THERMAL SOFTENING, ADHESIVE PROPERTIES AND GLASS TRANSITIONS IN LIGNIN, HEMICELLULOSE AND CELLULOSE

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Synopsis—The thermal softening of isolated samples of lignin, hemicellulose and cellulose has been investigated by observation of the thermally induced collapse of a column of powder under constant gravitational load. Softening temperatures of lignins ranged from 127–193°C. Birch xylan and pine glucomannan softened at 167° and 181°C, respectively. Sorption of water by lignin and hemicellulose caused pronounced decrease of the softening temperature—in some cases, to as low as 54°C. Softening points of both dry and moist lignins or hemicelluloses have been shown to correlate with the temperature at which the sample develops adhesive properties. The softening and adhesive behaviour has been explained in terms of the concept of the glass transition for amorphous polymers. Sorbed water is considered to act as a low molecular weight diluent in plasticising the polymer chains and lowering the glass transition temperature.

Celluloses were found to soften at temperatures greater than 230°C. In contrast to lignin and hemicellulose, sorption of water by the cellulose had negligible effect on the softening temperature. This difference was probably due to the crystalline nature of cellulose and indicated that water did not plasticise individual cellulose chains at the molecular level.

Introduction

PERHAPS the most important property of an amorphous polymer is its ability to undergo a glass transition. Profound changes in the mechanical behaviour of the polymer occur at the glass transition temperature. When its temperature falls below $-70°C$, rubber is transformed from an elastic material to a hard brittle solid. Polymethylmethacrylate is glass-like at room temperature, but above 70°C it becomes a deformable plastic. The present paper deals with the observation of glass transitions in the macromolecular constituents of wood.

Glass transitions are caused by increases in the movement of the polymer

molecules with increases in temperature. Below the glass transition, the polymer chains are anchored to each other by Van der Waals forces, hydrogen bonds or other attractive forces. Thermal motion is restricted to short chain segments or pendent groups. When the glass transition is approached, the chains acquire sufficient energy for large-scale movement with respect to each other. The glassy state breaks down and the polymer becomes soft or rubbery. For thermoplastic materials, the glass transition temperature is near the thermal softening temperature of the polymer. When a low molecular weight diluent is absorbed by the polymer, the glass transition temperature is usually lowered.[1] The reason for this is that the molecules of the diluent force apart the chains of the polymer and thereby decrease the energy required to allow the chains to develop large-scale molecular motion. Thus, sorbed diluents have a marked effect on the thermal softening of a polymer.

Wood is a mixture of three polymeric species—cellulose, hemicellulose and lignin. Cellulose is partly crystalline, whereas lignin and hemicellulose are considered amorphous. The following questions then arise—

  1. Do the amorphous constituents of wood undergo glass transitions? If so at what temperature do the transitions occur?
  2. Do low molecular weight sorbates such as water lower the glass transition temperature?

In order to answer these questions, some method of observing the glass transition is required. Hemicelluloses and lignins are almost always prepared in the form of powders and as such are not amenable to study by the usual methods applicable to void-free samples of solid polymers. After considerable trial and error, two methods were developed that gave indications of the glass transitions in powdered samples of isolated wood constituents. One involves the measurements of the thermal softening temperature of the powder.[2] In the second method, the temperature at which the powder develops adhesive properties is determined.[3] In subsequent sections of this paper, the two methods are described briefly and some results are discussed.

Thermal softening

THERMAL softening was observed as the collapse of a column of powder under constant load in a heated glass capillary tube. A diagram of the apparatus is shown in Fig. 1 and a photograph of its component parts is given in Fig. 2. The 3 mm internal diameter capillary was packed with the powdered sample. The powder was compressed by a plunger bearing a constant gravitational load of 300 g. The apparatus was placed in an oil bath and the temperature raised by 1.5°C per minute. At low temperatures, the powder sustained the load and the plunger did not move. As the temperature increased,

plunger movement began. At the softening temperature, the plunger moved quite rapidly compressing the powder into a solid plug at the bottom of the capillary. The position of the plunger was noted at 2 min intervals during a run. Fig. 3 shows the length of the plug of powder, normalised to unity,
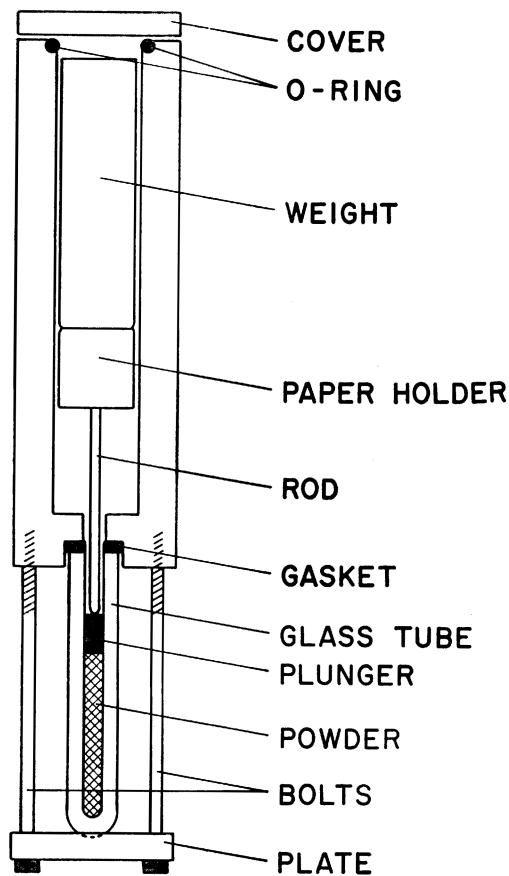

Fig. 1—Diagram of the softening point apparatus
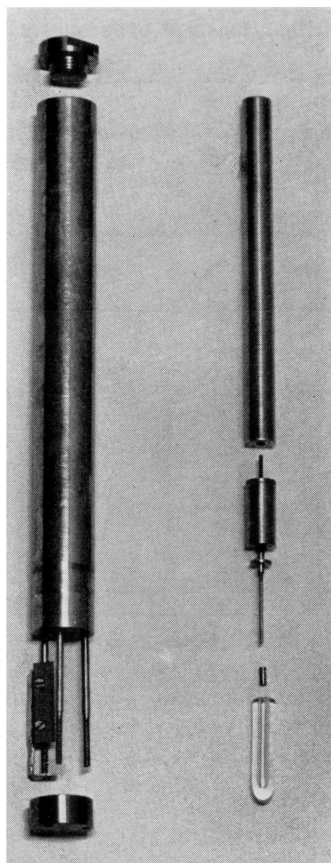
Fig. 2—Photograph of the parts of the softening point apparatus

plotted against the temperature for aspen dioxane lignin. A rapid decrease in length occurs when the column of powder collapses at around 120°C. The velocity of the plunger is also plotted against the temperature in Fig. 3. A sharp maximum is noted at 122°C, which is taken to be the softening temperature of the sample.

The apparatus was sealed to prevent any loss of vapour during a run. Thus, observations could be made on dry samples as well as on samples containing sorbed water vapour. The plunger was slightly fluted to allow free movement of gas. This eliminated back pressure on the plunger as the temperature was increased. In addition, blotting paper equilibrated to the same relative humidity as the sample was enclosed in a paper holder (see Fig. 1) in the body of the apparatus to minimise loss of moisture from the sample itself.
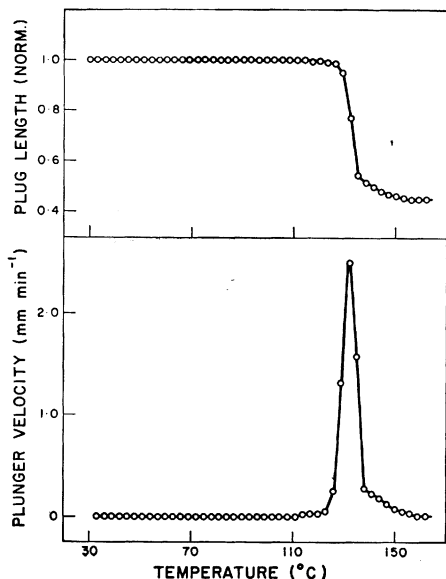
Fig. 3—Normalised plug length and plunger velocity plotted against temperature for dry aspen dioxane lignin
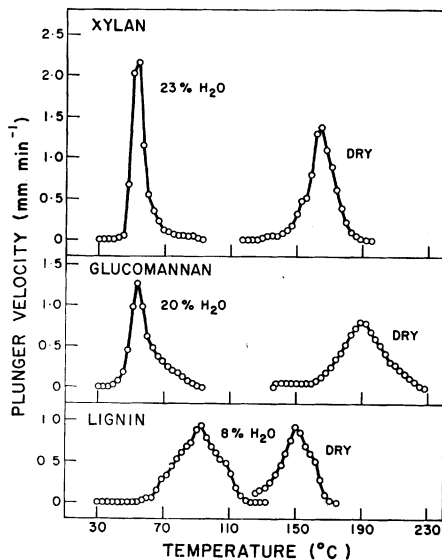
Fig. 4—Plunger velocity against temperature for spruce dioxane lignin III, pine glucomannan and birch potassium xylan both dry and equilibrated over saturated sodium chloride: water contents are shown near the peaks for the moist samples

Particle size was found to have little effect on the softening point measurement and no attempt was made therefore to use a uniform particle size with all samples. Fine powders such as the dioxane lignins were used as prepared. Coarse or fibrous samples were ground to 40 mesh before being used in the powder collapse apparatus. The powder collapse of samples of xylan, glucomannan and dioxane lignin is illustrated in Fig. 4. The softening temperatures were indicated by pronounced peaks in the plunger velocity curves.

Observations were made on dry samples as well as on material equilibrated at room temperature over saturated sodium chloride (76 per cent rh). It is apparent from Fig. 4 that water sorption by the lignin and the hemicelluloses caused a marked decrease in their softening temperatures.

Softening temperatures both dry $(T_s°)$ and moist (T_s) of several isolated lignins and hemicelluloses are listed in Table 1. Lignin shows quite a wide range of $T_s°$ values, the lowest being for spruce dioxane lignin I. This sample had the rather small molecular weight of 4 300, which was probably the reason for its low softening temperature.[2] Dry xylan and glucomannan softened between 165° and 185°C. The bonding temperatures $T_b°$ and T_b given in Table 1 will be discussed later in this paper.

TABLE 1—SOFTENING AND BONDING TEMPERATURES FOR DRY AND MOIST SAMPLES

Sample	Dry (°C)		Water uptake (g/100 g)	Moist (°C)	
	$T_s°$	$T_b°$		T_s	T_b*
Spruce periodate lignin	193	190	12.8	116	70
Birch periodate lignin	179	180	12.2	128	70
Spruce dioxane lignin I	127	110	7.7	72	50
Spruce dioxane lignin III	146	150	7.8	92	90
Aspen dioxane lignin	134	120	7.2	78	
Pine glucomannan	181	170	19.6	56	50
Birch potassium xylan	167	170	23.3	54	40
Sulphite pulp	231	—	12.2	222	—
Kraft pulp	245	—	12.4	239	—
Regenerated cellulose film	244	—	16.0	237	—

* T_b measured on specimens prepared in presence of excess water, then dried

Water uptake over saturated sodium chloride is also given in Table 1. Smallest sorption was shown by the dioxane lignins, yet, not unexpectedly, water uptake by the hemicelluloses was considerably greater. In all cases, the softening temperatures of the lignins and the hemicelluloses were decreased by the presence of water in the sample. The T_s values of about 55°C for the xylan and the glucomannan were particularly low.

Cellulose exhibited uniformly high $T_s°$ values as shown in Table 1. In addition, the softening temperature of cellulose was unchanged by water sorption. As shown in Fig. 5 for sulphite pulp, the plunger velocity curve for the moist sample flattened slightly, but no significant change in T_s was found. It is interesting to note from Table 1 that the pulps absorbed about as much water as the periodate lignins and considerably less than the hemicellulose samples. This result is in agreement with the findings of Christensen & Kelsey.[4]

The results for lignins and the hemicelluloses in Table 1 can be explained by the concepts of molecular motion in amorphous polymers outlined in the
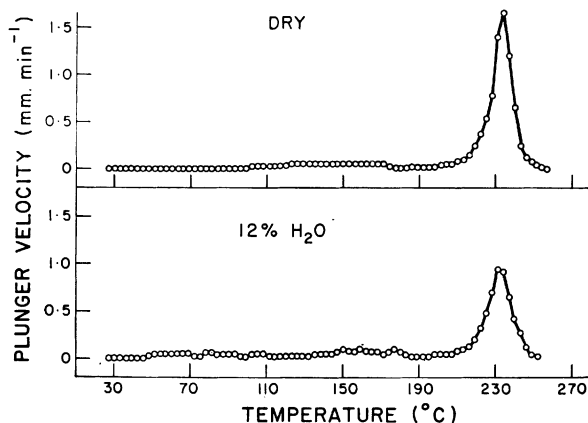
Fig. 5—Plunger velocity against temperature for sulphite pulp both dry and containing 12 per cent water

introduction. $T_s^°$ may be regarded as a glass transition temperature. Water acts as a low molecular weight diluent and lowers the glass transition temperature by plasticising the molecular chains of the lignin and the hemicellulose.

A quantitative treatment of the effect of a diluent on the glass transition temperature of a polymer has been given by Fujita & Kishimoto.[5] Their equation is—

$$Tg^° - Tg = (\beta/\alpha_2)C \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where $Tg^°$ = glass transition temperature of dry polymer,
  Tg = glass transition temperature of polymer containing diluent,
  C = concentration of diluent in g/g,
  α_2 = change in thermal expansion coefficient below and above Tg; $\alpha_2 = 4.8 \times 10^{-4}$ per °C,
  β = parameter representing the contribution of the diluent to the increase in free volume.

If $T_s^°$ and T_s values represent glass transition temperatures, then equation (1) should be applicable to the present results. In Fig. 6, data for many samples are plotted as the lowering of the softening temperature against the water uptake. It is seen that the points for lignins and hemicelluloses lie approximately on a straight line with slope corresponding to $\beta = 0.27$, which is reasonably close to the values of 0.37 and 0.30 found by Fujita & Kishimoto

for water sorbed on to polyvinyl acetate and polymethyl acrylate, respectively.[5] This agreement supports the concept that sorbed water acts as a diluent in lowering the glass transition temperatures of the amorphous components of wood.

As expected, the points for celluloses in Fig. 6 are well off the straight line through the points for the lignin and hemicellulose samples. Undoubtedly, the reason for this is the high crystallinity of cellulose. Recently, Manley[6] has proposed that the cellulose microfibrils are single crystals. Thus, it is possible that the softening temperatures of dry cellulose in Table 1 are, in fact, crystal melting points. Water cannot penetrate the cellulose lattice. Therefore, water would not plasticise individual cellulose molecules, but would be sorbed on to the surface of the crystalline microfibrils. If the
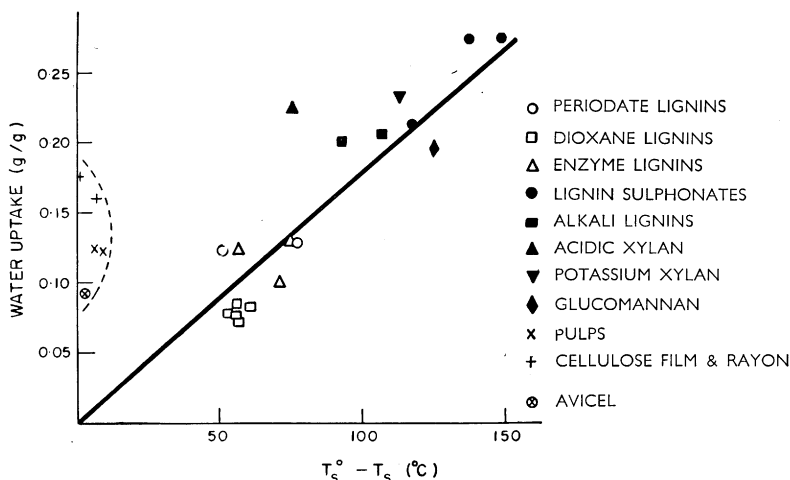
Fig. 6—Graph of $(T_s^\circ - T_s)$ against water uptake over saturated sodium chloride for several samples of lignin, hemicellulose and cellulose

cellulose contains regions in which the chains are disordered, water would penetrate these regions and perhaps plasticise sections of a particular chain; but other parts of the chain would be anchored in the crystalline regions and therefore would not be reached by the absorbed water molecules. Large-scale thermal motion of the chain would in consequence be unaffected by the presence of water in the cellulose.

The thermal softening and steam plasticising of lignin has been discussed by several authors in earlier papers. Lignin melting has been observed by Kleinert & Tayenthal[7] and by Björkman & Person.[8] Importance of the thermoplastic behaviour of lignin has been recognised in the mechanical defibring of wood,[9-11] chemical pulping,[8,12] wood stabilisation[13,14] and

the strength of veneers,[15] but there have been very few previous measurements of the actual softening temperatures of isolated lignins. Even less consideration has been given to the thermoplastic behaviour of the hemicelluloses. In part, this must be due to the fact that only recently have these non-glucan polysaccharides been prepared in relatively pure form. Cafferty, Glaudemans & Marchessault[16] have reported a softening temperature of 150°C for an O-acetyl glucuronoxylan from birch. This is in fair agreement with the T_s° value of 167°C in Table 1, considering the differences in the method of preparation of the two samples.

Adhesive properties

MARK *et al.*[17] have pointed out that the tack temperature of a polymer is one manifestation of the glass transition phenomenon. If two pieces of a polymer are brought into contact below the glass transition temperature, there can be no intermolecular diffusion of the chains from one surface to the other, because the chains are frozen. Thus, adhesion does not take place.
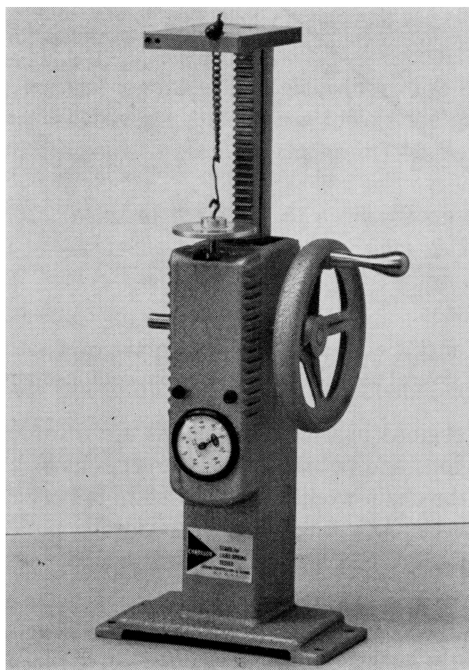

Fig. 7—Photograph of the Chatillon spring tester arranged to measure the force required to rupture a specimen

Above the glass transition, the polymer chains are mobile and can interpenetrate when the surfaces are pressed into contact. If the joint is then cooled, adhesion will occur. The temperature at which a plastic becomes tacky might be expected, therefore, to be in the vicinity of the glass transition temperature.

An interesting question is whether or not the amorphous components of wood show tack temperatures. This point was elucidated by recent work on the adhesive properties of lignin.[3] The method of measurement was to sandwich lignin powder between two $\frac{1}{2}$ in circles of filter paper, press the sandwich at various temperatures, then measure the force required to pull the

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SCOTCH TAPE OR
DENTAL CEMENT

LIGNIN OR
HEMICELLULOSE
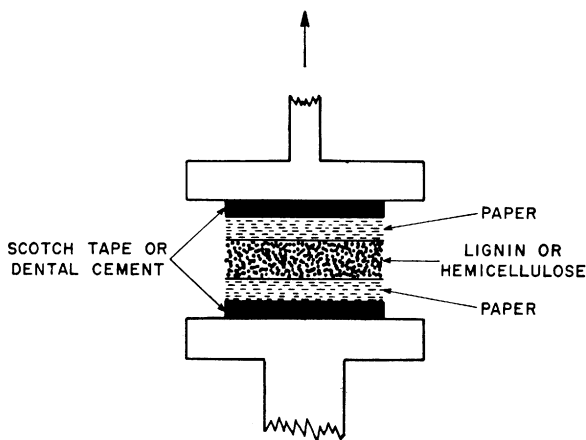
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Fig. 8—Diagram of a paper–lignin–paper sandwich: it was sometimes necessary to secure the specimen with dental cement rather than adhesive tape, because of the greater bond strength developed when hemicellulose was examined instead of lignin

pieces of filter paper apart. Pressing was done between two thermostated hot plates at temperatures ranging 25°–250°C and at a pressure of 1 260 g/cm². Specimens were then tested on the spring tester shown in Fig. 7. A drawing of the specimen mounted for testing is given in Fig. 8. The bond strength was the force per unit area required to rupture the sandwich. Specimens were pressed dry and soaking wet. Before testing, the specimens pressed wet were dried overnight in a stack of 200 sheets of filter paper.

An example of the type of data obtained is given in Fig. 9 for spruce dioxane lignin I. When pressed dry, the lignin developed bonding properties at around 130°C. The bonding temperature was lowered by 60°C when the lignin was pressed wet. The close parallel with the thermal softening behaviour is apparent.

The method was applied also to xylan and glucomannan. Some modifications were necessary. With lignin, the wet sandwich was made by suction of an aqueous suspension of lignin through the circle of filter paper, then placing a second wet piece of filter paper on the lignin layer to complete the sandwich.[3] A more convenient method with the hemicelluloses was to spread a paste of 2 parts water to 1 part hemicellulose on to a wet circle of filter paper, sandwich with a second wet circle of filter paper, then press at various temperatures. The pressing time of 15 min used with lignin was reduced to 5 min with xylan and glucomannan. The wet hemicelluloses above their softening temperatures were found to flow very readily and the longer pressing time was unnecessary. Besides, the bond strengths developed by the hemicelluloses were much greater than the paper–lignin–paper bond. Therefore, a stronger filter paper (Whatman No. 42) was used, which was secured by dental cement rather than the double-sided adhesive tape used for lignin sandwiches.

Graphs of bond strength against temperature of pressing are given in Fig. 9 for xylan and glucomannan. When pressed dry, the hemicelluloses bonded at temperatures above 170°C. In the wet state, bonding occurred at all temperatures of pressing, but the bond strength more than doubled at about 50°C, indicating a marked sudden increase in bonding at this temperature. Above 60°C, the wet pressed hemicellulose samples behaved like glue and bonded the two sheets so strongly that rupture invariably occurred in a paper layer.

The bond strength developed by some of the wet pressed lignin powders tended to decrease above 100°C. This was particularly evident for spruce and birch periodate lignin.[3] A likely explanation of this effect was that the water evaporated from the wet sandwich at the same time as the damp powder softened. At higher temperatures, evaporation may have taken place so quickly that the lignin dried before it had time to flow and thus to develop maximum adhesion.

It is interesting to compare the thermal softening temperature with the temperature at which bonding was produced or suddenly enhanced in a sample. This is illustrated in Fig. 9 by the proximity of T_s° and T_s (arrows) to the upward sloping portions in the graphs of bond strength against temperature of pressing. In Table 1, the minimum temperature at which bonding occurs is given both for the samples pressed dry (T_b°) and soaking wet (T_b). In the case of the hemicelluloses, T_b corresponds to the temperature at which a sudden increase in the bond strength occurred on wet pressing. Exact agreement between the bonding temperature and the softening temperature was not expected, because of the very different nature of the tests, but the correlation in Table 1 is good enough to indicate strongly that these two important phenomena arise from glass transitions in the lignins and the hemicelluloses.
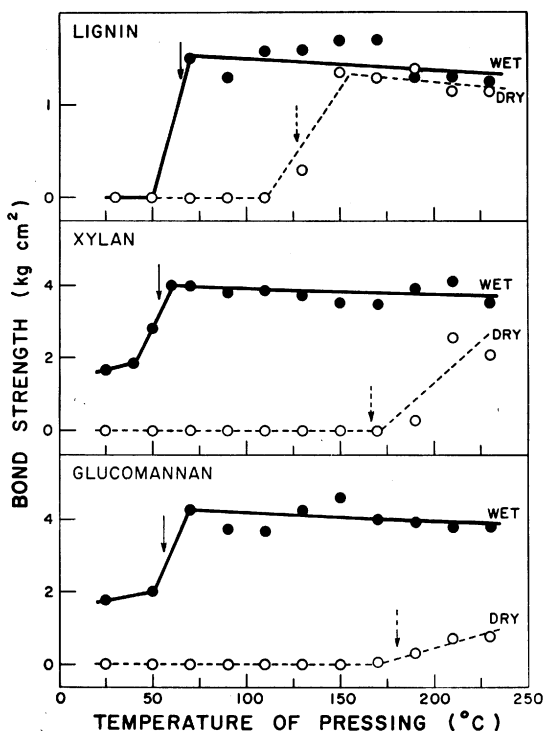
Fig. 9—Bond strength against temperature of pressing for spruce dioxane lignin I, birch potassium xylan and pine glucomannan: the dotted lines and hollow circles are for dry pressing; the solid line and filled circles are for pressing wet; softening temperatures of the dry samples are shown by the dotted arrows; the solid arrows are the T_s values at 10.7, 23.3 and 19.6 per cent of water for lignin, xylan and glucomannan, respectively

Discussion

PULP for papermaking is mostly cellulose, but it almost always contains some hemicellulose, frequently some lignin, too. These two amorphous constituents may comprise up to 40–50 per cent of a finished sheet of newsprint. On the papermachine, the sheet is consolidated by a rapidly varying pattern of temperature, pressure and moisture content. It is quite possible that in the dryers and calender stacks, temperatures and moisture contents are reached that correspond to the glass transition conditions of the amorphous

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components of the sheet. Remember that the softening temperature of birch xylan containing 23 per cent water is only 54°C. If the sheet is subjected to pressure while one of its macromolecular components is undergoing a glass transition, it is likely that the density, opacity and strength of the finished sheet will be affected.

It may be argued that the time intervals during which the sheet is held in the various nips of the drying and calendering sections are rather short—too short for the hemicellulose and lignin to be altered by glass transition phenomena. Mechanical relaxation times are remarkably temperature-dependent in the region of the transition. An increase of 20°C can alter the time scale of a particular physical effect by a factor of 10^6—that is, from seconds to microseconds.[18] Therefore, the temperature of the sheet at every stage in the papermachine will have an important bearing on the properties of the finished sheet.

An interesting principle emerges from a comparison of the temperature dependence of chemical reaction rates and of physical relaxation. The rate of an average organochemical reaction is doubled for every 10°C rise in temperature. This means that undesirable degradation of the wood constituents will be accelerated by a factor of 2 for each 10°C increment. Relaxation times decrease a thousandfold for an increase in 10°C near the glass transition. Thus, if it were feasible to heat the sheet up very rapidly, manipulate it under pressure and then cool it down rapidly, it might be possible to take advantage of the thermoplastic properties of the hemicellulose and the lignin without incurring the penalty of excessive degradation.

Let us now consider the failure of cellulose to be plasticised by water in the powder collapse apparatus. This was interpreted to mean that absorbed water does not increase the facility with which individual molecules of cellulose move with respect to each other. On the other hand, water appears to plasticise cellulose fibres in certain other types of observation. Robertson found that heating dry fibres decreased the extent to which they would re-swell when placed in water.[19] The decrease in reswelling capacity was greater as the time, temperature and the relative humidity at which the treatment was administered was increased. Robertson interpreted the effect as being due to the relaxation of frozen-in stress developed during drying. Increased humidity favoured a more rapid relaxation of the frozen-in stresses, because of the plasticising effect of the sorbed water. It seems likely that the stress relaxation takes place at the fibrillar rather than at the molecular level. The compound helical structure of the fibre will have a certain number of configuration-retaining linkages between adjacent microfibrils. These may be heat and moisture labile. When these linkages are broken, microfibrils may then move with respect to each other into more energetically favourable configurations.

Interfibrillar stresses are thereby released. A further example of the heat-labile interfibrillar linkages is given by the measurement by Stone & Scallan of the internal surface area of fibres.[20] The very large specific surfaces (140–200 m^2/g) of water-swollen solvent-exchanged fibres decreased progressively as the temperature was raised until, at 180°C, the specific surface was only 20 m^2/g. Stone & Scallan suggest that the decrease in surface area is due to pore closure, which occurs when the interfibrillar bonds supporting the open aerogel configuration are broken progressively by the applied heat. Thus, the loss of internal surface on heating is probably due to thermally induced shrinkage at the microfibrillar level. In contrast, the present results indicate that the powder collapse method measures transitions at the molecular level at which sorbed water has no effect on the large-scale motion of individual cellulose chains.

Finally, we may question the relevance of glass transitions to the interfibre bond. The adhesion experiments indicate that stronger bonding occurs above the glass transition temperatures of dry or moist hemicelluloses and lignin. With cellulose, the transition is above 230°C and is not lowered by moisture, yet wet pulp fibres bond readily when dried at room temperature. This supports the well-known concept of a low molecular weight hemicellulose glue on the surface of the crystalline microfibrils that causes the fibres to bond together when dried from water. Stone[21] has shown that the specific energy of bond failure increases when the xylan content of the fibre increases up to 20 per cent of xylan. Sorption of xylan on to a fibre under the conditions of a kraft cook has been conclusively demonstrated by Clayton & Stone[22] and Luce[23] has detected recently, by a chemical peeling technique, a hemicellulose-rich layer on kraft fibres. The notoriously poor papermaking properties of cotton and high alpha-content pulps may possibly be due to absence of hemicellulose on the fibre surface. In addition, perhaps the glue can consist of a layer of low molecular weight, disordered cellulose molecules on the surface of the fibre. This may explain the bonding properties of hollow filament rayon observed by Robertson.[24]

Notwithstanding the plausibility of the above concept, the nature of the cellulose interfibre bond is yet to be elucidated. Remaining questions can be stated thus—

1. Are cellulose fibres in paper held together by amorphous materials or is there some other mechanism of bonding?
2. If the bonding principle is amorphous, is the bond strength influenced by second order transition phenomena?

The answers to these questions are at present being sought in these laboratories.

Acknowledgements

References

1. Bueche, F., *Physical Properties of Polymers* (Interscience Publishers, New York, 1962)
2. Goring, D. A. I., *Pulp & Paper Mag. Can.*, 1963, **64** (12), T517–527
3. Gupta, P. R., Rezanowich, A. and Goring, D. A. I., *Pulp & Paper Mag. Can.*, 1962, **63** (1), T21–T30
4. Christensen, G. N. and Kelsey, K. E., *Austral. J. app. Sci.*, 1958, **9** (3), 265–282.
5. Fujita, H. and Kishimoto, A., *J. Polymer Sci.*, 1958, **28** (118), 547–567
6. Manley, R. St. J., *Nature*, 1964, **204** (4964), 1155–1157
7. Kleinert, T. and Tayenthal, K. von, *Angew. Chem.*, 1931, **44** (39), 788–791
8. Björkman, A. and Person, B., *Svensk Papperstidn.*, 1957, **60** (8), 285–292
9. Lagergren, S., Rydholm, S. and Stockman, L., *Svensk Papperstidn.*, 1957, **60** (17), 632–644
10. Luhde, F., *Pulp & Paper Mag. Can.*, 1960, **61** (11), T544–552
11. Atack, D. and Pye, I. T., *Pulp & Paper Mag. Can.*, 1964, **65** (9), T363–T376
12. Kleinert, T. N. and Marraccini, L. M., *Tappi*, 1964, **47** (10), 605–609
13. Baird, P. K. and Schwartz, S. L., *U.S. Forest Products Laboratory Report No. D*1928 (1952)
14. Stamm, A. J., *U.S. Forest Products Laboratory Report No.* 2129 (1960)
15. Higgins, H. G., *Austral. J. appl. Sci.*, 1953, **4** (1), 84–97
16. Gafferty, Patricia D., Glaudemans, C. P. J., Coalson, R. and Marchessault, R. H., *Svensk Papperstidn.*, 1964, **67** (21), 845–849
17. McLaren, A. D., Li, T. T., Rager, R. and Mark, H., *J. Polymer Sci.*, 1951, **7** (5), 463–471
18. Ferry, J. D., *Viscoelastic Properties of Polymers* (John Wiley, New York, 1961)
19. Robertson, A. A., *Pulp & Paper Mag. Can.*, 1964, **65** (3), T161–T168
20. Stone, J. E. and Scallan, A. M., *P.P.R.I.C. Technical Report* No. 382 (1964)
21. Stone, J. E., *Pulp & Paper Mag. Can.*, 1963, **64** (12), T528–T532
22. Clayton, D. W. and Stone, J. E., *Pulp & Paper Mag. Can.*, 1963, **64** (11), T459–T468
23. Luce, J. E., *Pulp & Paper Mag. Can.*, 1964, **65** (10), T419–T423
24. Robertson, A. A. and Mason, S. G., *Formation and Structure of Paper*, Ed. F. Bolam (Technical Section, B.P. & B.M.A., London, 1962), 639–647

Discussion

Dr O. L. Forgacs—We were interested in following up Goring's work on thermal softening in connection with a number of practical problems. To facilitate measurements, Gartaganis (of our laboratory) modified Goring's apparatus by adding to the top an extension that consisted of a transformer with a moving soft iron core. The core follows the position of the plunger and the resulting signal variation is rectified, amplified and recorded on a chart recorder. The plunger movement is amplified 15 times on the chart as the material softens.

With this gadget, we could obtain expanded thermal softening traces that are quite reproducible and quite different for different forms of lignin. Moreover, the curves are more complex than those of Goring's Fig. 3.

Apart from the general importance of taking thermal softening of papermaking materials into account, we consider this to be the essence of an analytical tool for polymers, the scope of which remains to be explored and evaluated.

Prof. A. E. G. Björkman—Compliments to Goring for another fine contribution to the physical chemistry of the main constituents of wood. Such results help us to understand better the behaviour of these materials as polymers, which is the one fundamental from which I believe we shall gain more during the next few years, particularly in woodpulping.

Equation (*1*) contains the parameter β, which concerns the increase in *free volume* that is connected with the solvent uptake. This concept is not commented on in detail. So far as I know, a solvent's plasticising effect can be explained solely by the extra free volume it introduces into a system, which gives polymer segments a better chance to move. It is important to know that this is the inherent result of the fibre separation mentioned in the paper.

I do not doubt that Goring's observations on T_m have a close connection with T_g, but is it correct to say that the actual T_g is measured? Most polymers show no change in macroscopic appearance when T_g is exceeded, but they become less brittle. In my experience, lignin seems to undergo a change that looks more like a T_m. Is there any chance of observing T_g, maybe at α and β

transitions, etc. by refined methods like NMR? On the other hand, if you have observed the real T_g values, is it possible to speak also about T_m values?

Finally, is not the large difference between the elongated hemicellulose molecules and the 'snake cages' of the lignin highly significant when it concerns their respective influence on fibre properties?

Dr H. G. Higgins—I have been interested in Goring's work over the last few years, because it gives a scientific explanation of various observations that we and many other people have made. In 1946, I published a paper in which the temperature range in the vicinity of 160°C was found to be quite critical for the plastic behaviour of dry plywood in compression as measured by residual deformation. At that time, I had no idea of the Asplund process. When I became aware of it, it seemed to me that the observations we had made could fit in very well with the effect of temperature in this process. In addition, we have recently studied the effect of temperature on the properties of neutral sulphite semi-chemical pulps and this work is being reported in *Tappi*. We have found certain critical effects in the vicinity of the lignin softening point, which may be explicable in terms of Goring's observations.

Dr D. A. I. Goring—I was very interested to read Back's contributions, particularly to see his Fig. 2 (page 570) in which there is an indication, because of the differences in the springback of a pressed pad, of a transition at 50°C that would perhaps correspond to a hemicellulose transition.

We have not made measurements of bonding in kraft paper, although interesting results might be found in the dry state. We did make adhesive measurements with milled cellulose and groundwood: they bonded very well when pressed wet at room temperature.

Then there is Hudson's crucial question. We all know, of course, that the cellulose fibre is plasticised by water: every housewife who irons knows this. Robertson has plenty of evidence for this; so have Stone and others. We think that our method measures the plasticisation of molecules by water and that Manley and others are right when they say that the elementary microfibril of cellulose is a single crystal and cannot be penetrated by water. Therefore, we think that our measurements are consistent with the fact that water does not plasticise cellulose at a molecular level. If I sound dogmatic, it is because I am nervous.

How, then, does water plasticise cellulose? It does so at the microfibrillar level. Instead of the bonds between molecules being loosened by water, bonds between microfibrils are loosened. If the fibre is then heated, deformed and dried, the intermicrofibrillar bonds form in different places and you have a differently shaped fibre. In this respect, the glass transition of cellulose may

not be very different from a glass transition of hemicellulose in origin. Significantly, Manley has recently shown that regenerated celluloses and celluloses precipitated from solution consist largely of 35 Å microfibrils.

I was glad to hear Forgacs' comments, because I have been very interested in his modification of our softening point device. His laboratory is producing plenty of reproducible data with this machine and their interpretations will be interesting.

In answer to Björkman's three points, yes, β is a parameter related to the free volume given to the system by the absorption of a low molecular weight diluent. It is the increase in the free volume that causes the lowering of the glass transition, although one would expect that, for a particular diluent molecule such as water and a particular type of polymer, the value of β would be about the same. From our paper, it is evident that we studied a wide range of wood constituents and obtained approximately equal values of β for the hemicelluloses and lignins.

It is also true that the glass transition itself is not necessarily equal to the transition detected mechanically. In fact, physical chemists like to think of a glass transition as a second order transition in volume in the graph of volume plotted against temperature. Thus, the glass transition detected dilatometrically does not occur at a temperature exactly equal to the thermal softening temperature, but I think that the majority of data in the polymer literature shows that the two transitions are rather close together. Additional second order transitions in volume also occur at temperatures much lower than the glass transition. In fact, the thermal expansion results I referred to earlier in the meeting arose out of an investigation of low temperature second order transitions in wood polymers. We found a transition in cellulose at about 25°C, which supported the recent work of Waba & Aziz.

On the question of the shape of the lignin and the hemicellulose molecules, it is likely that differences in the physical properties of lignins and hemicelluloses are dependent on the fact that the lignin molecule is spherical like a football and, in contrast, the hemicellulose molecule is extended like rather stiff string.

Finally, I apologise for misquoting from Higgins' paper: I will read it again. I was glad to learn that he has found results that supported our work.