

Prepared contributions

Effect of temperature on the compressibility of wet pulp pads— E. L. Back and K. G. Norberg, Central Laboratory, Swedish Fibre Building Board Industry, Stockholm

A GLASS transition temperature or a particle softening of certain pulp components will affect the compressibility of wet pulp pads. The strength of the paper products may also be affected, this strength comparison being made on products of equal density.

The data presented here refers to a mechanical Asplund pulp of 670 CSF, defibrated at a pressure of 10 atm with about 5 per cent loss in hemicelluloses. Pulp pads were pressed between 18 mesh wires in a hydraulic plane press with thermostated, oil-heated press platens and the gap width between the plates was recorded continuously. The press was loaded rapidly to various pressures—for example, from 8 to 200 kgf/cm² in 10 sec—the press water being removed effectively. After attaining constant gap width, the press was unloaded to 8 kgf/cm². The initial moisture ratio of the pads was 6.0 and the moisture ratio after pressing evaluated. The temperature in the pads was recorded as well.

Fig. 1 shows the gap width per dry unit of substance as a function of the press temperature at four levels of final press loads. The gap width decreases—that is, the compressibility increases fairly continuously with increasing pad temperature. Fig. 2 shows the percentage springback on deloading calculated as a percentage of the gap width under load as a function of the temperature and at various levels of moisture ratio after pressing. This springback falls off with temperature, apparently more rapidly above 50°C. The change in slope of the curve at 50°C is most significant at low moisture ratio. Since the relationship between the press opening at final load and the final moisture ratio of the pad was found to be independent of temperature, as expected, each level of moisture ratio corresponds to a given level of press opening at final load. Similar data at much lower moisture contents have been published by Jackson.⁽¹⁾

After drying the pads in hot air at 105°C and recording at 65 per cent rh equilibrium, their density at a given gap width in the press under final load still showed a significant effect of press temperature as shown in Fig. 3.

The tensile strength is of course primarily an effect of product density. Thus, to evaluate the bonding achieved, graphs of tensile strength against the press temperature should be presented at constant density levels. The left side of Fig. 4 refers to the experiments described above. At higher product densities, there appears to be a definite increase in strength with press temperature employed. The right side of Fig. 4 refers to experiments in which the pads were dried in the press and the press loads were varied with time of pressing.

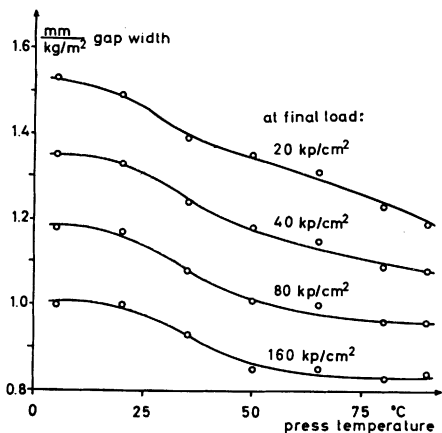


Fig. 1—The compressibility of pulp pads presented as gap width per unit of substance against the pad temperature at various levels of final press load

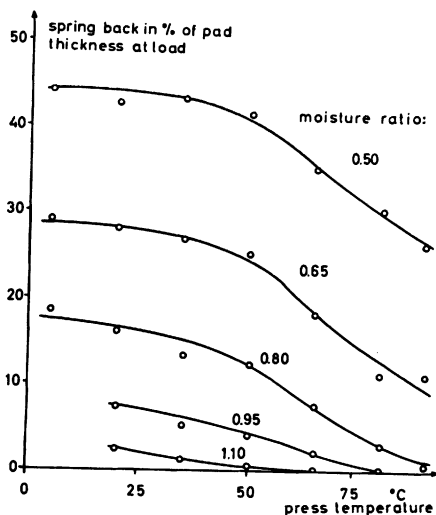


Fig. 2—The springback on deloading in percentage of pad thickness under load against the pad temperature data are given at five levels of moisture ratio in the pad, corresponding to gap widths 0.70, 1.00, 1.20, 1.35 and 1.50 mm per kgf/m²

Effects of cross-linking of cellulose ^(2,3) in these experiments were held at a minimum. A pulp of 760 CSF was used. Paper products of equal density here show significantly higher tensile strength with higher press platen temperatures. The bonding temperatures, assumed to correspond to 10–20 per cent pad moisture were in excess of 100°C, though they were of course lower than the press platen temperatures given in Fig. 4 and may be evaluated approximately from the experiments. For two of the measurements, the minimum bonding temperature is indicated in Fig. 4.

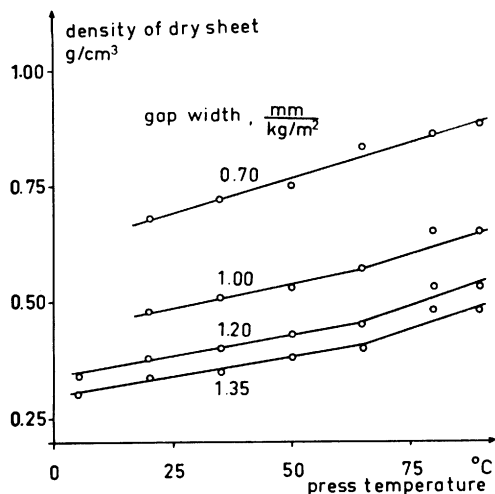


Fig. 3—The density of the pressed pads of Fig. 1 and 2 after hot air drying and conditioning at 65 per cent rh plotted against the press temperature employed; data given at various gap widths under final load

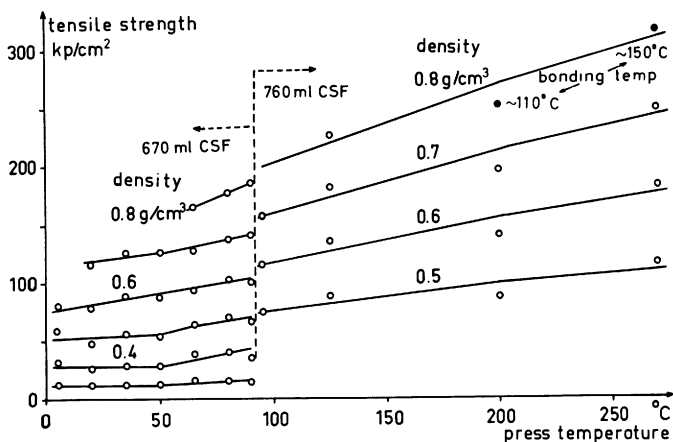


Fig. 4—The tensile strength of products against the press temperature, presented at various levels of product density: the left side refers to hot air drying after pressing (that is, to the pads of Fig. 3); the right side refers to drying in the press under load and, for two experimental points, the approximate bonding temperature is indicated

References

1. Jackson, M. and Ekstrom, L., *Svensk Papperstidn.*, 1964, **67** (20), 807-821
2. Back, E. L. and Klinga, L. O., *Svensk Papperstidn.*, 1963, **66** (19), 745-753
3. Back, E. L. and Klinga, L. O., *Tappi*, 1963, **46** (5), 284-288

**Dr F. L. Hudson, College of Science and Technology,
Manchester**

THE MOST surprising thing in the author's results is the high moist softening temperatures obtained for sulphate and kraft pulps and regenerated cellulose film. By measuring stress/strain relationships on fibres and yarns, Bryant & Walters⁽¹⁾ concluded that the glass transition temperatures of moist cotton, viscose rayon and wool fibre were below 0°C, though the glass transition temperatures for dry fibres were above 200°C. These figures will account for ironing properties, settability and general thermoplastic properties of moist cellulose,⁽²⁾ whereas Goring's figures would not. Is it possible that the apparatus he has used is making a distinction between fibrous and non-fibrous powders and failing to record a low glass transition for reasonably pure moist cellulose?

References

1. Bryant, G. M. and Walters, A. T., *Textile Research J.*, 1959, **29**, 215
2. Barkas, W. W., *The Mechanical Properties of Wood and Paper*, Ed. R. Meredith, (North-Holland Publishing Co., 1953), 54-55

Transcription of Discussion

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 paper-making 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

Discussion

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.