

The Sorption of Poly(Vinyl Acetate) on Cellulose. I. The Nature and Extent of the Sorbed Layer

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Synopsis

The sorption of poly(vinyl acetate) from benzene solution onto cellulose fibers has been investigated with particular attention to the nature and extent of the sorbed layer of polymer. The cellulose substrate has been varied by swelling pretreatments with water, ethylenediamine, and 18% sodium hydroxide. The density of the sorbed polymer after drying was found to be similar to that of the bulk polymer (1.19–1.20 g/cm³). Water vapor sorption isotherms were used to evaluate the internal surface of cellulose and the decrease in the surface area accessible to water after sorption of the polymer. This decrease was considered equivalent to the area covered by sorbed polymer. The amount of polymer sorbed per unit area (5.0–5.5 mg PVAc sorbed from benzene per 1 m² of cellulose surface) was found to be substantially independent of the amount of sorbed polymer and of the swelling pretreatment, indicating that the thickness of the sorbed layer was quite uniform (40–50 Å). A comparison of the thickness of the sorbed layer in the dry state with the thickness of a monolayer with polymer molecules lying flat on the solid surface indicated that the fraction of the polymer segments attached directly to the surface was about 0.10. The amount of polymer sorbed per unit area of cellulose and consequently the thickness of the sorbed layer and the fraction of attachment can be affected by the nature of the solvent from which the polymer is sorbed.

INTRODUCTION

In many cases the adsorption isotherm of a polymer from solution onto a solid surface either reaches a marked plateau or tends toward a limiting value. This indicates the formation of a monolayer. But because the limiting weight of adsorbed polymer may be many times greater than that of a low molecular weight analogue under comparable conditions, the concept of a monolayer consisting of macromolecular coils attached only by some of their segments to the surface of a solid is often adopted.

The present work is an attempt to investigate the character of poly-(vinyl acetate) (PVAc) adsorbed from benzene solution onto cellulose fibers (see experimental section), particularly (1) the uniformity of the polymer layer adsorbed on cellulose; (2) the extent of the surface covered by polymer; and (3) the thickness of the adsorbed polymer layer in the dry state.

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In order to obtain information on these questions, the hydrophilic properties of cellulose and the relatively hydrophobic nature of PVAc were exploited. Measurements of water vapor sorption capacity of the cellulose as a function of the amount of sorbed polymer were used to evaluate the changes in water-accessible surface. If we assume that the decrease in water-accessible surface corresponds to the surface covered by polymer, then, knowing the density of sorbed polymer, we could calculate the thickness of polymer layer in the dry state.

EXPERIMENTAL

Materials

Sorbent. Standard laboratory blotters composed of a mixture of cotton, bleached sulfite hardwood, and softwood fibers having an α -cellulose content of 89.4%, ash 0.53%, and Cu number 1.0 were used in the form of strips $\frac{1}{4}$ in. wide. The sheets have an open structure, yet cohere adequately for handling and treatment. Sorption properties are similar to those of other cellulose samples, including purified cotton, and we have no reason to believe that the material is atypical.

Poly(vinyl Acetate). A commercial product, Gelva-15 (Monsanto), prepared from vinyl acetate monomer. The average molecular weight (by the osmotic pressure method) was given by the manufacturer as 90,000.

Solvents. Methanol was purified and dried by distillation using the method based on azeotroping with benzene. Benzene was dried over sodium wire, distilled, and stored under moisture-free conditions.

Preparation of Sorbents

Series A. The samples were immersed in water for 24 hr and then the water was removed by solvent exchange, through methanol to benzene. Every solvent replacement was repeated at least five times over a period of several days. The swollen samples were transferred, without removing the benzene, directly to the sorption tubes.

Series B. The samples were swollen for 24 hr in pure ethylenediamine, which was washed out with methanol. Then the same solvent exchange process as in series C was used.

Series C. The samples were swollen for 4 hr in a solution of sodium hydroxide, 18% by weight. The samples were then washed in water, in 1% acetic acid, and again in water. Finally the water was removed by means of methanol and benzene as in the previous series.

Sorption of Polymer

The sorption of PVAc on cellulose from benzene solution was carried out in glass-stoppered tubes. Approximately 1 g of sorbent, stored in benzene after the pretreatment described above, was placed in 50 ml of solution and

slowly shaken for five days in a water bath at 25°C. The sorption was measured from solutions of increasing concentration from 2 up to 50 g PVAc per litre. A known volume of solution before and after the sorption period was evaporated and dried in vacuo at 60°C to determine the concentration. The fiber samples were rinsed in pure benzene for 24 hr to remove the excess PVAc solution and dried in vacuo at 60°C. In order to remove the last traces of benzene, which would remain in cellulose even after prolonged drying and could influence the subsequent measurements, the dry samples were immersed in water for 24 hr and then, after drying from water at room temperature, were finally dried again in vacuo at 60°C. The amount of sorbed polymer could be determined from the dry weight after sorption and the difference in the concentration of solutions before and after the sorption period. The benzene carried by the sample from the solvent exchange was taken into account, but no correction for benzene adsorbed by the cellulose was made.

The amount of sorbed polymer was

$$m_2 = c_0 \cdot v_0 - c(v_0 + v_b)$$

where c_0 and c are the initial and equilibrium concentrations of PVAc in benzene, v_0 is the volume of solution added to the sample, and v_b is the volume of benzene retained in the sample after pretreatment.

The polymer sorbed per gram of cellulose was $m_2/(m_{12} - m_2)$, where m_2 is the amount of sorbed polymer and m_{12} the dry weight of the sample after sorption.

Density of Sample

The densities of samples with different amounts of sorbed polymer were measured in water by the electromagnetic float method^{1,2} in which the buoyancy of the submerged float and sample is balanced electromagnetically by a measured current passing through a solenoid. The samples were soaked for 24 hr in air-free distilled water before measurement in order to allow good penetration by water.

Sorption of Water Vapor

The sorption of water was measured at various relative vapor pressures of water ($P/P_0 = 0.5, 0.12, 0.19, \text{ and } 0.27$) produced by various water-sulfuric acid mixtures in a desiccator. The amount of sorbed water was determined from the difference in weight after a 48-hr sorption period and was expressed per gram of cellulose rather than per gram of cellulose plus sorbed polymer. The results of water sorption were used to calculate the amount of sorbed water in a monolayer and the surface area by the Brunauer, Emmett, and Teller (BET) method.³

After the measurement, the sorbed polymer was removed by means of a Soxhlet extraction with methanol for 24 hr. The samples were resoaked in water and dried at 60°C in vacuo and again the sorption of water was

measured in order to find out if the samples would reach the same water sorption capacity regardless of the amount of sorbed and removed polymer.

Heat of Wetting in Water

Using a method previously described,⁴ the heat evolved on contact between liquid water and samples containing various amounts of sorbed polymer was measured. The bulk polymer does not show a measurable heat effect by this method.

RESULTS

Sorption of PVAc

The sorption isotherms of PVAc from benzene solution on a cellulose treated with (A) water, (B) ethylenediamine, and (C) sodium hydroxide solution are shown in Figure 1. The isotherms have similar shapes, showing steeply increasing amounts of polymer sorbed at low equilibrium concentrations and a limiting plateau. No step in the adsorption isotherm was found up to almost 5% PVAc concentration, as was reported by Patat⁵ for PVAc adsorption on alumina and copper foil.

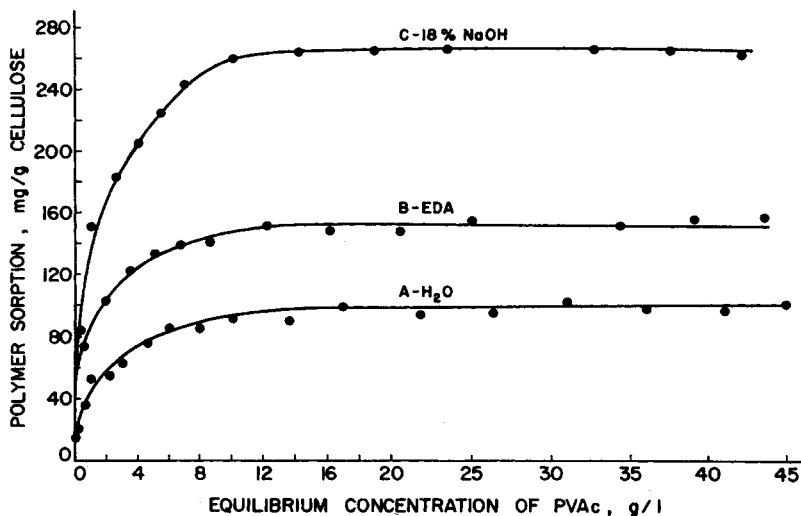


Fig. 1. Sorption of PVAc from benzene on cellulose swollen in water, ethylenediamine, and 18% sodium hydroxide.

Density of Sorbed Polymer

The changes of density as a function of the amount of sorbed PVAc are shown in Figure 2. The obviously regular dependence in all three series indicates the good penetration of samples by water and it is therefore possible to calculate the density of the sorbed polymer from these values with

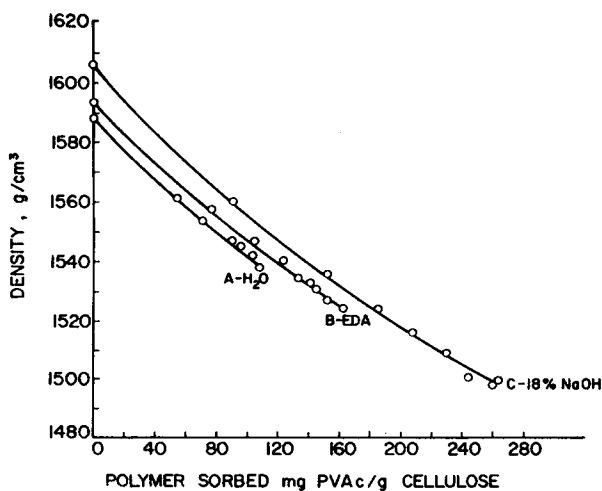


Fig. 2. Density in water of samples A, B, and C as a function of amount of sorbed PVAc.

some degree of confidence. Because the density is an additive quantity, the resulting value for a system of two components is given by the simple equation

$$d_{12} = \frac{m_1 + m_2}{v_1 + v_2}$$

Knowing the density of system d_{12} , the mass of both components, m_1 and m_2 , and the volume of cellulose v_1 , the volume v_2 , and hence the density d_2 of polymer were calculated. The results of all the measured samples are expressed in Table I as average values of at least two parallel measurements.

TABLE I
Density of Samples d_{12} and Calculated Density
of Sorbed Polymer d_2 Measured in Water

Series A			Series B			Series C		
PVAc, mg, per 1 g cell	d_{12}	d_2	PVAc, mg, per 1 g cell	d_{12}	d_2	PVAc, mg, per 1 g cell	d_{12}	d_2
0	1.5880		0	1.5962		0	1.6080	
53.3	1.5601	1.184	76.1	1.5585	1.207	89.7	1.5600	1.180
71.4	1.5535	1.190	103.5	1.5472	1.203	150.5	1.5366	1.185
88.8	1.5467	1.200	122.1	1.5413	1.208	182.8	1.5240	1.187
94.2	1.5456	1.208	131.3	1.5350	1.194	206.1	1.5169	1.191
102.8	1.5422	1.209	139.4	1.5336	1.201	227.0	1.5089	1.188
104.1	1.5378	1.183	144.0	1.5310	1.200	242.4	1.4996	1.177
			149.8	1.5264	1.188	263.3	q.4990	1.191
			148.0	1.5280	1.193	260.9	1.4890	1.185
Av		1.196			1.198			1.187

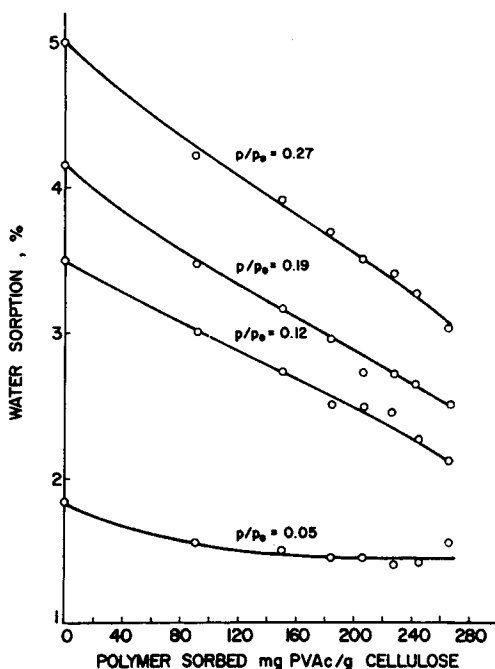


Fig. 3. Water sorption capacity of samples swollen in 18% sodium hydroxide C as a function of amount of sorbed PVAc at various relative pressures of water vapor.

The calculated values of the polymer density range from 1.183 to 1.208 g/cc and thus agree well with the density (1.18–1.21 g/cc) previously reported for solid PVAc.⁶

Influence of Sorbed Polymer on the Water Sorption Capacity

The results of water vapor sorption expressed as per cent water based on cellulose at $P/P_0 = 0.07, 0.12, 0.19,$ and 0.27 obtained for the samples in series C are shown in Figure 3. It is obvious that the accessibility of cellulose to water is sensitive to the amount of sorbed polymer and decreases regularly with increasing polymer content. To explain this behavior we assumed that the sorption sites for both polymer and water are the hydroxyl groups of cellulose. A mechanism will be proposed to support the suggestion that the loss of surface accessible to water vapor may be identified with the surface covered by the sorbed polymer. Such a picture is supported by the observation that after extracting the polymer from cellulose, all the samples again reached the same water sorption capacity as before polymer sorption.

Internal Surface of Cellulose Covered by Sorbed Polymer

To calculate the internal surface of cellulose, the sorption of water at the various relative water vapor pressures was used, assuming that the sorp-

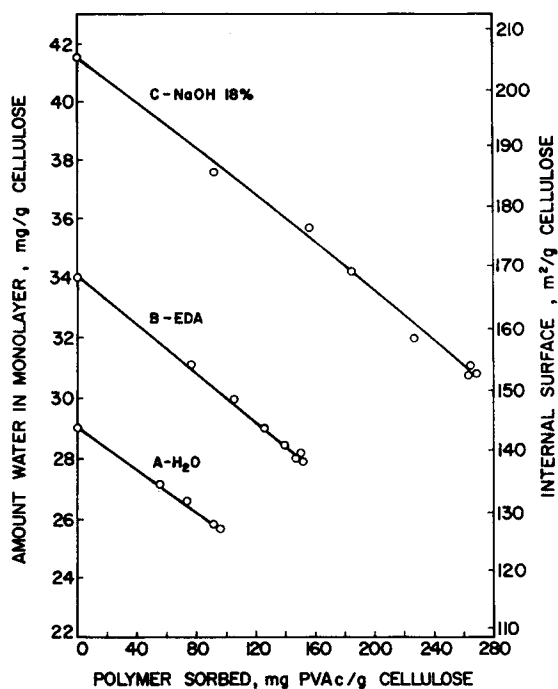


Fig. 4. The amount of water sorbed in a monolayer and the internal surface (BET) of samples A, B, and C per gram cellulose, as a function of the amount of sorbed PVAc.

tion isotherms of water are suitable for evaluating the contact area between the cellulose and water, i.e., the internal surface of the cellulose in the swollen state.⁷ The contact area is then developed when water molecules are allowed to enter the dry cellulose and break the hydrogen bonds between the hydroxyl groups of the cellulose chains. The previous cellulose-to-cellulose contact is replaced by cellulose-to-water contact. Thus, if some of the hydroxyl groups are not accessible to water because of sorbed polymer, the cellulose-water contact area would decrease.

Using the BET method, the amount of water in a monolayer at the cellulose-water interface was calculated and expressed as a function of the amount of sorbed polymer and plotted in Figure 4. To obtain the absolute value of internal surface from the known amount of water in a monolayer, the value of 14.8 \AA^2 per molecule of water was used.⁸ The decrease of internal surface in the case of series A was found to be $18 \text{ m}^2/\text{g}$ cellulose when the amount of sorbed polymer was 100 mg/g cellulose. In series B, the decrease is $29 \text{ m}^2/\text{g}$ at 150 mg/g and in series C, $52 \text{ m}^2/\text{g}$ corresponds to 260 mg polymer.

Thickness of the Sorbed Polymer Layer

Assuming that the surface area inaccessible to water is the area covered by polymer and knowing the volume of sorbed polymer, the thickness of

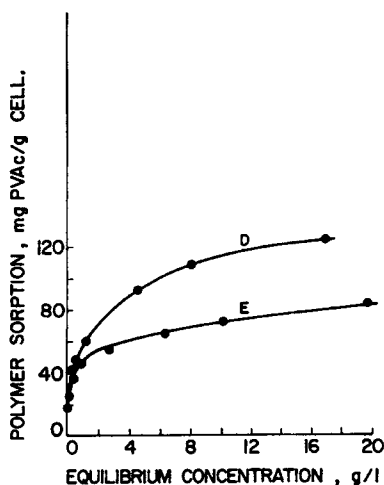


Fig. 5. Sorption of PVAc from benzene (D) and benzene-acetone mixture (E) on cellulose swollen in water.

polymer layer in the dry state could be calculated. Because of the linear relation between the amount of sorbed polymer and the decrease of surface area, a uniform coverage of surface by polymer is indicated. The average thicknesses are as follows: series A, 47 Å; series B, 43 Å; series C, 42 Å.

The fraction of segments attached directly to the solid surface could be calculated from the thickness of the sorbed layer and the thickness of a monolayer with polymer molecules lying flat on the solid surface, which is reported in the case of PVAc to be 4.7 Å.⁹ It turns out that about 90% of the polymer is without direct contact with cellulose and therefore the fraction of segments attached to the surface is about 0.11 in the case of series B and C and 0.10 in series A.

Because the thickness of a polymer layer and the amount of sorbed polymer are often compared with the size of macromolecules in solution, additional measurements were carried out. Two series of water-swollen and identically treated cellulose samples were used for PVAc sorption, the first sorbed from benzene solution, the second from a mixture of benzene with 30 vol-% acetone. The isotherms are shown in Figure 5. The amount of sorbed polymer is less from the binary solvent and could be controlled by the ratio of benzene to acetone.^{10,11} The intrinsic viscosities of the two solutions are similar¹¹ (0.62 dl/g and 0.65 dl/g), so that no significant differences in the size of the polymer coil are indicated. The changes of internal surface accessible to water as a function of the amount of sorbed polymer are shown in Figure 6 and indicate that almost the same surface is covered by polymer in both cases but with a different amount of polymer. From benzene, 125 mg PVAc covers 27 m² and from the benzene-acetone mixture, 85 mg covers 26 m². Therefore the average thicknesses calculated for the polymer layers are 41 Å and 25 Å, respectively. The fact needs to

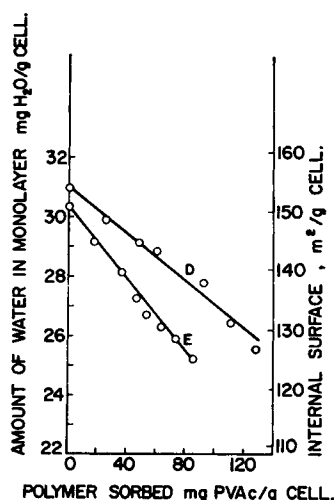


Fig. 6. The amount of water sorbed in a monolayer and the internal surface (BET) of samples D and E per gram cellulose, as a function of the amount of sorbed PVAc.

be stressed that these values were found for the dry state and therefore are hardly comparable with the thicknesses of layers sorbed on samples still immersed in solution. The removal of solvent during drying is accompanied by significant collapse of the sorbed layer, which is highly swollen with a low density¹² in contact with solvent but which has the density of solid polymer after drying.

The competitive effect of polymer and acetone for sorption sites can be taken into account to explain the differences in thickness. Some of the sites occupied by polymer in the presence of pure benzene become more inaccessible because of the attraction forces between acetone and cellulose and therefore less polymer is sorbed per unit area of solid. The subsequent drying leaves a layer with a thickness less than when all of the sites were available to the polymer. These results indicate how the character of the sorbed layer is influenced by the change of one of the sorption conditions.

Heat of Wetting (Immersion)

The heat which is evolved when a solid is immersed in a liquid depends on the energy of interaction between the solid and liquid and on the amount of liquid which is taken up by the solid. Therefore the samples which differ in the surface area accessible to water because of adsorbed hydrophobic polymer should evolve different amounts of heat when immersed in water. The heats of wetting as a function of the amount of sorbed polymer are shown in Figure 7. It is obvious that the heat evolved depends on the content of polymer, but the dependence is not linear. Thus the changes in surface area cannot be evaluated on the basis of heats of immersion.

Some explanation of the behavior could be found by trying to analyze the mechanism of wetting. Very simply speaking, we can imagine that the

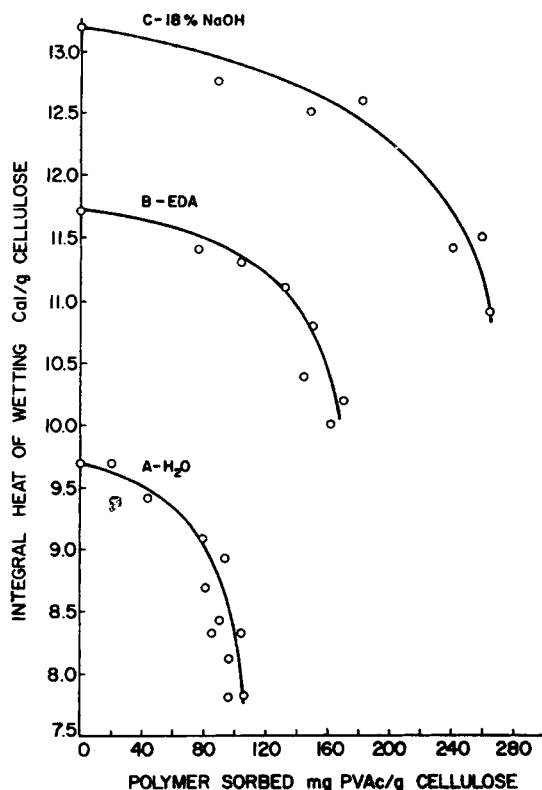


Fig. 7. Heat of swelling in water of samples A, B, and C as a function of the amount of sorbed PVAc.

final heat effect of wetting in the case of swelling material derives from two basic processes. One is the exothermic process when the water molecules are attached to the hydrophilic surface and the second one is endothermic when water molecules create new surface by breaking the hydrogen bonds between cellulose chains. Because the samples were dried after sorption of polymer, the pores existing in swollen state have collapsed together with the adsorbed polymer. Thus some parts of the cellulose structure with polymer layer between them are held together under greater attraction forces than previous cellulose-to-cellulose bonds.

The whole structure becomes more resistant to swelling and more work has to be done to dissociate the cellulose structural elements, which means that more heat is consumed in the swelling process. The final heat effect is lower than expected on the basis of proportionality to the decrease of water-accessible surface.

DISCUSSION

One of the basic problems in polymer sorption from a solution onto a solid surface is the structure of the sorbed layer. It is generally accepted

that the polymer molecules are often adsorbed as random coils much as they exist in solution. In this configuration, relatively few monomer units function as anchor segments and the absorbed layer has considerable thickness.

A limited amount of work has been reported on the determination of the thickness of the sorbed layer and the fraction of segments sorbed on the surface. Methods based on viscometry,¹³⁻²⁰ ellipsometry,²¹⁻²³ surface potential,²⁴ infrared spectra,²⁵⁻²⁸ x-rays,³¹ sedimentation velocity,²⁶ and dropping mercury electrode^{29,30} have been used. These attempts have met with varying success and the results are often at variance even with similar systems and techniques.

These methods are in general applicable to measurements of the sorbed layer in the continued presence of the solvent. Moreover, they are applicable only in the case of smooth surfaces of nonporous solids and are usually not suitable for cellulose materials having an irregular surface and a porous fine structure. Thus a different approach has been chosen with rather different objectives. The extent and thickness of the sorbed layer have been measured after the polymer has been dried down by removal of the solvent.

The main problem is to determine the surface that is accessible to the polymer. A broad range of pore sizes exists in cellulosic materials and most of the internal surface, being connected with the smaller pores, is not accessible to the larger polymer molecules.

Water vapor sorption isotherms were used to calculate accessible areas by the BET method before and after polymer sorption and these revealed the decreases that have been reported. That the decreases were due to sorbed polymer was demonstrated by extracting polymer from appropriate samples with methanol in a Soxhlet. The water sorption of the extracted cellulose, after swelling in water and drying, was identical with that of the original sample.

The decrease in the indicated area when polymer was present is identified with the area covered by the sorbed polymer layer and was found to be proportional to the amount of polymer sorbed. This identification requires an assumption, either that the water vapor does not sorb on exposed PVAc surfaces or that there is negligible exposed PVAc under the conditions of the experiment. There are no data to support the first assumption, but the latter appears plausible.

We assume that when the sample with sorbed polymer is dried from benzene, the polymer-coated surfaces are drawn together and bonded and are subsequently unavailable for water vapor sorption. This explanation is partially supported by an experiment in which samples before and after polymer sorption were dried from benzene in a stream of dry nitrogen, thus preserving, at least partially, their expanded structure.³² The surface areas of the samples were measured by standard nitrogen sorption techniques.³³ The sample without polymer had an available surface area of 50 m²/g, while for the sample with sorbed polymer it was only 11 m²/g. The difference

means that the presence of polymer had resulted in some collapse of the porous structure and we assume that all pores containing polymer are closed. After a wetting-drying cycle, both samples showed complete collapse and the nitrogen sorption areas were reduced to 1.2 and 1.1 m²/g, respectively.

The following simplified scheme is used to illustrate the assumed behavior.



(a) The sample of cellulose swollen in water, water replaced by methanol and finally by benzene—the open structure with different sizes of pores remains. (b) The sorption of PVAc from benzene—only the bigger pores are accessible to the polymer. (c) The benzene is removed from the sample—the pores with sorbed polymer collapse. (d) The sample is reswollen in water and dried—all the remaining pores collapse. (e) The sorption of water—only the pores without polymer are accessible to the water molecules.

Although a dependence of water vapor sorption on the amount of sorbed polymer has been demonstrated and is quantitatively reasonable, there remains some question about the validity of evaluating surface areas using water vapor. Opinions have been expressed that the addition of water to cellulose is a bulk phenomenon,³⁴⁻³⁷ equivalent to a solution process, and does not form a basis for demonstrating or measuring internal surfaces. On the other hand, the values of surface areas by nitrogen and water vapor sorption have sometimes been found to be in good agreement^{7,32,42} for swollen solvent-exchanged cellulose. However water vapor sorption measurements may give low values for the area³⁸⁻⁴¹ for materials other than cellulose, such as silica, quartz, or carbon black.

There is thus some uncertainty concerning the absolute values of the surface covered by the polymer, and therefore of the absolute thickness of the sorbed layer. Even though the values we have recorded may be only relative, their systematic behavior attests to their significance and provides a basis for drawing some conclusions about the nature of the sorbed layer.

SUMMARY AND CONCLUSIONS

Measurements of density, water vapor sorption, and heats of wetting have been made on cellulose fibers, with and without sorbed polymer. These measurements on dried fibers have been used to reach some conclusions about the nature and extent of the sorbed polymer layer.

(1) The thickness of the sorbed layer or the amount of polymer sorbed per unit area of cellulose is substantially unaffected by swelling pretreatment of the fibers.

(2) The thickness of the sorbed layer is independent of the amount of polymer sorbed from a given solvent and the isotherm, therefore, measures surface coverage.

(3) The thickness of the sorbed layer can be affected by the nature of the solvent.

(4) The area occupied by sorbed polymer on swollen, solvent-exchanged cellulose is up to 50 times greater than the superficial area. Internal surfaces are therefore involved.

(5) The thickness of the sorbed layer after drying indicates that the fraction of segments in contact with the surface is about 0.10.

References

1. S. H. Mhatre and J. M. Preston, *J. Text. Inst.*, **40**, T831 (1949).
2. Kozler, M., Fainberg, E. Z., and Mikhailov, N. V., *Vysokomol. Soedin. (Polym. Sci. USSR)*, **2**, 444 (1960); B. Alince, *Svensk Papperstidn.*, **65**, 216 (1962).
3. Brunauer, S., Emmett, P. H., and Teller, E., *J. Amer. Chem. Soc.*, **60**, 309 (1938).
4. Kuniak, L., and Alince, B., *Drevarsky Vyskum (Slovak)*, **2**, 67 (1965).
5. Patat, F., and Nitschmann, R., *Monatsh. Chem.*, **95**, 716 (1964).
6. Brandrup, J., and Immergut, E. H., *Polymer Handbook*, Interscience, New York, 1966, p. IV-92.
7. Stamm, A. J., *Tappi*, **40**, 761 (1957).
8. Harkins, W. D., *The Physical Chemistry of Surface Film*, Reinhold, New York, 1952, p. 235.
9. Shick, M. J., *J. Polym. Sci.*, **25**, 465 (1957).
10. Luce, J. E., Ph.D. Thesis, McGill University, Montreal, 1960.
11. Chan, F. S., and Robertson, A. A., *J. Colloid Interfac. Sci.*, in press, 1970.
12. Patat, F., Killmann, E., and Schliebener, C., *Fortschr. Hochpolym. Forsch.*, **3**, 332 (1964).
13. Ohrn, O., *Ark. Kemi*, **12**, 397 (1958).
14. Ohrn, O., *J. Polym. Sci.*, **17**, 137 (1955).
15. Tuijman, C. A. F., and Hermans, J. J., *J. Polym. Sci.*, **25**, 385 (1958).
16. Fendler, H. G., and Stuart, H. A., *Makromol. Chem.*, **21**, 193 (1956).
17. Rowland, F. W., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, New York, 1963.
18. Rowland, F. W., and Eirich, F. R., *J. Polym. Sci. A-1*, **4**, 2033 (1966).
19. Rowland, F. W., Bulas, R., Rothstein, E., and Eirich, F. R., *Ind. Eng. Chem.*, **57**, 46 (1965).
20. M. M. Huque, M. Fishman, and D. A. I. Goring, *J. Phys. Chem.*, **63**, 766 (1959).
21. Stromberg, R. R., Passaglia, E., and Tutas, D. J., *J. Res. Natl. Bur. Std.*, **A67**, 431 (1963).
22. Passaglia, E., and Stromberg, R. R., *Polymer Preprints*, **5**, 508 (1964).
23. Stromberg, R. R., Tutas, D. U., and Passaglia, E., *J. Phys. Chem.*, **69**, 3955 (1965).
24. Gottlieb, H. M., *J. Phys. Chem.*, **64**, 427 (1960).
25. Fontana, B. J., and Thomas, J. R., *J. Phys. Chem.*, **65**, 480 (1961).
26. Fontana, B. J., *J. Phys. Chem.*, **67**, 2360 (1963).
27. Thies, C., Peyser, P., and Ullman, R., Proceedings of the 4th International Congress of Surface Activity Sept. 1964, Vol. II, Brussels.
28. Peyser, P., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, New York, 1964.
29. Miller, I. R., and Graham, D., *J. Amer. Chem. Soc.*, **78**, 3577 (1956).
30. Miller, I. R., *Trans. Faraday Soc.*, **57**, 301 (1961).

31. Greenland, D. J., *J. Colloid Sci.*, **18**, 647 (1963).
32. Merchant, M. W., *Tappi*, **40**, 771 (1957).
33. Scallan, A. M., private communication.
34. Hermans, P. H., *Physics and Chemistry of Cellulose Fibres*, Elsevier, Amsterdam, 1949, p. 181.
35. Barkas, W. W., *The Swelling of Wood Under Stress*, H.M.S.O., London, 1949, p. 11.
36. Morton, W. E., and Hearle, J. W. S., *Physical Properties of Textile Fibres*, Butterworths, London, 1962, p. 233.
37. Greyson, J., and Levi, A. A., *J. Polym. Sci. A-1*, **1**, 3333 (1963).
38. Young, G. J., *J. Colloid Sci.*, **13**, 67 (1958).
39. Dzhigit, O. M., Kiselev, A. V., and Muttik, G. G., *Kolloid Zh.*, **23**, 553 (1961).
40. Whalen, J. W., *J. Phys. Chem.*, **65**, 1976 (1961).
41. G. J. Young, J. J. Chessik, F. H. Healey, and A. C. Zettlemoyer, *J. Phys. Chem.*, **58**, 313 (1954).
42. Stamm, A. J., *Wood and Cellulose Science*, Ronald Press, New York, 1964.

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