# Interactions of Phenolic Resin Alkalinity, Moisture Content, and Cure Behavior

**Linda F. Lorenz and Alfred W. Christiansen***

*Forest Products Laboratory, USDA Forest Service, One Gifford Pinchot Driue, Madison, Wisconsin 53705-2398*

The results of a dynamic mechanical analysis technique (DMA), already developed for estimating the extent of residual cure of phenol-formaldehyde resol resins, depend on the moisture content of the resin. For two resins, different but regular relationships were found between DMA-sample moisture content and the resultant tan delta area, which is measured to determine residual cure of samples, Moisture content also appears to be important for cure determinations by differential scanning calorimetry. The research reported here showed that alkali content, extent of precure, and relative humidity affect the equilibrium moisture content of phenol-formaldehyde resol resins.

## Introduction

**The** rate of cure of phenol–formaldehyde (PF) resol resins is affected by formulation, synthesis procedure, catalysts, and specialized additives that form a specific resin, even when the various types of phenolic resins are cured under identical environmental conditions. Variation in curing can affect such critical resin properties as brittleness, total extent of cure, and ability to penetrate wood adherends. In this research, we refine techniques (Follensbee et al., 1993; Christiansen et al., 1993) used to study the effects of temperature, moisture content (MC), and time on the cure of several different phenolic resol resins.

Determining the effectiveness of a resin for bonding wood usually involves bonding larger assemblies of wood with appropriate quantities of the resin, preparing samples from the assemblies, and measuring the strength needed to break the samples parallel or perpendicular to the bondlines. This process is time-consuming and wastes some experimental resin and wood. We are developing laboratory techniques using dynamic mechanical analysis (DMA) to measure the mechanical aspects of resin cure using small resin samples. The DMA directly measures mechanical properties, such as resin stiffness, from the initial liquid state of the resin to its final cured solid state. The DMA technique indicates when resin integrity is sufficiently developed to form strong bonds. The techniques make possible a more direct correlation between the mechanical aspects of resin cure behavior and the physical and chemical properties of the resin.

Previous work using DMA (Myers et al., 1991; Follensbee et al., 1993; Christiansen et al., 1993) established procedures for measuring the mechanical response of a resin to curing, which we call mechanical cure. The area under the tan delta curve (TDA) during isothermal heating was used as a measure of residual mechanical cure in a sample. In those previous studies, the size of the TDA was increased by conditioning the samples at 92% relative humidity (RH) overnight (Follensbee, 1990; Geimer et al., 1990). The procedures that were developed, however, did not determine the exact MC levels of the samples, nor did they take into account how the different alkalinities of the resins would affect moisture uptake.

Two factors that may affect resin moisture content are alkali content and extent of previous cure. In predominantly solid resin, water will likely act as a plasticizer, as it does for the amorphous components of wood (Goring, 1963), aiding molecular movement and, thus, reactivity. Alkali is hydrophilic. Therefore, in a resin sample being analyzed for residual cure, the alkali level and the environment to which the sample was last exposed will affect the reactivity measured. To prepare for a major study that will use DMA to measure cure of various PF resins under different curing conditions, we conducted preliminary investigations of variables suspected of being important for measuring TDAs. The research reported here shows how alkalinity and humidity effect the MC of PF resins and how that relates to cure behavior as measured by DMA.

## Methods

**Resin Properties.** Four PF resins manufactured by Neste Resins Corporation (Springfield, OR) were used. These resins, designated A–D, were chosen to provide a wide range of curing behavior and varied responses to high moisture environments during wood bonding. (Commercial designations for each resin are as follows: A is resin CB 101; B is resin CB 303; C is resin CB 303HM; D is resin CB 368.)

Percent oven-dry solids (nonvolatiles) was determined by heating a l-g sample of liquid resin in a 68-mm-diameter aluminum dish at 125°C for 1.75 h, according to Method 2.2 of the West Coast Adhesive Manufacturers Association (1957). Viscosity was estimated by comparison with Gardner–Holdt bubble viscosity standards. Alkalinity was determined by dissolving the resin in distilled water and titrating to pH 3.5 with 0.1 N HCI using a pH meter. Free formaldehyde was determined by a hydroxylamine hydrochloride procedure (Walker, 1972) (Table 1). Sodium hydroxide added to increase alkalinity was an analytical reagent in pellet form from Mallinckrodt Specialty Chemicals Co. (Paris, KY).

**DMA Measurements.** The dynamic mechanical analyzer subjects a material to controlled mechanical oscillation and measures the in-phase and out-of-phase response of the sample. Storage modulus G' and loss modulus G" are calculated, respectively, from these responses. The loss tangent, or tan delta, is given by G"/G' and represents the ratio of energy dissipated to *energy* stored per cycle. These properties can be monitored as a specimen is subjected to either a constant heating rate or isothermal heating. In this work, samples previously cured to some extent (precured) were analyzed to determine residual mechanical

**Table 1. Resin Properties**

| resin | non-volatiles (wt %)[a] | pH | kinematic viscosity ($m^2/s \times 10^6$) | alkalinity (wt % NaOH)[a] | free formaldehyde (wt %)[a] |
|---|---|---|---|---|---|
| A | 39.9 | 10.2 | 230 | 3.1 | <1 |
| B | 42.8 | 11.6 | 630 | 6.7 | 0 |
| C | 42.9 | 11.5 | 630 | 6.4 | 0 |
| D | 54.3 | 8.1 | 50–65 | 0.4 | 15 |

[a] Percentage of total resin (solids plus water).

cure. The area under the tan delta curve (TDA) during isothermal heating was used as a measure of residual mechanical cure in a sample.

The DMA measurements were made with a Du Pont (now serviced by TA Instruments, New Castle, DE) 983 Dynamic Mechanical Analyzer operated in the resonant frequency mode at an oscillation amplitude of either 0.10 or 0.30 mm. Samples (35 by 10 by 0.25 mm) were clamped horizontally between serrated clamp grips with a torque of 0.70 N·m for soft samples and 1.15 N·m for hard samples.

The substrate for DMA analysis was glass microfiber filter material (GFF) obtained as 15-cm-diameter circles, type GF/C, from Whatman International Ltd. (Hillsboro, OR). A sample was prepared on a clean sheet of glass by covering a 35 by 10 mm strip of GFF with PF resin and letting the resin soak into the glass filter for a few minutes. Excess resin was squeezed out by hand using a soft rubber roller, and the sample was hung up to dry for about 0.5 h at ambient conditions. The sample was weighed and either analyzed in the DMA immediately (uncured) or heated in an oven for a predetermined length of time (precure treatment). After a precure treatment, the sample was conditioned for 6-24 h in a conditioning jar to a moisture content of 45-95%. For the few samples that needed to be dried to MC levels as low as 19%, they were put either into a desiccator containing anhydrous calcium sulfate drying agent or into a conditioning room at 34°C, 20% RH for up to 24 h. The thickness and width dimensions of the sample were measured before it was clamped in the grips of the DMA Some DMA procedures were modified from those originally described by Follensbee (1993).

**Relative Humidity Equilibrations.** Resin samples on GFF were equilibrated at specific RH values in small (400 mL) jars containing beakers of saturated salt solutions. The samples were placed on small perforated platforms that rested on top of the beakers. The following salts were used in saturated solutions to provide the RH levels for conditioning samples: $MgCl_2 \cdot 6H_2O$ for 33% RH; $Mg(NO_3)_2 \cdot 6H_2O$ for 53% RH; NaCl for 75% RH; KBr for 79% RH; $KNO_3$ for 92% RH (Lange, 1961).

**General Procedures.** To prepare samples for weight-change experiments, strips of GFF were weighed and impregnated with PF resin as for DMA tests. Strips containing liquid resin were held by metal clips suspended from a balance and weighed wet. They were dried at ambient conditions for approximately 0.5 h and weighed. Samples were then subjected to various treatments for the specific tests described below. The equilibrium moisture content (EMC) of a sample is usually attained in 1-3 days in a humidity-conditioning jar.

After tests were completed, samples were weighed at the final moisture condition and heated at 125°C for 1.75 h to obtain oven-dry weights (ODWS) that were used to calculate MC levels. Some of the MC values, however, included mass losses due to condensation reactions during the oven-drying. To account for these condensation losses, additional resin samples were dried over Drierite for 24 h to 3 days, weighed, oven-dried, and reweighed. The differences in these two weights were due to condensation reactions and were subtracted from the previous weight losses.

## Specific Tests

**Effect of Alkalinity on Uncured Resin Moisture Content.** To determine the effect of the alkali content of a resin on the EMC of the uncured resin, various amounts of sodium hydroxide were added to resins A and D. For resin D, the final levels of sodium hydroxide in solution were 0.4, 1.04, 1.67,2.31, and 2.93% (weight basis). For resin A, the final levels of sodium hydroxide were 3.1, 4.1, 5.1, and 6.1% (weight basis). The resin-impregnated GFF samples were dried over Drierite for 24 h and equilibrated at 75% or 92% RH for 3 days. The MC levels were then determined as described above.

**Effect of Relative Humidity on Uncured Resin Moisture Content.** To determine how the MC of samples is affected by the RH at which they are conditioned, samples of resin A (3.1 wt % alkali) and resin C (6.4 wt % alkali) were prepared as described in the General Procedures section. The samples were put in individual jars containing saturated salt solutions to condition at five different RH levels (33, 53, 75, 79, and 92%). Each sample was weighed after 1,3, and 7 days. The EMC values were then determined as described previously.

**Effect of Extent of Cure on Solid Resin Moisture Content.** To test the effect of extent of cure on subsequent moisture absorption, samples of resins A, B, and C were prepared as described in the General Procedures section and precured in a forced draft oven at 125 or 140°C for 2, 4, or 8 min. The EMC values of the resin samples were determined after equilibrating at 92% RH for 3 days.

**Effect of Moisture Content on TDA Values of Uncured Samples.** Samples of resin A and resin B were dried at ambient conditions for various times to produce different MC levels before being weighed prior to a DMA scan. To obtain more consistent results, the time between preparing the samples and analyzing them for residual cure by DMA was held to 6 h or less (samples 1 day or older had TDAs that were two-thirds to one-half those of samples that were analyzed within several hours). Samples taken out of the DMA grips were immediately weighed to obtain dry weights for calculations of their MC levels.

## Results and Discussion

**Effect of Alkalinity on Uncured Resin Moisture Content.** As the alkali content of resins D and A increased, their EMC levels also increased (Figure 1), but not in direct proportion to the relative changes of alkali content. For resin D, as the aikali content increased by a factor of 7.3, the EMC at 92% RH increased by a factor of 1.3. At 75% RH, the EMC increased by only a factor of 1.1. For resin A, which started with a higher alkali content, as the alkali content increased by a factor of 2, the EMC at 92% RH increased by a factor of 1.6. At 75% RH, the EMC increased by a factor of 2. Data for unmodified resin B, manufactured with a high alkali content, are shown for comparison. At each RH, it appears that one curve

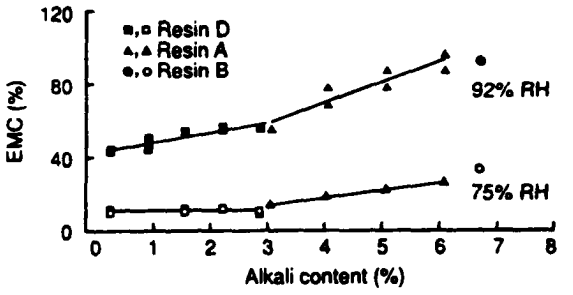


**Figure 1.** Effect of increased alkali content on the equilibrium moisture content.

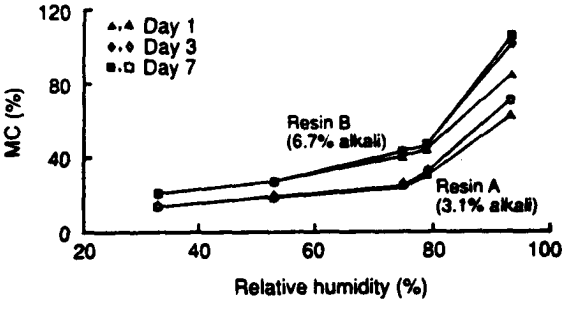


**Figure 2.** Effects of relative humidity and conditioning time over saturated salt solutions on the moisture content levels of uncured resins.

might fit through the EMC against alkali content data for all three resins.

If alkali alone were responsible for moisture absoption of the resins, MC increases would be proportionate to the relative amounts of alkali and the relationships would extrapolate back toward the origin of Figure 1. Since this is not the case, we reason that other factors are affecting the moisture content. One of these is that a portion of the alkali is combining with the acidic phenolic hydroxyl groups, even in this solid phase, to form phenate ions, which may have a different water-absorbing capacity than the sum of what the phenolic hydroxyls and the alkali would hold. However, the levels of moisture absorption contributed by nonalkaline moieties should he indicated by extrapolating the EMC values back to zero alkali, that is, to the y-axis of Figure 1. We do not have enough data to determine whether that extrapolation should be linear with alkali content, as shown for each resin, or whether it might follow the trend of the several resins together. If the overall trend for combining the data from the several resins is correct, it appears that almost half of the moisture absorbed when the resins contain 6% alkali would be absorbed by resin if no alkali were present. We reason that polar functional groups on the organic molecules, specifically hydroxymethyl and phenolic hydroxyl groups, contributed to moisture absorption as hydroxyl groups do in cellulose and its derivatives (Savage, 1965).

**Effect of Relative Humidity on Uncured Resin Moisture Contennt.** The effect of conditioning an uncured resin at different RH values on the MC of the uncured resin was determined. Figure 2 shows the resulting MC levels of resins A and B at five different RH levels at 1–7 days. Results showed that MC of uncured resin on GFF can be adjusted by conditioning at specific RH values. Except for the samples conditioned at 92% RH, the MC levels of the samples did not change significantly after 1 day.

Samples at the highest RH levels gradually darkened. Resin C was initially darker than resin A and was black

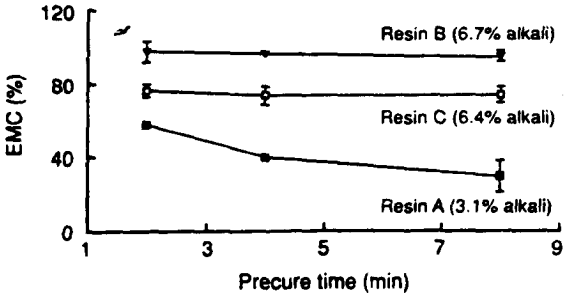


**Figure 3.** Effect of precure time at 125 °C on equilibrium moisture content. (Equilibrated at 92% relative humidity; each data point represents two samples for resins A and C and three samples for resin B. Error bars for some data points are smaller than the symbols.)

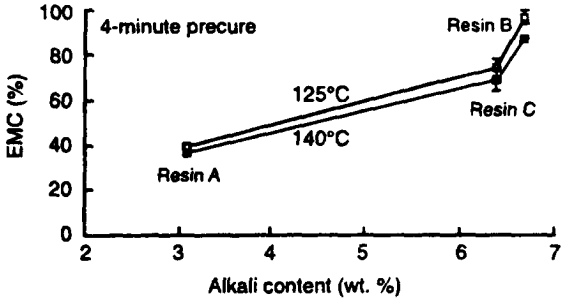


**Figure 4.** Effect of alkali content on equilibrium moisture content after three resins of different alkali content (equilibrated at 92% relative humidity) have been precured at 125 or 140 °C for 4 min. Each data point represents two samples. Error bars for some data points are smaller than the symbols.

after conditioning for 7 days at 92% RH. Resin A was tan after conditioning for 7 days at 33% or 53%, but was dark red at 92% RH. We assumed the darker colors were caused by oxidation reactions.

**Effect of Extent of Cure on Solid Resin Moisture Content.** The results for precuring resins A,B, and C at 125°C show that, as precure time increases, the ability of the resins to reabsorb moisture decreases (Figure 3). The 1oss of hygroscopicity is less, in absolute terms, for mains B and C than for A.

Using higher cure temperatures to increase precure also yields resins with depressed abilities to absorb water. Pairs of resin samples A, B, and C were cured for 4 min at either 125 or 140°C (Figure 4). Samples cured at 140°C had lower EMC ,levels than did those cured at 125°C.

The amount of alkali in the partially cured resins appears to also influence the amount of moisture regained in cured samples. As the alkali amount increased between resins from 3.1% for A to 6.4% for C to 6.7% for B, the moisture regained also increased (Figure 4), although other aspects of resin structure may have played a role. This result of increased EMC from increased alkali is similar to the data shown in Figure 1 for uncured resins.

**Effect of Moisture Content on TDA Values.** Preliminary runs showed that TDAs determined for several samples of the same resin at constant alkali and precure conditions, but different MC levels, varied by a factor of 3. Low MC in phenolic resins can suppress measurable cure in differential scanning calorimetry (Myers et al., 1991; Wang et al., 1995). In the present experiments, TDAs of the samples precured at 115°C for 5 min and then conditioned to various MC levels followed regular relationships with mass loss. Over the

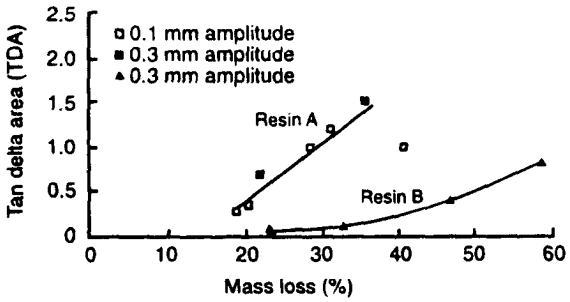


**Figure 5.** Effect of moisture content (measured as mass loss) for uncured samples on the tan delta area values obtained by isothermal dynamic mechanical analysis during cure of resins A and B at 200 °C.

MC range covered by data, the differences of mass loss were attributed to differences of MC absorbed by the precured samples (Figure 5). (The amount of mass lost by continuation of the condensation reactions is assumed constant because the precure and final DMA cure conditions were the same for all samples of each resin.) As the MC of the resin sample increased, the TDA increased. We do not yet understand why the relationship is linear in one case and curvilinear in the other. Future work will determine the relationship between TDA and MC for several different resins at several extents of precure. A regular relationship between MC and **TDA** values could make it easier to compare, at the same MC, TDAs for samples of a resin at different extents of cure or compare samples of different phenolic resins.

## conclusions

The equilibrium moisture content levels of alkaline-catalyzed phenolic resin samples increase as the alkali content increases. The amount of alkali, however, does not determine the total moisture content (MC} some moisture-holding capacity must be attributed to the organic polymer itself.

As the extent of cure of phenolic resin samples increases, the ability of the material to absorb moisture decreases slightly, at least for samples equilibrated at 92% relative humidity.

Tan delta areas obtained by dynamic mechanical analysis increase regularly, though differently, with MC for two phenolic resins. If these regular relationships are general, they would allow comparison of different resins, or a resin at different states of cure, at similar MC values.

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