

MOISTURE DEPENDENT SOFTENING BEHAVIOR OF WOOD

*Christopher A. Lenth*¹†

Scientist
Forest Research, Inc.
Private Bag 3020
Rotorua, New Zealand

Frederick A. Kamke†

Professor
Department Wood Science and Forest Products
Virginia Tech
Blacksburg, VA 24061-0503

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ABSTRACT

An improved understanding of material behavior during the manufacture of wood-based composites can increase the efficiency of wood utilization and provide insight into the development of new processes and products that manipulate the viscoelastic nature of wood. One specific area where additional knowledge can be of great benefit is the influence of heat and moisture on the softening behavior of wood.

The thermal softening behavior of wood at four moisture levels from 0 to 20% was evaluated using dielectric thermal analysis (DETA). Coincident *in situ* relaxations attributed to the softening of amorphous wood components in the range of 20 to 200°C were observed and found to exhibit the characteristics of a glass transition. The moisture dependence of this transition was characterized, and differences in the observed T_g were detected between juvenile and mature wood. Time-temperature superposition was also shown to be applicable to the wood and water system.

Keywords: Viscoelastic behavior, wood, thermal softening, high-temperature, glass transition.

INTRODUCTION

The viscoelastic character of wood is manipulated in many aspects of timber processing: from lumber drying to mechanical pulping. However, the nature of wood's viscoelastic response is poorly understood, and even less adequately defined. The manufacture of high performance, high value composite products from rapidly grown raw material represents just one potential area where increased knowledge of the viscoelastic behavior of wood could greatly benefit the forest products industry.

The hot-press consolidation process employed in the manufacture of wood-based

composite products creates an environment that accentuates viscoelastic behavior. This viscoelastic behavior results in densification from transverse compression of the constituent wood elements. Wood densification can have both permanent and recoverable components, which together have significant influence on the physical and mechanical properties of the composite product. It is known that the local environment of moisture content and temperature during hot-pressing influences densification, density gradient formation, and non-recoverable strain. Furthermore, it has been observed that the increased density, and other physical or chemical changes, result in modified wood properties. These changes have considerable implications for improved product performance and new product development, yet their nature and the mechanisms responsible for them remain essentially unresolved.

¹ Formerly Graduate Research Assistant, Department Wood Science and Forest Products, Virginia Tech, Blacksburg, Virginia 24061-0503.

† Member of SWST.

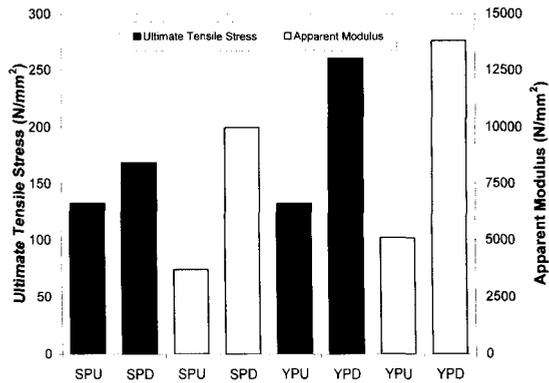


FIG. 1. Preliminary tensile results for samples of southern pine and yellow-poplar densified to 50% strain at 160°C, as well as undensified controls. SPU refers to undensified southern pine, YPD is densified yellow-poplar, etc.

The overall goal of this research effort is to characterize the viscoelastic behavior of wood as it pertains to conditions found during hot-pressing. The initial phase of this work involved investigations of the relationship between wood and water at conditions relevant to the hot-pressing of wood composites (Lenth and Kamke 2001). The current study investigated the thermal *softening* of the constituent wood polymers, and the influence of wood moisture content on viscoelastic behavior. The viscoelastic behavior was probed through observation of the glass transition temperature (T_g) of *in situ* amorphous components of wood via dielectric analysis.

One outcome of this research is demonstrating the feasibility of enhancing wood properties using relatively simple and inexpensive procedures. Preliminary investigations in this area indicate that the tensile strength and stiffness of densified southern pine and yellow-poplar are considerably higher than that of undensified material (Fig. 1). Many of the gains in strength and stiffness resulting from transverse compression are due to those properties' being closely linked to wood density (Armstrong et al. 1984). Such material enhancement could be performed either on-line or off-line during composite manufacture. Unfortunately, we do not understand the intricacies of

this process, nor are we aware of the full implications on product performance. If this process could be defined and harnessed, rapid growth, low-density timber could supply a significant segment of the industry. In effect, density, and thus strength and stiffness, would become another manufacturing variable, to be manipulated at will.

While converting juvenile wood and low-density wood into high performance products may require more involved processing techniques and increased manufacturing time, the extra effort can be considered as a trade-off for a 50- to 75-year decrease in rotation times. The key to success in this endeavor is application of a fundamental materials science approach to product and process development, founded on a solid understanding of material behavior under processing conditions.

BACKGROUND

Deformation of the wood component and development of density gradients during hot-pressing are very influential on resultant board properties. The time-dependent compression strain in a wood composite is influenced by temperature and moisture content changes during hot-pressing, during which the wood material may exhibit both glassy and rubbery phase behavior (Wolcott et al. 1990). Wood, though a complex natural polymeric composite material, exhibits physical and mechanical characteristics similar to simpler and more well-defined synthetic polymers. Shutler (1992) found that moist yellow-poplar samples tested in compression exhibit similar mechanical behavior to flexible polyurethane foams. Salmen (1984) and Kelley et al. (1987) have demonstrated application of the polymer science principal of time-temperature superposition to the softening of wood. Wolcott et al. (1990, 1994) extended this work by employing time-temperature-moisture content superposition as a method to explain the time-dependent behavior of wood during the hot-pressing of wood-based composites.

For characterizing the influence of moisture

on softening behavior in hygroscopic materials such as wood, a problem exists in that common methods involve temperature scans, which, in an effort to detect a discontinuity in material response, cause a change of moisture content. It is well known that decreasing moisture content increases the T_g of amorphous polymers like lignin and hemicelluloses. When the response to a mechanical stress is used to detect the T_g , as in dynamic mechanical analysis, the effects of declining moisture content become even more complex. If a mechanical stress is applied, desorption of a sample during testing could yield a reduced apparent T_g due to mechano-sorptive phenomena (Casey 1987). If the moisture content is allowed to drift during testing, the desired discontinuity becomes a subtle transition that may not be detectable before the wood polymer components begin to decompose (Wolcott et al. 1994). Some studies have been successful in maintaining saturation of sealed specimens as the temperature is increased (Salmen 1984; Irvine 1984; Takahashi et al. 1998; Uhmeier et al. 1998). In order to maintain constant specimen moisture content, specimens must either be sealed, which interferes with most types of measurements, or experiments must be carried out in an environment that can maintain constant EMC conditions as the specimen temperature is elevated.

The hemicelluloses, lignin, and amorphous cellulose components of wood have all been shown to exhibit thermal softening characteristics related to the glass transition when isolated individually (Goring 1963; Cousins 1976, 1978; Salmen and Back 1977; Back and Salmen 1978; Irvine 1984). While these results are important and some congruence exists among them, differing methods of extracting and preparing the wood constituents, as well as inconsistencies in techniques for detecting transitional behavior, limit their ability to describe the softening behavior of whole wood. It is also questionable if the extracted compounds accurately represent the behavior of the *in situ* wood components.

In copolymers containing more than one

amorphous component, more than one glass transition, indicative of large-scale segmental motion in the polymer chain, may be observed. These transitions are typically labeled as α transitions. Other transitions may be observed at lower temperature in the glassy state, which are labeled β transitions or secondary transitions. The β transitions are associated with localized molecular motions, and perhaps due to motions of side-groups in the polymer. Unfortunately, this naming convention is not universally accepted (Aklonis and MacKnight 1983).

Since wood is a complex biological polymer composite with distinct molecular domains, the observed softening behavior of neat wood consists of one or more rather broad transitions as determined by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and dielectric thermal analysis (DETA) (Salmen 1984; Wert et al. 1984; Kelley et al. 1987). Where a single transition has been observed in solid neat wood, it is generally attributed to softening of *in situ* lignin (Chow and Pickles 1971; Funakoshi et al. 1979; Atack 1981; Irvine 1984; Östberg et al. 1990; Takahashi et al. 1998; Uhmeier et al. 1998). Studies by Höglund et al. (1976) and Becker and Noack (1968) have also reported softening behavior in wood; however, they do not attribute it to specific wood constituents. In the temperature range from -20 to 192°C , two separate softening peaks have been observed by researchers using both dynamic and static mechanical methods for various species of solid wood with moisture contents from dry to saturation. These peaks have been attributed to relaxations in either (a) the hemicellulose and lignin fractions, (Hillis and Rosa 1978; Kelley et al. 1987) or (b) crystalline and amorphous regions in wood (Wert et al. 1984). Table 1 summarizes the softening temperatures reported for wood in the available literature.

Dielectric thermal analysis (DETA) is an increasingly popular technique for exploring molecular phenomena such as relaxations within polymers and is especially effective for observation of polar molecules where energy

TABLE 1. Reported softening temperatures for wood.

Source	Technique	Species	Measurement frequency (Hz)	Moisture content (%)	Softening temperature ^a T _g (°C)
Kelley et al. 1987	DMTA	spruce	1	30	60
				20	60
				10	80
				5	115
Salmen 1984	DMTA	spruce	0.05	saturated	82
					85
					95
					100
Atack 1981	Torsional Pendulum	spruce	1 ^a	saturated	85
Becker and Noack 1968	Torsional Pendulum	beech	0.5–3	saturated	80
				26	85
				20.5	95
Höglund et al 1976	Torsional Pendulum	various	1 ^a	saturated	80
					110
Sadoh 1981	Torsional Pendulum	birch	0.02	saturated	80
				dry	235
Wert et al. 1984	Torsional Pendulum	spruce	1	dry	132 & 192
Hillis and Rosa 1978	Static Torsion	pine	N/A	saturated	80 & 92
Takahashi et al. 1998	Radial Compression	various	N/A	saturated	80
Uhmeier et al. 1998	Radial Compression	spruce	N/A	saturated	85
Funakoshi et al. 1979	DTA	birch	N/A	dry	210
				25	62
Irvine 1984	DTA	Eucalyptus	N/A	16	68
				12	82
				7	108
				25	60
				20	60
				17	60
Östberg et al. 1990	DSC	Spruce	N/A	15.5	61
				13	63
				11.5	65
				8	70
				8	73
				7	81
				6.5	86

^a Approximate values.

absorption is due primarily to reorientation of permanent dipoles (Hedvig 1977). While dielectric analysis has been practiced for decades, modern dielectric equipment provides for simultaneous acquisition of data across a wide range of frequencies using a variety of sensor configurations.

In DETA an oscillating, low voltage electrical field is applied to the sample. The sample acts as both a resistor and capacitor, displacing the electric charge (Fig. 2). The complex dielectric constant (ϵ^*) can be determined by measuring the change in the amplitude and

phase of the returning electrical current (Cowie 1991). The complex dielectric constant can be further resolved into the dielectric permittivity (ϵ'), a measure of the electrical energy stored and subsequently released by the material, and the dielectric loss factor (ϵ''), an indication of the energy dissipated within the material (Cowie 1991; Torgovnikov 1993).

During a DETA experiment, atoms, ions, molecules, and polar groups within the analyzed material align or attempt to align themselves with the direction of the applied electrical field. The relaxation times required for

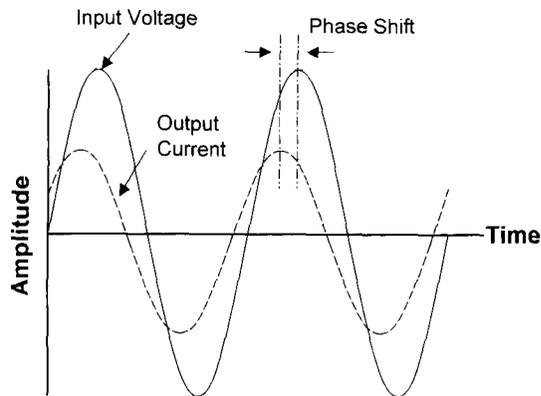


FIG. 2. Schematic representation of the behavior of input voltage and output current in DETA (Adapted from Cowie 1991).

the displaced items to return to an unperturbed position when the field is reversed give rise to distinct regimes of polarization for the material. This continuum of time-dependent polarizations can be thought of as a spectrum of relaxation times. As a result, the dielectric properties of a material exhibit a strong dependence on the frequency of the applied electromagnetic field. The dielectric response of wood and wood composites results primarily from ionic, dipole, and interfacial polarizations (Torgovnikov 1993).

Qualitatively, the dielectric permittivity can be considered analogous to the mechanical compliance, while the dielectric loss factor is more closely related to the mechanical loss modulus (Cowie 1991). However, the dielectric loss tangent ($\tan \delta = \epsilon''/\epsilon'$) is the parameter that reflects most closely the response of the mechanical loss factor, E'' . Transitional behavior in solid materials during a temperature scan is generally manifested as a peak in dielectric loss factor and loss tangent. When directly compared, DETA and DMTA measurements return comparable values for α and β transitions in polymers, and also exhibit similar characteristics when the frequency dependence of those transitions is investigated (McCrum et al. 1967; Wetton et al. 1986). DETA has been shown to be complementary to the standard techniques of DSC and DMA

for measuring relaxation phenomena in polymers (Rials 1992; Connolly and Tobias 1992). Eaton et al. (1976), Wert et al. (1984), and Mizumachi (1991) have used DETA to observe transitions in cellulose and its derivatives, wood, and wood polymer composites, respectively.

EXPERIMENTAL

Mature log sections of yellow-poplar (*Liriodendron tulipifera*) and loblolly pine (*Pinus taeda*) were cut into cants. These cants were further separated into juvenile, mature, and intermediate portions. Juvenile wood was defined as the wood inside the tenth growth ring and mature wood as that material outside the thirtieth growth ring, as per Kretschmann and Bendsten (1992). The wood material was then end-sealed and allowed to air dry at ambient laboratory conditions for approximately 12 months.

Specimens were created by first cutting 3-mm slices from the tangential surface of the seasoned cants. These slices were then machined into veneer strips with a uniform thickness of 2-mm in the radial direction using an abrasive planer. The veneers were further trimmed to dimensions of approximately 80 by 100 mm. Six replicate specimens of both mature and juvenile wood were fabricated for each species. Specimens were then separated into two groups of 12 samples, containing 3 replicates each of juvenile and mature wood for both species. Four testing conditions were investigated: 20, 12, 5, and 0% moisture content. Higher moisture levels were not investigated because the DETA was unable to resolve consistent results at moisture levels above 20%. Each group of 12 specimens was subsequently tested at two of the four moisture content conditions.

Once machined, the specimens were dried in a convection oven at 102°C to obtain the oven-dry weight. The perimeter edges of the dried samples were then sealed with a 2-mm layer of silicon sealant to prevent moisture loss during subsequent testing. Edge-sealed

specimens were then oven-dried a second time at 102°C. One half of the dried and edge-sealed specimens were allowed to equilibrate to a nominal EMC of 12% in an environment chamber at 20 (\pm)1°C and 65 (\pm)2% relative humidity. The remaining 12 were placed in a separate environment cabinet at 25 (\pm)1°C and 95 (\pm)2% relative humidity and equilibrated to a nominal EMC of 20%. Once the specimens had reached equilibrium, they were sealed in plastic bags and left in their respective environments until testing. After being tested at 20% EMC, that group of 12 specimens was re-equilibrated to 5% nominal EMC in the laboratory before testing a second time. Likewise, after testing at 12% EMC, the remaining 12 specimens were dried at 102°C in a convection oven and tested again in the oven-dry condition.

Dielectric thermal analysis was performed with a Eumetric System III MicroDielectrometer from Micromet Instruments. The dielectric properties of specimens were evaluated at frequencies ranging from 0.1 Hz to 100 kHz. Specimens conditioned to higher moisture contents exhibited a more descriptive dielectric response at higher frequencies, whereas dry specimens were more responsive to lower frequencies. In the standard configuration of this instrument for bulk dielectric analysis, the test specimen is placed between two parallel electrodes and the gain and phase of an electrical signal passing through the test specimen is compared to a known capacitance.

Temperature scans were carried out using an MP-1200/QC Programmable MiniPress networked with the Micromet[™] System III microdielectric analyzer. The press had 10-mm \times 20-mm (4 in. \times 8 in.) electronically heated platens, and its computer control was integrated with the data acquisition and control features of the dielectric instrument. The electrode assembly was placed between the platens of the press, and a thermocouple for measurement of sample temperature was connected to the dielectric data acquisition system. The system was calibrated prior to each scan

by measuring the dielectric properties of an air gap of fixed distance between the electrodes.

Equilibrated specimens were sealed in plastic bags until just prior to testing, at which time they were quickly weighed and placed between the electrodes. The press was closed under an air pressure of 276 kPa (40 lb/in.²). This yielded a net compressive force on the specimens of 7.6 kg/cm² (108 lb/in.²). The press was programmed to heat at 5°C per minute, and the temperature ramp and dielectric data acquisition were started simultaneously. Dielectric property data for the specimens at each of the measurement frequencies were collected simultaneously with temperature data, as the sample was heated. To minimize moisture loss during testing, the experiments were terminated when the specimen temperature reached 95°C. At that time, the press was opened, and the specimens were immediately removed and weighed to quantify moisture lost during the test. This protocol was carried out for specimens at 20, 12, and 5% EMC. Due to their higher softening temperature, the oven-dry specimens were heated to 225°C before the experiments were terminated.

RESULTS AND DISCUSSION

Moisture and frequency affects on softening behavior

The shortcoming of most previous work to characterize the moisture dependence of the glass transition(s) in wood is that they were unable to maintain constant moisture content of specimens during temperature scans. The method of edge-sealing specimens, when used with the dielectric technique in this study, was effective in minimizing the moisture lost during experiments. The loss of weight of the specimens ranged from less than 1% for the dry specimens to approximately 4% for the 20% moisture content specimens.

Figure 3 illustrates the dielectric behavior as a function of temperature for oven-dry southern pine juvenile wood, which is characteristic of the wood specimens in this study. Both the dielectric loss factor and the permittivity in-

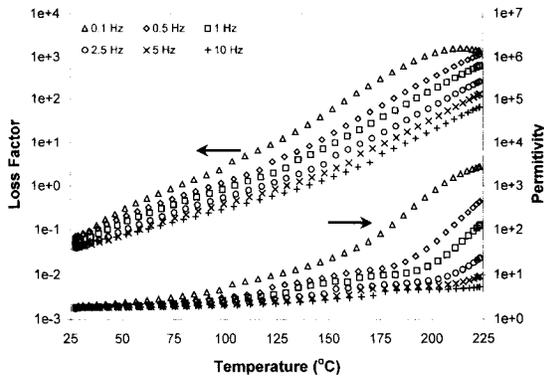


FIG. 3. Dielectric permittivity (right axis) and dielectric loss factor (left axis) versus temperature for southern pine juvenile wood at 0% moisture content. Six measurement frequencies are shown.

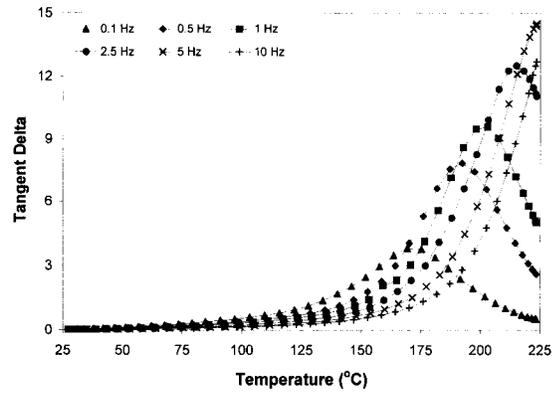


FIG. 4. Dielectric loss tangent versus temperature for southern pine juvenile wood at 0% moisture content. Six measurement frequencies are shown.

crease with temperature. An increase in the slope of the permittivity function beginning above 160°C indicates that the polarization behavior of the material is changing at that point. Specifically, the amount of energy stored and subsequently released by the capacitive function of the material is increasing at a greater rate with temperature. The magnitude of the observed dielectric response increases with decreasing frequency. This is due to the fact that at each measurement frequency, only the polarization of entities within the material possessing characteristic relaxation times less than that measurement frequency can be observed. Lower frequencies allow more time for displaced entities to relax themselves between successive cycles.

Discontinuities in the dielectric behavior of polymers are more easily observed by examining the dielectric loss tangent ($\tan \delta$), which is equal to the loss factor divided by the permittivity. Secondary transitions in polymers are generally associated with peaks in $\tan \delta$ (Cowie 1991; McCrum et al. 1967). Figures 4–7 show the dielectric $\tan \delta$ response observed for southern pine juvenile wood at 0, 5, 12, and 20% moisture content, respectively. These plots are again characteristic of all sample types that were studied. The other three wood types exhibited similar behavior, with the peak temperatures shifted slightly up or

down. Each figure displays data collected at the six frequencies of measurement for which the $\tan \delta$ function is most responsive. Peaks in the $\tan \delta$ function correspond to the temperature at which a dielectric softening (i.e., a relaxation process) was observed at that frequency in the sample. In the discussion that follows, focus is placed on results obtained at 1 Hz, as that measurement frequency most closely represents the time domains used in the consolidation of a wood-based composite. At 1 Hz, a maximum in $\tan \delta$, corresponding to this relaxation process, can be observed in Fig. 4 near 200°C for southern pine juvenile wood at 0% MC and near 90°C in Fig. 5 at

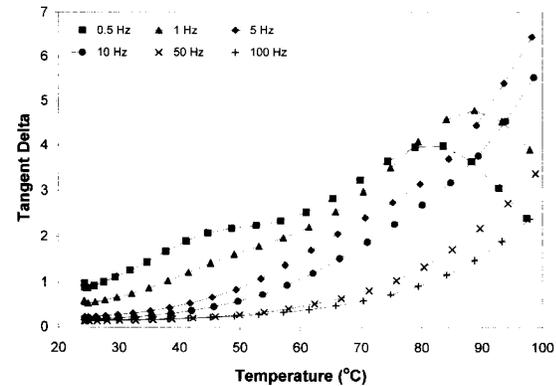


FIG. 5. Dielectric loss tangent versus temperature for southern pine juvenile wood at 5% moisture content. Six measurement frequencies are shown.

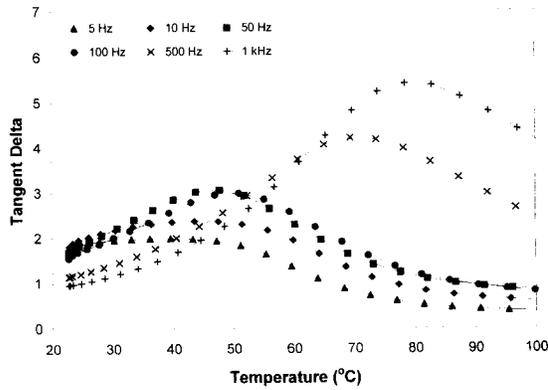


FIG. 6. Dielectric loss tangent versus temperature for southern pine juvenile wood at 12% moisture content. Six measurement frequencies are shown.

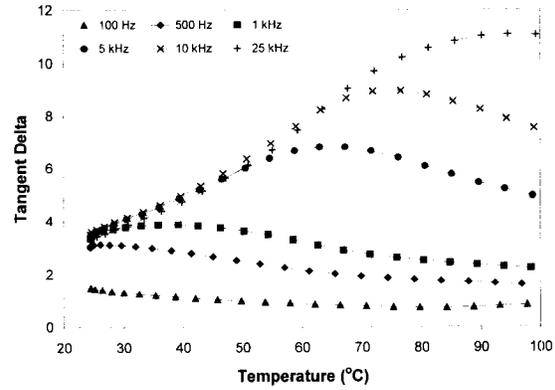


FIG. 7. Dielectric loss tangent versus temperature for southern pine juvenile wood at 20% moisture content. Six measurement frequencies are shown.

5% MC. The relaxation near 200°C for dry wood at 1 Hz agrees with the reported range of 192–235°C for a glass transition of *in situ* wood polymers observed by dynamic mechanical means (Sadoh 1981; Funakoshi et al. 1979; and Wert et al. 1984). For any given frequency, the temperature at which a peak in $\tan \delta$ occurs is shifted towards lower temperatures as moisture level increases. This trend has been reported by all researchers who have studied the softening or relaxation behavior of wood across a range of moisture contents (Table 1). The temperature-dependent $\tan \delta$ response for specimens conditioned to 12 and 20% moisture content can be observed in Figs. 6 and 7, respectively. The influence of moisture on the dielectric behavior of wood was also manifested in the fact that the frequencies at which relaxation processes can be observed, increased as moisture content was increased. It is also evident in Figs. 4–7 that increasing moisture level broadens the $\tan \delta$ peaks representing the dielectric relaxation. To some extent, this phenomena has also been reported for other techniques used to investigate the glass transition of wood (Salmen 1984; Kelley et al. 1987). In the DETA, this peak broadening represents the contribution of an increasing number of polarizing species to the dielectric response. The breadth of the relax-

ation peaks must be kept in mind when interpreting the results at high moisture levels.

The frequency dependence of a relaxation process can be evaluated by investigating the relationship of measurement frequency with the temperature corresponding to the maximum value of $\tan \delta$ (T_{\max}). A common method of quantifying the frequency dependence of a relaxation process is after the method of Arrhenius, which involves plotting the log of the measurement frequency against the reciprocal of T_{\max} . The slope of this plot is then related to the apparent activation energy of the relaxation process through the form of the Arrhenius equation given below:

$$\log f = \log f_0 - \frac{E_a}{RT} \quad (1)$$

Here f is the frequency of measurement, f_0 is a pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, and T is the Kelvin temperature at the $\tan \delta$ peak.

Figures 8 and 9 display Arrhenius plots for the frequency dependence of the dielectric relaxation process. The strong and well-defined frequency dependence of the observed dielectric relaxation delineates it as a transition, while the temperature range at which it is observed further suggests that is an α transition (Kelley et al. 1987). Table 2 lists the slope and intercept of linear fits to the relationships

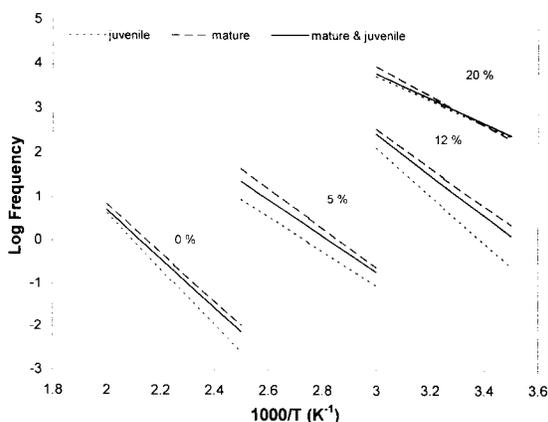


FIG. 8. Arrhenius plot of log frequency against reciprocal of absolute temperature for the T_{max} of the dielectric relaxation process in southern pine at 0, 5, 12, and 20% moisture content.

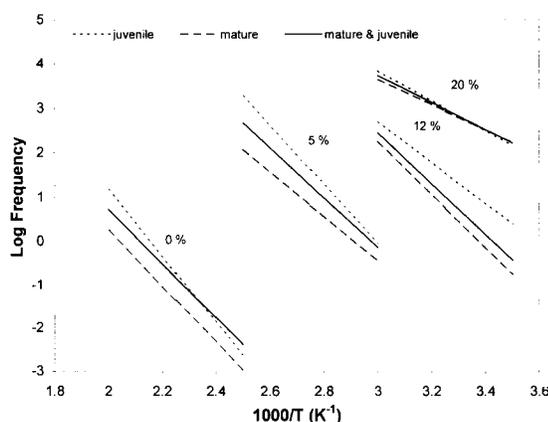


FIG. 9. Arrhenius plot of log frequency against reciprocal of absolute temperature for the T_{max} of the dielectric relaxation process in yellow-poplar at 0, 5, 12, and 20% moisture content.

shown in Figs. 8 and 9. The apparent activation energies calculated for southern pine and yellow-poplar mature wood, juvenile wood, and the two wood types combined, at each of the four moisture conditions, are also provided in Table 2. A test for independence between regression lines (Neter and Wasserman 1974) revealed the Arrhenius relationships for mature and juvenile wood to be statistically independent at a significance level of $\alpha < 0.005$ for both southern pine and yellow-poplar at all four moisture conditions. The T_g of juvenile wood was lower than mature wood in the yellow-poplar specimens. However, the opposite trend was revealed for southern pine. No attempt was made to explain this result.

The apparent activation energy determined for the observed relaxation processes tends to decrease with increasing moisture content, and ranges from near 50 kJ/mole at 20% moisture content to approximately 140 kJ/mole for dry wood. These activation energies are much lower than the values for the *in situ* α transition (T_g) of lignin of 339 kJ/mole (MC = 15%) reported by Kelley et al. (1987) and 395 kJ/mole (water saturated) by Salmen (1984), both using the DMTA. For polymers in general, the apparent activation energy for a glass transition is thought to be greater than or equal

to around 40 kJ/mole, with a tendency to increase with increasing T_g (Salmen 1984). Activation energies of 117 kJ/mole (dielectric) and 104 kJ/mole (mechanical) have been reported for the α transition near 80°C of side-branched polyethylene (McCrum et al. 1967). Dielectrically and mechanically observed α transitions in the same material generally yield equivalent E_a values (McCrum et al. 1967).

Figure 10 displays the temperature of the observed relaxation at 1 Hz as a function of moisture content. Relaxation temperature values at 1 Hz were obtained from the regression equations for log frequency against $1,000/T_{max}$. At 1 Hz, the data points at 20% moisture content represent extrapolated values based on the regression parameters reported in Table 2, as the DETA temperature scans did not extend to sub-ambient conditions. The data recorded in this study do not exhibit the plateau at 5–10% MC observed by some researchers for *in situ* α transition(s) in wood (Irvine 1984; Kelley et al. 1987; Ostberg et al. 1990). The decrease in the temperature of the relaxation process is curvilinear with moisture content, but it continues to decrease above 10%, similar to the behavior reported by Irvine (1984) for isolated hemicellulose and by Back and Salmen (1982)

TABLE 2. Parameters of the Arrhenius relationship for frequency dependence of the super-ambient dielectric relaxation in southern pine and yellow-poplar.

M.C. (%)	Species	Wood type	Log frequency vs. $1,000/T$ (K^{-1})		Activation energy (ΔE_a , $kJ\text{-mole}^{-1}$)
			slope	intercept	
0	southern pine	juvenile	-6.42	13.46	122.93
		mature	-5.68	12.22	108.76
		combined	-5.67	13.46	108.57
	yellow-poplar	juvenile	-7.58	13.12	145.14
		mature	-6.43	16.34	123.12
		combined	-6.22	13.17	119.10
5	southern pine	juvenile	-4.01	10.98	76.78
		mature	-4.58	13.11	87.70
		combined	-4.18	11.81	80.04
	yellow-poplar	juvenile	-6.60	19.77	126.38
		mature	-5.06	14.73	96.89
		combined	-5.63	16.75	107.80
12	southern pine	juvenile	-5.49	18.60	105.12
		mature	-4.40	15.75	84.25
		combined	-4.68	16.35	89.61
	yellow-poplar	juvenile	-4.65	16.66	89.04
		mature	-6.03	20.35	115.46
		combined	-5.76	19.73	110.29
20	southern pine	juvenile	-2.71	11.85	51.89
		mature	-3.27	13.75	62.61
		combined	-2.75	12.02	52.66
	yellow-poplar	juvenile	-3.35	13.88	64.15
		mature	-2.83	12.13	54.19
		combined	-3.01	12.75	57.63

for isolated amorphous cellulose and hemicellulose.

Also included in Fig. 10 are the T_g versus moisture content relationships for the α_1 (lig-

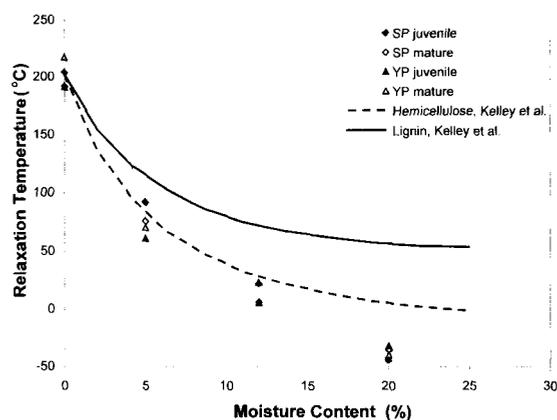


FIG. 10. Plot of relaxation temperature at 1 Hz against moisture content. Lines represent data of Kelley et al. (1987) summarized by the Kwei model.

nin) and α_2 (hemicellulose) transitions reported by Kelley et al. (1987) as summarized by the Kwei model. The Kwei equation has been used by several researchers (Kelley et al. 1987; Wolcott et al. 1990) to describe the depression of the T_g in wood due to increasing moisture content and has the form:

$$T_g = \frac{(W_1 T_{g1} + kW_2 T_{g2})}{(W_1 + kW_2) + qW_1 W_2}, \quad (2)$$

where W and T_g represent the weight fraction and glass transition temperature of the polymer (1) and diluent (2) (Kelley et al. 1987). The constants q and k represent adjustable parameters accounting for secondary interactions and free volume considerations, respectively. However, since it is believed that the relaxation behavior observed by the DETA represents the collective response of more than one distinct polymeric component, this model was not fit to the data from this study.

The relationship of relaxation temperature with moisture content observed in this work is quite similar to that reported for the T_g of hemicellulose by Kelley et al. (1987), especially at moisture contents up to 10%. Unfortunately, they were unable to resolve an apparent activation energy for this relaxation process at a measurement frequency that could be compared to the results of this study. The agreement between these results, however, suggests that the observed dielectric relaxation may be the glass transition of the *in situ* hemicelluloses and the amorphous component of cellulose, or indeed a blend of the relaxation events associated with all the amorphous components combined.

Similar agreement between transitions reported by DMTA and DETA techniques has been reported for glass transitions in other polymers (McCrum 1967; Wetton et al. 1986). While the two techniques have been shown to be complementary, it is likely that they respond differently to increases in the amount of moisture in a material. The dynamic bending properties evaluated by the DMTA are likely to achieve a level of diminishing returns where additional increases in moisture no longer influence the material behavior. This relationship is akin to the influence of the fiber saturation point on the mechanical strength of wood. The magnitude of the relaxations probed by the DMTA makes it sensitive to motions in polymer chain segments. The plasticization effect of water on these chain segments will likely be much greater for the initial layer of water molecules, and subsequently less for each additional layer as the forces attracting the water molecules to the substrate decrease. This behavior is certainly tied closely to the sorptive behavior of the polymer/diluent system. Thus the T_g of the less sorptive lignin would plateau at a lower moisture content than that of the more sorptive hemicellulose, as indicated by the results of Kelley et al. (1987). This idea is supported by results on the softening of isolated lignin and carbohydrates, in which the lignin T_g reaches a plateau with increasing moisture content, while the T_g of hemicellu-

lose and amorphous cellulose continue to decline markedly as moisture levels increase above 20% (Salmen and Back 1977; Irvine 1984). The dynamic motion of polymer chain segments evaluated by the DMTA may also be restricted by confines within the wood structure, or by association with inflexible components in the wood cell wall, such as crystalline cellulose.

DETA, on the other hand, will respond differently to changing levels of moisture. The dielectric response of wood consists mainly of dipolar and interfacial polarizations. Since the plasticizing water molecules are themselves dipoles, as well as contributors to interfacial polarization (Torgovnikov 1993), addition of water will have a complex effect on the dielectric response of hydrophilic polymers. The proximity of the polarizing dipoles to the backbone, and the amount to which they are influenced by the configurational motions of the polymer chain will directly affect the correlation between dielectric and mechanical properties (Ferry 1980). The accumulation of additional water will add more dipoles to the material which are decreasingly responsive to the motions of the polymer backbone. This would suggest that the correlation between DMTA and DETA decreases with increasing moisture content. The dielectric response may not reflect a "plateauing" effect with increasing moisture, more likely to be observed is a continued decline in the relaxation temperature of the polymer/plasticizer system with increasing levels of water. Using DETA, the delineation of the behavior of moisture from that of the polymer/diluent system is obviously complex, and interpretation of results is further disadvantaged by the lack of similar studies for comparison. However, the obvious frequency dependence of the observed relaxations, and the modest agreement with transition temperatures observed using other techniques, lend merit and validity to the identification of the observed relaxations as glass transitions of wood polymers.

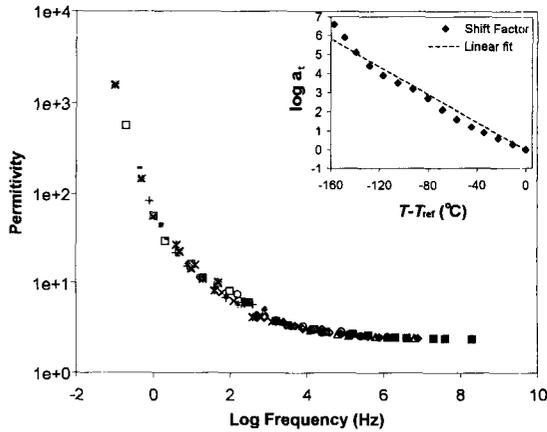


FIG. 11. Master curve for permittivity versus log frequency for yellow-poplar juvenile wood at 0% moisture content. The observed T_g of 198°C is used as the reference temperature.

Time-temperature superposition

An equivalence between time and temperature in their influence on viscoelastic response has been thoroughly demonstrated for amorphous polymers (Ferry 1980; Aklonis and MacKnight 1983; Cowie 1991). The time-temperature superposition (TTSP) principle was developed to reduce the amount of experimental effort required in determining time-dependent material properties. This technique can also be employed to evaluate the compliance of experimental results with theoretical relationships for amorphous polymers. Application of TTSP has been demonstrated to be effective for wood at various levels of hydration (Salmen 1984; Kelley et al. 1987; Wolcott et al. 1994).

At moisture levels of 0, 5, and 12%, curves of log permittivity were shifted horizontally along the log frequency axis to a reference temperature corresponding to that experimental temperature closest to the observed 1 Hz relaxation temperature (T_g). At 20% moisture content, the lowest experimental temperature (near 40°C) was chosen as a reference temperature, because the 1 Hz extrapolation of the observed T_g was well below the range of temperature over which permittivity data was collected. Master curves for the permittivity of

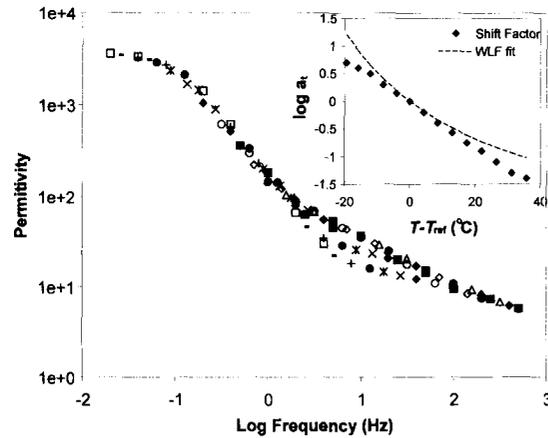


FIG. 12. Master curve for permittivity versus log frequency for yellow-poplar juvenile wood at 5% moisture content. The observed T_g of 61°C is used as the reference temperature.

yellow-poplar juvenile wood at the four different moisture levels are given in Figs. 11 through 14. At 0% moisture content, the master curves appear very smooth, while a moderate amount of scatter exists in those generated at 5 and 12%. Similar to the procedure of Salmen (1984) and Kelley et al. (1987), vertical shifts were not performed. The shift factors used in generating the master curves are plotted against the difference between the measurement temperature and the reference temperature ($T - T_{ref}$), and displayed in the upper right hand corner of Figs. 11 through 14.

Glassy, amorphous polymers are expected to comply with the Williams-Landel-Ferry (WLF) equation above their T_g up to $T_g + 100^\circ\text{C}$. For an arbitrarily chosen reference temperature, the WLF equation has the form (Aklonis and MacKnight 1983):

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (3)$$

Here $\log a_T$ is the shift factor, C_1 is a constant proportional to the fractional free volume of the polymer system (f_g) at the glass transition, and C_2 is a constant that relates the free volume and its coefficient of thermal expansion (α_f). When $T_{ref} = T_g$, values of C_1 and C_2 de-

TABLE 3. Parameters of both the fitted WLF equation and a linear fit to the shift factor data.

Wood type	Moisture content	WLF parameters				Linear fit parameters	
		C_1	C_2	f_g	α_f	Slope	R^2
Southern pine juvenile	0	—	—	—	—	-0.02	0.92
	5	6.7	281.9	0.065	$2.3e^{-4}$	-0.03	0.99
	12	5.9	234.8	0.074	$3.2e^{-4}$	-0.02	0.99
	20	5.5	388.2	0.079	$2.0e^{-4}$	-0.01	0.99
Southern pine mature	0	—	—	—	—	-0.02	0.90
	5	5.7	191.2	0.076	$3.9e^{-4}$	-0.03	0.98
	12	4.6	191.8	0.094	$4.9e^{-4}$	-0.02	0.99
	20	2.6	135.7	0.167	$1.2e^{-3}$	-0.01	0.98
Yellow-poplar juvenile	0	—	—	—	—	-0.04	0.97
	5	2.94	66.4	0.148	$2.2e^{-3}$	-0.04	0.99
	12	2.05	71.5	0.212	$2.9e^{-3}$	-0.02	0.93
	20	3.00	179.8	0.144	$6.3e^{-4}$	-0.01	0.90
Yellow-poplar mature	0	—	—	—	—	-0.03	0.92
	5	7.3	194.3	0.059	$3.0e^{-4}$	-0.04	0.99
	12	3.4	117.0	0.128	$1.1e^{-3}$	-0.02	0.98
	20	3.6	234.8	0.121	$5.1e^{-4}$	-0.01	0.99
	universal ^a	17.4	51.6	0.025	$4.8e^{-4}$	—	—

^a Aklonis and MacKnight (1983), Young and Lovell (1991).

terminated by fitting the WLF equation to the shift factor data can determine the suitability of the WLF and associated free volume relationships for describing the viscoelastic relaxation process in question. Table 3 collects the values of C_1 and C_2 as well as corresponding estimates of f_g and α_f obtained by a Levenberg Marquardt nonlinear regression of the WLF equation on the shift factor data. Parameters of the fit to the WLF equation are reported for

master curves at 5, 12, and 20% moisture content. At 0%, the limits of temperature within which the data were obtained, were insufficient for the generation of shift factors in the range of application for the WLF equation, which is T_g to $T_g + 100^\circ\text{C}$. In Table 3 the "universal" constants reported by Aklonis and MacKnight (1983) for $T_{\text{ref}} = T_g$ are given for comparison as are corresponding values of f_g and α_f (Young and Lovell 1991). Also provided in Table 3 are the parameters of an empirical linear fit to the shift factor data for all moisture contents. In Figs. 11–14, the fitted WLF equation is superimposed onto the shift factor plots of master curves obtained from experiments at 5, 12, and 20% moisture content, whereas the linear fit is superimposed on those master curves from the 0% moisture content specimens.

The shift factors do appear to be effectively described by linear empirical models, and the slope values are in reasonable agreement with those reported at lower moisture levels by Wolcott (1989) for relaxation modulus and creep compliance in wood. The increased deviation from those results with increasing moisture content can be explicated with the same arguments used previously to explain

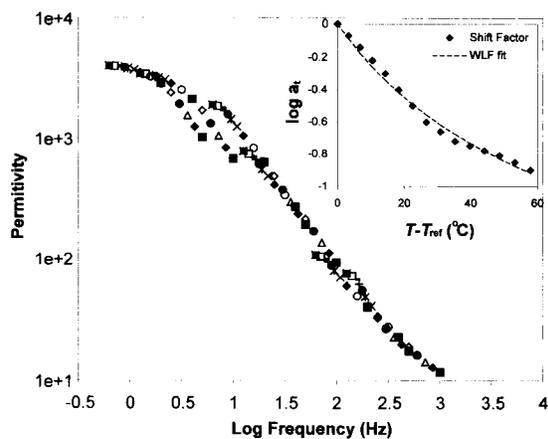


FIG. 13. Master curve for permittivity versus log frequency for yellow-poplar juvenile wood at 12% moisture content. 40°C was used as the reference temperature.

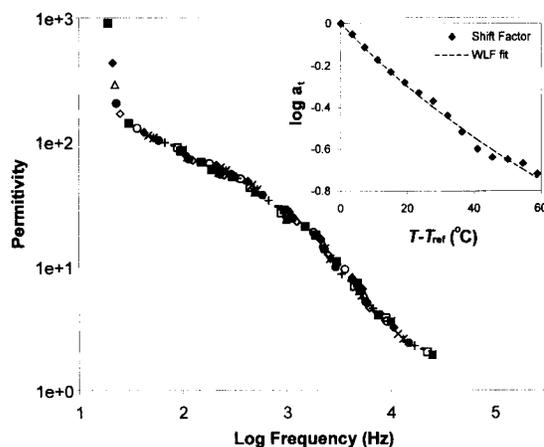


FIG. 14. Master curve for permittivity E' versus log frequency for yellow-poplar juvenile wood at 20% moisture content. 40°C was used as the reference temperature.

differences between the results of mechanical and dielectric analyses. Reasonable agreement between the values of the fitted WLF constants and the “universal” constants suggests that the observed viscoelastic process does follow WLF behavior. The shift factor plots inset in the master curves illustrate this association. The WLF constants in Table 3 are also somewhat in agreement with those reported by Salmen (1984) for water-saturated wood ($C_1 = 18.18$, $C_2 = 77.2$) and Kelley et al. (1987) for wood plasticized with ethyl formamide. The experimentally determined values for the fractional free volume at T_g (f_g , Table 3) of the samples tested are considerably higher than the universal value reported for amorphous polymers of 0.025 (Young and Lovell 1991) and that reported for water-saturated wood by Kelly et al. (1987) of 0.024. It must again be noted that influence of the measurement technique certainly bears upon this comparison. Values of f_g tend to increase with increasing moisture content. This trend follows the intuitive idea that the free volume of the system increases as it is swollen with adsorbed moisture. With regard to the thermal expansion coefficient of the free volume (α_f), there are no trends apparent with regard to wood type or moisture level.

Reasonable compliance with the WLF

equation, and moderate agreement between the constants derived from these dielectric experiments with those reported for mechanical tests on a similar system, suggest that the observed dipole response involves changes in backbone configuration that are associated with the glass transition (Ferry 1980). Corroborated by the evidence found in its frequency dependence, the temperature dependence of the shift factors suggests that the observed dielectric relaxation represents a transition. The fact that no β or lower transitions have been observed for wood in or above the ambient temperature range, indicates that this relaxation is an α transition, which is associated with large-scale molecular mobility. Furthermore, the fact that the observed relaxation is coincident at low moisture levels with the reported T_g of *in situ* wood polymers, leads to the belief that this relaxation process represents the glass transition of hemicellulose and the amorphous cellulose components or a relaxation of all amorphous components of wood. It is postulated that these wood components will dominate the dielectric response of wood in the conditions studied due to: 1) their greater proportion of dipolar groups, 2) the proximity of these dipoles to the backbone chain, and 3) their degree of coupling with the conformational motions of the backbone polymer chain (Ferry 1980).

The nature of the DETA technique, however, makes it difficult to differentiate which individual *in situ* components are responsible for the observed dispersion. The DETA is also not ideally suited for measurements in polymer systems where high moisture levels create a heavy dipolar response that can cloud observation of the targeted relaxation. As moisture levels increase in a hydrated system, the dispersion of the observed dielectric behavior is most likely a manifestation of the “gross” dipolar response of all of the hygroscopic polymer components and their bound moisture to the applied electrical field.

CONCLUSIONS

Dielectric thermal analysis (DETA) was used to observe moisture-dependent relaxation

behavior in juvenile and mature wood of southern pine and yellow-poplar. This dielectric relaxation process exhibited the frequency dependence and Williams Landel Ferry (WLF) compliance characteristic of an α (glass) transition. The observed T_g was consistent with reported values for wood, in particular those for hemicellulose and amorphous cellulose components of wood at low to moderate moisture contents. However, at higher moisture levels the DETA was not sensitive enough to polymer chain behavior to definitively differentiate the relaxation behavior of the individual amorphous wood components from the dipolar activity of the adsorbed water.

The moisture dependence of the observed transition was significantly different for mature and juvenile wood. At moisture levels up to 12%, yellow-poplar juvenile wood exhibited a lower T_g than mature wood. For southern pine this trend was inexplicably reversed. The time-temperature superposition principle (TTSP) was shown to effectively demonstrate frequency-temperature equivalence for the dielectric response of wood up to 20% moisture content.

This work adds new information to the knowledge base regarding material behavior during the manufacture of wood-based composites. These results can be combined with those from previous work to provide further insight into response of wood to hot-pressing environments, and will assist in further clarifying the complex influence of moisture on the thermal softening of wood.

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