SYNTHESIS OF GUAR GUM-*GRAFT*-POLY(ACRYLAMIDE-*CO*-DIALLYLDIMETHYLAMMONIUM CHLORIDE) AND ITS APPLICATION IN THE PULP AND PAPER INDUSTRY

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The synthesis and characterization of a novel fixative, guar gum-*graft*-poly(acrylamide-*co*-diallyldimethylammonium chloride) (GG-*g*-p(AM-*co*-DADMAC)) polymer is described. The grafted polymer proved to be effective at adsorbing hydrophobic wood resin particles onto papermaking fibre surfaces, thus removing wood resins from the water phase where they have a tendency to aggregate and form troublesome deposits. The new polymer combines 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.

INTRODUCTION

The aggregation and deposition of hydrophobic wood resins in the papermaking process has been an ongoing problem for the pulp and paper industry for many years. Wood resins are very sticky in nature and tend to deposit onto surfaces they come in contact with, resulting in downtime of the paper machine and loss in production efficiency. Alum has been employed initially to neutralize the anionic charge present on the wood resins and other anionic substances present in the process water (Koppinen 2007; Pruszynski 2003). However, with the trend in commercial paper making towards neutral pH (Roberts 1996), issues associated with alum usage have been reported. Alum has been found to be ineffective as a pitch control agent at neutral and alkaline pH, and increased sulfate levels have resulted in increase corrosivity of process waters (Laubach and Greer 1991).

A range of synthetic water-soluble polymers, such as, polyamines, poly-diallyl-dimethylammonium chloride (pDADMAC) (Wågberg and Ödberg 1991; Sundberg, A. et al. 1993; Yu et al. 2003; Richardson et al. 2002), polyacrylamides (pAM) (Maher et al. 2005; Kekkonen et al. 2001), polyvinylamines (pVAm) (Richardson et al. 2002; Moormann-Schmitz and Esser 2001), polyethylenimines (pEI) (Yu et al. 2003; Richardson et al. 2002; Moormann-Schmitz and Esser 2001; Richardson et al. 1997;

Winter et al. 1992) and more recently poly(acrylamide-co-DADMAC) block co-polymers (Maher et al. 2005; Richardson et al. 2003) have been used as alternative pitch control agents in the papermaking process. Cationic polymers have been found to perform better than alum (Pruszynski 2003), as they not only neutralize the anionic substances present but also can act as bridging agents, attaching the wood resin particles onto papermaking fibres and reducing their concentration in the process water, without adding any further financial implications. Polymers of quaternized ammonium salts such as pDADMAC have been reported to perform better than polyvinylamines and primary/secondary/tertiary polyethylenimines over a wide pH range (Pruszynski 2003). The degree of charge on the polyethylenimines is affected by pH (Pruszynski 2003), and these polymers lose a significant amount of charge at neutral and higher pH (Pruszynski 2003; Richardson et al. 2002, 2003; Dechandt et al. 2003).

There is increasing interest in the use of natural stabilizers such as guar gum, pectic acids, and galactoglucomannans to reduce the deposition of the wood resins (Sundberg et al. 1996; Otero et al. 2000; Hannuksela and Holmbom 2004; Saarimaa 2006). These natural polymers interact with the wood resin colloids and reduce their tendency to deposit and at the same time increase the strength of paper (Rojas and Neuman 1999). Guar gum is a galactomannan consisting of a $(1{\rightarrow}4)$-linked β-D-mannopyranose backbone with branch points from their 6-positions linked to α-D-galactose (*i.e.* $1{\rightarrow}6$-linked-α-D-galactopyranose) (Moe et al. 1947; Behari et al. 2001). There are between 1.5 and 2 mannose residues for every galactose residue (Fig. 1) (Moe et al. 1947).
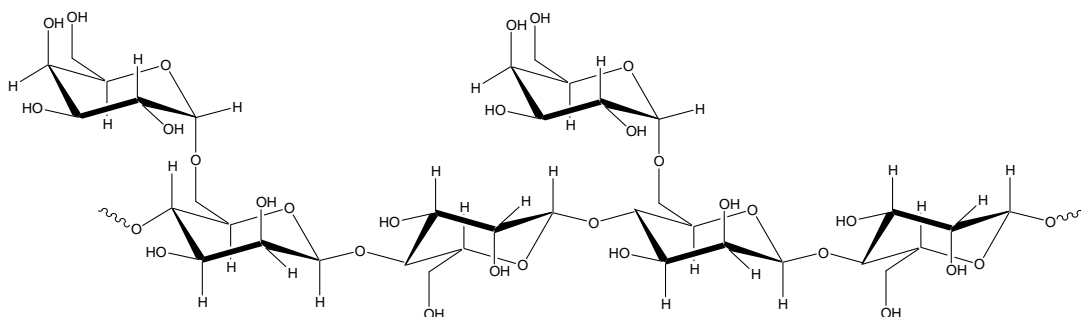

Figure 1. Principal structure of guar gum (Moe et al. 1947; Hall et al. 1999)

Guar gum is similar to galactoglucomannans, which are the principal hemicelluloses in softwoods (Panda 2004) in terms of the presence of both galactose and mannose. This structural similarity favours its use in mimicking the role of hemicellulose in wood and increasing the strength of paper by promoting hydrogen bonding amongst fibers.

A number of researchers have grafted synthetic cationic polymers onto natural polymers of starch and guar gum using graft copolymerization methods developed by Mino and Kaizerman (1958) and Nayak and Singh (2001a), using a ceric ion initiator, grafted poly(acrylamide) (pAM) to hydroxypropyl guar gum. Lu et al. (2004) grafted pAM and pDADMAC onto starch using a modified complex initiation system of cerium(IV) sulphate (Ce(IV)S) and potassium persulphate (KPS, $K_2S_2O_8$) under a nitrogen atmosphere. They showed that the Ce (IV)S-KPS initiation system resulted in

greater grafting efficiency than using either Ce(IV)S or KPS alone. This discovery enabled Lu et al. (2004) to theorise that Ce(IV) is reduced when the starch is oxidized. The Ce(III) species is further oxidized to Ce(IV) by KPS, to facilitate a continuous supply of free radicals.

This paper describes the synthesis and characterization of a new grafted guar-g-p(AM-co-DADMAC) copolymer using similar methods as Lu et al. (2004). The intention of producing the new polymer was to combine the benefits of both guar gum and commercial polymers to improve the efficiency of the polymers used to control wood resin deposition in the papermaking process. An added benefit in developing a new fixative that comprises a natural polymer is the reduction in the dependency of oil-based hydrocarbons for the fixation of wood extractives. This is important with the ever-increasing cost of extracting crude oil and its refinement towards petrochemicals (*i.e.* synthetic polymers). An evaluation of the new polymer and a comparison with commercially available polymers used in controlling pitch deposition was undertaken.

EXPERIMENTAL

Purification of Guar Gum

Purification of guar (Fluka, CAS: 9000-30-0) was carried out using the process reported by Rayment et al. (1995). Approximately 10 g of guar gum was boiled with 40 mL of 70% ethanol for 1 h under reflux. The sample was filtered, washed with 95% ethanol, and oven dried before use.

Graft Copolymerisation

The grafting procedure was based largely on the methods developed by Lu et al. (2004) and Nayak and Singh (2001b). A solution of purified guar gum (1 g) in water (108 g) was prepared in a three-neck round-bottom flask. Ethanol (80 g), hexane (40 g), and paraffin oil (2 g) were added to the solution, which was then heated to 60°C. Hexane and paraffin oil were added to create hydrophobic nucleating regions (*i.e.* droplets). The ethanol comprised 20% of the total reaction solution weight as recommended by Okieimen (2003), who showed that the graft level and grafting efficiency of the ceric ion (CeIV) process was improved at this level.

Copper sulphate (2 mL) and sulfuric acid (12 mL) were added by syringe through sealed stoppers to the guar gum/hexane/ethanol solution. An initiator solution (4 mL) of 0.167 M cerous (III) sulphate (Ce(III)S) and 0.167 M potassium persulphate (KPS, $K_2S_2O_8$) was added. Lu et al. (2004) noted that the Ce(IV)S-KPS initiation system depended on the acid concentration of the system. It has been reported that the SO_4^{2-} ions of sulfuric acid promote DADMAC grafting onto the backbone of starch (Bowman & Cha 2003). Sulfate ions (SO_4^{2-}) are also known to facilitate re-oxidation of Ce^{+3} to Ce^{+4} by maintaining the supply of SO_4^{2-} ions, which are primarily supplied by persulfate $(S_2O_8)^{2-}$. Too high a concentration of acid has been reported to degrade the starch backbone, resulting in low grafting (Lu et al. 2004).

After the first addition of initiator, 3 mL of 0.3 M diallyldimethylammonium chloride (DADMAC) was added to begin the grafting. Initiator solution (2 mL) was

added at 30 minute intervals a further 4 times during the reaction. This follows suggestions by Lu et al. (2004) whereby AM was believed to inhibit the grafting of DADMAC due to the much higher reactivity of AM.

Following each addition of initiator, 40 mL of a dilute mixture of acrylamide (AM) (61.25 x 10^{-3} M AM) and DADMAC (3.75 x 10^{-3} M DADMAC) monomers was pumped into the reaction vessel at a flow rate of 4 mL/min.

Fresh initiator was added throughout the reaction to encourage growth of the grafted co-polymer side-chains as the cerous sulphate (Ce(III)S) initiator, catalysed by potassium persulphate (KPS), can be rapidly consumed (Lu et al. 2004). Lu et al. (2004) concluded that the appropriate molar ratio of $[S_2O_8^{2-}]$ to $[Ce^{4+}]$ should be 5:2, this ratio was maintained throughout the reaction. In the final reaction solution of 400mL the concentration of Ce(III)S and KPS were 2.0 x 10^{-3} M and 5.0 x 10^{-3} M respectively.

The reaction sequence was terminated with the addition of hydroquinone. The copper sulphate concentration was 5.0 x 10^{-4} M in the final reaction solution of 400 mL.

The polymer was precipitated in 1 L of cold acetone. The white, swollen precipitate was dried in a vacuum oven at 40°C. The dry precipitate was then washed to remove monomers and homopolymers by soxhlet reflux at ~85°C with a 1:1 v/v mixture of acetone and glacial acetic acid for 3 hours. The polymer was then washed with absolute ethanol and dried in a vacuum oven at 40°C to constant weight.

To test the polymer for the mass of grafted AM and DADMAC 0.1 g of the final polymer was hydrolysed in 25 mL of 1M HCl and then refluxed for 3 hours at 70°C. The solution was neutralised with 25 mL of 1M NaOH, and the previously grafted side-chains of AM and DADMAC were precipitated with 10 mL 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 (200 x 200 micrometer aperture, 4400 to 750 cm^{-1} wavelength, 16 scans, 8 cm^{-1} resolution, liquid nitrogen cooled (77 K) Mercury Cadmium Tellurium (HgCdTe or MCT) detector).

NMR

Proton nuclear magnetic resonance spectra were recorded in deuterium oxide (D_2O) at 25°C on a Varian Mercury 2000 Spectrometer operating at 300 MHz. Chemical shifts were recorded as δ values in parts per million (ppm) and indirectly referenced via the solvent resonance (*i.e.* HOD). A trace amount of thionyl chloride was added to the sample in order to dissolve the GG-*g*-p(AM-*co*-DADMAC) in D_2O.

Cationic Degree

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

gram of GG-*g*-p(AM-*co*-DADMAC). The eq/dry g is then multiplied by 161.7 g/eq (*i.e.* molar mass of a DADMAC unit) and converted to a percent in order to yield cationic degree (DC) in % (w/w).

Commercial Cationic Polymers

Five different types of cationic polymers that are used commercially in the Pulp and Paper industry were obtained from Norske Skog Boyer. The five cationic polymers were labeled Fix A to Fix E. The polymers were chosen from a more extensive range that had been previously evaluated by McLean et al. (2010). Table 1 summarizes the information available for each of the polymers. The molar masses of the polymers were determined from viscosity measurements using an Ubbelohde viscometer and the Mark-Houwink equation. The viscosities of the polymer solutions were measured in distilled water.

Table 1. Physical Properties of Cationic Polymers

Label	Chemistry	% Solids	Molar Mass[1]	Intrinsic Viscosity	Viscosity Av Molar mass
FixA	pDADMAC	21	Medium	22.9	2.3×10^4
FixB	cPAM	58	High	91.0	5.9×10^7
FixC	Guar gum	100		12[2]	1.6×10^{6} [3]
FixD	p(AM-co-DADMAC)	63	Medium	51.7	[4]
FixE	PEI	26	Low	4.5	6.0×10^3

[1] Low MW= $<10^4$, Medium MW= 10^4-10^6, High MW=$>10^7$, c-cationic, PAM-polyacrylamide
[2]. Samavati (2007)
[3] Robinson (1982)
[4] Mark-Houwink constants K and a not available for the calculation of molar mass

Wood Resin Deposition

Model wood resin colloidal dispersions were prepared by mixing oleic acid (Aldrich 99+% purity), triolein (Sigma 99 % purity), and abietic acid (Aldrich 70 % purity technical grade) in acetone (99.5% purity) to a volume of distilled water which was added 1 mM KNO_3 and had been pH adjusted to 5.5. The dispersion was then dialysed to remove the acetone using cellulose membrane tubing (Sigma D-9402, 76 mm wide, > 12,000 MW) and a wash solution of distilled water, the pH of which was adjusted to 5.5 with HNO_3 and containing 1 mM KNO_3. Dialysis was carried out over 24 hours with the wash water being changed every 30 minutes for the first 5 hours. The concentrations of wood extractive components were 40 mg/L abietic acid, 40 mg/L oleic acid, and 55 mg/L triolein after dialysis. The average mean size of the wood resin colloids was found to be 0.45 microns using a Micrometrics Saturn Digisizer 5200 (McLean 2009).

Thermomechanical pulp (TMP) of *Pinus radiata* was collected from the primary refiners at Norske Skog's Boyer mill in Tasmania. The pulp was air dried and then

soxhlet extracted with hexane to remove extractives. The pulp was kept in the freezer at minus 4°C until ready for use. The fibres were rehydrated to 1% consistency by adding 4 g oven dry fibre to the wood resin colloidal solutions.

Deposition of wood resin onto the extractive–free thermomechanical wood fibres was conducted using a similar method used by Maher (2007) and McLean (2010), by stirring 400 mL of the model wood resin solutions in glass jars using a paddle stirrer (Cole Palmer, PE coated). All depositions were conducted over a period of 30 minutes in a 50°C temperature bath with paddles stirring at a constant rate of 330 rpm. 1 mL of 0.5 M pH buffer was added to each jar prior to adding the 4 g of soxhlet extracted TMP fibres. Three amine buffers were used to control the pH. Tris(hydroxymethyl)-aminomethane (pKa 8.06) and ethylenediamine (pKa 6.85) were obtained from Aldrich and prepared in distilled water. N, O-dimethylhydroxylamine was obtained by distilling (at 100°C) the hydrochloride salt with a molar excess of KOH to obtain the free amine with a yield of 82.5%. Each buffer solution was titrated with 1 M HCl until the pH of the buffer equalled the pKa of the amine. 1.6 mL of $0.5^{w}/_{o}$ fixative was added targeting 2 kg of 'as received' fixative per oven dried tonne of TMP.

Wood Resin Analysis

The amount of wood resin in the suspension before deposition and after deposition was analysed by gas chromatography (McLean et al. 2003). The quantity of wood resin in the total sample was analysed along with the quantity in a sample that was centrifuged (1800 rpm for 10 minutes which corresponded to 500 G) and another sample that was filtered through 0.2 µm filter. 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.

The wood resin was extracted from the fibre suspensions using tertiary-butyl methyl ether (*t*-BME) (Aldrich 99.8% purity HPLC). 100 μL of internal standard was added. The internal standard was a solution of toluene (Aldrich 99.8% HPLC), which in 100 μL contained ~55 µg of each of the following standards: pentadecanoic acid (Aldrich 99+ %), heptadecanoic acid (Sigma 99% purity), 1, 3-dipalmitoyl-2-oleoyl-glycerol (DOG) (Sigma 99% purity), and cholesteryl stearate (Sigma 99% purity). The pH was adjusted to 3.5 using 0.79 M HNO_3 in order for efficient triglyceride extraction (Örså and Holmbom 1994). This was repeated in duplicate for each of the samples both before and after the deposition studies.

The extracted samples were blown to dryness with laboratory air, then silylated using a combination of 100 μL of pyridine (Aldrich 99+% purity) and 100 μL of BSA (N,O-bis(trimethylsilyl)-acetamide, Sigma 90% purity) followed by 20 minutes in a 60°C oven. The GC vials were cooled to room temperature and then filled to 1 mL with toluene. The silylated samples were analysed using programmed injection temperature on-column high temperature gas chromatography with a flame ionisation detector (PVT-HTGC-FID). Samples were analysed using a Varian 3800 GC equipped with a Varian 8400 autosampler. The 1 μL samples were injected onto a 15 metre Phenomenex[®] 100% polydimethylsiloxane (ZB-1, 15m x 0.53mm ID x 0.15μm FT) Zebron[TM] capillary GC

column. The injector temperature was held at 90°C for the first 30 seconds after injection and then increased to 325°C at a rate of 200°C/min. The oven/column temperature was held at 90°C for the first 1.5 minutes after injection and then increased to 320°C at a rate of 12°C/min. The FID temperature was held at 350°C for the entire duration of the ~ 33 minute programs. Ultra-high purity helium was used as the carrier gas, and the column was held at a constant pressure of 3.0 psi with a corresponding linear velocity of 54.8 cm/s. GC data were analysed using the Varian Star 5.5 software package.

RESULTS AND DISCUSSION

Graft Level

The percentage of grafting (PG) and grafting efficiency (GE) were calculated according to the method of Lu et al. (2004) and Gao et al. (1998) as follows:

PG (%) = (weight of grafted p (AM-*co*-DADMAC) ÷ weight of GG) × 100

GE (%) = (weight of grafted chains ÷ weight of reacted monomers) × 100

The weight of grafted polymer was determined after washing of the polymer to remove unreacted monomers and homopolymers. The weight of the grafted chains was calculated from the difference in weight between the purified product and the guar gum added. The weight of homopolymers formed was determined from the difference between the impure product and the purified product, while the weight of reacted monomers was determined from the difference between the amount of monomers added and the weight of the homopolymers.

The GG-*g*-p(AM-*co*-DADMAC) yielded a PG of 85%, which is at the low end of the results of Lu et al. (2004) (*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. (2004).

In order to show that grafting had taken place, Fourier transform infra-red spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopic analysis of the product were undertaken. The FTIR spectra of purified guar gum and the grafted product are shown in Fig. 2. The broad peak at 3343 cm^{-1} indicates the presence of (OH) stretching vibrations of the guar gum backbone (Behari et al. 2001; Singh et al. 2004; Nada et al. 2007; Lin et al. 1988). The peak at 3195 cm^{-1} can be assigned to N-H stretching vibrations from the acrylamide (AM) unit of the copolymer (Nayak and Singh 2001b; Das et al. 1998; Lanthong et al. 2006; Liu et al. 2007) and indicates the presence of AM in the grafted copolymer. Sharp peaks at 1655 and 1611 cm^{-1} are assigned to CO (carbonyl) stretching and NH bending vibrations of AM respectively (Bowman and Cha 2003; Vu and Cabestany 1991).

To confirm the grafting of DADMAC on the guar backbone, comparative studies were carried out using ^{1}H NMR of grafted copolymer and purified guar gum. The signals obtained in the purified guar gum spectrum were verified with published data and were found to be consistent with the literature.
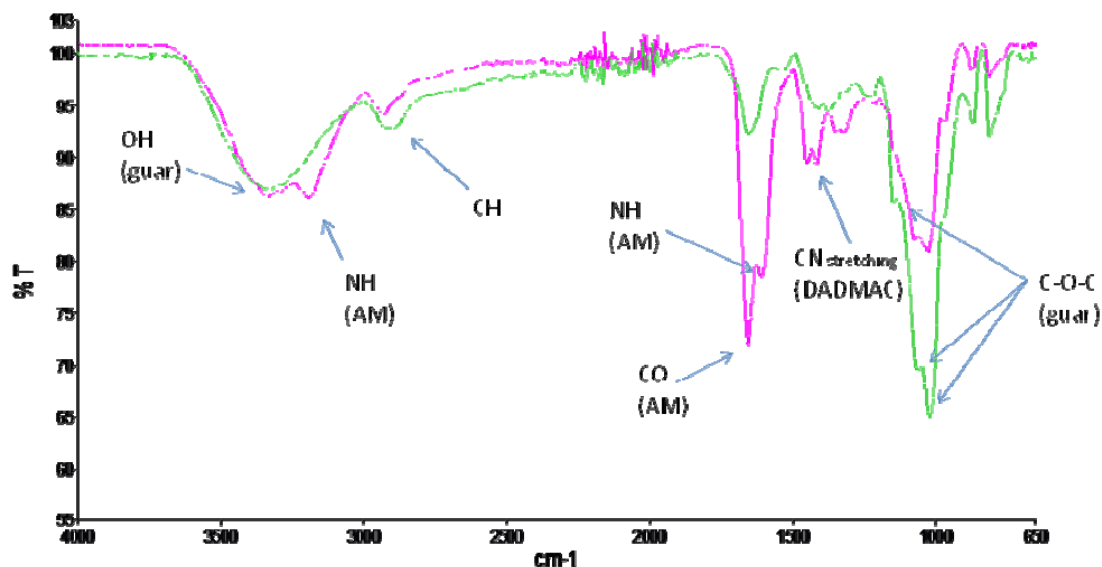
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Figure 2. FTIR spectra of purified guar gum (green line) and guar-*g*-p(AM-*co*-DADMAC) grafted copolymer (pink line)

The ^{1}H-NMR spectrum of GG-*g*-p(AM-*co*-DADMAC), in Fig. 3, shows the characteristic methyl (1), methylene (2) and methine (3) non-equivalent proton shifts
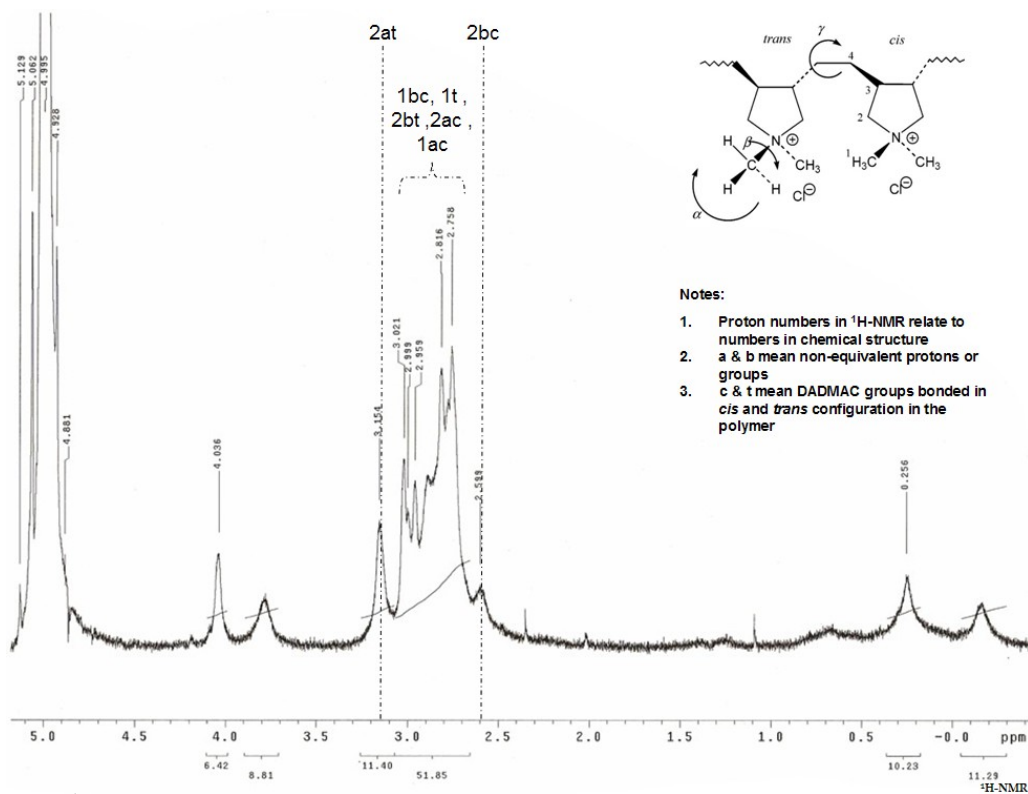

Figure 3. ^{1}H-NMR spectra of GG-*g*-p(AM-*co*-DADMAC) synthesized in this work. Peak assignment was correlated with literature values published by Kriz et al.(2001)

identified in both the *cis* and *trans* configurations of the DADMAC groups present in the grafted copolymer (Kriz et al. 2001). These signals were not found in the ^{1}H NMR spectrum of purified guar gum, and their presence in the ^{1}H-NMR of GG-*g*-p(AM-*co*-DADMAC) confirms the presence of DADMAC

Charge Measurements

The GG-*g*-p(AM-*co*-DADMAC) had a degree of charge (DC) of 10.34%, which was lower than the values of 22% to 32% for starch-*g*-p(AM-*co*-DADMAC) of Lu et al. (2004).

Evaluation in Controlling Wood Resin Deposition

The effectiveness of the new GG-g-p(AM-co-DADMAC) grafted copolymer in controlling wood resin deposition was assessed by carrying out deposition experiments. The amount of wood resin attached to the wood fibres was measured at a polymer addition of 2 kg (as received)/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. This value was considered in order to be able to perform the experiments close to mill current operational methodology using the newly synthesised polymer. The new grafted polymer was labeled Fix F.
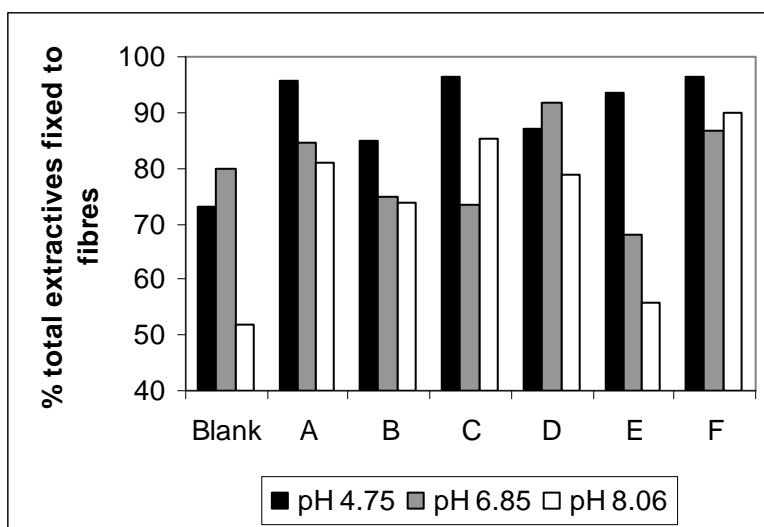

Figure 4. Effect of polymer on fixing wood resins onto fibres at a range of pH

The blank sample, containing only wood resin colloids, TMP fibres, and no fixative, was found to have a relatively high percentage of extractives fixed to the fibres at both pH 4.75 and pH 6.85. This result was typical of the behavior found for extractives from *Pinus radiata* (Maher 2007), which show a higher affinity for the TMP fibre surface than results reported for spruce. The higher resin acid content of the *radiata* extracts may be the reason for this behavior. At higher pH the fixation onto the fibres in the absence of fixative significantly decreases. This is likely to be a result of the increased solubility of the resin acid component of the radiata extracts at this pH.

Fix F was found to be perform well over the whole pH range evaluated for attaching the wood resins onto the fibres, as shown in Fig. 4. At pH 4.75 it performed as well as Polymers A, C, and E within experimental error (approx. 5%) by increasing the amount of wood extractives bound to fibre from 72% with no fixative to over 95% upon the addition of fix F. At pH 6.85 it increased the amount of fibre-bound extractives from 80% to 87% and performed as well as polymers A and D within experimental error, while at pH 8.06 it increased the fibre bound extractives from 50% to 90%, outperforming the other polymers.

These preliminary results indicate the potential of the new grafted polymer F for use in the pulp and paper industry as a solution to the problem of wood resins. Further work is needed to more fully characterize the polymer and understand its structure and where the grafting is. Additional work is also required to see the effect of different dose rates and comparison to other polymers at the same solids content.

CONCLUSIONS

The grafted copolymer (fix F) shows promise as an excellent fixative for binding wood extractives on the fibre surface. It performed well over a wide pH range. The product is unique as it takes advantage of the colloidal stabilising features of a natural product (Vercoe 2004) (*i.e.* guar gum) and the wood pitch fixative properties of a synthetic block copolymer (Richardson et al. 2003) (*i.e.* p(AM-co-DADMAC)) and also provides an alternative that reduces the reliance on pure synthetic polymers made from fossil fuels.

ACKNOWLEDGEMENTS

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