EFFECT OF RESIN MOLECULAR WEIGHT ON BONDING FLAKEBOARD

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ABSTRACT

Information on the effect of resin molecular weight on flakeboard properties is limited. A commercial phenol formaldehyde flakeboard resin was separated into two molecular weight fractions by diafiltration. Aspen flakeboards were prepared with the different resin fractions. Penetration characteristics of the different fractions were determined microscopically. Results indicate that both low and high molecular weight components of the resin are needed to achieve optimum board properties.

Keywords: Molecular weight, phenolic resin, diafiltration, wood adhesive, flakeboard.

INTRODUCTION

Data on the effect of resin molecular weight on flakeboard properties are very limited. Nearn (1974) pointed out that ultrafast adhesives required a surface primed with a low molecular weight resin to achieve a fully exterior bond. Wilson and coworkers (1979) observed in oak flakeboard that the molecular weight of the PF resin was significantly related to internal bond, but not to modulus of rupture. Gollob and coworkers (1985) found that in parallel-laminated panels a higher weight-average molecular weight (M_w) resin gave higher wood failure than a low M_w resin. This study was undertaken to examine the effect of resin molecular weight on aspen flakeboard.

MATERIALS AND METHODS

Fractionation

A commercial phenol formaldehyde (PF) flakeboard resin (Resin A) was separated into two molecular weight components by diafiltration. The diafiltration was carried out on an Amicon TC-5E thin channel ultrafilter equipped with an air-operated dual diaphragm pump and a 20 L stainless steel solution reservoir. The separation was done at room temperature with YM2 membranes (150-mm diameter, nominal 1,000 molecular weight cutoff). Tubing and gauges were wrapped with aluminum foil to keep out light. The resin was diluted to 10% solids with tap water prior to diafiltration. During the filtration, the volume was kept constant through the addition of water by siphoning. The two fractions were concentrated on the rotary evaporator with sufficient heat applied to maintain the temperature at 25 C. Sodium hydroxide adjustments were made by the addition of granular NaOH. Solids adjustments were made by the addition or removal of water.

The molecular weight distribution which resulted from the diafiltration of the phenol/formaldehyde resin is shown in Fig. 1. The chromatograms were obtained from a Sephacryl S-200 column with 0.1 N NaOH used as the eluant. The output was monitored with an ultraviolet detector at 254 nm and the number average
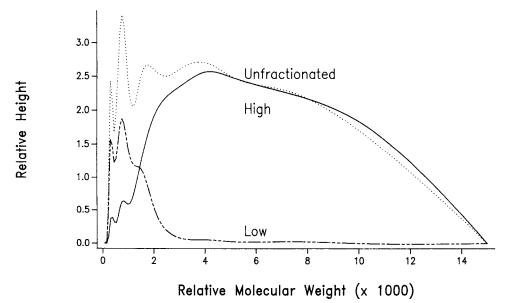
FIG. 1.   Molecular weight distribution of unfractionated Resin A and high and low molecular weight components of fractionated Resin A.

(M_n) and weight average (M_w) molecular weights determined relative to polystyrene standards. Twenty-seven percent of the mass separated as the low molecular weight fraction (<1,000, nominal) and was essentially free of high molecular weight material (>1,000, nominal). The balance of the material was found in the high molecular weight fraction. This latter fraction was predominantly high molecular weight, but did contain a component of low molecular weight.

Flakeboard preparation and testing

Aspen flakes (+16 mesh, random width, 0.5 mm thick, ~2.5 cm length) were sprayed with a wax emulsion followed by the binder. A Paasche handheld sprayer with a CFO-9 nozzle operated at an air pressure of 200–275 kPa was used for application of the wax at a 1% level and the binder at a 5.5% level. After forming, the mats were pressed to a nominal 9.5-mm thickness and 660 kg/m³ density at 205 C for seven minutes on a Wabash electric press.

TABLE 1.   Specifications of molecular weight fractions of Resin A.

Resin	Viscosity (Gardner-Holt)	Non-volatiles (%)	NaOH content	
			(%)	(NaOH/other solids)
Resin A	P	44.22	8.26	0.23
lmw¹ fraction	OOP	56.67	14.97	0.36
hmw¹ fraction	Q	38.02	6.21	0.20
Recombined fractions	QQR	44.36	8.34	0.23
Resin A + NaOH	R	47.19	12.45	0.36
hmw + NaOH	S	44.23	11.39	0.35
Recombined + NaOH	QR	46.95	12.13	0.35

¹ lmw = low molecular weight; hmw = high molecular weight.

TABLE 2. *Results of testing flakeboards prepared with different molecular weight fractions of Resin A adjusted to equal viscosity and percent NaOH.*

Resin fraction	Density (kg/m3)	Internal bond (kPa)	2 h boil		24 h soak	Thickness swell	
			Internal bond (kPa)	Thickness swell (%)	Water adsorption (%)	Center (%)	Edge (%)
Resin A	637 ± 12[1] (AC)[2]	885 ± 73 (B)	571 ± 34 (CD)	21.1 ± 1.1 (EF)	41.9 ± 3.8 (DE)	18.5 ± 2.1 (F)	24.9 ± 2.9 (CD)
lmw[3] fraction	615 ± 21 (E)	298 ± 52 (E)	2 ± 0 (H)	68.3 ± 5.6 (A)	90.5 ± 2.0 (A)	42.5 ± 3.8 (A)	44.9 ± 4.8 (A)
hmw[3] fraction	657 ± 20 (A)	892 ± 38 (B)	596 ± 52 (BC)	24.1 ± 1.2 (CD)	44.7 ± 5.4 (D)	20.5 ± 2.4 (DE)	25.9 ± 2.0 (C)
Recombined fractions	633 ± 17 (CDE)	867 ± 56 (BC)	528 ± 53 (D)	21.7 ± 1.3 (DE)	54.0 ± 3.2 (C)	21.3 ± 1.4 (CD)	25.9 ± 0.4 (C)
Resin A + NaOH	637 ± 11 (CD)	994 ± 61 (A)	749 ± 36 (A)	18.1 ± 0.8 (F)	45.0 ± 4.4 (D)	19.3 ± 0.9 (EF)	23.1 ± 0.9 (D)
hmw + NaOH	625 ± 13 (DE)	918 ± 38 (B)	779 ± 54 (A)	20.8 ± 1.1 (EF)	51.3 ± 4.8 (C)	23.2 ± 2.3 (B)	25.6 ± 1.4 (C)
Recombined + NaOH	633 ± 14 (CDE)	906 ± 34 (B)	642 ± 78 (B)	18.5 ± 0.7 (F)	60.0 ± 8.1 (B)	22.8 ± 0.8 (BC)	24.2 ± 0.8 (CD)

[1] Mean ± 95% confidence limits.
[2] See text for explanation of letters.
[3] lmw = low molecular weight; hmw = high molecular weight.

TABLE 3.   *Gel permeation chromatography and ^{13}C NMR characterization of liquid Resin A molecular weight fractions.*

Resin	M_n[1]	M_w[2]	M_w/M_n	Unsubst φOH	Subst φOH	-CH$_2$- φOH	-CH$_2$O- φOH	F/P[3]
Resin A	1,344	3,701	2.75	0.76	2.24	1.65	0.59	1.42
lmw[4]	602	1,034	1.72	1.18	1.82	1.12	0.70	1.26
lmw[4]	2,643	4,877	1.85	0.39	2.61	2.12	0.49	1.55

[1] Number average molecular weight.
[2] Weight average molecular weight.
[3] Formaldehyde/phenol ratio.
[4] lmw = low molecular weight; hmw = high molecular weight.

After trimming to 33 × 33 cm, the panels were conditioned at 50% relative humidity prior to testing. The panels were cut into 5.1-cm squares for internal bond tests and 15.2-cm squares for the 24-hour soak tests. The density, as-is internal bond, and 24-hour soak tests were conducted according to ASTM D1037. Additional samples (5.1 × 5.1 cm) were immersed in boiling water for two hours, dried overnight at 105 C, and then reconditioned to 50% relative humidity before measurement of the internal bond and thickness swell.

Twelve determinations of density, internal bond, 2-hour boil internal bond, and 2-hour boil thickness swell were made. Four specimens were tested after the 24-hour soak. The data presented in Tables 2 and 5 are the mean and 95% confidence limits of these determinations. The letters in parentheses following each mean result from an analysis of variance of the data with Duncan's multiple range test. Means with the same letter are not significantly different. A mean may have more than one letter associated with it to signify different groupings.

Microscopic examination

Droplets, approximately one millimeter in diameter, of each fraction were placed on uniform, microtomed aspen flakes for one-half hour and cured at 200 C, for 15 minutes. One typical droplet of each fraction was selected, embedded, cross-sectioned and examined by transmitted brightfield microscopy. Gross appearance of the fine resin droplets, gross (cellular) penetration, and cell-wall penetration of the various fractions were determined.

RESULTS AND DISCUSSION

Flakeboard panels prepared with the two different molecular weight fractions of diafiltered PF resin were tested to evaluate the effect of molecular weight, resin viscosity, and sodium hydroxide content. The resin specifications appear in Table

TABLE 4.   *High molecular weight Resin A panel preparation data.*

Resin description	Viscosity (Gardner-Holt)	Total solids (%)	Loading Total (%)	Loading Organic (%)	Loading NaOH (%)	Forming moisture (%)
Resin A	KL	44.04	5.50	4.43	1.07	11.6
hmw[1]/prop.[2] NaOH	HI	39.54	4.05	3.26	0.79	11.1
hmw/neat NaOH	I	41.30	4.33	3.26	1.07	11.4

[1] hmw = high molecular weight.
[2] Proportional.

TABLE 5. *Properties of flakeboard prepared with high molecular weight component of Resin A.*

Resin description	Density (kg/m3)	Internal bond (kPa)	2 h boil		Water absorption (%)	24 h soak	
			Internal bond (kPa)	Thickness swell (%)		Thickness swell	
						Center (%)	Edge (%)
Resin A	646 ± 13[1] (ABC)[2]	811 ± 50 (C)	421 ± 70 (E)	19.4 ± 2.1 (EF)	38.7 ± 3.8 (E)	16.5 ± 0.9 (G)	21.0 ± 0.7 (E)
hmw/prop.[3] NaOH	655 ± 16 (AB)	668 ± 34 (D)	264 ± 49 (G)	31.0 ± 2.6 (B)	52.7 ± 4.2 (C)	23.5 ± 1.6 (B)	28.1 ± 1.8 (B)
hmw/neat NaOH	653 ± 14 (AB)	672 ± 45 (D)	334 ± 31 (F)	25.6 ± 2.7 (C)	53.7 ± 6.6 (C)	22.3 ± 1.1 (BC)	25.3 ± 1.3 (C)

[1] Mean ± 95% confidence limits.
[2] See text for explanation of letters.
[3] Proportional.

TABLE 6. *Penetration characteristics of different fractions of Resin A on aspen microtomed flakes.*

Resin fraction	Cross-sectional appearance of resin droplet	Gross penetration	Cell wall darkening/penetration adjacent to adhesive
Resin A	Droplet very high, very large void space	None	Very slight darkening
lmw[1]	Droplet high, large void space	About 1–2 cells deep	Definite darkening
hmw[1]	Droplet very low (flat); no void space	None	Definite darkening
Resin A + NaOH	Droplet of medium height; medium size void space	About 1 cell deep	Definite darkening
hmw + NaOH	Droplet low, small void space	About 1 cell deep	Extensive darkening (up to 2 cells deep)

[1] lmw = low molecular weight; hmw = high molecular weight.

1, and the corresponding board test results appear in Table 2. Equivalent resin viscosities to achieve similar resin spraying patterns and consequently equivalent resin distribution were found to be extremely important. Another set of panels prepared with these same fractions, but with unequal viscosities, and hence different distributions of resin on the wood, had widely varying properties. The effects of the other resin variables were confounded and impossible to separate from the spraying variable.

The data in Table 2 indicate that the high molecular weight (hmw) fraction performed nearly as well as the unfractionated resin, although thickness swell was slightly higher for the hmw fraction. In contrast, the low molecular weight (lmw) material performed poorly alone and seemed to contribute little as a binder, as a bulking agent, or as a solvent to enhance the effectiveness of the high molecular weight material. If significant bulking or solvent effects were associated with the low molecular weight component, the hmw fraction should have shown much worse water resistance than the unfractionated resin, but it did not.

Sodium hydroxide was added to Resin A, the hmw fraction, and the recombined fractions to achieve the same NaOH/solids ratio present in the lmw fraction. This was done to determine if the poor results for the lmw fraction were related to the high NaOH content of this fraction. This increase in NaOH content resulted in improved or equivalent dry tensile strengths and a marked improvement in the tensile strengths after a 2-hour boil. In the case of Resin A, the water-related properties with and without added NaOH were equivalent. With the one exception of the 24-hour soak, center swell for the hmw fraction, the thickness swell for the recombined and hmw fractions remained the same or improved. In contrast, the water absorption increased for the latter two fractions. In no case, however, did the swell or absorption approach the poor values found for the lmw fraction. This indicates that the high NaOH content was not solely responsible for the poor properties observed with the lmw fraction.

The molecular weight and functional group characterization of the resin fractions are shown in Table 3. The data indicate, relative to phenolic hydroxyls, a higher concentration of substituted phenols and methylene linkages in the high molecular weight, more advanced fraction. This reflects the higher degree of
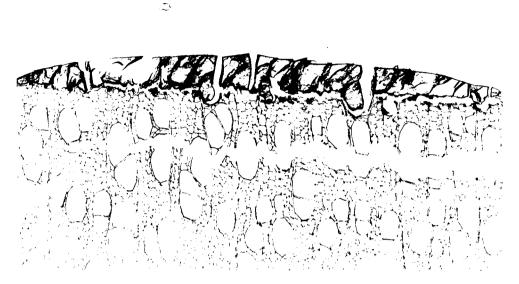
FIG. 2.   Droplet of high molecular weight fraction of Resin A cured on microtomed aspen flake. Droplet very low (flat) with no void space. 30×.

substitution: 2.6 out of the 3.0 reactive ortho and para positions on the phenol ring. Only 13% of the reactive positions on the ring are available for the additional curing reactions. In contrast, 39% of the reactive ring positions in the low molecular weight fraction are available for reaction.

Considering the potential for crosslinking through these available reactive sites, it did not seem reasonable that the performance of the hmw material would not be affected by the lmw fraction. To obtain the set of data just discussed, the panels were prepared from the hmw fraction at a resin loading of hmw material equivalent to the total loading of the unfractionated resin and not at the level of hmw material added with the unfractionated resin; i.e., high molecular weight material had been added in place of the low molecular weight component found in the unfractionated resin. To gain insight into this difference, additional panels were prepared with a hmw loading proportionately reduced to give a loading equivalent to hmw material applied with the neat resin. Also, two different levels of sodium hydroxide concentration were used. At the first level, the amount of NaOH was proportional to the amount of high molecular weight component present in the neat resin. At the second level, the concentration of sodium hydroxide corresponded to that found in the neat resin. The specific loadings and additional resin and board preparation data are given in Table 4. Resin solids and viscosity were adjusted to maintain equivalent resin distribution and moisture content.

The properties of the panels prepared with the two variations of hmw material, as well as an unfractionated Resin A control, are listed in Table 5. The panels prepared from the hmw component were comparable. Higher NaOH levels gave
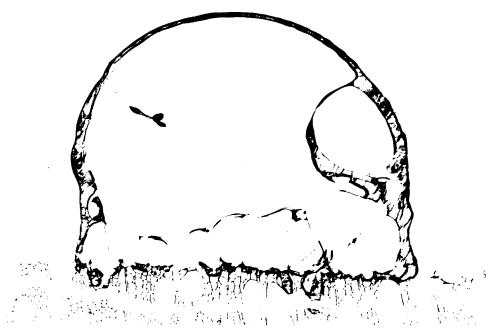
FIG. 3.   Droplet of Resin A cured on microtomed aspen flake. Droplet very high, with very large void space. 30×.

equivalent or slightly better results; however, both sets were inferior to the control panels which contained both the high and low molecular weight fractions of the resin. The high molecular weight material, when applied in proportion to the amount found in the neat resin, did not function as well as the neat resin. In comparison to the results from the earlier set with the hmw component at higher loading, there was a reduction in tensile strength and greater water absorption and thickness swell. The data from the first set do show that the hmw material can function alone. However, these data from the second set of panels demonstrate that when concentration or loading is taken into consideration, performance is improved by the presence of the lmw material. These more reactive lmw components likely serve to link the larger hmw polymers as the resin is cured.

A comparison was made of the penetration characteristics of the different fractions of Resin A. The results are summarized in Table 6. The hmw fraction seemed to spread out on the surface most readily with the formation of a large, flat droplet (Fig. 2) that lacked the interior void space present in the droplets of the other fractions (Fig. 3). The lmw fraction, which had yielded poor board properties (Table 2), had the highest NaOH level (15%, Table 1) and demonstrated the greatest gross penetration (1–2 cells, Table 6). It is possible that this high gross penetration does not leave sufficient adhesive at the glueline between the flakes for an adequate bond.

In this limited examination, NaOH levels did not seem to relate to levels of cell-wall penetration. Cell-wall penetration is the result of the complex interaction between the resin, the NaOH, and the chemical components of the wood. (Dark-

ening was assumed to reflect cell-wall penetration, although the color of the cured resin can influence this interpretation.) All fractions seemed to demonstrate at least some cell-wall penetration. Resin A had the least and the hmw fraction + NaOH had the greatest penetration (Table 6). This latter result is probably due to the NaOH, which characteristically opens up cell-wall structure. The combination of Resin A and NaOH, which demonstrated desirable board properties (Table 2), resulted in gross penetration about one cell deep and definite cell-wall penetration. This provided both the required mechanical interlocking at the surface and cell-wall penetration below the surface for bonding (Table 6).

The cause of the large void spaces within the droplets, from all the fractions except the hmw fraction, was not explored. These spaces are probably the result of gas formation during the resin curing process.

CONCLUSIONS

These results suggest the lmw fraction of the PF resin examined is of little influence as a bulking agent or solvent to enhance penetration of the high molecular weight component, nor alone is it effective as a binder. Optimum resin performance is achieved when both high and low molecular weight fractions are present with the lmw material acting to crosslink the larger oligomers. These conclusions are supported by the recent results of Steiner (1985) who indicated that a combination of lmw and hmw components was optimum for acid curing phenolic resins and Peterson (1985) who demonstrated that a high proportion (70%) of lmw resin (0–3,000 mw units) was optimum for southern hardwood flakeboard. The challenge for the resin chemist is to formulate resins with a range of molecular weight appropriate to the wood species and flakeboard process to be used.

ACKNOWLEDGMENTS

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