Relaxation behaviour of the amorphous components of wood

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The viscoelastic properties of wood were investigated using dynamic mechanical thermal analysis and differential scanning calorimetry. Under a limited set of conditions, two separate glass transitions (T_g) could be identified with both techniques. These two transitions were identified as arising from the amorphous lignin and hemicellulose matrix in the wood cell wall. Moisture dramatically affected the temperature at which the two dispersions occurred and, consequently, the ability to resolve their independent responses. The relationship between T_g and moisture for both components could be modelled with the Kwei equation, which accounts for the presence of secondary interactions. Annealing and specific interactions of a series of organic diluents were used in an attempt to enhance the resolution of the two components' values of T_g. Time–temperature superposition was shown to be applicable to wood plasticized with ethyl formamide, following Williams–Landel–Ferry behaviour over the temperature range T_g to $T_g + 85°$ C. These observations allow certain conclusions to be drawn concerning the applicability of existing models of the wood cell wall's supermolecular morphology. Most notably, models of the *in situ* morphology of the three wood components can be limited to those which consider the amorphous matrix of lignin and hemicellulose to be immiscible.

1. Introduction

Wood is a unique composite material which consists of three structural polymers, cellulose, hemicelluloses and lignin. The overall response to external stress of this composite is a consequence of interactions between the individual polymers. Little research has considered the behaviour of wood in terms of the morphology of the amorphous matrix of lignin and hemicelluloses. Attempts to characterize the supermolecular structure of the cell wall have been to elucidate the viscoelastic properties using creep experiments [1–4]. However, this type of analytical procedure suffers in that it treats the material as a homogeneous substrate. In addition, because of the long time-scale associated with creep experiments, it fails to detect molecular motion. To accurately assess the influence of such external perturbations as temperature or moisture, while minimizing anatomical effects, a shorter time-scale experiment is necessary which allows the observation of molecular motion.

Attempts to overcome these difficulties have concentrated on the viscoelastic behaviour of isolated wood components [5–11]. Techniques such as thermal, dielectric and dynamic mechanical analysis have led to an improved understanding of the effects of moisture and temperature on the response of the individual polymers of the cell wall. The thermal and viscoelastic properties of the amorphous component (lignin and hemicelluloses) have been found to be sensitive to diluents and heat [5–10], while the properties of the semi-crystalline cellulose depend more on per cent

crystallinity [11]. However, all work with isolated wood components suffers from the deficiency that the isolated polymer is either modified or incompletely represents the polymeric component *in situ*. Furthermore, the extent to which secondary interactions, arising as a consequence of the intimate association of the wood polymers, influence the composite's viscoelastic response cannot be evaluated.

Recently, several researchers have attempted to apply analytical techniques which are sensitive to the response on a molecular level directly to whole wood [12–14]. These methods include dynamic mechanical, dielectric and thermal analysis. This approach provides the opportunity to study the response of individual wood components *in situ* to an applied perturbation. This allows for a greater understanding of the contributions made by individual wood polymers, as well as their interaction, to composite properties. The viscoelastic behaviour of wood [12] and various types of paper [15, 16] have been studied by Salmen and co-workers. These materials were found to exhibit a response typical of amorphous materials undergoing a thermal transition from the glassy to the rubbery state, i.e. a glass transition (T_g). The temperature at which this transition occurred was found to depend on the concentration of the individual wood component, the frequency of the oscillation [12], and the presence and concentration of such diluents as water or ethylene glycol [16]. For whole wood, T_g was observed to plateau at relatively low moisture contents (< 5%), a behaviour which has previously been ascribed to

isolated lignin. Other organic diluents, such as dimethyl phthalate and ethylene glycol, did not exhibit this plateauing, and the depression of T_g was adequately modelled using the Kaelble equation. This relationship is broadly applicable to a variety of polymer/plasticizer systems as well as some copolymers.

Additional work has contributed to the understanding of the viscoelastic spectrum of this polymeric composite. Of considerable interest is the presence of a secondary dispersion at sub-ambient temperatures which has been observed with both dynamic mechanical thermal analysis (DMTA) [13] and dielectric analysis techniques [17]. The temperature at which this transition occurred, as well as its intensity, was found to depend heavily on the nature and concentration of the diluent. The origin of this dispersion has been ascribed to the interaction of the diluent with the hydroxyl groups of the various wood polymers [17]. A second alternative, motion of a functional group common to any given component, was ruled out [13].

Considerable ambiguity surrounds the assignment of dispersions that can be found in the viscoelastic spectrum of wood at elevated temperatures. Two high-temperature peaks in the tanδ curves of wood have recently been attributed to the carbohydrate components [13]. This conflicts with other reports [7, 12] which have identified lignin as one component producing a thermal transition at elevated temperature. Differential scanning calorimetry (DSC) of whole wood [7] has revealed a single transition between 50 and 120° C which was assigned to lignin. The same study noted that the T_g of isolated wood polymers was affected differently by water. While lignin's T_g reached a plateau at 50° C, the T_g of hemicelluloses were predicted to reach a minimum "well below room temperature" [7], although it was not observed.

Because of the importance of moisture on the processing of wood and pulp fibres, most recent studies have concentrated on the plasticization of wood with water. As an extension of these efforts, a variety of models [7, 9, 16] have been applied to account for the observed variation in T_g with moisture content (MC). While the conventional models work well at low moisture contents, they fail to correctly predict the viscoelastic response at higher MC ($> 10\%$) where T_g is observed to plateau. This limitation may result from a failure to explicitly consider secondary interactions such as hydrogen bonding. A model which takes secondary bonds into consideration has been proposed by Kwei [18]. In this model T_g is predicted as a function of blend composition, and two adjustable parameters, k (derived from free volume considerations) and q (proportional to the extent of secondary interactions present). The Kwei equation has been shown to accurately reflect the plateauing of T_g with increasing plasticizer content with blends of poly(methyl methacrylate) and phenol/formaldehyde.

It is the goal of this study to evaluate the viscoelastic response of wood in relation to the morphology of the amorphous matrix of lignin and hemicelluloses. By taking advantage of previously noted differences in the response to moisture and diluents, it should be possible to resolve the T_g of lignin and hemicelluloses into individual responses if these two polymers exist in the cell wall as an incompatible blend. The applicability of the Kwei model to account for the behaviour of the T_g of wood plasticized with water will be investigated.

2. Experimental procedure
2.1. Dynamic mechanical thermal analysis
A Polymer Laboratories' Dynamic Mechanical Thermal Analyzer, DMTA, interfaced to a Hewlett-Packard 9816 microcomputer was used to determine E' and tanδ. Temperature scans were performed at a heating rate of 5 deg min^{-1}, a frequency of 1 Hz, and a strain level of 1%. Sample geometry involved a dual cantilever beam with dimensions of 3 mm thick and 6 mm wide across the radial face with a 14 mm free length. Diluent content was measured before the scan and the sample chamber flushed with nitrogen, after which the sample was rapidly cooled to $-140°$ C using liquid nitrogen, before commencing the scan.

Apparent activation energies (E_a) were determined by evaluating the effect of frequency on the peak temperature of the various relaxation processes. A good approximation can be obtained with a modified form of the Arrhenius equation given below:

$$\log f = \log f_0 - E_a/RT \tag{1}$$

Here f is the frequency of vibration, f_0 is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant and T is the tanδ peak temperature. The frequencies utilized were 0.33, 1.0, 3.0, 10.0 and 30 Hz.

2.2. Differential scanning calorimetry (DSC)
A Perkin-Elmer DSC4 equipped with a Thermal Analysis Data Station was used for the thermal analysis. Sealed large-volume capsules were filled with approximately 40 mg of ground wood. The scans were made at a heating rate of 10 deg min^{-1}, under a dry nitrogen atmosphere.

2.3. Materials
Two species of wood were used for these studies: Sitka spruce (*Picea sitchensis* Bong. Carr.) and sugar maple (*Acer saccharum* Marsh.). The organic diluents (formamide, dimethyl formamide, diethyl formamide and ethyl formamide) were used as purchased.

3. Results and discussion
The phase morphology and structure of multicomponent polymer systems such as blends or block copolymers have been studied extensively by DSC and DMTA [19, 20]. The success of these techniques lies in their ability to differentiate between the single T_g of a homogeneous polymer system and the individual thermal transitions of a heterogeneous material. This differentiation defines the degree of compatibility (or incompatibility) of a polymer mixture. Since analogies can be drawn between the wood cell wall, which is comprised of three individual polymeric components, and synthetic polymer composites, it follows that these analytical techniques should be sensitive to
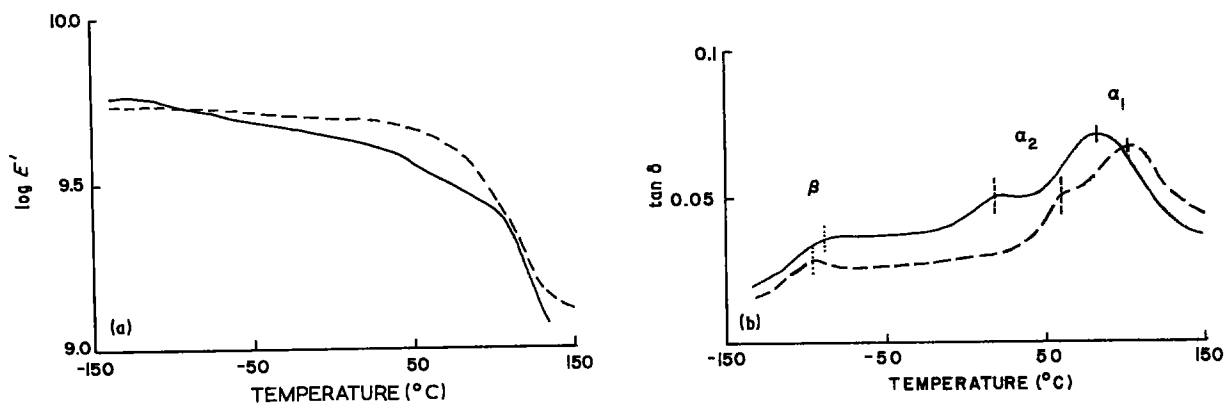
Figure 1 Comparison of (a) storage modulus (E') and (b) $\tan\delta$ response of (——) spruce and (– – –) maple at 10% moisture content.

the thermal transitions associated with the wood's amorphous components of lignin and hemicelluloses. The observation of one or more values of T_g, and the effect of various diluents on the viscoelastic response, can both be related to morphological models of the wood cell wall's amorphous matrix.

3.1. DMTA at various moisture contents

The dynamic mechanical spectra of a hardwood (maple) and a softwood (spruce) test specimen are shown in Fig. 1. They reveal remarkable similarities with regard to three features common to both species. The $\tan\delta$ response reveals a low temperature (β) transition at between -90 and $-110°$ C, followed at higher temperature by a broad transition (α_1) centred around 80 to 100° C; and a shoulder (α_2) between 10 and 60° C. No substantial loss in the storage modulus (E') was evident over the temperature range of the β-dispersion; however, a dramatic decrease in E' is associated with the high-temperature (α_1 and α_2) transitions. The behaviour of the β transition is characteristic of a secondary dispersion involving only small-scale molecular motion, while the storage modulus decrease at the α transitions implies large-scale segmental motion which is characteristic of a glass transition (see e.g. [19]).

The superior resolution of the α_1 and α_2 peaks for spruce as compared to maple can be rationalized on the basis of differences in both density and frequency of crosslinking in lignin. The greater heterogeneity of softwood as compared to hardwood lignin [21, 22] can

be expected to result in the formation of more distinct lignin domains. These may result in superior resolution.

The presence of a low molecular weight species often serves to plasticize an amorphous polymer. Plasticization causes a reduction of the energy required to initiate chain mobility [23]. Water has been found to plasticize cell wall components. Consequently, the precise temperature at which the α dispersions are found in the wood spectra can be expected to vary with moisture content. Fig. 2 shows that this is the case. The plasticizing efficiency of water, however, varies considerably for the two α relaxations. At low MC the α_1 and α_2 transitions are barely detectable at temperatures well above 100° C, and are indistinguishable from each other. Whereas the α_1 peak temperature declines to 60° C with MC rising to 10%, after which it remains constant, the α_2 peak continues to decline to sub-ambient temperatures with MC rising to 30%.

It should be noted that the sensitivity of these transitions to moisture complicates the DMTA analysis since the relative humidity of the sample chamber is difficult to control. This variation results in a loss of moisture in the sample during the scan. Moisture loss can lead to a broadening of the $\tan\delta$ response, an effect which would be most pronounced for the samples with a $\tan\delta$ peak around 100° C (at MC > 7%).

Fig. 2 shows that the β dispersion varies with MC as well. This is surprising since secondary relaxations are generally not influenced by the presence of plasticizers [17].
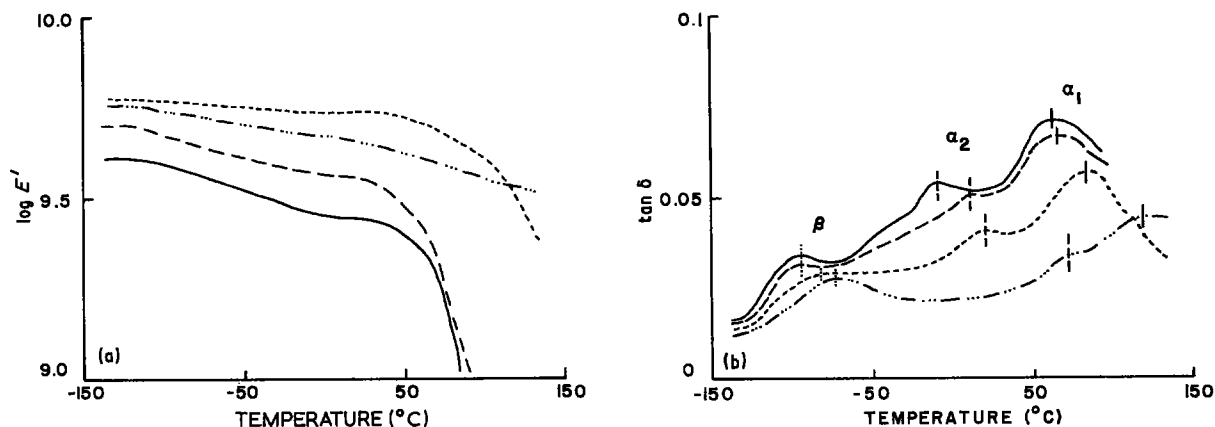

Figure 2 The effect of moisture content on the dynamic mechanical response (a) log E' and (b) $\tan\delta$ of spruce wood. Moisture contents are (– · –) 5%, (– – –) 10%, (— —) 20% and (——) 30%).

The evaluation of the effect of frequency on the tanδ peak temperature allows the determination of an apparent activation energy (E_a) of the relaxation using a modified form of the Arrhenius equation (Equation 1). For the α_1 transition, an E_a of 339 kJ mol^{-1} (MC = 15%) was calculated, and this compares favourably with the 395 kJ mol^{-1} figure reported by Salmen [12] for water-saturated wood over a similar frequency range. Both of these values are typical of the activation energy of a glass transition (T_g) which occurs around 100°C [24]. Insufficient resolution prevented the calculation of E_a for the α_2 dispersion. The β dispersion had an E_a of 102 kJ mol^{-1}, and a relaxation peak with similarly low E_a has been noted for a variety of hydrophilic polymers, including carbohydrates, under high humidity conditions [17]. All three observations, absence of modulus drop, moisture sensitivity, and low E_a, are consistent with the earlier assignment of this peak to site exchange of water.

The experimental evidence from the DMTA studies supports the identification of the two high-temperature transitions, α_1 and α_2, as T_g values. This is the first experimental evidence of two distinct transitions, presumably arising from two distinct polymeric components of the amorphous cell wall matrix. Although it is tempting to assign these peaks to lignin and hemicellulose, further evidence is required. The β dispersion can be attributed to site exchange of moisture.

3.2. DSC at various moisture contents

Differential scanning calorimetry provides an additional method for studying the nature of the observed thermal transitions. Fig. 3 shows a series of DSC scans made on milled spruce wood equilibrated at a moisture content of about 20%. The initial scan shows an endothermic peak at about 50°C which is not evident
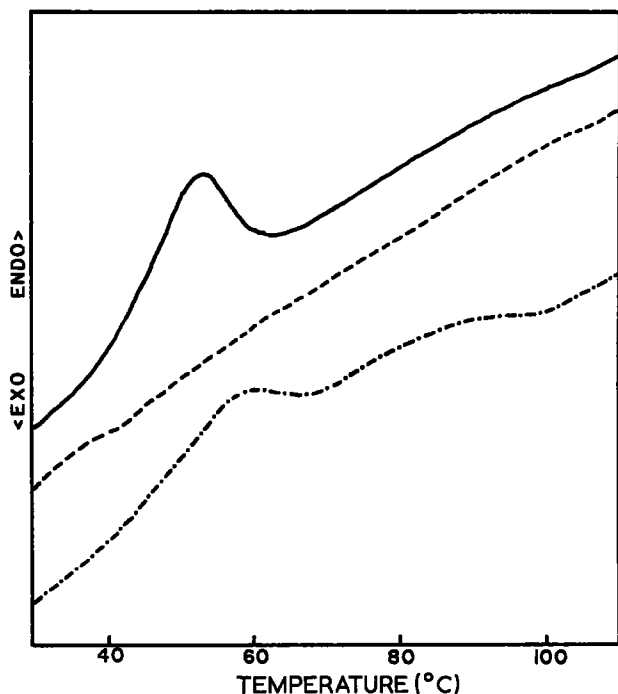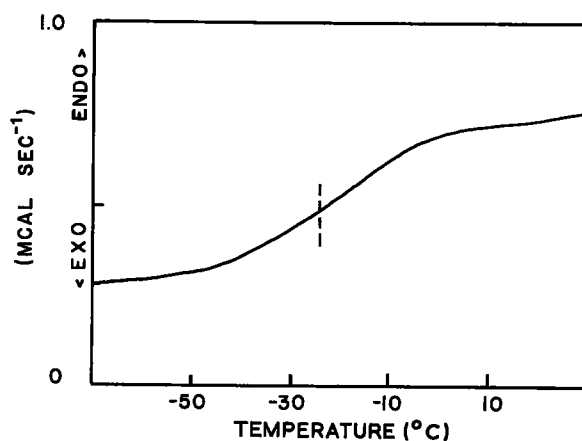
Figure 4 Sub-ambient differential scanning calorimetry trace of spruce wood (MC = 25% CAL × 10^{-3}sec^{-1} = 4.184 × 10^{-3} × J sec^{-1}).

after cooling and immediately rescanning. However, after annealing at 40°C for 24 h the endothermic peak reappears, although at a slightly higher temperature and somewhat reduced intensity. This phenomenon is known as enthalpy relaxation [20]; it results from the slow approach to conformational equilibrium which is characteristic of glassy materials and has been observed in lignin derivatives [23]. The observation of enthalpy relaxation is clearly associated with a T_g. The recorded relaxation peak at ca. 60°C agrees well with the tanδ peak at similar moisture content (Fig. 2).

A second transition, at −22°C, is revealed by sub-ambient DSC (Fig. 4). In the absence of any sub-T_g annealing treatment, this transition exhibits the characteristic baseline discontinuity of a second-order, thermodynamic event, i.e. a glass transition. The presence of these two thermal events in the DSC experiment corresponds to the α_1 and α_2 peaks in the dynamic mechanical spectrum (Figs 1 and 2), and this confirms two separate glass transitions arising from the amorphous component of wood.

It should be noted that the temperature difference between the DMTA peaks and the DSC events can be attributed primarily to frequency effects and the use of solid wood in the DMTA. Both of these variables effectively increase the observed T_g values in DMTA [7, 12].

3.3. Compliance with the Kwei model

Having established the presence of two distinct glassy polymers in the amorphous component in wood it is of interest to study their response to plasticization. Water was shown to affect the α_1 and α_2 transitions. Isolated lignin and hemicellulose polymers have been reported to respond differently to the presence of moisture [7, 9, 16]. Several models have been employed to predict the response of the amorphous component's T_g to absorbed moisture, but provide a good fit only at moisture contents below about 10% [9, 16].

One possible explanation for this limited range of application is that these models are based almost entirely on free-volume considerations and fail to consider the role of secondary interactions between the diluent and polymer. One model which does allow for strong secondary interactions such as hydrogen

Figure 3 Differential scanning calorimetry of spruce wood (MC = 25%): (——) initial scan, (———) immediate re-scan and (—··—) scan after annealing at 40°C for 24 h.
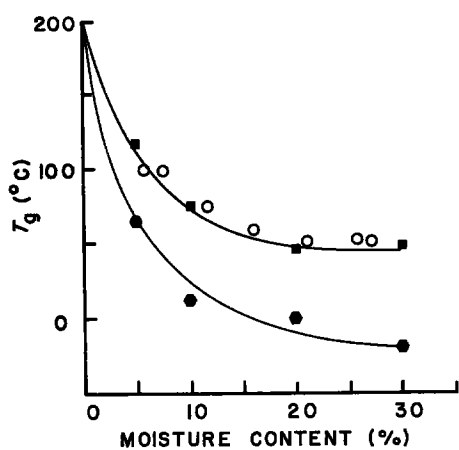
Figure 5 The effect of moisture content on the glass transition of spruce wood. (●) α_1 (this work), (■) α_2 (this work), (O) α_2 from Irvine [7]. The solid lines are predictions from the Kwei model using the parameters shown in Table I.

bonding is that by Kwei [18]:

$$T_g = (W_1 T_{g1} + kW_2 T_{g2})/(W_1 + kW_2) + qW_1 W_2$$

(2)

in which W and T_g represent the weight fraction and glass transition temperature of polymer and diluent (designated as Components 1 and 2, respectively), and q represents an adjustable parameter accounting for secondary interactions. The adjustable parameter k is derived from free-volume considerations.

Fig. 5 shows a plot of the α_1 and α_2 transition as a function of moisture content. Also included are the data of Irvine [7] for the T_g observed by thermal analysis of lignin in whole wood. There is remarkable agreement between all data. The α_1 transition reaches a plateau at ca. 70°C at an MC of 10%. The α_2 transition continues to decline to lower temperatures before levelling off at about −20°C as the MC approaches 30%. The lines represent the best fit from the Kwei equation for the three data sets, with the parameters used being summarized in Table I. On the basis of their distinctively different responses to plasticization by water, this analysis allows the assignment of α_1 and α_2 dispersions in the DMTA spectrum of wood to the T_g of lignin and hemicellulose, respectively.

Considering the excellent fit provided by the Kwei equation for both lignin and hemicelluloses, a brief examination of the adjustable q parameter is warranted. Intuitively, a higher q value for lignin than for hemicelluloses agrees with the concept that greater interaction occurs between water and the phenolic hydroxyl groups of lignin than between water and the primary and secondary hydroxyls of the hemicellu-

TABLE I Best fit values of the Kwei equation parameters k and q for wood components from various sources

Wood component and technique	k	q
Lignin (DMTA)*	10	585
Lignin (DSC)†	10	585
Hemicellulose (DMTA)*	13	355

*This work.
†From Irvine [7].

TABLE II Best fit values of the Kwei equation parameters k and q and phenolic hydroxyl content for three isolated lignin preparations

Lignin type and source	k	q	Ph-OH/C_9
Milled wood lignin [7]	8.7	590	0.26 to 0.27 [33]
Periodate lignin [9]	5.8	650	0.35 [34]
Kraft lignin [16]	7.2	740	0.43 to 0.47 [33]

loses. The relationship between the magnitude of q and the extent of interaction between water and specific functional groups of the wood polymers is tested in Fig. 6, which shows a plot of T_g for several isolated lignin preparations at varying moisture contents. Using the Kwei parameters shown in Table II, an excellent fit is observed between experimental data and model. This suggests that q decreases with phenolic hydroxyl content. Expressed another way, the theoretical term that accounts for secondary interactions decreases as the number of sites that provide for strong secondary interactions decreases. Although far from conclusive, this result does strengthen the argument that q provides a relative measure of secondary interactions which successfully accounts for unusual variations in T_g with moisture content for lignin and hemicelluloses.

3.4. Individual peak enhancement

With the identification of two separate T_g values for lignin and hemicellulose, an attempt was made to improve peak resolution with two experiments. For incompatible polymer blends or incompatible block copolymers, annealing above the T_g of both components allows for more complete phase separation [25]. A second method for peak resolution is preferential plasticization of the individual components with selected diluents. Both of these experiments were conducted with wood.

Wood samples were dried in a forced-air oven or under vacuum and rehydrated under a saturated atmosphere. It was hoped that the drying would serve as an annealing treatment and that vacuum drying could be used to account for the effects of moisture hysteresis [26]. Drying was limited to 30 min at 110°C to minimize possible degradation [27].
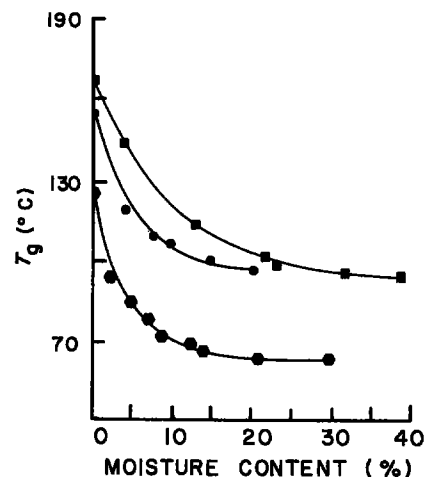

Figure 6 The effect of moisture content on (●) periodate lignin, (■) kraft lignin and (●) milled wood lignin. The solid lines represent predictions from the Kwei model using the parameters in Table II.
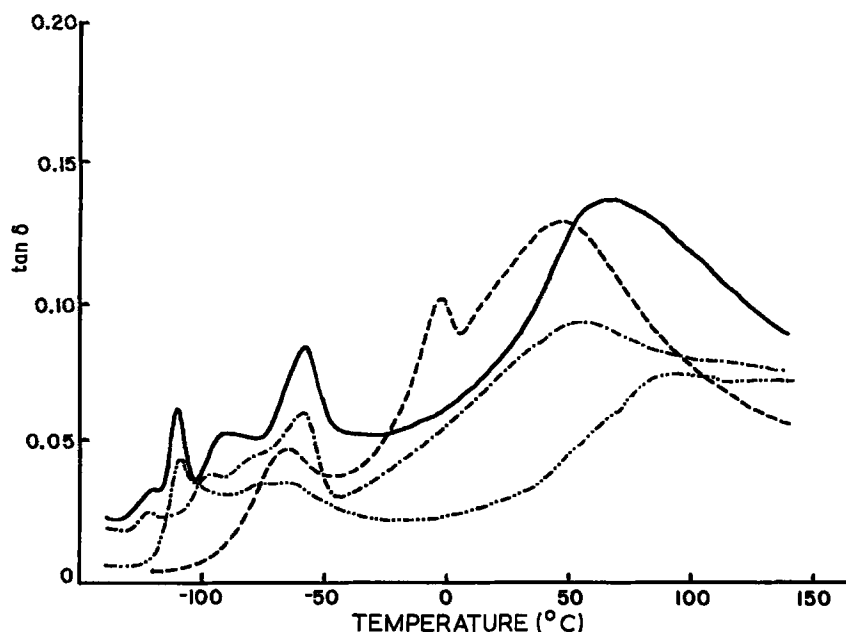
Figure 7 The tanδ response for spruce wood saturated with (— — —) formamide, (————) ethyl formamide, (— · —) dimethyl formamide and (— · · —) diethyl formamide. For solubility parameters see Table III.

The DMTA analysis of samples which were dehydrated and rehydrated failed to produce the expected enhanced resolution of the two tanδ peaks. The major difference between the control and the two dehydrated/rehydrated samples was due to moisture hysteresis. A comparison of the oven- and vacuum-dried samples showed some minor differences that could be attributed to exposure to high temperatures. The response for the oven-dried wood showed a second small dissipative response that was not present in the vacuum-dried sample. However, the effects of annealing were not as significant as hoped.

The second set of experiments involved a series of non-aqueous diluents. Four formamides with solubility parameters between 19.2 and 9.6 cal$^{1/2}$ cm$^{-3/2}$ (80 and 40 J$^{1/2}$ cm$^{-3/2}$) were chosen as potential selective plasticizers (Table III). The solubility parameter of lignin has been estimated to be between 10.5 and 11.2 cal$^{1/2}$ cm$^{-3/2}$ (44 and 47 J$^{1/2}$ cm$^{-3/2}$) by calculation from group contribution theory (e.g. [28]) while that of hemicellulose was taken to the 16 cal$^{1/2}$ cm$^{-3/2}$ (67 J$^{1/2}$ cm$^{-3/2}$) in accordance with that of amorphous cellulose [29]. It was hoped that formamide and ethyl formamide would preferentially interact with the hemicelluloses while dimethyl and diethyl formamide would be more attracted to lignin. The DMTA response for spruce saturated with each of the formamides is shown in Fig. 7.

The two obvious features of the DMTA response are the numerous peaks at low temperature and the single broad high-temperature peak. The relatively

sharp tanδ peaks can be related to the melting temperature (T_m) or T_g of the free diluent in the wood. These occur in the temperature range between −124 and 0°C, and they are summarized in Table III. At lower concentrations of each diluent, the transition is still present though at a reduced intensity and higher temperature. The motion of a side-group should be relatively independent of diluent type and concentration, but the activation energy of the transition, calculated from Equation 1, is found to vary considerably with diluent type (Table IV). This supports the hypothesis that the transition must be attributed to the motion of a diluent (i.e. site exchange) rather than a specific side-group of a wood component.

The second prominent feature of the DMTA response in Fig. 7 is the breadth of the high temperature tanδ peak. A broad tanδ peak is indicative of a heterogeneous material with a variety of dissipative mechanisms [30]. Thus, the original goal of finding diluents which preferentially interact with one of the amorphous components was not realized. Based solely on solubility parameters, selectivity might be expected; but in many cases interaction of polymer and solvent depend on more complex mechanisms than simple matching of solubility parameters. Despite the failure to resolve T_g values more distinctly, some general trends could be identified.

If the four formamides are distinguished by the strength of their hydrogen-bonding potential (see Table III) then a relationship between T_g and solubility parameter is evident. For the solvents with

TABLE III Selected physical properties of diluents and wood components

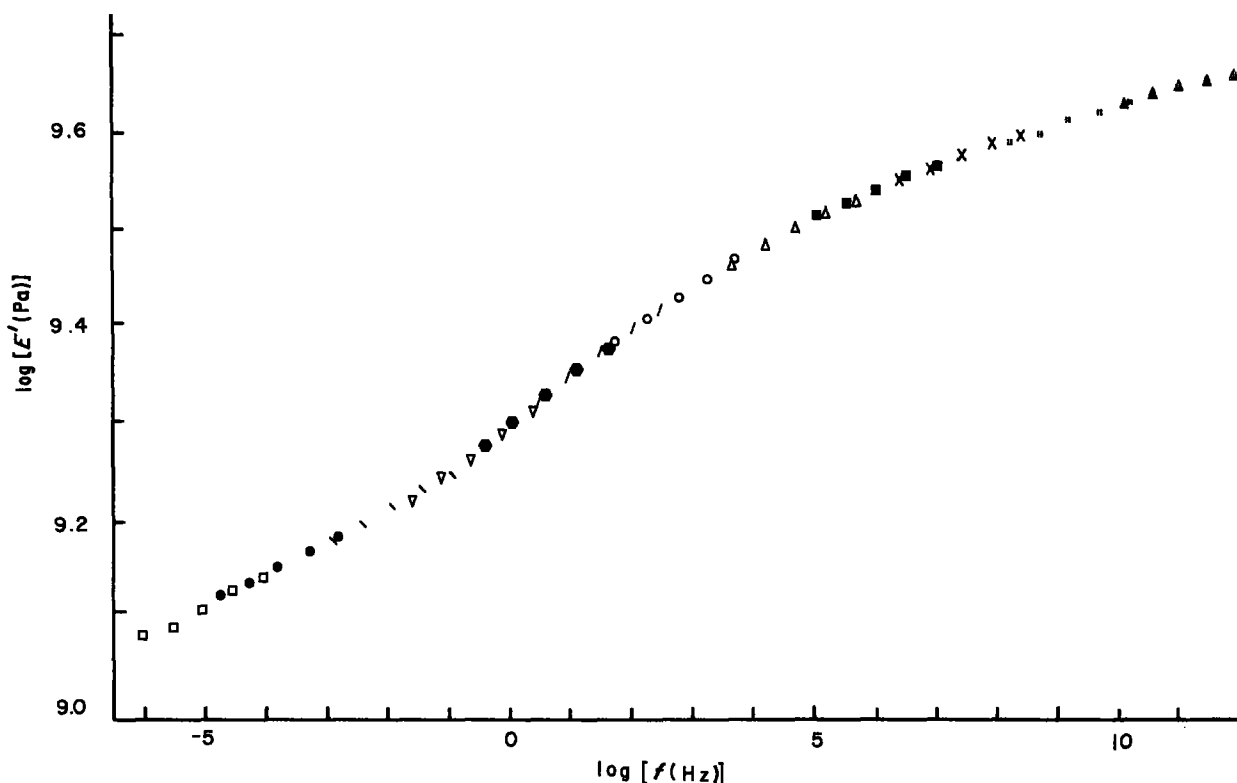| Diluent	Solubility parameter (cal$^{1/2}$ cm$^{-3/2}$)	Hydrogen bonding	T_m or (T_g) (°C)
Water	23.1 [29]	Strong	0* (− 137 [16])
Formamide	19.2 [29]	Strong	− 2*
Ethyl formamide	13.9 [29]	Strong	− 55*
Dimethyl formamide	12.1 [29]	Moderate	− 61*
Diethyl formamide	9.6 [29]	Moderate	(− 124)*
Cellulose (hemicellulose)	16.0 [29]	−	(200 [16])
Lignin	10.6 [35] to 11.2 [28]	−	(200 [16])

*Experimental value from DSC.

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Figure 8 Master curve of log E' against frequency for spruce plasticized with ethyl formamide. The reference temperature is 60° C.

strong hydrogen-bonding potential formamide is a more effective plasticizer than ethyl formamide as evidenced by the lower T_g. While for the solvents with moderate hydrogen-bonding potential, dimethyl formamide is a more effective plasticizer than diethyl formamide. While difficult to quantify exactly, the magnitude of the tanδ response was greater for both strong hydrogen-bonding solvents than for the corresponding two moderate hydrogen-bonding solvents.

3.5. Time–temperature superposition (Ttsp)

The correspondence between time and temperature for influencing a viscoelastic response has been demonstrated numerous times for a variety of amorphous materials [31, 32]. The most prominent of these works was that of Williams, Landel and Ferry [31]. The generality of Ttsp has important implications in the area of mechanical refining of wood. Ttsp would allow one to define conditions that might reduce the energy requirements for the refining of wood, if the lignin were above its T_g.

The application of Ttsp has previously been demonstrated for water-saturated wood [12]. In the present study the application of Ttsp to wood plasticized with non-aqueous diluents was tested. The results are shown in the master curve of the log E' data (Fig. 8).

TABLE IV Effects of various diluents at 20 wt % on the activation energy of the beta-dispersion in spruce wood

Diluent	E_a (kJ mol^{-1})
Water	85
Formamide	–*
Ethyl formamide	148
Dimethyl formamide	169
Diethyl formamide	188

*Poorly resolved peak temperatures.

The curve was obtained by a horizontal shift of the log E' response at different frequencies and a single temperature. The fit of the data is remarkable considering the complexity of the system. Note that the vertical corrections for density and temperature differences [19], which are derived from the kinetic theory of rubber elasticity, were not required.

The shift factor, log a_t, can be plotted against the temperature difference to form a second curve (Fig. 9). A reference temperature (T_{ref}) of 60° C was used for the shift-factor plot. Above its T_g a glassy polymer is expected to obey the Williams–Landel–Ferry (WLF) equation [31]:

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

where C_1 and C_2 represent constants, and t is the temperature at which the measurement is taken. The major portion of the shift-factor plot $(-30$ to $56°$ C)
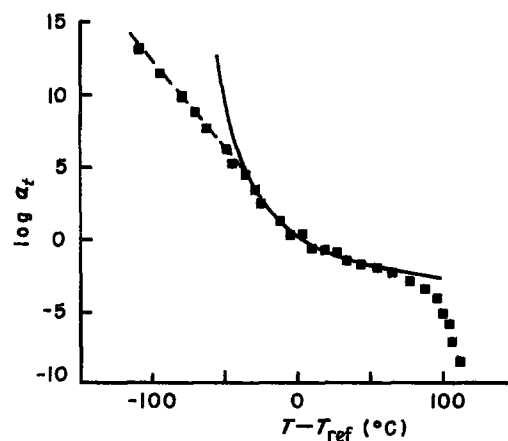

Figure 9 Plot of shift factors used in the construction of the master curve (Fig. 8) against temperature difference $(T - T_{ref})$. The solid line is the WLF equation; reference temperature is 60° C.

fits the WLF equation, and this is illustrated by the agreement of the "universal" WLF constants, typical of glassy polymers above their T_g, with the experimental ones. The values from the curved portion of Fig. 9 are $C_1 = 17.7$ and $C_2 = 52.1$, compared to 17.44 and 51.6 for the "universal" constants.

For the shift-factor curve below $(T - T_{ref}) = 30°\,C$ there is deviation from the WLF equation. This corresponds to a real temperature of $30°\,C$. Deviation from WLF behaviour indicates that a different type of dissipative mechanism takes control below $30°\,C$. This temperature corresponds approximately to the T_g of ethyl-formamide-plasticized wood. A similar deviation from WLF behaviour was also found for water-saturated wood [12]. For most glassy polymers the WLF equation is only valid for the range T_g to $(T_g + 100°\,C)$ [32]. In this study the WLF equation held up to $(T_g + 85°\,C)$, which is a slightly higher range than that found for water-saturated wood. Again, deviation from WLF indicates a different type of dissipative mechanism dominating.

4. Conclusions

Analysis of the relaxation processes of wood with both DMTA and DSC has demonstrated two separate T_g values representative of two distinct amorphous polymers. At 30% moisture content the T_g of in situ lignin is $60°\,C$ and the T_g of in situ hemicelluloses is $-10°\,C$, as measured by DMTA at 1 Hz. The temperature of these T_g values is heavily dependent on both moisture content and frequency. The DSC analysis also showed two separate values of T_g. The observation of enthalpy relaxation by DSC confirmed the DMTA tanδ peak as a T_g. The T_g depression of both amorphous wood components by moisture could be followed by the Kwei model. This model also appears to qualitatively account for the strength and number of secondary interactions. A low-temperature $(-100$ to $-50°\,C)$ β dispersion was also observed. This dispersion was attributed to site exchange of diluent rather than to small-scale motions of specific side-groups on one of the individual wood components.

With the observation of two separate T_g values one can confirm the immiscibility of the two amorphous wood polymers, lignin and hemicelluloses. However, from the results of this study one cannot distinguish between the models of Salmen [12] and Gravitis and Erins [21, 22], both of which describe a heterogeneous amorphous wood structure.

Two different approaches were used in an attempt to further resolve the two individual T_g values. Annealing above the highest T_g and the use of a series of formamides both failed to sharpen the response of the individual T_g values. However, annealing and rehydration revealed the effects of moisture hysteresis. The use of a series of formamides revealed that a higher solubility parameter and a stronger hydrogen-bonding potential contribute to the effectiveness of a plasticizer for wood.

Finally the applicability of time–temperature superposition to wood was confirmed for the second time. The WLF equation was found to be valid over the range T_g to $(T_g + 85°\,C)$ with constants of $C_1 = 17.7$

and $C_2 = 52.1$. Outside this range, presumably, other dissipative mechanisms become important as indicated by the departure from WLF behaviour.

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