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Viscoelastic properties of *in situ* lignin under water-saturated conditions

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The viscoelastic properties of wood under water-saturated conditions have been studied in the temperature range 20 to 140° C at frequencies ranging between 0.05 and 20 Hz. It is demonstrated that the major transition in this temperature range is related to a *glass transition*, i.e. the glass transition of the *in situ* lignin. The difference in softening behaviour along and across the fibre direction is shown to be related to the stiffening effect of the cellulose microfibrils preferentially aligned along the fibre direction. The softening behaviour is also estimated for frequencies applicable to wood defibration processes, $\sim 10^4$ Hz. The implications of the wood properties under these conditions are discussed.

1. Introduction

The softening of lignin is an important parameter to be considered in the mechanical pulping of wood, and the pulp properties may be varied substantially by variation of the process temperature relative to the glass transition temperature of the water-saturated lignin.

The glass transition temperature for water-saturated lignin has been determined on isolated lignins [1–3] as well as on the wood composite [3, 4] with fairly good agreement. Reports on the viscoelastic properties of lignin and also of wood under water-saturated conditions are, however, rare. The extensive studies of Becker and Noack [5, 6] on wood at various moisture contents do not cover the water-saturated state.

Due to the changes in structure that occur during the isolation of lignin from wood material, the viscoelastic properties of such isolated lignins may be of little relevance to the conditions prevailing in mechanical pulping. Experiments have therefore here been performed on wood in an attempt not only to describe the viscoelastic properties of the wood but also to relate these properties to the properties of the lignin material present.

Wood can be envisaged as a composite material with reinforcing fibres embedded in a matrix of lignin, a three-dimensional polyphenolic polymer. The fibres are in turn composed of cellulosic microfibrils in a matrix composed of both hemicelluloses and lignin. The total lignin content of the wood is about 28% (softwood). Due to the high degree of orientation of the microfibrils in the axial direction of the fibres, the wood is highly anisotropic. Thus the matrix lignin is more limiting in determining the mechanical properties of wood along the fibre direction than across the fibre direction. Under water-soaked conditions where the amorphous carbohydrate components of wood (mainly hemicelluloses) are already softened at room temperature [7], the properties of the lignin exert a particularly great influence on the properties of the wood. The glass transition temperature for lignin under these conditions has been found to vary between 80 and 100° C depending on the frequency of measurement [3, 4, 8]. This softening of lignin results in a major reduction in the elastic modulus of the wood, particularly in the direction across the fibres [8, 9]. The results here reported consist mainly of measurements on water-soaked wood samples in the cross-fibre direction between 20 and 140° C. For comparison, reference is made to some tests in the fibre direction.

2. Experimental procedure

The wood specimens were cut from green logs of a 50 year old tree of Norway spruce, *Picea abies.* Heartwood was selected in order that a large enough specimen could be cut out to give ade-

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quate testing loads. Samples for tests across the fibre direction were dumb-bell shaped with a cross-section of 15 mm x 50 mm, while samples for test along the fibre direction were made with a cross-section of 7 mm x 7 mm. Prior to testing, the wood samples were steam treated for 1 h at 135° C and then soaked in water at the same temperature to saturate the wood fully. The preconditioning at 135° C was also done to eliminate the effects of the irreversible softening taking place above 100° C [8, 9].

Dynamic mechanical properties of the water-saturated wood were measured at temperatures between 20 and 140° C. Forced sinusoidal vibrations in the frequency range 0.05 to 20 Hz were applied using a servohydraulic universal testing machine of the Material Testing System (MTS) equipped with an autoclave to provide water-saturated conditions up to 140° C. Deformation was measured with an extensometer attached to the specimen, while the load was measured with a load cell outside the autoclave connected through bellows to the sample. Below 100° C the water-saturated samples were sprayed with hot water, while above 100° C saturated steam was used. Above 100° C, i.e. above 1 atm, the excess load of the steam pressure was compensated for. The temperature was measured with a small thermocouple placed inside the specimen.

The sinusoidal vibrations were performed with zero mean stress. In all cases the amplitude was varied within the linear viscoelastic range, i.e. up to 0.1% deformation [10], and data have been obtained by extrapolation to zero deformation. Dynamic mechanical properties were calculated from the means of each ten consecutive loops. The complex modulus $|E^*|$ is by definition

$$|E^*| = \sigma_0/\epsilon_0 \qquad (1)$$

where σ_0 and ϵ_0 are respectively the stress and the strain amplitude. The loss modulus E'' was calculated from the mean area D of a single hysteresis loop

$$E'' = D/(\pi\epsilon_0^2) \qquad (2)$$

The storage modulus E' was then obtained from the relation

$$|E^*| = (E'^2 + E''^2)^{1/2} \qquad (3)$$

and the mechanical loss coefficient $\tan\delta$ was obtained as

$$\tan\delta = E''/E' \qquad (4)$$

The moduli are based on the macroscopic dimensions of the wood specimen at 20° C, 65% r.h., its void volume thus being included.

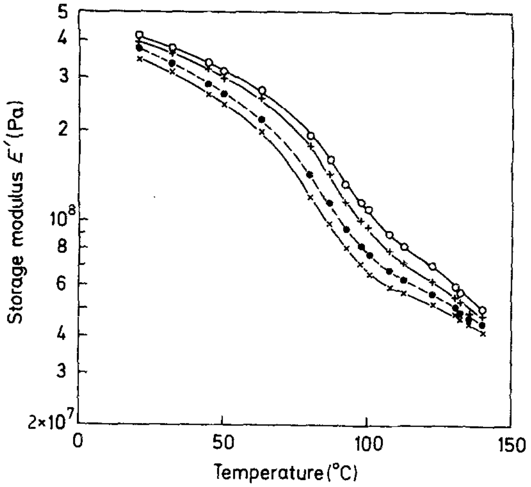

Figure 1 Storage modulus E' as a function of temperature for water-saturated wood across the fibre direction. Frequencies: × 0.05, ● 0.5, + 5, ○ 20 Hz.

3. Dynamic mechanical properties

Fig. 1 gives data for the storage modulus E' as a function of temperature at different frequencies. The data show the typical behaviour of a visco-elastic material with a second-order transition, here situated in the range of 60 to 120° C. Fig. 2 gives the corresponding data for the mechanical loss coefficient $\tan\delta$, with peaks at different frequencies in the temperature range corresponding to the transition region. The transition temperature, taken as the temperature of maximum $\tan\delta$, shifts to higher temperature as the frequency increases. This is analogous to the behaviour of second-order transitions in regular polymers. The

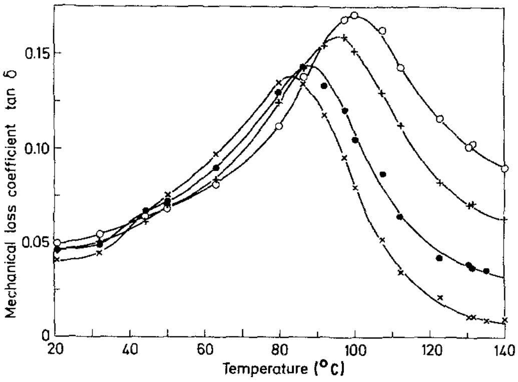

Figure 2 Mechanical loss coefficient $\tan\delta$ as a function of temperature for water-saturated wood across the fibre direction. Frequencies: × 0.05, ● 0.5, + 5, ○ 20 Hz.

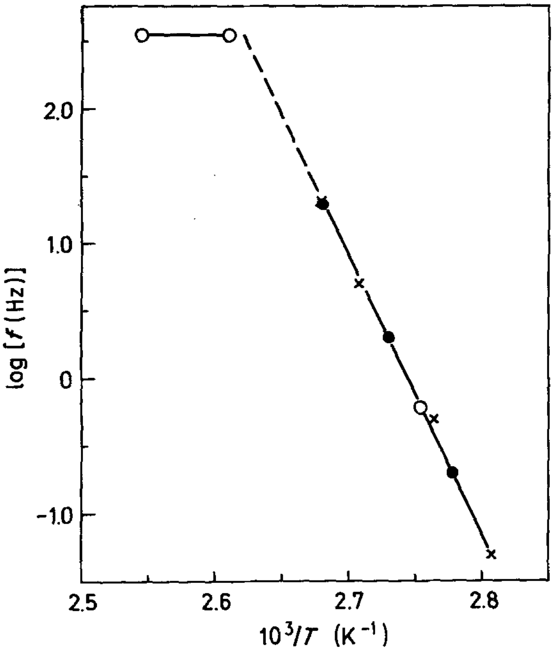

Figure 3 Arrhenius plot of log frequency against reciprocal of absolute temperature for the major transition in water-saturated wood across the fibre direction. × present work, • corresponding measurements by Salmén and Fellers [9], ○ measurements of Becker *et al.* [12].

frequency dependence for a second-order transition can be expressed by an Arrhenius-type equation given by

$$f = f_0 \exp(-\Delta H_a/RT) \qquad (5)$$

where f is frequency, f_0 is pre-exponential factor, ΔH_a is the apparent activation energy ($\mathrm{J\,mol^{-1}}$), R is the gas constant ($8.3143\,\mathrm{J\,mol^{-1}\,K^{-1}}$) and T is temperature (K). This equation also applies over a limited frequency range for the glass transition which more generally follows the Williams–Landel–Ferry (WLF) equation [11]. Fig. 3 gives an Arrhenius plot of measured data of the transition temperature across the fibre direction of water-saturated wood samples at various frequencies. From the slope, an apparent activation energy of $395\,\mathrm{kJ\,mol^{-1}}$ may be calculated. Data of Becker *et al.* [12] measured in torsion on wet spruce samples cut with the longitudinal direction across the fibres are also included in Fig. 3. Their data agree reasonably well with the relation found between frequency and inverse temperature, although a slight shift to higher temperatures at the highest frequency is noted. For a glass transition a significant deviation from the Arrhenius equation occurs at high frequencies. The data of Sadoh [4] at 0.02 Hz indicating a transition at about 80° C also fit the relation well. Generally the apparent activation energy ΔH_a for a glass transition has a value of about $40\,\mathrm{kJ\,mol^{-1}}$ and upwards, with a general trend towards an increase in ΔH_a with increasing T_g [13, 14]. A comparison may be made with polystyrene which has a T_g of 100° C and a ΔH_a of $423\,\mathrm{kJ\,mol^{-1}}$ [15] and polycarbonate with a T_g of 150° C and a ΔH_a of $481\,\mathrm{kJ\,mol^{-1}}$ [16]. The value calculated for the activation energy of the measured transition in water-saturated wood is therefore in the range expected for a glass transition.

For synthetic polymers the transition temperature has been found to rise by between 15 and 50° C per 100 MPa increase in pressure [13]. Atack has also noticed an increase of the same order in the transition temperature for wood with increasing pressure [17]. In the present investigation the increase in pressure is at the most 0.4 MPa. This pressure increase can be considered negligible in its effect on the transition temperature.

4. Time–temperature superpositioning

To determine whether time–temperature superposition is applicable to the dynamic mechanical behaviour of wood or *in situ* lignin, cross plots of E' and E'' against log frequency were made. These curves are then translated to master curves of E' in Fig. 4 and E'' in Fig. 5 by horizontal shifting. The reference temperature has here been set arbitrarily at 112.3° C. For clarity the data for E'' below 79.7° C have been omitted, since these data overlap to such an extent that any shift to con-

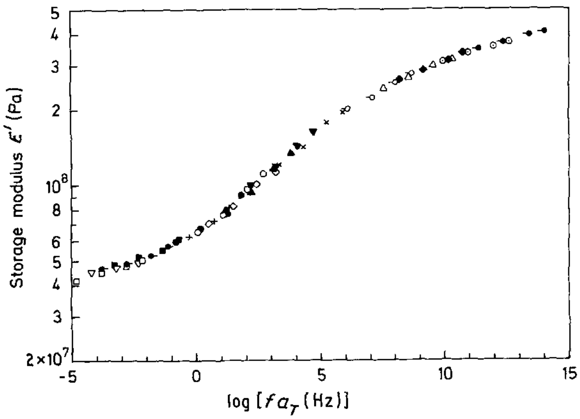

Figure 4 Master curve for the storage modulus E' versus frequency f times shift factor, a_T. The reference temperature where the shift factor is unity is 112.3° C.

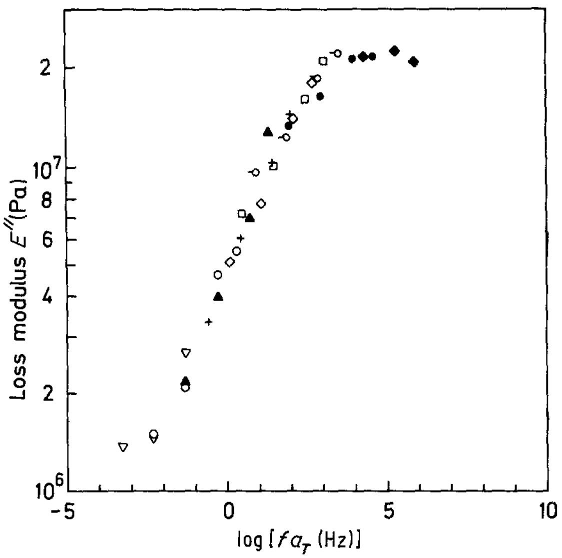

Figure 5 Master curve of the loss modulus E'' against frequency f times shift factor a_T. The reference temperature where the shift factor is unity is 112.3° C.

struct a master curve becomes meaningless. Since the elastic modulus is given in terms of a modulus related to the dimensions at 20° C and 65% r.h. the master curves are corrected for the change in specimen volume with temperature.

For amorphous polymers a small correction factor is normally used:

$$E(T_0) = E(T)\frac{\rho_0 T_0}{\rho T} \qquad (6)$$

where ρ is the density and T the temperature in degrees kelvin [11]. The expression is derived from the kinetic theory of rubber elasticity, and its validity for the composite system of wood is therefore questionable. For this reason no temperature correction has been applied here to the individual curves in the construction of the master curves.

Obviously both E' and E'' give smooth master curves. In the temperature range above the glass transition temperature of the lignin it may be assumed that the shift will follow the WLF equation. In this case, with an arbitrary reference temperature, the WLF equation is expressed as

$$\log a_T = \frac{C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})} \qquad (7)$$

In Fig. 6 the shift factors a_T used for the construction of the master curves for E' and E'' are given as a function of the temperature difference

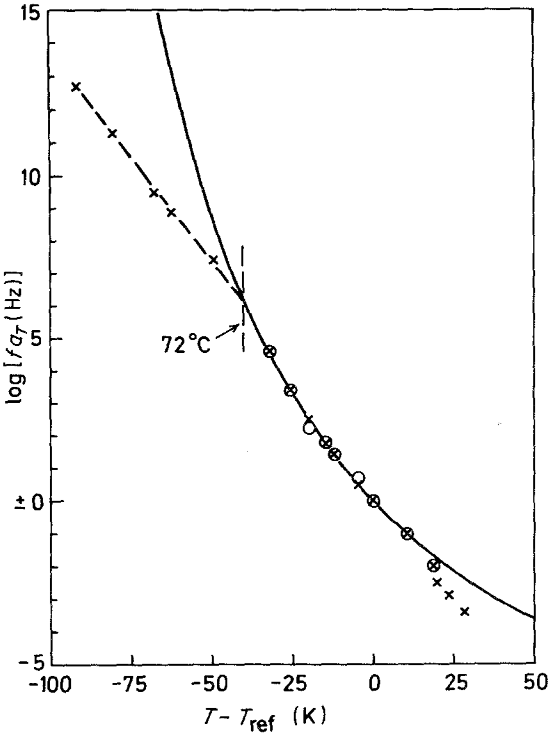

Figure 6 Shift factors against temperature difference $(T - T_{\text{ref}})$ for the master curves in Figs. 4 and 5. × from E', ○ from E''. The WLF equation derived is also included (full curve). The reference temperature is 112.3° C.

$(T - T_{\text{ref}})$ together with the WLF equation derived. There is clearly a good agreement between the shift factors for both E' and E''. Above ~72° C the shift factor follows the prediction of the WLF equation, indiating that this temperature is the glass transition of the wood or the *in situ* lignin at very low frequencies. This temperature is also in agreement with the Arrhenius plot in Fig. 3 and should correspond approximately to a dilatometrically determined glass transition temperature, i.e. a transition at about 10^{-4} Hz [13, 14]. Below 72° C the shift factor follows an Arrhenius-type of behaviour. Normally the WLF equation is applicable in the range from T_g to $T_g + 100°$ C. However, in the present case the shift factor deviates above 130° C, i.e. above $T_g + 55°$ C. Above this temperature other types of mechanism with different rate constants apparently prevail. A similar behaviour may be envisaged from the data presented by Höglund *et al.* [8] showing an increasing softening above this temperature.

If the transition temperature T_g, in this case 72° C, is chosen as the reference temperature, the WLF constants may be determined as $C_1 = -$

18.18 and $C_2 = 77.19$. In this case, the fractional free volume f_g at T_g and the volumetric expansion coefficient of the free volume, α_f, may be estimated from the following equations:

$$C_1 = B/(2.303 f_g) \tag{8}$$

$$C_2 = f_g/\alpha_f \tag{9}$$

where B is a constant set equal to unity [18]. For these measurements on wood f_g is estimated at 0.024 and α_f at 3.1×10^{-4} deg^{-1}, quite reasonable values considering the complexity of the system.

For the WLF temperature dependence there is no unique definition of activation energy. An apparent activation energy, dependent on the temperature difference $(T - T_g)$, is often defined [11] as

$$\Delta H_a = 2.303R \frac{d \log a_T}{d(1/T)} \tag{10}$$

In the vicinity of the glass transition temperature, $T_g = 72°$ C, the activation energy for the wet wood or for the *in situ* lignin can thus be approximately determined as 450 kJ mol^{-1}. As the apparent activation energy is greater the lower the frequency of the measurement, this value is quite reasonable in comparison with the value given by the Arrhenius plot.

5. Behaviour along and across the fibre direction

Fibres are almost perfectly aligned in the longitudinal direction of the tree. Within the fibres the cellulose microfibrils are preferentially aligned along rather than across the fibre axis. Since the cellulose microfibrils constitute the reinforcing elements in the fibre structure, it is thus not surprising that both fibres and wood are much stiffer along than across the fibre direction. This is reflected in the softening of wood under conditions of lignin softening as exemplified in Fig. 7 which shows the mechanical loss coefficient tan δ for water-saturated wood between 20 and 140° C.

To facilitate a comparison of the transition regions along and across the fibre direction, a normalization procedure independent of the geometry of the sample and of the structural arrangement of the constituents is required. A suitable normalization of the loss coefficient can be achieved by setting its maximum equal to 1. Thus the normalized loss factor $(\tan \delta)_n$ is given by

$$(\tan \delta)_n = \frac{\tan \delta}{(\tan \delta)_{max}} \tag{11}$$

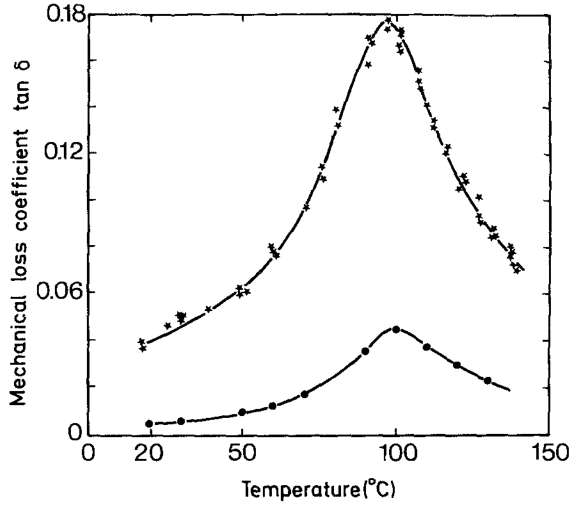

Figure 7 Mechanical loss coefficient as a function of temperature for water-saturated wood samples ★ across and ● along the fibre direction at a frequency of 10 Hz.

where $(\tan \delta)_{max}$ is the maximum loss coefficient.

In Fig. 8, these normalized loss coefficients $(\tan \delta)_n$ are compared for the two directions in wood. The close correlation between the shapes of the curves indicates that the viscoelastic properties of the wood at temperatures around 100° C are dominated by the lignin irrespective of the direction along or across the fibres. The discrepancy at lower temperatures may be due to the tail end of a transition below the measured range. This softening has a greater influence on the cross direction properties.

A small difference between the softening temperatures along and across the fibre direction may be noticed, but it is too small to have any signifi-

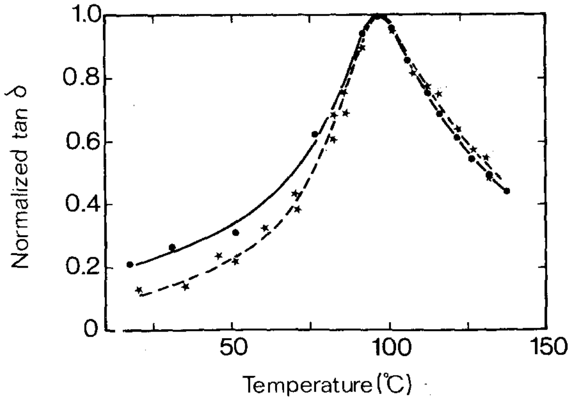

Figure 8 Relative mechanical loss coefficient versus temperature for water-saturated wood samples ★ along and ● across the fibre direction at a frequency of 10 Hz.

cance. In the case of the loss moduli [9], the difference between the temperatures of the maximum loss modulus along and across the fibre direction is greater than the corresponding difference in temperatures of the maximum mechanical loss coefficient, but these curves are severely affected by an additional loss apparent across the fibres, probably due to the existence of a broad transition region at the lower end of the measured temperature range. Measurements by Becker *et al.* [12] have indicated a somewhat greater difference for high frequency measurements, although this is obscured by differences in frequencies along and across the fibre directions in the tests compared. For other materials such as epoxy resin, Yang *et al.* [19] have noticed no shift in the softening maximum of the epoxy or of the dispersion curve for laminates of fibre-reinforced epoxy resin with different stacking sequences, despite the different stress states.

6. Applications to mechanical pulping

The softening of wood under water-saturated conditions has a great impact on the pulp properties achieved in mechanical pulping. Both the separation of the fibres and the subsequent development of their flexibility are believed to be dependent on the softness of the lignin. In commercial operations, mechanical refining and grinding take place at temperatures between 100 and 160° C and at frequencies in the kHz range [3, 12, 20], i.e. at frequencies appreciably higher than the frequencies here studied.

Using the established WLF equation and, beyond its applicable range, estimated Arrhenius-type equations, it is possible to transform the master curve data of the modulus into modulus–temperature relations at these high frequencies. In refiner operations the frequencies to which the wood chips are subjected have been estimated to be between $10^{3.5}$ and $10^{4.5}$ Hz [3, 12]. The same frequency range has also been given for mechanical treatment in grinding operations [20, 21].

In Fig. 9 calculated relations for the storage modulus E' at frequencies of 5 Hz and 10^4 Hz are compared. For comparison the measured data at a frequency of 5 Hz have also been included. If it is assumed that the wood or the *in situ* lignin follows the established WLF type of behaviour over the entire temperature range from T_g to $T_g + 100°$ C, as is usual for polymers, a broadening of the transition region at the higher frequency

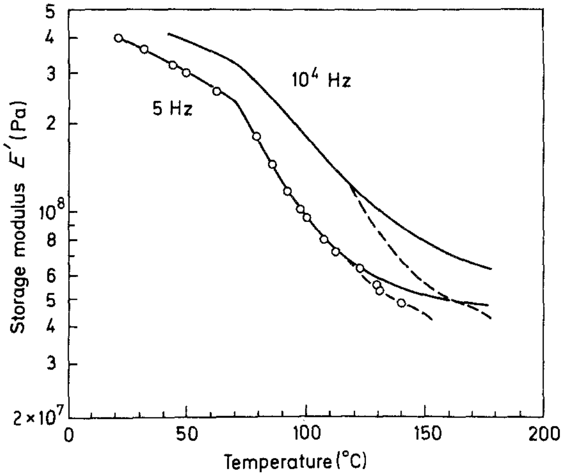

Figure 9 Calculated modulus–temperature relationship at different frequencies for the storage modulus E'. The curves are calculated from the established WLF equation and below 72° C the estimated Arrhenius relation for the shift factors. The broken curves above 130° C refer to an estimated Arrhenius relation for the shift factor. For comparison, measured data at a frequency of 5 Hz are included.

is readily apparent. Irvine [3] has speculated on the implications of such softening behaviour of wood for the defibration processes. In this context it should however be pointed out that the estimated WLF equation is found to apply only up to a temperature of 130° C. Conclusions drawn without taking this fact into consideration are thus questionable. Above 130° C other mechanisms than the glass transition of the lignin apparently have a marked influence. In this range the rate constant from the experimental data may be approximated by an Arrhenius-type of behaviour with an activation energy of 570 kJ mol^{-1} as indicated by the broken curves in Fig. 9. It is probable that several processes are taking place here simultaneously.

The broadening in the WLF region related to lignin softening seems nevertheless to have little influence on the total width of the softening range encompassing all softening processes. In fact when the torsional data of Becker *et al.* [12] at frequencies of around 1 and 10^3 Hz are examined, there is no indication of any broadening of the total softening region with increasing frequency. In this case, however, the measurement frequency varied somewhat with the change in moduli with temperature.

The range of the glass transition of the lignin within wood appears to be rather broad. The fact that the properties of mechanical pulps change sharply over a relatively narrow temperature range of the defibration process is, as pointed out by Irvine [3], not therefore related to a sudden change of the lignin material from a glassy to rubbery material. It should be recognized that a fracture process such as defibration cannot be simply related to the viscoelastic properties of the material. The separation and flexibilization of the fibres is instead related to a fatigue-type behaviour [9]. The degree of softness of the wood components certainly influences this fatigue process and may thus determine the pulp quality under certain loading conditions. An increase in temperature increases the fraction of fully separated fibres but also renders them less susceptible to bonding.

7. Conclusions

Measurements on water-saturated wood have shown that the transition normally experienced in the vicinity of 100° C can be related to the *glass transition* of water-saturated *in situ* lignin. This transition follows a WLF type of behaviour with a limiting activation energy of 450 kJ mol^{-1} and a glass transition temperature at low frequencies of 72° C.

The softenings along and across the fibre direction are shown to be due to the same phenomenon, and their difference is merely a reflection of the high degree of anisotropy of the microfibrils within the wood fibres.

It is shown that the WLF equation has narrower limits when applied to the softening of wood than for normal synthetic polymers. It is thus argued that the expected broadening of the lignin softening region of wood by an increase in frequency from 1 to 10^4 Hz does not appear to be significant, due to interaction with other softening mechanisms.

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