

Phenol-Formaldehyde Resin Curing and Bonding in Steam-Injection Pressing

Part II. Differences Between Rates of Chemical and Mechanical Responses to Resin Cure

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Summary

Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were applied to samples of phenol-formaldehyde resole resins that had been previously exposed to dry precure conditions. The area under tan delta curves during DMA isothermal scans of such samples decreased as the degree of precure increased; this area was used as an empirical measure of the rate of mechanical cure for phenolic resins. Similarly, the DSC exotherm area decreased with greater sample precure; this area was used to measure the rate of chemical cure. Rates of mechanical and chemical cure differed for different resins and with temperature. Under dry precure conditions at 115° and 140°C, a high degree of mechanical cure was achieved at a low degree of chemical cure.

Introduction

Many problems encountered in the bonding of wood are associated with moisture and temperature. This is especially true in the hot pressing of wood composites, where conditions are severe and change rapidly. Researchers have used various methods to determine the response of a thermosetting resin to the major environmental variables affecting cure. Gel permeation chromatography has been useful in determining changes in molecular structure during the early stage of cure while the resin is still in a liquid state (Wagner and Greff 1971; Duval *et al.* 1972). Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and differential scanning calorimetry (DSC) have all been useful in following the reactions into the solid stages of cure (Myers *et al.* 1991; Young 1986). However, none of the last three methods differentiates chain extension from crosslinking reactions. In contrast, dynamic mechanical analysis (DMA) measures changes in the mechanical response of a curing resin. Such changes are a more direct result of the molecular crosslinking that occurs during resin cure (Babayevsky and Gillham 1973; Provder *et al.* 1984; Strauss 1980; Young 1986; Follensbee 1990). The storage modulus and relative rigidity have been used to quantify the extent of cure occurring during ele-

vated-temperature dynamic mechanical measurements (Babayevsky and Gillham 1973; Provder *et al.* 1984; Strauss 1980; Young 1986), but not to measure residual cure in samples previously exposed to curing conditions.

The storage modulus represents the elastic response of the system; the loss modulus represents the viscous response of the system, in which some of the mechanical energy put into the system is lost as heat in molecular movement. Tan delta is the dimensionless ratio of loss modulus to storage modulus. A peak in tan delta is frequently used to designate the temperature or time at which a material transition occurs.

We previously developed DMA techniques and empirical data analysis procedures with the potential for quantitatively describing the extent of cure in terms of the mechanical response of aqueous thermosetting resins as affected by temperature and moisture over time (Follensbee 1990; Geimer *et al.* 1990). The techniques were developed to measure the residual cure of partially precured samples, not to measure initial cure taking place during DMA scan. The storage, or elastic, modulus of precured samples (before scanning by DMA) rose with precure time to a plateau value, beyond which increased levels of precure had no effect. However, tan delta area values continued to change until longer precure times were reached. Thus, at higher extents of cure, tan delta area values were more sensitive to precure than were storage modulus values. Also, storage modulus values at

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Table 1. Properties of resins

Resin type	Viscosity (mPa-s)	Free formaldehyde (percent) ^a	pH	Total alkalinity (percent) ^b
1-B	601	0.2	12.4	6.55 ^c
2-C	396	1.1	10.4	3.30
2-D	815	0.5	10.4	3.60

^a Weight percentage of total resin (solids plus water).

^b Weight percentage of total resin expressed as sodium hydroxide.

^c Measured after 1 year storage at -20°C .

storing the containers in a freezer; previous work (Myers *et al.* 1991) had shown no change in resin viscosity over 16 weeks at -20°C . A container was thawed briefly to prepare samples, and each container of resin was discarded after four such uses.

Procedures

General sample preparation

Samples for both DMA and DSC were prepared by dipping a 150-by 12.5-by 0.2-mm strip of Whatman GF/C⁴ glass microfiber filter in the resin for 25 min so that the strip was fully impregnated with resin (Step 1, Figure 1). The samples were then laid flat on a sheet of clean glass, and the excess resin was squeezed out with a soft rubber roller. The resin loading in the strips was typically 0.6 to 0.7 g/m (dry basis, width and thickness standardized).

The resin-impregnated strips were thoroughly dried (Step 2) in two phases. The samples were first suspended by one end from a line for about 0.5 h at ambient conditions, by which time they had lost enough water to become tacky. They were then cut into 35-mm-long pieces, which were dried overnight in a desiccator containing phosphorous pentoxide. This stringent drying was necessary to prevent sample blistering or cracking by moisture escape during subsequent precure. The weight and dimensions of the samples were measured to determine resin loading (based on constant filter thickness and a standard width). The samples were precured in a dry oven (Step 3). We define precuring as heating an uncured sample for a specified time at a specified temperature and relative humidity (RH). Varying precure time or temperature provided samples covering over a range of cure states. All experiments reported here involved only precure in a dry air oven, so that precure occurred at essentially 0-percent RH. Samples were precured at 115°C and 140°C ; those temperatures are within the range of industrial panel pressing operations and are different enough to show effects of temperature on reaction rates, without the reactions being too fast or slow. The reproducibility of results was checked by performing two or three runs at each of several resin, time, and temperature combinations.

After precure, samples were conditioned overnight (Step 4) at room temperature in a desiccator at 91 percent RH (in air over a saturated aqueous barium chloride solution). The resultant samples possessed approximately 29 to 70 percent moisture (Myers *et al.* 1991), depending on resin alkalinity. We feel this moistening step improved reproducibility and helped to distinguish the resins in the subsequent DMA and DSC scans (Follensbee 1990). Width and thickness were measured before the samples were clamped into the grips of the DMA. Conditioned samples were quickly transferred for analysis by either DMA or DSC. For DMA runs, the gap between the grips was measured before starting. Loss of moisture from the samples was minimized by keeping the time between removal from the desiccator to the start of the DMA scan as short as possible, usually 4 min or less (Follensbee 1990).

⁴ The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Dynamic mechanical analysis

The DMA experiments (Step 5) were conducted on a Du Pont 983 Dynamic Mechanical Analyzer equipped with an environmental chamber capable of isothermal or controlled heating rate operation from -150°C to 500°C . The sample was clamped between the ends of two parallel arms (approximately 9 mm apart). The driving arm underwent small oscillations in the plane of the sample. The clamp faces were serrated for these experiments (Follensbee 1990).

The DMA experiments were run in the resonant frequency mode at 150°C . This temperature is higher than that obtained in the core of many composite boards during hot pressing but is well below the temperature where degradation appears in the resin. (Degradation was suspected during several DMA isothermal cure trials at 180°C and 210°C because the storage modulus slowly decreased with time after cure was achieved.) The DMA temperature increased from room temperature to the isothermal temperature in 2 min.

Differential scanning calorimetric analysis

Samples for DSC (Step 5) and DMA were taken from the same precured strips. Small portions (8 to 10 mg) of precured and conditioned sample were put one layer deep in capsules, which then were quickly sealed. The samples were scanned in a Perkin-Elmer DSC-2 differential scanning calorimeter at $10^{\circ}\text{C}/\text{min}$ from 20°C to 200°C . Perkin-Elmer stainless-steel large-volume capsules fitted with a fluorocarbon rubber O-ring prevented the release of volatile components below the 200°C limit. Recorded temperatures were corrected for thermal lag using a correction based on the melting point of an indium standard. Cure exotherm heats were expressed as joules per gram of resin solids.

Temperature-scanning DSC experiments were performed rather than isothermal ones to avoid the substantial transitory peaks experienced in the calorimeter as it heats quickly to the isothermal temperature.

Results and Discussion

Dynamic mechanical analysis

Measures of mechanical cure

We first examined several features of the DMA response as possible measures of mechanical cure.

Figure 3 shows shear storage modulus G' , shear loss modulus G'' , and temperature during a DMA scan of a sample of Resin 2-C precured for 2 min at 115°C . As

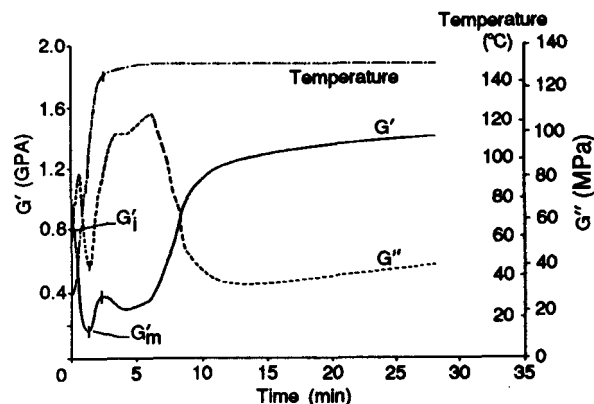


Fig. 3. Isothermal (150°C) DMA measurements of G' (shear modulus), G'' (loss modulus), and temperature for Resin 2-C after precure for 2 min at 115°C and subsequent conditioning at 91 percent RH.

the temperature increased to the isothermal temperature during the first two minutes, the sample softened somewhat, as shown by the drop in G' . During this initial 2-min period, the resin went through a transition, as shown by the G peak, and the sample lost essentially all its water (Myers *et al.* 1991). From about 2 to 12 min, further polymerization and crosslinking presumably occurred, whereby G' eventually rose to a "plateau" value higher than the room temperature value. During this period, G'' generally rose and then fell, indicating a major change in the resin. The rise of G' and fall of G'' probably occurred because crosslinking became sufficient to stiffen the resin and to inhibit large-scale molecular movement. After 12 min, the G' value slowly continued to rise, which might indicate slow continuing cure. The G'' value also increased slowly after this point. This slow increase in loss modulus is not understood. One possible explanation is that an annealing process took place to achieve more unhindered configurations.

One possible measure of extent of precure is the initial storage modulus G'_i near room temperature at the beginning of the DMA measurements. Values of G'_i at 40°C for Resin 2-C are given in Table 2, and the behavior of G'_i as a function of precure time at 115°C for the three resins is shown in Figure 4. The G'_i value increased with increased precure time for the formula 2 resins but not for resin formula 1.

Another conceivable measure of precure is the minimum storage modulus value G'_m for each DMA curve, which was caused by the initial softening. However, G'_m did not show a consistent trend with increased cure (Table 2). The usefulness of G'_m values is somewhat more uncertain than that of G'_i values because the initial softening and subsequent crosslinking overlap at higher degrees of precure and because dimensions should change as water is lost and the sample is heated to 150°C.

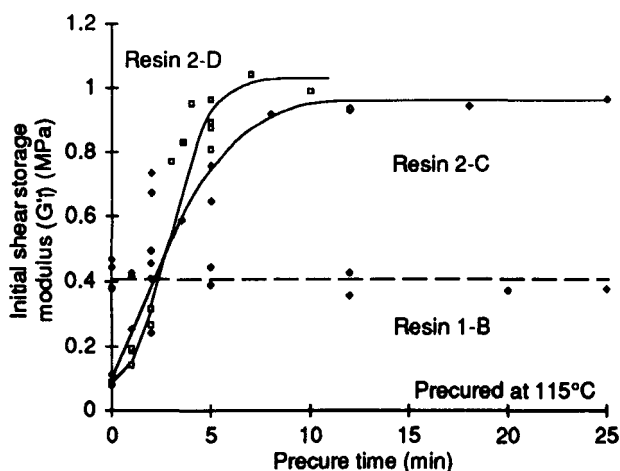


Fig. 4. Change of initial shear storage modulus G' , with precure time at 115°C for Resins 1 and 2. (DMA measurements at 150°C on samples conditioned at 91 percent RH.)

Table 2. Shear storage modulus values for precured Resin 2-C samples during DMA measurements

Precure time at 115°C (min)	Shear storage modulus (MPa) ^a		
	G'_i	G'_m	G'_f
0	0.11	0.03	1.46
1	0.26	0.08	1.47
2	0.67	0.17	1.28
3.5	0.59	0.11	1.01
5	0.64	0.60	1.07
5	0.76	0.21	1.07
12	0.93	0.49	1.09
12	0.93	0.55	1.10
25	0.96	0.62	1.15

^a G'_i is storage modulus at 40°C during initial heating in DMA. G'_m is minimum storage modulus value, which occurs at end of initial softening period in DMA. G'_f is storage modulus value taken at 14 min into DMA run; it is representative of final modulus attained during DMA run.

The final storage modulus values attained after cure, represented in Table 2 by the G'_f values at 14 min, were most often in the opposite order expected from the initial precure treatment: those samples precured longest showed lower G'_f values than those of samples with shorter precure time, as noted previously (Folensbee 1990).

Figure 2 shows the typical behavior of the tan delta area for Resin 2-C measured during isothermal DMA runs after precuring samples for three different times at one precure temperature. The area under the tan delta curve decreased with precure time. This trend was verified by more extensive experiments, as illustrated for Resin 1-B in Figure 5. Tan delta peaks are usually thought to represent transitions in material behavior on a molecular or submolecular level. The immobilization of molecules and portions of molecules

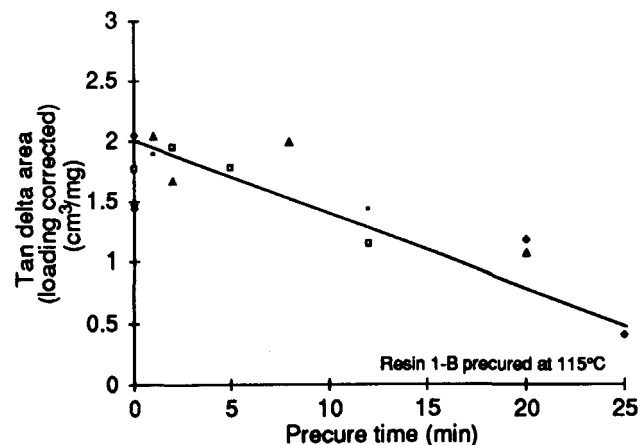


Fig. 5. Decrease of tan delta area with precure time at 115°C for Resin 1-B. (DMA measurements at 150°C on samples conditioned to 91 percent RH.) Filled squares - analysis during 1st month of storage at -20°C; filled diamonds - 2nd month; filled triangles - 6th month; open squares - 8th month; open diamonds - 12th month; open triangles - 22nd month.

by crosslinking and increasing steric hindrance should affect tan delta. The tan delta area measurement sums the amount of such activity retained by the resin before the DMA measurement.

The reason for several stray points in Figures 4 and 5 is not clear, although some of the most deviant points were obtained on resin stored in the frozen state for over 6 months. If such aging sensitivity does exist, this technique may prove useful for following the storage stability of resins or following their response to other treatments, additives, or synthesis procedures. We drew the curves in the tan delta area to de-emphasize any data obtained after long storage, and we eliminated data in subsequent figures for resin stored for long periods.

These comparisons reinforce the conclusion of a previous study (Follensbee 1990) that the tan delta area offers good potential as an empirical mechanical measure of precure.

Effects of resin type and temperature

The behavior of tan delta area with advancing cure was quite different for Resin 1 than for Resin 2, as shown in Figure 6. Resins 2-C and 2-D showed similar, fast decreases of tan delta area with precure time at 115°C; the area reached a plateau at very low values after about 10 min. In contrast, Resin 1-B showed a much slower decrease of tan delta area with precure time; the area fell to about one-third the initial value after 20 min, with no definite sign of reaching a plateau. The much slower decline of tan delta area for Resin 1-B indicates that the rate of mechanical cure of Resin 1 was not as great as that of the Resin 2 under these particular conditions, despite the initially higher molecular weight and catalyst content of Resin 1. The percentage of mechanical cure, calculated using Equation 1, is shown in Figure 7. By this measure, Resin 2 achieved over 90 percent cure in about 5 min, whereas Resin 1 required 25 min to achieve 80 percent cure.

Resin samples cured at 140°C (Fig. 8) attained equal precure in shorter times than samples cured at 115°C (Fig. 7). Resins 2-C and 2-D cured completely within 2 min at 140°C. Resin 1-B was only 95 percent cured after 8 min of precure. The 2-min precure for Resin 2 is the same magnitude of time used in steam injection pressing of 13-mm-thick phenolic-bonded flakeboards (Geimer 1982).

Attempts to examine the kinetics of mechanical cure were hampered by data scatter, possibly from the effects of resin aging.

Differential scanning calorimetry

In contrast to the DMA results, the results of the DSC experiments on samples precured at 115°C (Fig. 9) indicate that comparatively little chemical curing occur-

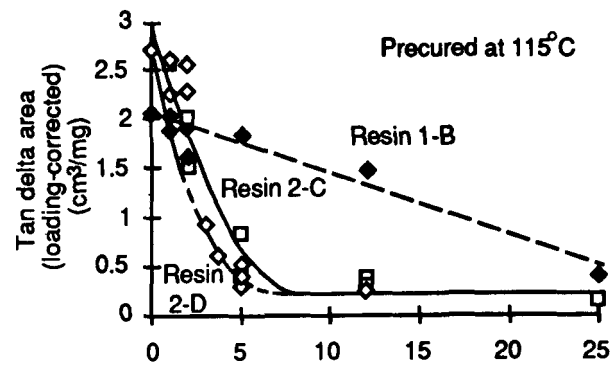


Fig. 6. Decrease in tan delta with precure time at 115°C for Resins 1 and 2. (DMA measurements at 150°C on samples conditioned to 91 percent RH.)

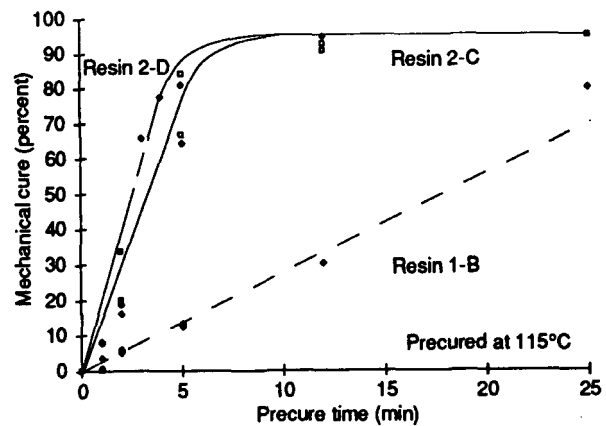


Fig. 7. Mechanical cure increase with precure time at 115°C for Resins 1 and 2. (DMA measurements at 150°C on samples conditioned to 91 percent RH.)

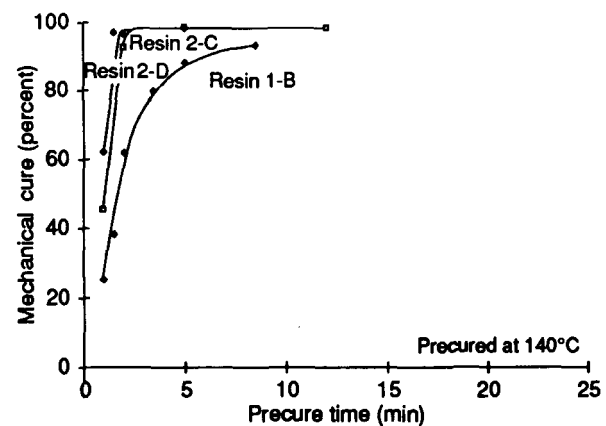


Fig. 8. Mechanical cure increase with precure time at 140°C for Resins 1 and 2. (DMA measurements at 150°C on samples conditioned to 91 percent RH.)

red during the oven precure. Chemical cure of phenolic resins is limited by the maximum temperature reached (Schindlbauer *et al.* 1976). Resin 1-B showed an extremely slow decrease of residual heat

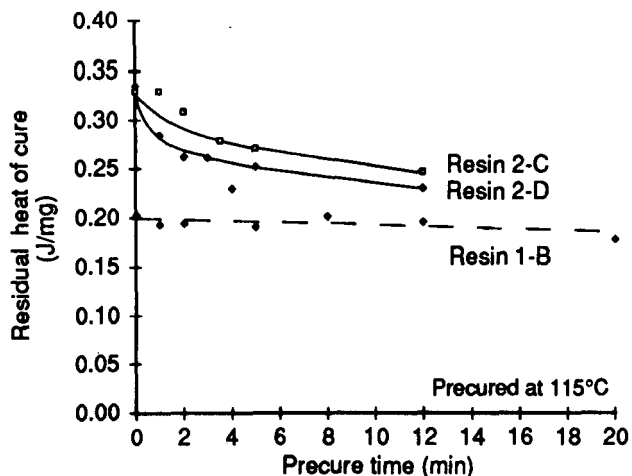


Fig. 9. Decreased in residual heat of cure with precure time at 115°C for Resins 1 and 2 (DSC scans at 10°C/min to 200°C on samples conditioned to 91 percent RH.)

with precure time up to 20 min. Although Resin 2 showed an initially fast decrease of residual heat of cure, within 12 min of precure time the cure reached a plateau at a high level of residual heat of cure (low precure).

Relationship between chemical and mechanical cure

Chemical cure, calculated as percentage of cure from Equation 2, for Resin 2-C is compared to mechanical cure in Figure 10. The mechanical cure attained a nearly asymptotic value in the 80-percent cure range, whereas the chemical cure reached its asymptotic value in the 20-percent range. Hsu and Lee (1989) reported that mechanical cure also precedes chemical cure for a low-shrinking unsaturated polyester resin. They observe a tan delta value of 1 (which is associated with the gel point for many thermosets) at chemical conversion of less than 1 percent; furthermore, storage and shear moduli reached plateau values at 5 percent conversion, at which point the samples were already hard and resistant to solvent etch-

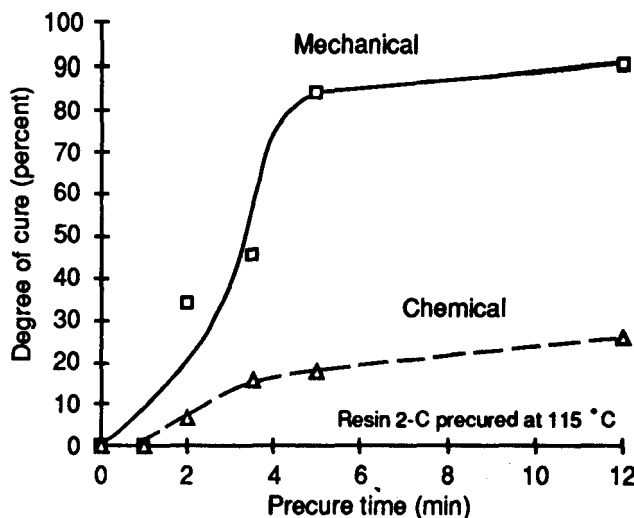


Fig. 10. Comparison of mechanical and chemical measures of cure for samples taken from the same specimens of Resin 2-C precured at 115°C. (DMA and DSC measurements on samples conditioned to 91 percent RH.)

ing. Grentzer *et al.* (1981) found that fractional cure of epoxy-amine coatings measured by shear storage modulus was complete much before chemical conversion measured by DSC analysis.

The difference in the rate of development of chemical and mechanical measures of cure invites a correlation of the two. Plotting one measure against the other provides a condensed description of the cure behavior of a resin under particular temperature and humidity conditions. We refer to this relationship as a chemical-mechanical pathway. Such chemical-mechanical pathway plots are shown for the three resins at two precure temperatures (115°C and 140°C) in Figure 11. The precure times are listed beside each data point. A higher precure temperature for Resin 1-B caused greater acceleration in the mechanical cure than in the chemical cure. A higher precure temperature for either Resin 2-C or Resin 2-D increased the chemical cure a bit more than it did the mechanical cure, but mechanical cure was generally still faster at the higher tempera-

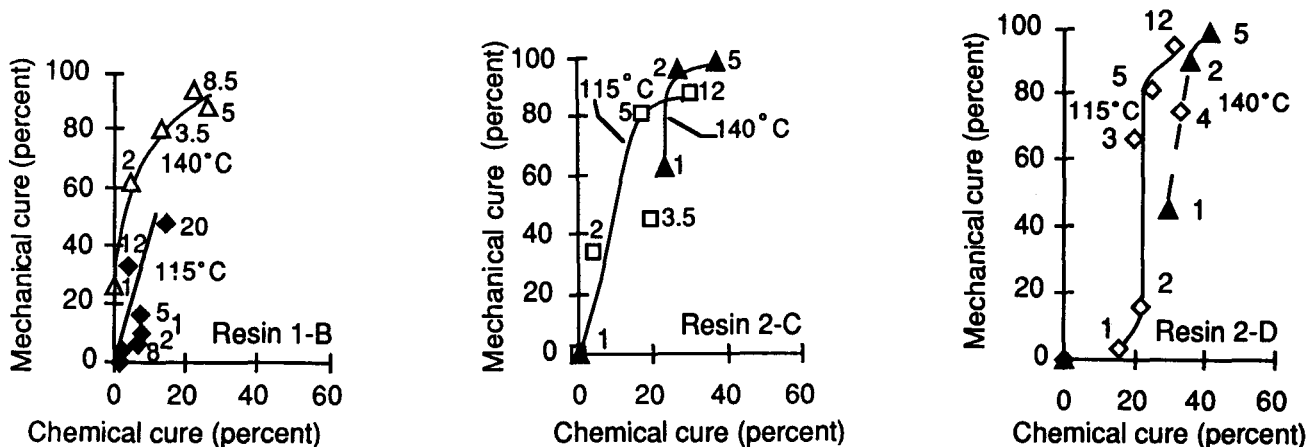


Fig. 11. Chemical-mechanical pathway plots for cure of Resins 1-B and 2-C and D precured at 115°C or 140°C and reconditioned to 91 percent RH before DMA or DSC measurement. (Number near each data point indicates precure time in minutes for sample.)

ture. The data for Resins 2-C and 2-D show that the chemical-mechanical pathway plots for these resins differ, particularly in the first few minutes of reaction.

Conclusions

1. Tan delta area determined by DMA can be used as an empirical quantitative measure of mechanical cure for aqueous phenolic resole resins. It is sensitive to resin precure, synthesis, and storage conditions.
2. For dry precure conditions, mechanical cure, measured by the tan delta area, proceeds more rapidly than chemical cure, measured by DSC. Most of the DMA-measured cure was completed before 50 percent of DSC-measured cure occurred.
3. The concept of a chemical-mechanical cure pathway can be used to differentiate resins by their chemical (thermal) and mechanical responses to cure. Plots of such a pathway may change with precuring temperature.

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