

## Thermoplastic Behavior of Lignin with Various Synthetic Plasticizers

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### Synopsis

The thermoplasticization of thiolignin (TL) and dioxane lignin (DL) with various synthetic plasticizers has been investigated. The thermal softening temperatures  $T_s$  of the lignin-plasticizer systems were measured applying the flow tester technique which is useful for investigating the thermal properties of polymers. It was found that the  $T_s$  of the lignins were lowered considerably as the solubility parameters (after Hildebrand) of the plasticizers approach close to that of lignin, namely, around 11. The lowering in the  $T_s$  of the lignins with the plasticizers was described by a linear equation with respect to the plasticizer concentration which ranged up to 20 wt-%. The sorption of the limited amounts (< 5%) of water to the lignins also considerably decreased the  $T_s$ , however, the extent of lowering in the  $T_s$  by water sorption is less than that by the plasticizer addition at their contents over about 15%. The relationship of  $T_s$  to water content (up to about 30%) was curved, not linear. It was clearly shown that a combined use of the plasticizer and water brought about the most effective plasticizing for the lignins compared with the use of either of those alone.

### INTRODUCTION

The thermoplastic properties of lignin are likely to be of interest in connection with several areas in the pulp and paper, fiberboard, and veneer industries. Fiberboard is usually manufactured by a thermomechanical process in which the steamed wood chips are first defibrated in a disc refiner, followed by hot pressing of the sheet formed from the defibrated pulps. Clearly, the thermoplastic properties of lignin will be one of the most important factors for promoting the thermal adhesion of the fiberboard pulps from which the board is formed by hot pressing.

It seems possible that, if the thermal softening of lignin in the fiberboard pulps can be modified, qualities such as the strength and density of the finished board will be improved because of an increase in interfiber bonding. Furthermore, if it is possible to facilitate the thermal softening of pulping waste lignins such as thiolignin by use of certain compounds other than water, it will be expected that such plasticized lignins may be utilized as adhesives for fiberboard manufacture.

Concerning the thermoplasticization of lignin with water, we can see that there are several references in the literature as to the softening of various types of lignins or woods.<sup>1-8</sup> Goring et al.<sup>2-4</sup> have investigated the adhesive properties and thermal softening of isolated lignins and the thermoplastic and adhesive behavior of fiberboard pulps from steamed wood. Takamura<sup>7</sup>

has shown that the softening of wood components, especially lignin and hemicellulose, is markedly dependent on their water contents. Hatakeyama et al.<sup>8</sup> have determined the thermal softening temperature of various isolated lignins by measuring the variation in their infrared spectra with temperature.

However, no investigation have yet been made of the way in which the lignin is plasticized with certain organic plasticizers. This problem is considered to be quite important and of interest.

The purpose of the present work is to determine whether the lignin is plasticized by the synthetic plasticizers and what kind of plasticizer would be expected to be effective. The experimental results are interpreted by the concepts of the solubility parameter defined by Hildebrand<sup>9</sup> and by the equations proposed for the glass transition phenomena in general synthetic polymer-plasticizer systems.

## EXPERIMENTAL

### Materials

**Lignins.** Thioglignin (TL) and dioxane lignin (DL) were used as lignin specimens. TL was commercial thioglignin produced from soft wood; it was repeatedly washed with hot water, dried, and then purified by precipitation from dioxane solution into ethyl ether.<sup>10</sup> DL was produced as follows: Ethanol-benzene-extracted wood meal of red pine was refluxed for 8 hr at 80°C with dioxane containing 0.5% hydrochloric acid. The extract was concentrated *in vacuo* at 20°C and poured into a large amount of water. The precipitate was centrifuged, washed, and dried. The product was further purified by dissolving it in dioxane and precipitating into ethyl ether.<sup>11</sup>

**Plasticizers.** The plasticizers used and their some properties are listed in Table I. All of them were reagent grade and used without further purification. These plasticizers are classified into the following four series: (1) dialkyl phthalate, (2) trialkyl phosphate, (3) aliphatic acid esters, and (4) other compounds, and differ from one another in the number of carbon atoms (from C<sub>1</sub> to C<sub>12</sub>) in their alkyl residues.

### Estimation of Solubility Parameter

The solubility parameter,  $\delta$  value, of the various plasticizers used in the present work was calculated by using the following equation:<sup>9</sup>

$$\delta = [(\Delta H - RT)d / M]^{1/2} \quad (1)$$

where  $\Delta H$  = latent heat of vaporization (cal/mole);  $T$  = bp (°K);  $R$  = gas constant;  $M$  = molecular weight; and  $d$  = specific gravity (g/ml). When the values of  $\Delta H$  were unknown, the  $\delta$  values were estimated from the structural formula and specific gravity of the plasticizers by using the molar attraction constants tabulated by Small.<sup>12</sup> The equation is

$$\delta = d\Sigma G / M \quad (2)$$

where  $\Sigma G$  is the sum for all the atoms and groupings in the plasticizer molecule. Some of the  $\delta$  values calculated as described above were confirmed by

TABLE I  
Plasticizers and their Solubility Parameter Values and Plasticizing Effects  
for Dioxane Lignin

Designation	Chemical formula	Solubility parameter	$T_s$ , °C for DL <sup>a</sup>
<b>Phthalic acid esters</b>			
dimethyl phthalate	$C_6H_4(COOCH_3)_2$	10.5	62
diethyl phthalate	$C_6H_4(COOC_2H_5)_2$	9.95	72
dibutyl phthalate	$C_6H_4(COOC_4H_9)_2$	9.4	110
dihexyl phthalate	$C_6H_4(COOC_6H_{13})_2$	9.1	117
diheptyl phthalate	$C_6H_4(COOC_7H_{15})_2$	9.0	132
di- <i>n</i> -octyl phthalate	$C_6H_4(COOC_8H_{17})_2$	8.9	135
diisooctyl phthalate	$C_6H_4(COOC_8H_{17})_2$	8.8	137
di(2-ethylhexyl) phthalate	$C_6H_4(COOC_8H_{17})_2$	8.75	137
di- <i>n</i> -decyl phthalate	$C_6H_4(COOC_{10}H_{21})_2$	8.9	135
diisodecyl phthalate	$C_6H_4(COOC_{10}H_{21})_2$	8.75	135
di- <i>n</i> -lauryl phthalate	$C_6H_4(COOC_{12}H_{25})_2$	8.8	137
diphenyl phthalate	$C_6H_4(COOC_6H_5)_2$	12.8	98
<b>Phosphoric acid esters</b>			
triethyl phosphate	$(C_2H_5O)_3PO$	9.65	67
tributyl phosphate	$(C_4H_9O)_3PO$	9.0	71
triphenyl phosphate	$(C_6H_5O)_3PO$	10.4	73
tricresyl phosphate	$(CH_3C_6H_4O)_3PO$	9.7	101
cresyldiphenyl phosphate	$(CH_3C_6H_4O)(C_6H_5O)_2PO$	10.6	80
diphenyl-2-ethylhexyl phosphate	$(C_6H_5O)(C_6H_5O)_2PO$	9.6	94
trichloroethyl phosphate	$(ClCH_2CH_2O)_3PO$	10.9	80
<b>Aliphatic acid esters and others</b>			
dibutyl maleate	$C_4H_9OCO(CH)_2COOC_4H_9$	9.0	97
di- <i>n</i> -octyl maleate	$C_8H_{17}OCO(CH)_2COOC_8H_{17}$	8.8	133
di- <i>n</i> -octyl adipate	$C_8H_{17}OCO(CH_2)_4COOC_8H_{17}$	8.6	140
di(2-ethylhexyl) adipate	$C_8H_{17}OCO(CH_2)_4COOC_8H_{17}$	8.5	139
diisooctyl adipate	$C_8H_{17}OCO(CH_2)_4COOC_8H_{17}$	8.5	138
di- <i>n</i> -octyl sebacate	$C_8H_{17}OCO(CH_2)_8COOC_8H_{17}$	8.7	139
di(2-ethylhexyl) sebacate	$C_8H_{17}OCO(CH_2)_8COOC_8H_{17}$	8.4	139
<i>n</i> -butyl oleate	$C_{17}H_{33}COOC_4H_9$	8.3	140
methyl abietate	$C_{19}H_{39}COOCH_3$	7.8	140
butyl stearate	$C_{17}H_{33}COOC_4H_9$	7.9	139
di(2-ethylhexyl)azelate	$C_8H_{17}OCO(CH_2)_7COOC_8H_{17}$	8.4	138
<i>o</i> -nitrodiphenyl	$C_6H_5C_6H_4NO_2$	11.0	80
camphor	$C_{10}H_{16}O$	7.55	138

<sup>a</sup> Plasticizer concentration was 20 wt-%, and the  $T_s$  for the original DL was 138°C.

direct comparison with the known values from reference<sup>13</sup>. The  $\delta$  values estimated are shown in Table I.

### Measurement of Thermal Softening

The thermal softening temperature  $T_s$  of the lignin samples was measured using the Koka-shiki flow tester Model 301,<sup>14</sup> manufactured by Shimadzu Seisakusho Co. Ltd. (Japan). This machine is attached to an automatic recorder and heating device controlled at a constant rate. A schematic diagram of a part of the flow tester, the heating device, is shown in Figure 1. The principle of the measurement of  $T_s$  by this method is similar to that of the "powder collapse method" which was previously developed by Goring.<sup>3</sup> A detailed procedure for measurement is as follows.

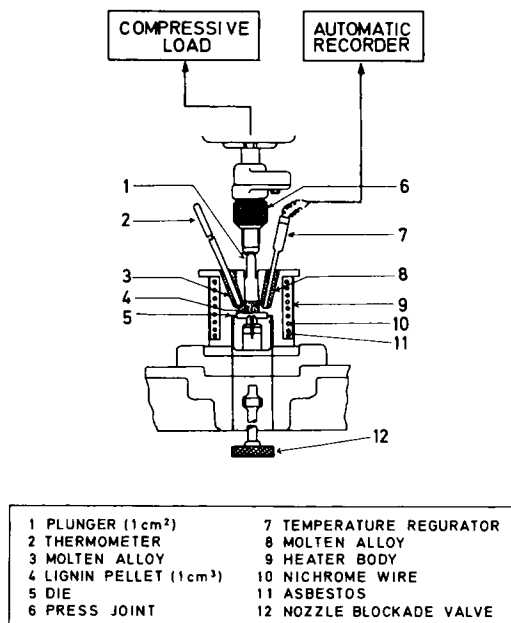


Fig. 1. Diagram of part of flow tester (heating device).

**Preparation of Lignin-Plasticizer Mixtures.** The weighed lignin samples were mixed with a definite weight of plasticizer diluted with ethyl ether. Then, the mixture was freed of ethyl ether under reduced pressure. When water was used as an additive, lignin-water mixtures were prepared by mixing the lignin samples with excess water, followed by vacuum drying to give a prescribed water content. On addition of both plasticizer and water to lignin, water was added to lignin samples previously mixed with plasticizer by the method described above.

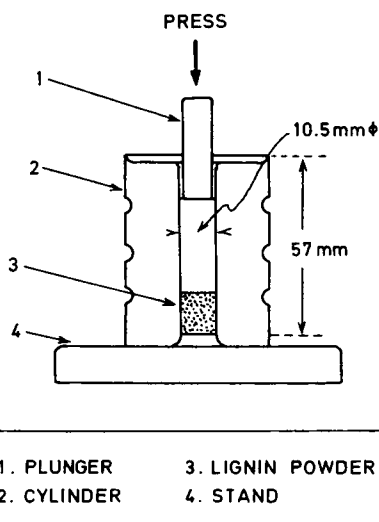


Fig. 2. Molding press for making a lignin pellet.

TABLE II  
Description of "Plasticization Pattern" shown in Figure 3

Notation	Region	Explanation	Remarks
AB	softening region	softening curve	the sample is gradually being deformed by a compressive load, and the small void in the sample is reduced
$T_s$ , °C		softening temperature	the small void in the sample has disappeared; the appearance of the sample pellet has become a homogeneous transparent matter or a single solid phase
BC	steady region	steady curve	the region in which the position of the plunger varies much less with temperature, and the sample does not manifest an apparent state of liquid flow within a limited observation time
$T_f$ , °C		flow temperature	the plunger begins to fall apparently; this is also read off by the dial gauge attached to the flow tester
CD	flow region	flow curve	the region in which the sample obviously flows through a nozzle placed at the bottom of the cylinder which is inserted the sample

**Measurement of Thermal Softening Temperature ( $T_s$ ):** The lignin-plasticizer mixtures, 0.7 or 1.0 g, were molded into cylindrical pellets 10.5 mm in diameter, using the molding press shown in Figure 2. The solid pellet was then set in the flow tester by inserting it into a hollow cylinder compartment mounted with a die having a small nozzle as shown in Figure 1. The pellet was preheated under a constant compressive load, 3 kg/cm<sup>2</sup>, through the plunger for 10 min at a temperature 30° below the  $T_s$  of samples which was roughly predetermined without preheating. After preheating, the temperature of the sample pellet was elevated at a constant rate, 3°C/min, under a constant compressive load of 10 kg/cm<sup>2</sup> with the aid of the plunger. Compressive deformation of the sample pellet is gradually increased with increasing temperature, that is, with the time course of heating. The length of fall of the plunger responds sensitively to this deformation and is depicted by the automatic recorder attached to the flow tester. Figure 3 represents an example of such a "plasticization pattern," and Table II is a description of the plasticization pattern in Figure 3.

The  $T_s$  was obtained from the point of intersection determined by extrapo-

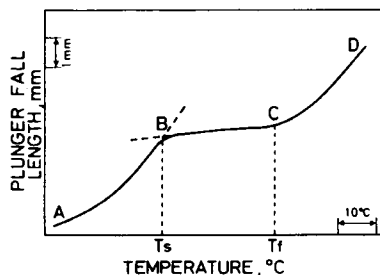


Fig. 3. Plasticization pattern.

lating the linear portion of AB and BC curves as given in Figure 3. The plasticizing effect of the different plasticizers was judged by an extent of a lowering in such a  $T_s$ . Preliminary tests were made of the effect on the  $T_s$  measurement of (a) compression load on the plunger, and (b) rate of heating. An increase in compression load produced a decrease in  $T_s$ , but the difference was small, between 5 and 10 kg/cm<sup>2</sup>. For example, the  $T_s$  values were obtained to be 177° and 174°C at 5 and 10 kg/cm<sup>2</sup>, respectively, for the original TL. A faster rate of heating, e.g., 6°C/min, gave a high  $T_s$  value. However, there was a negligible difference in  $T_s$  measured at 3°C/min and 1°C/min of the heating rates. Therefore, the standard heating conditions described above were adopted in all further experiments.

Almost all the runs were done in duplicate, and the excellent reproducibility was confirmed in all cases.

## RESULTS AND DISCUSSION

### Effect of Plasticizer Properties

Concerning the plasticization of the lignins with homologous series of dialkyl phthalates, Figure 4, shows the variation of the  $T_s$ . The  $T_s$  values were lowered with decrease in the number of carbon atoms in the alkyl residue. Therefore, dimethyl phthalate (DMP) which has one carbon atom in the alkyl residue showed the greatest plasticizing effect on the lignins. For example, the  $T_s$  values of dioxane lignin were found to be 138°C for the original DL and 62°C for the DL containing 20 wt-% of DMP. Similarly, the  $T_s$  of thiolignin containing the same amounts of DMP decreased to 70°C, whereas that of the original TL was found to be 174°C. For the series of the phthalate esters having the carbon atoms number of eight or above, i.e., dioctyl phthalate (DOP) or higher dialkyl phthalates, their  $T_s$  agreed very closely with those of the original lignins. That is, their plasticizing effects were not observed.

The plasticizer should, in most cases, have a high degree of solvent power for the polymer and should be compatible with the polymer system.<sup>15</sup> As a general rule, the concept of the so-called "solubility parameter," which was

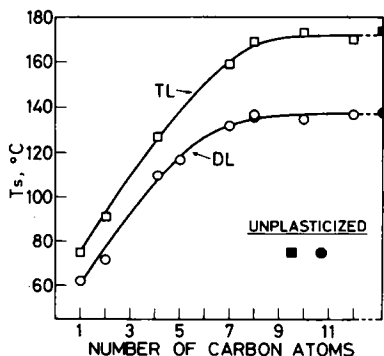


Fig. 4. Effect of the number of carbon atoms in the alkyl residue of a series of dialkyl phthalates on the thermal softening temperatures of thiolignin and dioxane lignin. Plasticizer concentration: 20 wt-% based on the lignin-plasticizer mixtures.

proposed as an indication of solubility and compatibility of substances by Hildebrand,<sup>9</sup> has been well adapted to general polymer-plasticizer systems. The solubility parameter  $\delta$  is defined as the square root of the cohesive energy density (CED) by the relation

$$\delta = (CED)^{1/2} = (\Delta E / V)^{1/2} \quad (3)$$

where  $\Delta E$  is the molar energy of vaporization and  $V$  is the molar volume. Polymers, in general, exhibit maximum solubility in solvents with  $\delta$  values closest to their own.

Thus, in selecting a suitable plasticizer for lignin, it is necessary to choose a plasticizer with a solubility parameter as close to that of lignin as possible. Schuerch<sup>16</sup> has shown that the ability of solvents to dissolve or swell a variety of isolated lignins increases as the solubility parameters of the solvents approach a value of around 11 and as their hydrogen-bonding capacities increase. From the investigation by Schuerch, the solubility parameter of lignin may be taken to be approximately 11. The  $\delta$  values for the plasticizers used in the present work are given in Table I. The series of these plasticizers have little or no hydrogen-bonding capacities because they are fully esterified.

Figure 5 shows the  $T_s$  of plasticized lignins as a function of the solubility parameter of a series of dialkyl phthalates. It can be seen that the plasticizers with  $\delta$  values closest to around 11 show low  $T_s$  values, i.e., high plasticizing effect, whereas the plasticizers with  $\delta$  values other than 11 show high  $T_s$  and therefore low plasticizing effect. It is evident that the plasticization of lignin with plasticizers can be interpreted on the basis of the concept of the theory of solubility parameter.<sup>9</sup> If there is good compatibility between lignin and plasticizer molecules owing to the similarity in their solubility parameters, the forces between the lignin molecules are reduced, thereby carrying an increase in chain mobility, which, in turn, leads to a "softening" or "plasticization" of the lignin.

In addition, for all other series of the plasticizers, it was found that better plasticization occurs when the  $\delta$  values were as close as possible to that of lignin, i.e., around 11. In other words, the smaller the number of carbon atoms in the alkyl residue of these esters, the lower the  $T_s$  of the lignins containing

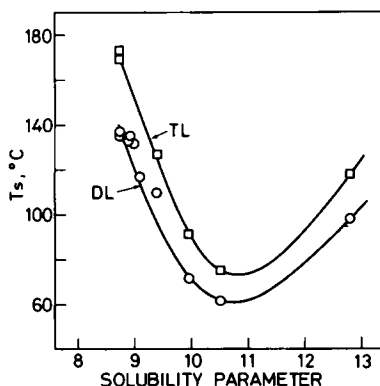


Fig. 5. Effect of solubility parameters of plasticizers on the thermal softening temperatures of thiolignin and dioxane lignin. Plasticizers: dialkyl phthalates except for diphenyl phthalate having a  $\delta$  value of 12.8; plasticizer concentration: see Fig. 4.

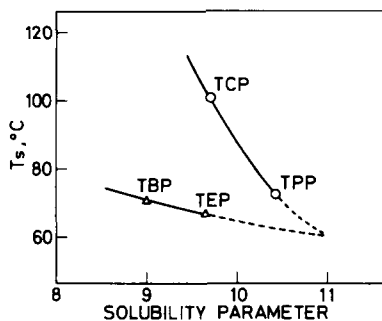


Fig. 6. Relation between solubility parameters of a series of phosphoric esters and the thermal softening temperatures of dioxane lignin. TCP, TPP, TBP, and TEP refer to tricresyl, triphenyl, tributyl, and triethyl phosphate, respectively. Plasticizer concentration: same as in Fig. 4.

the plasticizer. The values of  $T_s$  for plasticized DL are described in Table I. The relationship between the  $\delta$  values and the  $T_s$  as to the phosphoric esters is illustrated graphically in Figure 6.

Comparing the about 30 varieties of the plasticizers subjected to the thermal softening measurements of TL and DL, markedly effective plasticizers were as follows: (a) dimethyl phthalate (10.5), (b) triethyl phosphate (9.66), (c) tributyl phosphate (9.00), (d) diethyl phthalate (9.95), (e) triphenyl phosphate (10.4), (f) *o*-nitrodiphenyl (11.0), (g) trichlorethyl phosphate (10.9), (h) dibutyl maleate (9.0). The numbers in parentheses refer to the  $\delta$  values of the plasticizers.

### Effect of Plasticizer Concentration

The effects of the concentration of the plasticizers (DMP and TBP) on the  $T_s$  values for DL and TL are shown in Figure 7. There is a marked lowering of the  $T_s$  with increase in plasticizer concentration. The plot of  $T_s$  versus plasticizer concentration gave a straight line in all cases.

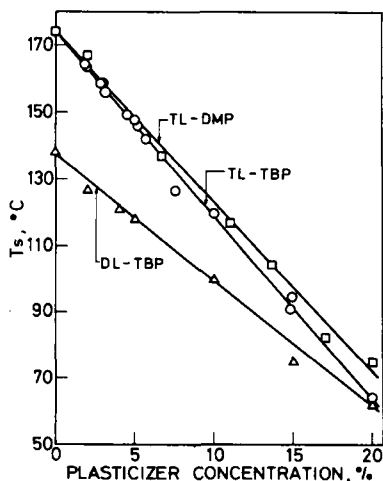


Fig. 7. Decrease in thermal softening temperatures with plasticizer concentration for thiolig-nin and dioxane lignin. Plasticizer concentration: plasticizer  $\times$  100/lignin + plasticizer.



It is considered that the sorption of plasticizers to lignin lowers the  $T_s$  in the same manner a diluent will lower the glass transition temperature of an amorphous polymer. It is generally agreed that the lowering of the glass transition temperature for most systems is directly proportional to the diluent concentration in the polymeric material.

The empirical equation relating the glass transition temperature depression to the diluent content<sup>17</sup> is

$$T_g = T_g^0 - kW_2 \quad (4)$$

where  $T_g^0$  = glass transition temperature of unplasticized polymer (°K);  $T_g$  = glass transition temperature of polymer + diluent (°K);  $W_2$  = weight fraction of diluent (g/g); and  $k$  = empirical constant. Equation (4) is valid at relatively low dilution (<20%) if the diluent and polymer are compatible, whereas a parabolic function is required to cover the entire region of diluent concentration.

If  $T_s$  as measured by the flow tester method in the present work corresponds to a glass transition temperature, eq. (4) should be applicable to the present results. The linear relationship in Figure 7 clearly shows that the lowering in the  $T_s$  of the lignins by the plasticizers can be interpreted by means of eq. (4). The average  $k$  values calculated using eq. (4) were: 540°, 510°, and 380°K for the TL-TBP, TL-DMP, and DL-DMP systems, respectively. This may be compared with  $k$  values which range from 200° to 500°K for polystyrene and several plasticizers such as tricresyl phosphate, methyl salicylate, or ethyl acetate.<sup>17,18</sup> The agreement is fairly good considering the differences in the materials and experimental techniques.

Many theories have been proposed to explain the lowering of glass transition temperature by a plasticizer. These all result in the form of eq. (4). The equation derived by Fujita and Kishimoto<sup>19</sup> is based on the iso-free volume concept and is as follows:

$$T_g = T_g^0 - \beta W_2 / \alpha \quad (5)$$

where  $\alpha$  is the difference between the thermal expansion coefficient above and below the transition temperature (the value of  $\alpha$  is a constant value of  $4.8 \times 10^{-4}$  per degree) and  $\beta$  is a parameter representing the contribution of diluent to the increase of free volume. From the results shown in Figure 7, the values for  $\beta$  calculated by means of eq. (5) were found to be 0.26, 0.25, and 0.18 for the TL-TBP, TL-DMP, and DL-DMP systems, respectively. With water as diluent, Goring<sup>3</sup> has found  $\beta$  for isolated lignins and hemicelluloses to have the value of 0.27, and Fujita and Kishimoto<sup>19</sup> have shown  $\beta$  for water sorbed onto poly(vinyl acetate) and poly(methyl acrylate) equal to 0.37 and 0.30, respectively. The values for  $\beta$  obtained in the present work were similar to those described above.

Thus, the lowering of the thermal softening temperature of lignin with plasticizer may be interpreted by the principles and concepts appropriate to glass transition phenomena in synthetic amorphous polymers.

### Effect of Water Sorption

The sorption of water by TL and DL also led to a considerable decrease in the thermal softening temperatures. This is shown in Figure 8. The  $T_s$

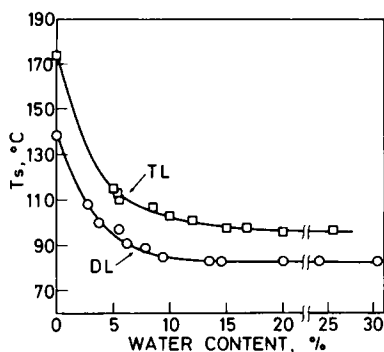


Fig. 8. Variation of thermal softening temperature with water sorption for thiolignin and dioxane lignin.

values for TL and DL were found to be about 115° and 95°C, respectively, at a water content of 5%, and were not lowered to below about 100° and 85°C, respectively even at a water content of 10% or above. It is clear that a lowering in  $T_s$  with a few per cent (<5%) of water is pronounced, however, further addition of water shows comparatively little effect on the  $T_s$ . Furthermore, curved plots in the relationship of  $T_s$  to water content show that eqs. (4) and (5) fail for this lignin-water system over the wide ranges of water content of 0–30%. Similar curved plots between  $T_s$  and water content have been obtained for periodate lignin by Goring,<sup>3</sup> and later for Björkman's lignin by Takamura.<sup>7</sup>

The solubility parameter for water is 23.4,<sup>9</sup> and this is markedly different from that of lignin, i.e., around 11. Thus, water is a poor solvent for lignin. It is, therefore, unlikely that the thermal softening of lignin with water is related to the compatibility between the two substances, in contrast to general polymer-plasticizer systems in which the concept of solubility parameter is applicable.

Schuerch<sup>16</sup> has shown that the ability of solvents to dissolve or swell several isolated lignins is closely correlated with the "hydrogen bonding capacities,"  $\Delta\mu$  after Gordy,<sup>9,20</sup> of the solvents as well as their solubility parameters. As is well known, water has very high hydrogen-bonding capacity value ( $\Delta\mu$ ). Thus, it is likely that the release of the intermolecular hydrogen bonds within the lignin matrix is the cause of the water-induced thermal softening of lignin.

### Plasticization by the Combined Use of Plasticizer and Water

As described above, both the synthetic plasticizer and water have shown effective plasticization for the lignins. If such synthetic plasticizers are incorporated with water, then a more pronounced thermoplasticizing effect on lignin would be expected. With this in mind, the following series of experiments were made: (a) addition of various amounts of water onto the TL plasticized with a definite amount of TBP; (b) addition of various amounts of TBP onto the moistened TL.

The results are shown in Figures 9 and 10 for the experimental series of (a) and (b), respectively. As shown in these figures, it is clear that the combined

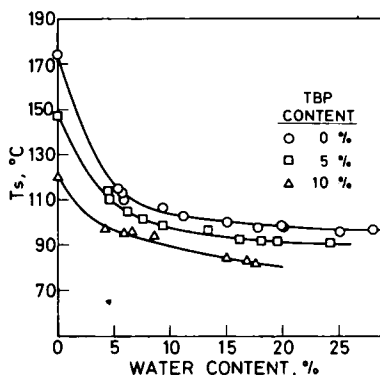


Fig. 9. Plasticization by combined use of plasticizer and water. Effect of the addition of water to thiolignin containing a definite amount of TBP.

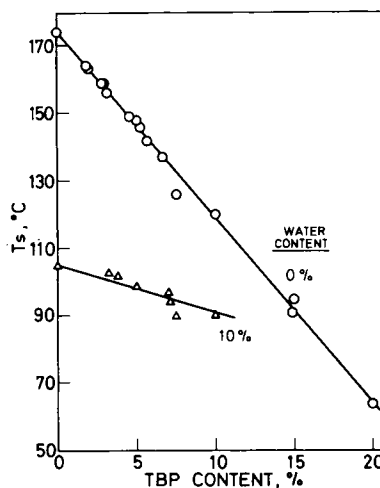


Fig. 10. Plasticization by combined use of plasticizer and water. Effect of the addition of TBP to thiolignin containing water of about 10%.

use of the plasticizer (TBP) and water produced a greater lowering in  $T_g$  compared with the use of either alone.

The fact that the plasticizing effects of plasticizer and water reinforce each other is similar to the behavior in solvent power of mixed solvents for isolated lignins. Schuerch<sup>16</sup> has shown that whenever a hydroxylated solvent, such as water or the lower alcohols, is mixed with a solvent of low hydrogen-bonding capacity and a  $\delta$  value of 9 or greater, the solubility of lignin is greater in the mixture than in either solvent alone. It may be concluded, thus, that the combined use of plasticizer and water is most effective for the thermal softening of lignin.

## CONCLUSIONS

1. The  $T_g$  values of thiolignin and dioxane lignin were lowered markedly with decrease in the number of carbon atoms in the alkyl residue of plasticizers such as a series of dialkyl phthalates or trialkyl phosphates.

2. High plasticizing effect, i.e., low  $T_s$ , was found when the  $\delta$  values (solubility parameters) of plasticizers approach as close as possible that of lignin, around 11.

3. The lowering in  $T_s$  of lignin with plasticizer concentration was described by a linear equation which has been proposed to explain a glass transition phenomena in synthetic amorphous polymers.

4. The lowering in  $T_s$  with small amounts of water was considerable, however, further addition of water showed comparatively little effect on the  $T_s$ .

5. When a synthetic plasticizer, such as tributyl phosphate, was incorporated with water, more effective plasticization was produced than that obtained by a use of either of these compounds alone.

In connection with the present work, it has been found that the thiolignin plasticized with synthetic plasticizers can be utilized as adhesives in fiberboard manufacture in order to improve the board qualities. This work will be reported in detail in a later paper.

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