CHARACTERIZATION OF CHEMICAL PROPERTIES AND FLOW PARAMETERS OF POWDERED PHENOL-FORMALDEHYDE RESINS

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ABSTRACT

A range of powdered phenol-formaldehyde resins was studied to examine the relationships between chemical structures and cure and flow parameters. Nine commercially available powdered waferboard/ oriented strandboard resins and six laboratory-synthesized resins were chemically characterized by gel permeation chromatography and proton magnetic resonance spectroscopy. The flow properties of the resins were determined using thermal mechanical analysis and other empirical techniques. Those resins containing greater proportions of low molecular weight species tended to exhibit greater total flow than higher molecular weight resins, with most of this flow occurring at lower temperatures. For similar molecular weight distributions, resins containing fewer methylol groups exhibited more flow. A liquid resin sample converted to a powder by spray-drying showed a higher degree of condensation than the same resin converted by freeze-drying. A resin sample that had been stored for over seven years exhibited a major shift to higher molecular weight values and greatly reduced flow compared to a fresh sample of the same resin.

Keywords: Phenol-formaldehyde, molecular weight, flow measurement.

INTRODUCTION

Powdered adhesive resins based on phenol and formaldehyde have been used by the North American waferboard and oriented strandboard (OSB) industries since 1975. Advantages over their liquid counterparts include lower resin quantity requirements in panel manufacture, better resin distribution on wood flakes, and shorter possible panel pressing times. Since different regions of the vertical plane of a panel experience different conditions during hot-pressing, flakeboards are often manufactured with adhesive systems incorporating resins of two different formulations for the face and core. Core resins have been developed for use in the middle layers of the panel, where the temperature rise is less rapid and the final temperature attained is lower than in the face layers on the outside of the panel.

The apparent trend in resin manufacture seems to have been the production of core resins of increasingly greater molecular weights. Since the chemical structures of these resins are closer to that of the final, cured, cross-linked structure, faster curing times are possible. Some adverse effects have been observed with these resins. Pre-cure of the resin may occur, and it would appear that in some cases insufficient flow of the resin (Go 1988) and subsequent reduced penetration of the resin into the wood flakes have occurred, leading to unsatisfactory bonding.

The importance of attaining adequate resin flow in the formation of bonds in plywood has been recognized. Resins of high viscosity do not spread well and produce thick glue lines. On the other hand, resins of very low viscosity may

overpenetrate the veneers leaving starved glue lines (Gupta and Sehgal 1979). This dependence on viscosity and its effect on flow become more critical at lower wood moisture contents.

Little work on the flow properties of powdered resin systems has been reported. Jones (1952) studied the molecular weights, flow and melt viscosities of a series of powdered novolak resins. A smooth relationship was found between flow (as measured by the distance a resin pellet flowed down an inclined, heated glass plate) and the number average molecular weight (M_n). Higher values of M_n yielded less flow. Katovic and Stefanic (1985) used the technique of thermal mechanical analysis (TMA) to study powdered novolaks. Two distinct levels of penetration of the TMA probe were noted. The first, around 95 C, was ascribed to the visual melting of the resin, but the nature of the second region, around 115 C, was not discussed. A study of powdered waferboard resins (Go 1988) indicated that poor resin flow was associated with low internal bond strengths. It was suggested that resin flow was only of importance at borderline moisture contents, pressing times or both. Flow was assessed qualitatively from the surface appearance of the waferboard panels.

A research program was initiated to investigate the relationship of cure and flow parameters in powdered phenol-formaldehyde resins to waferboard/OSB bond performance. One purpose of this study was to develop detailed descriptions of the chemical structures and flow characteristics of a number of commercially available and laboratory-synthesized resins. The effects of the molecular weight distributions and reactivities of the resins on their flow properties were then determined. Laboratory resins were synthesized first to show that resins having similar properties to commercial resins could be prepared in the laboratory; second to produce a range of "purer" resins containing none of the various additives that may be added to commercial resins; and third to incorporate a bromine label that could be used in subsequent studies to map the distribution of the resins at a glue line. The additives in the commercial resin formulations may be included for a number of purposes. They may aid efficient particle formation during spray-drying; they may aid in the release of finished panels from the press platens; or they may act as flow promoters or cure promoters. Thus, some of the additives may mask or enhance certain characteristics of the resins. The bromine label was incorporated in the form of *meta*-bromophenol. The bromine atom in the molecule is *ortho-*, *para*-directing in relation to its own position and thus *meta*-bromophenol will promote reactions at the same ring positions as does pure phenol. It was assumed that the *meta*-bromophenol was evenly incorporated into all molecules across the molecular weight distribution.

EXPERIMENTAL

Materials

Nine samples of commercially available waferboard/OSB resins were used. Eight different formulations were studied using fresh samples of resin. Resins A and B were designated as face resins by their manufacturers, Resins C, D1 and D2 were designated for use throughout the panel and Resins E, F, G and H were designated as core resins. Resins D1 and D2 were samples produced by the same manufacturer and were identified by the same designation. Resin D1 was a fresh
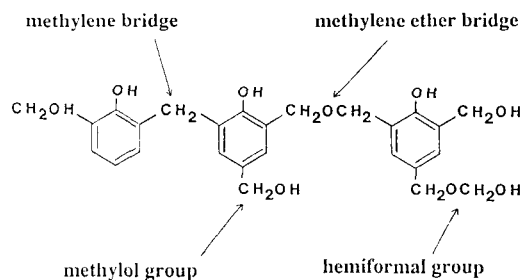
FIG. 1. Representative structure of a phenol-formaldehyde resin molecule, showing the functional groups present.

sample of the resin, whereas Resin D2 had been stored in the laboratory (at room temperature) for over seven years. Resin D2 was included in the study to determine if any discernible transformations occurred to the resin during storage.

Six resins were synthesized in the laboratory. Phenol, formaldehyde, and sodium hydroxide (molar ratio 1.0:2.0:0.2 and 1.0:2.0:0.4) were reacted in a resin kettle. For all the resins, 10% of the phenol content, by weight, was replaced by *meta*-bromophenol, for use in a subsequent study. The cooking times for the resins, the cooking temperature schedule used and the viscosities of the liquid resins as measured by Gardner-Holt viscosity tubes are shown in Fig. 1. Thus a series of resins with different molecular weight ranges and different reactivities were produced. The liquid resins produced were freeze-dried and ground to the powdered form (to pass a 200-mesh, i.e., 75-μm, screen). A portion of one liquid resin was spray-dried to the powdered form. Two different formaldehyde solutions were used for Cooks 1–3 and Cooks 4–6. Also, two levels of sodium hydroxide were used in the synthesis of the laboratory resins. The first level used (sodium hydroxide:phenol molar ratio 0.4:1.0, Cooks 1–3) produced resins with higher pH values than those of the commercial resins. In an attempt to minimize the differences between the laboratory and commercial resins, a second, lower level of sodium hydroxide (sodium hydroxide:phenol molar ratio 0.2:1.0, Cooks 4–6) was used. This produced pH values much closer to those of the commercial resins.

^{1}H-Nuclear magnetic resonance spectroscopy

^{1}H-nuclear magnetic resonance (NMR) spectroscopy provides information about the relative proportions of the different functional groups present in the resins. The resin samples were acetylated in a solution of anhydrous pyridine and freshly distilled acetic anhydride prior to analysis. After precipitation in water, the acetylated material was extracted into dichloromethane and rinsed three times each with aqueous hydrochloric acid (2%), aqueous sodium bicarbonate (7%), and distilled water. The extract was dried over magnesium sulphate overnight, filtered, flash evaporated, and placed in a vacuum over phosphorus pentoxide for 24 hours. The samples were then dissolved in deuterated chloroform. The ^{1}H-NMR spectra were obtained on a Varian XL-300 instrument using tetramethylsilane as the internal reference. Two acetylated samples of each resin were prepared, and two integrations were performed on the spectrum from each sample. The average of these four integrations was used in subsequent calculations. The relative propor-

tions of the different functional groups were calculated according to the equations developed by Woodbrey et al. (1965); Steiner (1975); and Gollob (1983).

Gel permeation chromatography

The molecular weight distributions of the resins were determined by gel permeation chromatography (GPC). A Spectra-Physics 8810 pump was used to pump the tetrahydrofuran (THF) solvent through a Rheodyne 7125 injector loop to the Varian Micropak TSK exclusion column series at a rate of 1.0 ml/min. The resins were analyzed in the acetylated state as 0.5% w/v solutions in THF. A 5-cm GH8P guard column was used, followed by four analytical columns (1000H, 2500H, 3000H and 4000H), each 25 cm in length. A Kratos Spectroflow 757 UV/VIS detector was used at a wavelength of 280 nm. The output signal was sent to a Spectra-Physics 4290 integrator equipped with a memory module and GPC-Plus microchip. The columns were calibrated using polystyrene standards. Five replications were performed for each sample.

Thermal mechanical analysis

Dimensional changes taking place in a powdered resin sample during its melting and subsequent cure, as a function of temperature, can be monitored by thermal mechanical analysis (TMA). A Perkin-Elmer TMS-2 instrument was used for the analyses. For each analysis a resin sample (15 ± 2 mg) was weighed into an small aluminum sample pan and an aluminum lid placed on top of the resin. A probe was lowered onto the lid and a weight of 300 g was applied to the probe, producing a pressure of 95.2 kPa over the area of the lid. The resin sample was then enclosed in a furnace. The temperature range scanned was 20–200 C at 10 C/min. As the temperature of the resin increased it melted and flowed. The resulting drop in the probe level was measured by a linear displacement transducer and recorded on an X-Y plotter. The level of the probe was then recalculated as a percentage of its original height. Three replications were performed for each resin.

Fusion diameter

The determination of the fusion diameter is a measure of the fluidity of a fusible resin when subjected to a specific temperature and pressure. Cylindrical pellets (12.0 mm in diameter, 5.0 mm in height) were prepared from 0.5 g resin using a steel die. Each pellet was placed on a preheated glass plate on a hot-plate at 140 C. A second preheated glass plate was placed on top of the pellet followed by a weight sufficient to deliver an initial force of 0.47 MPa. After three minutes the weight was removed and the diameter of the pellet measured at four places to calculate an average value. Three replications were performed for each resin.

Stroke cure time

The time taken for a sample of powdered resin to melt and then harden on a hot-plate is a measure of its reactivity at high temperature. The stroke-cure time is somewhat of a subjective measurement but does provide a basic indication of the reactivity of a resin. A 0.25-g sample of powdered resin was placed on a pre-heated glass slide on a hot-plate at 150 ± 2 C. The resin was spread with a small steel spatula and alternatively smoothed and patted. The resin was worked until

TABLE 1. *Chemical characteristics of laboratory resins.*

Resin	Functional groups[1]					F:P[2]	M_n[3]	M_w[3]	pH[4]
	-H	-CH₂OH	-CH₂-O-CH₂-	-CH₂-	-CH₂-O-CH₂OH				
Cook 1	0.26	0.98	0.00	1.73	0.02	1.98	1,669	18,688	9.87
Cook 2	0.26	1.00	0.00	1.69	0.04	2.00	1,564	7,577	9.92
Cook 3	0.27	1.13	0.00	1.56	0.04	2.02	1,264	4,853	9.65
Cook 4	0.09	1.11	0.00	1.70	0.09	2.15	1,454	5,187	8.89
Cook 5	0.11	1.25	0.00	1.56	0.09	2.20	1,160	4,660	8.93
Cook 6	0.09	1.27	0.00	1.54	0.08	2.21	1,126	2,484	8.77
Cook 5 (s.d.)[5]	0.12	1.12	0.00	1.71	0.05	2.07	1,388	6,437	8.80

[1] The total of the functional groups per phenolic nucleus is 3. The other ring positions are occupied by the hydroxyl group and unreactive meta sites.
[2] F:P = formaldehyde:phenol molar ratio.
[3] Molecular weight values are for the resins in the acetylated condition.
[4] pH of 2% w/v aqueous solution.
[5] Spray-dried sample.

strings no longer formed when the spatula was momentarily raised. Three replications were performed for each resin.

RESULTS AND DISCUSSION

Chemical structures and molecular weight distributions

Laboratory resins. — The relative proportions of the different functional groups present in the laboratory resins as found from the ^{1}H-NMR spectroscopy analyses and the molecular weight values calculated from the GPC results are shown in Table 1. The typical functional groups present in phenolic resins are illustrated in Fig. 2. Within each series of cooks, the relative proportion of methylol groups decreased with longer synthesis time. The corresponding increase in the relative proportion of methylene bridges was in agreement with the accepted mechanism of the condensation reactions of phenol-formaldehyde resins (Martin 1956; Megson 1958). The molecular weight distributions of the laboratory resins (Fig. 3) show a shift to increasingly higher molecular weight values from Cook 6 to Cook 4 and from Cook 3 to Cook 1. As the molecular weights increase the relative proportion of low molecular weight species (below 1,000 molecular weight units) is seen to decrease.

It is interesting to note the differences between the samples of Cook 5, which were either freeze-dried or spray-dried. The spray-dried sample contained fewer methylol groups and hemiformal groups and a correspondingly greater proportion of methylene linkages than did the freeze-dried sample. This indicates that the resin had undergone a greater extent of condensation during the spray-drying procedure than during the freeze-drying procedure. The temperature used in the spray-dryer was 200 C. However, the resin droplets sprayed into the drying chamber would not attain this temperature because of their short residence time. It would appear, though, that the temperature attained was sufficient to cause some additional condensation of the resin.

The molecular weight distributions of the freeze-dried and spray-dried samples of Cook 5 are shown in Fig. 4. A distinct shift to higher molecular weight values is evident for the spray-dried sample. This supports the ^{1}H-NMR results. The distribution of the spray-dried sample was very close to that of Cook 4. It appears
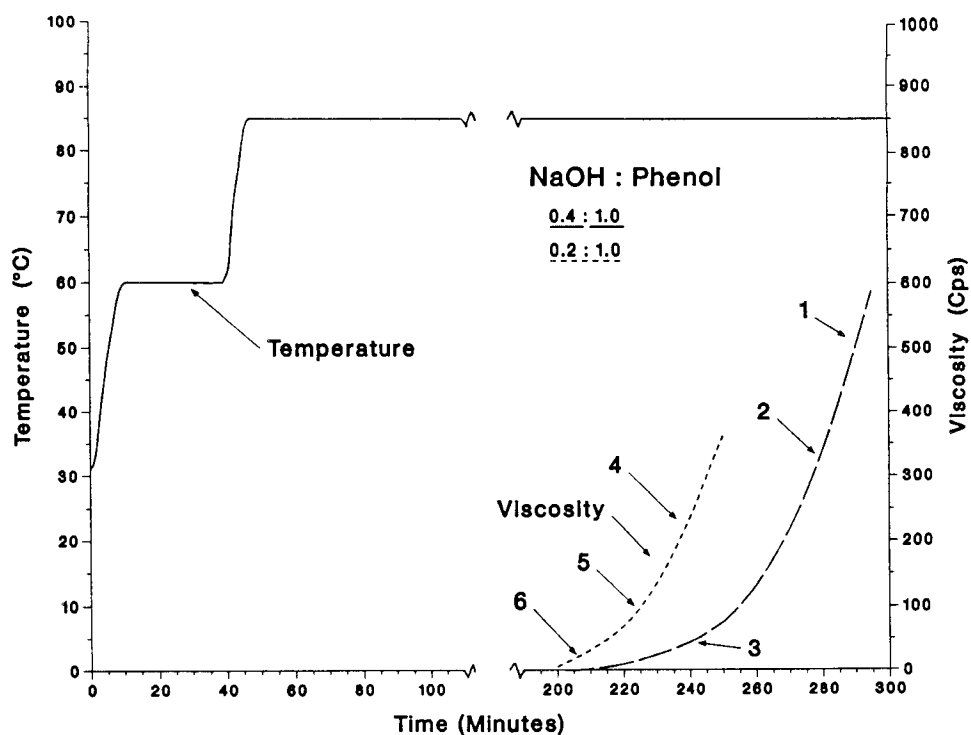
FIG. 2. Cooking temperature schedule and resin viscosities as a function of cooking time for liquid resin syntheses. The arrows and numbers indicate the points at which the synthesis of each resin was ended by rapid cooling. Formaldehyde : phenol ratio, 2.0:1.0.
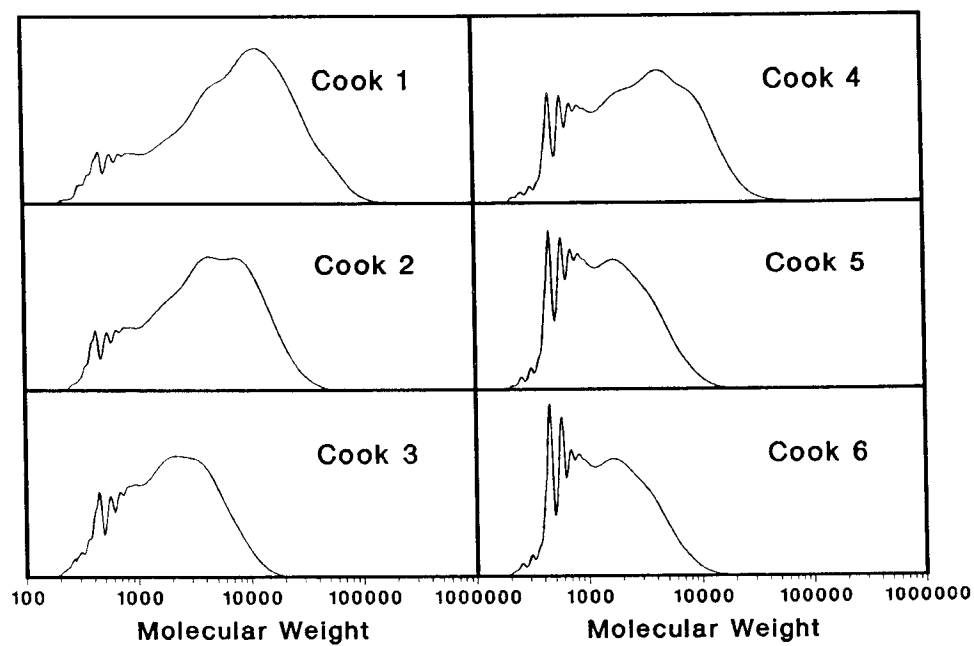

FIG. 3. Molecular weight distributions of spray-dried laboratory resins (acetylated form).
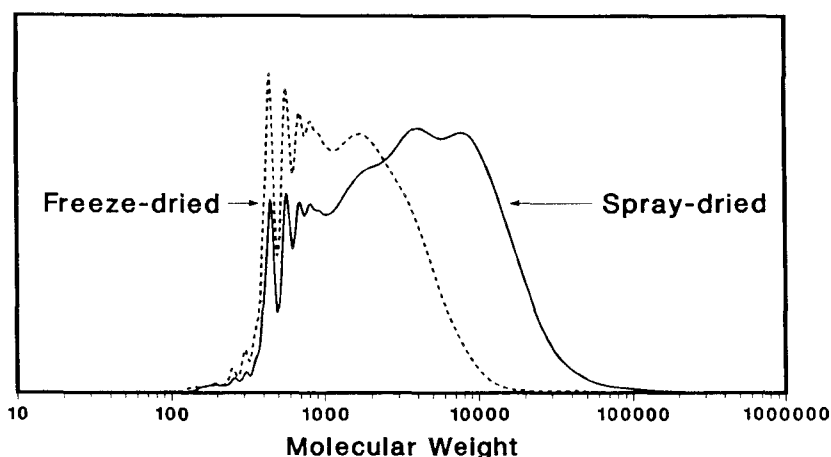
Fig. 4.   Molecular weight distributions of Cook 5 after freeze-drying and spray-drying (acetylated form).

that the spray-drying procedure produced an amount of condensation equivalent to approximately 10–15 minutes of cooking during the synthesis stage (the difference in the cooking times of Cook 5 and Cook 4). This suggests that the spray-drier can be used as a reactor in the preparation of resins. It is known that close attention to spray-drying conditions is necessary to produce the desired distribution of particle sizes. In addition it seems to be possible to alter the chemical attributes of a resin by manipulating the drying conditions.

Commercial resins.—The relative proportions of the functional groups present in the commercial powdered resins are shown in Table 2. All but two of the commercial resins had bound formaldehyde : phenol (F:P) ratios of close to or greater than 2.0:1.0. The bound F:P ratio is not necessarily the same as the ratio charged in the reactor vessel at the start of the cook, since some formaldehyde may be lost during the synthesis, for example, by the Cannizzaro reaction, whereby the formaldehyde undergoes self-oxidation-and-reduction. However, the bound

TABLE 2.   *Chemical characteristics of commercial resins.*

| Resin | Functional groups[1] | | | | | F:P[2] | M_n[3] | M_w[3] | pH[4] |
	-H	-CH$_2$OH	-CH$_2$-O-CH$_2$-	-CH$_2$-	-CH$_2$-O-CH$_2$OH				
A	0.93	0.38	0.18	1.51	0.00	1.32	720	3,497	8.16
B	0.25	1.16	0.01	1.53	0.05	2.03	905	2,242	8.56
C	0.41	0.97	0.07	1.50	0.05	1.90	742	2,710	9.02
D1	0.33	1.07	0.04	1.51	0.05	1.97	1,018	2,507	8.34
D2	0.51	0.72	0.24	1.48	0.05	1.78	1,226	13,386	8.95
E	0.13	1.19	0.04	1.56	0.08	2.16	1,080	2,945	8.93
F	0.03	1.32	0.03	1.56	0.06	2.24	963	1,769	8.82
G	0.05	1.25	0.00	1.64	0.06	2.19	1,418	7,613	8.94
H	0.08	1.03	0.20	1.64	0.04	2.13	954	4,179	9.38

[1] The total of the functional groups per phenolic nucleus is 3. The other ring positions are occupied by the hydroxyl group and unreactive meta sites.
[2] F:P = formaldehyde : phenol molar ratio.
[3] Molecular weight values are for the resins in the acetylated condition.
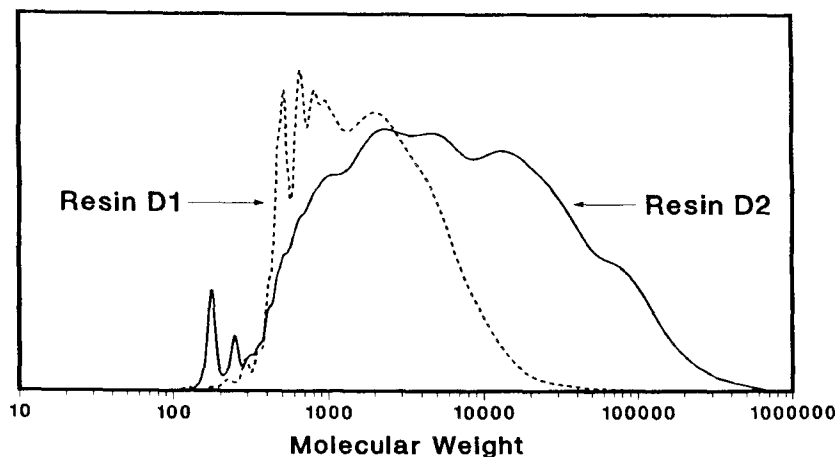[4] pH of 2% w/v aqueous solution.

FIG. 5.   Molecular weight distributions of Resin D1 and Resin D2 (acetylated form).

F:P ratio does give a good indication of the conditions used in the preparation of the resin. The majority of the resins were clearly of the resol type, having a F:P ratio of greater than 1.0:1.0. Resin A had a lower bound F:P ratio than the others, as a result of a high proportion of unreacted ring positions and a low proportion of free methylol groups. Resin A would therefore have been expected to be the slowest curing of the commercial resins. Resin D2 also had a lower bound F:P ratio than the others and, in particular, a lower ratio than a fresh sample of the same resin (Resin D1). This may have been due to an initial lower F:P ratio in the cook or the loss of formaldehyde to the atmosphere during storage. The low proportion of methylol groups and the high proportion of ether linkages in Resin D2 compared to Resin D1 indicate that condensation reactions likely took place during storage. These condensation reactions would have been between two methylol groups leading to an increase in the average molecular size.

The molecular weight distributions of Resins D1 and D2 are compared in Fig. 5. If it is assumed that the manufacturer's formulation of the resin did not change greatly over the period when Resin D2 was being stored, it can be seen that substantial changes were undergone by the resin during the storage time. The resin peaks are much less discernible in the aged resin and the molecular weight distribution has shifted towards much higher values. Far fewer low molecular weight species are present in Resin D2. The low molecular weight peak that is discernible in Resin D2 is probably due to free phenol. The free phenol, having no methylol groups, would be less likely than low molecular weight methylolated phenols to take place in any condensation reactions occurring during the storage at ambient temperature.

Flow properties

Laboratory resins. — The flow characteristics of the laboratory resins determined from the TMA results are shown in Fig. 6. All the laboratory resins exhibited a two-stage flow process. As the temperature rises, the resin melts and densifies and the level of the probe drops. The condensation reactions that take place as the temperature rises further cause the rate of the drop in the level of the probe to
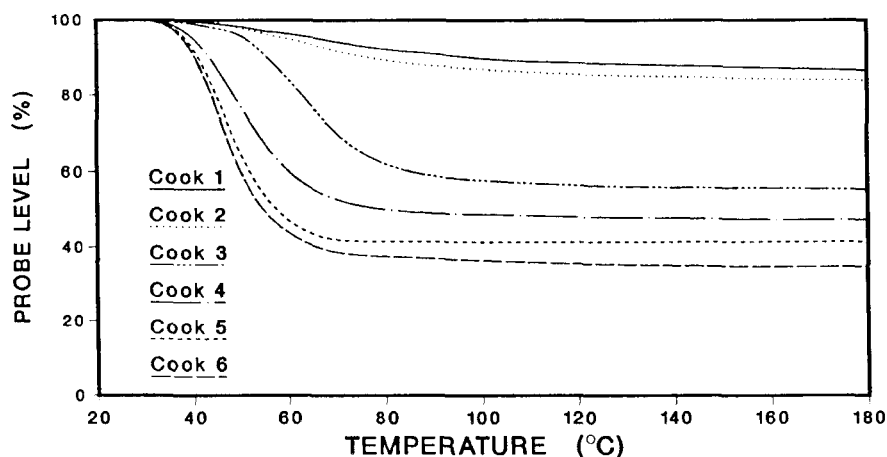
FIG. 6.   TMA flow characteristics of spray-dried laboratory resins.

decrease as the average size of the resin molecules increases. Increasingly less flow occurs as the resin molecules become progressively larger, until the fully cured state of the resin is reached and no further flow takes place. This flow behavior seems typical of resol resins. From the molecular weight distributions and TMA flow characteristics of the laboratory resins, the extent of the flow is seen to decline within each set of cooks, as the proportion of lower molecular weight species in the resin is reduced. In addition the temperature at which flow is initiated increases and the temperature at which the rate of flow is a maximum also increases as the proportion of lower molecular weight molecules decreases.

Commercial resins.—The values of the flow parameters measured from the TMA results for the commercial resins are shown in Table 3. The analysis of the TMA results for the commercial resins is not as straightforward as for the laboratory resins. This is, in part, because the progressional decrease in the free methylol group content that accompanies the increase in the molecular weight in the laboratory resins is not found for the commercial resins since a variety of reactant ratios and cooking schedules were probably used in their preparation. Also, some

TABLE 3.   *Summary of physical properties of commercial resins.*

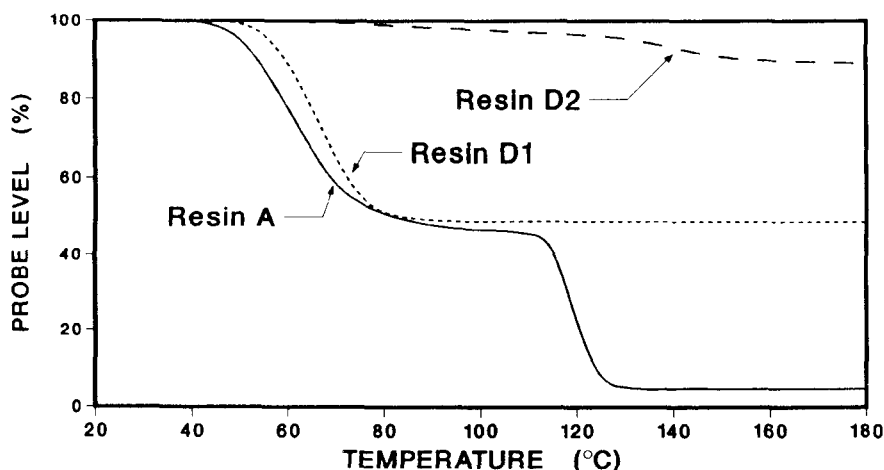| Resin	Stroke cure time (sec)	Fusion diameter (mm)	TMA Initial flow temp. (C)	TMA Max flow temp. (C)	TMA Final probe level (% initial)
A	40–50	44	45	55–75	47
				115–125	7
B	50–55	34	45	50–65	42
C	10–20	38	57	80–110	38
D1	15–20	26	50	60–70	49
D2	—	16	80	—	90
E	15–20	24	48	65–85	30
F	10–15	21	55	80–90	41
G	—	18	53	80–100	50
H	—	28	55	—	86

Note: Heating rate for TMA was 10 C/min.

FIG. 7.   TMA flow characteristics of three commercial resins.

of the previously mentioned additives that may be present can complicate the analysis. It was still possible, however, to rationalize the TMA results for the commercial resins considering the relative proportions of low molecular weight species, which would increase flow, and the relative proportions of methylol groups, which would tend to decrease cure time, thus reducing flow.

Most of the commercial resins exhibited a two-stage flow process whereby the probe gradually fell as the resin melted until it reached a level where it remained as the resin attained the fully cured condition. Resin A, however, exhibited two distinct drops in the level of the probe (Fig. 7). The first took place over the temperature range 55–70 C and levelled off at around 100 C. At 110 C another drop in the probe level started, of slightly less magnitude than the first, and was complete by 130 C. The molecular weight distribution of Resin A showed it to contain a relatively high proportion of monomers, dimers, and trimers compared to the other resins. As mentioned earlier, the ^{1}H-NMR results indicated that fewer methylol groups, through which cross-linking could occur, were present in Resin A than in the other resins. These factors would combine to cause the first drop, attributable to melting (Katovic and Stefanic 1985) to be the most rapid of the commercial resins. The second stage of flow is most likely due to the smaller molecules being able to undergo further flow in the molten state before condensation reactions had progressed to a sufficient extent to produce a cured mass. This behavior is more typical of resins of a novolak nature (Katovic and Stefanic 1985) where additional curing agents (e.g., hexamethylenetetramine or additional formaldehyde) usually have to be introduced to produce total cure. It would thus appear likely that Resin A contained a proportion of molecules that were novolak in nature.

The effect of room temperature aging on the flow of the resins is also shown in Fig. 7. Resin D1 displayed flow characteristics typical of the commercial resins whereas Resin D2 exhibited greatly reduced flow. This is a result of the much higher molecular weight distribution present in Resin D2, presumably due to the condensation of low molecular weight molecules to larger molecules during storage. The presence of the free phenol peak in Resin D2 and its absence in Resin
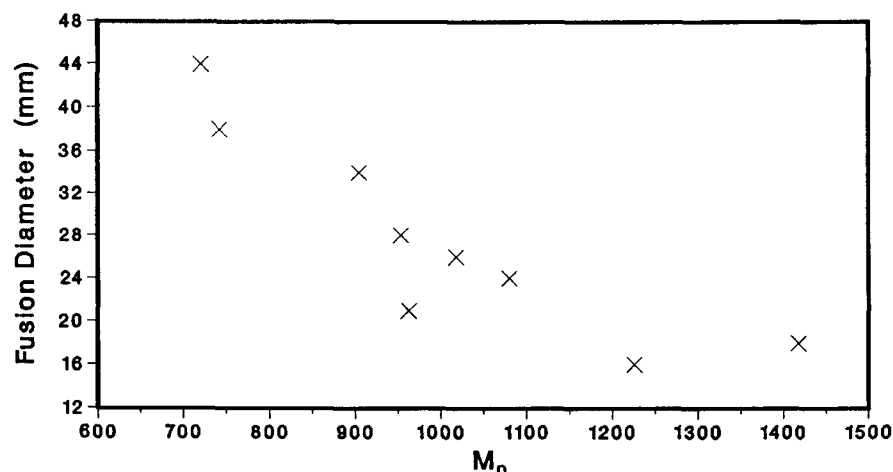
FIG. 8. Fusion diameter of commercial resins as a function of number average molecular weight.

D1 seem to indicate that the formulation of the resin did, in fact, change between the production of the two batches. However, it seems highly unlikely that any change in the formulation would account for the magnitude of the differences in molecular weight distributions and flow properties observed between the two resins. Practical experience in waferboard mills has shown that resins have a practical storage life and tend to lose their "tack" after that time. The changes undergone during storage appear to be associated with condensation reactions, loss of reactivity and reduction of flow capacity.

The relationship between number average molecular weight and fusion diameter for the commercial resins is shown in Fig. 8. The decrease in fusion diameter as M_n increases is in agreement with the flow characteristics indicated by TMA. A plot of fusion diameter as a function of weight average molecular weight (M_w) showed a less conclusive relationship, except at high values of M_w. M_w is often the molecular weight parameter chosen to describe a resin since for a number of properties larger molecules tend to have a greater influence on the value of that property than do the smaller molecules. The value for M_n gives an equal importance to all sizes of molecules in its calculation of molecular weight (unlike M_w). From the better correlation observed between fusion diameter and M_n, it would appear that flow is influenced as much, if not more, by the small molecules present in a resin as by the large ones.

The stroke cure times given in Table 3 show the relationship between reactivity and flow. Resins with longer cure times (less reactive) tend to start to flow at lower temperatures (as measured by the temperature at which the initial drop in the TMA probe level occurs), have maximum flow levels (as measured by the maximum slope in the plot of the drop of the TMA probe against temperature) at lower temperatures and exhibit more total flow (as measured by the final TMA probe level) than do resins with shorter cure times. This is to be expected since higher molecular weight resins, containing fewer small molecules, would be expected to attain the cured state more rapidly, allowing less time for flow to take place in a resin that already has a reduced flow capacity compared to a lower
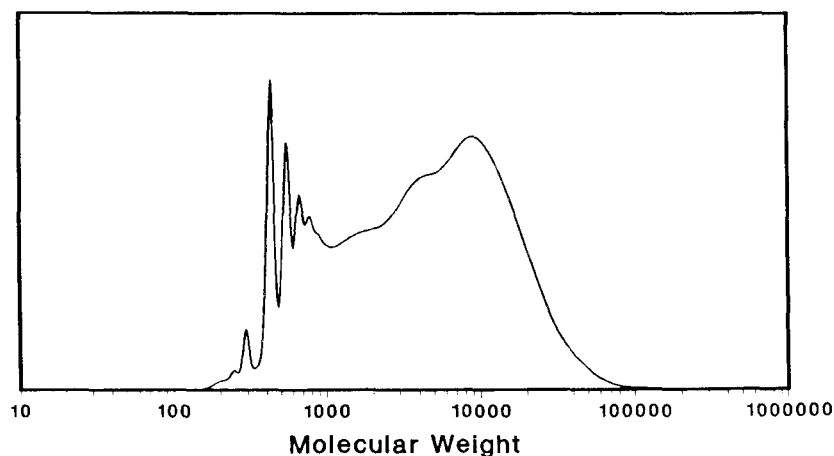
FIG. 9.   Molecular weight distribution of Resin G (acetylated form).

molecular weight resin (assuming other factors to be held constant, e.g., methylol content).

The molecular weight distribution of one resin, Resin G (Fig. 9) illustrates one approach that may be used to achieve the short pressing times desired, while at the same time maintain the necessary flow to produce adequate bonding. The high molecular weight peak was shifted to quite high values, yet peaks corresponding to trimers were still very much in evidence. This distribution would be unlikely using a standard cooking schedule. To achieve this distribution, low molecular weight phenolics would have to be added near the end of the cook, or the resin would have to be prepared by blending two or more resins. This approach of blending resins would appear to offer a practical approach to combining two or more resin systems into one that would exhibit the desired advantageous characteristics of each component.

SUMMARY

The characterization of the chemical structures of laboratory-synthesized and commercial phenol-formaldehyde powdered resins established that resins containing greater proportions of low molecular weight species exhibit flow at lower temperatures and greater total flow. For resins exhibiting similar molecular weight distributions, those resins containing fewer methylol groups also showed more flow. Flow, as measured by fusion diameter, was seen to be closely related to M_n. All but one of the commercial resins were distinctly of the resol type. Spray-drying of a liquid resin to the powdered form caused greater condensation of the resin molecules than did conversion by freeze-drying. Storage of a resin for a long period of time led to an increase in its molecular weight and a reduction in its ability to flow.

REFERENCES

Go, H. 1988. New developments in waferboard/OSB resin technology. Particleboard/Composite Materials Symposium, Washington State University, Pullman, WA, 123–132.

GOLLOB, L. H. 1983. The interaction of formulation parameters with chemical structure and adhesive performance of phenol-formaldehyde resins. Ph.D. dissertation, Oregon State University, Corvallis, OR.

GUPTA, R. C., AND V. K. SEHGAL. 1979. Effect of viscosity and molecular weight of lignin-phenol-formaldehyde-resin on the glue adhesion strength of plywood. Holz- und Holzverwertung 31:7–9.

JONES, T. T. 1952. The melt viscosity of some phenol formaldehyde novolak resins. J. Appl. Chem. 2:134–149.

KATOVIC, Z., AND M. STEFANIC. 1985. Intermolecular hydrogen bonding in novolaks. Ind. Eng. Chem., Prod. Res. Div. 24:1117–1130.

MARTIN, R. W. 1956. The chemistry of phenolic resins. John Wiley and Sons Inc., New York.

MEGSON, N. J. L. 1958. Phenolic resin chemistry. Butterworths Scientific Publications, London.

STEINER, P. R. 1975. Phenol-formaldehyde wood adhesive characterization by proton magnetic resonance spectroscopy. J. Appl. Polym. Sci. 19:215–225.

WOODBREY, J. C., H. P. HIGGENBOTTOM, AND H. M. CULBERTSON. 1965. Proton magnetic resonance study on the structures of phenol-formaldehyde resins. J. Polym. Sci. A 3:1079–1106.