

The Role of Porosity in Polyethylenimine Adsorption onto Cellulosic Fibers

B. ALINCE, *Pulp and Paper Research Institute of Canada, 3420 University St., Montreal, Quebec, Canada, H3A 2A7*

Synopsis

The total adsorption of a given polyethylenimine on pulp fibers, the porosity of which was altered by different drying conditions, was determined and compared with the available internal surface of the fibers. Since polymer adsorption takes place in an aqueous environment, the pore volume and the internal surface of pores as a function of their size were determined from a first benzene desorption isotherm, measured on fibers in which water was replaced by benzene to preserve their swollen structure. The total adsorption of a given polyethylenimine was found to be in a direct relation to the internal surface available in pores larger than a certain size, regardless of the total porosity. Consequently, it is concluded that the adsorption capacity is determined by the accessible surface.

INTRODUCTION

Polyelectrolytes are used to modify the surface characteristics of pulp fibers and other solids dispersed in water, which constitute the materials for making paper. In a typical case, a cationic polyelectrolyte is employed to promote attraction between pulp fibers and small particles of colloidal dimensions, all negatively charged, thus improving their retention. Increase of interfiber bonding, and consequently strength of paper, and control of liquid movement within the porous structure of paper due to the alteration of surface energy of fibers are other examples of the use of such polymers. The polymer's effectiveness is related to many factors, but its performance as a surface modifier rests in its ability to adsorb. Since the process of polymer adsorption from solution is rather complicated, the lack of knowledge often prevents us from full utilization of the polymer potential.

Generally, the total amount of adsorbed polymer is a product of a specific adsorption per unit area and the surface area upon which the adsorption takes place. The specific adsorption per unit area may vary with the molar mass of the polymer, the nature of the surface, and the configuration of polymer in solution and on the surface. In the case of a polyelectrolyte, its ionic character adds to the complication because of specific interaction with solids also containing ionizable groups. The extent of surface is particularly important when dealing with a porous substrate where the polymer can be excluded, due to its size, from entering the pore. The failure to take into account the accessibility of the internal surface to the polymer may lead to erroneous conclusions concerning the adsorption mechanism. A typical example is the relation between the adsorption capacity and the molar mass. It has been found that on cellulosic fibers and other microporous substrates the extent of polyethylenimine adsorption increases with decreasing molar mass.¹⁻⁵ How-

ever, on substrates with large pores the relation was reversed² in accordance with the usual findings in polymer adsorption. Such behavior indicates that with decreasing size of the polymer molecule more internal surface becomes available. Electron probe microanalysis has confirmed that polyethylenimine of low molar mass can penetrate into the wall of cellulose but that of higher molar mass is mostly excluded.⁶

Here an attempt is made to correlate the adsorption capacity with the internal surface of pores. The conditions under which the adsorption was investigated were chosen so that the polymer was practically uncharged because the ionic character of polyethylenimine presents two problems. First, the adsorption capacity is pH-dependent⁷⁻¹⁰; at low pH adsorption decreases because the molecule assumes an extended configuration due to an increased ionization and repulsion between its ionic groups. Consequently, it lies flat on the surface and less can be accommodated on a given surface than when it is in the form of coil at higher pH. Second, it has been reported^{7,8,10} that because of its cationic character the adsorption capacity depends on carboxyl content of cellulose, apparently due to ion exchange or complex formation. In this case the accessibility of the anionic groups would affect the amount of polymer adsorbed. The adsorption was therefore carried at pH around 10 where the polyethylenimine ionization is minimized^{9,11} and in the presence of 0.1M NaCl. Under these conditions the polymer molecule in solution should assume a configuration of a coil and the specific adsorption should not be affected by formation of a complex with the acidic groups of cellulose. The adsorption of a given polyethylenimine was performed on fibers, the porous structure of which was altered by different drying conditions. Because the adsorption takes place in an aqueous environment the porosity of swollen fibers must be considered.

EXPERIMENTAL

Materials

Dissolving Pulp. Never dried (ND), dried at 105°C, and reswollen (D) and dried a second time (2D).

Polyethylenimine. Polymine P (BASF). $\bar{M}_m = 6 \times 10^5$ determined by light scattering.¹²

Methods

Total Polymer Adsorption. Fibers (0.5 g) were placed in a stoppered tube containing 50 cm³ of 1% polymer solution, NaCl to give 0.1M, and adjusted to pH 10. The polymer concentration used is far above that required for saturation adsorption.^{1,4,5,10} After 48 h in temperature-controlled (25°C) shaker bath, the fibers were separated from the solution, washed with pH adjusted water in order to remove any excess of polymer, dried, and analyzed for nitrogen using the Kjeldahl method. The nitrogen content was converted to polyethylenimine by multiplying by 3.07. The amount of adsorbed polymer was also calculated from the change in polymer concentration of the supernatant before and after the sorption period. The Rayleigh interference refractometer was used for determination of the polymer concentration. Both methods gave similar results.

TABLE I
Polyethylenimine Adsorption on Microcrystalline Cellulose (Avicel)

Sample	\bar{M}_m^a	Specific adsorption ^b (mg/m ²)	Disintegrated		Aggregated	
			Adsorption capacity ^c (mg/g)	Covered surface ^d (m ² /g)	Adsorption capacity (mg/g)	Covered surface ^d (m ² /g)
PEI 12	8×10^2	0.7	14.0	20.0	7.5	10.7
Polymin P	6×10^5	1.9	36.0	18.9	10.5	5.8
PEI 600	5×10^6	3.0	59.0	19.7	5.5	1.9

^a From light-scattering.²⁴

^b Calculated from $A = 0.095 \bar{M}_m^{0.225}$.

^c From Ref. 14.

^d Calculated from ads. capacity and specific adsorption.

Porosity of Swollen Fibers

A method described elsewhere¹³ using the first benzene desorption isotherm was employed. Water-swollen fibers were solvent-exchanged through methanol to benzene and without drying from benzene placed in a vacuum sorption apparatus. The samples were allowed to equilibrate in an atmosphere of saturated benzene vapors, and then, by gradually lowering the benzene vapor pressure, the first desorption isotherm was obtained. The changes in the weight of the sample, representing the amount of desorbed benzene at given relative benzene vapor pressure, were recorded by means of a Cahn Electrobalance. The pore size distribution and the pore volume were calculated from the desorption isotherm. The total pore volume was comparable to that determined by a solute exclusion technique in water. The surfaces associated with given pore sizes were calculated assuming uniform cylindrical capillary pores.

RESULTS AND DISCUSSION

Accessibility of Surface

In order to demonstrate how the accessibility of the surface affects the adsorption capacity, the total adsorption of three polyethylenimines of different molar mass on microcrystalline cellulose (Avicel) is presented in Table I. Avicel was employed in the form of powder, which consists of aggregates of single microcrystals, and after disintegration at high shear in a Waring blender as well. The aggregates represent a porous solid with only a fraction of the internal surface accessible.

The adsorption capacity on the disintegrated Avicel clearly shows the dependence on molar mass.¹⁴ The increased adsorption, as molar mass increases, indicates that the polymer does not adsorb in its extended form lying flat on the surface. Such a configuration would be unrealistic anyhow, because at the high pH and in the presence of salt the polymer is practically uncharged and coils up. It has been shown that it acts essentially as an impermeable sphere.² Thus, assuming that the polymer will deposit on the solid surface as a monolayer of undeformed closely packed (hexagonal) spheres the specific adsorption A in mg/m² can be calculated using the formula

TABLE II
Adsorption of Polymin P on Fibers Treated with 0, 1, 5, and 10% NaOH¹⁴

NaOH (%)	WRV ^a (g H ₂ O/g fiber)	Ads. cap. (mg/g fiber)
0	0.7	16
1	0.9	25
5	1.0	30
10	1.1	35

^aWater retention value.

$A = 0.095 \bar{M}_m^{0.225}$.⁵ The \bar{M}_m values for the three polymers employed, and given in Table I, are then used to calculate the extent of the surface covered. As seen in the table this surface for each of the polymer is around 20 m²/g. This would represent the total exposed surface of the disintegrated Avicel, which is accessible to all the polymers regardless of their size.

In the case of the aggregated Avicel the adsorption capacity differs from that obtained on the disintegrated sample and the difference increases with the size of the polymer molecule. Now the largest polymer shows the least adsorption. Using the data for specific adsorption, it can be seen from Table I that the internal surface covered decreases with the molar mass of the polymer. Considering the porous character of the aggregates, it is conceivable that the lower accessibility results from steric hindrance and, as the polymer size increases, it is excluded from an increasing portion of the pores. Thus the total surface upon which it can adsorb decreases. This conclusion is strongly supported by a study of fractionated polyethylenimine adsorption on porous silica gel² and porous glass.⁵ Another example of the dominant role that accessibility has on adsorption capacity is provided in the study of polyethylenimine adsorption on pulp fibers which have been swollen to varying degree in aqueous NaOH.¹⁴ The swelling, evaluated by measuring the water retention value, and the corresponding adsorption capacity are given in Table II. The water retention value, expressed as the amount of water held in the fiber wall, reflects the total pore volume. As seen in the table the polymer adsorption increases with the porosity, thus indicating an increased accessibility of the internal surface to the polymer.

Correlation between Adsorption Capacity and Porous Structure

Provided that the porous structure of samples of different porosities is known, a comparison with adsorption capacity can be made. The fibers were employed in a never dried state, dried at 105°C in oven, and dried again after reswelling in order to alter their porosity. Since the adsorption takes place in an aqueous environment, characterization of the wet porous structure, particularly the pore size distribution and the internal surface of the swollen fibers, is of importance. Dry fibers have a negligible porosity, but after swelling in water a considerable porosity develops.

The total porosity can be evaluated from the amount of water held within the cell wall, but the pore size distribution remains unknown. The gas adsorption technique, frequently used for porosity analysis, requires a dry

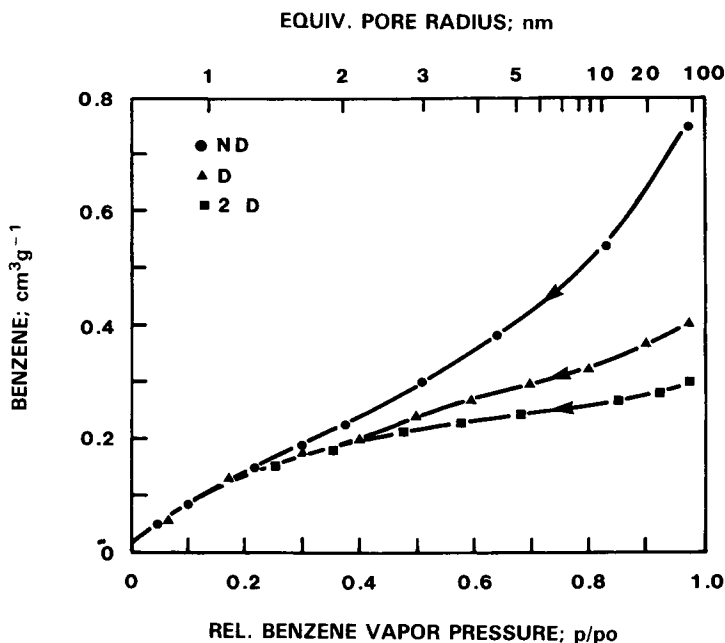


Fig. 1. First benzene desorption isotherm measured on never dried (ND) fibers, dried and reswollen (D), and again dried and reswollen (2D). Radius of capillary that would empty at a given relative benzene vapor pressure indicated on top.

sample, which requires obtaining an aerogel with the porous structure preserved. Simple evaporation of water collapses the gel to a non-porous solid.^{13,15} Freeze-drying is also ineffective in preserving the swollen structure of cellulose.^{13,15,16} The solvent exchange technique, in which the water is consecutively replaced by alcohol and by a nonplanar organic liquid, which is finally evaporated, is successful for producing a highly expanded aerogel. However, it has been shown that a considerable shrinkage occurs upon the removal of the last liquid.¹³ A modification of the solvent-exchange technique, using carbon dioxide as the last liquid that is removed above its critical temperature,^{17,18} results in an even more expanded structure but the total pore volume is still below the volume of water held in a swollen sample. Another method devised for pore size analysis, without drying the sample, is based on an exclusion of probes of different size (dextran, polyethyleneglycol)¹⁹⁻²² from the swollen sample. Although excellent for determining the total pore volume, it is subject to criticism,^{23,24} which makes it questionable as a method for determining pore size distribution.

The technique employed here is basically the solvent-exchange method, but, instead of drying the last liquid prior to gas adsorption, the first desorption isotherm of the last liquid, benzene, was recorded.¹³

In Figure 1 are shown the first benzene desorption isotherms measured on the three samples used. The radius of capillary that would empty at a given benzene partial vapor pressure p/p_0 , and calculated from Kelvin's equation, is shown at the top. The volume of benzene at $p/p_0 = 0.98$ represents the volume of all pores of radius up to 100 nm. For never-dried, dried (and

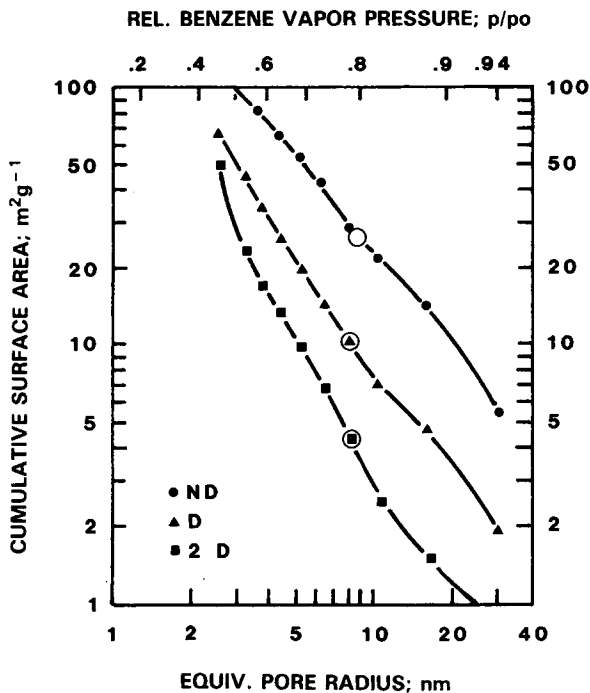


Fig. 2. Cumulative surface area in pores above and including a given equivalent pore radius calculated from the first benzene desorption isotherm. (Pores are assumed to be uniform and cylindrical capillaries.) Relative benzene vapor pressure at which a capillary of given radius would empty is shown on top. The large dots indicate the surface required to accommodate the polymer adsorbed; calculated from total adsorption and specific adsorption $1.9 \text{ mg}/m^2$.

reswollen), and twice-dried fibers it is 0.75 , 0.40 , and $0.30 \text{ cm}^3/g$, respectively, which are values comparable to the volume of water in swollen samples. The total internal surface area, calculated by the BET method, is $340 \text{ m}^2/g$ for the never-dried fibers and $325 \text{ m}^2/g$ for the dried and reswollen samples. The rather small difference in total internal surface, which is predominantly associated with small pores, indicates that the large pores are responsible for the considerable difference in the total pore volume. This is, after all, quite obvious from comparison of the isotherms.

The isotherms were used to obtain the volume of pores of a given average radius and the surface associated with those pores was calculated, assuming cylindrical pores. Figure 2 shows the cumulative surface area in all pores above and including the given pore radius of fibers subjected to the three different pretreatments.

The actual absolute values of pore size and internal surface are to be taken with some reservation because of the necessary assumptions for computation—uniform and cylindrical pores and rigidity of porous structure during benzene desorption. However, the measurements are reproducible and the results provide a basis for comparing the porous structure of the substrate when subjected to various pretreatments.

The adsorption capacity of the three samples, shown in Table III, compares reasonably well with their internal surface. The ratio of polymer adsorption is

TABLE III
Adsorption of Polymin P on Pulp Fibers of Different Porosity
and the Required Internal Surface Area

Sample	Adsorption capacity (mg/g)	Ratio	Internal ^a surface (m ² /g)
ND	50.5	6.3	26.6
D	19.6	2.4	10.3
2D	8.0	1.0	4.2

^a Calculated from adsorption capacity and specific adsorption 1.9 mg/m².

6.3:2.4:1, which is similar to the ratio of their surface area in Figure 2. However, this relation is noticeable at any given pore size, and, consequently, it is difficult to say if there is a limiting pore size below which the polymer is excluded from entering.

In order to get some indication about the accessible pores one might use the specific adsorption of 1.9 mg/m² obtained for this polymer (Table I) and calculate the area required to accommodate the amount of polymer adsorbed. The extent of surface required, shown in Table III and Figure 2, is found in pores of radius larger than about 8 nm. If taken rigorously this would mean that pores smaller than the size of polymer are accessible because the equivalent hydrodynamic spherical radius of the polymer, calculated from the Einstein-Stokes equation $[\eta] = 2.5 (Na/\bar{M}_m)(4/3)\pi R^3$, is larger. Using the intrinsic viscosity $[\eta] = 23.1 \text{ cm}^3 \text{ g}^{-1}$ and the molar mass $\bar{M}_m = 6 \times 10^5$ daltons taken from Ref. 12, the value of 12.8 nm is obtained.

There are several reasons for the apparent discrepancy. First, the pore radius calculated from Kelvin's equation is not corrected for the thickness of benzene multilayer that remains on the pore walls after desorption. The actual thickness is not known, but it is estimated that for benzene it is 1–2 nm.⁵ Still, even after correcting the "Kelvin radius" by adding the adsorbed layer, the pore size will be less than the size of the polymer.

The second reason relates to the polymer itself which has a very broad molar mass distribution.¹² Consequently, provided that there is enough polymer present, pores smaller than the average polymer size will be accessible to the fraction of lower molar mass. The evidence for this is provided by polyethylenimine adsorption on porous glass with a very narrow distribution of pores.⁵ The polymer, identical with that used here, adsorbed in the amount of 67.2 and 31 mg/g on a glass having pore radii of 10 and 4 nm, respectively, i.e., below the average equivalent hydrodynamic radius of the polymer.

However, the above assumes that the polymer behaves like a rigid sphere. A simple consideration of density shows that the polymer chain is rather loosely packed. The volume of a sphere having 12.8 nm radius is about 8800 nm³ while the volume of a molecule of molar mass 6×10^5 and density 1 g/cm³ is about 1000 nm³. This means that each polymer molecule is associated with 7800 nm³ of water. Consequently, the coil might be easily deformable and enter a pore, the aperture of which is less than the hydrodynamic dimensions of the polymer.

Regardless of the absolute values, the correlation between the extent of polymer adsorption and the porosity of the substrate indicates that the adsorption capacity is determined by the accessibility of the internal surface. It appears that for this polymer cylindrical pores of a "Kelvin radius" above 8 nm are accessible.

CONCLUSION

The attempt to correlate the adsorption capacity and porous structure of fiber provides, at least in a relative sense, a confirmation that the accessibility of surface within the pores is the dominant factor in polymer adsorption. Regardless of porosity, the total adsorption of a given polyethylenimine is directly related to the internal surface available in pores larger than a certain size.

The limited accessibility of internal surface of swollen cellulose to polymer accounts for the observation that, although the specific adsorption per unit area increases with the molar mass, the total adsorption of polyethylenimine on fibers is usually found to decrease with increasing size of the polymer.

References

1. W. A. Kindler and J. W. Swanson, *J. Polym. Sci. A-2*, **9**, 853 (1971).
2. R. E. Hostetler and J. W. Swanson, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 29 (1974).
3. J. C. Kane, V. K. LaMer, and H. B. Linford, *J. Am. Chem. Soc.*, **86**, 3450 (1964).
4. D. Horn and J. Melzer, *Transactions 6th Fundamental Research Symposium Fiber-Water Interactions in Papermaking*, Oxford University Press, Oxford, 1979, Vol. 1, p. 129.
5. J. C. Day, Ph.D. dissertation, McGill University, Montreal, 1976.
6. R. Nelson, *164th ACS National Meeting, Cell Wood and Fiber Chem. Div.*, New York, Am. Chem. Soc., Washington, DC, 1972.
7. K. V. Sarakanen, F. Dinkler, and V. Stannett, *Tappi*, **49**(1), 4 (1966).
8. G. G. Allan and W. M. Reif, *Svensk Papperstidn.*, **74**(2), 25 (1971).
9. E. Strazdins, *Tappi*, **57**(12), 76 (1974).
10. P. E. Trout, *Tappi*, **34**(12), 539 (1951).
11. G. M. Lindqvist and R. A. Stratton, *J. Colloid Interface Sci.*, **55**(1), 45 (1976).
12. D. Horn, in *Polymeric Amines and Ammonium Salts*, E. J. Goethals, Ed. Pergamon, New York, 1980, p. 338.
13. B. Alince, *Colloid Polym. Sci.*, **253**, 720 (1975).
14. B. Alince, *Cell. Chem. Technol.*, **8**(6), 573 (1974).
15. J. E. Stone, A. M. Scallan, and G. M. A. Aberson, *Pulp Paper Mag. Can.*, **67**, 263 (1966).
16. M. V. Merchant, *Tappi*, **40**, 771 (1957).
17. R. A. Sommers, *Tappi*, **46**(9), 562 (1963).
18. R. C. Weatherwax and D. F. Caulfield, *Tappi*, **54**(6), 985 (1971).
19. J. E. Stone and A. M. Scallan, *Pulp Paper Mag. Can.*, **69**(12), T288 (1968).
20. J. E. Stone and A. M. Scallan, *Cell. Chem. Technol.*, **2**(3), 343 (1968).
21. L. G. Aggebrandt and O. Samuelson, *J. Appl. Polym. Sci.*, **8**(6), 2801 (1964).
22. R. Nelson and D. W. Oliver, *J. Polym. Sci. Part C Polym. Symp.*, **36**, 305 (1971).
23. J. C. Day, B. Alince, and A. A. Robertson, *Cell. Chem. Technol.*, **13**(3), 317 (1979).
24. T. Lindström, in *Paper Structure and Properties*, J. A. Bristow and P. Kolseth, Eds., Dekker, New York, Basel, 1986, p. 75.

Received November 28, 1988

Accepted December 12, 1988