

# Some Laws of a Lignin Plasticization

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**ABSTRACT:** A comparison of the plasticizing efficiency of a series of molecules introduced in dry and hydrated Kraft lignin demonstrated that the plasticization mechanisms are different before and after sorption site saturation. Lignins were plasticized in two steps and glass transition decrease was determined from DSC measurements. "Specific sorption plasticizers," such as water, are very efficient in low content because of their functionality and accessibility to sorption sites. The plasticizing efficiency does not depend on

the solubility parameter, and is well quantified, considering the molar concentration of donor/acceptor functions. After saturation of sorption sites (in wet conditions), the plasticizing efficiency depends on the solubility parameter, which should be close to that of the polymer matrix. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1445–1451, 2006

**Key words:** lignin; plasticization; coplasticization; glass transition

## INTRODUCTION

As a result of strong interactions between hydroxyl groups, natural polymers must be plasticized to obtain soft materials. A great deal of literature focuses on the plasticization and the modeling of glass transition decrease of proteins, polysaccharides, and lignin based polymers. Two types of equations are proposed to predict the glass transition of a polymer plasticizer blend from the glass transitions of the individual species. The Bueche equation,<sup>1</sup> derived from the free volume approach, proposes average  $T_g$  values weighted by volume fractions and by the volume expansion variations between glassy and rubbery states. The Couchman equation,<sup>2</sup> derived from a thermodynamic approach, implies weight fractions and heat capacity changes during glass transition. This equation has also been improved assuming the dependence of  $\Delta C_p$  with temperature,<sup>3</sup> and has been extended to the blend of three components.<sup>4,5</sup> Since the cohesion of biopolymers is mainly insured by hydrogen bonds, another Couchman or Gordon Taylor derived equation has been proposed to take into account these strong interactions, adding a quadratic term to the basic expression (e.g., the Kwei equation<sup>6</sup> was applied to lignin plasticization by water).

All of these models imply a continuation of plasticizer action, from the first molecules introduced into the polymer network, to the use of a plasticizer at high content.

If we look, however, at the literature focusing on the mechanisms of water bonding to biopolymers, e.g., the modeling of water sorption isotherms, water acts differently depending on its content. It is sorbed successively on primary sites, in a multilayer form, and then condenses into a liquid phase.<sup>7</sup> The first step of sorption can be easily explained considering stoichiometric ratios of water and sorption sites; for example, water has been shown to be doubly hydrogen bonded on polysaccharide sites.<sup>8,9</sup> Recently we proposed that starch saturation by glycerol was obtained with the same stoichiometric ratio (2 glucose units/1 glycerol).<sup>10</sup> In the presence of low water content (<6%), glycerol and water share one sorption site by a glucose unit; at higher water content (under 57% relative humidity), more sites are used, and a 3 : 3 : 1 glucose/water/glycerol stoichiometry is proposed).

Our objective in this study was to establish whether there was a change of mechanism related to a  $T_g$  decrease after the specific sorption site saturation point. Ternary blends were studied, i.e., polymer/water/plasticizer systems. By working with a panel of very different plasticizers, we examined which species had the best plasticizing effect before and after site saturation. This qualitative approach should be sufficient to point out the eventual change of mechanism. The molecular modeling part is not discussed in this article.

Starch (whose plasticization is widely studied in literature) is not the best biopolymer with which to test "non specific" plasticizers (non donor/acceptor, non interacting by H bonds), because of their low solubility in polysaccharides. On the contrary, lignin is a good model because of (i) its aromatic structure—

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large aromatic molecules can play the role of classical (non specific) plasticizers, and (ii) its high hydroxyl content—lignin can be plasticized by specific sorbants.

## EXPERIMENTAL

### Material

The series of plasticizers was defined to have a list of nonvolatile molecules, representing different possible plasticization mechanisms:

- donor/acceptor molecules: donor/acceptor blends are all currently used to make lignin solutions in solvents
- pure acceptor molecules
- poly(ethylene glycol) molecules: ethylene glycol is given as a very good plasticizer for lignin<sup>11</sup> and the use of oligomers of poly(ethylene glycol) allows modulation of this acceptor character
- aromatic molecules showing a similar structure to lignin repetition units (classical strategy for plasticizing)
- organic acids *Plasticizers*: Ethylene glycol (EG) (99%, Aldrich, Noisy le Grand, France), adipic acid (99%, Aldrich), succinic acid (99%, Aldrich), 1,4-diazobicyclo[2,2,2]octane (98%, Aldrich), diethylene glycol (DEG) (99%, Aldrich), tetra(ethylene glycol) (TEEG) (99%, Aldrich), hexa(ethylene glycol) (HEG) (97%, Aldrich), poly(ethylene glycol) dimethyl ether (PEGDM-250) ( $M_n \approx 250$ , Aldrich), poly(ethylene glycol) dimethyl ether (PEGDM-500) ( $M_n \approx 500$ , Aldrich), ethylene carbonate (98%, Aldrich), propylene carbonate (99%, Aldrich), 6-caprolactone monomer (99%, Aldrich), triethylene glycol (TEG) (99%, Acros Organics, Noisy le Grand, France), vanillin (97%, Fluka, St. Quentin Falavier, France), acetovanillone (97%, Fluka), acetosyringone (97%, Fluka), homovanilic acid (99%, Fluka), ferulic acid (99%, Fluka), lactic acid (100%, LabOSI, Elancourt, France), ethanol (95–96%, SDS, Peypin, France).
- Kraft lignin was provided by Westvaco, Charleston, SC; commercial name, Indulin AT, pine lignin 97%, pH of 2% aqueous solution at 25°C: 6.5. No treatment was applied to the commercial product.
- Lignin–plasticizer blends were obtained by evaporating a solution of plasticizers (e.g., water for EG and ethanol for vanillin). In the first step, the plasticizer solution was blended manually with the lignin powder. The quantity of solution was adjusted to homogeneously wet the powder; the use of a plasticizer solution allows a better dispersion, especially when incorporating low amounts of plasticizer (scattered  $T_g$  data were previously obtained from a direct incorporation).

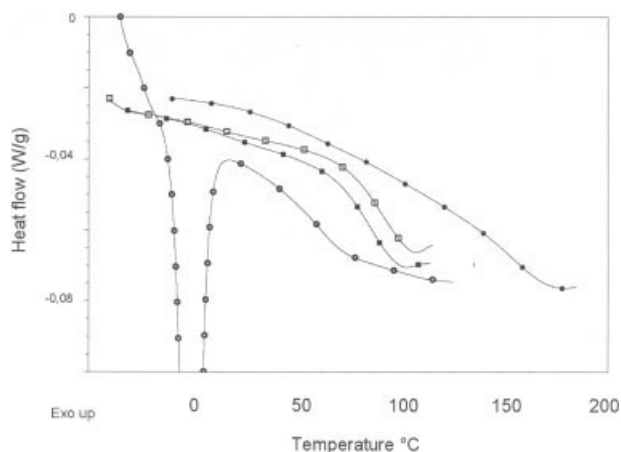
Impregnated powder – ethanol or water – was then dried 2 h at 70°C for complete ethanol removal, or to reach a water concentration lower than water solubility under 80% relative humidity (RH). After drying, the product was ground manually and stored 1 day at 80% RH. The hydrated product was then stored 1 day at 80°C in hermetic glass to allow complete plasticizer diffusion (at 80°C/80% RH all plasticized samples can be considered to be at rubbery state or near  $T_g$ ; see Fig. 6). The product is then equilibrated at convenient RH and 20°C for further analyses.

- Acetylated (100%) samples were obtained by the following procedure. Samples were submitted to acetylation in a mixture of acetic anhydride and pyridine (1 : 1, v/v) for 24 h at room temperature. The reaction products were then poured into ice water and extracted with dichloromethane. Organic layers were washed with saturated sodium chloride solutions. Assuming a 100% reaction yield, an average concentration of 4.6 mol acetylated OH/1000 g lignin was calculated. This concentration was used for the synthesis of other acetyl esters.
- *Partially acetylated lignin*: The target quantity of acetyl anhydride is added to the lignin pyridine solution at room temperature. The sample is treated by four ethanol/toluene (1:1) coevaporations. The final product is washed in water.

### Methods

Glass transition temperatures were determined by DSC (differential scanning calorimetry; TA Instrument 2920). Samples between 30 and 50 mg were placed in high volume hermetic pans. The heat cycles applied were –45 to 160°C at a rate of 5°C min<sup>-1</sup> for the first scan and –45 to 210°C at the same rate for the second scan (cooling rate between the two scans, 20°C min<sup>-1</sup>). The pans were either opened (0% RH) or closed (80% RH). Samples tested at 80% RH were preconditioned in a climatic oven (SECASI Technologies). Glass transition temperature was determined from the second run. Examples of DSC traces are shown in Figure 1. For the determination of the glass transition of lignin with low water content, an adapted procedure was defined. Samples of dry lignin, rehydrated at 40% RH, were taken at different times of sorption (before equilibrium). Samples were submitted to DSC analysis, and then DSC pans were drilled and submitted to thermogravimetric analysis to determine the water content.

*Water sorption isotherms*: Samples (500 mg), initially dried for 12 h at 80°C, were equilibrated in humidity controlled ventilated ovens and regularly weighed until constant. Water contents were expressed in reference to the dry product.

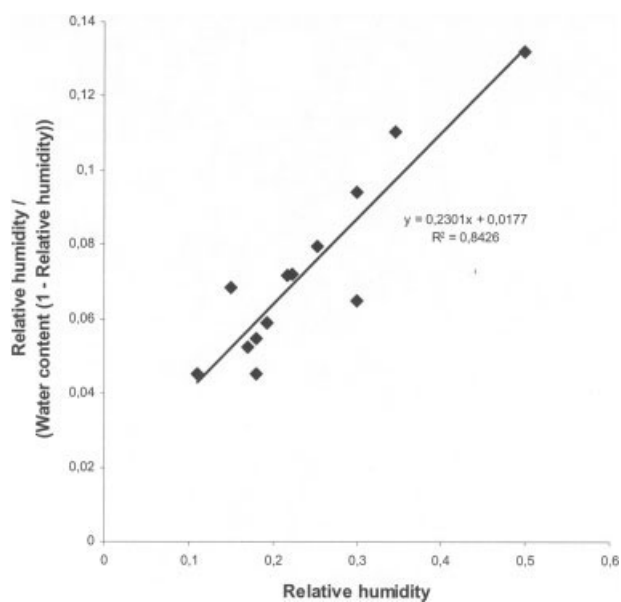


**Figure 1** Examples of DSC traces (2nd run) •, dry Kraft lignin; □, Kraft lignin hydrated at 32% RH; ■, Kraft lignin hydrated at 57% RH; ○, Kraft formulated with 30% water.

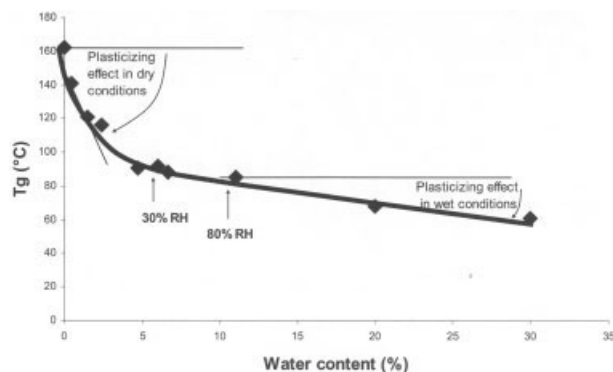
## RESULTS AND DISCUSSION

### Lignin/water systems

Figure 2 shows the BET plot of Kraft lignin water sorption. The use of the BET equation<sup>12</sup> between 30 and 50% RH leads to the determination of 4% water (weight content) for the saturation of primary sites in Kraft lignin. From different model structures of lignins proposed in the literature,<sup>13</sup> we determined an average OH content of 1.4 OH per monomeric unit (phenolic + aliphatic alcohols + carboxylic acids). If all of these sites are saturated by monofunctional water, a theoretical water concentration of 12.8% can be calculated. If water is supposed to be bifunctional (as proposed for polysaccharides<sup>8,9</sup>), a 6.4% concentration



**Figure 2** BET plot of Kraft lignin water sorption (25°C).



**Figure 3** Evolution of  $T_g$  as a function of water content.

can be calculated, which is closer to the experimental BET value. At 30% RH, the water concentration is higher than the experimental and the calculated values of the saturation point. In the following experiments, we will consider this RH as the saturation point.

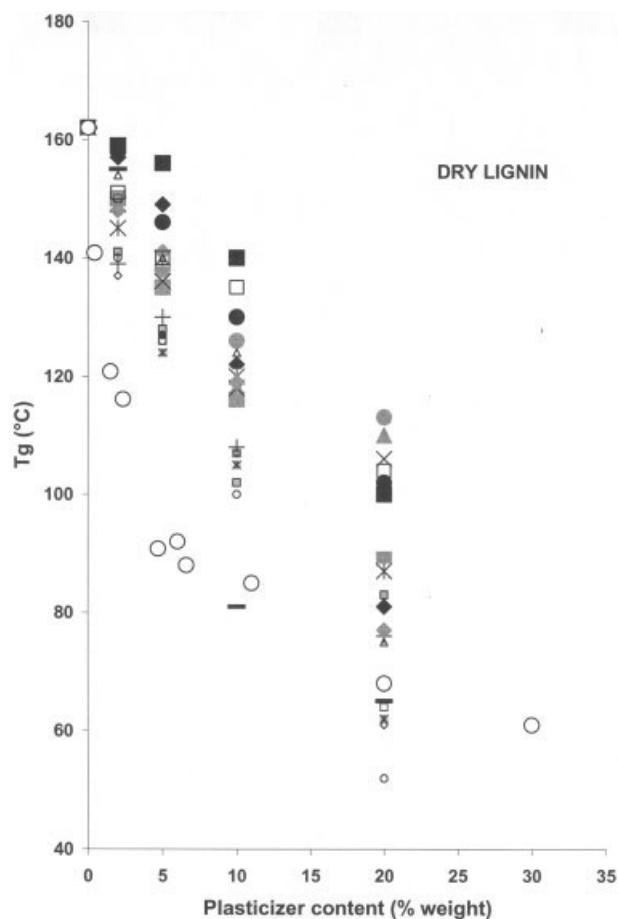
Figure 3 shows the glass transition variation of Kraft lignin as a function of water content. High concentrations could be tested by using high pressure DSC cells. A pseudo linear decrease of the glass transition is observed between 5 and 30% water. Sakata and Senju,<sup>14</sup> who measured the same kind of formulations, observed a plateau for the glass transition, perhaps due to differences in characterization methods (possible water loss, measurement of thermal softening temperature instead of  $T_g$ ).

Schematically,  $T_g$  decreases in two steps as a function of water content. In the first step, a high decrease was observed. This was also the case in Sakata and Senju's work.<sup>14</sup> The second step of  $T_g$  decrease, which occurs after specific site saturation, was characterized by low slope of the straight line. A clear change in behavior was observed before and after saturation.

The three component solubility parameters of lignin and water were calculated using the Van Krevelen group contribution method.<sup>15</sup> The distance in Hansen space between lignin and water is very high ( $\Delta\delta = 26.7$  (J/cm<sup>3</sup>)<sup>0.5</sup>). Although it is an efficient plasticizer, water is not compatible with lignin in terms of solubility parameters. After site saturation, the low slope of  $T_g$  decrease is on the contrary well connected to this high difference in terms of solubility parameters.

### Lignin plasticizer systems

Figure 4 shows the variation of  $T_g$  as a function of plasticizer contents expressed in weight. Assuming a classical plasticizer effect (increased chain spacing, increase of free volume), the more compatible the structure introduced in the polymer matrix, the better the plasticization effect. To quantify compatibility, Han-



**Figure 4** Plasticization of dry Kraft lignin by different plasticizers. Plasticizer concentration expressed in weight content. ○, water; □, EG; •, DEG; ◊, TEG; ▨, TTEG; ◻, HEG; ◇, PEGDM-250; ▩, PEGDM-500; ■, vanillin; ●, acetosyringone; ◆, acetovanillone; △, homovanilic acid; ⊙, ferulic acid; ✕, ethylene carbonate; ×, propylene carbonate; +, caprolactone; ▨, adipic acid; △, succinic acid; ✕, lactic acid; −, DEBCO.

sen three-dimensional parameters were calculated using the group contribution method of Van Krevelen.<sup>15</sup> The compatibility with lignin was evaluated by the distance in the 3D Hansen referential between the lignin and the plasticizer. These values are reported in Table I. To quantify the plasticizer effect, we used the slope of linear regression of  $T_g$  as a function of plasticizer content. The  $T_g$  decrease is evidently not strictly linear (average  $R^2$  linear regression parameter = 0.95), but a linear fit allows calculation of an overall plasticizing effect in the range tested, quantified by a single parameter, allowing the comparison of different types of plasticizers. The slope can be calculated with a molar concentration of plasticizer or by weight content (Table I).

The correlation between the plasticizer efficiency and the distance to lignin in the Hansen referential is theoretically a decreasing function. This is not the

case: water exhibits a more efficient plasticizing effect despite of its incompatibility with lignin.

Most of the models describing  $T_g$  decrease use a plasticizer concentration expressed as weight content and which is eventually corrected by the densities to express a volume fraction. The idea is to consider a blend of two independent species, and to make a weighted average of their  $T_g$ 's. Unfortunately, if specific interactions exist, the plasticizer action is localized at a specific place on the macromolecule, and the plasticizer effect is theoretically better evaluated by using the molar concentration of H bonds developed by the plasticizer. Ideally one should know the real functionality of the plasticizer. An attempt was made to predict the functionality of the molecules assuming (i) a functionality equal to 1 for ethers, hydroxyls, carbonyls, aldehydes, carboxylic acids (delocalized hydrogen), amines; and (ii) a functionality equal to 2 for esters and carbonates (Table I). The plasticizing efficiency of water is totally different when expressed as a function of weight (Fig. 4) or mole (Fig. 5) contents. In terms of weight concentration, water is the best plasticizer, while in terms of molar concentration, water has the same plasticizer efficiency as other plasticizers. In Figure 5, a unique plasticizer behavior, whatever the plasticizer, is observed until around 4 mol of H bonds/1000 g lignin (see data surrounded by full line). After that point, data are spread. Ethylene glycol seems to deviate from this unique behavior probably because of an overestimation of its functionality. The specific concentration is close to the 4.4 mol of H bonds and would correspond to the lignin saturation from BET method.

Considering a purely H bond breaking mechanism, an apparent plasticizer functionality can be calculated from a plasticizer "scaled" efficiency. In this way, a plasticizer efficiency normalized to that of water (i.e., scaled) was calculated. If the plasticizer action is only "stoichiometric" (neutralization of OH sites), the ratio of plasticizer efficiency to half of water efficiency is directly linked to the plasticizer functionality, as water is known to be doubly hydrogen bonded.<sup>8,9</sup> The values are reported in Table I. When comparing this scaled plasticizer efficiency to the predicted functionality, several comments can be made:

- For poly(ethylene glycol) samples (from DEG to PEGDM ether 500), the experimental ratio directly corresponds to the number of hydroxyl and ether functions.
- The relationship between the experimental ratio and predicted functionality is not as easily correlated for other molecules, but a maximum difference of 1 unit is observed. Generally the scaled plasticizer efficiency is higher than the predicted functionality. This confirms that the H bond breaking mechanism is not the only role of the

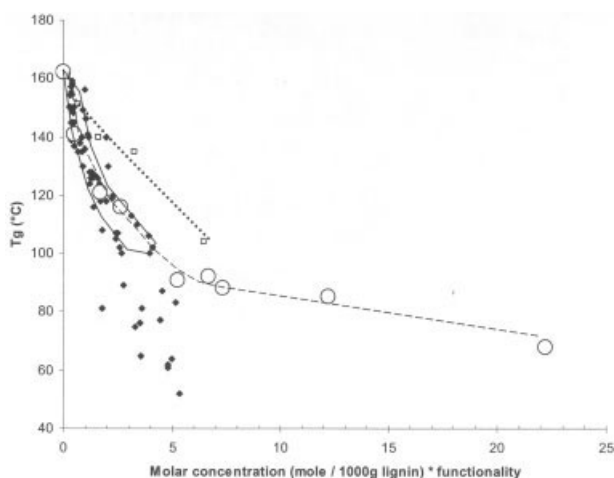


**TABLE I**  
**Plasticizer Efficiency Evaluated by  $dT_g/d$ Concentration at 0% RH and 80% RH, and Comparison of Plasticizer Scaled Efficiency (Ratio with Half of Water Efficiency) and Plasticizer Functionality**

Plasticizer	Distance to lignin in Hansen referential ( $J/cm^3$ ) <sup>0.5</sup>	Plasticizer efficiency				Calculated functionality	Plasticizer scaled efficiency	
		Concentration (mole/1000 g of lignin)		Concentration (weight/100 g of lignin)			0% RH	80% RH
		0% RH	80% RH	0% RH	80% RH			
Water	26.68	33	2	1872	123	2	2	2
Ethylene glycol	14.68	17	11	288	202	2	1.0	9.8
Diethylene glycol	13.44	59	21	555	200	3	3.6	18.6
Triethylene glycol	13.46	79	46	526	330	4	4.8	40.8
Tetraethylene glycol	13.72	73	38	375	194	5	4.4	33.8
Hexaethylene glycol	14.27	136	69	480	244	7	8.2	61.4
PEG dimethyl ether ( $M_n$ 250)	18.74	117	53	469	212	6	7.1	47.2
PEG dimethyl ether ( $M_n$ 500)	18.04	240	120	480	240	12	14.5	106.6
Ethylene carbonate	16.63	31	12	356	156	2	1.9	10.6
Propylene carbonate	14.91	27	13	269	170	2	1.6	11.6
Caprolactone	18.52	46	15	401	150	2	2.8	13.4
1,4-Diazabicyclo[2,2,2]octane	21.28	58	19	517	166	2	3.5	16.8
Vanillin	3.82	48	35	317	253	3	2.9	31.2
Acetosyringone	9.55	60	36	305	183	4	3.6	32
Acetovanillone	7.58	69	45	418	270	3	4.2	40
Ferulic acid	10.16	45	38	230	195	3	2.7	33.8
Homovanillic acid	7.84	78	57	431	311	3	4.7	50.6
Adipic acid	17.14	52	22	356	152	2	3.2	19.6
Lactic acid	12.18	37	18	473	222	2	2.2	16
Succinic acid	15.32	28	13	240	109	2	1.7	11.6

plasticizers. When the scaled plasticizer efficiency is lower, several explanations can be proposed: (i) EG could interact in a dimer form (functionality = 1), or could involve one intramolecular H bond (functionality = 1 instead of 2); (ii) the attribution of a functionality equal to 2 for esters, carbonates, and acids could be an overestimation for steric reasons.

Previous authors have shown a relationship between plasticizer efficiency and the solubility parameter on dry lignin. These results are not in contradiction with the present work, as the reported relationships were shown in a homologous series, e.g., phtalates differing from their alkyl chain length, but identical considering their functionality.

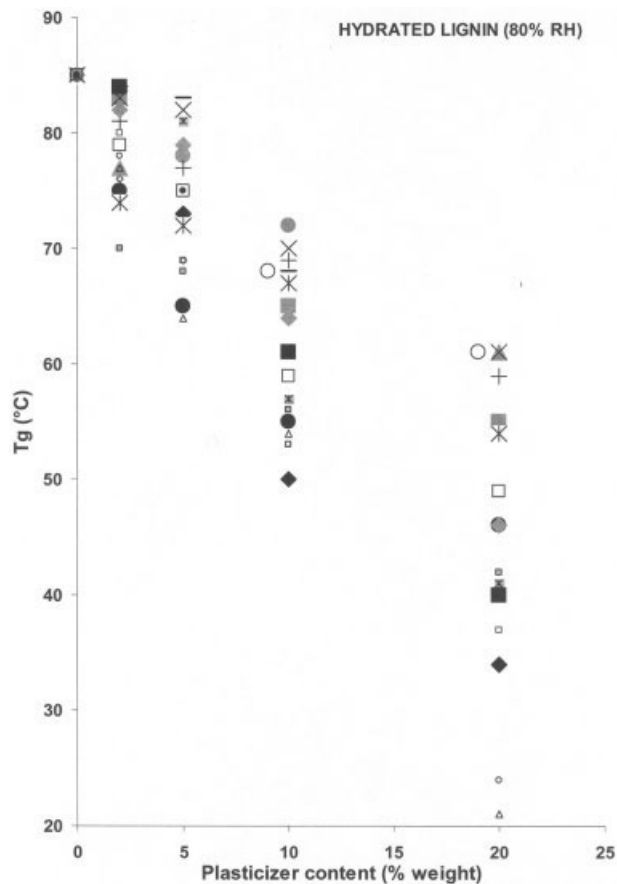


**Figure 5** Plasticization of dry Kraft lignin by different plasticizers. Plasticizer concentration expressed in mole of functions involved in hydrogen bonds. —○—, Water; —□—, EG; —◆—, all other plasticizers.

### Lignin/water/plasticizer systems

To test the water plasticizer systems in conditions of total saturation of sorption sites by water, we decided to use an 80% RH, leading to a water concentration larger than saturation. As samples can have different water sorption isotherms, they probably do not strictly contain the same water content. When considering that water is in excess, slight concentration variation does not drastically change the plasticizing behavior.

All the data obtained at 80% RH are presented in Figure 6. The abscissae of water data points were obtained by subtracting the water content at 80% RH from the total water content. Expressed in mole or weight concentration, water has the lowest activity. No master curve was observed in the correlation between  $T_g$  and molar concentration of H bonds, even at low plasticizer contents. This shows that the plasticization mechanism is no longer controlled by plasticizer polymer specific interactions.

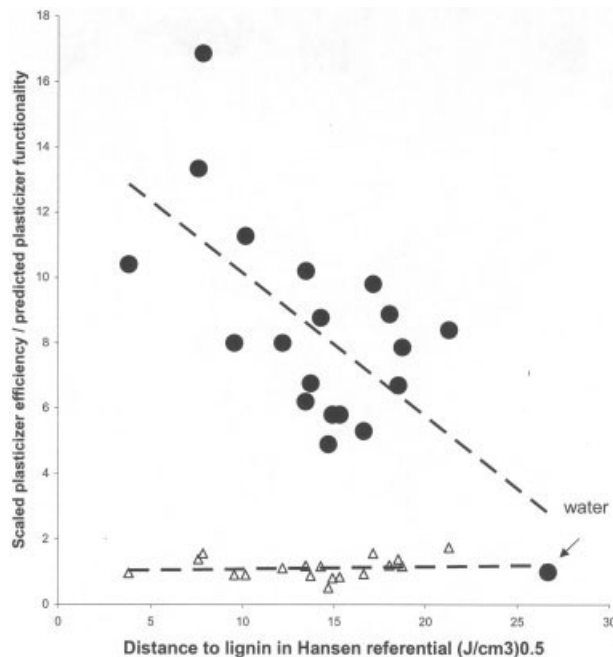


**Figure 6** Plasticization of Kraft lignin under 80% RH by different plasticizers. Plasticizer concentration expressed in weight content. Same symbols as in Figure 4.

The scaled efficiency has no relationship to the functionality (Table I) but shows a scattered correlation with the solubility parameter: Figure 7 shows a decreasing relationship of the ratio scaled efficiency/predicted functionality for hydrated plasticized lignin. On the contrary, for dry lignin, this ratio was nearly 1 and it was not correlated to the solubility parameter.

### Lignin acetylation

Considering that lignin plasticization mechanism is closely related to the availability of OH functions, we decided to compare quantitatively internal and external plasticization of lignin. Acetates (the shortest hydrophobic ester derivative) were chosen for internal plasticization to limit the action of ester groups to the disappearance of OH groups (the other mechanism being the chain extender action). The 100% acetylated sample has an average glass transition around 100°C, which is close to the water saturated sample. The weight uptake after total acetylation allows to calculate the OH content: 4.6 mol/1000 g lignin, which is close to other estimations of the saturation point.

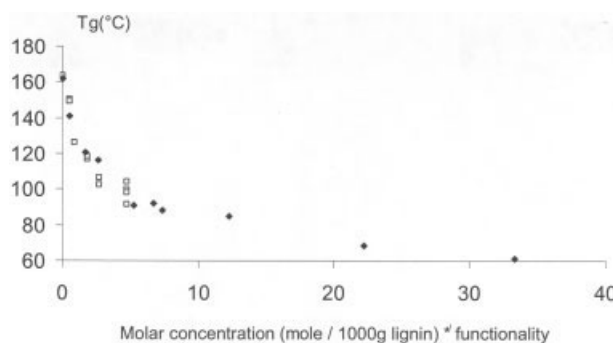


**Figure 7** Ratio of experimental functionality to predicted functionality. The experimental functionality is obtained from the ratio of the plasticizer efficiency (with a concentration expressed in mole) to half of water plasticizing efficiency. ●, at 80% RH; △, at 0% RH.

Figure 8 shows the glass transition of partially acetylated samples. As previously, the concentration is expressed in mole of modified OH bonds. Using this scale, and considering a double bonded water, the variation of the  $T_g$  of acetylated lignin and plasticized lignin are roughly the same until the saturation point. This confirms the existence of a chemical mechanism (OH bond breaking) until the saturation point.

## CONCLUSIONS

The mechanisms of lignin plasticization are totally different in dry and in wet conditions. The change of



**Figure 8** Plasticization of Kraft lignin by water ◆ and by acetate grafting □. Plasticizer concentration expressed in mole of OH sorbed or grafted.

mechanism can be defined from the  $T_g$  value at the saturation point, which is located around 100°C.

- Unsaturated lignin (dry lignin, plasticized by low amounts of plasticizers) is better plasticized by molecules that can be involved in H bonds. Poly-(ethylene glycol) molecules show a plasticizer efficiency proportional to the concentration of oxygen atoms. The functionality of water sorbed on lignin is 2. The functionality of EG is 1, possibly due to EG intramolecular H bond formation. Molecules showing a high ratio of functionality/molecular weight, like water, have an apparent high plasticizer efficiency when expressed by weight content. When plasticizer efficiency is expressed by molar concentration, water is only a *standard* plasticizer.
- A saturated polymer is better plasticized by molecules with a solubility parameter close to that of the matrix. Consequently, although dry lignin is highly plasticized by water, saturated lignin is poorly plasticized by water. On the contrary, vanillin-like molecules have a good efficiency in the presence of water.

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