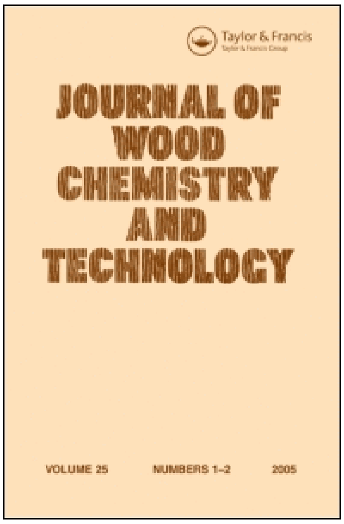

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Evaluation of Various Phenolformaldehyde Resins in the Phenolformaldehyde Resin—Polyethyleneoxide Dual Retention Aid System

Karen R. Stack[a]; Lawrence A. Dunn[a]; Noel K. Roberts[a]
[a] Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

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EVALUATION OF VARIOUS PHENOLFORMALDEHYDE RESINS IN THE PHENOLFORMALDEHYDE RESIN - POLYETHYLENEOXIDE DUAL RETENTION AID SYSTEM

Karen R. Stack, Lawrence A. Dunn, Noel K. Roberts
Chemistry Department, University of Tasmania,
GPO Box 252C, Hobart, Tasmania, Australia.

ABSTRACT

Retention performance of the polyethylene oxide (PEO)-phenolformaldehyde resin (PFR) retention aid system is affected by the chemical structure and the molecular weight distribution of PFR. ^{13}C NMR and high performance liquid chromatography have been used to characterise various resole and novolak-based resins. Of the resins examined, those with the highest molecular weight gave the greatest retention improvement. The type of substitution around the aromatic ring of the resin appears to affect the interaction with PEO and the size and structure of the network formed when PFR and PEO are mixed together.

INTRODUCTION

Phenolformaldehyde resin (PFR) and high molecular weight polyethylene oxide (PEO) have been successfully used as a dual retention aid system in the papermaking industry since the early eighties[1-4]. Various mechanisms have been proposed for how the dual retention aid system improves fibre retention. It has been proposed that PFR is adsorbed onto the fibres providing binding sites for the PEO to attach to and bridge the fibers[5]. Lindstrom et al[6,7] proposed that PEO and PFR interact to form a network structure which traps fibres as it is being formed. In both mechanisms the role of the PFR is to provide binding sites for the PEO via hydrogen bonding between the ether oxygens and the phenolic hydroxyls.

Several factors have been found to affect the interaction between PEO and PFR both in the absence and presence of pulp fibers[8,9]. The type of resin, in particular, appears to affect the interaction and retention aid performance of PEO and PFR. However, no detailed study has been reported. This paper presents results of a study in which a series of resins have been evaluated in conjunction with PEO as retention aids.

PFR is a complex mixture of polyphenolics, differing in molecular weight, shape and degree of substitution with methylol groups and methylene linkages. The nature and concentration of the components depend on the reaction conditions such as the formaldehyde to phenol ratio (F:P), the type and quantity of catalyst, time and temperature of the reaction[10-16].

The resins can be divided into two groups[17]:

1) Novolaks, which are prepared under acidic conditions with a formaldehyde:phenol (F:P) ratio smaller than one. In a novolak, phenol rings are connected via methylene bridges and their general structure is represented by formula 1 in Figure 1.

2) Resoles, which are prepared under basic conditions with a F:P ratio larger than one. The

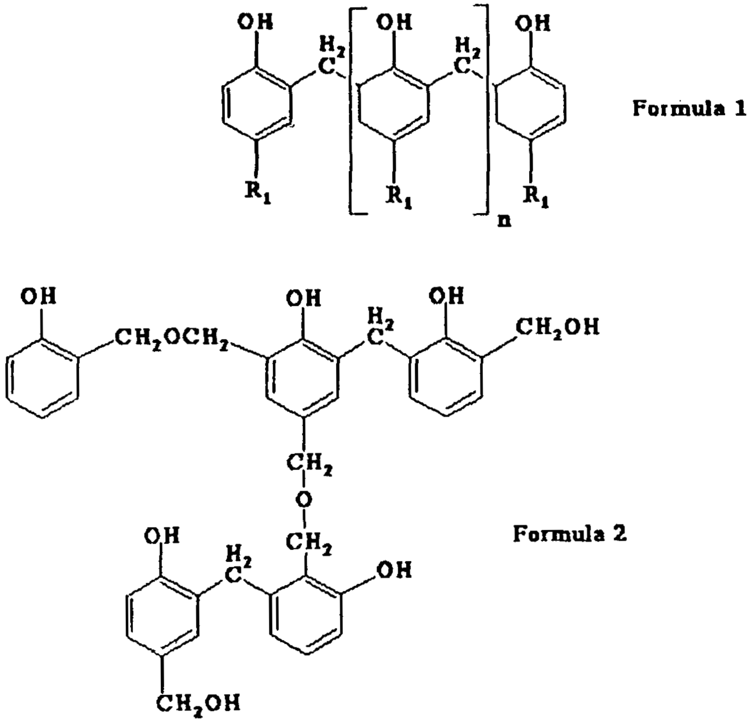

FIGURE 1: Chemical Structure of Novolak (Formula 1) and Resole (Formula 2) type PF Resins.

structure of a resole is quite different from a novolak due to the presence of methylene and ether bridges and methylol groups and to branching. This branching is dependent on the F:P ratio, the catalyst used and the condensation temperature. The structure of a resole would comprise elements such as those in formula 2 in Figure 1.

High molecular weight phenol-formaldehyde resoles are typically used with high molecular weight PEO to improve fiber retention in the Newsprint industry.

Until recently, little has been reported concerning the relationship between molecular structure and end-use properties of PFR due to the complexity of the material and lack of suitable instrumentation and techniques to adequately characterise the resins. High performance liquid chromatography (HPLC)[18], size exclusion chromatography[19-21], nuclear magnetic resonance[21-24] and infra-red[25] spectroscopy are some of the techniques now being used by researchers to analyse PFR. ^{13}C NMR and HPLC have been applied in this study to define the important molecular properties of a PFR needed for it to combine with PEO and improve fibre retention in the papermaking process.

RESULTS AND DISCUSSION

Physical properties of Resins

Experimental resins were kindly prepared and donated by ICI Australia and CHEMPLEX Australia Ltd. The exact conditions under which the resins were manufactured, that is, the formaldehyde to phenol ratio (F:P) , amount of catalyst and reaction time were not supplied for commercial reasons. From the information supplied by the manufacturers the resins differ from each other in the following ways:

1. Resin A is lightly condensed.
2. The F:P ratio of Resins B-G varied as follows,

$$B, C, D, E < F < G$$

3. Resins H and I had the same F:P ratio and alkalinity as Resin E, however the reaction time varied as follows,

$$E < H < I$$

TABLE 1: Summary of the physical properties of various phenolformaldehyde resins

Resin	Type	Alkalinity %	Viscosity cP	M_n	M_w
A	Resole	0.27	*	410	530
B	"	5.9	*	1550	5200
C	"	7.1	*	1200	18300
D	"	5.7	*	1180	16800
E	"	7.5	1872	1280	25800
F	"	5.3	3104	1080	5700
G	"	5.2	856	*	*
H	"	7.3	2480	*	*
I	"	7.4	5504	*	*
J	Novolak	8	58	**	**
K	"	7.4	292	**	**
L	"	8.7	188	**	**
M	"	9.3	162	**	**

* Resins had condensed and unable to measure.

** Resins not measured because of a problem with column.

Four novolak-based resins (Resins J-M) were also evaluated. These were received as the sodium salts with NaOH being added to raise the pH of the solution to approximately 12.

Table 1 summarises the physical properties of the resins. The alkalinity, viscosity, and relative molecular weights, M_n and M_w, were measured for most of the resins. Some of the resins had solidified before all the alkalinity and viscosity measurements had been completed and so some of the data is not available for these resins. The molecular weight distribution of the resins were measured using gel permeation chromatography, GPC. Some problems were experienced in dissolving some of the resins in THF, in particular the more condensed resins such as Resin G-I were completely insoluble. Column performance was found to change significantly over the course of the study. Resins J-M were not measured because of the unreliability of the column.

Differences in the alkalinity of the resins were evident indicating that the NaOH contents were different. Resin A had the lowest alkalinity of the resins while Resins F and G were slightly lower than that of the other resins. The novolak-based resins had the highest alkalinity.

Differences in solution viscosity were also evident in those resins that were measured. Viscosity is generally used as a guide to the molecular weight of the resins. The novolak resins had the lowest solution viscosities. Most of the resoles had high viscosities due to aging and condensation of the resins.

HPLC analysis of PFR

High performance liquid chromatography (HPLC) reverse phase chromatography was used to investigate the components in the resins. Separation of the components in the resin by the column is based on differences in molecular weight and chemical structure of the components. Figure 2 presents the chromatograph trace of a lightly condensed, low relative molecular weight resin

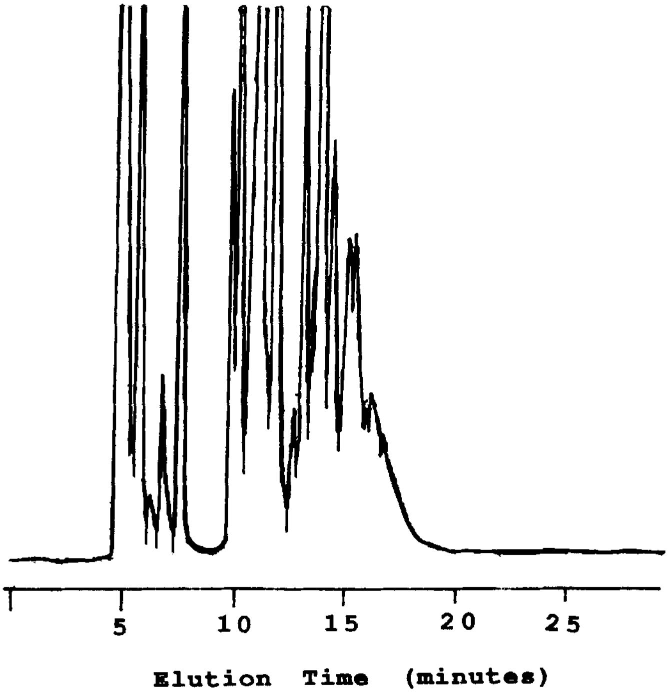

FIGURE 2: HPLC Chromatograph of lightly condensed resin, Resin A.

(Resin A). A predominance of components eluting at low elution times is evident. For the other resins, the chromatograph trace has a broad band of components eluting late in the column (Figure 3). This material forms the bulk of the material in the sample. This broad band is believed to be composed of the higher molecular weight components. The equipment was unable to adequately separate out this material further.

Differences in the position of the major band (Table 2) between the novolak-based resins (Resin J-M)

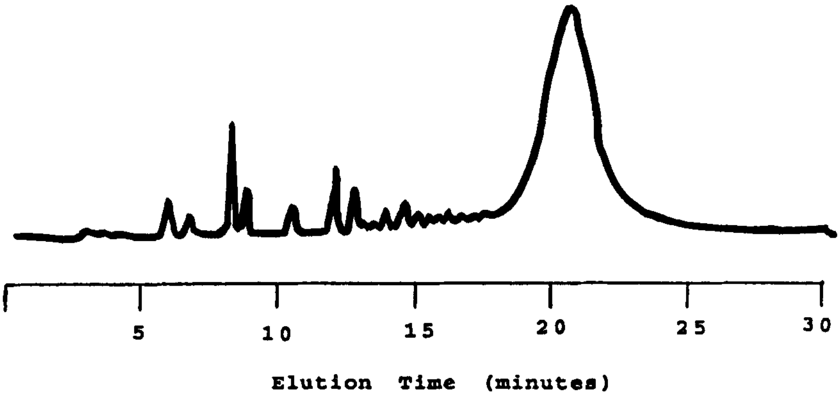

FIGURE 3: Typical HPLC Chromatograph of PF Resin.

TABLE 2: Comparison of the major peak position and area in the HPLC chromatographs of the PF Resins.

Group	Resin	Elution Time	%Area
Resoles	A	5.6	29.0
	B	20.4	29.1
	C	20.2	41.3
	D	20.0	70.5
	E	19.9	63.9
	F	19.0	75.2
	J	22.2	65.8
Novolaks	K	22.3	66.5
	L	22.7	74.2
	M	22.7	76.3

and the resoles (Resin A-I) are evident, reflecting a difference in the chemical structure of the resins.

Some minor variations in the position and intensity of the earlier eluting peaks occurs between the resins. These minor differences reflect the differences in the chemical structure within the resins due to differences in reaction conditions.

Some variation in the area under the major band is also evident (Table 2). The resins with the lower band area have less of the higher molecular weight material present and those with the greater area have less of the lower molecular weight species present.

There appears to be no direct correlation between the major band area in the HPLC chromatographs and the relative molecular weights of the resins obtained from GPC.

^{13}C NMR analysis of PF Resins

Quantitative ^{13}C NMR has been used to study the differences in structure between the resins. The novolak-based resins can be characterised by a lack of peaks in the region 50-95 ppm (Figure 4) unlike the resoles (Figure 5) which have peaks present at 64 and 66 ppm due to methylol side chains and in some cases peaks at 85-90 ppm due to hemiformal side chains on the aromatic ring[23].

Table 3 summarises the relative proportion of unsubstituted C-2,C-4 and C-6, methylol side chains and methylene bridges that have been determined from integration of the area under the various peaks in the NMR spectra. Some discrepancies exist between the

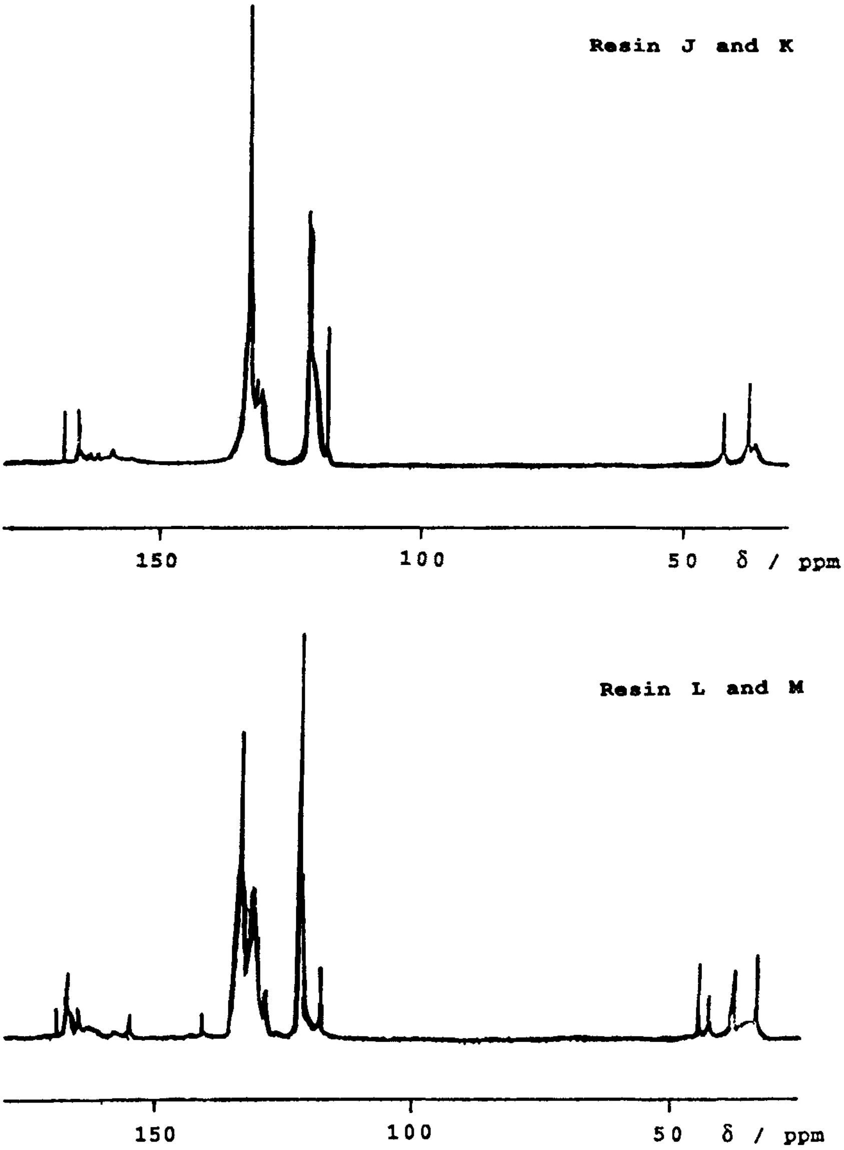

FIGURE 4: ^{13}C NMR of Novolak - based resins

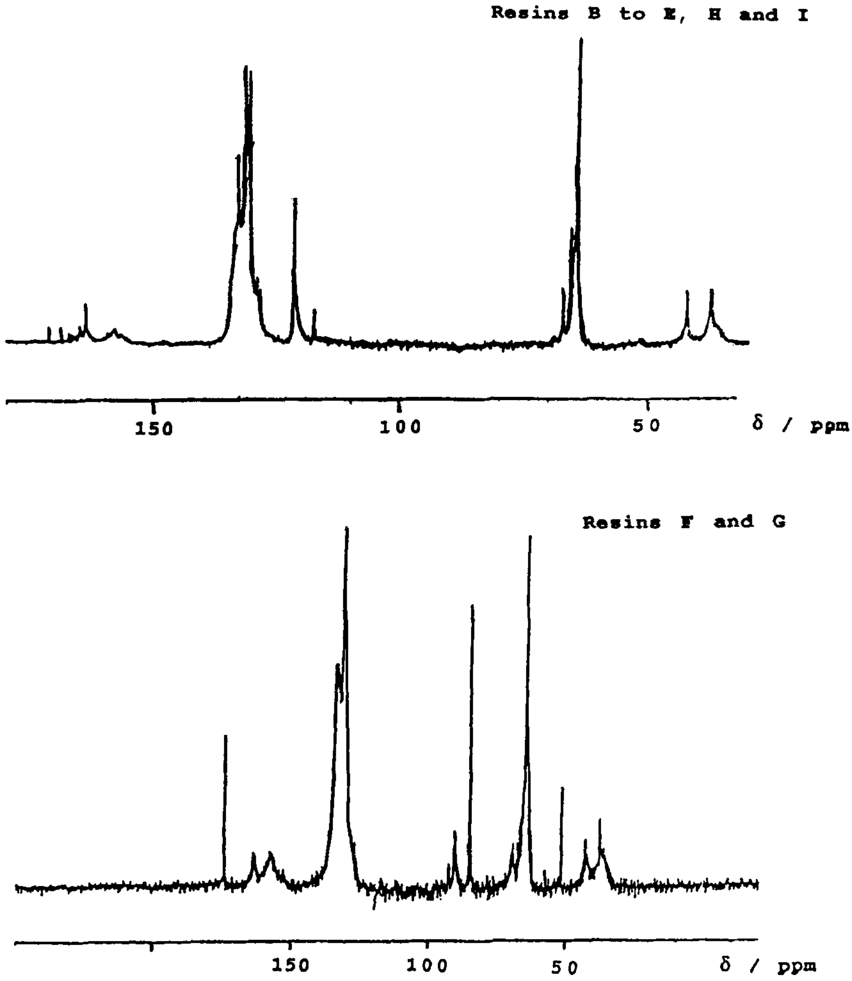

FIGURE 5: ^{13}C NMR of resole resins

TABLE 3: Substitution around aromatic ring for PF Resins using quantitative ^{13}C NMR.

Resin	phenolic C1 150-170 ppm	subs C2,C4, C6 125-135 ppm	unsub (C2,C6) , C4 114-120 ppm	hemiformal 80-95 ppm	methylol 60-67 ppm	methylene bridges 30-42 ppm
B	0.82	2.70	0.47		1.62	1.27
C	0.77	2.88	0.35		1.83	1.02
D	0.61	2.78	0.61		1.62	0.98
E	0.71	2.80	0.50		1.74	0.98
F	0.80	3.10		0.70	1.80	0.91
H	0.79	2.80	0.44		1.56	1.10
I	0.72	2.80	0.47		1.92	0.91
J	0.66	1.40	1.94			0.77
K	0.70	1.48	1.86			0.70
L	0.62	1.66	1.73			1.18
M	0.54	1.80	1.60			1.06

calculated values in Table 3. Theoretically there should be one phenolic C-1 carbon per aromatic ring in all the PFRs. The calculated amount of phenolic C-1 carbon per aromatic ring was less than one, varying from 0.54 to 0.96 carbons. The signal to noise ratio in this region of the spectra is large compared to the other regions. This would introduce a greater degree of error in the integration of the area under the peaks. A 25 second relaxation time was used to ensure complete relaxation

TABLE 4: Ortho and Para substitution around the aromatic of the PF Resins.

Resin	Unsub Carbons		Methylol		methylene bridges		
	C2,C6 ortho 120ppm	C4 para 116ppm	ortho 66ppm	para 63ppm	p-p 42ppm	o-p 36ppm	o-o 30ppm
B	0.36	0.05	0.14	1.48	0.29	0.98	0
C	0.32	0.03	0.22	1.61	0.33	0.69	0
D	0.56	0.05	0.13	1.49	0.29	0.68	0
E	0.47	0.03	0.21	1.53	0.20	0.68	0
F	0	0	0.42	1.57	0.27	0.64	0
H	0.39	0.05	0.16	1.37	0.33	0.77	0
I	0.47	0	0.30	1.62	0.28	0.63	0
J	1.68	0.26	0	0	0.23	0.54	0
K	1.67	0.19	0	0	0.19	0.51	0
L	1.52	0.21	0	0	0.30	0.59	0.29
M	1.41	0.19	0	0	0.28	0.42	0.36

of all carbons, particularly the phenolic ones which are known to relax slowly. This time is much longer than the values reported in the literature in which quantitative NMR has been used to study PFR[21-23].

The number of the substituted groups on the aromatic ring i.e., methylene bridges and methylol groups (30-125 ppm region) do not add together to the value determined directly from the number of substituted carbons on the aromatic ring (125-135 ppm region). One possible reason for this is an under-estimation of the number of methylene bridges arising from signal suppression due to restricted molecular motions with severe branching and crosslinking[22].

Although problems are evident with the ^{13}C NMR results, a large amount of useful information is present concerning the relative differences in substitution and branching in the various resins examined. Table 4 summarises the relative proportion of ortho and para substitution around the aromatic ring for the resins evaluated. Less substitution and branching and a lower ratio of ortho to para substitution around the aromatic ring were observed to be present in the novolak-based resins compared to the resoles examined. The type of methylene bridging, in the novolak-based resins, was found to differ. Resins J and K were found to contain only two types of linkages, namely o-p and p-p bridging while Resins L and M had all three types of bridging (o-o, o-p, p-p). This latter group of resins (Resins L and M) also showed a greater degree of condensation compared to Resin J and K. A larger proportion of higher molecular weight material was evident in the HPLC chromatographs and the NMR spectra indicated more substitution around the aromatic ring (Tables 3 and 4).

The formation of o-o linkages is believed to occur after all the para-carbons are consumed. In the condensation of novolak resins, p-p methylene bonds occur first, followed by o-p methylene bonds. The o-o methylene bonds link the initially formed branched o-p and p-p polymer molecules.

The resoles evaluated can be grouped into two classes. One group containing methylol side groups with methylene bridges linking aromatic rings in either an o-p or p-p arrangement (Resins A- E, H, I); the second group (Resins F, G)) contained hemiformal groups in addition to the methylol groups and methylene bridges. Resin F exhibited a greater degree of substitution around the aromatic ring as the NMR spectra (Table 2) showed a complete absence of unsubstituted C-2, C-4 and C-6 carbons. No evidence emerged of obvious differences between the two types of resoles in the number of methylol groups and methylene bridges present. The additional substituted sites in Resins F appear to be taken up by the hemiformal groups.

The para position in the resoles is almost completely substituted. This position has been found to be more reactive toward formaldehyde than the ortho position under alkaline conditions. The resulting para-methylols are also more reactive than the ortho-methylols in condensation reactions[21,26] thus resulting in the formation of p-p methylene bridges followed by o-p methylene bridges.

Complex Formation between PEO and PFR.

When PEO and PFR are mixed together, in the absence of pulp, a complex forms which separates from the solution[9]. It is generally accepted that the interaction is due to hydrogen bonding between the ether oxygens of the PEO molecule and the phenolic hydroxyl groups of the PFR molecule[6,7].

The amount of PFR interacting with PEO is dependent on pH, ionic strength, shear, temperature, PEO molecular weight and the type of PFR[9].

Figures 6 and 7 show the effect of the addition of different PFRs on the interaction between the resins and PEO. No interaction at all was observed with Resin A. Resins F and J were found to interact the most with PEO, followed by Resin E, while Resins J-M and B-D interact

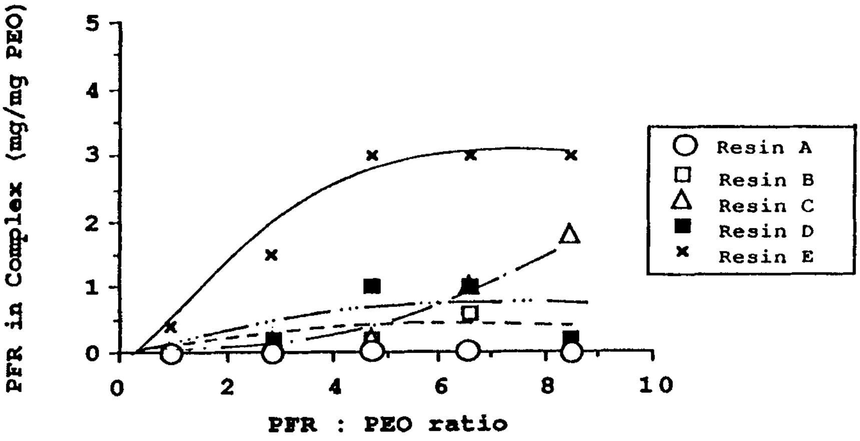

FIGURE 6: Effect of PFR (Resin A to E) on the amount of PFR interacting with PEO.

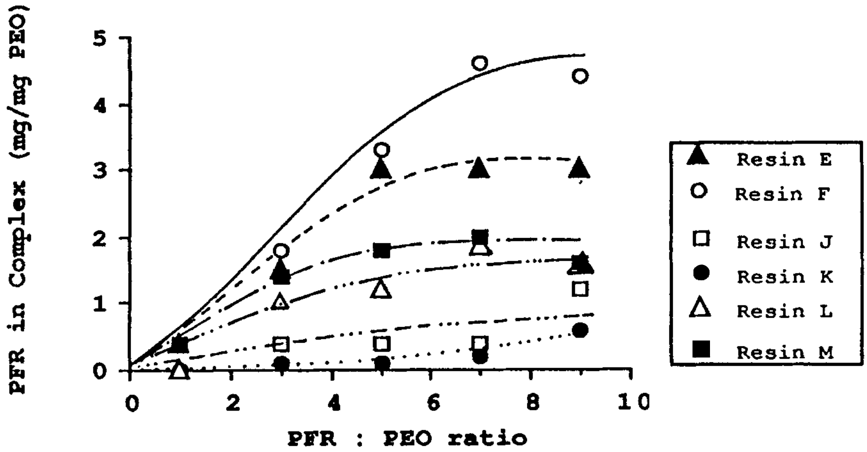

FIGURE 7 : Effect of PFR (Resin E, F, J to M)) on the amount of PFR interacting with PEO.

to similar extents even though the two groups differ structurally.

No clear correlation between molecular weight and interaction with PEO is evident though the resin with the greatest molecular weight (Resins E, H, I) did show the greatest interaction with PEO and the resins with the lowest molecular weights (Resins A and E) interacted the least.

The presence of the methylol side chains on the resoles appear to play very little role in the interaction with PEO. The novolaks, which do not possess these groups, interact to the same extent as the resoles. However, the presence of the hemiformal side chains in Resins F and G do appear to enhance their interaction. These resins, even though they do not have the highest molecular weights, are able to bind to a greater extent than the other resins. The enhanced interaction is possibly due to a hydrophobic interaction between the hemiformal groups and the ethylene groups of the PEO chain.

Retention Performance of PFR and PEO

Figure 8 presents the retention performance of the various PFRs with PEO at a PFR:PEO ratio of 1 and 5. Differences in the nature of the performance of the resoles and the novolak-based resins are evident. At a PFR:PEO ratio of 1, the novolak-based resins and most of the resole resins improve fibre retention to the same extent. As the PFR:PEO ratio increased to 5, the performance of the novolak-based resins decreased while that of the resoles remained the same.

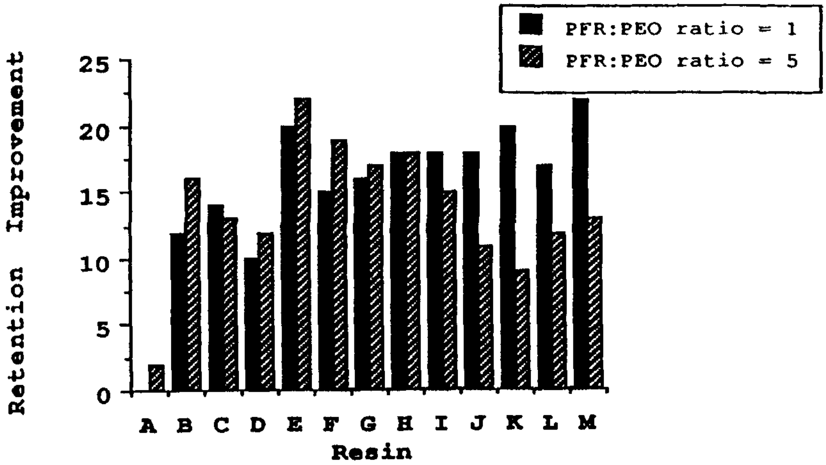

FIGURE 8 : Retention performance of PEO with various PF Resins.

Within the resoles and novolak-based resins, no clear correlation with molecular weight is evident. Resin E, with the highest molecular weight of the series Resins A to G, gave the greatest retention improvement of the resoles. The more condensed versions of this resin, Resins H and I, did not perform as well. The lightly condensed resin (Resin A) gave the least retention performance.

The resin that interacted the most with PEO (Resin F) was found not to give the highest retention improvement.

It is proposed that PFR and PEO improves fibre retention by forming a network structure that traps the fines and fibres. The flocs formed are stabilised by interaction with the surrounding fibres[8]. The size of the network formed by PEO and PFR appears to be critical in the retention performance. Its size is influenced by the molecular weight of PEO as well as the structure and molecular weight of the PFR[9]. The higher molecular weight polymers are believed to form a larger mesh size in the network which can then trap more fines in the network as it is being formed.

The chemical structure of the various PF Resins, in particular the accessibility of the phenolic hydroxyls, appear to play an important role in the interaction between PEO and PFR and their retention performance. It is proposed that the phenolic hydroxyls of the novolak-based resins are more accessible for binding to PEO than are those of the resoles. The novolaks have no bulky side groups around the aromatic ring and are more linear. Complexation between PEO and PFR results in the conformation of the PEO molecule undergoing change and coiling up to adopt a more contracted configuration. The novolak-based resins appear to be able to contract the PEO molecules to a greater extent than the resoles as the PFR:PEO ratio is increased. This results in a more compact network which is not as effective as trapping fines and hence reduces their retention performance.

The phenolic hydroxlys of the resoles are not as accessible for binding, however, their higher molecular weights can compensate for this reduced interaction with PEO. Thus the quantity of resin interacting with PEO is similar for the novolaks and most of the resoles. The network structure formed by the resoles is thus more open than that produced by the novolak-based resins with their greater interaction of phenolic hydroxyls, particularly as the PFR:PEO ratio increases. This can explain the differences in retention performance between the types of resins.

PF Resins such as Resin F, which is able to interact more with PEO because of secondary binding forces between their hemiformal groups and the PEO molecule, are also believed to form a slightly more compact network structure and are thus not able to trap as much material as the structure formed by Resin E.

Further condensation of Resin E to increase its molecular weight did not increase fibre retention above that of Resin E. It appears that the additional condensation of the resin producing a more bulkier, crosslinked molecule may in fact result in a decrease in the interaction of the molecule with PEO.

EXPERIMENTAL

Materials

Resoles and novolak-based phenolformaldehyde resins were kindly prepared under differing reaction conditions by ICI Australia and Chemplex Australia Ltd. for evaluation. All resins were supplied as aqueous solutions of the sodium salt.

Polyethylene oxide with a molar mass of approximately five million was supplied by Union Carbide. A 0.1 % (wt/wt) solution was prepared by slow addition of the powder to a beaker of distilled water being stirred by a magnetic stirrer. The solution was stirred for 90 minutes.

Pulp samples were prepared using thermomechanical pulp produced from *Pinus radiata*. Fines content of the pulp was 65 to 70 % and pulp consistency was 0.5%. The fibre suspensions had a pH of 5 and a conductivity of 600μS/cm.

Methods

PF Resin Analysis

Percent solids was determined, on the resin as received from the manufacturer, by drying 5 ml overnight at 120°C and expressing the dry weight as a percentage of the weight of liquid resin .

Total alkalinity was determined by titrating 1-2 g (± 0.01 g) resin diluted with 150 ml distilled water with 0.25M HCl to pH 7.0 and using the following formula:

$$\%\mathrm{NaOH} = \frac{\mathrm{Titre} \times \mathrm{N} \times 40 \times 100}{1000 \times \mathrm{sample\ weight}}$$

where % NaOH is the total alkalinity, titre is the volume of HCl titrated and N is the molarity of the HCl solution.

Viscosity measurements were performed, at 20°C, on 400 ml of the neat resin using a Brookfield Viscometer fitted with a No. 2 spindle operating at 20 rev min^{-1}. The reading was converted to centipoise by using the conversion table provided with the instrument.

Molecular weight distribution of the resins was measured using gel permeation chromatography (GPC). A Varian 5020 LC with a Varian 9060 polychrom detector was used, fitted with an Ultrapac Column TSK G2000HXL, 7.8 x 300 mm, 5 mm particle size. Tetrahydrafuran, THF, was used as the solvent. The resins were found to be insoluble in the THF so 4 to 5 drops of trichloroacetic acid (10% solution in THF)[27] were added to 2 to 3 ml of neat resin (40% solids) and the volume made up to 25 ml with THF. Polystyrene was used for calibration of the column over the molecular weight range of 400 to 35,000. Calibration was carried out prior to each set of measurements.

High Performance Liquid Chromatography (HPLC), was used to investigate the composition of each resin. 0.5ml of neat resin was diluted to 50 ml in water:methanol (80:20) solvent. Samples were injected into the Varian 5020 analytical liquid chromatograph, fitted with a Varian 9060 Polychrom detector and a Waters U Bondapak 5 micron 4.6mm id x 25cm column. A solvent gradient programme starting at 20% methanol:80% water and going to 100% methanol after 20 minutes,then being held for 5 minutes, with a flowrate of 1 ml/minute was used. Absorbance at 278nm and 220nm wavelength were used for monitoring of the components on the displays on the instrument and the D5654 data system.

^{13}C nuclear magnetic resonance spectra (NMR) were obtained using a Bruker AM300 Nuclear Magnetic Resonance Spectrameter. Two to three ml of each resin was dissolved in an equivalent amount of D_2O. Spectra were run with a pulse width of 4.1 µs (90°),a pulse delay of 25 s, 25,000 Hz spectral width, 0.32 s acquisition time, 16K data points and 4Hz line broadening. Grated decoupling was used to suppress the Nuclear Overhauser Effect. Chemical shifts were measured relative to tetramethylsilane (TMS).

Integration of the area under the various chemical shifts is carried out. The number of groups per aromatic were calculated by summing the area under the peaks in the aromatic region, 116-172 ppm, and then normalising it by setting it equal to six carbons. The relative proportions of the areas of each region was then determined and normalised. The C-3 and C-5 carbons, assumed to be unsubstituted, were set equal to 2 carbons. The substituted C-2, C-4 and C-6 were then determined by subtracting 2 from the value calculated for the 127-135 ppm region.

Complex Formation

PFR and PEO solutions were mixed together in a dynamic drainage jar under the same conditions used in the retention experiments. The concentration of PFR added to the jar was varied from 0 to 22.5 mg/l while the concentration of PEO was maintained at 2.5 mg/l. HCL was used to adjust the pH of the solution to 5. The amount of PFR interacting with the PEO was calculated by analysing the filtrate from the drainage jar and subtracting the amount of polymer present from the original solution. PFR concentration in the filtrate was determined by measuring the absorbance of the peak at 285nm in the ultraviolet (UV) spectrum. The pH of the solution was adjusted to 12 with NaOH prior to the UV absorbance measurement in order to dissolve any colloidal PFR. Colloidal PFR was found to pass through the screen in the drainage jar.

Retention Aid Performance

Retention measurements were made using a dynamic drainage jar fitted with a piece of machine fabric. A stirrer speed of 1100rpm was used. 500ml of 0.5% pulp concentration was added to the jar, followed by PFR. Ten seconds later, PEO was added. The suspension was stirred for a further 20 seconds before the drainage clamp was removed. The volume of filtrate drained in the next 30 seconds was collected, filtered, dried and weighed. Fibre retention (FR) was calculated from equation[1], using the fibre concentration (C_S) of the pulp added to the jar and the fibre concentration (C_f) of the filtrate drained:-

$$FR = (C_S - C_f) \cdot 100/C_s \qquad [1]$$

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