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THE TRANSPORT OF WATER IN CELLULOSIC MATERIALS

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Synopsis The mechanisms involved in the transport of water in high polymers are reviewed. The discussion is mainly based on intact capillary-free models where the solution-diffusion mechanism is operative. The different patterns of behaviour which have been found for the sorption isotherms and the concentration dependence of the diffusion constants will be presented. Examples of the behaviour found with cellulose itself, two cellulose derivatives and with grafted cellulose and celullose acetate will be discussed in detail. In particular, experiments concerned with the sorption of water into wood pulp and grafted wood pulp will be presented and some theoretical and practical aspects of the results obtained considered.

Introduction

TWO general mechanisms of water transport in cellulosic materials are possible, in principle. These are activated diffusion and capillary flow. Both have a number of ramifications and variations. In the case of highly swollen membranes, such as wet cellophane, hydraulic flow may be also involved, but this is still controversial. With highly porous cellulosic materials such as paper, pore flow may be accompanied by a surface 'hopping' type of mechanism; the latter has been little explored but is of great interest to papermakers. It can explain in part why the water vapour permeability of paper made from highly beaten pulp is not too much different from a more open structured paper. An extremely interesting discussion of the role of surface diffusion in water transport through paper itself has been presented by Corte.(1a–c) The general subject of water sorption and transport in wood and cellulose has been discussed in detail by Stamm.(2) The sorption of water in wood pulp fibres has been extended to extremely high humidities, where capillary condensation into pores becomes a major factor. Research in this field has

Under the chairmanship of Prof. M. Judt been pioneered by Stone and Scallan.(3, 4) This paper will discuss the solution and diffusion of water into essentially pore free cellulosic materials and will reflect in essence the approach of the polymer chemist to such problems. Two cellulose derivatives, secondary cellulose acetate and ethyl cellulose, which have quite different water transport behaviours, will be discussed in some detail. In addition, the effect of grafting synthetic polymers onto wood pulp on water transport and the development of 'super absorbing' cellulosic materials will be more briefly described. This paper will concentrate on the research conducted by the authors and their colleagues and is not intended to be a general review of the subject.

Experimental

THE cellulose acetate used had a degree of substitution of 2·25, whereas the ethyl cellulose had a D.S. of 2·55. Films were cast from acetone solution and were dried under high vacuum at 50° C to constant weight.

The sorption isotherms and the sorption-desorption rates were determined with a quartz helix microbalance and a Cahn electronic microbalance; both were enclosed in a water jacketed glass vessel, through which constant temperature water was circulated. Details of the equipment used have been described previously.(5, 6)

The permeability and diffusion coefficients were measured, using an all glass high vacuum time lag equipment of the type described originally by Barrer and Skirrow.(7) Details of the modifications used in the present equipment have been described elsewhere.(8)

Although there are no particular difficulties in measuring the sorption isotherms or the permeability coefficients, the measurement of the diffusion coefficients can present considerable problems in the case of water. If the sorption or desorption rates are used, these are subject to considerable errors due to the heat generated or lost from the condensation or evaporation of the water in or from the cellulosic material. These errors can be reduced, if the sorption or desorption increments are kept small; a full discussion of this treatment has been presented elsewhere both for fibres(9) and films.(10) The necessary corrections were small in the case of the cellulose ether, discussed in this work.

The use of the time lag method for determining diffusivities is complicated in the case of water vapour by adsorption of water on the glass receiving volume of the equipment. Errors due to this effect have been reduced to reasonable proportions by using a gravimetric method of monitoring the downstream water flux,(11) by using all steel equipment(12) and by the authors and their colleagues in the present work by collecting the downstream water vapour in the receiving section of the apparatus in a pre-wetted condition. Details of this method have been described by Yasuda and Stannett.(8) The general problem of measuring water diffusion and solution in high polymers has also been discussed by the same authors.(13)

The methods used in this research are effective, although somewhat conventional. It should be pointed out that quite different methods have been developed, notably the use of the vibroscope for fibers(14) and of NMR techniques(15, 16); the latter can also yield valuable information regarding the state of the sorbed water.

The methods and materials used in the studies of the sorption and transport of water in the grafted cellulose fibres will be included in that section.

Results and discussion

THE sorption isotherms for cellulose acetate and ethyl cellulose are shown in Figs. 1 and 2. Both are of the normal BET III type; cellulose acetate absorbs about twice as much water as ethyl cellulose. This, presumably, reflects the higher degree of substitution of the ether plus the influence of the more polar acetate groups.

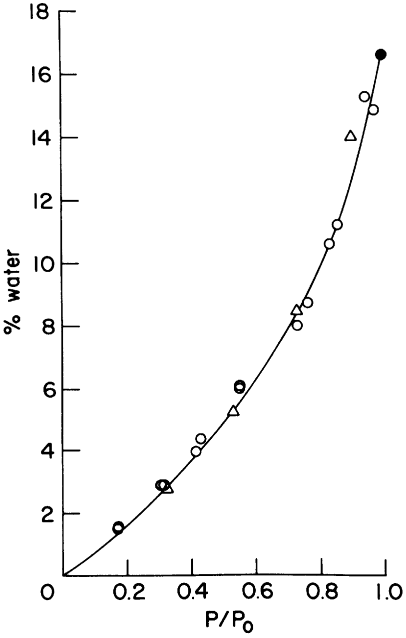

Fig. 1—Sorption isotherm for water in cellulose acetate at 25° C. ○ gravimetric values; ● liquid water; △ *P/D* values

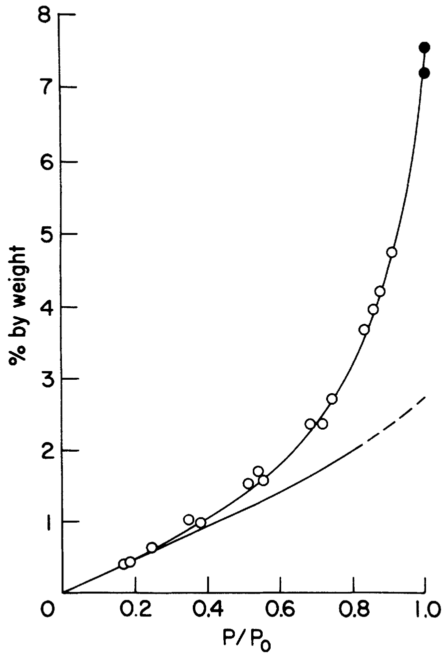

Fig. 2—Sorption isotherm for water in ethyl cellulose at 25° C. ○ gravimetric values; ● liquid water; line represents *P*/*D* values

The permeability coefficients for water in cellulose acetate are presented as a function of the relative vapour pressure in Fig. 3. There is a considerable increase in permeability with vapour pressure. The water vapour transmission in ethyl cellulose, normalised to one centimetre thickness, is shown in Fig. 4. The slope of the curve gives the permeability coefficient; it can be seen that up to about 50 per cent relative humidity ($p/p_0 = 0{\cdot}5$), the permeability coefficient is a constant and then increases somewhat, but only by about 30 per cent. The diffusion coefficients for cellulose acetate estimated from the time lags are presented as a function of the relative vapour pressure in Fig. 5. In the case of ethyl cellulose, the diffusion coefficients were estimated both by the time lag method and from the rates of sorption and desorption and are shown in Fig. 6. The experimental details and the theoretical bases for these measurements are given in full in references(6, 7) and (17). There is a fourth method of estimating the diffusion coefficient; that is by dividing the permeability coefficient by the solubility coefficient, estimated from the

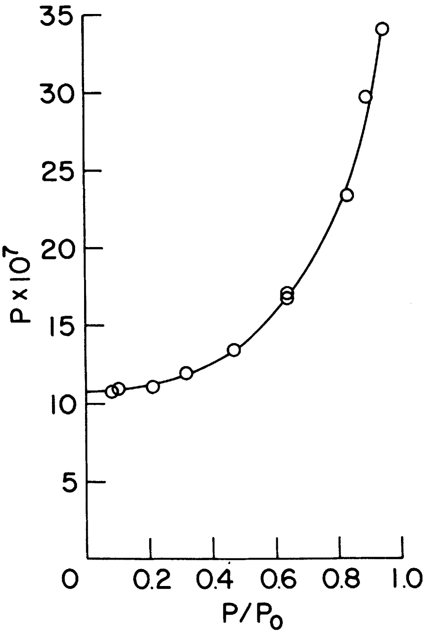

Fig. 3—Permeability coefficients of cellulose acetate at 25° C. Units. CCS·STP/CM²/CM/sec/CM

sorption isotherm. When the sorption isotherm is not linear, i.e. Henry's law is not obeyed, and the diffusion coefficients are concentration dependent, we have

$$\bar{P} = \frac{1}{p}\int_0^p P(p)\,\mathrm{d}p$$

and

$$\bar{S} = \frac{1}{p}\int_0^p S(p)\,\mathrm{d}p,$$

leading to

$$\bar{D} = \frac{\bar{P}}{\bar{S}} = \frac{1}{c}\int_0^c D(c)\,\mathrm{d}c.$$

where $\bar{P}$, $\bar{S}$ and $\bar{D}$ are the values of the coefficients averaged from zero to the pressures and concentrations used in the measurements. $P(p)$, $S(p)$ and $D(c)$ are the differential values.

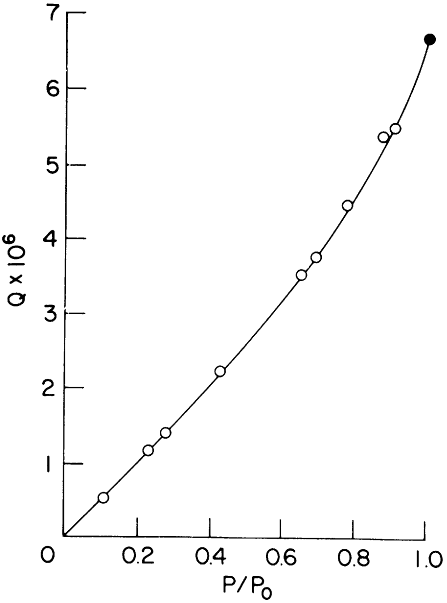

Fig. 4—Water vapour transmission through ethyl cellulose at 25° C. ● liquid point. Units CCS·STP/CM^2/CM/sec

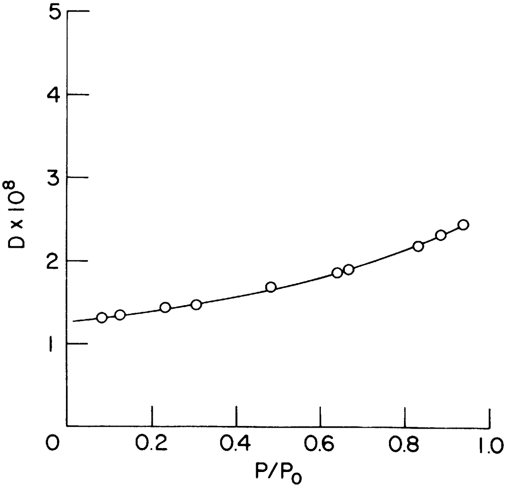

Fig. 5—Diffusion coefficients for water in cellulose acetate at 25° C

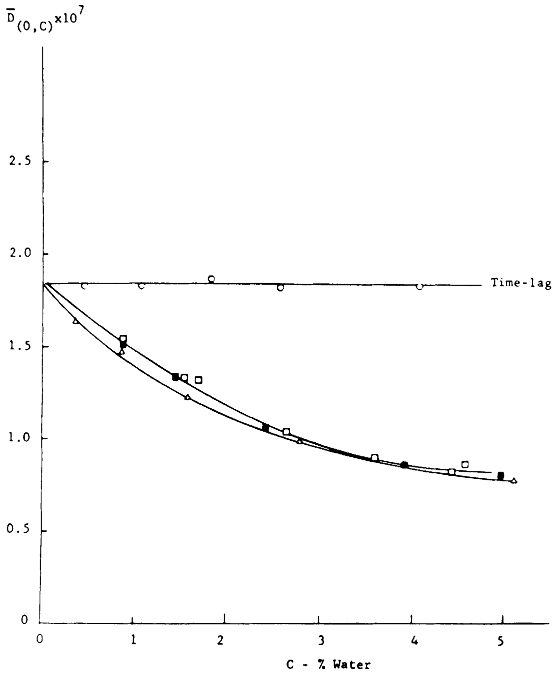

Fig. 6—Diffusion coefficients for water in ethyl cellulose at 25° C. ○ time lag method; □ sorption; ■ desorption; △ *P*/*S* (taken from reference 6)

In the case of cellulose acetate only the time lags and the quotient of the permeability and solubility coefficients were obtained. With ethyl cellulose all four methods of estimating the mean diffusion coefficients were obtained; these are included in Fig. 6. The sorption and desorption values were corrected for the small temperature changes occurring during the processes by the method described in reference.(10)

The values obtained for the diffusion coefficients, estimated in four different ways, are presented as a function of the water content of the ethyl cellulose in Fig. 6. There is a gratifying agreement between the sorption, desorption and *P*/*S* values; they all decrease with increasing water content. The time lag values, on the other hand, are remarkably constant. All the values coincide at zero water content. The decrease in the diffusion coefficients with increasing water content is a natural consequence of the clustering phenomenon, to be discussed later, thus, following the arguments of Barrer and Barrie(11) and others.(6)

The flux $J = -D_T \cdot \partial C_1/\partial x$, where D_T is the true diffusion coefficient and C_1 the concentration of mobile isolated molecules.

J must also equal $-D \cdot \partial C/\partial X$, where D is the measured diffusion coefficient and C the total concentration of water, i.e. isolated molecules and clustered water.

Hence $D = D_T \cdot \partial C_1/\partial C$.

Since the ratio C_1/C decreases as the concentration increases, the measured value of D also decreases.

The constant value of the time lag diffusion coefficient is puzzling since it should include the time taken in cluster formation. It would appear that clusters are not formed under the conditions of the time lag experiments which are dynamic in nature. The other methods, on the other hand, are based on equilibrium measurements and the steady state permeation. The fact that the values converge at zero relative vapour pressure tends to confirm this explanation.

A sorption isotherm can be constructed for each cellulose derivative by dividing the permeability coefficients by the time lag diffusion coefficients and multiplying by the upstream pressures of each measurement. These are included with the measured sorption isotherms shown in Figs. 1 and 2. A pronounced difference can be seen. In the case of the cellulose acetate, the calculated isotherm coincides with the measured one. However with ethyl cellulose, the isotherm only coincides at very low relative vapour pressures, in fact can be considered as tangential. At high vapour pressures the estimated water content is far less than the actual, measured, value. A similar phenomenon has been found in a number of synthetic polymers. Polyoxymethylene follows the cellulose acetate mode, whereas polyvinyl chloride, rubber hydrochloride and polyethyl methacrylate follow the same pattern of behaviour as ethyl cellulose.(18)

The 'excess' water in ethyl cellulose has been ascribed to the clustering of the water molecules in the polymer. This was first described by Rouse(19) in 1947; water in the clusters would not diffuse so readily as isolated water molecules because of the extra energy needed to break a molecule from the cluster (Rouse).(19) This cannot be considered as too likely if the whole system is in quasi-equilibrium, since the chemical potentials of the water molecules should be equal. A second explanation is that the probability of an effective diffusive jump per water molecule would be less for a molecule contained in a cluster than if distributed in monomolecular solution in the polymer. There has been more direct evidence of gross clustering, including dielectric constant studies(20) and the onset of opacity(11); in an extreme case actual globules of water could be observed(22) with a phase contrast microscope. These examples are probably manifestations of 'free' water, a concept which is very familiar to cellulose and protein chemists. The development of NMR has shed considerable light on the state of water in cellulose and biological systems, for example.(15, 16, 23)

A less direct approach based on the statistical mechanics of solutions has been developed by Zimm(24) and by Zimm and Lundberg.(25) This method has been applied rather widely by polymer chemists whose systems rarely have sufficiently large clusters to be examined by physical means.

Zimm and Lundberg define a cluster integral, $G_{11}/\bar{v}_1$ for a two component system as:(25)

$$\frac{G_{11}}{\bar{v}_1} = -\phi_2 \left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{p,\,T} - 1$$

The subscript 1 refers to the solvent, in this case water, of partial molar volume $\bar{v}_1$. $\phi_1 = 1, -\phi_2$ is the volume fraction of the penetrant e.g. water, in the polymer and a_1 is the activity of the penetrant ($\sim p/p_0$) given the sorption isotherm; therefore the data can be plotted as a_1/ϕ_1 versus a_1 and differentiated to yield $G_{11}/\bar{v}_1$. The differentiation can be carried out graphically or analytically. The cluster integral multiplied by the volume fraction of penetrant gives an estimate of the mean number of penetrant molecules in excess of the mean number in the neighbourhood and is a measure of the clustering tendency of the penetrant molecules. When Henry's law is obeyed, as with a number of synthetic polymers and water, $G_{11}/\bar{v} = -1$. The quantity $1+G_{11}/\bar{v}$ gives, therefore, a measure of the average number of penetrant molecules which exist in a cluster. The calculated values for both cellulose derivative are given in Table 1 at various relative vapour pressures. It is clear that the tendency to cluster is much less with cellulose acetate. Furthermore, as would be expected, clustering becomes greater at higher relative vapour pressures.

TABLE 1—ESTIMATED MEAN CLUSTER SIZES FOR WATER IN ETHYL CELLULOSE AND CELLULOSE ACETATE AND THE VARIATION OF THE FLORY-HUGGINS INTERACTION PARAMETER AS A FUNCTION OF RELATIVE VAPOUR PRESSURE.

	$\phi_1 \cdot G_{11}/\bar{v}_1+1$ *values*				
$p/p_0 =$	*0·2*	*0·4*	*0·6*	*0·8*	$\frac{1}{\chi_0} \cdot \frac{\partial \chi_1}{\partial a_1}$
Ethyl cellulose	1·04	1·21	1·58	2·37	0·55
Cellulose acetate	1·13	0·91	1·08	1·71	~0

A highly favoured method for polymer chemists to describe a sorption isotherm is by the Flory–Huggins equation(26); in simplified form this can be given as

$$\ln a_1 = \ln\phi_1 + (1 - 1/r)\phi_2 + \chi\phi_2^2,$$

where r is the molar volume ratios for polymer and penetrant and is very large for high molecular weight polymers. χ is the polymer solvent interaction parameter and should be constant for random mixing at all activities. With clustering, over and above those associated with random mixing, χ will vary with activity as clusters will become more prevalent at higher activities. The degree of variation of the Flory–Huggins interaction parameter with activity could be regarded as another measure of clustering.(18, 27) This variation has been expressed as $1/\chi_0(\partial\chi/a_1)$ where χ_1 is the value of χ at zero concentration; these values are included in Table 1. The clustering tendency of water in ethyl cellulose is again indicated by these values. It is interesting that in the field of membrane technology, it has long been felt that polymers in which water does not cluster, are most effective as membranes for reverse osmosis. An interesting study of this approach has been published by Vieth, Douglas and Bloch(28) and tends to support such a correlation. In any case, ethyl cellulose is a very poor polymer for reverse osmosis membranes, whereas cellulose acetate, in which there is no clustering, is one of the most effective. The use of BET theory to describe water vapour sorption isotherms is favoured by many wood and cellulose chemists, but is not much used by polymer chemists, mainly because of the lack of any precise meaning of the internal surface in a homogeneous polymer.

Newer, fast developing, physical methods such as NMR, in concert with the use of statistical mechanics, will continue to shed more light on the all important problem of the actual state of sorbed water in polymers. This is of particular interest in wood, cellulose and biological systems.

The sorption and diffusion of water in grafted cellulose fibres(5)

THERE is another aspect of the transport of water in cellulosic materials which has occupied the attention of the authors for a number of years. This concerns the effect of grafting a synthetic polymer to cellulose on the water transport behaviour. The grafting can be carried out directly onto the pulp or other fibres and so provides a method of direct modification. The general methods of grafting to cellulose have been reviewed in detail and need not be repeated here.

Two areas of investigation will be briefly discussed, (a) the rendering of cellulose less sensitive to water and (b) the production of highly water sorbing cellulose fibres.

(a) *The reduction of the water sensitivity of wood pulp by grafting*(5)

The details of the grafting procedures have been described,(5) an 84 per cent alpha cellulose unbleached graft softwood pulp (Domtar Co., Canada) was used. The 'per cent' grafting is expressed as the weight of grafted polymer per 100 parts of the original pulp. Thus, a 70 per cent graft actually contains 41 per cent of polymer and 59 per cent of pulp. The sorption isotherms and the diffusion coefficients were measured as described in the experimental section.

The sorption isotherms of styrene grafted pulps are shown in Fig. 7. Marked reductions in the water content can be seen; however, these were calculated on the total weight; in Fig. 8 isotherms calculated on the pulp content only are presented. The reductions in water content are still substantial

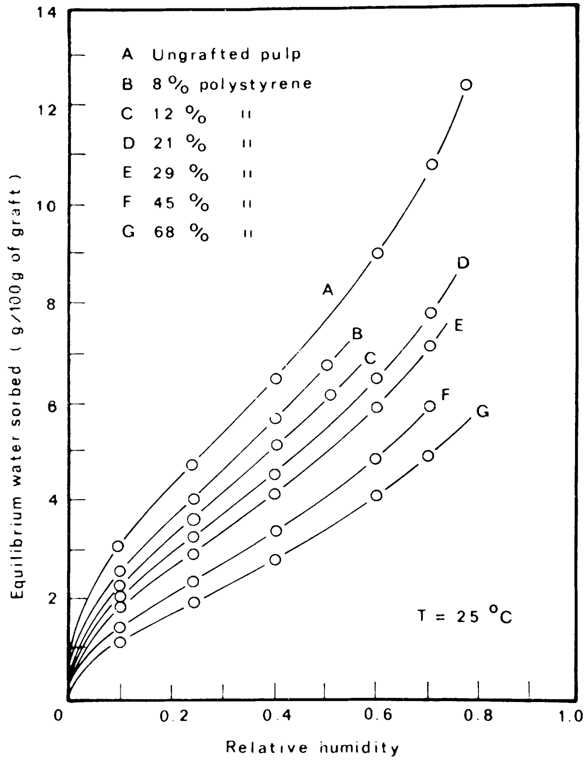

Fig. 7—Sorption isotherms for water in ungrafted and polystyrene grafted pulp at 25° C (taken from reference 5)

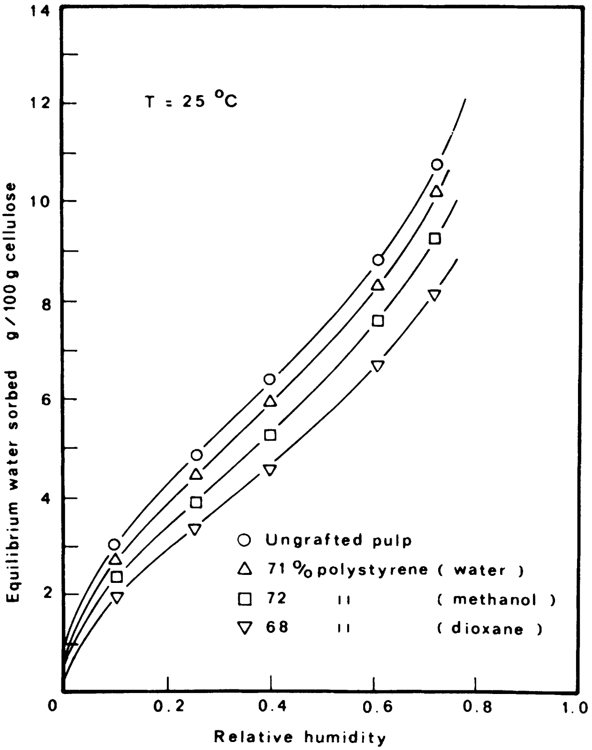

Fig. 8—Sorption isotherms for water in ungrafted and polystyrene grafted pulp at 25° C. The grafting was effected by irradiating the pulp in monomer solutions containing water, methanol and dioxane. The water contents have been calculated on the pulp content only (taken from reference 5)

and depend on the medium in which the grafting is conducted. With water in the grafting solution, it is believed that the grafted polystyrene side chains are coiled tightly and have the least effect. With the wet dioxane, the polystyrene chains are believed to be more extended and have a far greater effect on the water sorption. From the point of view of dimensional stability or electrical characteristics, the overall water absorption is important; this has been reduced from about 11 to 4·5 per cent at 70 per cent relative humidity with a 68 per cent graft. The decreases were also estimated at 5 and at 75 per cent relative humidities and were found to be 40 and 25 per cent respectively. The density of the sample was 1·361 compared with a calculated value of

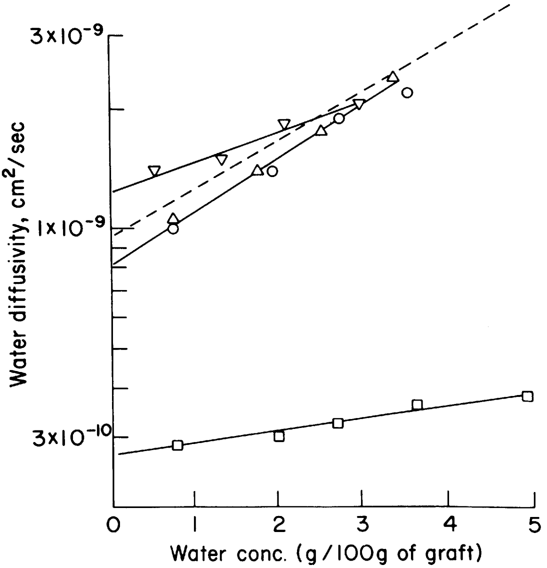

Fig. 9—Diffusion coefficients for water in grafted pulp at 25° C: ▽ 8 per cent polystyrene; △ 7 per cent polyacrylonitrile; ○ 9 per cent polyethyl acrylate; □ 11 per cent polyacrylic acid, dotted line, ungrafted pulp. The equilibrium water contents at 75 per cent RH were 10·7, 11·5, 11·6 and 14·4 per cent respectively and 11·5 per cent for the ungrafted control (adapted from reference 5)

1·289. These two pieces of evidence suggest that the polystyrene molecules may be present as isolated molecules leading to tighter packing.

Turning now to the diffusion coefficients, it can be seen that these increase somewhat less with increasing water concentration than with the ungrafted pulp (see Fig. 9, for example). The values of the diffusion coefficients extrapolated to zero water content are shown graphically in Fig. 10 as a function of the polystyrene content. These increase with the degree of grafting; presumably even in the dioxane grafting system there is some opening of the structure by the grafted side chains, which eases the diffusion process.

In addition to styrene, a number of polar monomers were grafted to similar degrees. The effect of these on the diffusion coefficient is included in Fig. 9. It is interesting that a small amount of polar polymer, particularly acrylic acid, reduces the diffusion coefficients considerably. The equilibrium

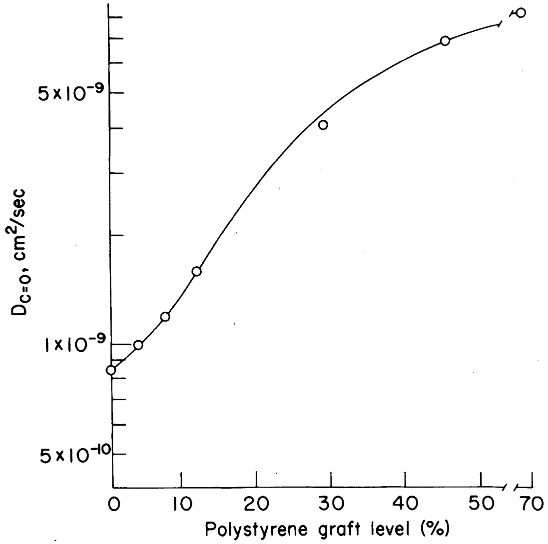

Fig. 10—Effect of polystyrene graft level on the diffusion coefficients for water, extrapolated to zero water content at 25° C (taken from reference 5)

water contents, on the other hand, are somewhat larger; these are included in the figure caption. However the water content increases by less than 25 per cent, whereas the diffusion coefficients decrease by more than threefold. The actual rate of penetration of water, therefore, is considerably reduced by the grafting of a water sensitive polar monomer. Polystyrene reduces the water content but increases the diffusivity; again the overall rate of penetration is decreased. A reasonable optimisation of both effects was achieved using a copolymer of acrylonitrile and styrene. This has a practical application in the use of dry wood pulp for the insulation of telephone cables. When such cables are broken, the ingress of water is so rapid that repairs cannot be effected. However, grafting an acrylonitrile-styrene copolymer increased the time taken to reach intolerable levels of the dissipation factor from four hours to several hundred hours. This is sufficient time to effect repairs. In addition, the dielectric constant was 1·30 for the grafted pulp compared to 1·75 ungrafted. Less pulp is therefore needed to achieve equal capacitance, resulting in the possibility of smaller diameter cables.

(b) *Highly water sorbing cellulose fibres*

There has been great interest in recent years in the development of polymers which have a tremendous capacity for water.(29) These have a very large market in various applications, notably in catamenial devices, disposable diapers and for various surgical uses. Among the types of polymers under study are crosslinked water soluble synthetic polymers and cellulose derivatives, including carboxy methyl cellulose(30) and graft copolymers. Two types of the latter are under active development, grafted starch(31) and cellulose.(32–35) Two approaches have been taken—the grafting of acrylonitrile and acrylate esters, followed by hydrolysis(32–35) and the direct grafting of water soluble polymers.(36) The latter approach has been taken by the present authors.

When substantial amounts of say acrylic acid are grafted to cellulose, there is only a modest increase in the water sorption. This is because the crystalline regions of the cellulose restrict the swelling. However, if the grafted material is treated with a solvent for the cellulose and the solvent then removed, the grafted side-chains prevent the recrystallisation to a large extent and allow considerable swelling to occur.

Examples of this behaviour are shown in Table 2 for acrylic acid grafted to viscose and to cellophane; similar results have been obtained with wood-pulp. Tremendous degrees of swelling can be achieved, particularly if the sodium salt of the polyacrylic acid side chains is formed. Up to 4 000 per cent of water can be retained after centrifugation under 900 × gravity for 30 minutes(3, 4) with grafted wood pulp. Fibre saturation point measurements, using the Stone and Scallan method, showed that the sorption was in the fibre

TABLE 2—SORPTION OF WATER AND WATER VAPOUR BY CELLULOSE GRAFTED WITH ACRYLIC ACID

	Per cent water sorption at 25° C			
Material *RH*	*25*	*50*	*75*	*100*
Cellophane				
(Control)	8·5	15·0	22·0	32·0
46 % Graft	8·3	14·6	23·5	45·0
46 % Graft (Decrystallised)	18·5	30·0	41·5	2 940
Rayon				
(Control)	9·0	14·5	20·0	35·0
108 % Graft	8·6	14·3	21·5	43·0
108 % Graft (Decrystallised)	22·0	36·0	48·5	3 250*

* Measured by centrifugation procedure.

walls rather than in the lumen or interfibre capillaries. This latter observation was made by Lepoutre, Hui and Robertson,(34) who have carried out the most extensive and meaningful work in this field. Their work was based, mainly, on the hydrolysed polyacrylonitrile graft approach. Since the application of these unique grafted celluloses mainly involves physiological fluids, such as blood and urine, the effect of salts, pH and other variables as opposed to pure water is of particular interest. This field is one of the most interesting, academically and industrially, areas of research concerning the transport of water in cellulosic materials and is still completely in its infancy.

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Discussion

Dr J. D. Peel Is decrystallised cellophane transparent or are the pores large enough to make it opaque?

Stannett No, it is completely transparent. In fact, the increase in volume when you add water is very dramatic indeed.

Mr E. T. Anderton Would you like to comment on the ageing effect on absorbency and the transport of water in ordinary pulps?

Stannett I've done very little in that field. It definitely decreases with ageing, but I can't add anything more to that.

Mr J. W. Swanson I would like to comment on the loss of absorbency of pulps with ageing. Work we published in 1959 {*TAPPI* **42**, 812–818 (Oct. 1959)} showed clearly that this is caused by vapour-phase redistribution of fatty materials that are present in all woodpulps. Subsequent work has shown that these vapours distribute at predictable rates through the fibre structure and adsorb on the unbonded fibre surfaces both physically and chemically. Depending on the moisture content of the paper these fatty materials may actually penetrate the cell wall to considerable depths and react there chemically.

Prof. R. H. Marchessault I really have difficulty in imagining the model that applies in this high swelling fibre because the native cellulose would have a different starting morphology than the rayon. Since you graft to roughly the same level in both cases and decrystallise one expects that decrystallisation will not be as effective in the case of native cellulose as in the case of rayon. Hence the final two structures would probably not be identical.

Stannett Well I can't say for woodpulp it's too complicated, that's

Under the chairmanship of Prof. M. Judt why I like to work with rayon and cellophane but I imagine it would start off very highly crystalline. I'm not sure whether they are folded or extended but a whole array of crystals may be taking up to 60–70 per cent or, in the case of cotton, 80 per cent of the structure. Then you dissolve it and it becomes completely amorphous. The strange thing is that rayon and cotton maintain a skin structure as they swell, unlike woodpulp.

Dr D. A. I. Goring I was interested in your comments on clusters slowing the diffusion of water through the ethyl cellulose. Aliphatic alcohols in solution are envisaged as having water molecules clustered round the hydrocarbon end in a kind of clathrate formation. Do you see water molecules in an ethyl cellulose membrane clustering round the ethyl groups as a sort of partial clathrate formation. Why this wouldn't happen so much in cellulose acetate or indeed cellulose is that you don't have such big hydrocarbon entities.

Stannett That is a good point, but as far as I know nobody knows where the clusters are. There seems to be something almost like a nucleation of some kind. Methanol can also cluster in some polymers.

Dr A. H. Nissan Don't let's jump to conclusions too fast. Starkweather, using Zimm's methods, calculated and published two years ago an account of clustering around cellulose. He gets clusters of up to 16 molecules. His method of calculation is graphical and doesn't lend itself to accurate results at high moisture contents. He says indefinitely large clusters appear on cellulose. These are pure thermodynamics data obtained from adsorption. He had done it for cellulose, nylon, and other materials.

Prof. M. Judt You say that you noticed an opacifying effect which you relate to the clustering effect. Would the degree of opacity be a measure of the number of clusters?

Stannett Most of the polymers don't exhibit opacity but ethyl cellulose does.

Goring If there are clusters on cellulose, does a cellulose membrane exhibit the same symptoms as an ethyl cellulose membrane?

Stannett I have not looked at cellophane because it swells so much but I would expect clustering to occur. Dr Mason did high pressure permeating through swollen cellophane and he showed evidence of hydraulic flow where there must be clusters joined together in some continuous channel of some kind.

Dr J. M. Haynes I was interested to hear you associate opacity with clustering of water molecules. As you probably know there are many other types of explanation for this kind of phenomenon occurring in porous media, some of which are associated with scattering at capillary interfaces, others with density fluctuations in the liquid under a large negative pressure close to the bottom of the van der Waals curve. Clustering, however, would seem to be an explanation which is specific to water. Can you say whether the opacity is observed with other liquids in these materials?

Stannett In polyvinyl acetate with phase contrast microscopy you see little globules of water. But opacity did develop in ethyl cellulose and it was ascribed to clusters becoming large enough to scatter light.

Marchessault I'd like to go back to your adsorption isotherms on the pulp. I am wondering whether the decreased adsorption in the case of the polystyrene graft data that you showed is related to the method of grafting. Is there some amount of cross-linking here? I say this because I always had the impression that in most of these grafting cases, certainly on native cellulose, the effect of the insertive synthetic polymer was essentially to just be there and not hinder the adsorption of the cellulose itself. Now I could imagine that if your grafted material tended to be cross-linked it would literally prevent the cellulose from creating its own pore space. My impression was that normally when you insert grafting you do not hinder the adsorption capacity of the cellulose itself.

Stannett Yes, I didn't go into that because of lack of time. The curve I showed had three isotherms and the same amount of polystyrene grafted by different methods bear out pretty well what you say, but I hadn't thought too much of cross-linking. When you graft with just water swollen cellulose the polystyrene is very coiled and opens the structure in a way Dr Scallan shows, and then it can't collapse, and so you get very little improvement. In dioxane and water the monomer and polymer are both soluble. We chose that material for a little test tube experiment so everything would dissolve in that mixture and then I visualised the grafted polystryene being very much more homogeneous and filling up pores and so on. Hydrolysis experiments showed that grafted polystyrene is not cross-linked. We have never tried to deliberate cross-linking and perhaps we could try that.

Mr P. Howarth We have heard a lot this week about clustering. We've been doing some work at UMIST examining, by interference microscopy, the distribution of adhesives in pigment coating layers. We find considerable clustering with styrene-acrylic, for example, and we have been in touch with Dr Heiser in America who has found this with another adhesive. Could we say that when one material is distributed within the matrix of another, clustering is the natural phenomenon rather than uniform distribution. Are we moving into that sort of position.

Stannett I wouldn't go so far as to say that but certainly it is much more common than we had hitherto thought. There is some very interesting work by Manfred Gordon who put water in benzene and found that the water was clustered in the benzene. So it occurs in liquid-liquid mixture also. In fact he applied a modified polymerisation theory to try to explain how the clusters developed with increasing water content in the benzene although you also get some turbidity developing eventually.