Development of Dynamic Mechanical Methods to Characterize the Cure State of Phenolic Resole Resins

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SYNOPSIS

We are interested in using dynamic mechanical analysis (DMA) to measure the degree of cure achieved by aqueous phenol–formaldehyde (PF) resole resins as a result of previous exposures to various temperature–humidity–time regimes. We developed procedures that permit the obtaining of data that properly characterize and quantify the DMA behavior of these aqueous systems. Particularly important factors are substrate selection, sample clamping geometry, and sample humidification prior to analysis. In this report, we illustrate the problems encountered and the steps that we adopted to resolve them. We also present preliminary DMA data that illustrate some approaches for measuring the degree of cure achieved during previous resin exposures. One especially promising approach employs the area under the tan delta curve during isothermal scanning as an inverse measure of precure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

We are engaged in a program whose overall goal is to improve both the processing efficiency and the mechanical properties of phenol–formaldehyde (PF) bonded flakeboard made by the steam injection pressing process.[1] Our approach to that practical goal is to achieve a better understanding of the effects of the steam injection pressing variables on the development of resin cure and bonding. These variables include temperature, moisture level, time, pressure, and resin type. Each of these variables can be expected to exert a strong influence on the rate and extent of cure of aqueous PF resins. Moreover, the rate of transition (cure) from a soluble liquid to an insoluble, but heat softenable, gel and finally to an infusible solid will differ among phenolic resins synthesized by different procedures or from different ratios of ingredients. Differences of cure rate between phenolic resins affect such critical resin properties as substrate penetration, brittleness, and total extent of cure.

The primary focus of our program is the use of dynamic mechanical analysis (DMA) to measure the degree of cure achieved by aqueous PF resole resins subsequent to their exposure to combinations of temperature, humidity, and time. (Hereafter, we refer to this cure state as the degree of precure.) We intend to use the dynamic parameters of storage modulus (E'), loss modulus (E''), and tan delta (E''/E') to interpret the viscoelastic events that occur as a resole is heated, such as thermal softening, dehumidification, deplasticization, and gelation/crosslinking. This information will be used to estimate degrees of resin precure and will be correlated with measurements of degree of precure from differential scanning calorimetry (DSC).

This article primarily discusses the development of DMA procedures that will provide reproducible and interpretable data for PF resole resins. Accurate characterization of these water-based systems by DMA is hampered by the vaporization of water in the resin formulation and of water produced during the condensation reaction. These events cause sample shrinkage and eventual brittleness. Obtaining DMA data that properly characterize and quantify the curing reactions for these resins depends upon careful attention to several factors; these include

substrate selection, sample clamping geometry in the DMA, and proper sample humidification prior to analysis. Altering any of these factors can greatly influence the appearance of the DMA data and the utility of the technique for quantitatively estimating the degree of resin precure.

We felt that a description of some of the problems we have encountered, and of their resolution, would be useful to others attempting to apply DMA to PF resoles and to other water-based systems. This article is, therefore, technique-oriented. We identify some of the difficulties involved in obtaining reproducible, quantitative DMA data during the cure of aqueous PF resole resins, describe the procedures we developed to surmount those difficulties, and illustrate the behavior of PF resoles in DMA, with particular reference to determining extents of precure.

BACKGROUND

Phenol–Formaldehyde Chemistry

A PF resole resin passes through three stages as it cures: (A) liquid or solid material, which is generally soluble and fusible, (B) solid material, which is insoluble but softened by solvent and heat, and (C) which is both insoluble and infusible.

The reaction between phenol and formaldehyde occurs in two steps. In the first step, formaldehyde reacts with phenol monomer, yielding hydroxymethylphenols (Fig. 1). The products may possess different degrees of substitution, depending on the molar ratio of formaldehyde to phenol (F/P), and they form most easily in neutral or alkaline conditions.[2] In the second step, the hydroxymethylphenols react with one another or with phenol molecules. This step commonly results in methylene linkages, as shown in the pathway on the right side of Figure 1. The formation of methylene ether linkages is also possible (left side, Fig. 1), but is less common. A molecule of water is evolved as each link of the polymer chain is formed; hence the term "condensation reaction" is used for this second step. At temperatures above 150°C, methylene ether linkages can lose formaldehyde and convert to methylene linkages.[3]

The details of the polymerization vary depending on the resin formulation. A resole is formed at alkaline pH and in excess formaldehyde. Under alkaline conditions, formaldehyde reacts faster with
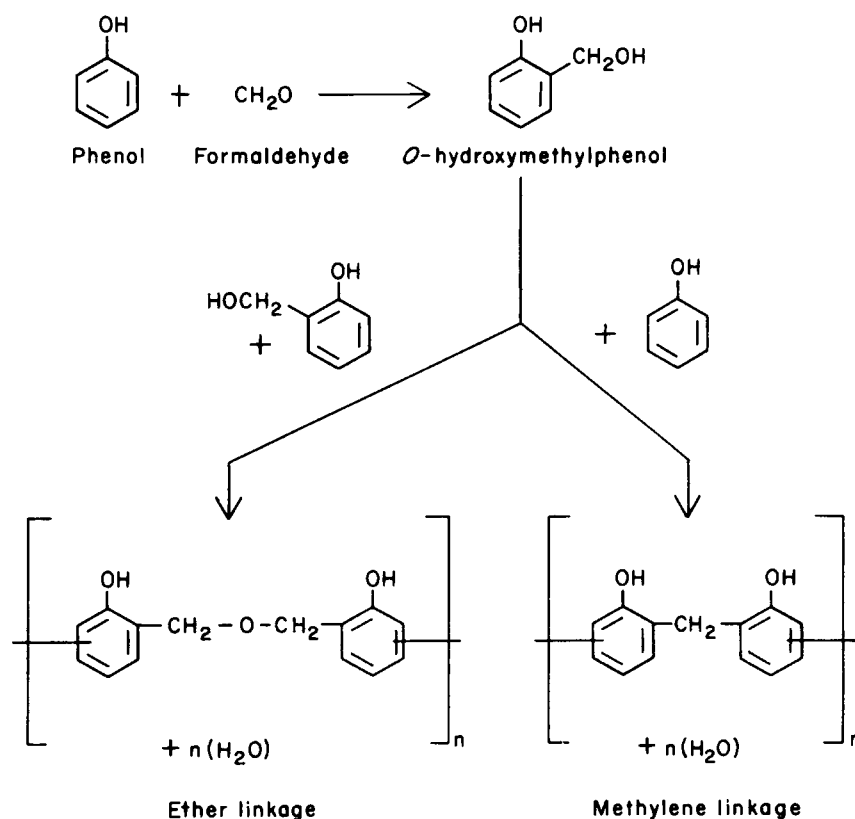
Figure 1 Possible reaction pathways for the cure of phenolic resole resins.

phenol than the subsequent condensations of hydroxymethylphenol groups.[3] The high F/P ratio allows for a high degree of hydroxymethylphenol substitution on each phenolic ring. In the A stage, the condensation of hydroxymethylphenols is allowed to continue to a limited degree before the reactions are stopped by cooling. At that point, some hydroxymethylphenol groups remain, and only heat is required for further polymerization and formation of a crosslinked network.

DMA for Measuring Degree of Resin Precure

A dynamic mechanical analyzer subjects a material to controlled mechanical oscillation and measures the in-phase and out-of-phase response of the sample, from which one calculates the storage modulus (E') and the loss modulus (E''), respectively. The loss tangent, or tan delta, is given by E''/E' and represents the ratio of energy dissipated to energy stored per cycle. These properties can be monitored as a specimen is subjected either to a constant heating rate scan or isothermal heating.

Gillham has carried out extensive work on solventless thermosets, such as epoxies.[4,5] He used the torsional braid analyzer (TBA), which monitors the dampening of oscillations of resin-impregnated braid. Gillham showed that the mechanical response of the resin is highly dependent upon two events: gelation, which results from chemical crosslinking, and vitrification, which results from physical immobilization of molecular segments. After the resin passes through vitrification, the rate of chemical crosslinking is greatly depressed. In fact, to continue crosslinking, the resin must normally be devitrified by increasing the temperature above the glass transition temperature. Gillham measured gelation and vitrification times at numerous cure temperatures with the TBA. His work led to an increased understanding of the relationships between cure temperature, vitrification, or glass transition temperature (T_g), extent of reaction, and cure kinetics of thermosets.

Strauss[6] measured the degree of cure of resole resins on a glass fabric support as samples were heated isothermally in a dynamic mechanical analyzer. He used the modulus values for uncured and final cured states as the zero and fully cured values. This procedure measures the extent of cure that has been achieved relative to the maximum possible at that same temperature. However, this procedure neglects the fact that the final moduli at 120°C and 140°C were much lower than the final moduli obtained at 150°C to 200°C, which were scattered in a small range of values.

Provder[7,8] showed how the increasing degree of cure during a constant heating rate scan could be measured by monitoring the rise in shear storage modulus G' (t, T) as a function of time, t, and temperature, T (see Fig. 6 in Ref. 8). As the temperature rises, the material initially softens, causing G' to fall and then level off at a plateau value, G'_o. During the subsequent cure regime, G' increases to another plateau value. A baseline thermal softening response for the final cured resin, G'_f (T), is obtained upon cooldown and reheating of the cured sample. The fractional degree of cure at any point in the scan may be calculated from the values of G'_o, $G'(t,T)$, and G'_f (T).

Landi and coworkers have used DMA to study the cure of PF novolac molding resins.[9] Because these materials are water insoluble powders and contain much lower formaldehyde to phenol ratios than do the PF resoles, the results of Landi and coworkers are not directly applicable to our investigation. However, it is important to note that they found the density and storage modulus to decrease with increasing T_g, that is, with increasing cure. This seems to imply that as cure continues, the PF structure becomes increasingly rigid and the chains are unable to reach a close packed, random arrangement.

Steiner and Warren[10] applied the TBA technique to aqueous PF resoles. They observed a fluctuating loss modulus as temperature increased and attributed this to simultaneous thermal softening and water loss. Their observed storage modulus showed a continuous rise to a plateau, similar to the behavior of a solventless thermoset.

Robert Young[11] used DMA to follow the storage modulus of PF resole prepreg (resole-impregnated cloth containing little water) during both rising temperature and isothermal scans. He attributed the modulus changes to thermal softening at moderate temperatures and cure at higher temperatures. Ultimately, the modulus rose to a high plateau. After correcting for the thermal softening effects on modulus, he used the rising modulus values in the higher temperature region to calculate apparent degrees of cure, essentially as suggested by Provder.[8] Initial experiments indicated good agreement between such calculated degrees of cure for samples on glass cloth and on wood strips.

So and Rudin[12] made phenolic resin–woodflour composites (60 wt % resin) to study the dynamic mechanical properties of the resin. The resin was synthesized for 2, 3.5, or 5.5 h at pH 8.3, using barium hydroxide as catalyst. Phenol-to-formaldehyde

mole ratio, curing pH, and curing time were also varied. Rectangular bars were formed by curing the resin–wood mixtures in a mold at 160°C. Values of G' for samples at ambient temperature did not show large differences, except smaller values were obtained when the time for curing at pH 6.5 was short (12 min). However, no quantitative measure of cure was given for the resin in the composite samples.

Kim et al.[13] used DMA to study the isothermal cure of phenolic resole resins. They used the time to reach a peak in the tan delta curve as an indication of when vitrification by network formation occurred. Also, they used the time at which two tangents to the G' curve intersect near the final G' plateau as a measure of cure time. Higher isothermal cure temperatures decreased both the tan delta peak time and cure time, as expected. Although no quantitative measure of cure was made, Kim et al. found that advancement of the resin during synthesis significantly decreased the tan delta peak time and intensity from the time just after addition of formaldehyde to 1.5 h later. Much smaller effects were seen for several samples taken over the next 2.5 h of synthesis.

Other Methods for Measuring Thermoset Cure

A number of other methods have been used to quantify the extent of reaction that an adhesive has already undergone as it ages or cures. Simple tests, such as viscosity and gel time determination, indicate the original state of the resin and provide information concerning reactivity during the initial stages of cure. Gel permeation chromatography (GPC) is used to separate the constituents of a resin by molecular size; but because the molecules must be soluble, this system is limited to analyzing resin in its initial form or the very early stages of cure. Infrared (IR) spectroscopy can follow reactions from liquids into the solid state, but the spectral bands for various chemical groups often overlap in the important "fingerprint" region, leading to difficulties in establishing baselines and in making quantitative determinations.[14]

Solid state nuclear magnetic resonance (NMR) spectroscopy has been used to follow the structural changes in phenolics as curing progresses.[11,15] Young's data (see Fig. 1 of Ref 11) show an initial rise in methylene ether content, followed by a decrease, indicating that initially formed ether links are easily broken and convert to more thermally stable methylene links.[11] Also, the peaks attributable to methylene content and 2,4,6-ring substitution both rise steadily throughout the experiment, indi-

cating that cure reactions are proceeding. The increasing number of methylene trisubstituted ring sites is necessary for the formation of a highly crosslinked network. Rates of the various reactions decreased near gelation or vitrification.

Differential scanning calorimetry (DSC) measures the cure of phenolic resins by sensing the exothermic heat output of small resin samples during controlled heating.[14,16] This device can be used to measure the residual heat of cure remaining in a sample that has already been partially cured. By subtracting the residual heat from the amount of heat available from an uncured sample of the resin, one gets a measure of the cure that occurred during a previous exposure. However, as with the other chemical methods, chain extension reactions are not differentiated from crosslinking reactions, and the data are not directly informative about mechanical property buildup. Thus, DSC can be used to complement DMA techniques.[14]

We noted earlier that our objective was to optimize the cure process for aqueous PF resoles as affected by steam-injection pressing variables, such as time, temperature, and humidity. Thus, we required a method for measuring relative degrees of precure in samples that had been previously exposed to different combinations of those variables. These earlier studies, and particularly those by Young,[11] indicated that DMA offered the greatest potential for that purpose.

EXPERIMENTAL

In this section, we describe the dynamic mechanical analyzer. We also summarize the procedure that we ultimately developed for obtaining DMA data during the cure of aqueous PF resins. The Technique Development section will detail the problems that were encountered and provide the rationale for the recommended procedures.

The Dynamic Mechanical Analyzer

All mechanical measurements were made using a Du Pont 983 Dynamic Mechanical Analyzer.* The sample, in the form of a small sheet or slab, is clamped between the ends of two parallel arms in either a vertical or a horizontal plane, depending

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* The use of trade, firm, or corporation names in this publication is for the information of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture of any product or service to the exclusion of others which may be suitable.

Sample orientation
for horizontal clamps

Sample orientation
for vertical clamps
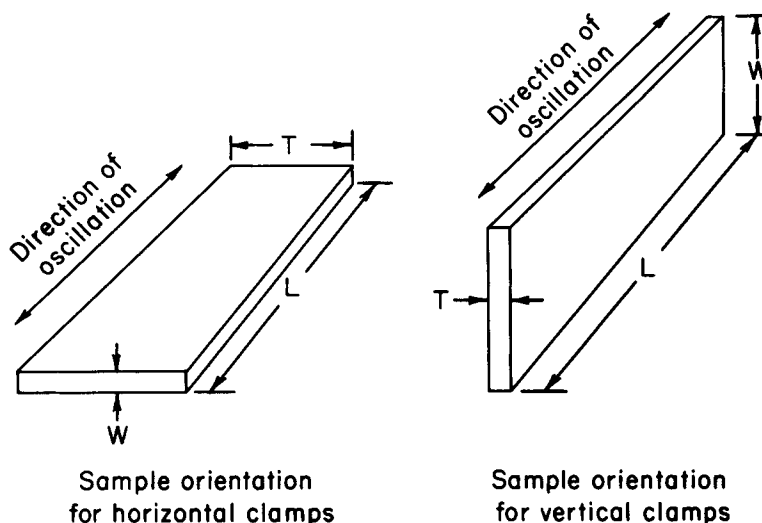
Figure 2 Sample geometry for horizontal and vertical clamping arrangements in the Du Pont 983 Dynamic Mechanical Analyzer.

upon its geometry and stiffness (Fig. 2); our initially flexible samples were clamped in the horizontal plane. One arm and the sample are forced into oscillation at a preselected amplitude by an electromagnetic driver. Energy dissipation by the sample causes the actual sample strain to be out of phase with the driver signal. The instrument detects this time shift as a phase angle, delta, from which tan delta is calculated.

The Du Pont 983 can operate in either of two modes: resonant frequency or fixed frequency. In the resonant frequency mode, the instrument operates on the principle of forced resonant vibratory motion at a fixed amplitude, which is selected by the operator. The storage modulus† is a function of the resonant frequency (detectable within the range 2 to 85 Hz). The storage modulus and the loss modulus are calculated by a program using iterative solutions to complex equations.[17] In the fixed frequency mode, the input energy is modulated to vibrate the sample at a constant frequency and amplitude. Again, storage and loss moduli are calculated by an iterative program.[17] Frequencies may be selected within the range of 0.001 to 10 Hz.

The heating chamber can accurately control temperature in the range $-150°C$ to $500°C$.[18] The temperature can be ramped (increased at a constant rate) at between $0.01°C/min$ and $50°C/min$, or held

constant for isothermal runs. The heating rate for our temperature scans was $5.0°C/min$. Sample temperature is monitored by a thermocouple placed about 1 mm from the edge of the sample, centered between the parallel arms. Typical response times to reach thermal equilibrium for isothermal testing range from 2 to 4 min. Nitrogen gas, at a rate of 1.0 L/min, feeds past the heating elements and through the DMA heating chamber. This sweeps any volatile gases away from the sample to ensure that the sample's gaseous environment stays nearly constant. Thermocouple studies showed that the temperature of the sample is unaffected by the stream of nitrogen gas. The equipment, as presently constituted, does not permit operation with moist air.

After deciding on the mode of operation, the operator programs the control parameters into the computer. The sample is then mounted in the clamps and the heating chamber with nitrogen supply is attached. From this point, all operations are controlled by the computer.

Selected DMA Parameters

We found the following sample and instrument parameters to be most suitable for studying our resole resins:

- Samples clamped horizontally between serrated clamp grips; sample dimensions: 35 mm by 12.5 mm by 0.3 mm, and 9 mm between clamps.
- Tolerable range for oscillation amplitude: 0.10 to 0.40 mm. At amplitudes less than 0.10 mm,

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† The instrument software initially calculates a shear storage modulus, G', and shear loss modulus, G''. Flexural storage and loss modului, E' and E'', respectively, are calculated by multiplying the respective shear values by the factor $2(1 + \sigma)$, where σ is Poisson's ratio, which is generally 0.33 for nonelastic polymers.

excessive noise occurred in the data collection system. At amplitudes above 0.40 mm, the electromagnetic driver shut off during sample curing, and the instrument stopped collecting data.

- Frequency of 1.0 Hz in the fixed frequency mode. Higher frequencies (e.g., greater than 5 Hz) often caused samples to shatter as they became brittle in later cure stages.
- Torque applied to clamps: 0.70 N-m for soft samples and 1.15 N-m for hard samples. Higher torques often led to sample buckling or resin being squeezed out between the clamps.

Sample Preparation Procedures

We eventually arrived at the following standard procedure for preparing samples for DMA experiments.

A strip of glass microfiber filter (Whatman GF/ C), measuring 150 mm × 12.5 mm × 0.2 mm, was immersed in a jar of phenolic resin. After soaking up resin for 25 min, the strip was removed from the jar and was laid flat on a clean sheet of glass. Excess resin was uniformly squeezed out using a soft rubber roller under hand pressure. The sample was then hung up to dry for about 0.5 h at ambient conditions.

When the sample became semidry (tacky), it was cut into pieces 35 mm long, which were dried overnight in a desiccator over phosphorous pentoxide. (Henceforth, this step will be referred to as "precure conditioning.") Subsequently, the dried sample's weight and length were measured to determine the resin loading (based on constant filter thickness and standard widths). The sample was then subjected to a precure treatment in an oven as dictated by the aims of the particular experiment.

After the oven precure treatment, the sample was conditioned overnight in a desiccator over saturated salt solution, usually $BaCl_2$, to provide 91% relative humidity (RH). (Henceforth, this step will be referred to as "pre-DMA conditioning.") The width and thickness were measured before the sample was clamped into the grips of the DMA, and the gap between the grips was measured. To minimize moisture loss from the samples, the time between removal of samples from the high humidity desiccator environment and initiation of the DMA scan was kept as short as possible, usually 4 min or less.

Resins

The resins used in this study were synthesized with formaldehyde to phenol molar ratios of 2.20 to give resins with viscosities suitable for flakeboard adhesives. Details of the synthesis and properties of these resins can be found in a previous publication.[14]

TECHNIQUE DEVELOPMENT

Sample Preparation

Substrate Selection

Because the resins start as aqueous solutions and are often still fusible when ready for dynamic mechanical analysis, a substrate was needed to enable us to handle the specimens and to support the resin during the DMA experiments. We found that the substrate must meet the following criteria:

1. Imbibe and support the resin, but not interfere with the curing reaction.
2. Maintain constant mechanical properties over a temperature range of 25°C to 200°C, so there is minimal interference with the mechanical properties of the resin.
3. Exhibit good wet strength properties, because an aqueous resin is to be applied.
4. Not be hygroscopic, so that it does not change its mechanical properties significantly over a wide range of relative humidities.
5. Possess a fine, porous structure, so that the resin does not contract within the substrate to leave voids.

The first substrate we tried, a cloth woven from fine glass fibers, satisfied the first four criteria. However, during heating in the DMA, the resin shrank away from the gaps between fibers, leaving voids throughout the specimen. Consequently, the apparent modulus decreased, rather than increased, as heating progressed.

Another substrate, laboratory filter paper, being hygroscopic, showed a significant variation in its storage modulus because of moisture loss during DMA scans between 25°C and 200°C. In addition, fiber orientation toward one direction in the paper could be a complicating factor. Other materials, including cotton fabric, rayon, ceramic cloth, kraft paper, and balsa wood, were rejected because of failure of one or more of the criteria discussed previously. One type of glass fiber filter cloth failed to withstand the shear forces of squeezing out excess resin with a roller.

A pure borosilicate glass microfiber filter (Whatman GF/C) proved to meet all of the necessary criteria. The filter material was able to absorb eight

times its weight of liquid resin, and loading was uniform along the length. This substance's storage modulus, about 1% to 3% that of a cured PF resin, changed little from 25°C to 200°C; it possessed good wet strength and was not hygroscopic. Most important, the fine-structured material possessed no directional properties, and temperature scans of resin-impregnated samples showed significant increases in storage modulus that were not always observable with the other substrates. To determine if the glass microfiber filter were truly inert, the reactivity of small samples of glass filter impregnated with uncured resin was compared to reactivity of samples of neat, uncured liquid resin in DSC temperature scanning experiments. Both types of sample showed the start of curing activity at about the same temperature, peak temperatures agreed within 1°C, and the heats of cure for the two samples, adjusted to the mass of resin solids, agreed within 3%.

Although resin shrinkage during a DMA scan does not cause disruptive voids to be formed in the microfiber filter, it does cause dimensional shrinkage of the entire sample. This is a potential problem for calculating modulus, because the calculation is based on a sample cross-sectional area that is usually measured just before the sample is mounted in the DMA clamps. However, measurements made before and after exposure to isothermal cures in the DMA at temperatures up to 150°C showed that sample width decreased between zero and 0.26 mm, and thickness decreased between zero and 0.02 mm (Table I). The effects of dimensions on modulus can be calculated from an equation of motion, which describes the deformation of a sample acted on by a flexural bending force.[17] In a simplified form, which takes into account only the dimensions of the sample, the equation is:

$$E' = K\left[\frac{2.66}{LWT} + \frac{L}{T^3W}\right]$$

where E' is the storage modulus, MPa, K is a factor varying with the frequency of oscillation, MPa-mm^3, L is the gap between pairs of DMA clamps, mm, T is the width of sample, mm, and W is the thickness of sample, mm.

Modulus values were calculated for the dimensions in Table I, and the differences between the standard values, based on initial dimensions, and the values based on final dimensions are given in the last column of Table I. The dimension changes produced a maximum error in the final storage modulus of only 2.4%. For fixed frequency operation, the term K does not vary. In resonant frequency operation, the frequency itself is a function of the dimensions. In the systems we investigated, the maximum change we calculate for K in resonant frequency is a 5% decrease.

Conditioning Procedures

Conditioning before Precure. After the filter material was saturated with resin, it was hung up to dry. When the resinous strip reached a semidry (tacky)

Table I Dimensional and Modulus Variations Caused by Sample Shrinkage

Precure	T_o, mm	T_f, mm	W_o, mm	W_f, mm	$\dfrac{(E'_f - E'_o)}{E'_o}$
105°C DMA Isotherm					
1 min, 140°C	12.86	12.71	0.34	0.34	0.015
2 min, 140°C	12.88	12.64	0.32	0.32	0.024
150°C DMA Isotherm					
1 min, 140°C	12.83	12.64	0.32	0.33	−0.011
2 min, 140°C	12.85	12.59	0.31	0.32	−0.006

(E'_o) final storage modulus calculated with sample dimensions measured prior to DMA run.
(E'_f) final storage modulus calculated with sample dimensions measured after DMA run.
(T_o) measured sample width prior to DMA run.
(T_f) measured sample width after DMA run.
(W_o) measured sample thickness prior to DMA run.
(W_f) measured sample thickness after DMA run.

state, it was thoroughly dried at room temperature overnight over phosphorous pentoxide in a desiccator (precure conditioning). The dried samples were then ready to be heated (partially cured prior to DMA analysis) for specified periods of time in a forced-circulation oven. This precure conditioning over phosphorous pentoxide was necessary to avoid blistering or cracking of the sample caused by rapid release of moisture when the wet sample was placed in the hot precure oven. If samples could be precured for short times at elevated humidity, this drying procedure would be unnecessary.

Conditioning after Precure. After exposure to a controlled precure condition, such as 2 min at 105°C, the samples were preconditioned overnight in a 91% RH environment (desiccators containing a saturated solution of barium chloride). This pre-DMA conditioning was necessary to achieve greater cure and to magnify modulus changes when the partially cured samples were subsequently tested in the DMA chamber.

Figure 3, for example, shows the difference in DMA behavior for 3 samples, each partially cured at 105°C for 1 min in a dry oven, but then pre-DMA

conditioned to either 91% RH (over a saturated barium chloride solution), 58% RH (sodium bromide solution), or 33% RH (magnesium chloride solution). Sample storage modulus was monitored during a ramped temperature increase of 5.0°C/min. The preconditioning humidity obviously had a marked effect on the storage modulus over the entire temperature range. At 91% RH, the water plasticized the resin to such an extent that the initial modulus was an order of magnitude less than that of the sample equilibrated to 33% RH. In the intermediate temperature range, thermal softening was pronounced in the stiffer, lower moisture content (33%- and 58%-equilibrated) samples. By the time the temperature reached approximately 105°C, the 33% RH sample apparently retained insufficient water to continue plasticization, and its modulus began to rise. However, the higher humidity samples maintained their low moduli until nearly 140°C, at which point their moduli began to rise rapidly because of cure. (The drop in modulus at about 150°C is probably caused by slippage in the unserrated clamps, as discussed later.)

Using higher levels of moisture in precured samples increased measurement sensitivity by dynamic
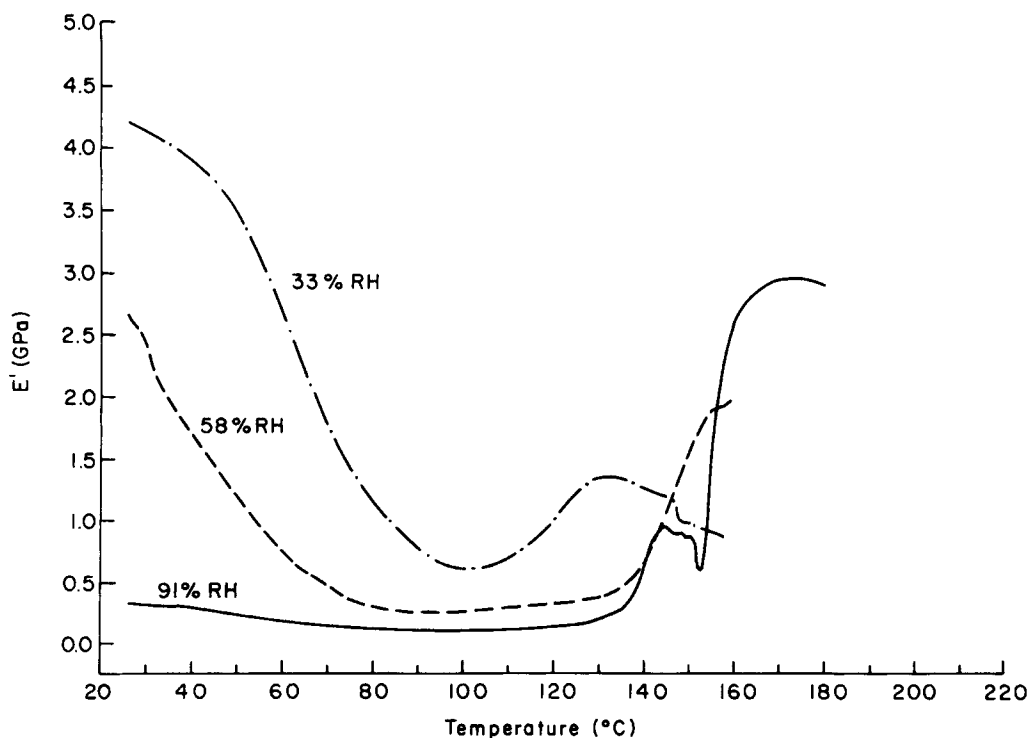
Figure 3 Influence of different initial sample moisture contents on the DMA storage modulus curves, at fixed frequency, of a phenolic resole resin at the same degrees of precure. Unserrated clamps were used. (Note the decrease in initial modulus as samples are conditioned at higher relative humidities prior to DMA analysis.)

mechanical analysis. This is shown in Figure 4 for isothermal runs at 150°C for two samples of a resin cured identically, but conditioned at different humidities before analysis: at 58% RH (top) and 91% RH (bottom). The range of moduli values for the sample conditioned at 91% RH was much larger than for the range of values measured for the sample conditioned at 58% RH. Even though PF resin samples typically retain only 1 to 2% water by the time the DMA temperature has increased to 110°C,[14] which would occur in less than 2 min here, the effect of the initial moisture on the modulus persisted until at least 7 min, indicating that the plasticization and chain mobility imparted by the water was somehow retained after the water escaped. Certainly, the water initially helped to separate the stiff, hydrogen bonded polymer chains and produce a looser, more random chain structure. Such structures apparently persisted during the rising temperature as the system dried and cured. We have also observed that the heats of reaction during DSC scans of initially liquid PF resins were decreased by 34% when the samples were dried to 2.4% moisture content prior to thermal scanning. Moreover, Katovic and Stefanic[19] report that the plasticizing effect of water on PF novolac resins persists over the range from 40°C to at least 110°C.

In view of these results, we selected the 91% RH preconditioning environment for subsequent work, because we felt it would emphasize differences in the DMA behavior of samples that had been precured to different extents.

We note additionally that overnight exposure was sufficient to ensure attainment of equilibrium moisture content in all samples. Samples of a resin subjected to different degrees of partial precure also showed only small differences in moisture content. However, the average sample moisture content increased significantly if the phenolic resin contained higher levels of sodium hydroxide.[14]

Sources of Variability

Resin advancement during storage is, of course, a potential source of variability.[14] Resole PF is capable of undergoing polymerization even at room temperature. To prevent any major changes with time, small jars of resin were kept frozen, except when they were thawed for sample preparation. As a precautionary measure, each jar of resin was discarded after four uses for sample preparation. During this period, the resin typically underwent an increase in viscosity from 450 MPa to about 600 MPa.
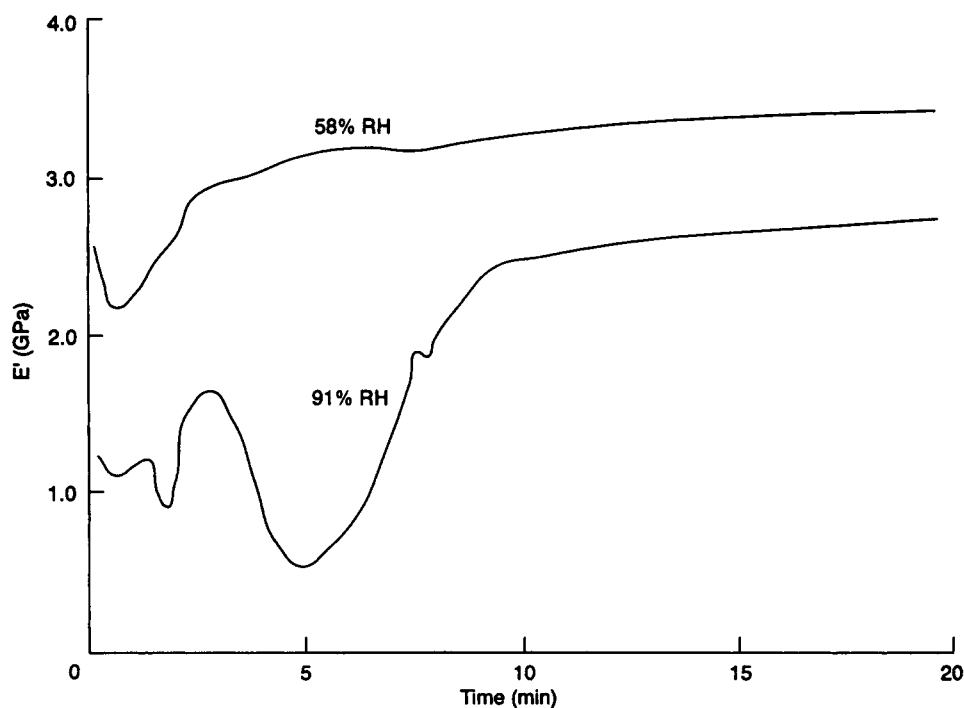
Figure 4   Influence of humidity preconditioning on DMA storage modulus (resonant frequency) of samples cured identically. (Modulus was measured during isothermal curing at 150°C.)

Errors developed if too much time was taken between removing a sample from the preconditioning desiccator and initiating a DMA scan. As a sample was removed from the 91% RH conditioning desiccator, moisture was lost to the atmosphere. This resulted in loss of plasticization and an increase in sample modulus. Figure 5 illustrates this for samples conditioned at 91% RH after receiving various levels of precure. The modulus of these samples was then monitored in the DMA over a period of time without using the heating chamber. Though the modulus curves rise at the same rate, the greatest relative changes are occurring in the less-cured, softer samples. To minimize errors from solvent evaporation, we recommend that the mounting time be kept constant and as short as possible.

Another source of variability is the clamping procedure. Care must be taken to apply the same torque every time, especially with soft samples. Even though a sample is tightly mounted in the clamps, it may soften with heat and redistribute the resin in contact with the clamps. This softening in the resoles led to an unstable modulus region centered at 140°C, as shown in Figures 3 and 6, when all runs were made using flat clamp surfaces. It was originally thought that these fluctuations were caused by a resin transition. However, when slightly blunted

serrations (0.42 mm spacing, 0.076 mm deep, 0.016 mm flats across the tips) were cut into the surfaces of the clamps perpendicular to the sample length, this instability was eliminated or greatly reduced (Fig. 7).

Although the fixed frequency experiment was intended to provide sensitivity for soft samples and gives the potential for calculating activation energies, we found that the resonant frequency mode was more applicable to our needs. In the fixed frequency mode, the Du Pont 983 instrument had difficulties in following the rapid changes that occurred when a sample softened with heat and then rapidly increased in modulus. The DMA software program perceived these regions as extremely unstable and responded by shutting off the electromagnetic motor. Consequently, data were lost, as can be seen in Figures 6 and 8. Using the resonant frequency mode, however, such data gaps rarely occurred. Recently, we learned that lowering the threshold value for a parameter called the data factor would possibly eliminate the problem of gaps in data collected at fixed frequency, at the sacrifice of a noisier signal.

In summary, excellent reproducibility can be achieved in both isothermal and constant heating rate scans if proper attention is given to operating procedures. This is illustrated in Figure 6, which
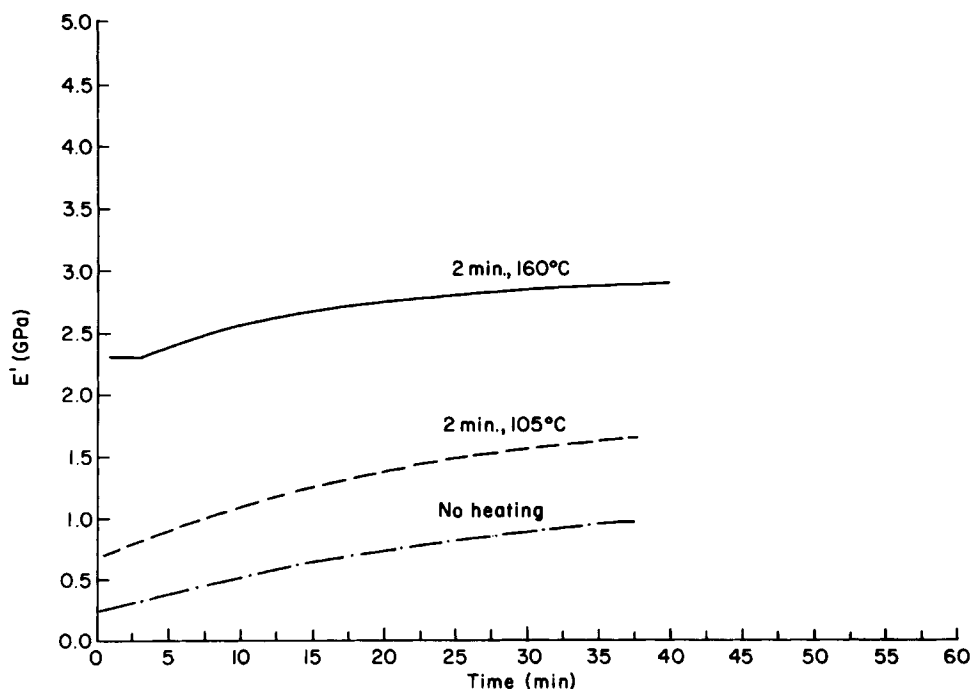

Figure 5   Changes in DMA storage modulus (fixed frequency) when samples preconditioned at 91% RH were allowed to release moisture to the atmosphere at room temperature. (Note that the vertical position of the modulus curve depends on the degree of precure.)
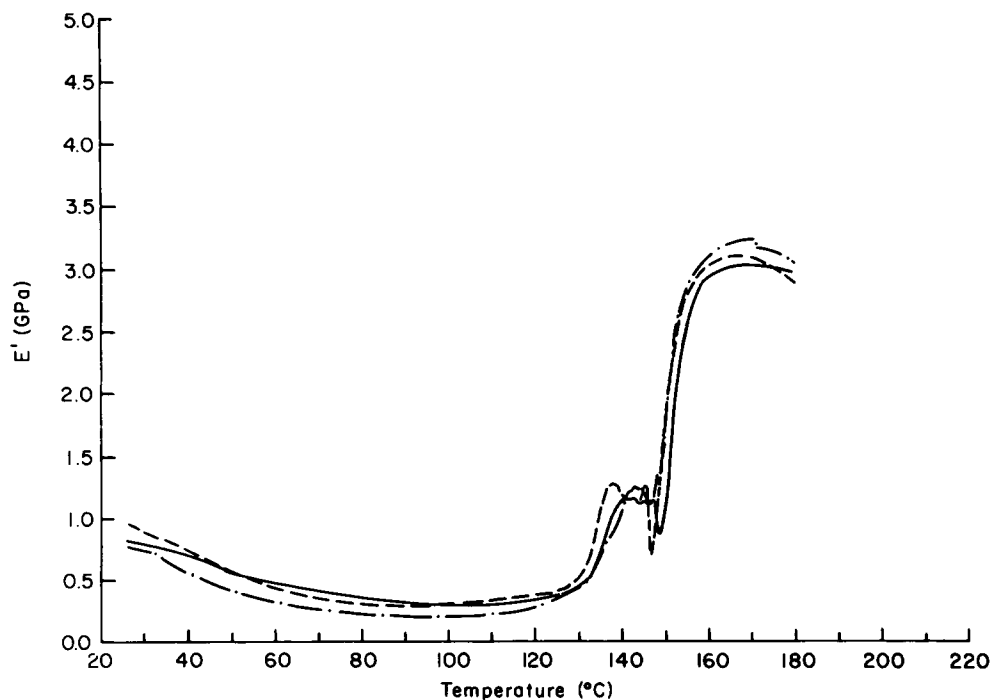
Figure 6   Reproducibility of modulus measurements (fixed frequency) for three samples of the same phenolic resin prepared in an identical manner. (All samples were precured 1 min at 105°C and then conditioned at 91% RH prior to scanning.)
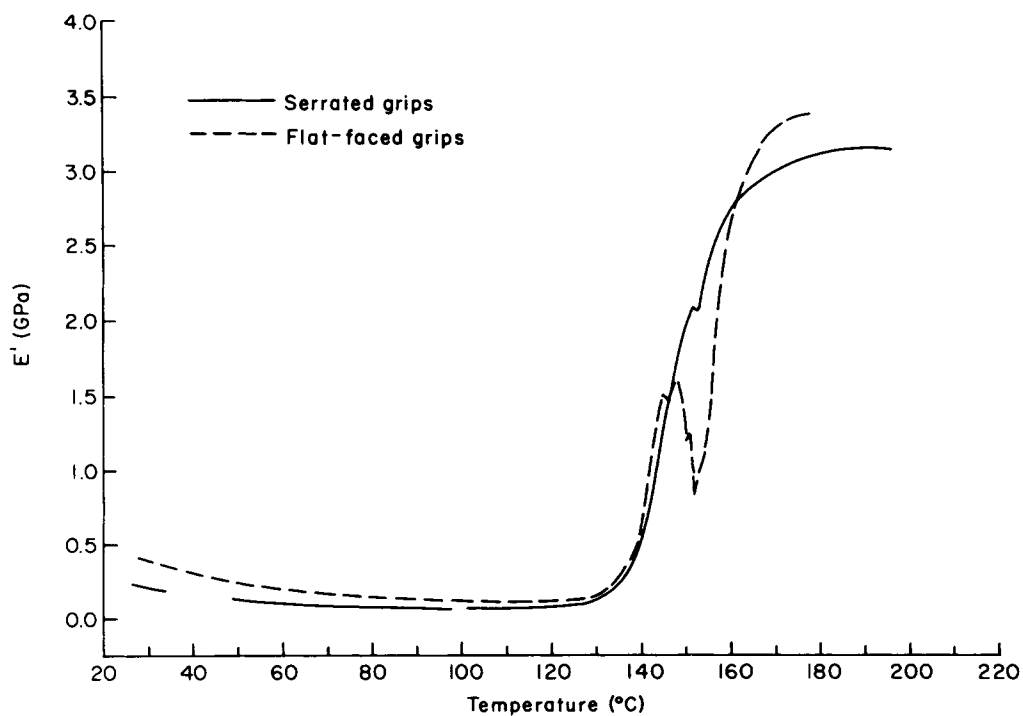

Figure 7   Influence of type of grip surface on DMA storage modulus data at fixed frequency. (Samples were not precured, but were conditioned at 91% RH prior to DMA scans. Note that the modulus "peak" centered at 145°C for samples gripped in smooth clamps disappeared when serrated clamps were used.)

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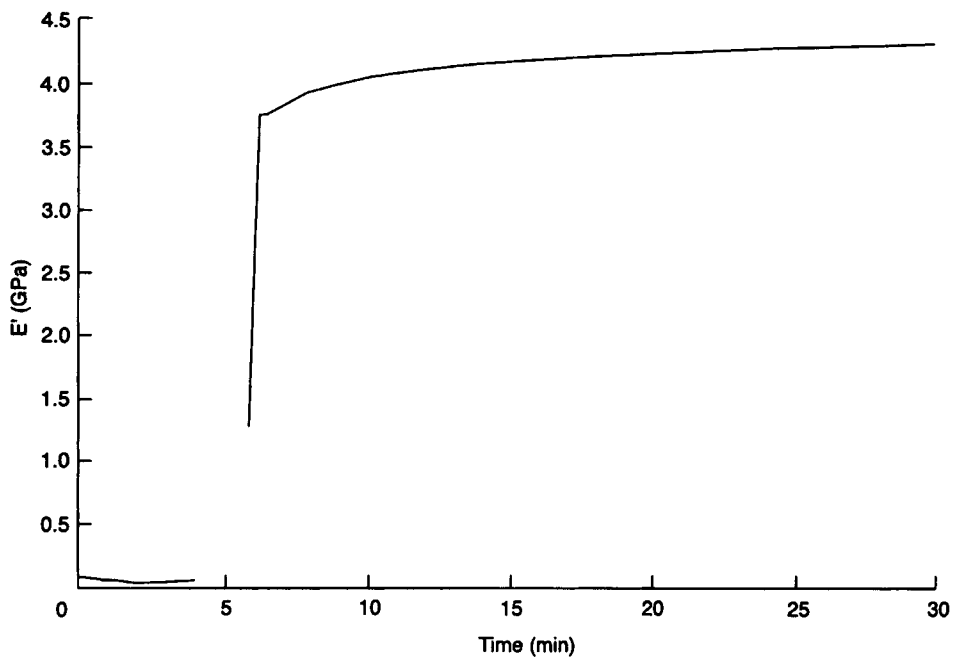
Figure 8 Critical gap in fixed frequency data collection while measuring DMA storage modulus during an isothermal run at 200°C.
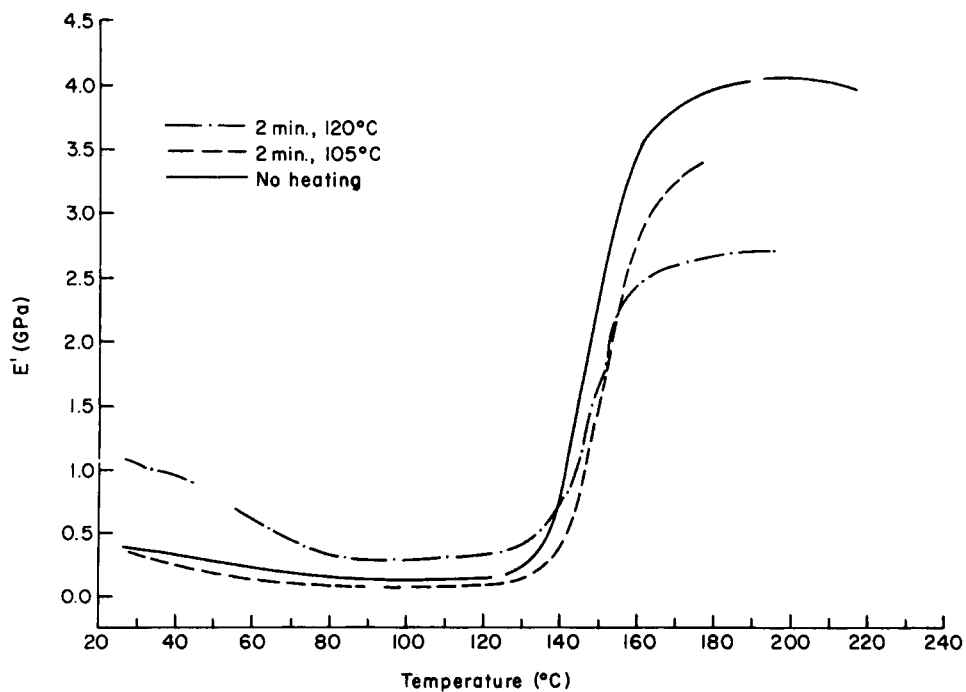
Figure 9 Effect of precure condition on storage modulus for phenolic samples. (Samples were conditioned at 91% prior to scan. Note the higher level of ultimate modulus attained when no precure heating was used.)
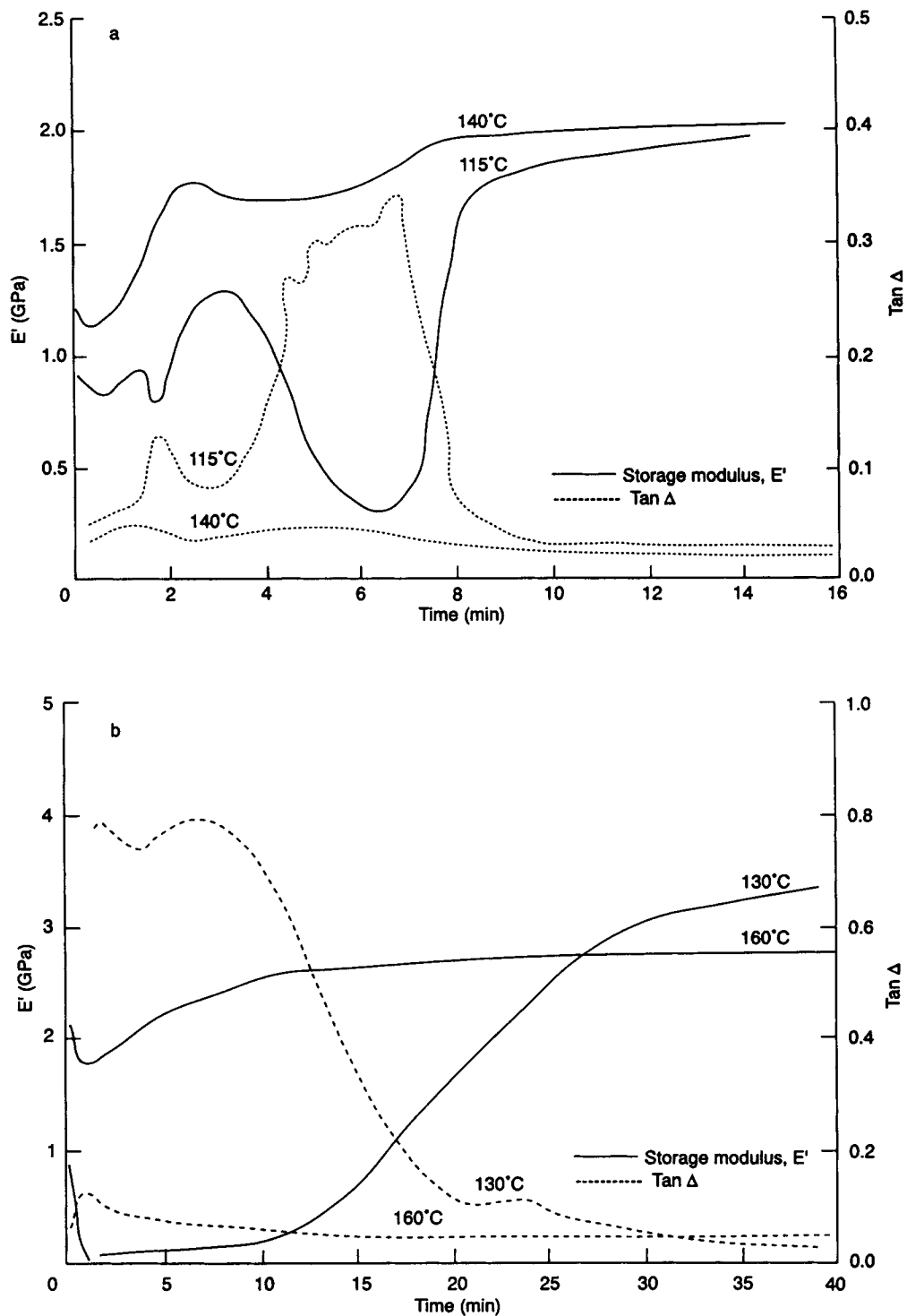
Figure 10   DMA storage modulus and tan delta curves for phenolic samples with different initial degrees of precure. In frame (a), for a test in resonant frequency mode, the sample cured for 2 min at 115°C was less cured than that cured for 2 min at 140°C. In frame (b), for a test in fixed frequency mode, the sample cured for 2 min at 130°C was less cured than that cured for 2 min at 160°C. (Note the larger area underneath the tan delta curve and larger modulus variation for the samples with less precure.)

shows constant rate heating scans on three samples of the same resin. All three specimens received identical treatment and were prepared from the same jar of resin; however, one specimen was prepared and tested one week after the other two.

Using DMA to Determine Extent and Rate of Cure

As mentioned earlier, our primary interest is in developing techniques for measuring the cure state of resin samples that have been subjected to actual or simulated steam injection pressing conditions for wood panels. We are interested in the development of cure during a DMA scan primarily insofar as it tells us something about the original cure state.

We considered several dynamic mechanical responses as predictors of a resin's pre-DMA state of cure. These divide into three groups, and we discuss them here with some preliminary data and comments about their utility for our purpose.

Magnitudes of Initial Moduli and Initial Thermal Softening

For samples preconditioned to 91% RH, the initial (25°C) storage modulus generally increased as the oven precure treatment became more severe (Figures 9 and 10). Opposite effects were observed with tan delta area (Fig. 11) and with the degree of thermal softening (decrease of modulus from initial values) below 100°C (Figs. 9 and 10). However, in addition to errors in these quantities caused by moisture loss during sample mounting and equilibration, we found them to be insensitive to changing cure state at higher degrees of cure, as illustrated for E' in Figure 11.

Modulus Buildup due to Cure at High Temperatures

Figure 12 illustrates the influence of isothermal DMA temperature on both the rate of modulus buildup and the final modulus achieved for samples of the same resin precured by the same amount. The higher modulus plateau achieved, in the higher DMA temperature scans, is consistent with the concept that a liquid state is maintained to a higher level of cure at the higher DMA temperature before the resin's glass transition increases to reach that temperature, at which point further reaction is inhibited.[5]

The S-shaped modulus curve, observed during cure in the DMA (Fig. 12), can be used to calculate apparent degrees of cure achieved along that curve.[7,8]
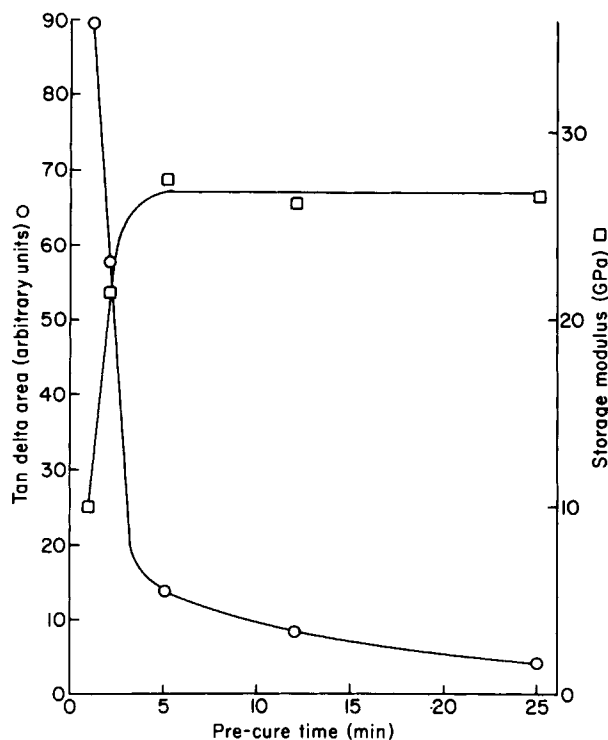
Figure 11 Tan delta area (circles) and initial storage modulus (squares) as a function of precure time at 115°C. (Isothermal DMA scans at 150°C. Note the greater sensitivity of tan delta to precure times between 5 and 25 min.)

We could follow similar procedures to calculate degrees of cure for each temperature scan, relative to its own maximum modulus or to a maximum modulus reached in a higher temperature scan. However, these calculations by themselves would not achieve our objective, which is to measure the degree of cure reached in the oven precure or other previous exposure. Achieving that objective is made more difficult by the finding that a higher temperature, and thus more curing, during precure frequently reduces the final modulus level (a possible measure of degree of cure) reached by a resin during a subsequent DMA scan (Figs. 9 and 10). We rationalize this observation by noting that the higher cure state achieved during precure is accompanied by a higher T_g. In that state, the molecules will be less able to react during a subsequent DMA constant heating rate scan because the sample is below its glass transition during much of the scan. It is worth noting here that both Megson[20] and Pritchett[21] have emphasized the rigidity of phenol–formaldehyde polymer chains and the likelihood of configurations being frozen and slow to respond to solvents or heat.
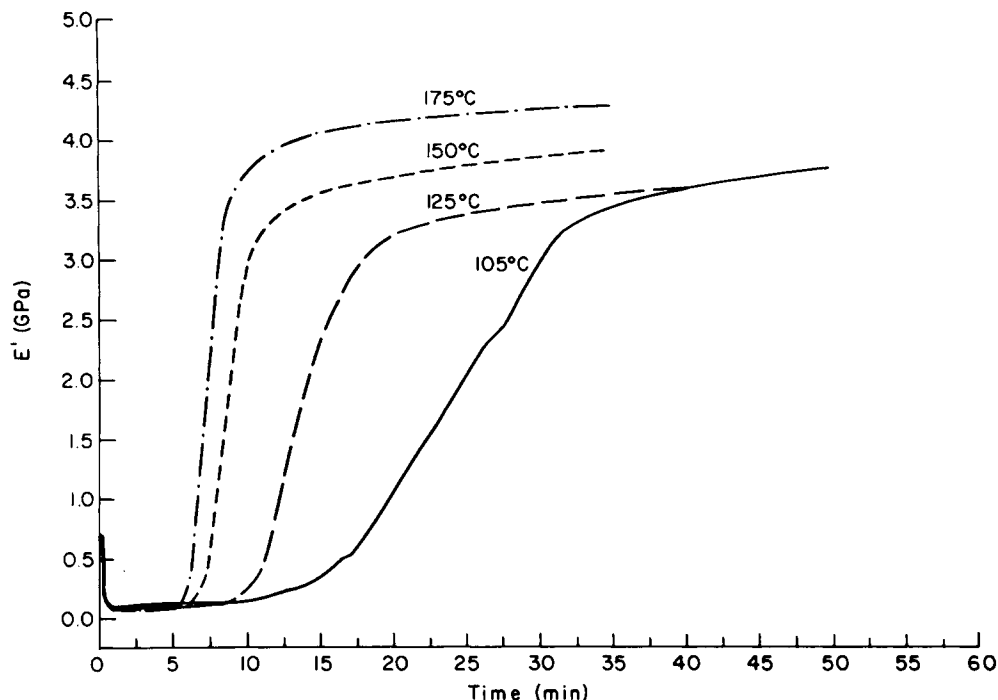
Figure 12   DMA storage modulus vs. time curves at various DMA isothermal temperatures for phenolic samples precured for 2 min at 105°C. (Samples conditioned at 91% RH prior to scans. Note that the curves for samples run at higher isothermal temperatures reach the modulus plateau more rapidly.)

Area under Tan Delta Curve

Preliminary experiments indicate that the area under the tan delta curve in an isothermal DMA scan in resonant frequency is a potentially useful measure of the degree of cure achieved in a sample prior to the DMA scan. In Figure 10(a), for example, the sample precured at 115°C exhibited a much larger tan delta peak at early times than did the sample precured at 140°C. Thus, the tan delta area (enclosed by the tan delta curve, by a horizontal baseline extrapolated back from its limiting value at high temperature, and by a vertical line at time zero) for the 115°C sample far exceeded the similarly determined area for the 140°C-precured sample. In other words, a large tan delta area implies that a sample possesses a large amount of residual cure potential, i.e., it was only lightly precured. Similar behavior is seen in the curves of Figure 10(b), which were obtained during fixed frequency measurements on samples of a resin precured for 2 min at the indicated temperatures. The rationale for these observations resides in the definition of tan delta as the ratio of loss modulus to storage modulus (E''/E'). A lightly precured sample will not only have a low initial E',

but it will also have a high E'' because it will be less crosslinked, have more molecular mobility, and absorb more mechanical energy. We use tan delta instead of E'', because the modulus ratio eliminates any variation due to sample size.

The effect of precure time upon the tan delta area of a resin is shown in Figure 11. The tan delta area decreased steadily with increasing precure time, falling some 20-fold between 1 and 25 min precure time. It is encouraging that the area appears to be more sensitive to changes at the higher cure levels. For example, between 5 and 25 min the area still fell nearly three-fold, whereas the initial E' values ($t = 0$) for samples with these precure times were essentially unchanged. We are investigating this tan delta area method further and will address its use for measuring both extent and rate of cure in greater detail in a future publication.

SUMMARY AND CONCLUSIONS

This investigation is part of a program aimed at understanding the influence of temperature, moisture, and time on the cure process of aqueous resole PF

resins. For that purpose we selected dynamic thermal analysis as the method of choice for measuring the degree of resin cure in samples previously exposed to combinations of those variables. We have described here the steps that we found necessary in order to surmount several problems encountered in attempting to obtain quantitative, reproducible DMA data on such samples. We have also examined here some alternative approaches to applying such DMA data for the purpose of measuring the extent of precure. Our major conclusions are as follows:

1. With proper attention to details of sample preparation and testing, reproducible DMA data can be obtained with aqueous resole PF resins. Most important are substrate selection, sample preconditioning, and sample clamp design.
2. The storage modulus ultimately attained in a DMA scan is affected by the amounts of precure and moisture existing in the sample prior to the DMA scan. This ultimate modulus increases with less precure and with greater starting moisture content. This behavior can be rationalized on the basis of changes in glass transition temperature caused by the level of cure and plasticization by water.
3. At any one initial moisture condition, the initial storage modulus values (at $t = 0$ in a DMA scan) rise with precure time to a plateau value, beyond which increasing levels of precure have no effect. If the moisture content of the sample is increased, the initial modulus decreases.
4. Preliminary results indicate that the area under the tan delta curve from an isothermal DMA scan offers promise as a relative measure of the degree of cure developed in samples prior to the scan.

FUTURE WORK

We plan to continue using DMA to study the influence of moisture and temperature on rate and extent of cure of resole PF resins. That work will include the use of a special environmental chamber for the DMA that will allow measurements under different relative humidities. Mechanical measurements will be paralleled with chemical analyses in an attempt to provide a chemical rationale for the observed effects.

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