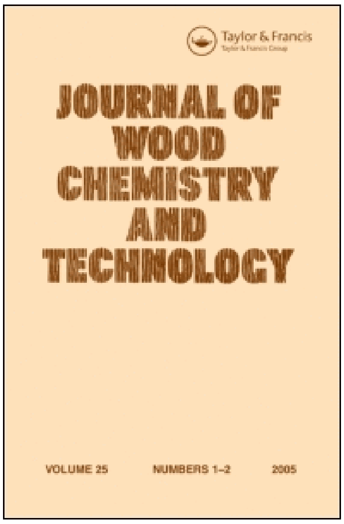

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Effects of Non-Aqueous Plasticizers on the Thermal Softening of Paper

Lennart Salmén[a]; Ernst Back[a]; Ylwa Alwarsdotter[a]
[a] Swedish Forest Products Research Laboratory, Stockholm, Sweden

To cite this Article Salmén, Lennart , Back, Ernst and Alwarsdotter, Ylwa(1984) 'Effects of Non-Aqueous Plasticizers on the Thermal Softening of Paper', Journal of Wood Chemistry and Technology, 4: 3, 347 — 365

To link to this Article: DOI: 10.1080/02773818408070654

URL: http://dx.doi.org/10.1080/02773818408070654

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 4(3), 347-365 (1984)

EFFECTS OF NON-AQUEOUS PLASTICIZERS ON THE THERMAL SOFTENING OF PAPER

Lennart Salmén, Ernst Back and Ylwa Alwarsdotter
Swedish Forest Products Research Laboratory
P.O. Box 5604, S-114 86 Stockholm, Sweden

Dedicated to Prof. J.L McCarthy on the
Occasion of his 70th Birthday

ABSTRACT

The stress-strain properties of a NSSC-fluting medium plasticized with various amounts of ethylene glycol have been measured over a temperature range up to 250°C. By comparison with delignified and hemicellulose-extracted samples it is concluded that the major softening is to a large extent caused by the lignin. It is shown that the Kaelble equation provides a good estimate of the glass transition temperature in lignin plasticizer systems. A reasonable correlation is also found between the measured softening in NSSC-papers containing ethylene glycol and the predictions of the plasticizing effect on lignin and carbohydrates based on the Kaelble approach. On this basis, the thermal softening of a NSSC-fluting medium and its lignin and carbohydrate polymers when plasticized by water is discussed, particularly in relation to the hot corrugating process.

INTRODUCTION

The softening of paper due to moisture can be detrimental or beneficial in product performance and in converting operations such as corrugating. In the hot corrugating process the paper must be soft enough to be formed into the flute profile, but it must emerge from the corrugating nip with a stable flute profile. Normally corrugation is carried out at a moisture content of 5 to

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9 % and with a press nip temperature substantially above 100°C. The best fluting medium is often based on NSSC-pulp containing about 24 % lignin with a 1.2 % sulphur content. It is suggested that the softening of the lignin in the corrugating nip is important for flute formation.[1]

This study was undertaken in order better to establish the effects of lignin softening on the mechanical properties of a fluting medium under corrugating conditions. Since it is difficult to maintain equilibrium conditions with small amounts of water in the paper above 100°C, ethylene glycol, a higher boiling compound with similar softening ability to that of water, was used. The softening effect of both non-aqueous solvents and water on all the polymeric paper components, i.e. cellulose, hemicelluloses and lignin, is discussed.

EXPERIMENTAL APPROACH

To study the plasticizing effects of water on NSSC-paper at temperatures above 100°C, measurements under pressure are required, which are rather tedious procedures. As an alternative approach a higher boiling compound with a plasticizing action similar to that of water has here been used.

A plasticizer is a substance, usually a monomer, added to a polymer to soften it, i.e. to lower its glass transition temperature and thereby its stiffness-temperature relationship. The softening ability of a plasticizer is related to its interaction with the polymer. This interaction can be partly described by comparing the solubility parameter δ, which is a measure of the intermolecular forces in the material. The relation of Kaelble[2] for estimating the reduction of the glass transition temperature for a given amount of added plasticizer is also based on this solubility parameter.

The plasticizer here chosen was ethylene glycol, a fairly good solvent for the wood polymers having a boiling point of

198°C. Ethylene glycol[3] has a solubility parameter δ of $33.4\cdot10^3$ $(J/m^3)^{\frac{1}{2}}$, which comes close to that of water[3] which is $48\cdot10^3$ $(J/m^3)^{\frac{1}{2}}$. Both ethylene glycol and water have high hydrogen bonding potentials. The softening temperature, i.e. the glass transition of the lignin, in wood samples whether immersed in ethylene glycol or water occurs at about 80°C at 0,02 Hz[4], this being the limiting softening temperature of lignin in these plasticizers. This means it is the lowest temperature attainable in these systems, independent of plasticizer concentration, above the limiting value. For comparison a few experiments with glycerol with a δ of $43.2\cdot10^3$ $(J/m^3)^{\frac{1}{2}}$ are also reported.

EXPERIMENTAL DETAILS

The papers here tested were based on a commercial NSSC-fluting medium containing 50 % birch and 50 % other hardwood species. For comparison, samples of this paper have been disintegrated and the pulp then delignified and in one case also hemicellulose extracted prior to the formation of isotropic handsheets. The delignification was performed in sodium chlorite and the hemicellulose was extracted with alkali according to a procedure of Spiegelberg[5]. The chemical compositions of all the papers, analysed and calculated according to a procedure outlined by Aurell[6], are given in Table 1. The degree of crystallinity was estimated from X-ray diffraction spectra of disintegrated samples, according to a procedure of Jayme and Knolle[7] and was calculated from the intensities of the crystalline and amorphous peaks.

All samples for mechanical tests were dried in vacuum at 65°C for 4 hours. Samples to be measured without plasticizer were then stored individually in sealed tubes containing water-free nitrogen gas. Other samples were placed in an autoclave at 65°C under low pressure for 20 days and exposed to various amounts of ethylene glycol or glycerol vapor. The ethylene glycol or glycerol absorbed was determined from the weight increase. The existence of residual

TABLE 1

Composition of Papers Investigated

	relative weight %			% crystallinity*
	cellulose	hemicellulose	lignin	
NSSC-fluting medium	48	29	23	65
delignified NSSC-pulp	70	29	1	74
delignified and hemicellulose extracted NSSC	89	10	1	76
kraft sack paper	77	16	7	70

* based on sum of cellulose and hemicellulose

amounts of water was checked by Karl Fischer titration[8] and limited to a maximum of 0.5 %.

The stress-strain tests were performed on an Alwetron TCT 20 [9], at a strain rate of 0.17 %/s. The test span was 100 mm and the strip width 15 mm. The samples were soaked in silicone oil in order to avoid contact with moist air and then clamped inside a thermostating chamber and heated or cooled to the test temperature by direct contact with the inert pre-thermostated silicone oil within a few seconds. For more details see[10].

The tensile properties were evaluated over the temperature range from -20°C to 200 or 250°C depending on the plasticizer content. One strip was measured for approximately each 2°C interval. The elastic modulus is given as the specific elastic modulus, i.e. as the elastic modulus divided by density. It is obtained by dividing the tensile stiffness by the dry basis weight of plasticizer-free samples. Transition temperatures were evaluated as maxima in the derivative curves of the logarithm of the modulus of elasticity against temperature.

RESULTS

Stress-strain Properties

The stress-strain properties of the NSSC-fluting medium have been measured at ethylene glycol contents of 0.0, 4.5, 6.4 and 12 % between 0°C and 200° to 250°C. In fig. 1 data for the specific elastic modulus are given as a function of temperature. For an ethylene glycol content of 12 % only the mean curve obtained is shown due to overlap with data for an ethylene glycol content of 6.4 %. It is apparent that the softening region is successively lowered by an increase in the ethylene glycol content. However at an ethylene glycol content of 12 % saturation seems to have occurred, i.e. a limiting softening temperature is reached. This behaviour is similar to that noticed with water as a plasticizer for wood [11] and various isolated lignin preparations[11,12,13].

For NSSC-fluting medium without plasticizer, the softening region has earlier been shown to consist of two glass transitions, one for lignin at 205°C and one for cellulose at 230°C [14]. For the samples containing ethylene glycol no such separation into several transitions is readily apparent. The reduction in the specific modulus is more distinct the higher the ethylene glycol content.

Corresponding data for the breaking elongation are given in fig. 2. Obviously a considerable increase in the breaking elongation accompanies the reduction in modulus of the papers, the increase being more distinct the higher the ethylene glycol content. For plasticizer-free samples such a marked increase in breaking elongation over a rather limited temperature range has been attributed to the softening of the lignin component[14] reflecting its plastic flow. A limiting breaking elongation is apparently reached at about 2.5 % elongation.

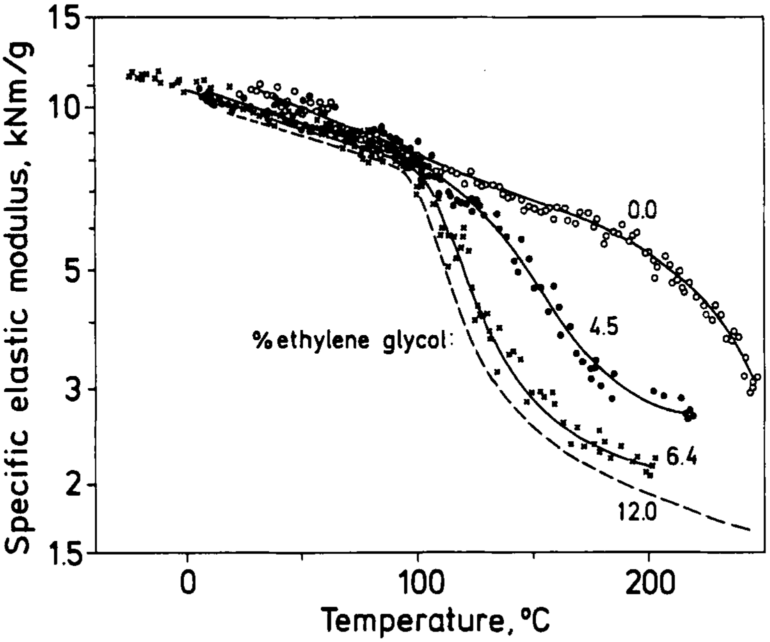

FIGURE 1. Specific elastic modulus versus temperature for NSSC fluting papers containing different amounts by weight of ethylene glycol.

For the breaking load the softening region is naturally less discernible, as seen in fig. 3. Ethylene glycol lowers the breaking load over almost the entire temperature range studied. The relatively broader softening region in this case is common for polymers and may be attributed to an early onset of pull-out of chains or fibers below the transition region[14].

Similar effects occur with glycerol as a softener as shown in fig. 4 which depicts the effect on the breaking elongation. The softening region is here somewhat broader than that with ethylene glycol. It is also difficult to determine an exact softening temperature from the corresponding data for the elastic modulus. A limiting breaking elongation of about 2.5 % is again reached.

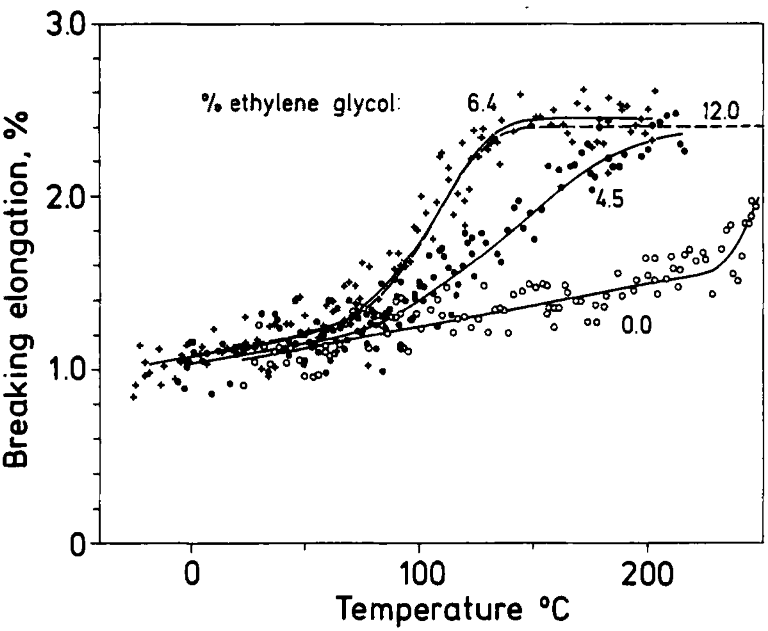

FIGURE 2. Breaking elongation *versus* temperature for the NSSC-papers in figure 1 with different amounts by weight of ethylene glycol.

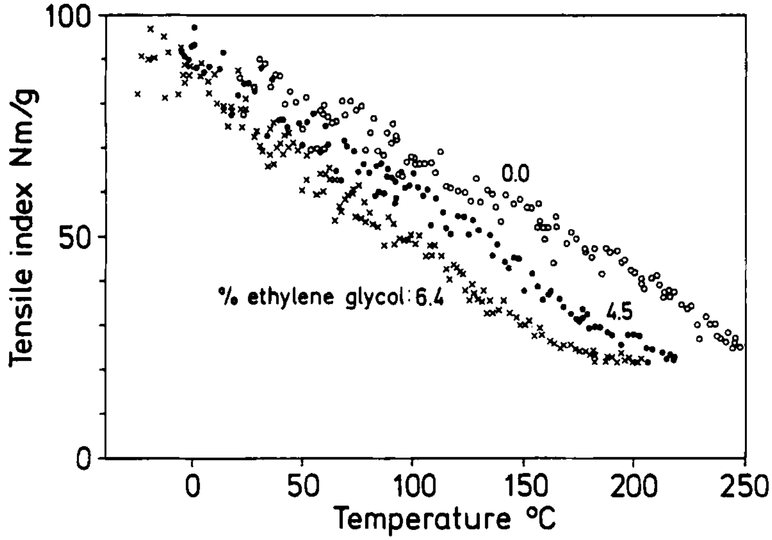

FIGURE 3. Breaking load *versus* temperature for the NSSC-papers in figures 1 and 2 with different amounts by weight of ethylene glycol.

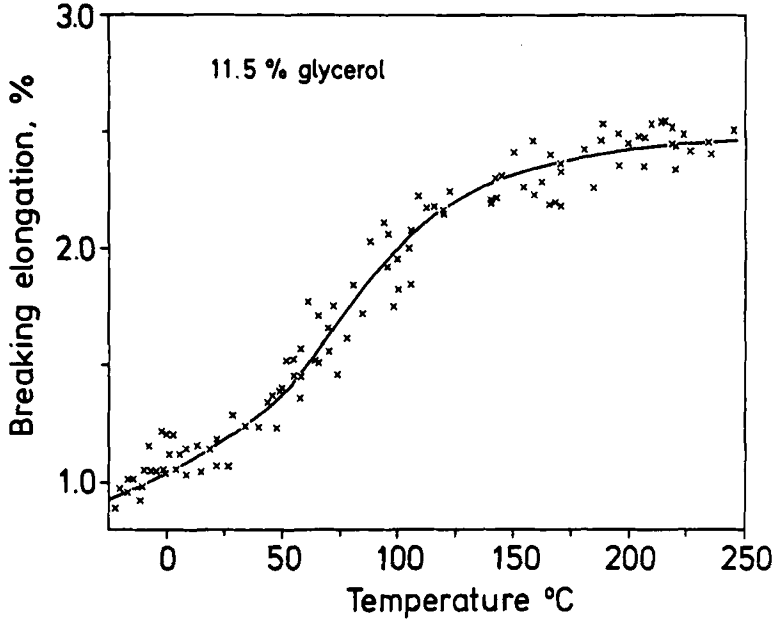

FIGURE 4 Breaking elongation *versus* temperature for the NSSC-papers of figures 1 to 3 containing 11.5 weight % of glycerol.

Effects of Chemical Composition

The influence on the elastic modulus of the corresponding papers plasticized with ethylene glycol of delignification with chlorite and of delignification with chlorite followed by extraction with alkali to remove hemicelluloses is shown in fig. 5. The minor differences in ethylene glycol content may be disregarded when discussing the softening behaviour. The reduction in modulus over the softening region is considerably reduced by chlorite delignification. The subsequent extraction of hemicelluloses has little further effect. It is thus reasonable to conclude that a significant part of the softening seen in NSSC-papers plasticized with ethylene glycol is due to the lignin component. In comparison, for plasticizer-free papers delignification causes a softening at 205°C to disappear while hemicellulose extraction has no apparent effect[14].

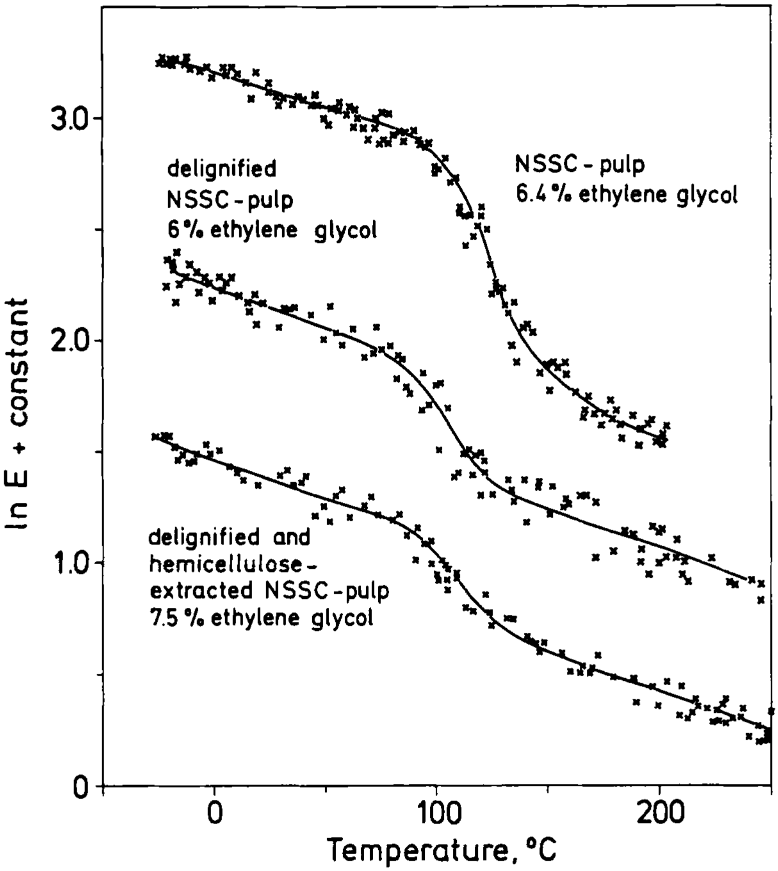

FIGURE 5. The natural logarithm of the specific elastic modulus, *ln* E versus temperature for papers of an NSSC-pulp, an NSSC-pulp delignified with chlorite and an NSSC-pulp both delignified and extracted with alkali to remove hemicelluloses - all plasticized with ethylene glycol. The curves have here been separated vertically by the addition of a constant, thus only the relative change with temperature is considered.

It is difficult to determine the effect of the extractions on the temperature of the softening due to the changes in chemical composition. Nevertheless, no major shift seems to have occurred.

In the corresponding data for the breaking elongation of the two extracted papers no abrupt increase which indicate the softening region is seen. On the other hand, at lower temperatures the extracted papers exhibit a greater increase in breaking elongation with temperature than the original NSSC-fluting medium. The same phenomenon has also been noticed for corresponding plasticizer-free papers of extracted NSSC-pulps compared with unextracted samples[14].

For other papers with a low lignin content such as a kraft sack paper the softening region for plasticized samples is comparable with that noticed for delignified NSSC-papers, as seen in fig. 6. Strictly speaking a softening region can only be discerned here as a discontinuity in the fairly linear behaviour of the elastic modulus versus temperature. These results do not permit this softening region in papers of low lignin content to be referred to any given component. It may be noticed that the degree of softening at the transition temperature seems to be rather unaffected by changes in hemicellulose content. For single pulp fibers, the relative composition, i.e. the amount of lignin or of hemicelluloses, has also been found to have little influence on the degree of reduction in the modulus caused by the softening of the hemicelluloses[16].

Calculating the Glass Transition in Polymer-plasticized Systems

Both empirical and theoretical equations have been put forward to describe the glass transition of a polymer-plasticizer mixture. Examples are that of Kelley and Bueche[17] relating T_g to free volume, that one of Couchman and Karasz[18] considering volume or entropy continuity conditions, that of Di Marzio and Gibbs[19] using a statistical mechanical interpretation of composition effects on T_g, that of Kaelble[2] relating T_g to the cohesive energy and lattice coordinate numbers and that of Nose[20] assuming a "hole theory". For practical purposes the choice can be made on the basis of the availability of the material parameters required in the respective equations.

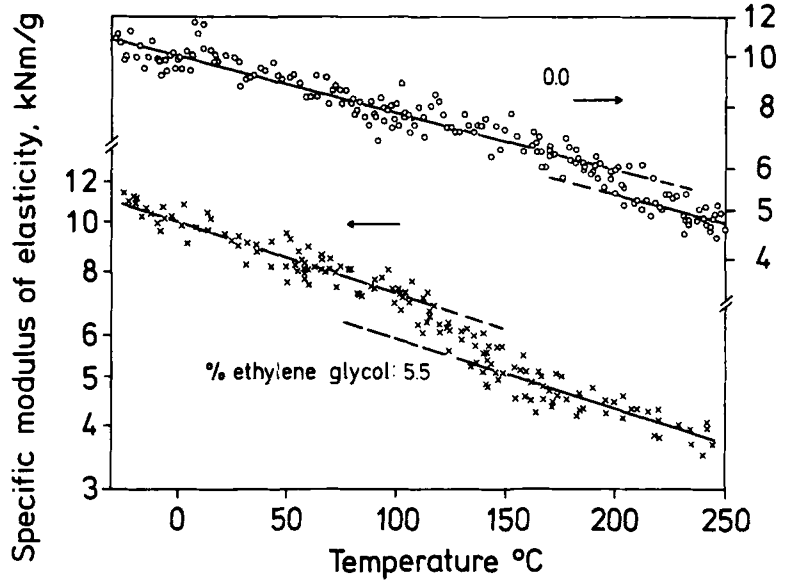

FIGURE 6. Specific elastic modulus *versus* temperature for a kraft sack paper without plasticizer - right-hand scale - and plasticized with 5.5 % by weight of ethylene glycol - left-hand scale.

The equation of Kaelble has been used by Salmén and Back to estimate the plasticizing effect of water on amorphous carbohydrates[1,21,22]. The corresponding application to other softeners does not differ in principle.

For lignin, the solubility parameter δ has been experimentally determined[12] to be about $22.5\cdot10^3(J/m^3)^{\frac{1}{2}}$. In fig. 7 the Kaelble equation is applied to the lignin and dimethyl phthalate system. This application is based on the data of table 2 and shows good agreement with experimental data of Sakata and Senju[12]. No limiting glass transition temperature is noticed in this case, probably due to the better compatibility of this plasticizer than for instance for water. For more polar plasticizers like ethylene glycol or water in particular, the free volume theories may have limitations. However, the drastic reductions in the T_g of various

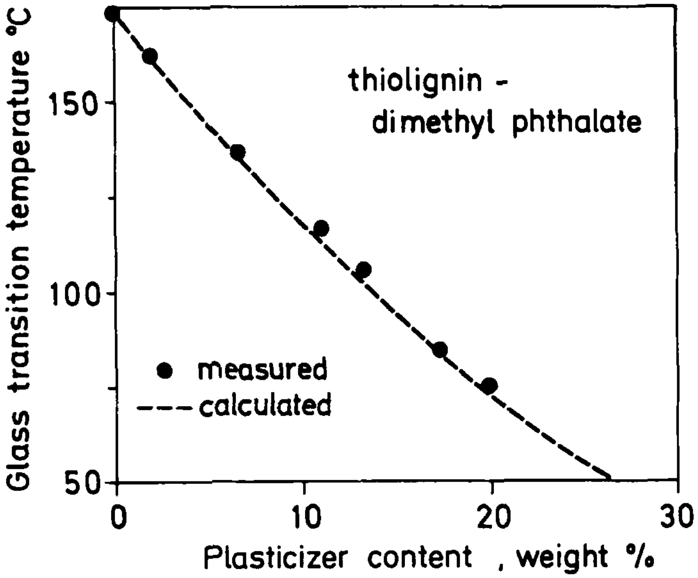

FIGURE 7. Glass transition temperature of thiolignin *versus* dimethyl phthalate content. The points refer to experimental data of Sakata and Senju[12]. The line represents calculations according to the Kaelble equation using parameters in table 2.

lignins caused by small amounts of water[12,13], e.g. for a thiolignin from 174°C down to 115°C by a moisture content of 5 % [12], is qualitatively predictable by the Kaelble equation[1]. Further addition of water has comparatively little effect, i.e. a limiting softening temperature is reached.

In applying this approach to the multicomponent polymer system of a NSSC-fluting there are several limitations to be considered. The distribution ratio of the plasticizer, here ethylene glycol, between the lignin and the amorphous carbohydrates is unknown. Here the distribution ratio for ethylene glycol is arbitrary set to 0.2 considering that cellulose has a higher absorption for hydrophilic monomers than lignin.

The crystallinity of the cellulose influences the calculations since plasticizers are generally absorbed only in the amorphous

TABLE 2

Material Parameters used for Calculations of Glass Transition Temperatures according to the Kaelble Equation*

	transition temperature	solubility parameter	molar volume	parameter
		δ	ν	h_D or h_p
	T_g (K)	$(J/m^3)^{\frac{1}{2}} \cdot 10^{-3}$	$m^3/mol \cdot 10^6$	dimensionless
water	136[26]	48.1[28]	18	71
ethylene glycol	155[26]	33.4[28]	56	96
dimethyl phthalate	195[27]	21.5[28]	163	95
cellulose	493[1]			151[1,21]
hemicellulose	493[1]			151[1]
lignin	478[1]	22.5	133	34
thiolignin	447[12]	22.5[12]		34

$$^{*}Tg = \left(Tg_p\, X_p + \frac{h_D}{h_p}\, Tg_D\, X_D\right) \Big/ \left(X_p + \frac{h_D}{h_p}\, X_D\right), \text{ where } h = \frac{2\,\delta^2 \cdot \nu}{R\, Tg}$$

regions of the polymers. Neglecting the differences noted between the glass transition temperatures of hemicelluloses and of amorphous cellulose[1,22] calculations are made for an amorphous carbohydrate fraction containing both cellulose and hemicellulose with a glass transition of 220°C. The crystalline fraction of the carbohydrates (cellulose and hemicellulose) may be given by X-ray diffraction data and is for the NSSC-fluting medium estimated to be about 65 % of the total carbohydrate fraction.

Figure 8 gives the estimated glass transition temperature as a function of the ethylene glycol content in the NSSC-fluting medium for the lignin and carbohydrate fractions. For the lignin plasticized with ethylene glycol a limiting softening temperature probably exists at 80°C, 0.02 Hz[4]. Considering the strain

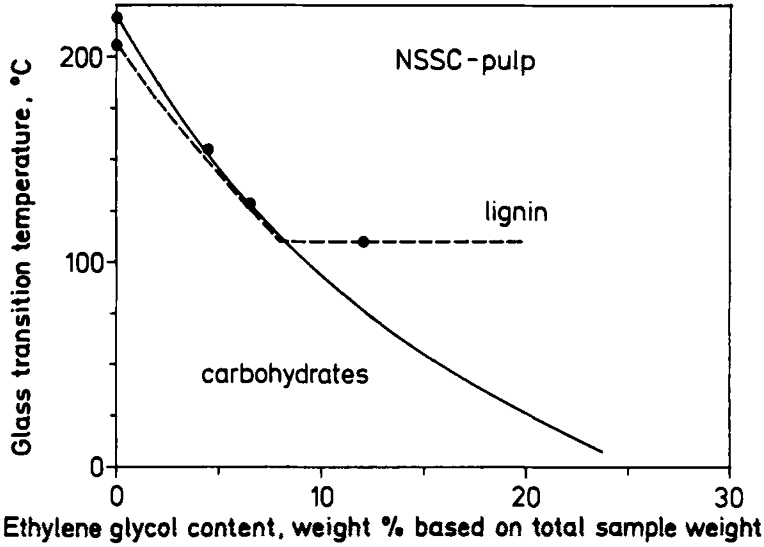

FIGURE 8. Glass transition temperatures of lignin and cellulose versus ethylene glycol content in an NSSC-pulp. The calculations are based on a lignin content of 23 %, a carbohydrate crystallinity of 65 % and a distribution ratio of ethylene glycol between lignin and amorphous carbohydrates of 0.2. The points refer to softening temperatures estimated from fig. 1.

rate here used and the increase in softening temperature with the increase in deformation rate, a softening temperature of 110°C is here more reasonable.

The calculations indicate only small differences in softening temperature between the lignin and the carbohydrate polymers of the NSSC-fluting medium with a low addition of ethylene glycol. This may explain why only a single transition region is observed in figures 1 and 5. The softening temperatures estimated from the inflection points in figure 1 are also included in figure 8. Obviously the observations have been rationalized on the basis of plausible values of the parameters used in this estimate. Better techniques of measuring absorption ratios and degrees of crystallinity are however necessary to obtain a more solid proof. Some measurements at higher plasticizer content might also support the picture given.

DISCUSSION

Obviously the lignin component of the NSSC-fluting medium has a large effect on the thermal softening of this paper. Part of this effect may be due to the sulphonation of the lignin in this paper.

Yeo and Eisenberg have recognized that, for a polyelectrolyte such as sulphonated lignin, the maximum loss coefficient increases and the rubbery modulus decreases with increasing plasticizer content[23]. Such behaviour is apparent in fig. 1. The more distinct softening region at a higher ethylene glycol content may thus be explained as being a consequence of the polyelectrolyte behaviour of the sulphonated lignin. This behaviour is opposite to the normal behaviour of plasticized polymers[24]. However the fact that the glass transitions of the lignin and of the carbohydrates occur at about the same temperature with increasing amount of plasticizer may also tend to narrow the softening region.

The softening occurring in delignified papers is probably due to the softening of the carbohydrate components. The softening temperatures measured for delignified NSSC-pulp and for the kraft sack paper also agree fairly well with predictions using the Kaelble approach for carbohydrates plasticized by ethylene glycol. It is however not yet possible to discriminate between the softening of hemicelluloses and the amorphous parts of cellulose.

With ethylene glycol as a plasticizer good agreement is apparently found between the experimental data and the results of calculations according to the approach of Kaelble. Due to the similar softening behaviour of water and ethylene glycol it may be assumed that the Kaelble approach may be considered to be valid also for lignin with water as a plasticizer. In fact the Kaelble equation has been shown to well predict the softening

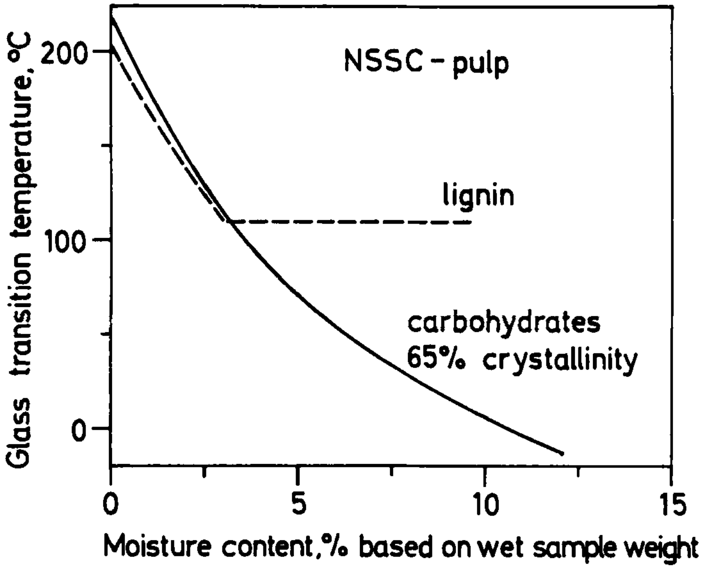

FIGURE 9. Influence of water on the softening temperatures in an NSSC-pulp. The calculations are based on a lignin content of 23 % and a distribution ratio of water between lignin and amorphous carbohydrates of 0.2.

effect of water on isolated lignin preparates[1,22]. For high yield pulps, softening effects on both the amorphous carbohydrates and on the lignin have to be considered. Figure 9 gives the results of such calculations for the components in NSSC-fluting medium again assuming a distribution ratio of 0.2 for water between lignin and amorphous carbohydrates. The limiting softening temperature for the lignin in this NSSC-fluting medium is here set to be about 110°C. This temperature is set higher than that normally quoted because attention has been given to the frequency dependence of this transition and to the web speed in the corrugator when the fluting medium is deformed. Also the NSSC-fluting medium contains 1.2 % sulphur and the limiting glass transition temperature of water-plasticized lignin is known to be lowered by increasing the degree of sulphonation[25].

Thus, while relatively small amounts of water may soften the carbohydrates even at room temperature, it is evident that the plasticization of the lignin component in NSSC-fluting is important in hot corrugation operations where web temperatures above 100°C are reached. With a moisture content between 5 and 9 %, a web temperature sufficiently above 100°C is necessary in the corrugating nip to achieve a good formation and flute profile. This may mean a surface temperature in the corrugator of about 170°C. Steam release from the paper web as it leaves the corrugating nip should quickly cool it below the softening temperature in order to solidify and stabilize the flute profile.

It should also be noticed that at moisture contents above 3 % two glass transitions in fact ought to be observable in the paper, one belonging to the carbohydrates, the other to the lignin. This should also be the case with ethylene glycol as a plasticizer (see fig. 8) where it should be more easy to observe. This is an interesting point for future studies.

ACKNOWLEDGEMENTS

The authors are grateful for the skilful technical assistance of Mr. Jan-Erik Wikén.

The present affiliation of Ylwa Alwarsdotter is Nymölla AB, S-295 03 Nymölla, Sweden.

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