

# Temperature dependence of the tensile properties of lignin/paper composites

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The mechanical properties of dioxane lignin (DL)/paper and kraft lignin (KL)/paper composites were investigated as functions of temperature and strain rate. The tensile properties of the lignin/paper composites were governed by the viscoelastic properties of lignins used as a matrix. In the temperature dependence of the tensile properties, the strength of DL/paper composite decreased at 70° and 130°C at which the elongation had maxima. This behaviour was caused by the viscoelastic properties of DL having two relaxations in the primary dispersion region at 120° and 160°C. In the case of KL/paper composite, a drastic decrease in the strength and maximum of elongation were observed at the glass transition of KL (140°C). The strain rate dependence of the strength of DL/paper composite showed behaviour typical of viscoelastic materials. The strength increased with increase of the strain rate and then decreased after reaching a maximum, which showed a transition from a brittle to a ductile type of fracture.

(Keywords: tensile properties; viscoelasticity; glass transition; hydrogen bond; lignin; composite)

## INTRODUCTION

Lignin is a polymer that is brittle at room temperature and does not have film-forming capability. The viscoelastic properties of polymers that show difficulty in forming films have usually been measured using composite samples of polymers with appropriate support. Generally, the performance of composite materials is dependent on the mechanical properties of both elements, that is supports and polymers used as matrix. However, if a material that is mechanically insensitive to time and temperature is chosen as the support (we call it a mechanically inert support), then mainly the mechanical properties (or viscoelastic properties) of polymers affect the performance of the composites. As mechanically inert supports, the metal plates<sup>1</sup>, glass braids<sup>2,3</sup>, metal springs<sup>4</sup>, glass cloths<sup>5</sup>, nylon fibres<sup>6</sup>, asbestos paper<sup>7</sup>, blotter paper<sup>7,8</sup>, or filter paper<sup>9-12</sup> have been used. Recently, we have reported on the dynamic viscoelastic properties of lignin and lignin-related polystyrene derivatives impregnated in filter paper, using a forced vibrational method, and have discussed the relaxation mechanisms of the polymers<sup>11,13,14</sup>. Filter paper is suitable for the support of lignins above room temperature, since a significant change in the mechanical properties of such paper is not observed over a temperature range between 30° and 200°C, and cellulose has good affinity for lignins. In practice, the technique of polymer/paper composites is used for reinforcement of weak papers such as non-woven<sup>15</sup>, dry-formed<sup>16</sup>, or wet-laid papers<sup>17-19</sup>. When the mechanical properties of lignin/filter paper composites are measured as a function of temperature, the

results should directly reflect the viscoelasticity of lignins.

In this paper, the temperature and strain rate (time) dependence of the tensile properties of lignins impregnated in filter paper were measured, and it was shown that the performance of the composites is governed by the viscoelastic properties of lignins. The viscoelastic properties of dioxane lignin (DL) prepared in the laboratory were compared with those of kraft lignin (KL) obtained as a by-product in the pulping process. Differences between DL/paper and KL/paper composites are also discussed in this paper.

## EXPERIMENTAL

### Materials

DL and KL were used as samples in this study. DL was prepared from softwood according to Junker's procedure<sup>20</sup> and KL was provided by Tokai Pulp Co. Ltd. Lignins were first dissolved in dioxane and then precipitated in water. This process was repeated twice, after which the lignins were dried *in vacuo* ( $10^{-4}$  mmHg) for 3 days at about 50°C.

The preparation of lignin/filter paper composites was carried out as follows. Strips of filter paper (Toyo filter paper No. 51) were immersed in 30% tetrahydrofuran solutions of lignins, dried at room temperature for 3 days and then *in vacuo* ( $10^{-4}$  mmHg) at 50°C for 3 days. The content of lignins was about 40% by weight.

The composite sample strips were cut into sections 5 mm in width and 100 mm in length for measurement of tensile properties. For the dynamic viscoelastic measure-

ments, the sections were 5 mm in width and 40 mm in length. The thickness of the composite strips was about 0.2 mm.

#### Measurements

Tensile properties were measured by using an Instron Universal Testing Instrument, model TM-M, equipped with a thermostat. The tests were conducted over a temperature range from 30° to 180°C at a crosshead speed of 1 cm min<sup>-1</sup>. The strain rate dependence of the tensile strength was measured at constant temperature of 30° (below  $T_g$ ), 110° (near  $T_g$ ) and 170°C (above  $T_g$ ) while the crosshead speed varied from 0.05 to 100 cm min<sup>-1</sup>. The gauge length was 50 mm.

The dynamic viscoelasticity of the composites was measured using a Rheovibron DDV-IIC viscoelastometer at a frequency of 110 Hz. The heating rate was 2°C min<sup>-1</sup>. The distance between chucks was 30 mm.

## RESULTS AND DISCUSSION

The viscoelastic properties of lignins were estimated using composites made of lignins and mechanically inert supports. Figure 1 shows the temperature dependence of the dynamic viscoelastic properties of lignin impregnated in filter paper. Data were shown only for the primary dispersion region. A peak appeared at about 135°C in the  $\tan \delta$  versus temperature curve of KL composite. In the case of DL, a broad peak appeared at 160°C along with a shoulder peak at 120°C.  $E'$  decreased gradually with temperature in both samples.  $E'$  of KL is higher than that of DL. The drastic change in the temperature dispersion of filter paper was not observed below 200°C. Therefore, changes in the dynamic mechanical properties of lignin/paper composites are attributed to the viscoelastic prop-

erties of lignins. It is suggested that KL has harder but more brittle properties than DL, since the KL composite has a higher  $E'$  value and a lower  $\tan \delta$  peak than DL composite. DL composite has two relaxations, which were observed also via dilatometry<sup>21</sup> and d.s.c.<sup>22</sup> Two glass transition temperatures ( $T_g$ ) in the primary dispersion region were reported in various synthetic polymers, e.g. crystalline isotactic polypropylene<sup>23</sup> and polymers having hydrogen bonding such as nylon<sup>24</sup>, poly(acrylonitrile)<sup>25</sup> and poly(vinyl alcohol)<sup>26</sup>. In these cases, this phenomenon was explained as resulting from the existence of two different kinds of aggregation states of molecules in the amorphous region; low  $T_g$  reflects a random state and high  $T_g$  reflects a dense state. It can be said that the above aggregation states of DL are related to the hydrogen bonding. Random and dense states are reflected by non- and tight hydrogen bonding, respectively. Therefore, the low-temperature relaxation at 120°C in  $\tan \delta$  may be caused by molecular motion in the randomly aggregated (non-hydrogen-bonding) region and the high-temperature relaxation at 140°C may be caused by the molecular motion in the densely aggregated (hydrogen-bonding) region.

Rupture of paper sheet occurs according to two kinds of mechanisms, i.e. the failure of fibre, and fibre-fibre bondings<sup>27</sup>. When polymers are added to paper, the strength of the paper should increase, since fibres are bound together and the stress transfer between fibres is improved<sup>16-19</sup>. The mechanical properties of polymer/paper composites are governed by the viscoelastic properties of the polymers that are added as binders even in only small amounts<sup>16</sup>. However, problems concerning the failure mechanisms of the composites remain to be solved. For example, distribution of polymers added, adhesion effect between polymers and fibres (interfacial rupture or cohesive rupture of polymers), and/or stress concentration in the composite which decreases the mechanical strength. The relationship between the ultimate tensile properties of the lignin/paper composites and the viscoelastic properties of lignins is important.

Figure 2 shows the tensile strength of lignin impregnated in filter paper at 30°C as a function of the weight fraction. The strength of the KL composite had reached a maximum at 27% of the weight fraction. On the other hand, in the case of DL the strength increased as the lignin content increased and reached a constant value. This agreed with the result obtained by Engman *et al.*<sup>17</sup> A difference in behaviour of the tensile strength between KL and DL composites is caused by a difference in the viscoelastic properties. The decrease in the strength of KL/paper composite above 27% may come from the brittle property of KL. As can be seen from Figure 1, the KL composite has a small  $\tan \delta$  peak around  $T_g$ . It is predicted from the shape of the  $\tan \delta$  peak, which defines the viscosity of polymers, that KL is a rather brittle polymer even above  $T_g$ . Microcracks are easily generated in the brittle KL matrix and weaken the composite at above 27% of the weight fraction. On the other hand, DL is a soft and viscous polymer compared with KL, judging from the shape of the  $\tan \delta$  curve and the magnitude of  $E'$  in Figure 1.

In Figure 3 the temperature dependence of the tensile properties of filter paper itself is presented in order to discuss the tensile properties of lignin/paper composites. The tensile strength decreased linearly from 12 MPa at 30°C to 8.5 MPa at 180°C. A slight increase in the

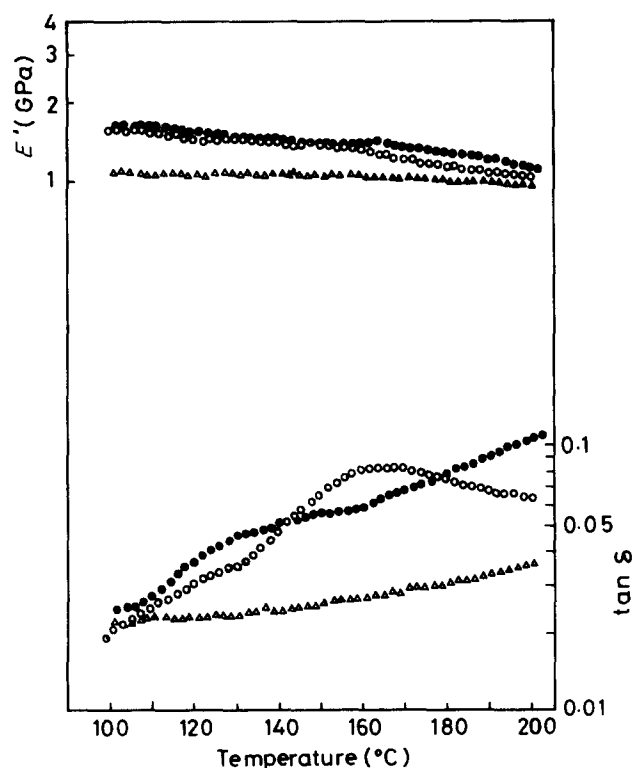


Figure 1 The temperature dependence of the dynamic viscoelasticity of lignin/filter paper composites and filter paper: ( $\Delta$ ) filter paper; ( $\circ$ ) DL/filter paper composite; ( $\bullet$ ) KL/filter paper composite

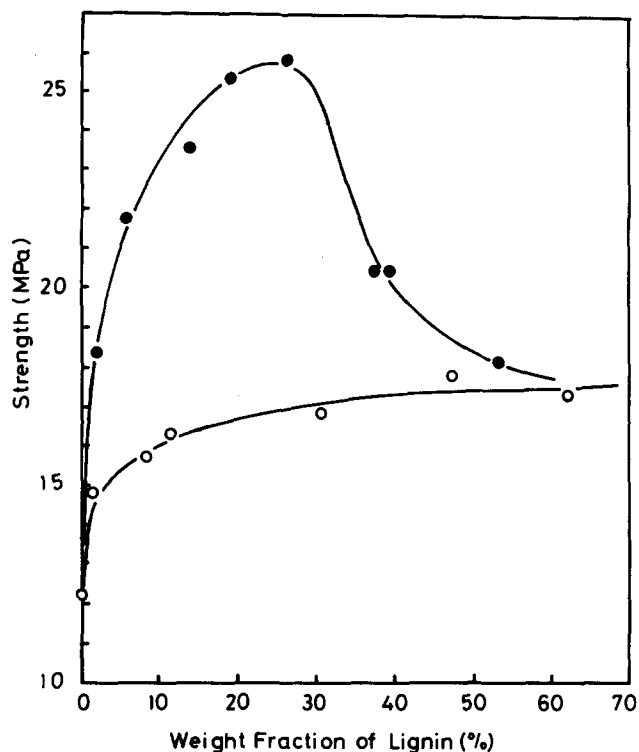


Figure 2 The tensile strength of lignin/filter paper composites as a function of weight fraction at 30°C: (●) KL/filter paper composite; (○) DL/filter paper composite

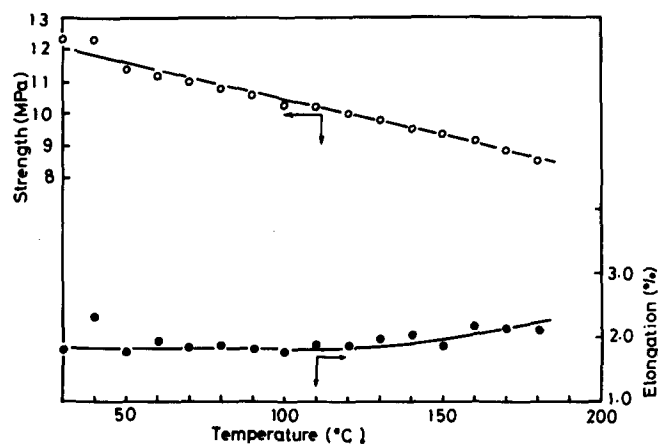


Figure 3 The temperature dependence of tensile properties of filter paper

elongation was observed after 150°C. The decrease in the tensile strength and increase in the elongation may be due to onset of softening in the vicinity of  $T_g$  ( $\sim 230^\circ\text{C}^{28}$ ) and/or breaking of hydrogen bonds. No drastic change in the tensile properties and the dynamic viscoelasticity of filter paper was observed as shown in Figure 1.

The temperature dependence of the tensile properties of lignin/paper composites is shown in Figure 4. The strength of KL composite decreased as the temperature increased and decreased markedly near  $T_g$  (130–140°C), reaching a maximum elongation at about 140°C. The decrease in the strength of DL composite was quite remarkable at 70° and 130°C. In the elongation *versus* temperature curve, two peaks were observed at about 70° and 130°C corresponding to a change in strength. It is clear that changes in temperature dependence of the tensile properties of the composites are governed by the

viscoelastic properties of lignins. The decrease in the strength and corresponding peaks at 70° and 140°C for DL composite agreed well with the two relaxation phenomena shown by the  $\tan \delta$  curve of DL in Figure 1. Increase in strength was observed between 100° and 120°C and this may be attributed to the transition from a random to a dense aggregation state of molecules caused during heating. In the case of KL composite, the strength decreased markedly and the peak elongation was observed at  $T_g$  (130°C), which showed the same behaviour as the dynamic viscoelastic properties of KL. Generally the fracture behaviour of viscoelastic bodies changes from a brittle to a ductile type at the glass transition temperature, which coincides with the drastic decrease in strength and maximum in elongation<sup>29</sup>. As shown in Figure 4, in the ductile fracture region (above  $T_g$ ), the reinforcement effect of the DL composite is ineffective. On the other hand, the KL composite is effective even above its  $T_g$ , showing a higher value of strength (more than 12 MPa for filter paper at around room temperature).

Figure 5 shows the strain rate dependence of the tensile strength of the DL/paper composite at constant temperatures, i.e. below  $T_g$  (30°C), near  $T_g$  (110°C) and above  $T_g$  (170°C). The strength increased at first and then decreased with the strain rate after having reached a maximum. The time dependence of the tensile behaviour of viscoelastic bodies at a constant temperature changes from a brittle to a ductile fracture pattern depending on the strain rate. Recently, Saito<sup>30</sup> has estimated the strain rate dependence of the strength of viscoelastic bodies using Hata's theory<sup>31,32</sup>. According to Hata's theory, the strength

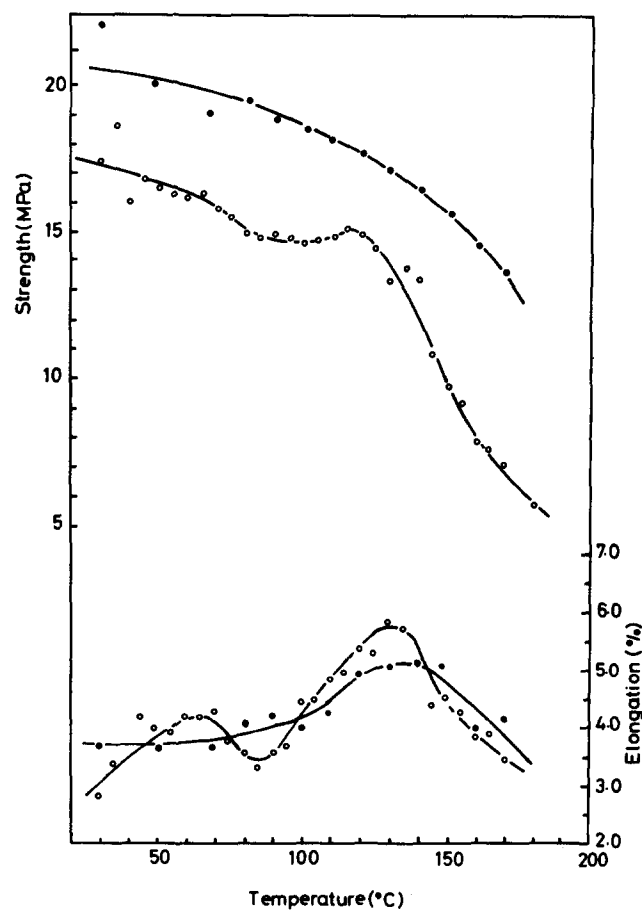
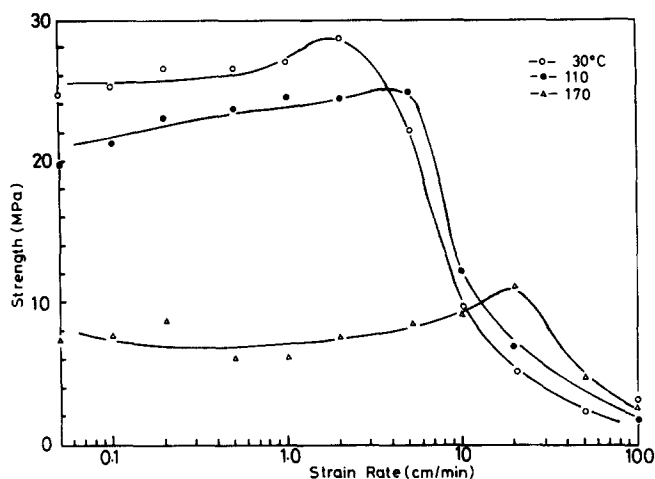


Figure 4 The temperature dependence of the tensile properties of lignin composites: (●) KL/filter paper; (○) DL/filter paper



**Figure 5** The strain rate dependence of the tensile strength of DL composite at constant temperature: (○) 30°C; (●) 110°C; (△) 170°C

increases with increasing strain rate in the low and medium rate region, and reaches a maximum, after which it decreases in the higher rate region. The maximum strength corresponds to the transition point between brittle and ductile fracturing. The result presented in *Figure 5* is consistent qualitatively with the pattern estimated by Saito and shows typical viscoelastic behaviour. Ductile fracture occurs in the lower strain rate region and brittle fracture in the higher strain rate region. The peak value can be considered as the point at which a transition from ductile to brittle fracture takes place, corresponding to  $T_g$  in the temperature dependence of the tensile strength or dynamic viscoelasticity. The peak strength at higher temperature was located in the higher strain rate region. The result in *Figure 5* indicates that impact strength of the lignin/paper composite is weak due to the brittle property of lignin.

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