

CHARACTERIZING WOOD COMPONENTS AS NETWORK POLYMERS BY DYNAMIC MECHANICAL ANALYSIS

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ABSTRACT

The characterization of structure-property relationships in wood components, such as lignin, is a critical aspect of utilization. This point has been emphasized recently with concerns directed toward the application of natural products as wood bonding agents. Dynamic mechanical analysis is a valuable technique for the study of these relations because of its sensitivity to variations in polymer structure.

Keywords: Dynamic mechanical analysis, thermosetting polymers, network structure, lignin.

INTRODUCTION

Dynamic mechanical analysis (DMA) is evolving as one of the most powerful tools available for the study of structure-property relationships in polymeric materials (Read and Dean 1978). Determined as a function of the frequency of an oscillating mechanical stress and temperature, the elastic modulus and internal friction are among the most fundamental dynamic mechanical properties relating polymer structure to end-use applications. Damping ability, which can be measured directly as the dynamic loss modulus, is sensitive to variations in molecular structure as seen through the intensity and position of both major and minor relaxation peaks.

The introduction of the torsional braid analyzer in 1962 (Lewis and Gillham 1962) significantly expanded applications of mechanical spectroscopy. Its unique capacity for handling samples incapable of supporting themselves made it ideal for monitoring the strength development of thermosetting resins as a result of crosslinking (Gillham 1979; Steiner and Warren 1981). In addition, this method has been used in the evaluation of low molecular weight wood components such as lignin in various applications (Braddon and Falkehag 1973; Young 1978). Automation improved the speed and sensitivity of subsequent instruments and greatly facilitated its application to network structure characterization. This is being recognized more and more as a critical parameter in the performance of adhesive bonds (Kotyev et al. 1981; Taki et al. 1982). Although the utility of dynamic mechanical analysis in defining polymer adhesion and fracture processes in terms of atomic molecular models has not yet been fully realized, it is clear that interpreting dynamic mechanical properties at the molecular level offers great opportunities for gaining a scientific understanding of the structure-property relationship of polymers and polymer composites, and for the practical selection

of adhesive and coating formulations for use in wood products. An example of this type is illustrated in the following communication.

EXPERIMENTAL

Thin, polymeric films of hydroxypropyl lignin (Glasser et al., 1983) cross-linked with hexamethylene di-isocyanate were cast from solution onto silicon-coated glass plates.¹ Chain extenders such as polyethylene and polybutadiene glycols were incorporated into some samples to increase film toughness and flexibility. The cure schedule included 15 minutes at room temperature to allow for solvent evaporation followed by 2 hours at 120 C. The film was then peeled from the glass surface and samples were punched out for determination of dynamic mechanical properties.

Dynamic mechanical analysis was conducted on a Perkin-Elmer TMS-2 Dynamic Thermomechanical Analyzer.² All samples were loaded at 0.5 grams at a frequency of 0.1 Hz using a square-wave impulse.

RESULTS AND DISCUSSION

The two most frequently employed stress forms in dynamic mechanical analysis are the square-wave and sine-wave. Of the two, the sine-wave is far more common, being found in all instrumentation today, and it demands brief discussion. As seen in Fig. 1, when a stress is varied sinusoidally through a sample, the response for an ideally elastic material is in phase with the stress wave, while a purely viscous material is 90° out of phase with the stress. However, for the viscoelastic materials commonly encountered, the strain is out of phase by some angle and can be resolved through the projection of vectors into $\tan \delta$: a measure of the internal friction or the ratio of the loss to the elastic modulus. With information on the complex modulus, the individual moduli can then be separated (Cowie 1973).

For rapid, qualitative evaluation of a material, the square-wave signal is of considerably greater value. For this case, the viscous component is shown by the curvilinear section indicative of a time-dependent response mechanism. Molecular transitions are most apparent in the height of the curved region (damping), but are also evident in the height of the linear or elastic region, as well as the ratio of the two components, which corresponds to the internal friction as defined by the phase angle (Rosen 1971) in the sine-wave impulse.

Figure 2 is a dynamic mechanical spectrum of a cured lignin-polyurethane resin using the square-wave signal. Within the glassy region, the material is characterized by a relatively high modulus as indicated by the shallow penetration depth (h) with very little viscous component (H-h) present since the curvilinear component is almost negligible (see inset). In the glass transition region, the onset of

¹ The films were prepared and supplied by Mr. V. P. Saraf, who is studying the effect of synthesis variables on performance properties of polyurethane films as part of an M.S. thesis at VPI & SU.

² These films were analyzed at the Perkin-Elmer Laboratories and are indicative of excellent resolution of the viscoelastic components. However, subsequent work with our own instrument has raised questions concerning reproducibility and quantitative data acquisition. Specifically, the asymmetry of the duty-cycle has eliminated the possibility of quantitative data, at the moment limiting applications to qualitative screening of materials.

RESULTANT STRAIN FOR STRESS FORMS COMMONLY
USED FOR DYNAMIC MECHANICAL ANALYSIS

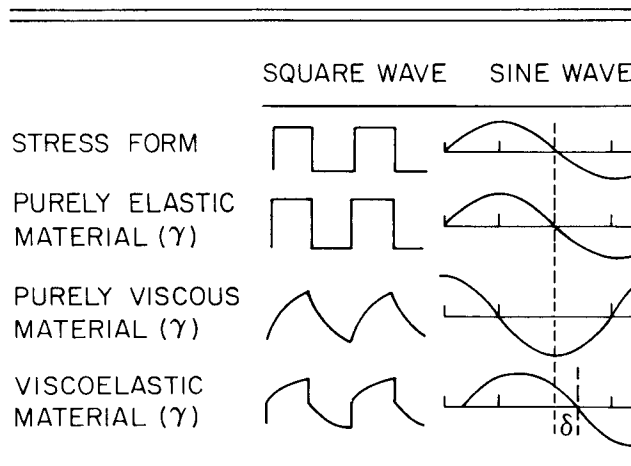


FIG. 1. Comparison of the material response for the square-wave and sine-wave stress forms commonly used in dynamic mechanical analysis.

which begins at 60 C, the viscous component shows a significant increase, particularly with respect to the elastic response region. At this same point, softening of the material becomes apparent, as evidenced by the offset of the probe from the zero baseline. In addition, a decrease in modulus is seen as the height of the linear region increases until a relatively stable plateau is reached up to approximately 200 C, where the viscous response again dominates, typical of network chain scission.

The sensitivity of this particular instrument to variations in network structure is illustrated in Fig. 3. Spectrum 1 is a lignin-polyurethane comprised solely of hydroxypropyl lignin with hexamethylene di-isocyanate as the crosslinking agent, while spectra 2 and 3 have long chain glycols added in increasing amounts. The net effect of the treatment is to increase the molecular weight of network chains between crosslinks. Although the overall appearances of the spectra are drastically different, closer inspection serves to differentiate the materials more accurately.

One of the most well-defined effects of crosslink density variations is on the glass transition temperature. In the material lacking any long-chain glycols, the T_g is found around 60 C as evidenced by the increased viscous component and is lowered almost 20 C as increasing amounts of chain builders are incorporated into the system. This is as expected, since as the molecular weight between crosslinks is increased, the amount of thermal energy required for chain motion is decreased, and the transition occurs at correspondingly lower temperatures. In addition, the offset from the zero baseline increases from spectrum 1 to 3, consistent with the premise that probe penetration will increase as the degree of crosslinking in the network is lowered. In addition, as seen in spectrum 2, the breadth of the glass transition region is considerably greater than in either of the other two materials. Although it is difficult to assign this influence at present, it

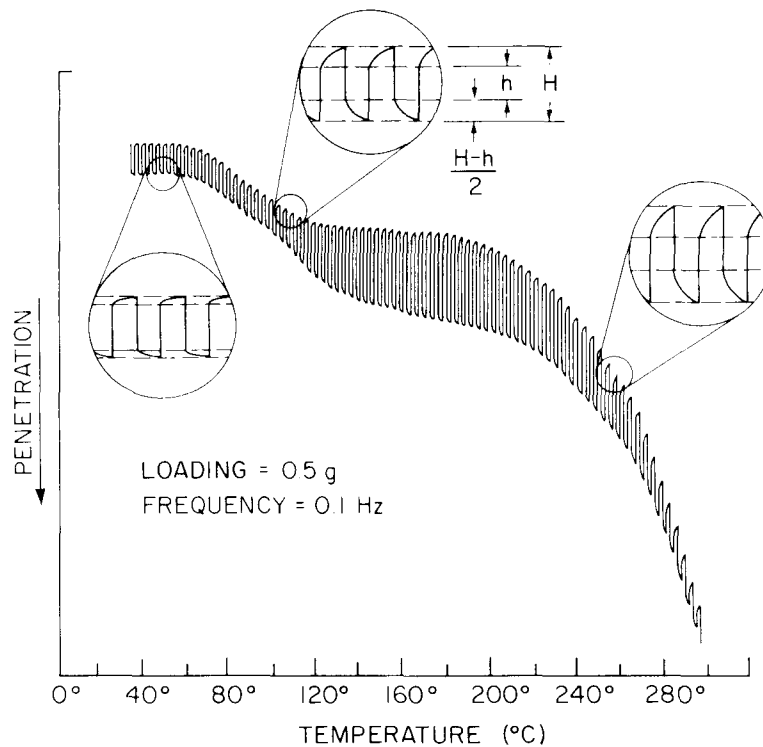


FIG. 2. Dynamic mechanical scan of a lignin-polyurethane film using the square-wave stress impulse.

is presumably the result of a greater dispersity of molecular weights within the network.

A particularly sensitive measure of crosslink density is the elastic modulus above the glass transition, in the rubbery plateau (Aklonis et al. 1972). Again, with reduced crosslinking from spectrum 1 to 3, the modulus in the rubbery region is lowered as seen by the height of the linear response, which is considerably greater in 3 than in either of the other spectra. Finally, differences are evident in the temperature at which chain scission and network degradation begin, which is seen as an increased viscous component and longer relaxation times.

CONCLUSIONS

Evaluating the influence of network structure on adhesive bond performance is a critical concern in successfully decoupling the interactive parameters directing the adhesion phenomenon in wood composites. Because of the insoluble, intractable nature of thermoset polymers, structural characterization has progressed slowly. However, dynamic mechanical analysis has advanced to the point where significant contributions are possible. The fundamental dynamic mechanical properties, the elastic modulus and damping, are extremely sensitive to the primary parameter describing polymeric networks, the crosslink density. Through a better understanding of structure-property relationships in network polymers and

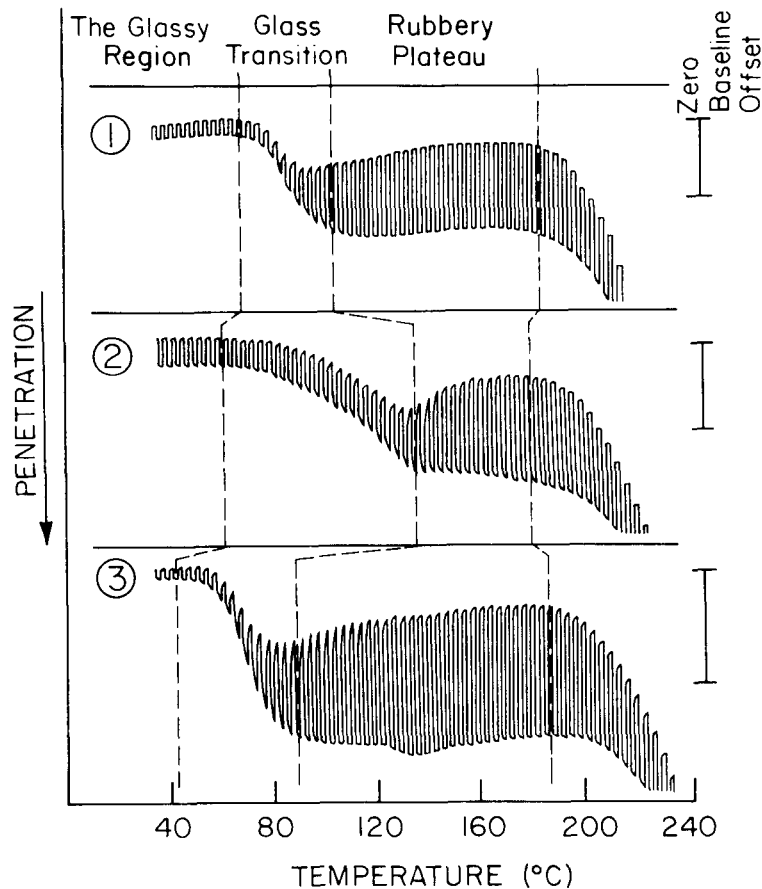


FIG. 3. Dynamic mechanical spectra of: 1) lignin polyurethane, 2) lignin-polybutadiene glycol polyurethane, and 3) lignin-polyethylene glycol polyurethane.

the influence of synthesis variables on the structure, the ability to engineer adhesive materials for specific applications would be available for wood composites as it already is for so many other composite materials.

The Perkin-Elmer Dynamic Mechanical Analyzer offers a relatively inexpensive alternative to mechanical spectroscopic instrumentation. However, problems arising with asymmetry of the duty-cycle make quantitative data impossible to access, restricting its utility to qualitative screening of materials.

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