	2.33(2.23)	35(40)	75(77)	0.9(1.1)	4.7(4.9)	4(29)	2.9(3.2)	12.2, 14.9*
40:60	+13	425(375)	17(19)	45(58)	38(42)	2.28(2.23)	36(40)	76(77)	0.9(1.1)	5.0(4.9)	6(29)	3.4(3.2)	0.22, 0.23% N
Itaconic Acid-Cationic Cellulose Blend (S401, S402/S407, S408)													
20:80	NS	380(375)	19(19)	56(58)	29(42)	2.4(2.23)	34(40)	75(77)	1.1(1.1)	6.3(4.9)	13(29)	3.7(3.2)	11.6, 12.0* 0.19, 0.22% N

\* meq/100g.

## APPENDIX 5: PUBLICATIONS

## Evaluation of Chemically Modified Cellulose from Cotton Linters

LOUISE A. TITCOMBE,\* JOHN B. BREMNER,\*\*  
M. IKO BURGAR,\*\*\* MICHAEL J. RIDD,†  
JIM FRENCH†† AND KENNETH N. MADDERN†††

\* Teaching Company Associate, University of Tasmania/APPM Group Research Unit PO Box 252C, Hobart, Tasmania, 7001.  
Full Member Appita.

\*\* Reader, Chemistry Department, University of Tasmania.  
BHP Research Laboratories, Clayton, Victoria, 3168.

† Professional Officer, Central Science Laboratory, University of Tasmania.

†† Supervisor Laboratory Services, APPM Group Research Unit, PO Box 201, Burnie Tasmania, 7320. Full Member Appita.

††† Research Manager, APPM Group Research Unit, Burnie, Tasmania. Full Member Appita.

### SUMMARY

The use of Australian cotton linters pulp in blends with imported pulp and recycled fibre at the Shoalhaven Mill, Associated Pulp and Paper Mills Limited (APPM) is limited by their poor bonding properties. This project aims to chemically modify cellulose so that a greater quantity of cotton linters may be incorporated into the paper without adversely affecting the sheet strength.

Reliable methods for evaluating chemically modified cellulose from cotton linters are essential. The development of such methods is complicated by the morphological complexity, crystallinity and insolubility of cellulose. The techniques developed to evaluate chemical modifications include small scale pulp evaluations, nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR), with support from elemental microanalyses.

A small scale method of pulp evaluation was desirable because of the cost of chemicals per modification and the physical constraints on large scale reactions. The method developed at APPM allows key strength and optical properties to be measured.

Initial pulp evaluations of several derivatives of cellulose using cooked, bleached cotton linters from Shoalhaven are described. Amidoethyl cellulose showed improved strength properties, but these were offset by the weakening effects of alkaline pretreatment.

The determination of degree of substitution (DS) is crucial for the evaluation of cellulose derivatives and the reproducibility of the syntheses of these derivatives, as properties vary considerably with changing DS; the position of substitution is also important. FTIR and NMR spectroscopic studies directed towards determining the DS and substituent positions have been undertaken on some derivatives of the Australian linters. Further studies are continuing.



L. A. Titcombe

J. B. Bremner

M. J. Ridd

J. French

K. N. Maddern

The use of cotton linters pulp in blends with imported pulp and recycled fibre at the Shoalhaven Mill, Associated Pulp and Paper Mills Limited (APPM) is limited by their poor bonding properties. Chemical modification of the linters is intended to overcome the inherent low tensile and bursting strength, and allow a greater quantity of linters to be incorporated into the paper. Strength increases may be obtained by chemical modifications which increase the conformability of the fibres, and/or intermolecular attractive forces.

It is essential that suitable methods of characterization be developed to evaluate the chemically modified celluloses from cotton linters. Both the degree of substitution (DS) and position of substitution need to be ascertained. Furthermore, characterization is complicated by the morphology, crystallinity and insolubility of cellulose. For the purposes of this project, nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy, small scale pulp evaluations and microanalytical determinations, have been investigated.

### SYNTHETIC METHODS FOR CHEMICALLY MODIFIED CELLULOSES

The cellulose used in this study was in the form of cooked, bleached linters from the final stage of the Shoalhaven cotton linters processing plant.

Cellulose derivatives have been largely prepared using reported methods. In particular, syntheses successfully completed include cyanoethyl cellulose(1,2), carboxymethyl cellulose(3) amidoethyl cellulose(2) and cellulose mesylate(1).

Reaction schemes are presented in Figure 1. While substitution mainly at the C<sub>6</sub> position would be expected normally, some substitution at C<sub>2</sub> and C<sub>3</sub> may also occur, and in the case of carboxymethylation, substitution at the C<sub>2</sub> hydroxyl is reported to predominate(4).

In combination with hydroxyethyl cellulose, the above derivatives will provide a database of known modifications used not only to develop methods of characterization, but also to provide a baseline for future novel modifications. According to the literature, the above mentioned derivatives pro-

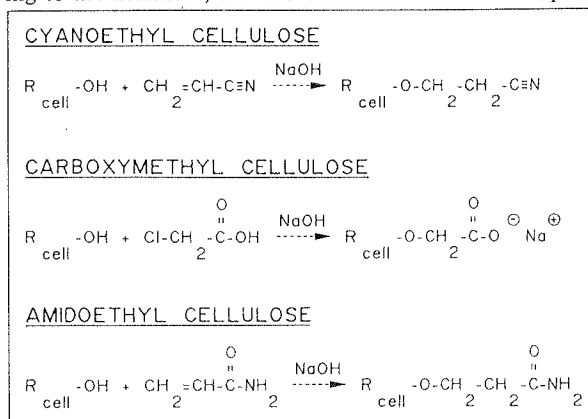


Fig. 1 — Reaction schemes for modified celluloses.

duce pulps with increased strength properties at low DS(2,3,5). In particular carboxymethylation and hydroxyethylation are generally reported to impart the greatest strength increases to cotton linters(6,7).

Problems have been encountered in replicating published syntheses. Cyanoethylation reactions were particularly prone to reproducibility problems. It is thought these problems may be attributed to differences in starting materials; celluloses with differing histories have differing reactivities. Similarly reagent accessibility and cellulose crystallinity greatly influence the outcome of a chemical modification.

The use of tetrabutylammonium fluoride (TBAF)(*cf* 19) to introduce a fluoro group has been extended to a reaction with cellulose mesylate. The derivative obtained, fluoro-deoxycellulose has been previously synthesized using potassium fluoride but has received little attention(8). The fluoro functionality should provide some interesting properties for investigation, and  $^{19}\text{F}$  has the added advantage of possessing similar NM properties to that of the  $^1\text{H}$  nucleus.

Cellulose mesylate was prepared using reported methods(1). The fluoro-deoxycellulose was then prepared by refluxing the mesylate precursor and TBAF in tetrahydrofuran and acetonitrile for up to 24 hours. The overall synthetic scheme is presented in Figure 2. The conditions used provide a good source of nucleophilic fluoride, which displaces the mesylate group.

#### MONITORING PROCEDURES

The methods developed to characterize chemically modified celluloses are required to provide information on both the degree and position of substitution. This is complicated by the structure of cotton linters, viz surface cellulose chains are more accessible than others, some regions of each polymer chain may be more exposed to reagents than others and finally, the hydroxyl groups of the anhydroglucopyranose unit have varying reactivities to different reagents. Evaluation of the pulp properties of chemically modified cotton linters is also crucial to the success of this project.

Of the available characterization methods, NMR and FTIR spectroscopy, pulp evaluation and microanalytical determinations have been used extensively in this work.

#### Nuclear magnetic resonance (NMR) spectroscopy

This technique has the potential to allow for qualitative and quantitative analysis. Studies may be performed in solution or in the solid state. However inherent problems exist with the analysis of cellulose in either solution or the solid state.

Solution NMR studies of cellulose derivatives are frequently reported in the literature and the corresponding DS usually cited. However closer inspection reveals that in most cases acid hydrolysed or partially degraded celluloses were used to effect dissolution and increase spectral resolution(*eg*, 9,10). A variety of solvent systems are available for NMR studies of celluloses, including *N*-methylmorpholine-*N*-oxide with dimethyl sulfoxide (MMNO-DMSO)(11). Initial trials using this solvent system were unsuccessful.

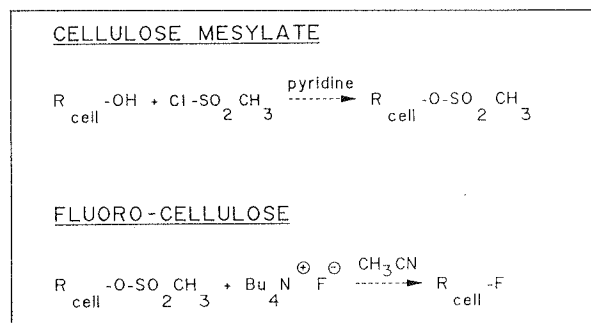


Fig. 2 — Synthesis of fluoro-deoxycellulose.

The dissolution of modified celluloses for solution state NMR analysis may lead to further chemical modification caused by interaction with the solvent system, resulting in decomposition or reversal of existing modifications, or cause the degradation of cellulose itself as is the case with MMNO-DMSO(12). The problem is compounded by the difficulty in ascertaining which, if any, of these side effects has occurred.

Analysis by solid state NMR offers the advantages of requiring minimal sample preparation and avoiding the dissolution problems of cellulose with suitable solvent systems. A significant disadvantage is the decreased resolution inherent with solid state NMR spectroscopy.

Characterization of cellulose derivatives was achieved using cross-polarization magic angle spinning (CP-MAS) solid state  $^{13}\text{C}$  NMR(13,14). The spectra thus obtained of cellulose and its derivatives (Fig. 3,4), agree with those reported in the literature(9,13,14). In particular carboxymethylation and cyanoethylation of cellulose were readily confirmed by  $^{13}\text{C}$  CP-MAS NMR spectroscopy by reference to

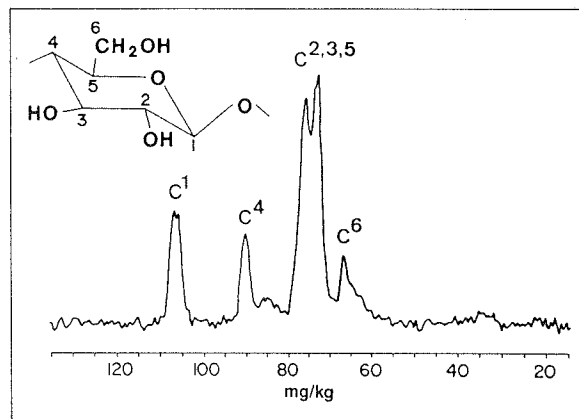


Fig. 3 —  $^{13}\text{C}$  CP-MAS NMR spectra of unmodified cotton linters.

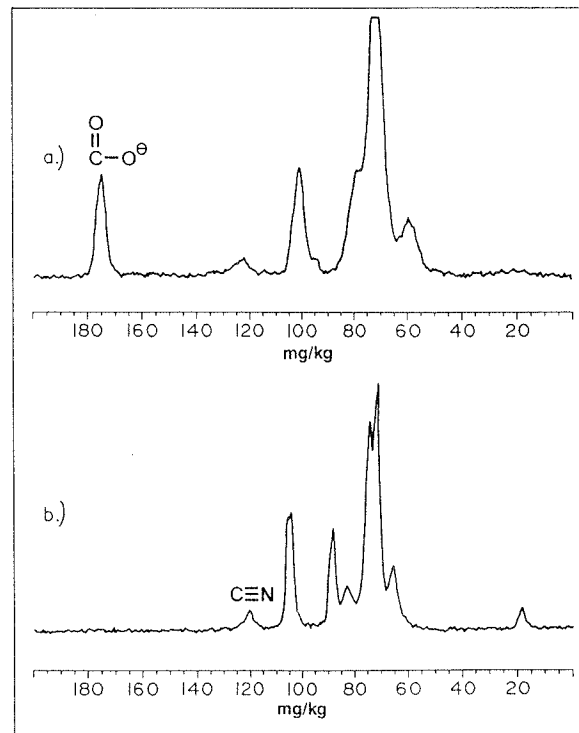


Fig. 4 —  $^{13}\text{C}$  CP-MAS NMR spectra of carboxymethyl cellulose and cyanoethyl cellulose.



the carboxyl ( $\delta 177$ /mg/kg) and nitrile ( $\delta 121$ /mg/kg) resonances, respectively.

In some instances, it is a relatively simple matter to ascertain whether a particular cellulose modification has been successful. This is illustrated by the synthesis of fluoro-deoxycellulose (Fig. 2). The  $^{13}\text{C}$  CP-MAS NMR spectrum of the precursor, cellulose mesylate clearly shows the presence of the methyl sulfonate group at  $\delta 39$ /mg/kg (Fig. 5a).

After treatment with the fluorinating agent the elemental microanalysis on the sample indicated a low sulfur value ( $\leq 2\%$ ) and the presence of fluorine ( $c/\%$ ). Most of the fluorine is likely to be attached at  $\text{C}_6$ , but this substituted carbon would be expected to resonate about 80 mg/kg and was masked by the other cellulose peaks in the  $^{13}\text{C}$  CP-MAS spectrum (Fig. 5b); evidence for the presence of aliphatic C-F groupings has been obtained from a  $^{19}\text{F}$  solution-phase NMR spectrum, however. Details of this work will be presented elsewhere.

Qualitative studies of modified celluloses using  $^{13}\text{C}$  CP-MAS NMR spectroscopy are relatively straightforward, provided substitution levels are not below c. 2%. However quantitative analysis to determine the DS is more complex. Despite the increased utilization of solid state NMR techniques with celluloses and advances in the interpretation of spectra of cotton and wood in recent years(15), DS determinations have not become commonplace because of the following complications: (i) low resolution spectra are typically obtained despite CP-MAS which yields finer spectral detail, (ii) integrations may not be relied upon if insufficient time is allowed for relaxation to occur between irradiations, (iii) measurement of spin-lattice relaxation parameters ( $T_1$ ) is crucial as  $T_1$ 's vary greatly for  $^{13}\text{C}$  nuclei and incorrect integrations will result if nuclei are not equally relaxed between pulses, (iv) the nuclear Overhauser enhancement effect is not the same for all nuclei, and (v) the intensity of signals in  $^{13}\text{C}$  is related to the degree of protonation; non-protonated carbon atoms have longer relaxation times and give small peaks (16). To the best of our knowledge, solid state DS analysis has been reported on one occasion only for ethyl hydrox-

yethyl cellulose (EHEC)(17), in an attempt to overcome the poor resolution caused by high viscosity EHEC solutions.

Investigations are currently being undertaken to overcome the inherent difficulties of  $^{13}\text{C}$  CP-MAS NMR spectroscopy to increase the reliability of this technique and allow DS determinations to be performed for a range of chemically modified celluloses.

#### Fourier transform infrared (FTIR) spectroscopy

Methods of FTIR analysis used to characterize cellulose in this work have included attenuated total reflectance, diffuse reflectance and incorporation into alkali-halide pressed discs. Attenuated total reflectance is only feasible on cotton linters made into handsheets and hence is not applicable to smaller scale modifications.

The most convenient method of characterization found thus far, uses alkali halide discs of the modified celluloses. Samples were initially ground in a Wiley mill. However, due to the small scale of most modifications, a domestic coffee grinder was considered more suitable and has proved satisfactory to date.

Qualitative FTIR studies of linters present no problem, provided substitution levels are 2% or greater. Typical examples of cellulose, cyanoethyl cellulose, azido-cellulose(18) and cellulose mesylate are presented in Figure 6. Unfortunately, the FTIR spectra of fluoro-deoxycellulose do not reveal the appropriate C-F absorbance, which is obscured beneath other cellulose peaks.

Quantitative FTIR analysis is desirable for DS determinations. Internal quantification is preferable to methods which require a calibration data set because of the wide range of cellulose derivatives to be synthesized. Currently a known mass of cyanoethyl cellulose is pressed into an alkali halide disc and quantification performed using the isolated nitrile peak in conjunction with Beer's Law. The relationship between absorbance/mg modified cellulose at  $2253\text{ cm}^{-1}$  ( $I_{2253}$ ) and microanalytically determined nitrogen content (%N) is  $I_{2253} = 0.0094 \times \%N$ . The results are shown in Figure 7.

#### Small scale pulp evaluations

Full pulp evaluation typically involves four different beating times and requires a total of 125 g oven dry (o.d.) pulp.

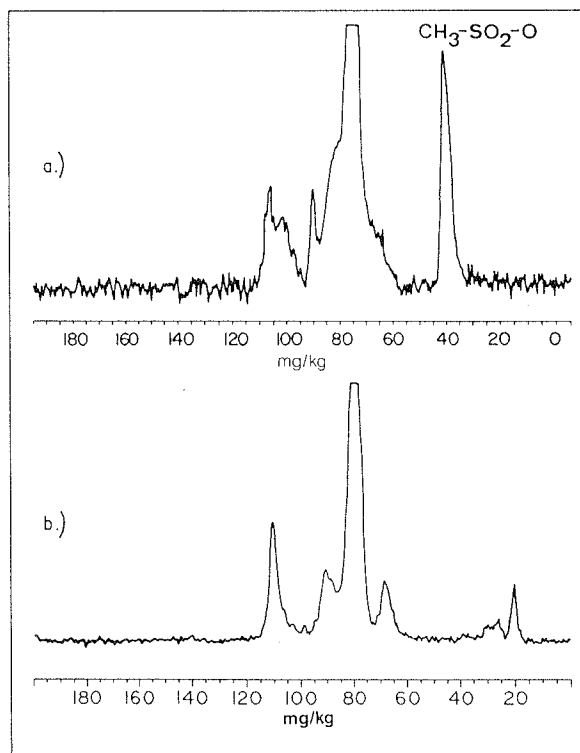


Fig. 5 —  $^{13}\text{C}$  CP-MAS NMR spectra of cellulose mesylate and fluoro-deoxycellulose.

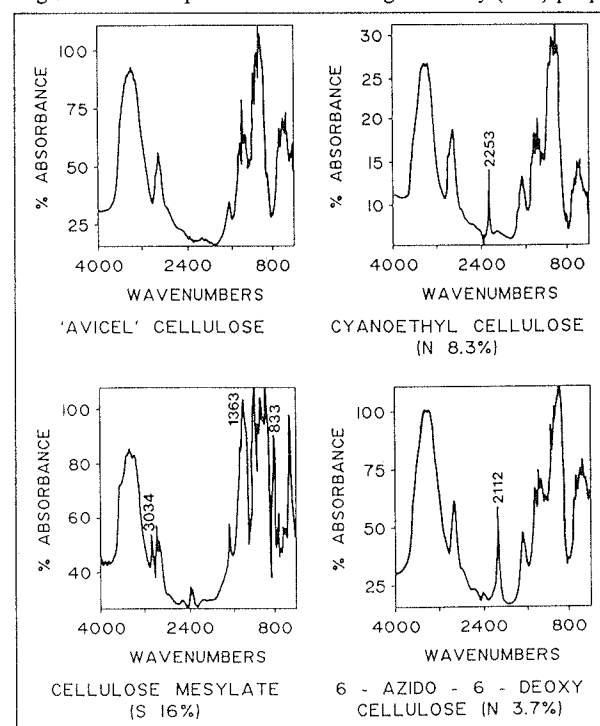


Fig. 6 Examples of FTIR spectra of cellulose and modified celluloses.

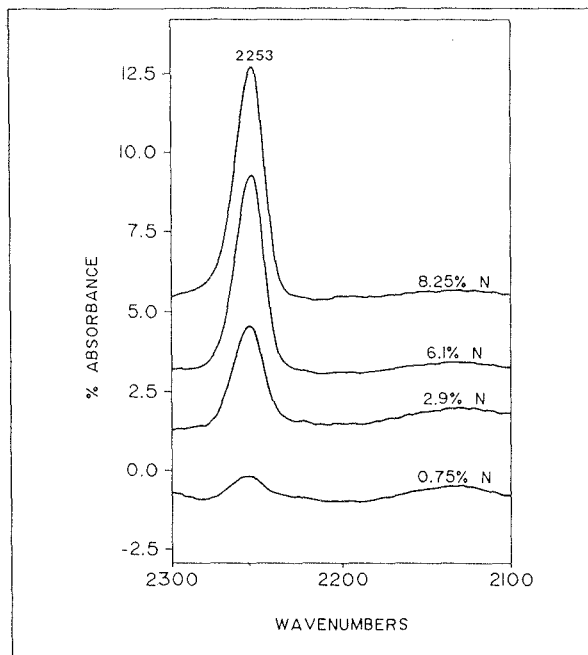


Fig. 7 Spectra of cyanoethyl cellulose as a function of nitrogen content in the region 2300 — 2100  $\text{cm}^{-1}$ .

A small scale method of pulp evaluation was desirable because of the cost of chemicals per modification and the physical constraints of large scale reactions (eg to modify 125 g o.d. pulp approximately 10 L of solvent would be required). A method has been developed at APPM to evaluate 5 g o.d. samples of chemically modified linters. Two 5 g o.d. samples are evaluated using a small blender and variable beating times, depending on freeness levels. Each 5 g sample yields pulp for freeness and three handsheets which allow fibre length, thickness, optical properties, finish, air permeance, tensile index, stretch, tensile energy absorption (TEA), stiffness, Z-direction tensile and zero span tensile strength to be measured.

The effects of beating in the small blender have been compared with pulp beaten in the PFI mill. The small blender produces pulps having lower freeness, higher tensile strength and lower air permeance at a given bulk than those obtained from the PFI mill. The procedures developed do not provide comprehensive evaluations but do allow for ranking of modified linters and estimation of strength properties relating the results to full scale evaluations conducted on unmodified linters. Based on these rankings the most promising chemical modifications will be scaled up and comprehensive pulp evaluations performed.

The desired changes in pulp properties on chemical modification of cotton linters are increased tensile index, Z-direction tensile and stiffness, with minimum bulk reduction. Other properties are to be maintained at their current levels.

**Pulp strength enhancement by chemical modification:** In the majority of cases studied to date, chemical modification has compensated for the effects of pretreatment (treatment with alkali, washing *etc*) to produce pulp properties nearly equivalent to the unmodified cotton linters. This is illustrated by a comparison of the tensile strength versus bulk for unmodified linters, pretreated linters (blank), and cyanoethylated linters (0.27%N, DS 0.032) (Fig. 8). Studies are currently being performed to reduce the detrimental effects of pretreatment on the strength of cotton linters.

Improved strength properties (Fig. 9) were obtained by treatment of linters with acrylamide (Fig. 1) to produce am-

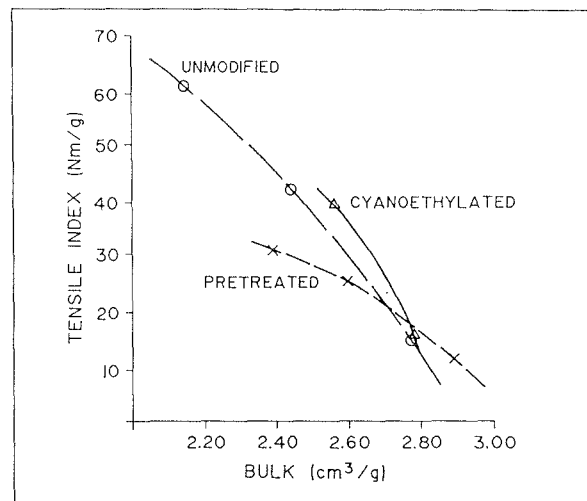


Fig. 8 Effect of pretreatment and cyanoethylation on the tensile index of cotton linters.

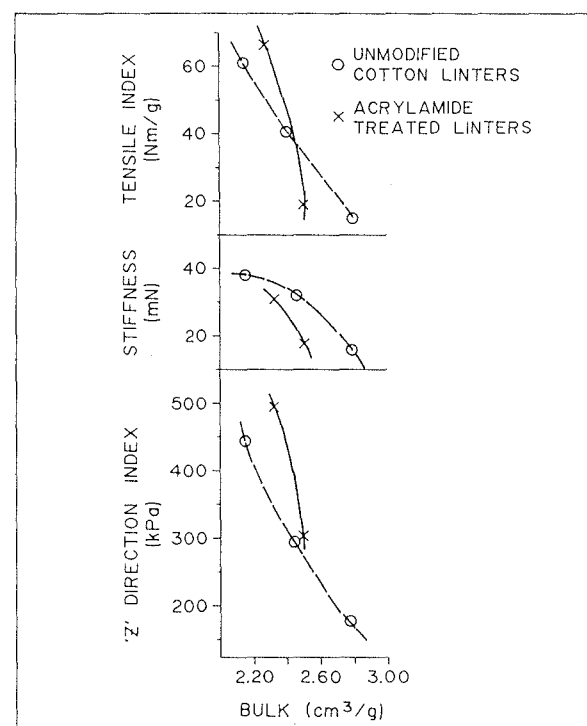


Fig. 9 Comparison of unmodified and acrylamide treated cotton linters for (i) tensile index, (ii) Z-direction index and (iii) stiffness versus bulk.

idoethyl cellulose (% 0.75% N). The modification was noted to produce adverse effects on optical properties. The substitution of acrylamide onto cellulose was detected by its effect upon pulp properties although it was difficult to detect by routine NMR and FTIR spectroscopic analysis, which have sensitivity problems below c.2%.

## CONCLUSION

The chemical modification of Australian cotton linters has been achieved using reported methods. Further emphasis will now be placed on the investigation of novel modifications to produce fibres with favourable papermaking properties, and value-added cellulose products.

It is possible to evaluate and monitor chemical changes using modern spectroscopic techniques (NMR and FTIR) and small scale pulp evaluation trials. In combination, these techniques can reveal information concerning the level of substitution, and the corresponding effect of derivatization on pulp properties. Microanalyses can also be used for monitoring substitution.

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