

THE INFLUENCE OF WATER ON THE GLASS TRANSITION TEMPERATURE OF CELLULOSE

N. L. SALMÉN and E. L. BACK, Swedish Forest Products Research Laboratory, Stockholm, Sweden

THE glass transition temperature is the temperature at which an amorphous polymer changes from a hard glassy form into a rubberlike elastic form or to a viscous fluid. At this glass transition, which is a secondary transition, the temperature derivatives of both physical and mechanical properties of the polymer change.

The glass transition temperature is related to a certain degree of movement of the main chain, for example rotation of a larger chain segment. This is explained by many theories as being related to the void volume of the polymer, that is the volume not occupied by molecules.

Above the glass transition temperature it is assumed that the void volume is so great that a large chain motion is possible and exists, for example a rotation of segments. From this it is apparent that a polymer, especially one with side groups, can have several secondary transitions, for example when the void volume is sufficient only for the rotation of one side group. The secondary transitions of cellulose are estimated to be at 220° C for the main chain movement, that is the true glass transition⁽¹⁻⁵⁾ and at 0° for movement in the gluco-pyranose ring.^(6, 7)

Water as plasticiser for cellulose

THE plasticising effect of water on cellulosic material is of great importance. Water is an effective softening agent for cellulose and is present in almost every process where cellulose is produced, converted and finished. This softening is of special interest for example for the press drying of hard fibre building board, where it gives the stiff fibres enough flexibility to create a large bonding area. Another example is the corrugating of fluting, where water makes the paper mouldable around the roll profile. The effect of water on the glass transition temperature of cellulose has, however, been studied very little.

Under the chairmanship of B. W. Attwood

Addition of plasticisers reduces the glass transition temperature for a polymer. Many theories have been proposed to explain and calculate this reduction and among the better ones is the approach of Kaelbe⁽⁸⁾ (Appendix) which considers the cohesive energies of the components. Here this approach is used to calculate the effect of water on the glass transition temperature of cellulose.

The glass transition temperatures of pure amorphous water and cellulose respectively, have been reported in the literature to be 136 K⁽⁹⁾ and 493 K⁽¹⁾ The molar cohesive energy for cellulose at the secondary transition at 273 K can be calculated to be 296 kJ/mol, using experimental data for the softening effect on this transition of water measured by Kaimins.⁽⁶⁾ This calculation of the constant h_p for cellulose is shown in Table 1.

TABLE 1—CALCULATION OF THE CONSTANT h_p FROM THE SYSTEM CELLULOSE-WATER AT THE PYRANOSE RING TRANSITION⁽⁶⁾ ACCORDING TO THE EQUATION OF KALBE

<i>System cellulose—water</i> ⁶			<i>The constant h_p for cellulose according to the equation of Kaelbe (J/mol K·10⁻²)</i>
<i>weight fraction H₂O (%)</i>	<i>mole fraction H₂O (%)</i>	<i>measured T_g syst. (K)</i>	
11	52.6	240	10.43
20.8	70.3	223	12.27
22	71.7	215	10.29
28	77.8	203	10.01
30.4	79.7	203	11.22
Mean value:			10.85

If the molar cohesive energy for cellulose is assumed to be the same at 273 K and at 493 K, the constant h in Kaelbe's equation for cellulose at the glass transition at 493 K can be calculated to be 633 J/mol K. Using this value of the constant h_p for cellulose at 493 K, Kaelbe's approach can now be compared with experimental data by Kargin⁽¹⁾ for the plasticised system cellulose—triethylphenylammoniumhydroxide. The glass transition temperature for triethylphenylammoniumhydroxide has here been estimated to be 120 K by extrapolating the data of the system mentioned above. Its molar cohesive energy has here been calculated according to Hayes⁽¹⁰⁾ to be 141 kJ/mol. From Fig. 1 it appears that Kaelbe's equation is in good agreement with the experimental data.

From the above mentioned values of the cohesive energies and glass transition temperatures the effect of water on the glass transition temperature for totally amorphous cellulose is also calculated according to the approach of Kaelbe and included in Fig. 1.

TABLE 2—DATA REQUIRED FOR CALCULATIONS OF PLASTICISED SYSTEMS ACCORDING TO THE APPROACH OF KALBE

Material	Cohesive energy density		Molar volume v ($m^3/mol \cdot 10^6$)	From equation (1) $\frac{h}{h}$ ($J/mol \cdot K \cdot 10^{-2}$)
	T_g (K)	δ^2 ($KJ/m^3 \cdot 10^{-3}$)		
Water	136 (9)	2 254 (8)	18 (8)	2.98
Dibutylphthalate	200	—	—	5.13
Triethylphenylam- moniumhydroxide	120	—	—	11.72
PVC	360 (15)	507 (18)	46 (8)	0.70
Nylon 6-6	370 (16)	774 (8)	209 (17)	4.70
Cellulose	493 (1)	—	—	6.33

For a given moisture content in the amorphous part, the moisture content of the total material will naturally depend on the degree of crystallinity of the cellulose material concerned. The crystallinity can for example vary for different cellulose fibre materials from 50 to 85 per cent and for viscose cellulose from 25 to 40 per cent.⁽¹¹⁾

Different test methods also give different estimates of the crystallinity.

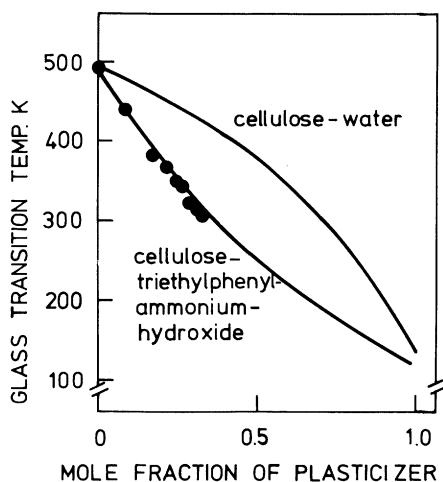


Fig. 1—The glass transition temperature for completely amorphous cellulose plasticised with two plasticisers. The lines are calculated theoretically according to Kaelbe's approach. Symbols give experimental values according to Kargin *et al.*⁽¹¹⁾

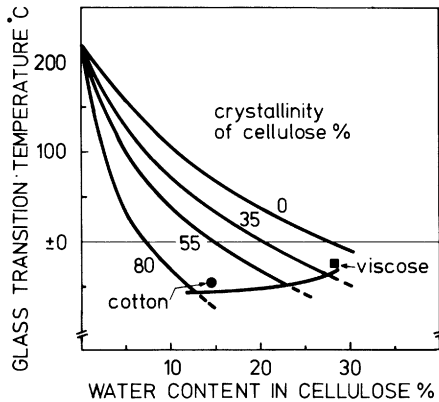


Fig. 2—The glass transition temperature for the cellulose-water system with cellulose of different degrees of crystallinity. The lines are calculated theoretically according to Kaelbe's approach

In Fig. 2 the data from Fig. 1 are recalculated and presented for cellulose of 35, 55 and 80 per cent crystallinity. In this way, the softening effect of water on cellulose is quantified. One objection remains. The approach of Kaelbe does not consider the chain stiffness or the chemical interaction between cellulose and water. The first one per cent of water is known to be bonded strongly to the cellulose, i.e. it is packed very closely. This could have a minor effect on the accuracy of the calculations.

Some measurements have been published by Naimark for the glass transition temperature of cellulose material saturated with water,⁽¹²⁾ which to some degree verify the relation. The glass transition temperature in systems saturated with water is stated to be about -25°C for viscose, and about -45°C for cotton cellulose. The water content excluding capillary water can according to Christensen be estimated in saturated viscose to be between 27.5 and 29.5 per cent and in saturated cotton cellulose to be about 14.5 per cent.⁽¹³⁾ These data have been plotted in Fig. 2, where they fit fairly well with the calculated lines.

NMR data by Ogiwara for the glass transition temperature of some cellulose materials softened with water have also been published.⁽¹⁴⁾ The cellulose is treated in different ways to give different degrees of crystallinity. In Fig. 3 the published data are given for cotton and for dissolving pulp of different crystallinities. It is evident that the experimental curves are very similar to those calculated according to Kaelbe's approach.

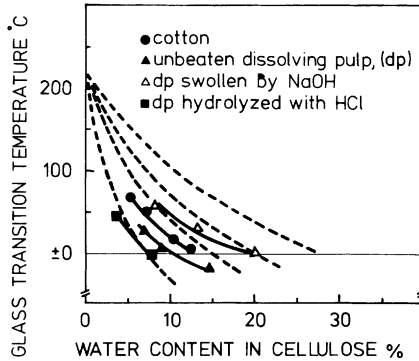


Fig. 3—The glass transition temperature for the cellulose-water system with cellulose of different degrees of crystallinity. Symbols give experimental values for cellulose treated to give different degrees of crystallinity according to Ogiwara *et al.*⁽¹⁴⁾ The broken lines are calculated theoretically according to Kaelbe as in Fig. 2

Glass transition in the paper-water system

NATURALLY, cellulosic material is often present together with hemicellulose and lignin. Cellulose and hemicellulose chains can, due to their similar chemical structures and properties, when existing in a homogeneous mixture form a system with a joint glass transition temperature, somewhere between that of the two components. The transition in the pyranose ring for holocellulose has been shown by Kaimins to be between the transition temperatures for xylan and cellulose.⁽⁷⁾

Native lignin is considerably more hydrophobic than cellulose, and in fibres exists partly separated from the hydrophilic cellulosic components. In some pulping processes the lignin becomes more hydrophilic by chemical reaction. Therefore its glass transition temperature could be thought to be lowered by water, as has been shown by Goring to be the case for periodate lignin and dioxane lignin.⁽³⁾ The lignin in the structure will certainly interact with the cellulosic compound and make the softening in the fibre or the wood material less distinct.

Also the morphological structure of fibres constructed of fibrils with unevenly distributed chemical components can influence the resulting softening at the glass transition due to anisotropic effects. This means that the softening can be more difficult to evaluate by mechanical methods.

With these drawbacks, the equation of Kaelbe and Fig. 2 can presently serve to summarise the softening effect of water on cellulosic materials.

Appendix

The glass transition temperature is, according to Kaelbe, related to the structural changes in the lattice.⁽⁸⁾ The relation is given by:

$$T_g = \frac{-U_g(Z_L - Z_G)}{\Delta C v_g Z_G} \approx \frac{U}{h}, \quad (1)$$

where T_g is the glass transition temperature, and U_g is the molar cohesive energy at the glass transition temperature, $\Delta C v_g$ is the difference between specific heats at constant volume above and below T_g , and Z_L and Z_G are lattice co-ordination numbers for the rubber state and the glass state respectively. The molar cohesive energy U can be considered to be rather independent of temperature and can be calculated from the cohesive energy density δ^2 and the molar volume v according:

$$U = \delta^2 v. \quad (2)$$

If the cohesive energy density δ^2 is not known, the cohesive energy U can be estimated according to Haye's empirical relation⁽¹⁰⁾ where the contributions of the structural groups to the cohesive energy are added.

If, according to Kaelbe, it is assumed that Hayes's summation of the molar cohesive energies is valid for different molecules in a mixture, equation (1) can be rearranged to read

$$T_g = \frac{T_{gP} X_P + (h_D/h_P) T_{gD} X_D}{X_P + (h_D/h_P) X_D}, \quad (3)$$

where X_P and X_D are the mole fractions for the polymer and the plasticiser respectively, and h_D and h_P are the constants in equation (1) for the plasticiser and the polymer.

For the examination of the approach of Kaelbe the equation (3) has been applied to two systems reported in the literature, using data for system components listed in Table 2.

Fig. 4 shows this comparison for the systems, almost amorphous polyvinyl chloride plasticised with dibutylphthalate, measured by Kargin,⁽¹⁵⁾ and partially crystalline polyhexamethylene adipamide, Nylon 6-6, plasticised with water measured by Woodward.⁽¹⁶⁾ In the calculations, the glass transition temperature of water according to Rasmussen and McKenzie has been set to 136 K.⁽⁹⁾ The crystallinity of Nylon 6-6 has here been calculated to be 44 per cent using the actual density and the densities of a completely amorphous and a completely crystalline Nylon 6-6 given by Starkweather.⁽¹⁷⁾ The plasticising effect must be calculated on the amorphous part of the polymer only. The molar cohesive energy of dibutylphthalate has been estimated from its structure according to Hayes's relation.⁽¹⁰⁾ As is evident from Fig. 4, the approach of Kaelbe describes the two systems sufficiently well.

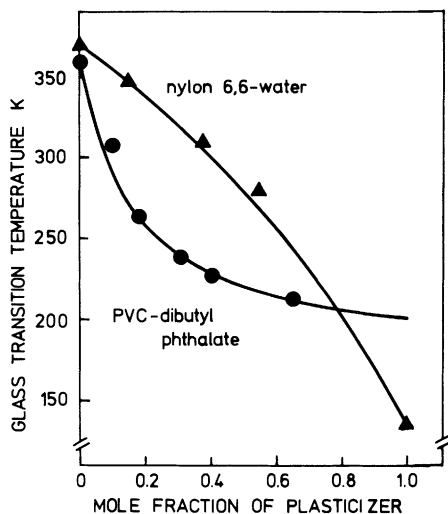


Fig. 4—The glass transition temperature for two polymer-plasticiser systems. The lines are calculated theoretically according to Kaelbe's approach. Symbols give experimental values according to Kargin⁽¹⁵⁾ and Woodward⁽¹⁶⁾

References

1. Kargin, V. A., Kozlov, P. V. and Wang, Nai-Ch'ang., *Doklady Akad. Nauk. SSSR*, 1960, **130** (2), 356-8
2. Alfthan, E., de Ruvo, A. and Brown, W., *Polymer*, 1973, **14**, 329
3. Goring, D. A. I., *Pulp Pap. Mag. Can.*, 1963, **64** (12), T-517
4. Back, E. L. and Didriksson, E. I. E., *Svensk Papperstid.*, 1969, **72** (21), 687
5. Naimark, N. I. and Fomenko, B. A., *Vysokomol. Soyed.*, 1971, **B13**, 45
6. Kaimins, I. F. and Ioelovich, M. Ya., *Vysokomol. Soyed.*, 1973, **B15** (10), 764
7. Kaimins, I. F. and Ioelovich, M. Ya., *Khim. Drev.*, 1974, (2), 10-13
8. Kaelbe, D. H., *Physical Chemistry of Adhesion*, (Wiley Interscience, New York, 1971)
9. Rasmussen, D. H. and MacKenzie, A. P., *J. Phys. Chem.*, 1971, **75** (7), 967
10. Hayes, R. A., *J. Appl. Poly. Sci.*, 1961, **5**, 318
11. Casey, J. P., *Pulp and Paper*, 2nd ed., (Interscience, New York, 1960), **1**, 19
12. Naimark, N. I., Fomenko, B. A. and Ingnatèva, E. V., *Vysokomol. Soyed.*, 1975, **B17** (5), 355
13. Christensen, P. K. and Giertz, H. W., *Consolidation of the Paper Web*, Ed. F. Bolam (Technical Section, B.P. & B.M.A., London, 1966), 59-84

14. Ogiwara, Y., Kuboto, H., Hayashi, S. and Mitomo, N., *J. Appl. Polymer Sci.*, 1970, **14**, 303
15. Kargin, V. A., Slonimsky, G. L. and Roguvina, L. Z., *Colloid J. USSR*, 1957, **19**, 153
16. Woodward, A. E., Crissman, J. M. and Sauer, J. A., *J. Polymer Sci.*, 1960, **44**, 23
17. Miller, R. L., 'Polymer Handbook', (Interscience, New York, 1960) Sect. III, 1-60.
18. Hansen, C. M., Dr.-diss., Danmarks Tekniska Högskola, Copenhagen, 1967

Transcription of Discussion

Discussion

Dr A. H. Nissan Mr Salmén, I was very intrigued with your first curve, which doesn't appear in the preprints, so I didn't have time to study it. It was a very extensive set of data on modulus as a function of temperature. May I have a copy of the data because I would like to see what the slope of the curve was between the log E and temperatures. Have you done any analysis on it?

Salmén We have analysis on it and it agrees with your theory.

Mr T. Lindström The main experimental support for your calculation is the data from Ogiwara *et al.* (*J. Appl. Polym. Sci.* 1970, **14**, 303) on the effects of crystallinity and the moisture content on the glass transition temperature of cellulose. The experimental technique that they used was N.M.R. spectroscopy, by plotting the half-width of the absorption peak versus moisture content they found there was a kink on the curve which they identified as the glass transition temperature. There are two points that I would like to make. Firstly, Carles and Scallan have published a similar paper (*J. Appl. Polym. Sci.* 1973, **17**, 1855), where they claim that the N.M.R. curve is smooth and they could not detect any kinks. My second point is that if such a kink exists how can we be sure that it is due to the glass transition temperature?

Salmén I am not an expert on N.M.R., so I cannot comment.

Prof. R. H. Marchessault Xylan has been shown to exist as a crystalline hydrate with between 1 or 2 water molecules per Xylose unit. The extreme limit of two water molecules would push the value beyond the 15 per cent moisture content that you were considering. We know that even 25 per cent would not be an unreasonable figure to consider. Did you take this into consideration?

Salmén No, we did not.

Under the chairmanship of B. W. Attwood