

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

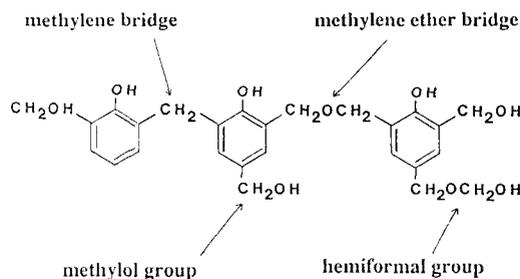


FIG. 1. Representative structure of a phenol-formaldehyde resin molecule, showing the functional groups present.

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- μ m, 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.

¹H-Nuclear magnetic resonance spectroscopy

¹H-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 ¹H-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 a 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 preheated 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	-CH ₂ OH	-CH ₂ - O-CH ₂ -	-CH ₂ -	-CH ₂ -O- CH ₂ OH				
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 ¹H-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 ¹H-NMR results. The distribution of the spray-dried sample was very close to that of Cook 4. It appears

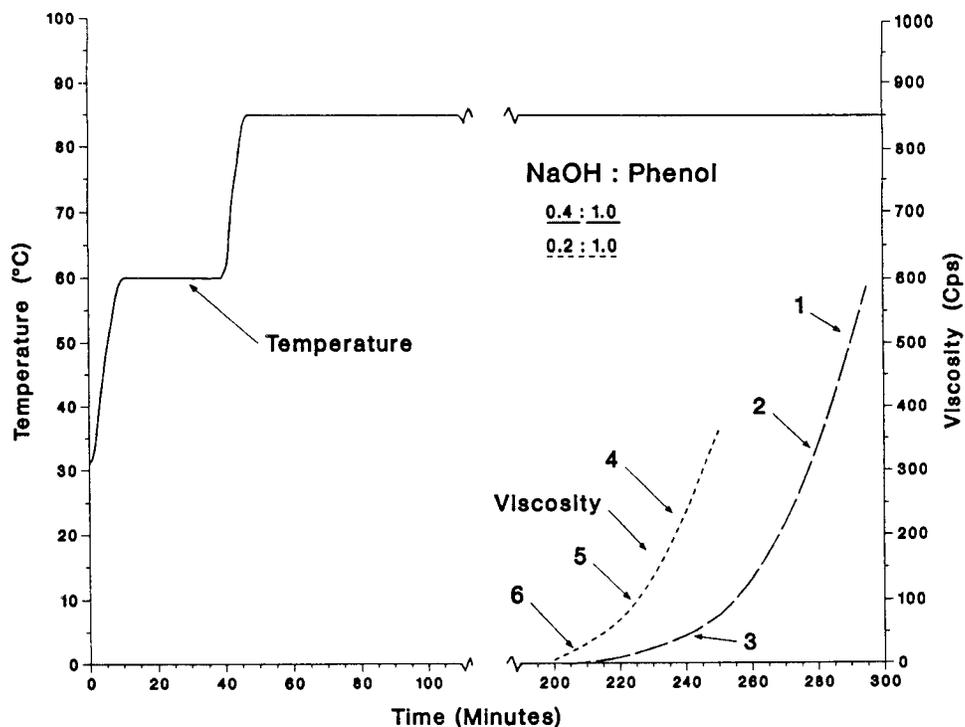


FIG. 2. Cooking temperature schedule and resin viscosities as a function of cooking time for liquid resin syntheses. The arrows and numbers indicate the points at which the synthesis of each resin was ended by rapid cooling. Formaldehyde : phenol ratio, 2.0:1.0.

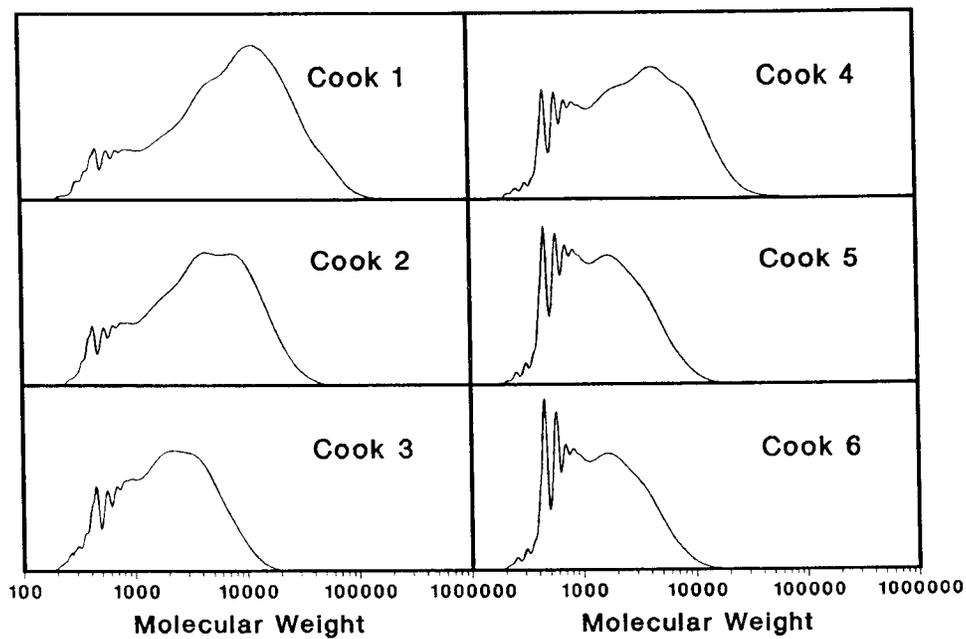


FIG. 3. Molecular weight distributions of spray-dried laboratory resins (acetylated form).

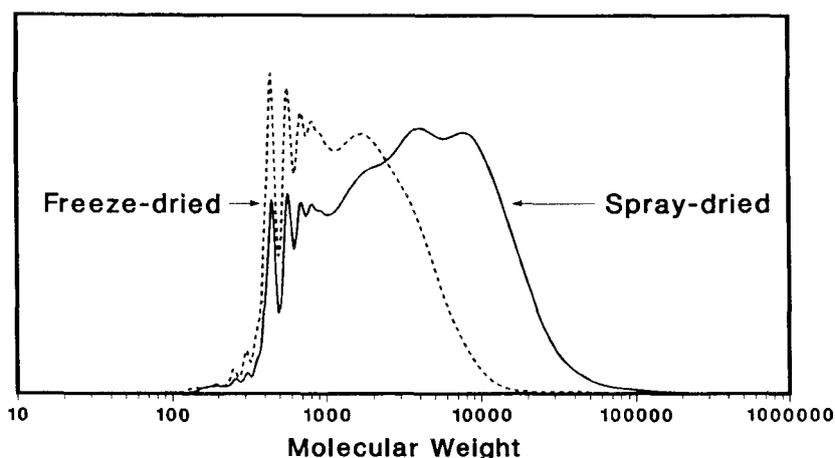


FIG. 4. Molecular weight distributions of Cook 5 after freeze-drying and spray-drying (acetylated form).

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	$\begin{matrix} -\text{CH}_2- \\ \\ \text{O}-\text{CH}_2- \end{matrix}$	-CH ₂ -	$\begin{matrix} -\text{CH}_2-\text{O}- \\ \\ \text{CH}_2\text{OH} \end{matrix}$				
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.

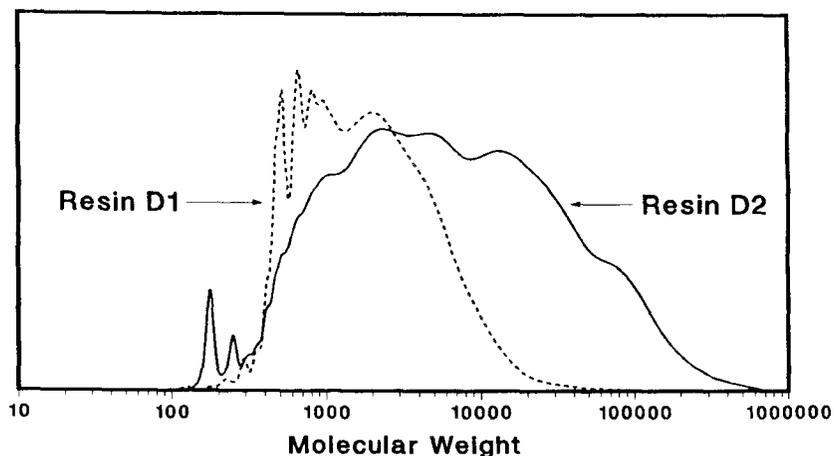


Fig. 5. Molecular weight distributions of Resin D1 and Resin D2 (acetylated form).

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

