

Use of a new novel grafted Guar Gum-copolymer as a pitch fixative

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SUMMARY

A novel fixative, guar gum-*graft*-poly(acrylamide-co-diallyldimethylammonium chloride) (*aka* GG-g-p(AM-co-DADMAC)) was developed. This new grafted polymer proved to be very effective at adsorbing hydrophobic wood resin particles onto papermaking fibre surfaces and thus removing the troublesome wood resins from the water phase where they have a tendency to aggregate and form troublesome deposits. The new polymer is unique in that it takes advantage of the colloidal stabilising features of a natural product, guar gum and the wood resin fixative properties of a synthetic polymer p(AM-co-DADMAC). GG-g-p(AM-co-DADMAC) was effective over the entire pH range as compared to other commercially available polymeric fixatives that were evaluated.

Keywords:

co-polymer, guar gum, poly(acrylamide-co-diallyldimethylammonium chloride), pDADMAC, wood resin fixatives, papermaking

INTRODUCTION

The deposition of hydrophobic wood resins in the papermaking process has been an ongoing problem for the pulp and paper industry for many years. Water soluble polymers are often used to reduce the problem. A range of synthetic water soluble polymers have been applied including polyamines, polyDADMAC (1-4), polyacrylamides (5, 6), polyvinylamines (4, 7), polyethylenimines (3, 4, 7-9), and more recently polyacrylamide polyDADMAC co-polymers (5, 10). These polymers are generally cationic in nature and readily interact with the negatively colloidal wood resins and remove them from the pulp and paper system by "fixation" to the wood fibres in the paper.

There is increasing interest in use of natural stabilizers such as guar gum, pectic acids and galactoglucomannins to reduce the deposition of the wood resins(11-14).

These natural polymers tend to stabilize the wood resin colloids and reduce their tendency to deposit. Guar gum is a galactomannan consisting of a (1→4)-linked β -D-mannopyranose backbone with branch points from their 6-positions linked to α -D-galactose (*i.e.* 1→6-linked- α -D-galactopyranose). There are between 1.5 - 2 mannose residues for every galactose residue (Figure 1).

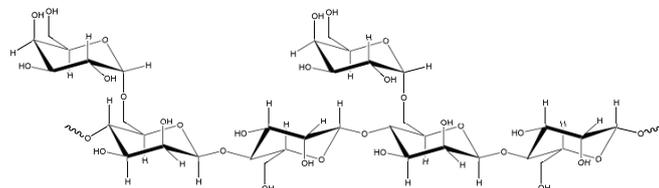


Figure 1. Principal structure of guar

Guar gum is similar to galactoglucomannans which are the principal hemicelluloses in softwoods (approximately 20%).(15) Their backbone is a linear or possibly slightly branched chain built up of (1→4)-linked β -D-glucopyranose and β -D-mannopyranose units (Figure 2).(15)

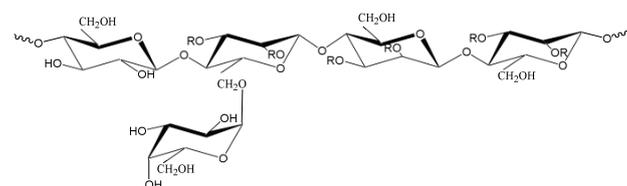


Figure 2. Principal structure of galactoglucomannans (R=H, CH₃). (15)

Guar gum is also similar to galactans which occur in minor quantities both in normal wood and tension wood, but high amounts are present in compression wood (about 10% of the wood weight).(15) The backbone of galactans, which is slightly branched, is built up of (1→4)-linked β -D-glucopyranose units substituted at C6 with α -D-galacturonic acid residues (Figure 3).(15)

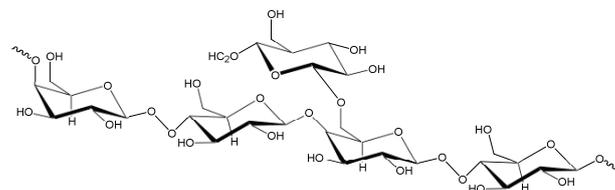


Figure 3. Principal structure of galactan in compression wood(15)

This paper evaluates the new grafted copolymer against other commercial polymers used for removal of wood resin deposition in the papermaking process.

EXPERIMENTAL

Graft Copolymerisation

The new polymer was prepared by reacting an aqueous guar gum solution with acrylamide (AM) and diallyldimethylammonium chloride (DADMAC) in the

presence of ethanol, hexane and paraffin according to a similar procedure as Lu *et al* (16) and Nayak and Singh (17). A complex initiation system of cerium sulphate (CS) and potassium persulphate (KPS) was used.

The reaction sequence was terminated with the addition of hydroquinone. The polymer was precipitated by adding 1L of cold acetone and allowed to settle in a separatory funnel. The white swollen precipitate was dried in a vacuum oven at 40°C. The dry precipitate was then washed of monomers and homopolymers by soxhlet reflux at ~85°C with a 50/50 weight mixture of acetone and glacial acetic acid for 3 hours. After reflux washing the final polymer was washed with ethanol and dried in a vacuum oven at 40°C.

To test the polymer for the mass of grafted AM and DADMAC 0.1g of the final polymer was hydrolysed in 25mL of 1M HCl and then refluxed for 3 hours at 70°C. The solution was neutralised with 25mL of 1M NaOH and the previously grafted side-chains of AM and DADMAC were precipitated with 10mL of cold methanol. The remaining product, guar gum, was dried in a vacuum oven at 40°C.

FTIR

The dried GG-g-p(AM-co-DADMAC) sample was mounted on a diamond compression cell and characterised by Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer Spectrum One FTIR with auto-image microscope. (200x200micron aperture, 4400 to 750cm⁻¹ wavelength, 16 scans, 8 cm⁻¹ resolution, liquid nitrogen cooled (77K) Mercury Cadmium Tellurium (HgCdTe or MCT) detector).

NMR

Proton nuclear magnetic resonance spectra were recorded in deuterium (D₂O) on a Varian Mercury 2000 Spectrometer operating at 300 MHz. Chemical shifts were recorded as Δ values in parts per million (ppm) and referenced to the solvent used (*i.e.* D₂O). A trace amount of thionyl chloride was added to the sample in order to dissolve the GG-g-p(AM-co-DADMAC) in D₂O by providing chloride for DADMAC (*i.e.* DADMA Chloride) any excess thionyl chloride would be converted to DCl with some sulphur dioxide gas which was vented.

Cationic Degree

The cationic degree for the GG-g-p(AM-co-DADMAC) was determined by titrating 0.1mL of 0.5% (as received, or wet) fixative with 0.001N sodium polyethylene sulphonate (PES-Na, MüttekTM [25053-27-4]) using the Au electrode MüttekTM PCD-02 (Particle Charge Detector) to determine the charge neutralisation endpoint held for five minutes. This yields charge in equivalents of charged functional groups per dry gram of GG-g-p(AM-co-DADMAC). The eq/dry g is then

multiplied by 161.67g/eq (*i.e.* molar mass of a DADMAC unit) and converted to a percent in order to yield cationic degree (DC) in % (w/w).

Wood resin Deposition

Wood resin was soxhlet extracted with hexane from thermomechanical pulp produced from wood chips of *Pinus Radiata* at the Norske Skog, Boyer Paper Mill in Tasmania, Australia.

Deposition of wood resin onto the extractive free-thermomechanical wood fibres was carried out by adding 400g of wood fibres at 1% solids into glass jars. The fibre suspensions were stirred using paddle stirrers (Cole Palmer, PE coated) at a stirring rate of 300 rpm for 30 minutes at 50 °C.

The amount of wood resin in the suspension before deposition and after deposition was analysed by gas chromatography as described previously (18). The wood resin was extracted from the fibre suspensions using tertiary-butyl methyl ether (*t*-BME). The quantity of wood resin in the total sample was analysed along with the quantity in a sample that was centrifuged and another sample that was filtered. The filtered sample yielded the soluble wood resin present while the difference between the centrifuged sample and the soluble sample yielded the amount of colloidal wood resin in the suspension. The difference between the total wood resin in the sample and the amount in the centrifuged sample yielded the amount bound to the fibres.

RESULTS AND DISCUSSION

Polymer characterization

The polymer was characterized. The GG-g-p(AM-co-DADMAC) yielded PG of 85%, which is at the low end of the results of Lu *et al* (16) (*i.e.* 85-168%) where starch was the trunk polymer. The GE of the GG-g-p(AM-co-DADMAC) was 79.16% as compared to a range of 50-86% from Lu *et al* (16).

The cationic degree (DC) for the GG-g-p(AM-co-DADMAC) was determined by titrating 0.1mL of 0.5% (as received, or wet) fixative with 0.001N sodium polyethylene sulphonate. The GG-g-p(AM-co-DADMAC) had a DC of 10.34%. The DC of the starch-g-p(AM-co-DADMAC) of Lu *et al* (16) had DC from 22% to 32%.

The FTIR scans, in Figure 4, show the characteristic absorption bands of AM at 1619 cm⁻¹ and 1658 cm⁻¹ due to -NH-. This FTIR of GG-g-p(AM-co-DADMAC) proves the presence of AM.

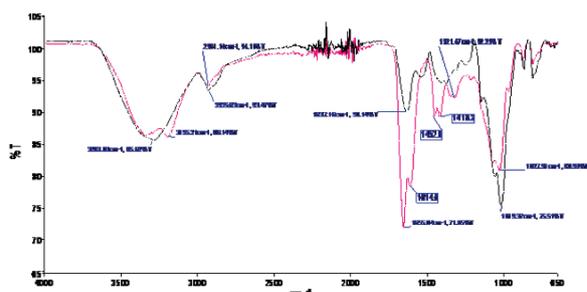


Figure 4. FTIR spectra of GG-g-p(AM-co-DADMAC) in pink. Neat guar gum in black.

To confirm that the GG-g-p(AM-co-DADMAC) contained DADMAC proton (^1H) nuclear magnetic resonance spectra of the sample were recorded in deuterium (D_2O).

Figure 5 shows the ^1H -NMR spectra for guar gum prior to grafting which shows the broad shifts from the hydrogen atoms within the mannose and galactose residues of the guar gum.

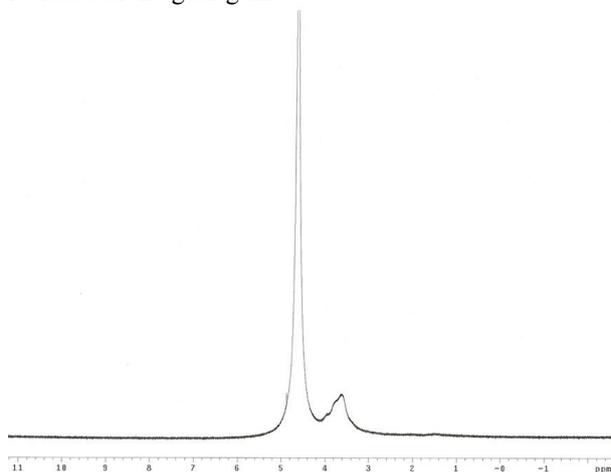


Figure 5. ^1H -NMR spectra of guar gum

^1H -NMR of GG-g-p(AM-co-DADMAC), in Figure 6, shows the characteristic methyl (1), methylene (2) and methine (3) non-equivalent proton shifts identified in both the *cis* and *trans* configurations of the DADMAC groups within the pDADMAC polymer chain (Kříž *et al*(19)). This ^1H -NMR of GG-g-p(AM-co-DADMAC) proves the presence of DADMAC.

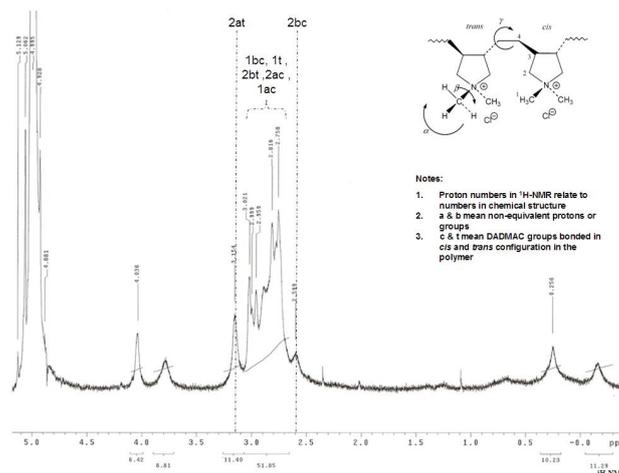


Figure 6. ^1H -NMR spectra of GG-g-p(AM-co-DADMAC)

Evaluation in controlling wood resin deposition

The effectiveness of the new GG-g-p(AM-co-DADMAC) polymer in controlling wood resin deposition was accessed by carrying out deposition experiments. The amount of wood resin attached to the wood fibres was measured at a polymer addition of 2kg/tonne (oven dried fibre) at three pH conditions (pH 4.75, 6.85 and 8.06) for a range of different polymeric fixatives that are used commercially to control wood resin deposition in the papermaking process. The new grafted polymer was labeled FixX.

The new grafted polymer GG-g-p(AM-co-DADMAC) (FixX) was found to be one of the best fixatives evaluated. At pH 4.75 it was found to increase the amount of wood resin attached to the fibres from 72% with no fixative to over 95%, as shown in Figure 7, and to reduce the amount of material present in the colloidal fraction, as shown in Figure 8.

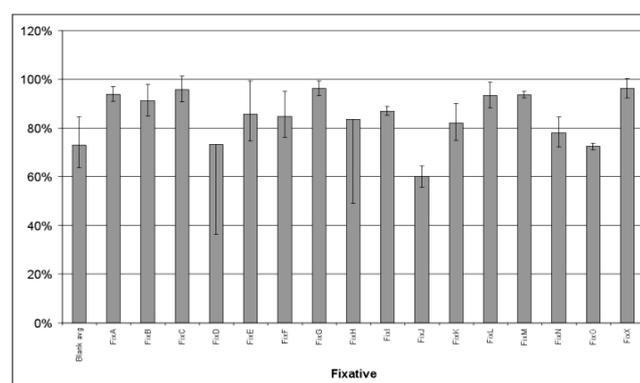


Figure 7. Percent of the total extractives fixed to the fibres after deposition at 4.75pH.

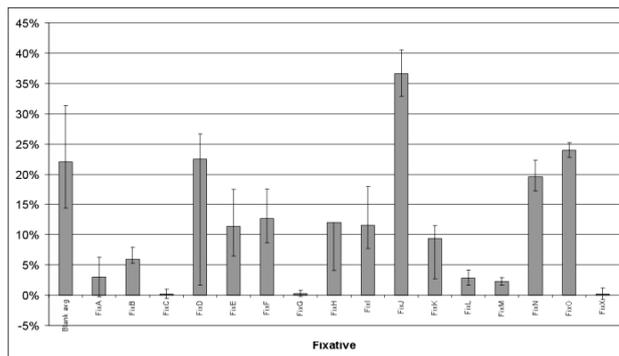


Figure 8. Percent of the total extractives in the colloidal phase after deposition at 4.75pH.

At 6.85pH, FixX is as good as the better performing fixatives at reducing the amount of wood resin in the colloidal phase (Figure 9) and attaching it to the fibres (Figure 10).

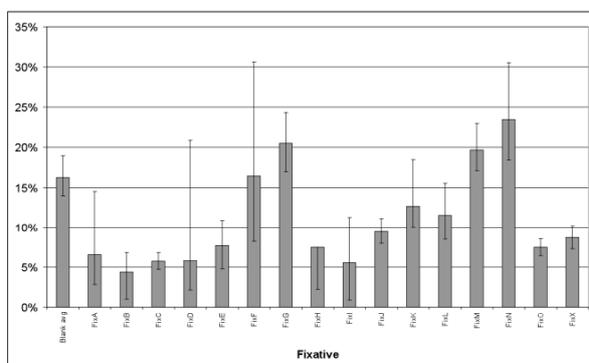


Figure 9. Percent of the total extractives in the colloidal phase after deposition at 6.85pH.

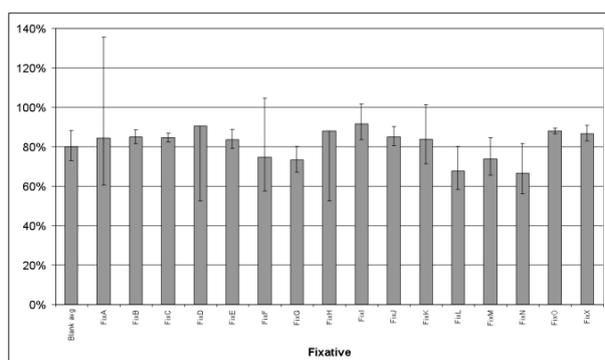


Figure 10. Percent of the total extractives fixed to the fibres after deposition at 6.85pH.

At pH 8.06, Fix X outperformed the other fixatives by decreasing the wood resin in the colloidal phase from 36% to almost zero as shown in Figure 11 and increasing the amount of wood resin bound to the fibres from 50% to close to 90% as shown in Figure 12. The other fixatives to perform almost as well as FixX were FixC (pDADMAC), and Fix G (guar gum).

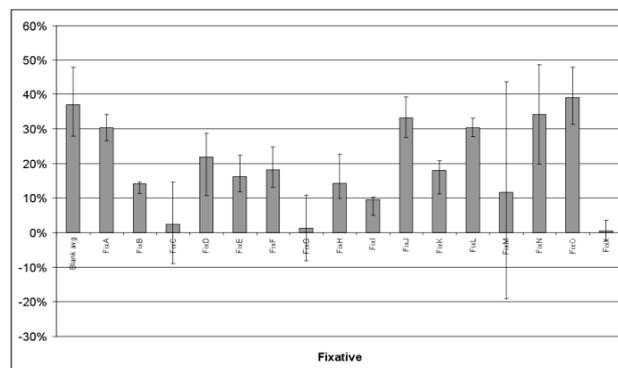


Figure 11. Percent of the total extractives in the colloidal phase after deposition at 8.06pH.

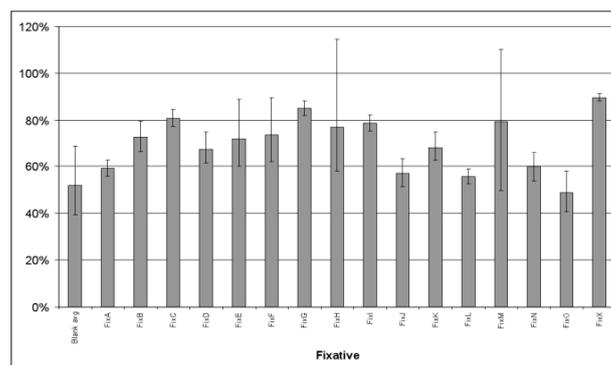


Figure 12. Percent of the total extractives fixed to the fibre after deposition at 8.06pH.

CONCLUSIONS

A novel fixative, guar gum-*graft*-poly(acrylamide-*co*-diallyldimethylammonium chloride) (*aka* GG-*g*-p(AM-*co*-DADMAC)) was developed for the first time. This new grafted polymer proved to be a good fixative as well as a good colloidal stabiliser, a combination of properties shared only by high molar mass pDADMAC. The product is unique in that it takes advantage of the colloidal stabilising features of a natural product(20) (*i.e.* guar gum) and the wood pitch fixative properties of a synthetic polymer(10) (*i.e.* p(AM-*co*-DADMAC)). GG-*g*-p(AM-*co*-DADMAC was effective over the entire pH range as compared to the other fixatives evaluated.

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