

Materials science approach to product development in decorative surfaces

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ABSTRACT: *Postforming grade, high-pressure decorative laminate is used as a case study to discuss how current material science techniques may be used to enhance the understanding of existing products and contribute to product and process improvements. Thermal analysis techniques were used to evaluate the impact of temperature and heating rate on the mechanical performance of the subject laminate systems. Dynamic mechanical analyses were particularly useful in defining the conditions for optimal postforming. Trials were performed on a stationary postforming machine to support these efforts.*

KEYWORDS: *Decorative papers, dynamic tests, high pressure, laminates, test methods, thermal analysis.*

High-pressure decorative laminates (HPDLs) can be made postformable by careful selection of both resin and paper raw material composition, and proper laminate processing history. The formaldehyde-to-melamine mole ratio in the melamine resin used to saturate the surface layers must be chosen to match the manufacturing process cycle. Excessive resin cross-link density will prevent formability. In addition, modifiers such as guanamine or sucrose can be added to create additional ductility and improved

formability. However, laminate surface properties, such as stain, scratch, and scuff resistance, may be compromised. Postforming places similar constraints on the core phenolic resin. Cotton linter can be added to increase the ability of paper layers to stretch around outside bends without tearing. Longer pulp fibers (less refining) also allow more paper stretch without tearing. Postforming grade papers are often buffered to higher pH values in comparison to standard HPDL papers, thus slowing the cure reaction.

Given proper resin and paper materials, saturation and drying must be controlled to appropriate resin and volatile contents. The relative degree of resin advancement during B staging and press curing builds the molecular structure required for subsequent formability.

This paper investigates the postformability of an HPDL as described above. Thermal analysis techniques were used to study laminate viscoelastic material property response changes during the forming process. Predicted trends in material response were verified using a consistently controlled postforming machine. Variations in paper and resin raw material were not considered.

Background

Dynamic mechanical thermal analysis has been successfully used to provide insight into the cross-linking reaction of various thermoset resins during cure. Tung and Dynes (1) studied the viscoelastic response of epoxy resins during isothermal cure and showed that the gel time of the thermosetting resin can be determined from the dynamic viscoelastic shear response. A linear correlation between gel time from a standard viscosity test and the crossover point of the storage and loss modulus ($G' = G''$ or $\tan \delta = 1$) was shown.

Extending thermal analysis techniques from isotropic resins to fiber- and particulate-reinforced

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materials (prepregs and consolidated laminates) is a challenge of growing importance. Keeling (2) used dynamic mechanical analysis to study the viscoelastic response of melamine and phenolic resin prepregs on various fiber substrates, including fiberglass, kraft paper, and alpha cellulose paper. The work used subsequent room temperature resonate frequency to predict the resin modulus development during cure. It was noted that separation of the composite laminate response into components due to the fiber, the resin, and the interface development is a considerable challenge.

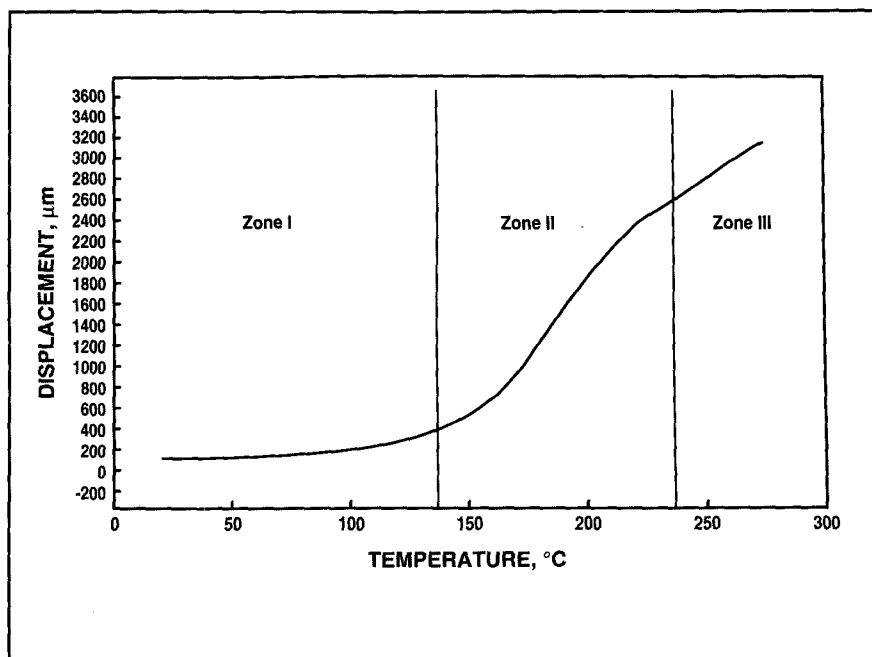
Jalbert (3) conducted dynamic mechanical testing of low-pressure melamine-based paper prepregs and showed that B-staged prepregs with similar resin contents, volatiles, and flow measures can result in different degrees of resin flow during subsequent press molding. It was suggested that the reduction in dynamic stiffness and the increase in peak tan delta are related to the degree of B stage in the prepreg. Less advanced prepregs showed more significant changes in viscoelastic response during a dynamic thermal ramp. Note that tan delta is defined as the ratio of the viscous damping response to the elastic stiffness response.

Analytical investigation

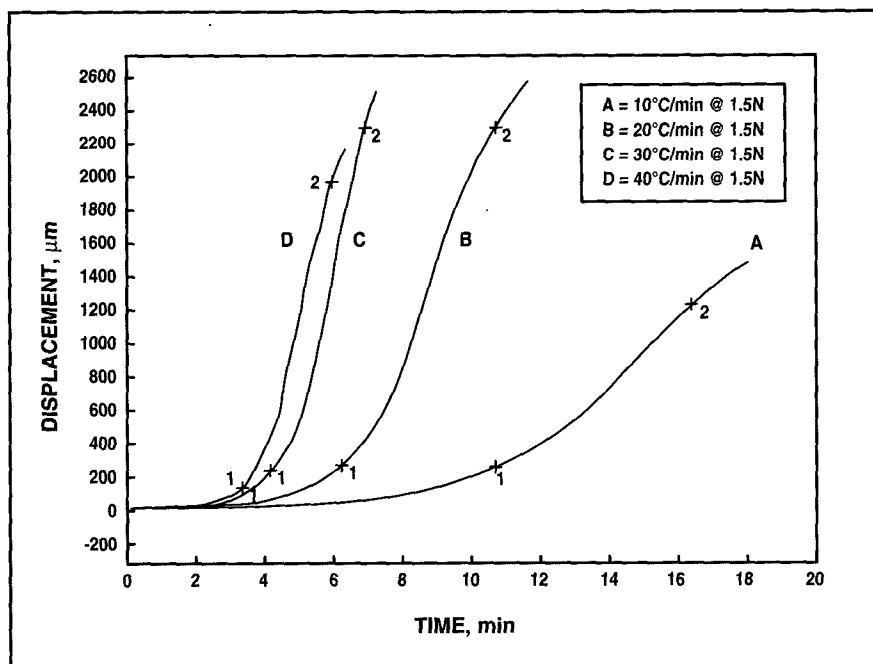
Material systems

A commercial postforming grade HPDL (PF42) was chosen for the completion of this study. As with most conventional HPDL, this is composed of multiple layers of phenolic-treated kraft paper, with a surface layer of melamine-treated decorative paper. The consolidated laminate is produced by subjecting this layout to temperature and pressure. The challenge in evaluating the performance of such a material system involves understanding the response of the constituent materials

1. Three zones of laminate response from TMA analyses of the melamine system



2. Deflection response of the melamine laminate system at heating rates of 10°C, 20°C, 30°C, and 40°C per min, measured by TMA

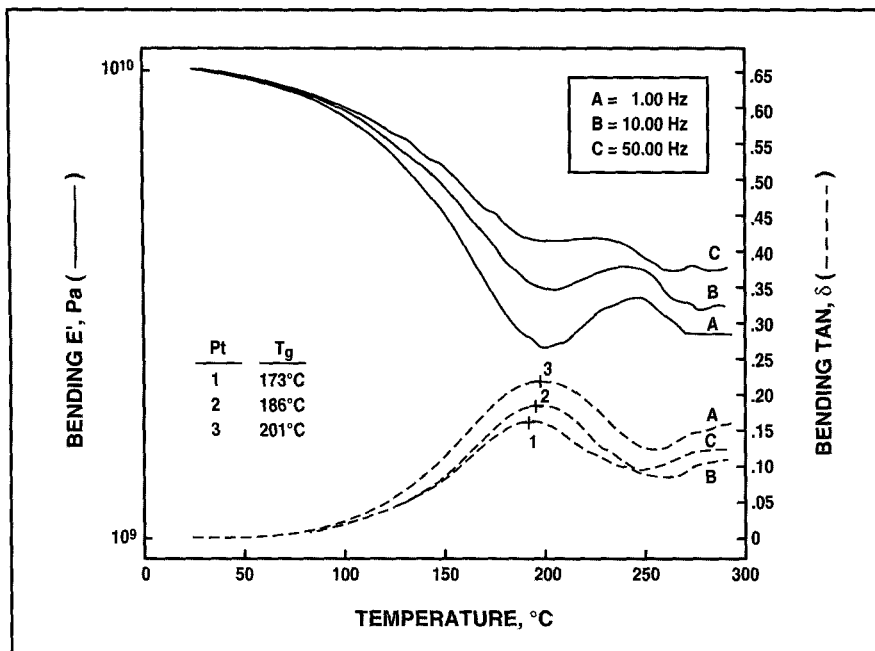


as well as their synergistic effects on the laminate behavior. While this level of understanding may not be necessary in evaluating an existing product with a proven track record,

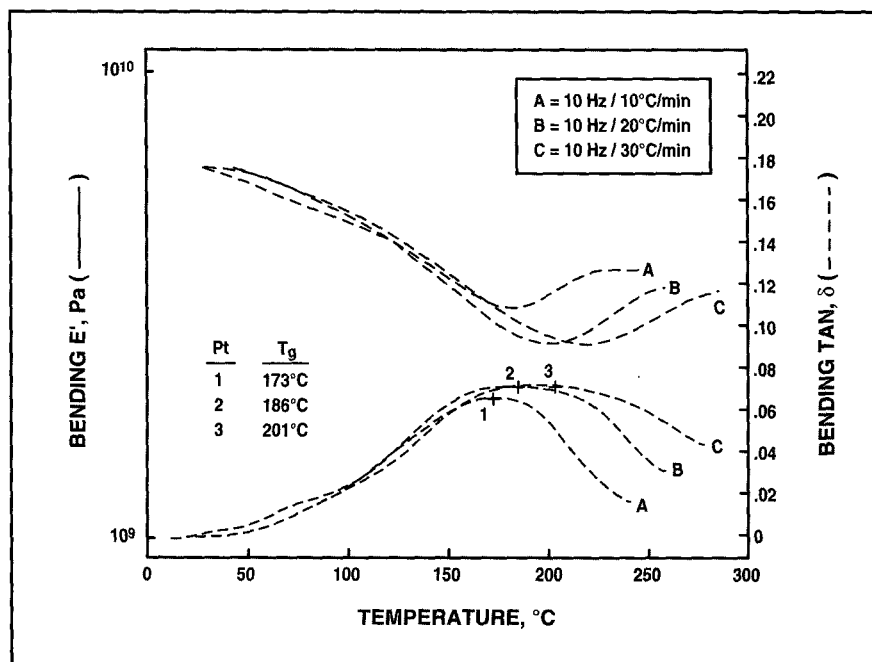
it is indispensable in developing new material or optimizing old products.

The application of this approach to the PF42 laminate resulted in the evaluation of three material systems: a melamine/decorative paper, a phe-

3. Frequency response of the melamine laminate system at 1 Hz, 10 Hz, and 50 Hz, from DMTA analyses



4. Dynamic response of the phenolic/kraft laminate at heating rates of 10°C, 20°C, and 30°C per min, from DMTA analyses. Peak values of tan δ are labeled.



nolic/kraft paper, and the PF42 product. Each of these was pressed using the standard cycle for PF42, the same press, and the same press operator for consistency. The melamine and phenolic laminates were laid up and

pressed to yield laminates with a nominal thickness of 0.75 mm (0.030 in.), while the PF42 laminates were fabricated to their standard 1.016 mm (0.040 in.) nominal thickness. All laminates in this study were subjected to

standard NEMA (4) testing to ensure postformability.

Thermomechanical analysis

Thermomechanical analysis (TMA) techniques were applied to the subject laminates. The goal of this testing was to observe the effects of temperature and heating rate on the softening and flexural behavior of the three laminate systems. The similarity between the selected TMA mode and actual postforming demands made the DMTA MkIII TMA mode the preferred choice over more classical TMA modes (e.g., flat probe or penetrating probe).

The large-deformation TMA mode of a Polymer Laboratories DMTA MkIII was selected for these tests. In this TMA configuration, a small, rectangular specimen (10.5 x 32.0 mm nominal) was mounted in single-cantilever fashion, and a constant force of 1.5 N was applied to the free end (5). This force was maintained, and the resultant specimen deflection was monitored through a regimen of increasing temperature. These tests were conducted at heating rates between 10°C and 40°C per min, through a temperature spectrum of 25–250°C.

Figures 1 and 2 display the results of TMA testing on the melamine laminate specimens. At all heating rates, the laminate exhibits a displacement profile that can be described by three general zones of material behavior (Fig. 1). Early in the heating profile, the rate at which deflection increases in response to rising temperature is relatively small and steady (Zone I). With increasing temperature, this behavior yields to a second zone of rapid deflection response (Zone II), which represents a temperature window corresponding to pronounced softening and flow behavior for the resin in the laminate (3). It is the deflection behavior observed in this second zone that is most desirable in the postforming process. Finally, the material reaches a third temperature zone in which

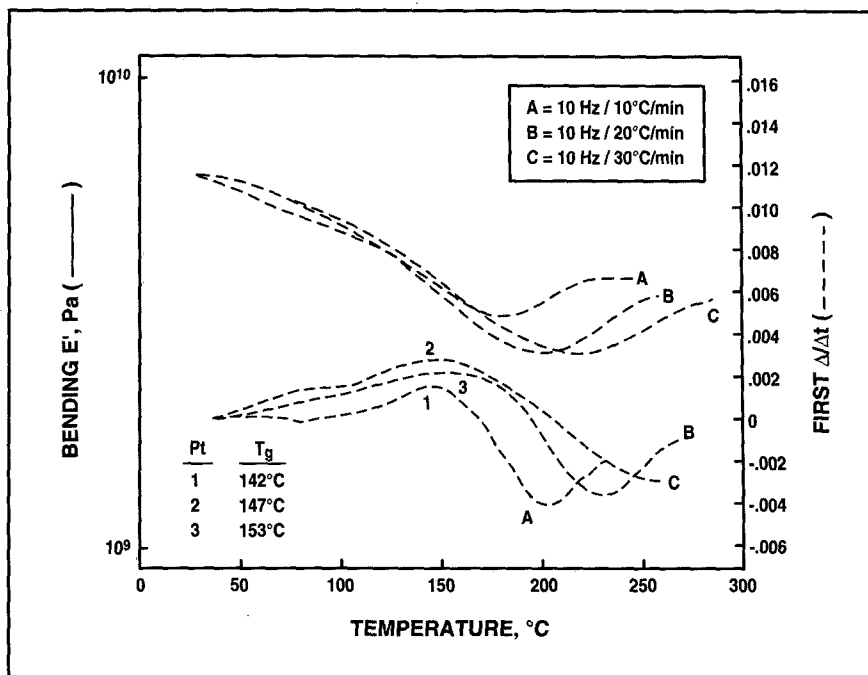
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the rate of deflection is again reduced (Zone III). This third zone of material response reflects the onset of an advanced state of cure in the resin system. The resin in the laminate has achieved a cross-link density that reduces the ability of resin to flow, thereby limiting formability.

The curves in Fig. 2 are labeled with numbers 1 and 2 at the approximate points of inflection into Zones I and II, respectively. These inflection points were selected using curve analysis software supplied with the analytical equipment. Table I displays the temperature values corresponding to these points for the melamine/paper results of Fig. 2, and for similar results obtained from identical testing of the phenol/kraft and PF42 laminate. Both of the latter laminate systems displayed a three-zone temperature response similar to the melamine, although the reduced resin content and stiffer paper of these materials combined to yield more gradual transitions in the displacement response.

The data in Table I provide an approximate picture of how the components of a postforming HPDL (e.g., melamine/paper or phenol/kraft) and the PF42 itself respond to the combination of force and temperature used in postforming. A few interesting points can be made about the data in Table I. The locations of the first transition temperatures suggest that, for both the melamine and phenolic resin systems, the onset of material softening is relatively independent of heating rate. The second transitions shift to higher temperatures with increasing heating rate. This trend is also apparent in both melamine and phenolic resin laminates, and suggests that faster heating rates in the postforming process may be useful in broadening the process range for successful forming. The position of these forming windows is revealing, because it supports the opinion that successful postformability is largely a function of the melamine/decorative surface.

5. Dynamic response of the phenolic/kraft laminate at heating rates of 10°C, 20°C, and 30°C per min, from DMTA analyses. Peak values of $-dE'/dt$ are labeled.



I. Key transition temperatures from TMA

Material system	Heating rate, °C/min	Transition 1, °C (Zone 1 - Zone 2)	Transition 2, °C (Zone 2 - Zone 3)
Melamine/ decorative paper	10	132	191
	20	132	221
	30	137	224
	40	134	236
Phenolic/ kraft	10	90	192
	20	87	217
	30	91	235
	40	85	238
PF42 commercial HPDL	10	109	196
	20	126	219
	30	132	233
	40	124	226

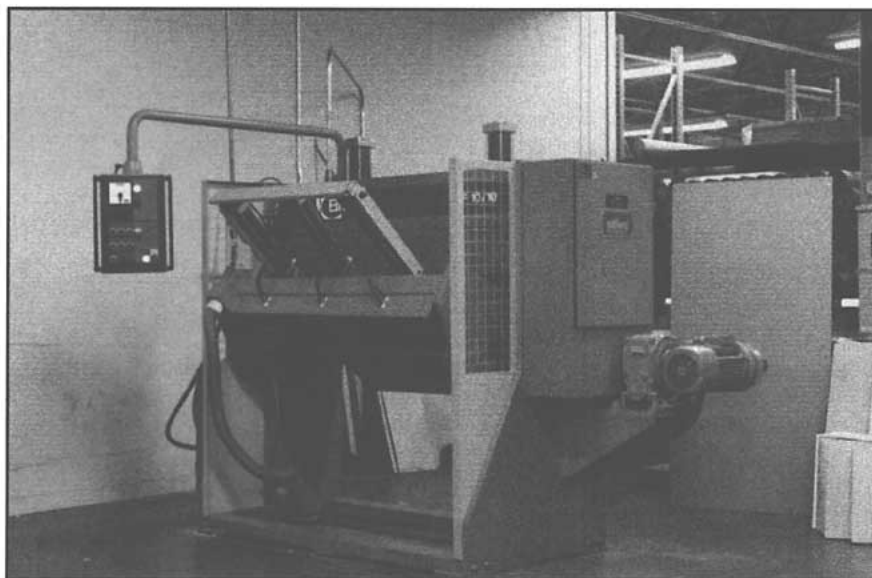
While this seems obvious, the aesthetics of the decorative surface being all-important, Table I illustrates the actual mechanics behind the observation. The apparent window of melamine flow (approximately 130–230°C) lies within that indicated for phenolic (approximately 90–240°C), which inherently places control of

successful forming in the melamine/decorative surface. Note that the apparent forming limits for the PF42 lie, for the most part, between those of the constituent laminates. In reality, achieving successful postforming at either extreme of this range (130–230°C [265–445°F]) is unlikely. At the low end, the laminate has not

II. Key transition temperatures from DMTA

Material system	Heating rate, °C/min	Peak tan delta, °C	Temp. (°C) at maximum -dE/dt
Melamine/decorative paper	10	176	149
	20	198	165
	30	212	174
Phenolic/kraft	10	173	142
	20	186	147
	30	201	153
PF42 commercial HPDL	10	175	144
	20	181	156
	30	205	170

6. Brandt Model PF10/10 postforming machine



achieved adequate flexibility. At the high end, not only has the resin reached an advanced cure and lost flexibility, but the point at which paper discoloration begins has been exceeded for certain paper/color combinations.

Dynamic mechanical thermal analysis (DMTA)

To gain more insight into the nature of the phenomena observed under TMA evaluation, dynamic mechanical analyses were performed on the three subject laminate systems. The DMTA instrument used in the preceding TMA testing was also se-

lected for these evaluations. The TMA specimen geometry was retained, and the specimens were again mounted in single-cantilever fashion. DMTA mode was selected for this part of the study, however, and it is in this mode that the instrument has its greatest utility. Unlike TMA mode, a static mode, DMTA subjects the specimen to a well controlled, oscillating deformation of specific magnitude and frequency. For these studies, the test frequencies and heating rates were varied, but a displacement amplitude of 90 μm (0.02% strain) was maintained in all testing.

Figure 3 displays DMTA data for the melamine laminate system, taken at frequencies of 1 Hz, 10 Hz, and 50 Hz, at a heating rate of 20°C/min. These data are intended to demonstrate the relative insensitivity of the thermal transitions to testing frequency in the subject laminates. In a homogeneous resin, or even a composite of high resin content, the selection of test frequency can be important, because changing frequencies shift the location of thermal events horizontally along the temperature axis (6). Depending on the nature of the resin, this effect can be significant. The melamine laminate was selected as an example because, as the subject system with the highest resin content, it has the greatest potential for frequency-dependent behavior. The phenol/kraft and PF42 laminates displayed even less response to changing frequency.

The behavior exhibited in Fig. 3 is not atypical of reinforced resin systems (7) and reflects the influence of the nonviscoelastic constituents of the composite. There is some question about the relationship between frequency and the magnitude of the properties measured, and Fig. 3 clearly illustrates frequency-induced shifting along the vertical axes. Previous experience applying DMTA to resin processing (extrusion processes) suggests that this frequency sensitivity may be used

III. Results of postforming trials

Machine platen temp.,		Time to 163°C (325°F), s (back surface)	Time to start bend, s	Heating rate (back side)		Springback	Cracking or crazing	Discolor	Other comments
°C	°F			°C/s	°F/s				
240	464	20	23	6.7	12.0	No	Yes	Yellow	Blister
230	446	20	20	6.7	12.0	No	1 side only	Yellow	-
230	446	20	23	6.7	12.0	No	Yes	Yellow	-
220	428	21	22	6.3	11.4	Slight 1 end	Slight 1 end	No	Acceptable
210	410	-	25	-	-	Slight 1 end	Slight 1 end	No	Acceptable
210	410	23	23	5.8	10.4	No	No	No	Acceptable
212	414	22	22	6.1	10.9	No	Slight 1 end	No	Acceptable
206	403	23	32	5.8	10.4	No	Yes	No	Acceptable
207	405	21	26	6.3	11.4	No	No	No	Acceptable
210	410	-	20	-	-	No	Slight 1 end	No	Acceptable
200	392	-	28	-	-	No	No	No	Acceptable
196	385	26	32	5.1	9.2	Slight	No	No	Acceptable
195	383	-	34	-	-	No	No	No	Acceptable
186	367	28	34	4.8	8.6	No	Slight 1 end	No	Marginal
170	338	45	65	2.9	5.3	Yes	Yes	No	-
170	338	-	45	-	-	Yes	-	-	-
170	338	-	31	-	-	Yes	-	-	-
167	333	-	23	-	-	Yes	-	-	-
157	315	-	20	-	-	Yes	-	-	-
150	302	-	-	-	-	No	Yes	No	-
145	293	-	16	-	-	Yes	-	-	-
140	284	-	-	-	-	Extensive	Yes	No	-
130	266	-	-	-	-	Extensive	-	-	Break

to investigate rate effects in the manufacturing process of a resin system (8). Such speculation, with respect to postforming HPDL, is outside the scope of this paper. For the purpose of this paper, the trends but not the magnitudes of the storage modulus (E') and $\tan \delta$ signals are of primary interest. Having eliminated frequency as a major variable in the behavior of the subject laminates, the focus can be reasonably limited to temperature and heating rate effects.

Figures 4 and 5 display these data for DMTA testing performed on specimens of the phenolic/kraft laminates at 10 Hz, under heating rates of 10°C, 20°C, and 30°C per min. Two material phenomena may be observed as results of heating rate studies, each reflecting the nature of the measurement from which it is drawn [i.e., $\tan \delta$ or storage modulus (E')]. The $\tan \delta$ reflects the loss or damping properties of the laminate

system. The peak value of $\tan \delta$, therefore, represents the point of maximum resin mobility in the material. For the subjects of this study, this point can be related to the temperature at which the greatest amount of the partially cross-linked resin has reached its minimum viscosity. At temperatures beyond the $\tan \delta$ peak, the cross-linking mechanism begins to reduce the amount and mobility of this resin.

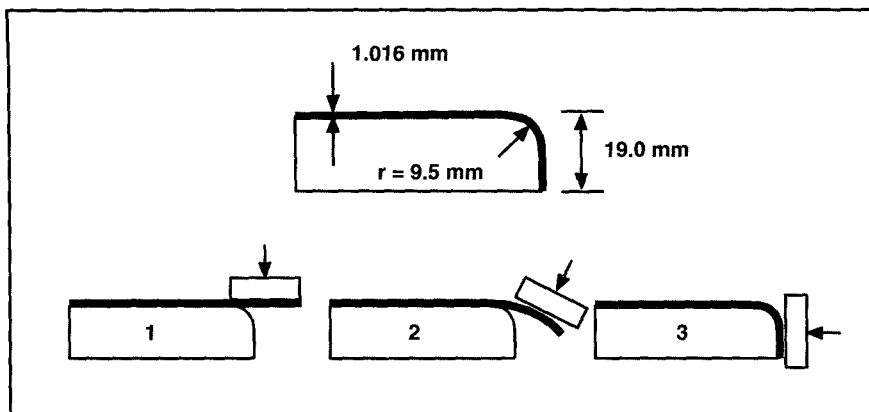
The quantity E' relates closely to the basic structural stiffness of a material; it proves to be a gauge of the material's potential to postform. Note that the points of minimum E' correspond closely to their related $\tan \delta$ peaks. At temperatures below the $\tan \delta$ peaks, both the E' and $\tan \delta$ traces superpose on one another well, regardless of heating rate. The effect of heating rate on the laminate behavior becomes more pronounced as the materials pass through their regions of maximum

softness. The shifting $\tan \delta$ values illustrated in Fig. 4 demonstrate this behavior clearly.

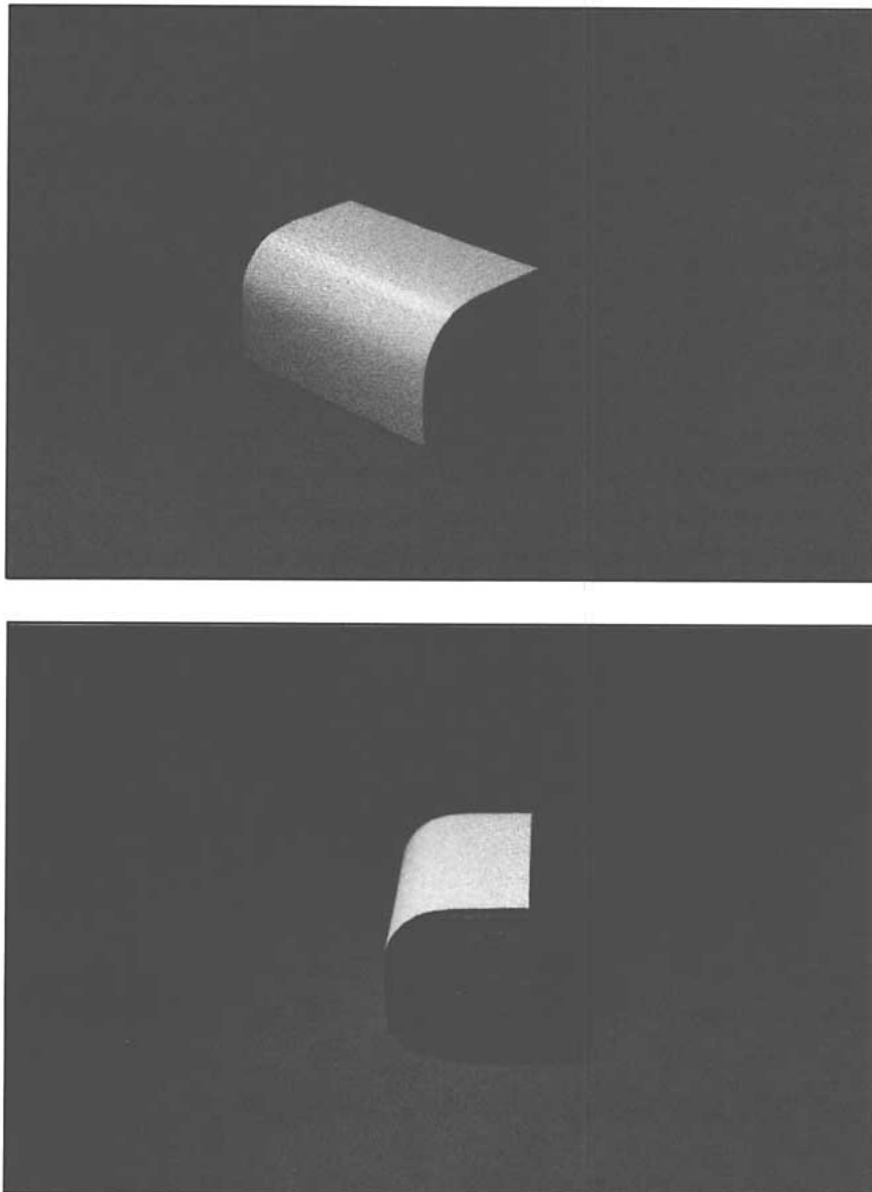
Figure 5 presents an analysis of the E' signal from Fig. 4. In this figure, the first derivative of the E' curve with respect to time ($-dE'/dt$) was calculated for all three heating rates. Using the peak of $(-dE'/dt)$ in this manner yields a definitive temperature at which the reduction of E' is at its maximum rate. This measurement could suggest a reasonable lower limit to successful postforming temperatures, because it invariably lies between the onset of softening suggested by TMA and the peak of the $\tan \delta$ curve for all of the subject laminates.

Table II presents these specific data for the phenolic/kraft system of Figs. 4 and 5 and the other subject laminate systems. Note that the temperature ranges presented in this table lie within those suggested

7. Schematic cross section of geometry studied and staged



8. Cross section of laminate showing successful forming without springback



through the TMA results of Table I. In addition, the DMTA data in Table II suggest a clear effect of heating rate on the location of these process windows. In general, Table II suggests a postforming window of approximately 30°C. The locations of these windows range from approximately 145–175°C for slower heating rates to 175–205°C for faster heating rates. Given the sensitivity of DMTA measurements, and their ability to measure material properties directly, it seems reasonable that useful postforming ranges could be approximated from the DMTA measurements reflected in Table II. Most importantly, the rationale for using these temperatures to define such a window of material behavior is based on reasonable interpretation of material properties.

Experimental verification

Postforming trials

A 1.016-mm (0.040-in.)-thick postforming grade HPDL (PF 350) was thermally postformed on a stationary postforming machine. The laminate material properties were verified to pass industry-standard NEMA testing (4) for a PF42-grade laminate. A Brandt PF10/10 stationary forming machine was used for the forming trials. Forming is accomplished over a 91.4-cm (36-in.) length by means of a conductive contact-style heat source, or platen. The forming motion is controlled with a pneumatic pressure beam and forming bar. This equipment was chosen for its ability to be programmed for precise and repeatable forming temperatures and motions. See Fig. 6. A 90° external radius of 9.5 mm (0.375 in.) was chosen for this study.

The preparation for forming procedures begins with a 19.0-mm (0.75-in.)-thick particle board (IM-2 grade) substrate, prelaminated with an overhang sufficient to form-cover the edge profile. Contact adhesive was applied to both surfaces of the over-

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hanging laminate. The postforming and bonding are achieved with a swiveling, heated, pressure-forming bar that automatically forms the overhanging surface around the profiled edge of the substrate by means of an electromechanical drive. See **Fig. 7**. The forming beam can make preselected stops at critical points around the profile. Most of the forming work discussed here was accomplished in a single motion, wrapping 90° in 16 seconds followed by a 10-second hold in the vertical position to set the adhesive on the edge.

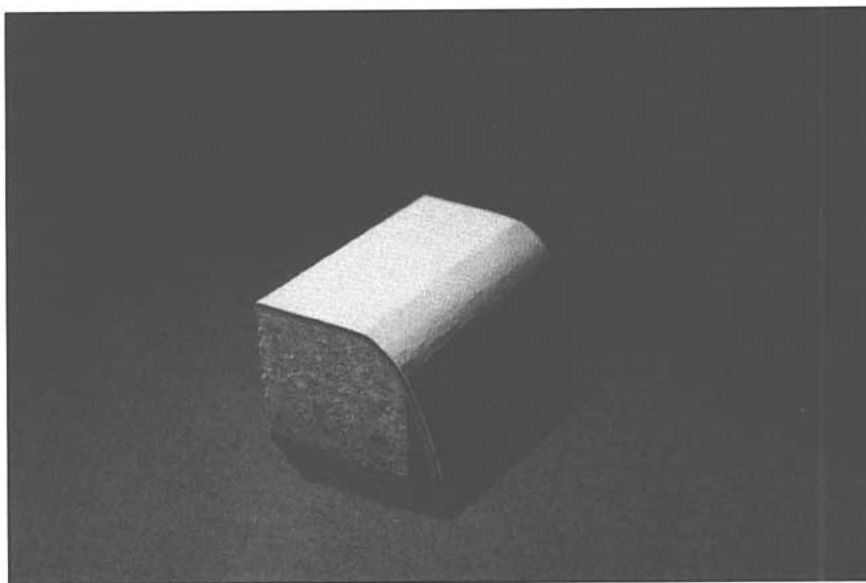
Forming conditions were varied by changing the forming platen temperature and maintaining a constant forming speed. The nature of the heating process does not allow the forming temperature and warmup rate in the laminate to be varied independently. A temperature-sensitive chalk was used on the laminate back surface to estimate the approximate heating rate. Note that the laminate top surface heating rate will be higher and the nominal laminate temperature will be lower than the estimates reported. **Table III** lists the results of a series of forming experiments. In general, the following progression of laminate forming response was observed through the test series as the platen temperature was increased: (a) cold bend: laminate fracture along edge profile, (b) large cracks/crazing/springback, (c) mild springback, (d) success, (e) crazing, (f) discoloration, (g) blistering.

Platen temperatures of 190–200°C (374–420°F) resulted in successful postforms for the combination of laminate, forming speed, and equipment studied. The corresponding laminate heating rate was estimated to be 3.1–5.1°C/s (5.6–9.1°F/s). Some slight effects were observed at the ends of the samples, indicating that uniform application of heat along the length of the bend is necessary.

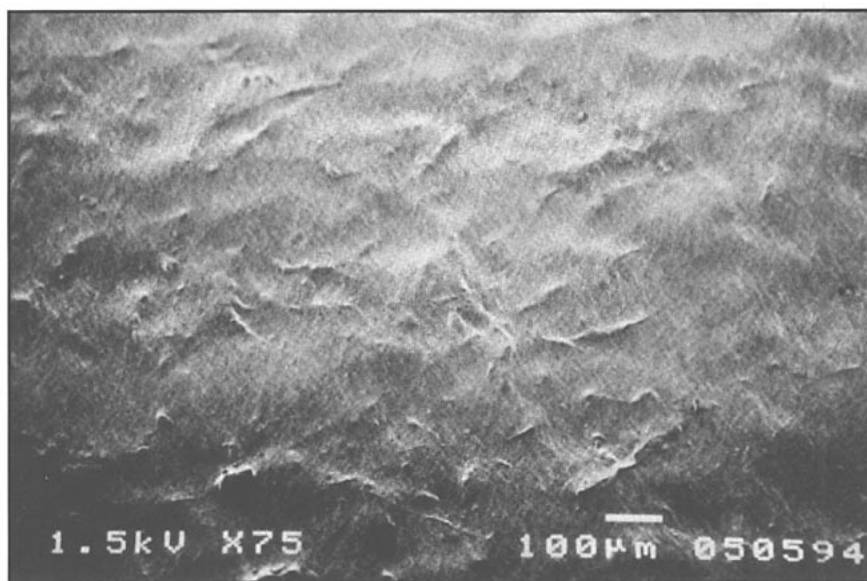
Photo-microscopy

Figures 8 and 9 illustrate the cross sections of typical formed edges with

9. Cross section of laminate showing springback



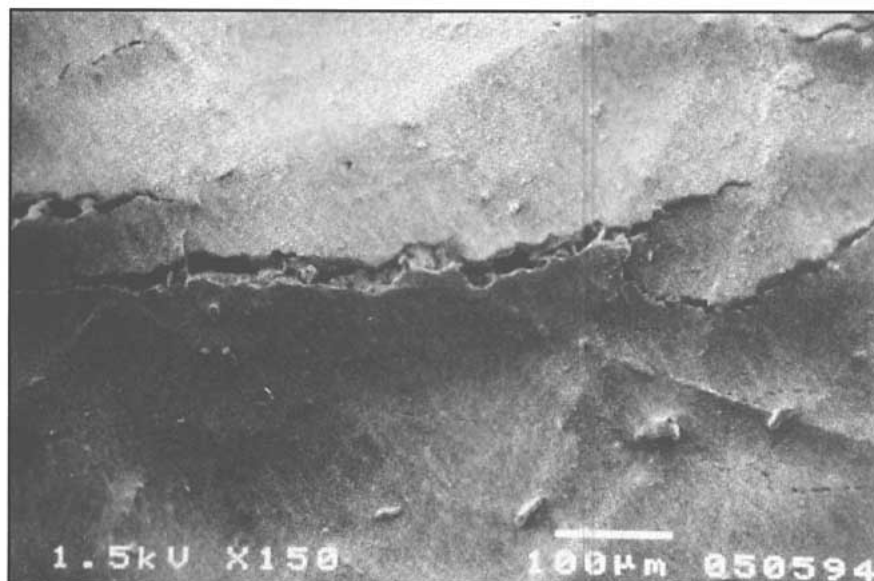
10. SEM photo of laminate surface after successful forming. Magnification 75X.



correct and incorrect temperature-time conditions. Figure 8 shows a properly formed edge with good surface finish and the laminate curvature matching the substrate curvature (minimizing mechanical load on the bond line). Figure 9 illustrates the possible failure modes when forming conditions are not matched to the laminate material. Forming with insufficient heat can result in both large surface cracking

and a significant springback (elastic recovery). The curvature mismatch between the laminate and the substrate can also apply undue mechanical load to the adhesive bond line. **Figure 10** illustrates the surface appearance of a typical decorative laminate after successful postforming. The photographs were obtained using a scanning electron microscope. The laminate surface shows a relatively smooth texture, free of imper-

11. SEM photo of laminate surface after improper forming. Note crazing due to poor resin flow and paper stretch. Magnification 75X.



fections, similar to the laminate surface as manufactured. The surface texture shown here is a matte finish. When the temperature and time of the postforming operation are not matched to the laminate material, less-than-ideal surface finish can result. **Figure 11** shows microscopic crazing as a result of forming the material at temperature-time conditions above the forming window for the laminate.

Summary and conclusions

In this effort, the performance of a commercial postforming-grade HPDL (PF42) was used as a case study. The goal of this study was to evaluate the ability of current materials science techniques to successfully measure and predict the performance of the PF42. Specifically, the thermal analysis techniques of thermomechanical analysis (TMA) and dynamic mechanical thermal analysis (DMTA) were used to measure and predict the effects of temperature and heating rate on postforming HPDL.

Both TMA and DMTA methods were successful in demonstrating the mechanisms of softening and cross-

linking associated with postforming laminate. In particular, DMTA techniques demonstrated the ability to monitor these mechanisms and suggested the development of a process window for postforming. A postforming window was defined for PF42 by using both the E' and $\tan \delta$ curves generated with DMTA testing. This method predicted a viable postforming range of approximately 30°C, which shifted according to heating rate. A range of 175–205°C was predicted for fast heating rates, based on data accumulated in DMTA testing at 30°C/min.

A state-of-the-art, static postforming machine was used in support of these efforts. Successful postforming was achieved using platen temperatures between 190°C and 220°C. Some question exists about the rate of heating that occurs in the laminate as a result of contact with the platen/forming bar. In addition, the actual temperatures established inside the laminate during this process are not well understood. These and several other difficulties became apparent in the attempt to compare field postforming results with the performance predictions generated using thermal analyses.

These levels of correlation must be achieved if thermal analysis techniques are to prove robust methods, useful in engineering complex material systems. This aspect of the study will be the focus of continued effort. **□**

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