IN-SITU CURE MONITORING OF ISOCYANATE ADHESIVES USING MICRODIELECTRIC ANALYSIS

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ABSTRACT

Recent advances in microelectronics have produced small electrodes that can be used for remote dielectric measurements. These miniature sensors are small enough to be embedded in a composite panel during manufacture with little disturbance to the manufacturing process. Small particleboard panels (5 by 4.5 by 0.25 in.) were manufactured with 6 percent polymeric diphenylmethane diisocyanate resin in a laboratory hot-press. A dielectric sensor was embedded in the core of each panel to measure both temperature and dielectric responses. The curing behavior of the particleboard furnish was also examined using dielectric analysis in a controlled oven and differential scanning calorimetry. Close agreement was found between the curing response detected by both these techniques. In addition, the curing response of particleboard furnish in a controlled oven was remarkably similar to that seen in situ during particleboard manufacture using four different platen temperatures. The contribution of moisture changes during pressing to the dielectric signal was evaluated. Finally, two different sensor designs were evaluated on a limited basis.

The hot-pressing operation is the focal point for the manufacture of most wood-based composites. During pressing, heat is transmitted into the product through a complicated heat and mass transfer process involving both conductive and convective mechanisms (4,6,8,9). Great strides have been made in recent years to understand these consolidation processes through in-situ monitoring of hot-pressing variables. In particular, internal mat temperature and moisture histories are studied for their influence on adhesive cure. Interpreting the influence of the transient humidity and temperature gradients within a mat on adhesive cure has been, at best, speculative.

The importance of adhesive cure to the integrity of the wood composite is emphasized by the volumes of research reports that address the issue. For the most part, this past work has been restricted to the controlled environment of the laboratory to investigate the physical and chemical processes of the curing reaction. Extending this information to the curing behavior of the resin in an actual production environment requires that a number of assumptions be made. Recently, a modified version of dielectric analysis (DEA) has been introduced that makes in-situ cure monitoring of thermosetting polymers a reality. Known as microdielectric spectroscopy, the utility of this analytical tool has been demonstrated for a variety of thermosetting polymers (2,5), including phenol-formaldehyde resins (10) and modified resorcinol-formaldehyde resins (11). The objective of this research is to investigate the application of microdielectric analysis to the study of the curing reaction of isocyanate adhesives as it relates to the overall mat consolidation process of particleboard.

METHODS AND MATERIALS

MICRODIELECTRIC THEORY

The primary objective of dielectric spectroscopy is the observation of dipole orientation and ion mobility within a material. Several excellent reviews on DEA are available (1,3). Of particular significance are the fundamental dielectric properties: permittivity (ε') and dielectric loss (ε''). Permittivity is a measure of the degree of alignment of dipoles and dielectric loss is a measure of the energy expended to align dipoles and transport ions. These parameters are analogous to the storage and loss modulus obtained from dynamic mechanical analysis. Also, it is common practice to express dielectric data as tan δ, defined as the ratio of the dielectric loss to permittivity ($\varepsilon''/\varepsilon'$) as is done with dynamic mechanical data. It is important to recognize that the dielectric loss parameter results from both a dipole term and an

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Forest Prod. J. 45(2):72-77.

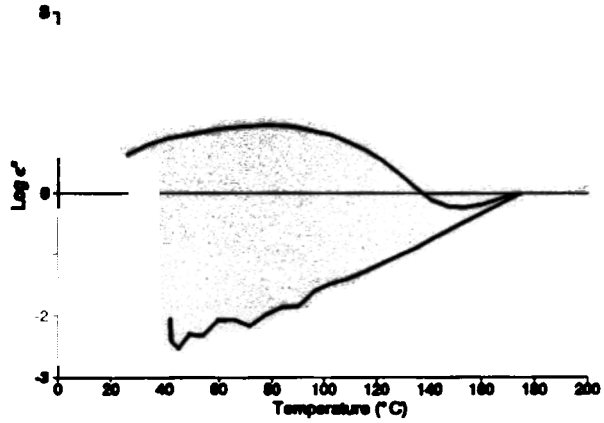

Figure 1. — Dielectric scan in the controlled oven for particleboard furnish with 6 percent MDI content.

ionic conductivity component (σ), as follows:

$$\varepsilon'' = D + \left(\frac{\sigma}{\omega} \times \varepsilon_0\right)$$

where:

D = a dipole contribution term

ω = frequency

ε_0 = absolute permittivity

At sufficiently low frequenies, then, σ can be made much larger than the dipole contribution term and easily measured.

During the isothermal cure of a thermosetting polymer, dipoles tend to orient preferentially along the field direction while ions move toward the electrodes. Initially, the mobility of these components is very high in the liquid resin. As the curing reaction progresses, which generates larger complex molecules, the movement of the ions and dipoles in the system becomes increasingly restricted. This result is manifested as longer dipole relaxation times relative to the experiment's cycle time (frequency). Eventually, as the difference between the relaxation time and cycle time increases, the dipoles will remain randomly oriented and ions will become all but immobilized. In essence, dielectric data provide information on material viscosity prior to vitrification and polymer rigidity in the glassy state. Therefore, DEA presents an opportunity to characterize the curing reaction of a thermosetting polymer by monitoring its rheological transformation.

In the past, the application of DEA has been limited due to experimental difficulties that required careful sample preparation and a high vacuum environment. Recent technological developments have avoided many of these obstacles by making it possible to build the electrode structure on an integrated circuit. This microdielectric sensor provides a fixed sample geometry, signal amplification, and local temperature measurement while expanding the available measurement frequencies to a range of 0.005 Hz to 100 kHz. Perhaps the most significant enhancement offered by this technology is the small size of the microsensor, which makes data collection from remote locations possible. Consequently, microdielectric analysis provides tremendous opportunities in the area of thermoset cure, both in terms of fundamental research efforts and production quality control.

PANEL MATERIALS

Southern pine particleboard furnish was obtained from commercial sources and was maintained at 6 percent equilibrium moisture content (MC) until use. All furnish was screened to remove fines and overs (passing 9 and holding 18 Tyler mesh). Ovendried furnish was prepared in a convection oven at 103°C. Furnish was prepared to 9 and 12 percent MCs by mixing a measured amount of liquid water with the 6 percent MC furnish and storing for 24 hours in a sealed plastic container.

Polymeric diphenylmethane diisocyanate (MDI) (Mondur MR-5) was gradually added to the particleboard furnish while manually stirring the mixture. A 6 percent resin level was selected because the resin could not be adequately distributed at lower amounts. Each panel was mixed in single batches immediately prior to pressing. The residual furnish mixture was used for controlled dielectric and calorimetry measurements.

DIELECTRIC ANALYSIS

DEA was performed using a Eumetrics System III Micro-Dielectric Analyzer equipped with a microprocessor-controlled oven. Most measurements were performed using a low conductivity sensor and signal converter. An interdigitated electrode (IDEX) sensor with a high conductivity signal converter was used for a single scan. All scans were performed at a frequency of 100 Hz. Although multifrequency scans are typically used for cure analysis, a single frequency was necessary to collect an adequate number of data points during the rapid temperature changes in the press. Temperature is detected using a Type J thermocouple integrated into the low conductivity sensor. However, a separate thermocouple was located adjacent to the IDEX sensor.

DEA was performed in both a microprocessor-controlled oven and in panels during pressing. For controlled oven scans, approximately 10 g of furnish and resin was applied to the DEA sensor and placed on the oven's heating stage. The furnish was pressed on the sensor with a metal plate and screw clamp. A glass cover was placed over the heating stage to minimize heat loss. Duplicate samples were tested with oven scans to verify repeatability.

Small particleboard panels (5 by 4.5 by 0.25 in.) were manufactured in a 6- by 6-inch laboratory hot-press. Panels were manually formed to a target density of 45 pcf. The DEA sensor was located in the center of the panel after forming 50 percent (by weight) of the panel. A small low density area was formed around the brittle low conductivity DEA sensor to prevent fracture. In addition, the sensor was backed with a 0.06-inch-thick piece of basswood to prevent bending in the pressed panel. These steps were not necessary for the tough IDEX sensor. The panels were pressed at the specified platen temperature for 15 minutes and were then removed from the press to cool. The DEA scan began as the panel was being loaded into the press. Press closure began 1 minute into the DEA scan and was completed in approximately 15 seconds. All panels were pressed to stops.

DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 2. Small samples of furnish (20 mg) were placed in o-ring-sealed, medium-pressure containers for analysis. The samples were scanned from 50° to 200°C at a heating rate of 10°C/min. Temperature and heat calibration was performed using an indium standard. Data were recorded on a strip recorder and manually digitized for computer analysis.

RESULTS AND DISCUSSION

CONTROLLED SCANS

A controlled DEA scan on particleboard furnish with a 6 percent MDI content is shown in **Figure 1**. The dielectric scan can be divided into four distinct regions that show: 1) the increase in dielectric loss (ε'') with increasing temperatures less than 75°C; 2) the decrease in ε'' between the inflection points displayed at 75° and 155°C; 3) the increase in ε'' for temperatures greater than 155°C; and 4) the relatively linear decrease in ε'' with temperature (a characteristic cooling curve for a fully cured polymer).

The early increases in ε'' seen in region 1 result from decreases in viscosity in the liquid MDI resin with increasing temperature. Evidence of the onset of cure is seen as a change in the slope of the curve at about 50°C, the reaction rate is not great enough to completely counteract the temperature-viscosity relationship. However, in region 2, the rapid progression of cure results in a significant decline of ε''. In this region, ε'' consistently decreases with the increased viscosity and decreased molecular mobility of the MDI resin and composite panel. Because this change is only associated with the changes in the physical properties of the resin, no direct interpretation can be made regarding the chemistry of polymeric network formation (i.e., urethane and urea bond formation) from this single scan. Simply stated, the inflection points displayed at 75° and 155°C denote the onset and culmination of cure as it is actually manifested in the panel. Region 3 results from the softening of the cured (solid) MDI resin and wood polymers. The cooling curve shows the characteristically linear relationship between the log of ε'' and temperature for a fully cured polymer (region 4). All the panels in this study were removed from the press and allowed to cool during the dielectric scan.

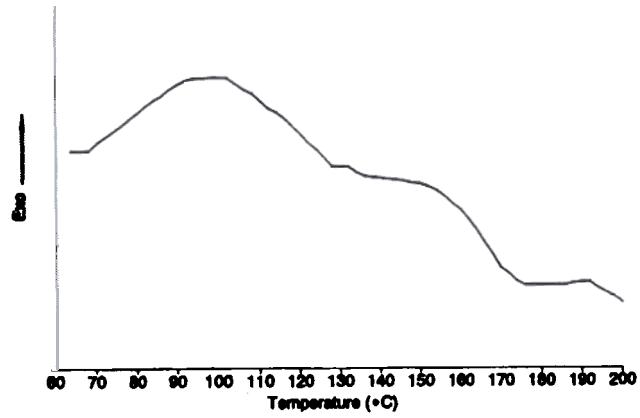

Figure 2. — Differential scanning calorimetry of particleboard furnish with 6 percent MDI content.

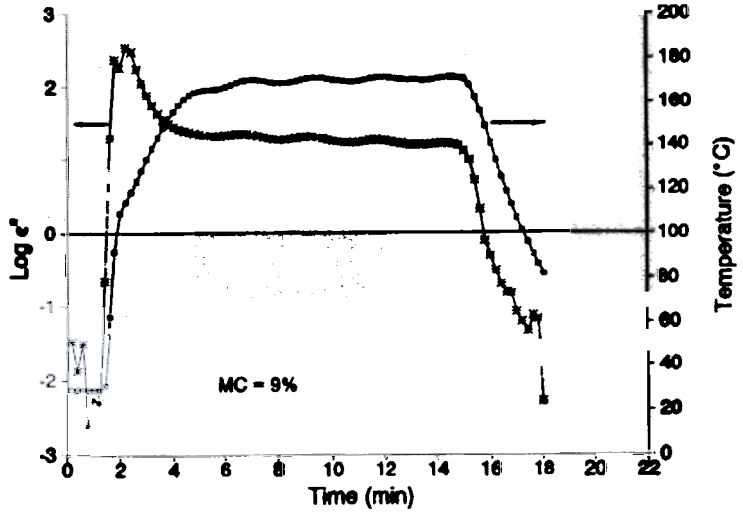

Figure 3. — Typical dielectric scan during particleboard pressing

A DSC scan of the particleboard furnish generated using a similar temperature history is shown for comparison in **Figure 2**. An exothermic peak located between 65° and 130°C results from the curing reaction of the MDI resin. Note that the onset of the curing reaction is observed at essentially the same temperature when determined by DSC as compared to DEA. However, DEA suggests that resin cure is not complete until a temperature of about 150°C, almost 20°C beyond that indicated by DSC. This apparent discrepancy can be accounted for in terms of the characteristics of the two analytical techniques. DSC senses heat flow from curing regardless of its influence on the physical properties of the resin. Reactions occurring early in the cure cycle (i.e., at low temperatures) produce significant amounts of heat, but have little influence on developing mechanical properties. However, network polymers are typically sensitive to small amounts of crosslinking when crosslink density is low. Therefore, reactions occurring late in the cure cycle may contribute significantly to increasing physical properties, but produce little heat. Since the dielectric sensor measures the mobility of ions and dipoles in the sample, it is inherently more sensitive to physical property changes and, therefore, the latter stages of cure.

PANEL SCANS

A typical DEA scan during panel pressing is shown in **Figure 3**. The panel was loaded into the press and the scan began at time equal to zero. Both temperature and ε'' remained constant until the press was closed at 1 minute. Both variables increased during the press closing time, which was approximately

45 seconds. During the remainder of the press cycle, the panel temperature asymptotically increased toward the platen temperature. However, ε″ continuously decreased as the MDI resin cured. As the platen temperature was approached inside the panel, small fluctuations can be seen in both the core temperature and ε″ resulting from the on-off temperature control in the press.

CURE KINETICS

Although Figure 3 is useful to observe the press cycle, the cure relationship is best understood when the press data are presented in a different manner. Figure 4 depicts the same cure data for four particleboard panels (6% MDI content) manufactured with identical press cycles and different platen temperatures. The data are presented as a function of temperature, rather than press time, for comparison with the controlled DEA scans. The magnitude of ε″ is influenced by the mechanical pressure producing physical contact between the particleboard furnish and the DEA sensor. Because pressure on the sensor could not be strictly regulated in the controlled and panel scans, the controlled scan data are vertically shifted. This vertical shift on the log scale is equivalent to a multiplier on a normal scale and merely serves to amplify the dielectric signal. This shift does not influence the temperature-curing relationship of the particleboard furnish and is performed to enhance the comparison of this relationship between controlled and panel scans.

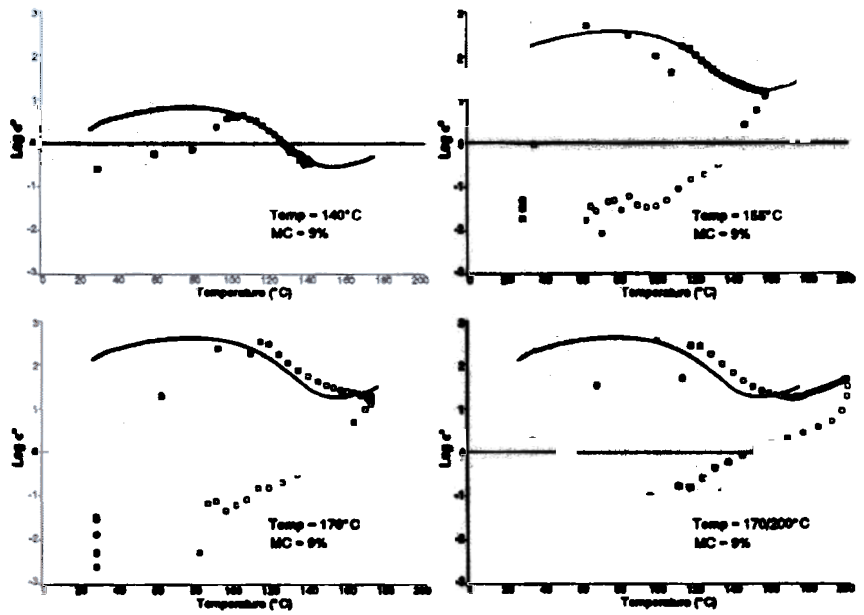

Figure 4. — Panel dielectric scans for particleboard panels manufactured with different platen temperatures (individual data points). A controlled oven scan is overlaid (solid line) for comparison.

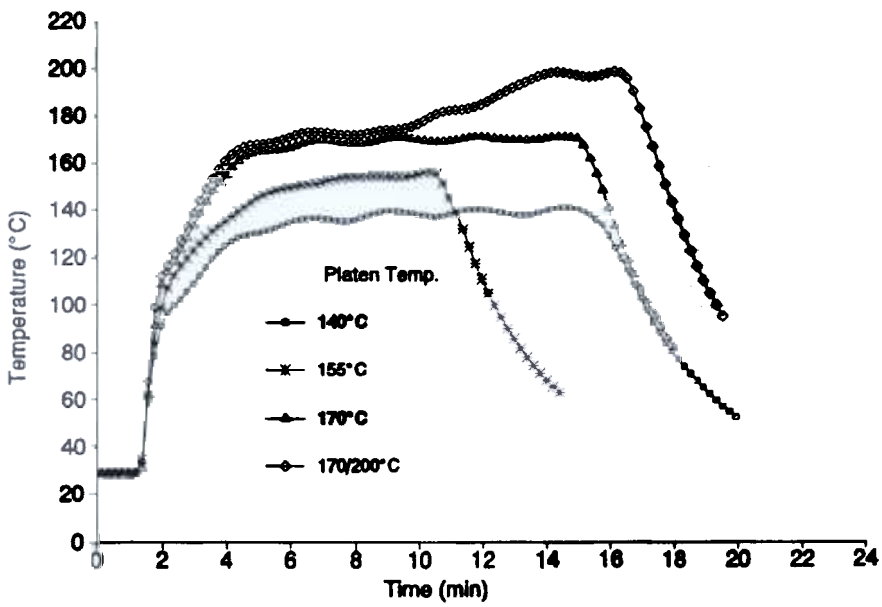

Figure 5. — Panel core temperature during hot-pressing

It can be seen in Figure 4 that the temperature-cure relationship between the controlled and panel scans are remarkably similar for the panels pressed at 140° and 155°C. For the two panels pressed with an initial platen temperature of 170°C, the magnitude and shape of the ε″ curve are again similar to the controlled scans; however, the cure appears to be shifted to higher temperatures. The apparent increase in cure temperatures with platen temperatures in particleboards can be explained using cure kinetics. In the controlled oven scans, the furnish was heated at a rate of 10°C/min. For panels with low platen temperatures, the heating rate inside the core of the panel was slower than panels pressed at high platen temperatures.

The relation of the internal heating rate and platen temperatures can be illustrated in the panel heating curves in Figure 5. After press closure (approximately 1 to 1-1/2 min.), the core of all panels heated rapidly to approximately 100°C. The heating rate then changes to a nearly linear increase in temperature with press time until the platen and core temperatures are equal. Measuring the slope of this portion of each heating curve shows that the heating rates for the 140°, 155°, 170°, and 170°/200°C panels were 14.0°, 13.5°, 22.8°, and 23.2 °C/min., respectively. Because the heating rate for the two high temperature panels was nearly double that of the low temperature panels and the controlled oven scans, the curing regime is apparently shifted to higher temperatures. This shift is actually manifested by the decrease in curing time at each temperature associated with the higher heating rates.

To determine if the 170°/200°C panel was completely cured, the platen temperature was increased to 200°C, 10

minutes into the DEA scan. Complete cure can be detected by the presence of region 3 (Fig. 4) where the log ε″ increases linearly with temperature. If the MDI has not completely cured, the log ε″ will continue to decrease. The DEA scan in **Figure 4** for this panel clearly shows the presence of region 3. The relatively linear decrease of log ε with temperature during panel cooling is similar to that seen in the controlled oven scan.

Influence of Moisture

Dielectric constants for wood are strongly influenced by MC (12). Differences in absolute MCs for the wood component would have little influence on detecting adhesive cure in panels because only the relative change in the dielectric constants are of interest. However, the decreasing MC of the wood component seen during hot-pressing (8) could present serious complications for using dielectrics to monitor adhesive cure because the dielectric signal could be a product of two major factors.

To determine the contribution of moisture changes during pressing to the decrease in ε″, panels were pressed with and without (i.e., neat wood) MDI resin at two different MCs. **Figures 6 and 7** show DEA scans for panels hot-pressed with ovendried and 9 percent MC wood, respectively. Panels were prepared and pressed with neat wood (i.e., without MDI resin) and 6 percent MDI resin. All panels were pressed with identical platen temperatures and press times.

Both the ovendried and 9 percent MC wood panels show a marked difference in the decrease of log ε″ with press time. This difference is most pronounced with the ovendried wood panels, indicating that moisture loss in the wood during pressing is likely to contribute to the overall dielectric response of the panel. This contribution does not, however, seem to dominate the dielectric response of the panel. This point is most evident in the similarities between the controlled and panel dielectric signals. Despite the inevitable differences that exist in the moisture changes that result in the oven samples and particleboard panels, the dielectric signals are remarkably similar.

More evidence of the role of moisture in the total dielectric signal can be seen in **Figure 7**. The erratic behavior of the dielectric signal for temperatures be-

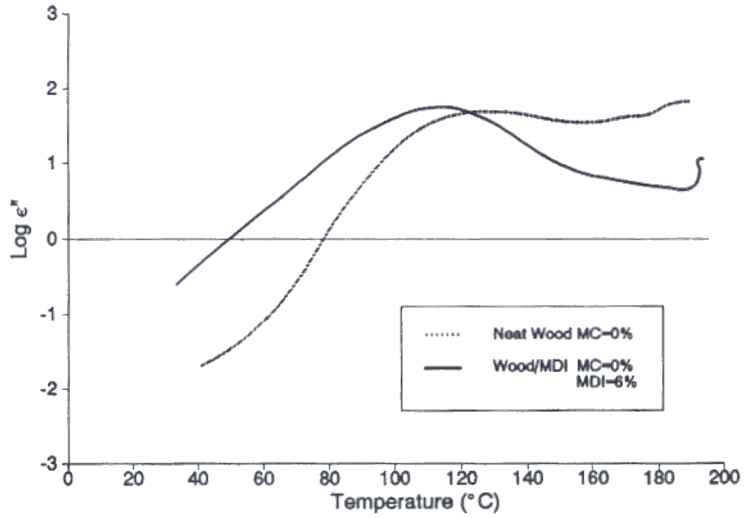

Figure 6. — Dielectric scans for particleboard panels pressed with ovendried wood. No MDI resin was included in the neat wood panel.

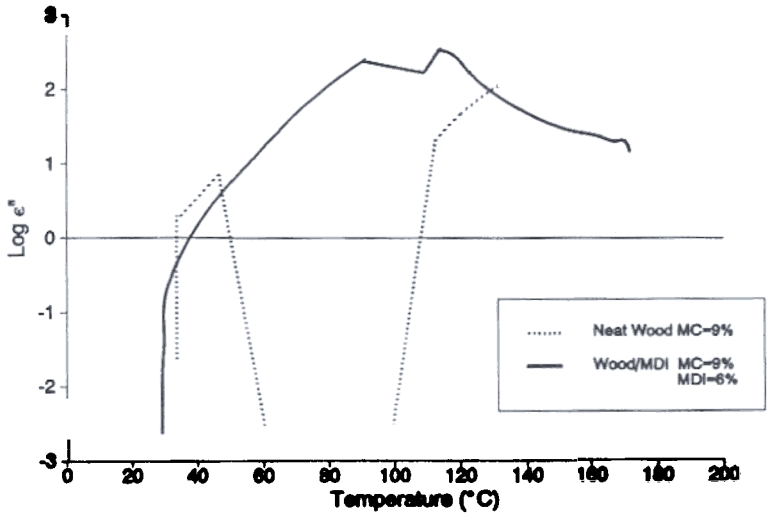

Figure 7. — Dielectric scans for particleboard panels pressed with wood with 9 percent moisture content. No MDI resin was included in the neat wood panel.

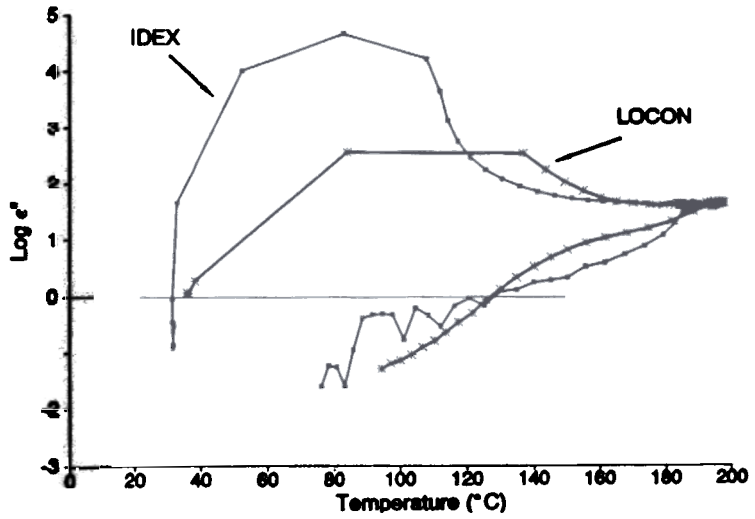

Figure 8. — Dielectric scans for particleboard panels made with both the low conductivity and IDEX sensor types.

low 100°C in the neat wood panels is characteristic of polarization on the dielectric sensor. The polarization is likely caused by the condensation of water vapor present in the particleboard panel. This would indicate a saturated gas environment is present in the panels for these temperatures. Kamke and Wolcott have observed saturated environments in flakeboard panels (8). This polarization is not readily evident in the panel with MDI resin. It is possible that much of the water vapor in these panels is being consumed in reactions with the MDI resin producing polyureas. This reaction is well known to exist and thought to contribute highly to the curing of MDI resin in wood composites (7).

The interactions of the resin, moisture, and wood to produce the total dielectric signal is clearly evident in these experiments. Combined, these components produce an interesting view of the panel formation. Separately, they indicate contributions of the individual components of interest.

SENSOR TYPE

The previous experiments were conducted with a microdielectric sensor that is sensitive to low conductivity materials (bulk conductivity range = 10^{-16} to 10^{-5} Siemens/cm). Other sensors are commercially available for high conductivity materials (bulk conductivity range = 10^{-8} to 10^{0} Siemens/cm). Also available as a more rugged, durable alternative is the interdigitated electrode sensor (IDEX), which can measure bulk conductivities ranging from 10^{-14} to 10^{0} Siemens/cm with careful interface selection. This particular sensor has an electrode spacing of .005 inch, compared to an electrode spacing of 0.0005 inch on the low conductivity sensor, which prevents polarization from occurring as readily. Also, the increased mechanical toughness of this sensor makes it better suited for high temperature/pressure applications and therefore increases the panel densities that can be studied.

A comparison of the dielectric signal detected by the conventional low conductivity and IDEX sensors is shown in Figure 8. The IDEX sensor produces a signal that more clearly depicts the early stages of the press cycle than the low conductivity sensor. This difference is likely produced from the decreased polarization on the IDEX sensor. It is interesting that the two scans converge at the end of the pressing cycle. This could indicate that the IDEX sensor is less sensitive to moisture changes than the low conductivity sensor. If differences in sensor types can be more clearly defined, techniques may be developed to use multiple sensors to depict different phenomena contributing to panel formation.

CONCLUSIONS

Microdielectric analysis provides a valuable tool for in-situ detection of panel formation. The technique is sensitive to the cure of polymeric MDI resins in particleboard panels. The dielectric signals produced from scans of particleboard panels during pressing were similar to those produced in a controlled oven scan with small amounts of furnish. The technique is sensitive to the cure differences that result with different heating rates. This fact must be considered when comparing the signal produced in both controlled and pressing conditions.

Moisture changes during pressing contribute to the overall dielectric signal of particleboard furnish. It is not possible to determine the exact contribution of moisture from this research; however, sensor polarization early in the press cycle is evident. The dielectric signal produced with neat wood is substantially different than that produced when MDI resin is included. In addition, the similarities between scans produced from small samples of particleboard furnish cured at controlled heating rates in an oven and those hot-pressed in panels, supports the theory that the curing of MDI resin dominates the dielectric signals seen in this research. The use of multifrequency scans may provide insight into the role of moisture in future research.

Qualitative differences are seen in the dielectric signals produced from particleboard panels monitored using low conductivity and IDEX microdielectric sensors. The signals are similar in the magnitude of the dielectric loss term (ε'') and temperatures corresponding to inflection points in signals. The IDEX sensor produces a more defined signal at early stages of the pressing cycle and is apparently less sensitive to polarization from water vapor.

Although microdielectric analysis shows great potential in the in-situ detection of adhesive cure during pressing of wood composites, additional research is needed to better define parameters such as sensor type, frequency of scans, and response of adhesive type. In addition, efforts must be made to increase the scan rate to better detect the early portions of the pressing cycle.

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