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THE EFFECT OF CELLULOSE ON THE STRUCTURE OF WATER: VIEW 2

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Synopsis The sonic tensile modulus (E) of paper decreases with moisture content (m). The slope of the decrease, $d \ln E/dm$, is constant up to a moisture content equal to the fibre saturation point of paper. This phenomenon seems consistent with the multilayer adsorption of water and its explanation provided by the polarisation theory of Polanyi. The energies of interactions between layers of adsorbed water indicate that hydrogen bonds between layers may contribute to the load carrying capacity of wet paper. This hydrogen bonding between layers implies a structured organisation throughout the adsorbed water that extends several layers from the cellulose surface. In this way, it appears that water near a cellulose surface is structured by the cellulose surface rather than destructured by it. One such model for structured water is presented.

Introduction

BASED largely on dilatometric measurements of wet and dry cellulose and related materials such as glucose, Ramiah and Goring(1, 2) proposed a model for water in the vicinity of a cellulosic surface. That model utilises the 'flickering cluster' concept of water introduced by Frank and Wen.(3) In Goring's model it is envisioned that the normal clustered arrangement of liquid water is altered by the cellulose surface. The usual hydrogen bonding among water molecules is viewed as limited to clusters some distance from the surface. The molecules in contact with the cellulosic surface are pictured as tightly bonded to the cellulose, but unbonded to the outer layers of water. In the sense that the local concentration of 'unbonded' water is increased by the presence of cellulose, cellulose is said to destructure the water.

Recent research on solutions of monosaccharides has uncovered evidence that strongly questions these conclusions. Using both dielectric and nuclear

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magnetic relaxation measurements, Tait and co-workers(4) found that the relaxation time of bulk water in glucose solutions is greater than that in pure water. Although the increase in relaxation time is small, it is significant and implies that glucose is surrounded by lattice water. In the sense that the local concentration of bonded water is increased by the presence of a glucose molecule, glucose is classified as a structure-maker. This conclusion is directly opposite to the hypothesis of Ramiah and Goring.

The model that Tait and co-workers employs to explain the structuring effect of glucose involves the placement of the pyranose ring into the tridymite structure of water with only slight distortions of the water lattice.(5) The oxygens on carbon atoms C_1 to C_4 of the pyranose ring replace four oxygens in the water lattice, forming strong hydrogen bonds with the water molecules in planes above and below the chair conformation of the pyranose ring. If such a model is valid for glucose, it is reasonable that the surface of cellulose, composed of anhydropyranose rings, can also be accommodated into the water lattice, augmenting the bonded clusters nearby and structuring the water.

The question of whether glucose molecules increase or decrease the hydrogen bonding of the nearby water molecules is unresolved. Ramiah and Goring's indirect method through dilatometry indicates structure-breaking, while Tait and co-workers' more convincing direct measurement of relaxation times indicates structure-making. There appears to be an alternate method for evaluating the effect of cellulose on water structure. Cellulose is a solid and what Nissan(6, 7) calls a 'hydrogen bond dominated solid'—a solid whose density of hydrogen bonds controls its tensile modulus. Measuring the effect of water on tensile modulus of cellulose to very high levels of moisture content can reveal something about the nature of water in the vicinity of a cellulosic surface.

Experimental

MEASUREMENTS have been made of the tensile modulus of paper as a function of moisture content. These measurements were made by a sonic pulse propagation technique at a frequency of 5 kHz.

The speed of sound propagation through kraft paper was determined by the multipoint method using the H. M. Morgan Co. Dynamic Modulus Tester PPM-5R over a wide range of moisture contents. The velocity was converted into a 'sonic' modulus by multiplying by the actual measured density of the sheet. The moisture content was varied over a wide range. The fibre saturation point was measured by the nonsolvent water method or polymer exclusion method introduced by Stone and Scallan.(8) In the version used (developed by Feist and Tarkow(9)), polyethylene glycol 9 000 is used as the excluded polymer.

Results and discussion

THE effect of water on modulus, although initially surprising, seems consistent with the polarisation theory of Polanyi,(10) and indicates a multilayer type of adsorption in which the water is structured by the surface of cellulose rather than destructured by it.

Fig. 1 is a plot of the natural logarithm of the modulus ratio—that is, the modulus of paper divided by its modulus at 50 per cent RH *vs.* the moisture content of the paper (weight of water/weight of dry fibre). This plot shows that as the moisture content increases, the logarithm of the tensile modulus drops off sharply with a constant slope all the way out to a moisture content equal to about 76 per cent.

This type of behaviour is entirely consistent with the hydrogen-bonded nature of paper. Nissan has shown(11) that the tensile modulus E of a hydrogen bonded network, such as paper, is simply proportional to the cube root of the number of effective hydrogen bonds per unit volume (n).

$$E = kn^{1/3}$$

Nissan's development also predicts the type of logarithmic drop-off of modulus with moisture content (m) that is observed.

$$\ln \frac{E}{E_{50}} = -Km$$

For paper, it is intuitively understandable that the tensile modulus must depend only upon the hydrogen bonds, because we know that the only connections between fibres or between fibrils within the cell wall are through hydrogen bonds. The initial modulus—that is, just the first part of the stress–strain curve—is determined by the weakest bonds in the system.

When kraft paper is modified by the introduction of chemical cross-links, similar results are found. The initial modulus still shows the same drop-off

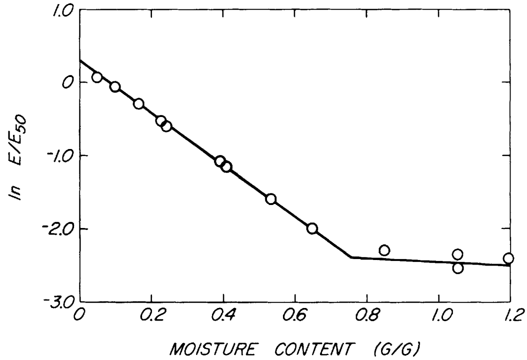

Fig. 1—Tensile modulus ratio of wet paper

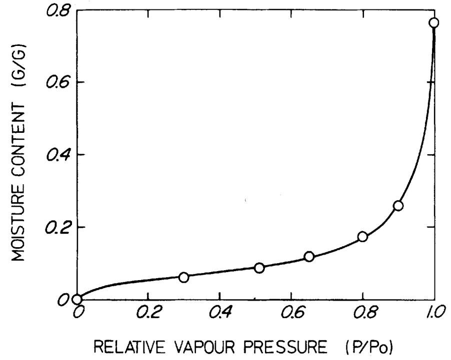

Fig. 2—Water sorption isotherm of kraft paper

with moisture content, but the break in the line occurs at a much smaller moisture content. The role of crosslinks in affecting this wet stiffening of paper is discussed in another section.(12)

The remarkable aspect of Fig. 1 is that the straight line extends all the way out to a moisture content of almost 80 per cent. This straight line means that the last 10 per cent moisture (say, moisture between 65 per cent and 75 per cent) has the same quantitative effect in reducing the ln of the tensile modulus as has the first 10 per cent moisture. That's remarkable in that we know that the last 10 per cent water is not even in contact with the cellulose, but is water in contact with only other water molecules.

The water adsorption isotherm for this kraft paper is a rather typical isotherm for cellulose (Fig. 2). The value for the moisture content at saturation is a real measurement, not an extrapolation. It is measured by the polymer exclusion method. It is interesting to note that this fibre saturation point has a value of 78 per cent, almost identical to (in fact, within experimental error of) the value at which the break occurs in the ln modulus plot (Fig. 1).

This agreement between fibre saturation point and the break in the ln modulus plot also holds for the crosslinked papers as well.(12)

It seems important here to review what is known about how water is adsorbed onto cellulosic surfaces.(13) It is known that about 6 to 8 per cent moisture corresponds to monolayer coverage. This moisture content occurs at about 50 per cent RH. Above 50 per cent RH, water molecules begin adsorbing upon other water molecules. Above 85 per cent RH, all of the water adsorbed is upon previously adsorbed water molecules. So it is difficult to see offhand how water at the high end of the isotherm can have the same

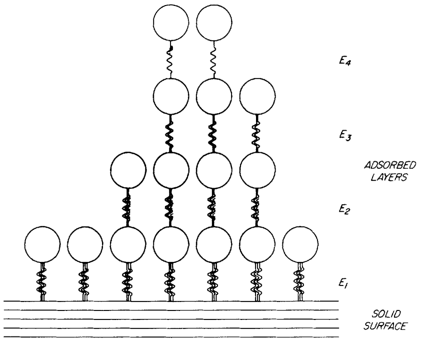

Fig. 3—Multilayer sorption

quantitative effect in lowering the ln of the tensile modulus as the water at the lower end has.

The polarisation theory that Polanyi developed 60 years ago provides some insight into this phenomenon.(10) The Polanyi theory has proven useful in explaining many aspects of adsorption phenomena in general and, in particular, has occasionally been used in the interpretation of water adsorption on high polymers.

According to both the polarisation theory and the multilayer adsorption theory, the forces involved are short range and only the first layer of adsorbed molecules is attracted strongly by the solid surface. The second layer is adsorbed essentially not by the solid surface but by the first adsorbed layer, and the adsorption thus propagates from layer to layer (Fig. 3).

The forces of attraction for each successive layer become progressively weaker. The energy of adsorption decreases and the potential field decreases with distance. If the adsorbed molecules constitute a plane array of dipoles, then that decrease is approximately exponential.

Based upon the Polanyi polarisation theory, equations have been developed that relate the relative vapour pressure of the adsorbate with the amount adsorbed.

$$\ln \frac{p_0}{K_3 p} = K_2 K_1{}^m \quad \text{(DeBoer and Zwikker}^{(14)}\text{)}$$

$$\ln \frac{p_0}{p} = K_2 K_1{}^m + K_4 \quad \text{(Bradley}^{(15)}\text{)}$$

where p/p_0 = relative vapour pressure
and m = moisture content

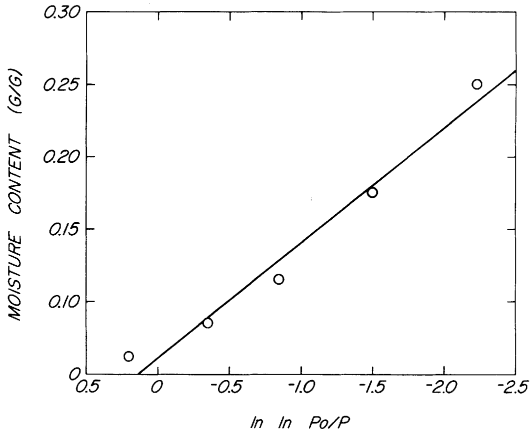

Fig. 4—Adsorption isotherm polarisation theory (Polanyi). The scales have been expanded so data are not condensed by taking the log of the log of p_0/p

These equations were derived independently from different starting assumptions by DeBoer and Zwikker in 1929(14) and Bradley in 1936,(15) who extended the theory to cover polar adsorption.

They both have essentially the same form in that they predict a linear relationship in plotting the log of the log of relative vapour pressure *versus* the amount adsorbed at that relative vapour pressure.

In 1950, Hoover and Mellon(16) applied this polarisation theory to sorption of water by high polymers and found that their experimental data for many polymers, including cellulose, fitted fairly well, in the relative humidity range from 30 to 90 per cent, to Bradley's equation in which $K_4 = 0$.

For kraft paper too, in this range, the fit is not bad either (Fig. 4). The five points shown in Fig. 4 correspond to the first five points of the original isotherm (Fig. 2). It is impossible to take the log of zero or to take the log of the log of 1. Besides, at the upper end of the range is the region where capillary condensation is thought to be occurring and the polarisation theory should not apply.

The fibre saturation point (FSP) is a measurement made not at a relative humidity of 1, but made by equilibrating the paper with a 3 per cent solution of polyethylene glycol (PEG) 9 000. The relative humidity of that solution is not 1 but about 0·99995, as estimated by Raoult's law. The log of the log of the reciprocal of that number can be evaluated.

When the fibre saturation point is included in the Bradley plot, it too falls

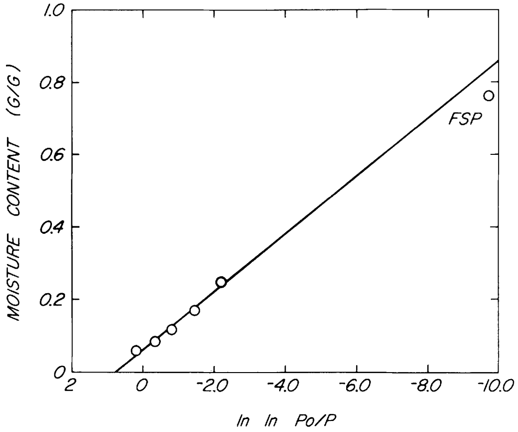

Fig. 5—Adsorption isotherm polarisation theory (Polanyi)

almost on the straight line (Fig. 5). This is perhaps fortuitous and deserves more detailed investigation to determine whether it is generally true that fibre saturation points for cellulosic materials determined by polymer exclusion are related to the relative vapour pressure through the Bradley formulation. There is perhaps a partial explanation for why this fibre saturation moisture content agrees with Polanyi's adsorption theory even into the high relative vapour pressure regions normally thought to govern capillary condensation. The advantage of the PEG method is that gross capillaries external to the cell wall are not included in an FSP measurement. The big capillaries within the cell wall in cellulose are quite different from the big capillaries in carbon black, for instance. In carbon black, big capillaries fill by true capillary condensation. In cellulose, the big capillaries don't pre-exist—that is they aren't there until the water makes them.(13) Almost 40 years ago, Stamm referred to these as transient capillaries.(17)

Cellulose can very appropriately be considered an almost poreless solid when dry. But upon wetting, long slit-like surfaces develop to adsorb the moisture (Fig. 6). Although there is a large volume increase in the amount of water adsorbed above, say, 85 per cent RH, there is no increase in surface area. That volume picked up at high humidities is accommodated by the swelling apart of pre-existing surfaces, and no new surfaces are formed.

If adsorption between cellulosic surfaces follows the multilayer or Polanyi scheme, then the forces of attraction between layers decreases toward the centre (Fig. 7). If a stress is applied to the solid surfaces that comprise the surfaces of a water-filled slit, then the restraining forces will be limited by the

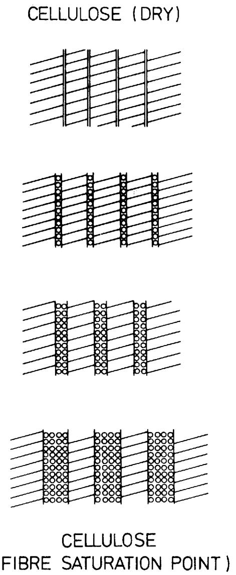

Fig. 6—On wetting, long slit-like surfaces develop to adsorb moisture

weakest forces between the adsorbed layers. As the number of layers increases, those forces that can act as restraints to the deforming stress become smaller. A hydrogen-bonded network in which there are many such slit-like connections in series will exhibit a tensile modulus that decreases with moisture content according to how the forces between the various layers decrease as the number of layers builds up.

That this decrease is logarithmic is evidenced from heats of wetting. Ashpole and Cooper(18) found that for a system as complex as the cellulose-water system, a surprisingly simple mathematical relationship exists between

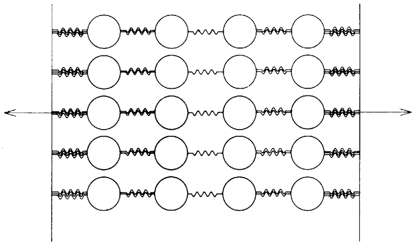

Fig. 7—Sorption in transient capillaries

moisture regain and heat of wetting. The logarithm of the heat of wetting ΔH_m, of cellulose at any moisture content 'm' is directly proportional to that moisture content.

$$\Delta H_m = \Delta H_0 \exp(-Km)$$

Anderson and McCarthy(19) used this Ashpole and Cooper relationship to derive an equation that describes the adsorption isotherm of water on cellulose and derived this expression between the reduced pressure and moisture content.

$$\ln \frac{p_0}{p} = \frac{18\beta\varepsilon}{RT} \exp(\beta m)$$

$$\ln \ln \frac{p_0}{p} = \ln K + \beta m$$

It should be pointed out that this expression is identical to the one derived by DeBoer and Zwikker and by Bradley using Polanyi's polarisation theory.

It seems, then, that the polarisation theory introduces a particular mechanism for the propagation of attractive forces through the sorbent, and is at least compatible with the view that the exponential functional relationship might exist between tensile modulus and moisture regain.

There is indeed additional evidence in the literature that helps support this belief. In 1952, Ashpole(20) pointed out a linear correlation between the tensile modulus of cellulosic fibres and their heats of wetting. This correlation, together with the exponential relationship between heat of wetting and moisture content, implies a linear relationship between the log of tensile modulus and moisture content.

It seems then that if the polarisation theory (or multilayer adsorption theory) predicts or implies the functional relationship between tensile modulus and moisture content, and that functional relationship holds all the way out to the fibre saturation point, something is revealed about the nature of the water in the vicinity of the cellulosic surface.

Goring's model for water in the vicinity of a cellulosic surface envisions the normal clustered arrangement of liquid water destructured by the cellulosic surface. The usual hydrogen bonding among water molecules is viewed as limited to clusters some distance from the surface. The molecules in contact with the cellulosic surface are pictured as tightly bonded to the cellulose, but unbonded to the outer layers of water. It is clear that such a model can not explain a fractional decrease in tensile modulus with added water that is constant up to the fibre saturation point, a moisture content equivalent to about eight layers of adsorbed water.

Indications from modulus measurements, however, are that real bonding

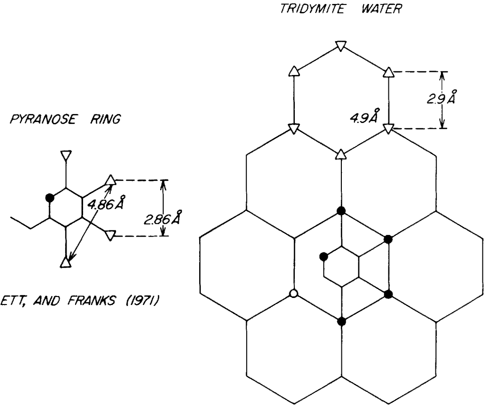

Fig. 8—Similarities and compatibilities of spacings in the pyranose ring with those in the tridymite structure of water

exists throughout the adsorbed water all the way up to the fibre saturation point, almost 80 per cent water in the case of this kraft paper. This is through several layers of adsorbed water. All the water up to the fibre saturation point behaves in the same way. When a stress is applied (at least at sonic frequencies), all of this water participates. There is no unbonded water that just goes along for the ride, but a completely hydrogen-bonded network of water exists between the cellulosic surfaces.

Byrd(21) has reported the onset of shrinkage forces in a wet web of alpha cellulose fibres at a moisture content that corresponds approximately to the fibre saturation point of the fibres.

There is nothing unusual about a fibre saturation point of 80 per cent. Never-dried pulps can have fibre saturation points of 200 per cent.(22) This moisture content approaches the consistency at which the wet web is lifted from the wire. It seems reasonable that load bearing by hydrogen bonds through water layers may account for the wet web strength; we know that at the consistency at which the web is lifted from the wire, there are no direct cellulose–cellulose hydrogen bonds between fibres.

If a hydrogen-bonded network exists between cellulosic surfaces, this network can be envisioned as arising from the similarities and compatibilities of the spacings in the pyranose ring with those in the tridymite structure of water (Fig. 8).(23, 5) Because of the close fit of the pyranose ring and the tridymite structure of water, the adsorbed water between two cellulosic surfaces can be viewed as a distorted ice-like cluster, hydrogen bonded throughout from one cellulose surface to the other (Fig. 9).

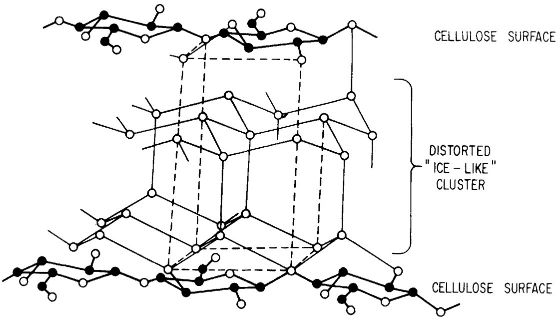

Fig. 9—Adsorbed water, like a distorted ice-like cluster, is hydrogen-bonded throughout

This 'ice-like' cluster is not intended to be crystalline, but rather liquid water which exhibits the flickering bond opening and closing associated with the flickering cluster model of water. This cluster would be indistinguishable from bulk water in many of its properties. But the proximity of the cellulosic surface with its permanent pyranose rings multiply-hydrogen-bonded into the network would tend to make the structure more permanent. To be physically significant a bond must be able to persist for some time, because, only if a bond persists for some time, can it be stressed. The persistence of bonding throughout the cluster allows the cluster to transmit a stress from one cellulose surface to the other if that stress is applied at a high enough rate of loading. At a high rate of loading such as that applied by sonic methods, an insufficient number of hydrogen bonds can open, and it has been shown by Nissan(6) that several nearby hydrogen bonds must open cooperatively to provide the mechanism of stress relaxation in hydrogen-bonded networks.

The fact that each increment of water up to the fibre saturation point appears to have the same quantitative effect in lowering the logarithm of the tensile modulus, indicates that the interaction between cellulose and water is extensive, and that the effects of water molecules not even in contact with the polysaccharide are felt.

There have been many investigations of the interactions between cellulose and water.(24–26) Most indicate a marked difference in the nature of bonding between the water adsorbed at low relative humidities and that adsorbed at higher relative humidities. The initial water adsorbed has been called 'bonded' water and corresponds to the first monolayer of adsorbed water which is usually completed by about 50 per cent RH on an ascending isotherm and is the water adsorbed at the highest Polanyi potential. This bound water has usually been reported to correspond to about the first 4 to 15 per cent water pickup,(25) depending greatly upon the surface area of the cellulose. Nissan(6) has pointed out that the effect of the first monolayer of water on the tensile modulus of paper should be different from the effect of subsequent layers. Although the points in Fig. 1 indicate a constant slope all the way out to 76 per cent water, there are indications of deviations at the low values of moisture content that might lead to a smaller slope below about 5 per cent adsorbed water as predicted by Nissan.(6) Further measurements at the low end of the isotherm are needed to verify this possibility.

The remarkable constancy of slope between monolayer coverage and fibre saturation point is unmistakable and indicates significant interactions between cellulose and water. Although this water may have different properties from 'bound' water, it is certainly not free water or bulk water. NMR measurements by Froix and Nelson(27) have verified the existence of 'bound' water. They have also shown a component of secondary bound water that extends up to the fibre saturation point of cotton. Although they include this water with what they call 'free' water to distinguish it from 'bound' water, they point out that it does not have the NMR properties of bulk water, but exhibits a line broadening indicative of restricted motion.

The fibre saturation point as measured by the exclusion of polyethylene glycol 9 000 is a measure of water within the cell wall pores that is inaccessible or cannot act as a solvent for the PEG of that molecular weight. If the water in these pores were unbonded water or destructured water, it would certainly be capable of acting as a solvent for solute molecules small enough to enter the pores. Rowland(28) has recently reported, however, that small water-soluble solute molecules characterised by limited hydrogen-bonding capabilities find only a fraction of the water in accessible pores available as solvent water. On the other hand, water-soluble solutes that hydrogen bond better than saccharides find all the water in an accessible pore available as solvent water.

The slope of the first line segment in Fig. 1 is $-3{\cdot}4$. This is not in agreement with the slopes of lines obtained by others who evaluated the effect of moisture on the tensile modulus of paper.(29, 30) It has been suggested elsewhere(31) that part of this difference may be explained by the differences in the rates of loading at which the measurements are made. A high rate of loading (sonic measurement) would allow for a higher proportion of hydrogen bonds to be effective, while measurements at low rates of loading (Instron method) would allow for stress relaxation processes involving flickering bond openings and closings to occur during the measurement. Further investigations of these differences are desirable. It is hoped that an analysis of the variations of slope of ln *E versus* moisture content at different rates of loading might reflect the spectrum of relaxation times involved.

The idea that structured water may extend several layers from a surface has been proposed as a general phenomenon.(32) Drost-Hansen has suggested that, for certain polar surfaces, the most reasonable model consists of a layer of ordered (structured) water at the solid surface, with the ordering extending into the bulk of the liquid, decreasing as a function of distance from the interface.

Conclusion

THE interaction between cellulose and water is of the utmost technological importance because this interaction governs all of the papermaking processes and many of the ultimate properties of paper. The purpose of this report has been to take a different look at the nature of water–cellulose interaction. It has been an attempt to use the flickering cluster model of water and the polarisation theory of adsorption to explain the remarkable effect water has in reducing the tensile modulus of paper. Its effect in reducing the log of the tensile modulus (measured sonically) is constant all the way to the fibre saturation point of the paper. This effect seems consistent with the old polarisation theory of adsorption and suggests a multilayer type of adsorption in which the water is structured by the cellulose rather than destructured by it.

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Transcription of Discussion

Discussion

Dr A. H. Nissan Playing the devil's advocate again: Even at the fibre saturation point we know that the cellulose structure has preserved its integrity; it is still a solid. A water molecule arriving looks around and it finds lots of water on which to alight or some hydroxyl group bonded to another cellulose molecule to break. Therefore a decreasing portion of the total water molecules arriving will settle on the hydroxyls of the cellulose. This decreasing portion bears a relation to the total as a ratio of the hydroxyl groups still unbroken to those that were there at the beginning. Therefore, supposing I said to you, Dr Caulfield: To me it looks as if we are again dealing with the structure of the paper, we are dealing with the structure of the cellulose, that the loss in the modulus or the increase in the arrival times of your stress was due to the fact that the phenomena that were initiated in the beginning are continuing and therefore whether the water is structured or not structured may well be described by other methods but your curves do not deal with that but deal merely with a number of hydrogen bonds broken by the water. How would you try to explain that to me?

Caulfield We have tried to measure the surface area as a function of the relative humidity by a number of methods, water adsorption and adsorption of gases on water swollen paper that had been dried by the critical point method and all of the evidence so far that we have accumulated seems to indicate that the surfaces stop increasing above 85 per cent RH. Once you add water above 85 per cent RH there is no newly exposed cellulosic surface. The water adsorbed above 85 per cent RH has to be adsorbed on other water molecules.

Prof. R. H. Marchessault I feel both speakers refer to a cellulose surface as something which is similar in the dry state and in the wet state; I submit that the surface in the dry state is not at all the same as in the wet state. I think Prof. Giertz in his reference to hemicellulose was getting at this point;

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certainly from what we know about the hydratability of xylan and what must be a slightly disordered cellulose surface, which I would expect at the surface of any crystalline cellulose microfibril, I would expect that the sharp boundary in the dry state would transform to a hydrated material gradient. In that sense the water in that hydrated layer would be ordered, in my opinion, and farther away it would gradually turn into the ultimate flickering cluster state, if that is the fashionable theory at the time.

Prof. H. W. Giertz Have you made the same studies on single fibres or cotton fibres?

Caulfield No.

Giertz Because the cotton fibre has about the same rupture strength when it is wet as when it is dry I would expect the *E*-modulus to be also very much the same for a wet cotton fibre as for a dry one. You are taking as your starting point a paper which is a network where all fibres are engaged in carrying the load and that nothing is changed in this picture when the paper becomes more and more moist. There is, however, another way of looking at paper and that is that paper is a network where not all fibres or segments are arranged in such a way that they really are carrying the load. We have active and passive segments. If that is the case then there is a much simpler explanation of the decrease of the *E*-modulus with moistening. The *E*-modulus is an indication of the amount of material carrying the load. Now, when moistening the paper the fibres will swell and expand laterally and that will cause straight and active segments to become curved and passive; and so they will not contribute to the *E*-modulus any longer. An indication of this is that if you take a paper conditioned at 90 per cent relative humidity you have of course a very low *E*-modulus; the primary part of the stress-strain curve is low compared with the dry paper. But at the end of the stress-strain curve you are getting a tertiary slope. This is typical for all papers having slack segments. When such segments are straightened out during the elongation of the paper they jump in and take the load and the *E*-modulus is increased. As you see, I am ready to explain your first observation of the decrease in *E*-modulus as an effect of changing the amount of active segments in the paper.

Caulfield I agree that it is a decrease in the number of load bearing elements but I think that the load bearing elements are hydrogen bonds rather than fibre segments. Although it may be stronger in breaking length it is weaker in tensile modulus. The tensile modulus of single fibres decrease with moisture content in just the same way as a paper sheet does.

Dr D. H. Page Perhaps the difference between the views of Goring and Caulfield may be reconciled as follows: Cellulose is a structure breaker for water and water is a structure breaker for cellulose. If we break down the structure of the cellulose we lower its modulus and that is the result that you have obtained. You may say that it can't be that because the specific surface doesn't continue to increase as we add more water. I don't think that matters. When we have a large amount of water in the cell wall we will have broken the structure quite a bit already and a little more breaking of the structure will hardly be measurable in terms of specific surface, but will have a dramatic effect on the elastic modulus.

Dr D. A. I. Goring I am particularly interested in what you think happens to water alongside a carbohydrate type of surface which hasn't got anything on the other side. You have approached the problem from the point of view of pores in water-swollen cellulose and you are interpreting the tensile strength of the fibre in terms of the properties of this water. Let us extrapolate it further. Suppose you have one fibre swimming around somewhere at the wet end of a paper machine and there is a cellulose molecule or hemicellulose molecule sticking out into the water, and there is nothing beyond except more water for a long way. How do you picture that water?

Caulfield I picture it as structured by the surface, whatever surface it is, cellulose or a glucose molecule that extends out, gradually fading away for a distance of say 8 to 10 layers.

Goring Suppose then that you measure the size of the molecule hydrodynamically for example. Suppose you take the molecule and measure its viscosity and therefore you measure the actual hydration envelope. You don't find a thick layer; you find about one water molecule per OH group.

Caulfield That might be involved in how quickly these things are changing too, or how quickly the cluster flickers for instance. Those measurements made by different methods (N.M.R. or dielectric relaxation) do indicate that there is a substantial hydration sphere associated with glucose and other molecules that contain pyranose rings.

Goring I think that this is the heart of the problem and I might say that this controversy as to whether molecules of this sort have large hydration layers around them, of, say, 10, 20 or 30 molecules, or whether the water is affected only in a narrow layer is a widespread one and still unresolved; not only for cellulose but also for the water in biological systems, the water against membranes, etc.

Caulfield There is an interesting way to approach the problem of forces between surfaces that does not involve a simple model. The Lifshitz-Dzyaloshinskii theory provides an expression for the force of attraction between two surfaces through a liquid layer. There have been spectacular advances in the last ten years along experimental lines and I would think that someone soon should be able to apply this theory to the attraction of two cellulosic surfaces across a water gap.

Mr J. R. Parker I am puzzled about one aspect of Dr Caulfield's approach to this. Maybe he can clarify it. It appears to me that the sonic velocity is being measured in a direction parallel to the fibre axes and therefore parallel to the fibrils, but the discussion hinges on the fact that the stretching will occur in the water layers, but this seems wrong to me. The fibrils within the fibres will carry the load. They will not be transmitted across the layers of water between those fibrils. These two directions are at right angles.

Caulfield These measurements were made on a machine made paper which of course means both a machine direction and a cross-machine direction. On Thursday you will see some more data on measurements in both directions. Our interpretation is not the that sound wave runs down the fibril, it runs across the hydrogen bonds.

Giertz This brings up the whole problem of the forces over the liquid layer between solid compounds. Dr Goring, if you have two cellulose or hemicellulose surfaces bounded by ordered water, are there any clusters present when the surfaces are close together?

Goring I don't know. The answer to that will give the alternative to Dr. Caulfield's model. What happens to the water if you have a small enough distance that the destructured layers actually touch? What happens when more water comes in? Is this normal water or is it effected by being sandwiched between two layers of destructured water? The theory that I have put forward really deals with a cellulose surface and an infinity of water on the other side. I think that your question is a new question which needs answering.

Giertz Well, can I ask you this: would you expect there to be forces in between the two surfaces? Secondly, when this water is evaporated, what happens to the fibrils on the two fibre surfaces if the fibrils can move?

Goring What you are really asking is how much water do you have to have for it to be statistical? Because the sort of structures that we are talking about are statistical animals, they occur because the water molecules are free to marry who they like and divorce and marry again very quickly.

Nissan On Friday I will try to synthesise these two views into one homogeneous structure. Actually we have been ignoring many studies that have been done outside paper. There have been studies on what happens to adsorbed molecules on cellulose. Professor Preston, for example, at Leeds University has demonstrated by electron diffraction studies on the adsorption of metal salts on cellulose that you get a pattern of structure which is not like the salt crystal or soaplike copper napthanate adsorbed, nor the basic Meyer-Misch structure but a structure which is new, namely, a surface ordered structure of the adsorbed molecules which has some depth in the third dimension. The questions that are arising here can be resolved by realising that the OH groups on cellulose are tied down. Therefore, if things are adsorbed onto them there must be a structure which is not tridymitic, nor is it cellulosic; it is a structure of its own. If, in fact, two surfaces are near each other, since the energy between water molecules in association with each other and that of cellulose to cellulose are practically the same, the composite would look as if it were one continuous structure.

Prof. B. K. Steenberg At the German Institut für mechanische Verfahrenstechnik, Mannheim, they are making stress-strain studies with an extremely delicate apparatus on pillars of very fine sand, pure silica moistened with distilled water. The remarkable thing is that they obtain stress-strain curves with loops etc. which are exactly of the same type as we find for paper. When then the water is evaporated the elastic modulus increases just as for paper. An explanation of the observed effect of water does not have to include unique properties of cellulose. This work is not published yet, but will be soon. Secondly, concepts like stress and strain and consequently modulus of elasticity are averaging concepts. They are fully defined in homogeneous materials but in particulate matters they lose their physical meaning. I think it would be dangerous to draw theoretical conclusions based on an assumption that we are dealing with homogeneous materials.