Preferred citation: B. Alince and T.G.M. van de Ven. Porosity of swollen pulp fibers evaluated by polymer adsorption. In **The Fundametals of Papermaking Materials**, *Trans. of the XIth Fund. Res. Symp. Cambridge, 1997*, (C.F. Baker, ed.), pp 771–788, FRC, Manchester, 2018. DOI: 10.15376/frc.1997.2.771.

POROSITY OF SWOLLEN PULP FIBERS EVALUATED BY POLYMER ADSORPTION

by

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ABSTRACT

Adsorption of polyethylenimine (PEI) of different sizes on swollen delignified pulp fibers indicates that for PEI molecules of diameter smaller than 25 nm, the accessible internal surface area within the pores in the cell wall is independent of the size of the PEI molecule. This suggests that a minimum pore radius R_{min} exists in the fiber wall (with the possible exception of very small pores of about 1 nm) through which all PEI molecules in the range 2-25 nm can pass freely. Since the molecules must be able to pass through pores with walls fully coated by PEI and since the thickness of an adsorbed PEI layer is comparable to the size of PEI in solution, the pore size must be at least 3 times the size of PEI, implying that R_{min} _ 40 nm. A value of the pore radius in the range 45-50 nm is found from estimates of the area of pores accessible to PEI and the corresponding pore volume. No pores are found in the range 3-40 nm. These findings differ from the pore radii obtained by the solute exclusion technique which usually are around 10 nm. The difference might be due to the ease with which the pores contract and expand under different conditions. Non-adsorbing molecules could cause the pores to contract due to depletion effects, while adsorbing molecules might cause pores to expand.

INTRODUCTION

The porosity of swollen cellulosic fibers is an important parameter to be considered when dealing with reactivity. Dry fibers are not "reactive" because they are nonporous and, therefore, the reactant has no access to the interior of the cell wall and the reaction takes place on the external surface only. Upon swelling, the porosity and the internal surface develops, making considerably more cellulosic chains available for a reaction to take place. Thus accessibility and reactivity are directly related. In order to quantify the relation, a knowledge of the porous structure and internal surface is desirable. As yet, no completely reliable method for analyzing the porous structure of swollen fibers has been developed. The problem is that most common techniques require dry samples and are, therefore, applicable only if the porous structure of the swollen fibers can be preserved through to the dry state. Methods such as freeze drying or solvent exchange drying produce samples with a considerable surface area, but it has been shown that a significant collapse, particularly of large pores, takes place during the removal of the last liquid (1,2). Methods designed to analyze the porous structure of swollen fibers, in particular the solute exclusion technique, are difficult to interpret in terms of size and distribution of pores for reasons discussed later on, although this method yields reliable results for the total amount of water associated with wet fiber walls (3).

In view of these problems, a more realistic evaluation of the pore structure might be obtained by using probes that interact with the surface, e.g., adsorbing water soluble polymers. In this paper we investigate the adsorption of polyethylenimine (PEI) into porous fibers and draw conclusions about the structure of the fiber wall, making use of comparisons with adsorption of PEI into porous glass.

PORE SIZE ANALYSIS WITH INTERACTING PROBES

The intention is to obtain information concerning the average size and the size distribution of pores in pulp fibers. For this purpose the adsorption of water soluble polymer of different molar mass is used and the adsorption is carried out on samples of known porosity (glass) and of unknown porosity (pulp fibers). The rationale is that if the specific adsorption of polymer per unit area is known, then the total surface area can be calculated from the total adsorption. Therefore on a porous substrate one can estimate the extent of the internal surface accessible to the polymer.
Using a polymer series of different molar mass and, consequently, size, allows one to obtain additional information. If the specific adsorption per unit area increases with the size of

polymer, then the total adsorption on a porous substrate will follow the same relation, as long as all the pores are accessible. By increasing the size of the polymer a point is reached where the relation between polymer size and its adsorption capacity breaks down, indicating that the polymer becomes too large to enter the pores. Thus, if the size of the pores is known (e.g., for porous glass), one can estimate the maximum size of a polymer molecule that can fully penetrate into the pore. Once this is known, then from a similar set of experiments performed on a sample of unknown pore size (i.e., pulp fibers), the point of break-down and thus the size of pores can be estimated.

In order to determine the relation between the polymer size and the accessible surface, the adsorption on glass with controlled size of pores was carried out using polymers of different size.

POLYETHYLENIMINE ADSORPTION ON GLASS

Water-soluble polyethylenimine (PEI) was chosen for several reasons. First, it readily adsorbs on both cellulosic fibers and glass. Second, it is available in a range of molar mass from several hundred up to several million Daltons. Third, PEI molecules are highly branched macromolecules which approximately maintain their shape upon adsorption. The main parameter affecting the adsorption capacity is the available surface area. This can be concluded from PEI adsorption studies on glass (4), clay (5), TiO_2 (6), microcrystalline cellulose (7), and fibers at low pH (8). Fourth, its positive charge, which results from protonation of amino groups, can be controlled by pH. At low pH the charge is pronounced, while around pH 10 PEI is almost uncharged and the macromolecules behave essentially as impermeable spheres (9). The experiments were performed at pH 10 in order to suppress the effect of charge, particularly the repulsion between macromolecules. This is quite important when dealing with adsorption on a porous substrate. One can imagine that when a highly charged polymer adsorbs at a pore entrance it can effectively prevent other macromolecules from entering the pore because of mutual repulsion.

The size of polymer in solution is a function of molar mass. In order to obtain the relation between the molar mass and the size of PEI polymer, data available in the literature (4,9,10) are listed in Table I. A plot of size versus $\bar{M}_m$ is presented in Fig. 1, which shows that the size (in nm) varies as $6.8 \cdot 10^{-2}\ M^{0.39}$. The exponent 0.39 is consistent with the fact that PEI is indeed a rather compact spherical molecule. The characteristics of glass with controlled pore size, as determined by benzene adsorption (4), are shown in Table II. Note that the pore size of the second and third sample are somewhat smaller than calculated from

the relation R = 2 V/A (R being the pore radius and V and A the pore volume and pore area, respectively), indicating that the pores are not smooth cylinders.

Data from ref. (4)				Data from ref. (9)				Data from ref. (10)			
Sample	$\bar{M}_m$ [5]	$[\eta]$ [2] cm^3g^{-1}	r [3] nm	Sample	$\bar{M}_m$ [4]	$[\eta]$ [2] cm^3g^{-1}	r [3] nm	Sample	$\bar{M}_m$ [1]	$[\eta]$ [2] cm^3g^{-1}	r [3] nm
PEI 18	5.4×10^3	7.1	1.8	1	2.1×10^3	7.5	1.4	PEI 3	4.0×10^2	5.2	0.7
PEI 50	1.5×10^4	7.4	2.6	2	5.3×10^3	9.8	2.0	PEI 6	1.1×10^3	5.9	1.0
PEI	6.0×10^4	16.0	5.3	3	1.0×10^3	9.9	2.5	PEI 12	8.0×10^3	6.7	2.0
				4	2.0×10^4	11.2	3.3	Polymin P	6.0×10^5	23.1	13.0
								PEI 600	5.0×10^6	37.6	30.0

1) $\bar{M}_m$ — mass average from light-scattering.
2) $[\eta]$ — intrinsic viscosity in 0.1 M NaCl.
3) r — equivalent radius calculated from Einstein-Stokes equation, $[\eta] = 2.5\ (N_{Av}/M)(4/3)\pi r^3$.
4) $\bar{M}_m$ — mass average from sedimentation equilibrium.
5) $\bar{M}_m$ — mass average calculated from $\bar{M}_n$ and $\bar{M}_m/\bar{M}_n$ ratio.

Table I: PEI Characteristics

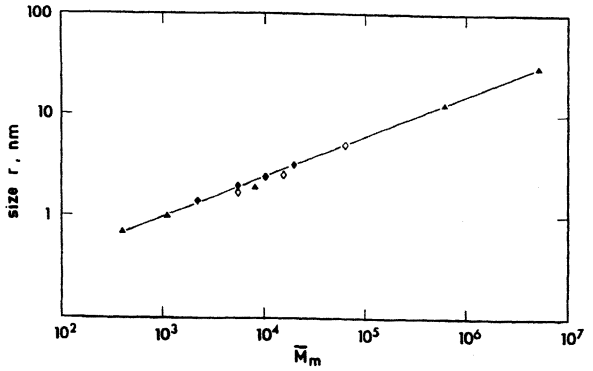

Fig. 1. Size (radius) versus molar mass of PEI compiled from data in literature (9,10).

Sample	Surface Area m^2g^{-1}	Pore Volume cm^3g^{-1}	Pore Radius nm	Pore Size Distribution[2)]
75 C	150	0.54	7	8
240 C	110	1.32	16	7
170 EN	105	1.49	20	14

1) CPG-10, Size 120/200 Mesh (C-Corning, EN-Electronucleonics)
2) Width of distribution (+/-% of radius) accounting for 80% of the pore volume.

Table II: Characteristics of Porous Glass Beads[1)] by Benzene Adsorption (4)

The adsorption of PEI per unit area, when depositing as a monolayer of randomly packed spherical molecules, should be
directly related to the size of the polymer. This has been experimentally confirmed (4), as shown in Fig. 2 where the adsorption per m^2 (left hand coordinate) on non-porous glass at pH 10 is plotted against the size of PEI. Included in Fig. 2 are data obtained on three samples of porous glass beads having different average pore sizes, taken from (4). The total adsorption capacity is expressed in mg per gram of glass (right hand coordinate). By dividing the total adsorption by the adsorption per m^2 the area covered by the polymer is obtained.

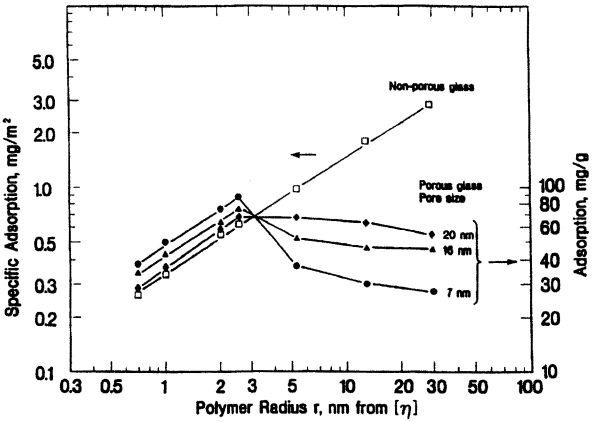

Fig. 2. Total PEI adsorption on glass as a function of polymer size at pH 10. Specific adsorption in mg/m^2 (left scale) on nonporous glass (□); adsorption capacity in mg/g (right scale) on glass with controlled pore size 7nm (●); 16 nm (Δ); and 20 nm (♦) in radius.

Up to the point where the linear relation breaks down, i.e., for a polymer radius in the range 2.5-5 nm, the surface area covered is close to the total surface listed in Table II. This means that all of it is accessible to the polymer. After the cut-off point, the polymer starts to have difficulty entering the pores and more so as the size of the pore decreases, which is what one would expect. Although there are no data for polymer radii between 2.5-5 nm, it can be assumed that the actual cut-off point in Fig. 2 for glass with a larger pore size should be located towards a larger size of polymer.

What is of interest is that the adsorption still continues, even when the average size of the polymer exceeds that of the average pore size. The most likely reason for this is the fact that the polymer is not monodisperse. Each sample contains a fraction of much smaller molecules than the average and, thus, while the larger ones are excluded, the smaller ones can still penetrate into the pore. This phenomenon was discussed in (11) in order to explain the shape of adsorption isotherms of PEI on pulp fibers, particularly the gradual increase of adsorption with increasing polymer concentration.

The cut-off point also provides other important information concerning the size of accessible pores. In order to be fully accessible, the pore must be several times larger than the polymer size. Since the cut-off point in Fig. 2 is in the range 2.5-5 nm and the pore sizes are 7, 16 and 20 nm, one can conclude that the polymer size must be 3 to 5 times smaller than the size of the pores to enter the pores freely. This is to be expected since a PEI molecule must be able to pass through a pore even after the wall is coated by a layer of PEI molecules.

POLYETHYLENIMINE ADSORPTION ON PULP FIBERS

The total adsorption in mg g^{-1} on dissolving pulp (designated as D), softwood bleached kraft (designated as B), and microcrystalline cellulose is shown in Fig. 3. All adsorption data represents maximum adsorption at pH 10 determined by nitrogen analysis of the samples after washing with distilled water to remove unadsorbed polymer (7,12). Also included is the specific adsorption in mg m^{-2} taken from Fig. 2 for comparison. The adsorption capacity of disintegrated nonporous microcrystalline cellulose follows the expected trend since all the surface is accessible to the polymer. From the total adsorption divided by the adsorption per m^2, the surface of this microcrystalline cellulose is found to be around 20 m^2 g^{-1}.

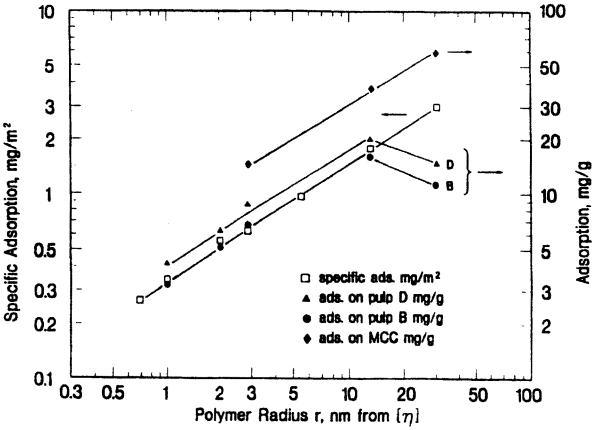

Fig. 3. Total PEI adsorption on pulp fibers as a function of polymer size at pH 10. Adsorption capacity in mg/g (right scale) on two pulp fibers and on microcrystalline cellulose compared with a specific adsorption in mg/m^2 (left scale).

The relation between PEI adsorption and its size on both fibers breaks down at a polymer radius above 13 nm rather than 2.5-5.0 nm, as was the case for porous glass. The interpretation then would be that the pore size of pulp must be larger than that of glass, having 20 nm pores.

The data presented in Fig. 3 also offer information concerning the distribution of pore size. Up to the cut-off point, the surface area occupied by PEI is about 10 m^2 per gram for pulp B regardless of the polymer size. This means, of course, that all the surface that is accessible to a 1 nm polymer is also accessible to 13 nm polymer. Since there is no additional surface within some smaller pores accessible only to smaller polymers, the apparent conclusion is that there is a minimum pore radius R_{min} within the range of pores accessible to the polymer. Assuming, in conformity with porous glass, that also in pulp fibers the pores are 3-5 times larger than the critical size of the PEI molecules that can

freely penetrate the pores, R_{min} _ 40-65 nm. Experiments on PEI adsorption (Polymin P) on cellulose fibers (8) at pH 6, at which conditions the PEI molecules have an expanded configuration, show that such swollen molecules have considerable difficulty in entering the pores, suggesting that polydispersity above R_{min} is not very large. Thus the data are consistent with a rather narrow pore size distribution around about 50 nm. Since the smallest size of PEI employed was about 1 nm, one cannot exclude the presence of pores smaller than 3 nm, based on the PEI adsorption data.

EVIDENCE FOR THE EXISTENCE OF LARGE PORES

Additional evidence that in swollen fibers large pores exist comes from estimating the pore size from the relation R = 2 V/A, where A is the surface area accessible to PEI molecules below the critical size and V the pore volume. For cylindrical pores this relation yields the radius of the pore, while for slit-like pores R is the width of the slit. The total pore volume can be estimated from the fiber saturation point (FSP) determined by solute exclusion (3). FSP-values are typically in the range 0.8-1.4 g H_2O/g fiber (13) and surface areas accessible to PEI are typically in the range 10-25 m^2/g (12). The average pore size R, calculated using the above values, is then around 110-160 nm, i.e., almost three times the suggested value of R_{min}. This is unrealistic since the dextran molecules used in FSP determinations should be able to enter such pores as such molecules typically have a diameter of 56 nm (3, 13). It has to be realized, however, that the FSP might include water in pockets which are accessible only via small pores. These pockets could represent a large volume but small surface area.

Besides large pores, there is also evidence for the existence of small pores, as suggested by benzene and nitrogen adsorption on swollen pulp fibers dried by the solvent exchange technique (1,2,14,15,16), indicating that the predominant size of the small pore is around 2 nm, i.e., too small for the polymer to enter. The volume of such pores is typically 0.1-0.3 cm^3/g, depending on the treatment and drying history of the fibers and the surface area within this group of pores is therefore 100-300 m^2/g.

The existence of both small and large pores can also be inferred from data for the water content of swollen fibers measured by the pressure plate technique, the data of which are comparable to the solute exclusion (17). For fibers having a FSP of about 1.2 cm^3/g the pore volume of different sizes is shown in Table III. These results show the presence of large pores > 100 nm, which contain a substantial amount of volume, but contribute little to the available surface area. As discussed, such large pores probably do not exist since they are not seen in solute exclusion experiments. Instead it is much more likely that there are

pockets of water in the fiber wall which are only accessible via small pores. These pockets can collapse and be emptied when an external pressure is applied. If true, they might account for about one-third of the water in the fiber wall.

Pore size (R), nm	0-10	10-100	100-1000
Pore volume (V), cm^3/g	0.2	0.6	0.4
Pore surface (A), m^2/g [1)]	200[2)]	24	1.6

[1)] Calculated from A = 2V/R, taking the dominant size R = 2 nm, and average size 50 and 500 nm, respectively.
[2)] The large surface area within the pores of dominant size 2 nm is not accessible to polymer.

Table III: Distribution of pores of swollen never dried pulp determined by pressure plate technique (17).

Another possibility to analyze the pore structure is to use data from the technique of the first desorption of benzene from swollen and solvent exchanged samples (1,2). These experiments show two types of pores: large collapsible pores for which the adsorption/desorption behavior is irreversible, and small rigid pores with reversible behavior. The size of these small pores is about 1-2 nm, i.e., the same as obtained by nitrogen adsorption. Data for four dissolving pulps subjected to different treatment (mercerization, drying) on which the adsorption of PEI is known are shown in Table IV. The pore volume accessible to the polymer is taken as the difference between the total volume of pores up to 100 nm (the limit for the benzene desorption technique) and the volume of pores up to 2 nm (inaccessible to polymer). The calculated average pore sizes of 45-50 nm are in the range of R_{min} estimated above from the assumption that the freely accessible pores should be 3-5 times larger than the size of polymer. Taken together, the data from the pressure plate, from benzene desorption on solvent exchanged fibers and from PEI-adsorption are consistent with a bimodal pore size distribution of small pores of about 2 nm and large pores of about 50 nm radius.

Sample		1	2	3	4
Pore volume of 0-100 nm pores	cm^3/g	0.75	0.65	0.56	0.40
Pore volume of 0-2 nm pores	cm^3/g	0.15	0.27	0.23	0.14
Pore volume (V) of 2-100 nm pores	cm^3/g	0.60	0.38	0.33	0.26
PEI adsorption[1)]	mg/g	50.5	31.0	28.2	19.6
Surface (A) [2)]	m^2/g	26.6	16.3	14.8	10.3
Pore size (R) [3)]	nm	45	47	45	50

[1)] Polymin P
[2)] Calculated from specific adsorption 1.9 mg/m^2 for Polymin P
[3)] Calculated from 2V/A

Table III: Distribution of pores of swollen never dried pulp determined by pressure plate technique (17).

REANALYSIS OF SOLUTE EXCLUSION DATA

The conclusion we reach in this paper, namely that swollen fibers contain no pores (or a negligible amount of pores) in the range 3-40 nm, seems to be at odds with conclusions from solute exclusion experiments performed with non-adsorbing polymers (dextrans), which usually show the presence of pores of about 10 nm where, according to PEI adsorption data, no pores exist. It is therefore of interest to reexamine the literature date on solute exclusion. Data from the paper by Stone and Scallan (3) are shown in Fig. 4, where we have plotted the ratio, σ, of inaccessible water to the totally inaccessible water which in this case is identical with the ratio of inaccessible pore volume to total pore volume, against the diameter, d, of the non-adsorbing molecules. It can be seen that the relation between σ and d is linear for small diameter probes.

To determine the relation between σ and d, we need to know the concentration of nonadsorbing polymer in the pores. It is well known that because of depletion layers near the pore wall (18,19), the concentration of nonadsorbing polymer in a pore is less than that

in the bulk. The exact profile can be calculated from theory and depends mainly on molecular weight M, the Flory-Huggins interaction parameter χ and polymer flexibility. Instead of calculating the profile we will simply assume a depletion layer thickness equal to the radius of the polymer and bulk concentration elsewhere in the pore.

For a given pore size distribution p(R):

$$\sigma(r) = 1 - \frac{1}{V}\int_0^\infty K(R,r)p(R)dR \qquad (1)$$

where V is the total pore volume and K(R,r) a function that depends on the geometry of the pores and the distribution of polymer in the pores. The integral in Eq. (1) represents the total

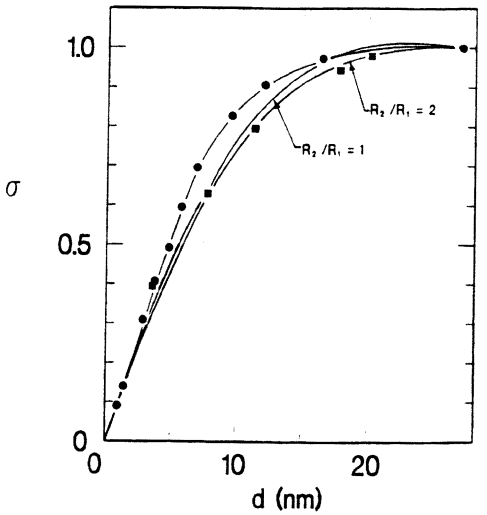

Fig. 4. The ratio, σ, of the inaccessible pore volume to the total pore volume, versus the diameter of the polymer, determined from size exclusion experiments (solid dots, data from ref. 3). Also shown are results of two calculations for $R_2/R_1 = 1$, $R_1 = 10$ nm and $R_2/R_1 = 2$, $R_1 = 7.3$ nm (solid lines) as well as predictions for a bimodal distribution consisting of 15% 1 nm pores and 85% 12 nm pores (squares).

accessible volume. Since the function K(R,r) is not precisely known, it is difficult to obtain the pore size distribution p(R) from measurements of $\sigma(r)$. Assuming cylindrical pores and including depletion, $K \propto (R - r)^2$ (20). For a pore size distribution characterized by a minimum pore size R_{min}, the relation between σ and the diameter, d, of the probe ($d = 2r$), for low values of d, reduces to

$$\sigma = k \frac{d}{R_{min}} \qquad (2)$$

k being a constant depending on p(R) and the geometry of the pores. For cylindrical pores and a monodisperse pore size distribution, we find that $k = 1$. Polydispersity lowers the value of k; e.g., for a distribution with no pores below R_1 and above R_2 and with the number of pores decreasing linearly in between, the value of k _ 0.73. Calculations from Eq. (1) for a monodisperse pore size distribution, and for a distribution with $R_2/R_1 = 2$, are shown in Fig. 4 and compared with experimental data. Also included in Fig. 4 are calculations based on a bimodal distribution, consisting of a monodisperse fraction of 1 nm pores constituting 15% of the pore volume, and another monodisperse fraction of 12 nm pores, taking up 85% of the pore volume. It can be seen from Fig. 4 that for this distribution the inaccessible volume is rather close to the calculations for a monomodal distribution. Thus the existence of small pores cannot be excluded and the possibility exists that the pore size distribution in pulp fibers is bimodal: small pores (presumably within the macrofibrils) and large pores (presumably between the macrofibrils). The suggestion of a bimodal distribution of pores has already been made (21), but the formation of large pores ranging between 100-1000 nm was considered to be the result of beating.

It can be seen that the initial slope is the same for the experimental and theoretical curves, but that the data for the inaccessible volume of pulp fibers lie slightly above the theoretical curve, i.e., the accessible volume is smaller than predicted. Since no such effect is seen in rigid porous glass (4), this reduction in accessible volume is possibly due to a contraction of the pores, caused by the osmotic stress difference between the pores and the bulk (the concentration in the pores being less). Also the geometry of the pores will affect the results. Slit-like pores will result in somewhat higher values of σ at intermediate pore diameters.

From Eq. (2) we can estimate the value of R_{min}. The experimental slope σ/d equals about 0.1 nm^{-1}, which results in a value of R_{min} of about 10 nm. Thus the size exclusion data are consistent with a rather monodisperse pore size distribution of 10 nm pores.

It is of interest to note that a similar average pore size of swollen fibers was obtained by using the NMR technique (22) with no indication of a broad distribution of pores.

There appears to be a discrepancy between the pore radius of fibers of about 10 nm obtained using dextran probes and the pore radius of about 50 nm using polymer adsorption. Some of the difference could be caused by the ease by which the cellulose wall swells and shrinks in response to different environments (1,23). Non-adsorbing molecules are expected to cause a contraction due to the depletion of polymer in the pores, while adsorbing molecules might expand the pores.

IMPLICATIONS FOR THE FIBER WALL STRUCTURE

Depending on the way the surface area of pulp fibers is measured, we can distinguish three distinct surface areas:

(i) the external surface area of the fiber, A_f;
(ii) the surface area, A_1, freely accessible to PEI molecules of diameter about 25 nm and smaller;
(iii) the surface area, A_2, accessible to small molecules (e.g., benzene, N_2), but not to polymers.

Typically $A_f \cong 0.5\text{-}1\ m^2/g$ (24), $A_1 \cong 10\text{-}25\ m^2/g$, $A_2 = 200\text{-}300\ m^2/g$.

Based on these facts we can speculate about the structure of a fiber wall. It is known that the fiber wall consists of macrofibrils which can be released, e.g., on beating. These macrofibrils in turn consist of microfibrils, typically with a cross section of 120 nm^2.

We further notice that A_1 and A_2 correspond closely to the total surface areas of the macrofibrils, A_{mf}, and of the microfibrils, $A_{\mu f}$:

$$A_{mf} \approx \frac{2}{\rho_{mf} r_{mf}} \quad ; \quad A_{\mu f} \approx \frac{2}{\rho_{\mu f} r_{\mu f}} \qquad (3)$$

where r_{mf} and $r_{\mu f}$ are the effective radii of the macro- and microfibrils of density ρ_{mf} and $\rho_{\mu f}$. Taking $r_{mf} = 100$ nm and $r_{\mu f} = 6$ nm results in $A_{mf} = 14\ m^2/g$ and $A_{\mu f} = 210\ m^2/g$, close to A_1 and A_2.

Since $A_l \cong A_{mf}$ it appears that much of the surface area of the macrofibrils is accessible to 25 nm PEI molecules, while the surface area of the microfibrils is inaccessible to them. The spacings between the macrofibrils must be large enough that 25 nm PEI molecules can freely pass through, even after the macrofibrils are coated by a monolayer of PEI molecules. We have seen that for glass beads with rigid pores of roughly cylindrical shape, the pore size is 3-5 times larger than the critical size of a PEI molecules which can freely penetrate the pores. If the same were true for pulp fibers, the radius of the large pores would be around 40-65 nm. However pulp fibers are not rigid and probably the pores are not cylindrical.

There are many structures compatible with the PEI adsorption data on fibers. One possibility is that there are cylindrical pores of radius larger than 40 nm. Another, more likely, possibility is the existence of slit-like openings between macrofibrils (of width _ 40 nm) which give access to the concentric layer structure of the cell wall (25). If this is the case, the number of such openings must be very large since the polymer adsorption is very fast (11), indicating that most of the accessible surface area can be rapidly reached by adsorbing macromolecules.

CONCLUDING REMARKS

We have shown that when PEI is present in swollen delignified fibers practically no pores exist with a radius in the range 3-40 nm. Larger pores of about 50 nm are present, possibly as openings between macrofibrils. The presence of small pores (around 1-2 nm), the existence of which is suggested from benzene and nitrogen adsorption data on solvent exchanged pulps and from results of the pressure plate technique on never dried fibers, cannot be excluded from our experiments as all probes used were too large to enter these pores. Indirectly, PEI adsorption supports the presence of small pores since values of the pore radius calculated from pore volume and area are consistent with pore volumes from which the volume of the small pores is subtracted.

ACKNOWLEDGEMENTS

The authors acknowledge the valuable discussions with Dr. A. Scallan.

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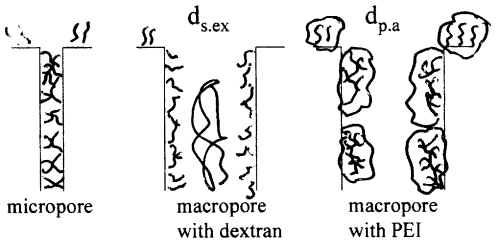
Transcription of Discussion

Porosity of Swollen Pulp Fibres evaluated by Polymer Adsorption

Dr Theo van de Ven, Director, Paprican/McGill, Canada

Editors note 1: The table on p.781 in vol. 2 is incorrectly labelled. It should read "Table 4: Distribution of pores by benzene desorption on solvent exchange pulps (1)

Editors note 2: extra slide used in Dr van de Ven's presentation to which some of the discussion refers.



Professor Tom Lindström, Royal Institute of Technology (KTH), Sweden

You have the assumption about adsorption and what you are saying is that the adsorption per square metre is independent of substrate. Still you are talking about charge interactions in your last slide. How do you reconcile that?

Theo van de Ven

This is not difficult to reconcile. Presumably the PEI will still have a little bit of residual charge but you also have to remember that the pH in this hemi-cellulose layer may be much lower than the pH outside and so when the PEI molecule gets in a micropore it is in an ideal position to react with the carboxylic groups of the hemicellulose.

Tom Lindström

What you are saying is that the adsorbed amount is related directly to the surface area. This is generally not the case for polyelectrolytes adsorbing onto charged surfaces. Could you offer an explanation?

Theo van de Ven

We have looked at clay, titanium dioxide, microcrystalline cellulose, glass and latex and we find about the same amount of PEI in terms of milligrammes per metre squared on all those surfaces. It all is consistent with random depositing of molecules on these surfaces. So as long as it sits on the surface and takes up a certain amount of space, and as long as there is a driving force for attraction, the available surface area seems to be the main factor determining the adsorption capacity of these branched molecules.

Tom Lindström

Then I have another question regarding the size. You are assuming when you look at the glass bead data that the adsorption goes down for high molecular weight PEI. I'm not sure it is really necessary to assume that the adsorbed electrolyte blocks the entrance to the other molecules because you have an equilibrium situation and the polymers can diffuse back and forth. So then my question is if you really extend your adsorption experiment not within the framework of two minutes but if you extend them to say four or five hours you would probably have another kinetics that is depending on the readsorption and desorption of polyelectrolytes moving into the structure which gives you a completely different pattern of adsorption for the high molecular weights polymer.

Theo van de Ven

I agree in principle. However, the PEI is highly irreversibly adsorbed at low ionic strengths. If you go to ionic strengths of about 0.01 molar or higher the PEI becomes reversibly adsorbed and follows some kind of Langmuir of fibre kinetics. But at low ionic salts we don't see these effects.

Peter Wrist, Consultant, Peter E Wrist, USA

You found that there are basically two distinct groups of pores, micro and macro. Would you care to speculate on what physical features these correspond to in term of microcrystalline structure of the fibre?

Theo van de Ven

I guess I more or less already did. If you take the microfibrils and take out the lignin, the dimension of the remaining hole is close to a few nanometres according to the data of Goring and Kerr. So I think those are the mircopores. If you swell the fibre wall, the thickness of the lamellae is much thicker than an individual fibril, so you have many fibrils in such a lamellae and the distance between them corresponds to the macropores.

Lars Ödberg, Vice President Basic Research, STFI, Sweden

I have some comments on the NMR measurements. First I would like to correct a misconception and that is you have to know the area and volume when you do these. If you really had to do that it wouldn't be good because then you would already know the size . When we get that ß parameter is that we measure at a high relative humidity. We measure both the adsorbed amount and the relaxation time at something like 90% RH and get ß parameters without any kind of assumption on volumes and areas. I would stress that as I know some referees think that you have to know it.

Theo van de Ven

The reason I did is because in some papers you have done so.

Lars Ödberg

There are three ways of measuring the ß parameter but if you want to do it from first principles then that is possible also. What I wanted to say is that I can reconcile your measurement with NMR also. With NMR you have to think about the fact that the molecules can diffuse during the time of the measurement and can probe different pores and probe both the micropores and macropores they will find an average pore size which could be an average of the small and the large pore section. I think in our NMR measurements we have done after a water retention value treatment the macropore's water would still be there but you can reconcile it. I have a question also about your microcrystalline cellulose. This is something totally different and that is you said that you expected a different type of adsorption for that but microcrystalline cellulose is not crystalline its just fibres. Fibres that have been chopped up. If you look in a microscope it's just fibres that you have taken away maybe 3-5% of the fibrous material. I should expect the same kind of adsorption behaviour on micros but maybe those microcrystalline cellulose was made from something completely different.

Theo van de Ven

It was completely disintegrated when we did the experiment.

Lars Ödberg

OK, then it could be a completely different matter.

Professor Jacques Silvy, Universidade de Beira Interior, Portugal

Your conclusions are ever on the white board. There are as many pore size distributions as we have phenomena to interpret or methods to determine it. We don't worry about that because we do that to make applications where we need some physical adaptation to the phenomena no matter of the differences between the pore size distributions we have if it satisfies our application. When we speak about fluid flow, for example, we need to know the pore size distribution. In that case what we call size is the ratio between the volume and area wetted by the fluid. Therefore the pore size in that case is the distribution of the volume to area. Then it would be very difficult to find the size of the pores in the case of this interconnected network. The pores are not circular, they are not slits, they look much more like stars. How could you define the size of a star? In practice

it runs very well because the hydrodynamic parameter we need is really the ratio of the volume of liquid to the area wetted and in statistical geometry when we look at this very complicated network either in the cell wall or in the paper we can be sure that theoretically size dimension is the mean cord that you can statistically measure in the space of the pore and this satisfies the experiments. Therefore my comment is, that no matter is the disagreement in the pore size distributions, everybody can be right if he chooses the right parameter according to his experiment.

Theo van de Ven

Obviously the problem is that you don't know the geometry of the pore and the size and thus one is dealing with two unknowns. That doesn't detract from the fact that the pore will have some kind of geometry, there may be a connected network, but there are still pores. I don't think that the pores I talked about can be probed hydrodynamically because the pores are too small. You can probe the pores between the fibres by hydrodynamics but I don't think you can probe the pores within the fibre wall in the same way.

Dr Lennart Salmén, Head of Fiber Physics, STFI, Sweden

You said that by taking away lignin you create micropores. Can you then explain that going from TMP to kraft pulp you are shifting the pore size distribution towards larger pores.

Theo van de Ven

How did you determine the pore size distribution?

Lennart Salmén

Both solute exclusion and NMR measurement indicates this shift.

Theo van de Ven

I think that I have addressed both of those techniques.

Mike Ragauskas, Associate Professor, IPST, USA

Your comments on the micropore and how they are filled by hemicelluloses are interesting but I wonder since a significant portion of the hemicelluloses in a kraft pulp are redeposited is it right to assume that you have a uniform distribution down the pore of hemicelluloses?

Theo van de Ven

I am not claiming that it has to be uniform. This was just a cartoon to illustrate how we could possibly reconcile the methods of solute exclusion and polymer adsorption.

Mark Ragauskas

Would that change if you now have patches without hemicelluloses?

Theo van de Ven

I guess you could form bottlenecks which would prevent molecules from going into other volumes of water.

Mark Ragauskas

Or could you even have a funnel shape?

Professor Robert H Pelton, Senior Scientist, McMaster University, Canada

You're proposing these molecular hydrogels which I like. Do you think that they would possibly exist on the exterior surface of the fibres and if so can you comment on their influence on fibre/fibre bonding and colloidal deposition.

Theo van de Ven

I do think they exist. The reason is if you consider the surface charge density of the fibre wall and calculate it from either the micropores or the macropores you get the same value. So I presume you will see the same on the external surface as well and so I would think that the outside wall of the fibre has the same surface charge density and the same

kind of structure as the pore wall. I agree fully with you that this will have a large effect on interactions of materials with fibres, such as fillers with fibres, fibres with fibres and so on. I don't think people have looked in much detail at these types of interactions and tried to extract information about surface gels. It must have a significant effect.

Lars Wågberg, Research Manager, SCA Research AB, Sweden

Your cartoon looks nice when you have all the surfaces saturated with PEI molecules inside a pore. If you still agree that we have charges on these polymers and we assume that we have partially saturated 50% of the charges within the pore leaving the other charges naked for adsorption by polymers. Couldn't you envisage that you can get bridging inside the pore and a subsequent closure of that kind of pores. This means that you don't get this nice filling as you have in this case when further polymers are added.

Theo van de Ven

I guess this would be possible. It depends on the shape and size of the polymers you want to put in the micropores. You could certainly bridge the two walls together with some polymer.

Lars Wågberg

That also means that you can get a closure of that pore which then will not have available for the further polymer adsorption.

Theo van de Ven

It is a possibility.

John Waterhouse, Senior Associate Scientist, IPST, USA

I just want a point of clarification. In the works of say Caufield and Weatherwax they looked at BET surface area going from the never dried to the dried state and various ways of preserving the never dried state, and they demonstrated that getting to the 100 and 300 metre squared per gramme range that critical point drying was the preferred method, and so I am a little bit confused as to why when you solvent exchange from benzene you end up with such high surface areas. I would have thought that in partially drying the

mircopores would perhaps be first to disappear and you would have something in the 60 metre squared per gramme range. Perhaps you can clear this up?

Theo van de Ven

That's certainly true. It's well known that if you dry fibres completely from water you only see the external area, and you don't see any porosity anymore. If you do partial drying you can see anything between the external surface area and 300m²/g. In benzene desorption you do the calculation not from dried pulp, but you obtain the pore sizes from the Kelvin equation. The macropores are emptied first.

John Waterhouse

You made the comment that you were happy to see that there was an agreement with the BET surface area.

Theo van de Ven

In this sense it is just a right order of magnitude. You see a big contribution to the surface area from micropores. I don't claim exact agreement.