

Swelling of Particulate Polymers Enmeshed in Poly(tetrafluoroethylene)

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Synopsis

It was demonstrated that swelling of cross-linked polymers can be monitored much more conveniently and reproducibly after that polymer has been comminuted to a fine powder, and then fabricated mechanically into a tough microporous composite film consisting of the particulate matter (>80%) enmeshed in poly(tetrafluoroethylene) [PTFE; <20%]. The latter component provides the physical integrity that affords ease of handling and ensures permanent entrapment of the particles even after 100 cycles of swelling and desiccation to the original dry state. The PTFE microfiber network, however, does not affect adversely either the physicochemical properties of the particles or the permeability to fluids. Kinetic studies in 10 replicates have shown that the void space (0.3 to 0.6 mL/g of composite) is filled by capillary action within the first few minutes of contact with the liquid, and that swelling to the equilibrium state (2 to 90 mL/g of composite) usually occurs within 0.5 to 2 hours thereafter, depending primarily upon the surface to volume ratio of the particles. The magnitude of swelling at equilibrium, however, is dependent only on the thermodynamic state of the gelled polymer in excess liquid, and is reproducible usually within 0.2%.

INTRODUCTION

We reported^{1,2} that tough flexible microporous sheets can be produced from dough-like mixtures of particulate matter and aqueous poly(tetrafluoroethylene) (PTFE) emulsions by a work-intensive procedure using an ordinary rubber mill. In so doing, the PTFE microspheres are converted into microfibers that separate and enmesh the particles. When dry, these composite sheets consist of >80% particles and <20% PTFE by weight. They are very porous (usually >40% voids, with pore-size distributions that are uniformly below 0.5 μ). As such they are effective filters that remove suspensoids >0.5 μ from permeating fluids.¹

Since the particles are isolated and not physically bound to one another or to the PTFE microfibers, the physical integrity of these composite sheets is provided entirely by the entangled web of PTFE microfibers produced during milling. The tensile strength (wet or dry) of the composite sheets range from 200 to 2000 psi depending upon the work-intensive procedure. The other physical properties, such as hydrophilicity and absorptivity, depend on the choice of particles; thus sheets made from hydrophilic particles, such as methylcellulose are hydrophilic; those made from hydrophobic particles, such as poly(styrene) are hydrophobic; and those made from absorptive particles, such as charcoal, are highly absorptive.

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Because the enmeshed particles are not lost even if handled very roughly, and the reactivity of the particles is not affected adversely by being entangled in the web of PTFE microfibrils, these microporous composites have proven to be ideally suited for sorption of gases and liquids in various applications. Thus, composites of this sort have been used to monitor adsorption of organic vapors and H_2S on charcoal,^{3,4} and also to study absorption of organic vapors by polymers⁵ such as poly(methylmethacrylate), poly(vinyl chloride) and poly(vinyl fluoride).

We also reported⁶ that microporous composites made from water-swelling cross-linked dextrans are useful as dressings for infected wounds. In this connection it was necessary to evaluate a large number of other water-swelling polymers. In so doing, we discovered that the microporous structure of these composites retained the rapid equilibration advantage associated with microparticles, and also provided the ease of handling associated with a flexible polymeric film of good physical integrity. This publication reports some of the results of these swelling studies, which led to a convenient general procedure with excellent reproducibility for measuring swelling of cross-linked polymers.

EXPERIMENTAL

Preparation of Microporous Particulate-PTFE Composite Films

Using Hydrophobic Particles

Examples of such particles (>0.1 to 40μ) are: poly(ethylene), poly(propylene), poly(styrene), or poly(acrylate). To 45 g of Teflon-30B aqueous emulsion, which contains 61% PTFE and 8% nonionic surfactant (such as *p*-nonylphenoxypolyethyleneoxide), was added 100 g of the hydrophobic particles. The mixture was kneaded at room temperature by means of a mortar and pestle until a dough-like consistency was established. The dough was worked on a rubber mill operating in its friction mode at $50^\circ C$ to form a weak continuous band about 1 mm thick. The band was removed from the mill, folded several times, rotated 90° , and then repassed through the rollers spaced 10 mm apart. The rectangular slab obtained thereby (about 10 cm wide, 15 cm long and 1 cm thick) was folded on itself three times to form a slab about $10 \times 5 \times 3$ cm³. This was repassed through the rollers along the 10 cm axis (i.e., 90° displaced from its last direction of pass through the rollers) to form a rectangular slab about 5 cm wide, 30 cm long, and 1 cm thick. This was again folded on itself three times to form a slab about $5 \times 10 \times 3$ cm³. The toughness of the dough increased with each pass through the rollers. The folding, rotating 90° , and rerolling sequence was repeated a total of about 12 cycles until the dough became too resistive to allow continued working. The rectangular slab was saturated with water. The rubber mill was changed from its friction mode to its calendaring mode, and the slab was calendared such that the thickness was reduced from 10 mm to 0.25 mm in about 10 passes through the rollers in the same direction to form a ribbon about 10 cm wide, 600 cm long, and 0.025 cm thick. This ribbon was saturated with water, and then folded on itself to the center a

total of five times to form a stack of 64 0.25 mm layers. This layered stack (about 2 cm thick, 10 cm long, and 9 cm wide) was recalendered along the 10-cm axis (i.e., 90° rotated from its former direction of calendering) to produce again a ribbon about 0.25 mm thick, 10 cm wide, and 600 cm long. The ribbon was sprayed with water, refolded on itself six times to form a stack of 128 layers, each 0.25 mm thick. This layered stack (about $3 \times 10 \times 5$ cm³) was calendered in turn as described above to form a ribbon about 5 cm wide, 75 cm long, and 0.4 cm thick. This ribbon was cut into fifteen 5-cm squares, which were then calendered biaxially into 16-cm squares about 0.04 cm thick. The squares were washed overnight in a bath of warm running water to remove the nonionic soap that was introduced as a component of the Teflon-30B emulsion. The squares were damp dried between two paper towels and weighed. The samples were then air dried and reweighed. The porosity (i.e., volume of void space per unit bulk volume of membrane) was calculated from this difference in weight. The porosity determined thereby ranged from 0.2 to 0.5, depending upon the water content at the last pass through the rollers. The tensile strength of these composite sheets (wet or dry) was > 250 psi and usually about 500 psi.

Using Hydrophilic Non-Water-Swellable Particles

Examples of such particles (0.1 – 15 μ) are: powdered kaolin, calcium carbonate, vermiculite, and zeolite. The powder (120 g) was added with stirring to a mixture of water (60 mL) and Teflon-30B aqueous emulsion (60 g), to form a watery paste. Additional powdered particulate (60 g) was mixed into the watery paste to form a stiff dough. The dough was worked on the rubber mill kept at 50°C as described above to form a kid-leather-like microporous sheet about 0.25 mm thick, the tensile strength of which was about 450 psi. The porosity (0.3 – 0.7) and poresize distribution (< 1 μ) is dependent in large part upon the water content of the composition at the end of the calendering procedure, whereas the tensile strength (300 – 600 psi) depends in large part upon the number of passes through the rollers. When the three-phase composite is dried, the space occupied by the water phase becomes the void space of the now microporous structure.

Using Water-Swellable Particles

Examples of such particles (0.5 to 40 μ) are cross-linked dextrans (Sephadex G-25-40; Sigma Chemical Co), base-hydrolyzed starch-polyacrylonitrile graft copolymer (Super-Slurper, manufactured by General Mills Inc.), and poly(acrylamide) (Bio-Gel P-4; Bio-Rad Laboratories). Because spherical particles with diameters greater than 40 μ are sometimes more difficult to work into a sheet of good physical integrity, particles of this ilk were comminuted to a fine powder in a Spex Freezer Mill kept at liquid nitrogen temperature. To the water-swellable particles (50 g) contained in a 1-liter beaker was added with continuous stirring 150 mL of water in 10 mL portions. Thereafter, 23 g of Teflon-30B emulsion dispersed in 60 g of water was added dropwise to the continuously stirred mass of water-swollen particles. The mixture was then worked on the rubber mill (essentially as described above with the exception that additional water was not added after each cycle)

to give a water-swellaible microporous sheet 1 mm thick (Fig. 1) the tensile strength of which was > 250 psi.

Swelling of Particles (80%) Enmeshed in PTFE (20%) Microporous Films

Ten samples of approximately the same size ($3 \times 3 \times 0.03$ cm³) and weight (0.3 g) were cut from different sections of the same microporous composite sheet made as described above. The ten samples were air dried at 20°C and 50% relative humidity (RH), and then weighed on a Mettler AE 160 balance to the nearest tenth of a milligram. The samples were dried further in a vacuum oven kept at 100°C and then reweighed to determine the weight of absorbed water vapor per gram of film at 20°C and 50% RH. The samples were then placed at 30-s intervals on the surface of the test liquid contained in a petri dish 14 cm in diameter. The weight of liquid absorbed by each sample was determined periodically as follows: The first sample was removed at time t , placed between multiple layers of soft filter paper and damp dried. The sample was placed in a closed weighing flask and weighed

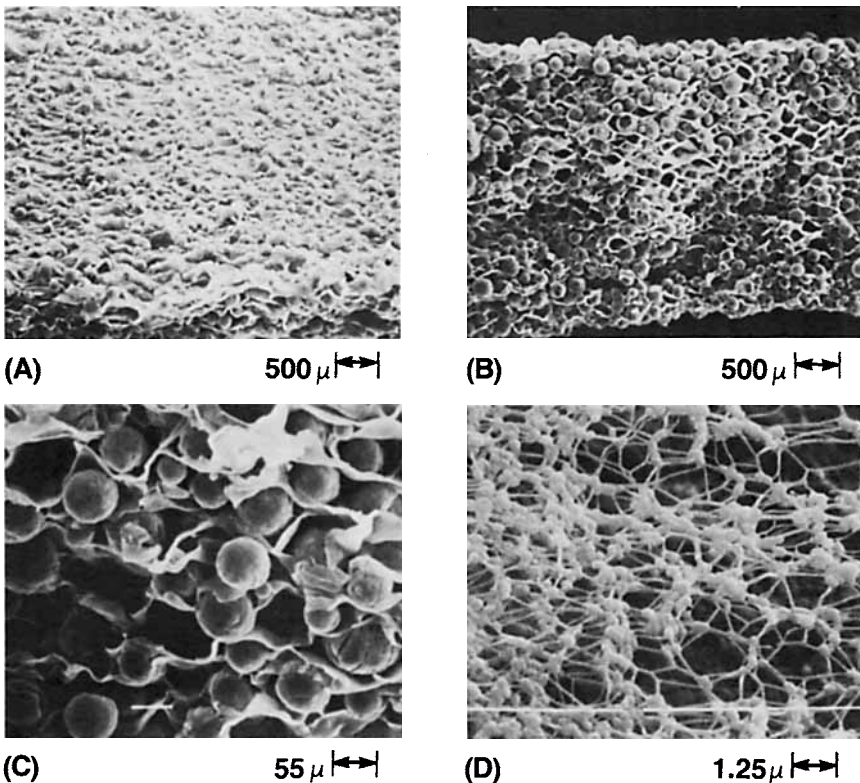


Fig. 1. SEM photomicrographs of a microporous composite sheet consisting of Sephadex microspheres (G-25-40) enmeshed in PTFE (ca. 20% by weight). (A) Top surface and a small portion of the freeze-fractured edge viewed at a 45° angle from the horizontal plane. (B) Freeze-fractured edge, viewed at a 0° angle from the horizontal plane. (C) Tenfold enlargement of "B." (D) Forty-four-fold enlargement of "C" showing an area of the PTFE entangled component that enmeshes the Sephadex microspheres.

to the nearest 0.1 mg. The sample was then replaced on the surface of the liquid. In like fashion, the weight of liquid absorbed by the other nine samples was determined in 30-s intervals so that the entire scan of liquid uptake by the 10 samples was completed in 5 min. Such scans were made periodically as needed to determine the time required to establish saturation to swelling equilibrium. The final scan was made after the samples were allowed to remain in contact with the test liquid for a total of 18 h. The volume, V , of liquid (i.e., weight of liquid absorbed divided by its density) per gram of composite was then plotted as a function of accumulated time, t , of contact with the liquid as noted in Figures 6, 7, and 8. The time, τ , required to attain apparent equilibrium (i.e., about 98% of absorption capacity at $t = \text{infinity}$), the volumes of liquid absorbed per gram of composite at apparent equilibrium and at $t = 18$ h are collected in Tables I and II.

TABLE I
Absorption of Water by Particles in PTFE Composite Films

Film No	Particulate	%PTFE	mL of water absorbed per mL of film
A. Non-water-swellable particles			
1.	vermiculite	15	0.51
2.	kaolin	15	0.57
3.	zeolite	15	0.53
4.	calcium carbonate	15	0.52
5.	calcium carbonate	40	0.40
6.	poly(ethylene)	15	0.43
B. Water-swellable particles			
7.	cellulose	15	0.91
8.	collagen	15	1.2
9.	Sepharose 4B-200 ^a	15	1.30
10.	Chitosan ^b	15	1.68
11.	Chitin ^c	15	1.85
12.	Corn Starch	15	1.77
13.	OCH ₂ CO ₂ H modified starch	15	1.50
14.	OCH ₂ CO ₂ Na modified starch	15	6.8
15.	Sephadex G-25-80 ^e	15	2.22
16.	Sephadex G-25-150	40	1.76
17.	Sephadex G-25-150	60	0.80
18.	alginate acid	15	2.86
19.	Super-Slurper	15	93
20.	Super-Slurper ^f	43	20
21.	Super-Slurper ^g converted to the acid form	15	1.67
22.	sulfonated styrene-co-divinylbenzene(1%)	30	25
23.	DEAE-Sephadex ^g	50	39
C. Mixtures of particles			
24.	Super-Slurper (43%) + kaolin(21%)	36	6.3
25.	Super-Slurper (33%) + kaolin(33%)	34	2.3
26.	DEAE-Sephadex (33%) + kaolin(33%)	34	4.0

^a Cross-linked agarose.

^b Polyglucosamine.

^c Poly-*N*-acetylglucosamine.

^d β -1,4-linked polyglucose.

^e Dextran cross-linked with epichlorohydrin.

^f Cellulose chain extended with polyacrylonitrile and then hydrolyzed.

^g Diethylaminoethyl-modified Sephadex.

TABLE II
Absorption of Liquids by Particles (80%) Enmeshed in PTFE (20%)

Particulate	Liquid Absorbed at r.t.	τ Time (in min) to reach plateau of saturation	$V_{(t=\tau)}$ mL liquid per gram of composite absorbed at $t = \tau$	Time study	$V_{(t=18)}$ mL liquid per gram of composite absorbed at $t = 18$ h
Kaolin	water	2	0.39 ± 0.06		0.40 ± 0.04
	methanol	2	0.37 ± 0.01		0.37 ± 0.01
CaCO ₃	water	2	0.36 ± 0.07		0.36 ± 0.04
	methanol	2	0.35 ± 0.01		0.35 ± 0.01
Sty-Co-DVB ^b	water ^a	^a	^a	^a	0.62^a
	heptane	5	0.65 ± 0.04	Fig. 8	0.65 ± 0.02
	methanol	5	0.69 ± 0.03		0.69 ± 0.02
	acetone	5	1.21 ± 0.09	Fig. 8	1.22 ± 0.07
	CCl ₄	30	3.05 ± 0.03	Fig. 8	3.12 ± 0.01
X-linked polyacrylamide ^c	CHCl ₃	30	3.48 ± 0.03	Fig. 8	3.53 ± 0.01
	methanol	20	0.12 ± 0.02	Fig. 7	0.16 ± 0.02
X-linked dextran ^d	water	30	3.20 ± 0.08	Fig. 7	3.39 ± 0.01
	water	90	2.23 ± 0.06	Fig. 6	2.25 ± 0.06
	heptane	10	0.40 ± 0.04	Fig. 6	0.40 ± 0.04
	methanol	90	1.21 ± 0.04^e	Fig. 6	1.31 ± 0.02^e
	heptane	90	1.28 ± 0.04^f		1.30 ± 0.04^f
	water	90	1.54 ± 0.06^f		1.57 ± 0.05^f

^a Water capacity of the composite sample before removal of the surfactant as described in the Experimental.

^b BioBeads SX-2, comminuted to 1 to 10 μ m.

^c Bio-Gel P6, comminuted to 0.5 to 5 μ m.

^d Sephadex G-25-40, 10 to 40 μ m.

^e Chemical modification occurred during this time study as described in the text.

^f Capacity for absorption of heptane and water after chemical modification that occurred during the methanol time study.

RESULTS and DISCUSSION

Physical Characterization of Composite Membranes

A typical microstructure of particles enmeshed in PTFE networks is shown in Figures 1(A) and 1(B), which are SEM photomicrographs of the top surface and freeze-fractured edge view, respectively, of a membrane made from Sephadex G-25-40 (i.e., cross-linked dextran beads about 10 to 40 μ in diameter) and PTFE emulsion as described in the Experimental section. The uniform distribution of isolated particles in multiple planes that parallel the surface of the composite sheet is clearly visible. The void space around each spherical particle [Fig. 1(C)] represents the size of that particle in its water-swollen state prior to freeze fracture and subsequent desiccation in vacuum. Although the PTFE mesh that surrounds each particle appears to be a continuous sheet in Figure 1(C), it is in reality a fibrous network that resembles a fishnet [Fig. 1(D)].

A "fishnet" pattern of fibrillated PTFE is obtained only when the particulate component of the composite mixture is a water-swollen material and therefore relatively soft. When the particulate component is a hard,

nonwater-swellaible irregular-shaped material, very long fibers (i.e., > 1 mm in length < 0.1 μ in width) are produced during milling, and consequently tough composite membranes are fabricated more easily from the latter than from the former. Although the porosity of membranes made from non-swellaible particles is less than those made from water-swellaible particles (Table I), the three-dimensional patterns for the particle distributions of both types of composites are essentially the same and about as shown in Figure 1.

Because of the open-cell structure (Fig. 1), all such membranes (Table I) made from hydrophilic particles absorb water readily despite that these particles are isolated and restrained by a network of PTFE microfibers. The volume of water absorbed by membranes made from hydrophilic (but non-water-swellaible) particles, such as kaolin and calcium carbonate, is equal to its void space (usually from 0.3 to 0.6 mL per mL of the bulk volume of the composite (Table I) depending upon the final water content at the termination point of sample preparation as described in the Experimental section). This absorption occurs via capillary action, and is reproducible to within 2%, provided that it occurs unidirectionally (i.e., from the bottom surface to the top surface of the microporous film) to allow for free escape of displaced air.

The volume of water absorbed by composite membranes made from water-swellaible particles, however, depends on the absorptivity of the particle. Thus, the volume of liquid absorbed per gram of composite membrane (Table I) ranges from about 1 mL for particles such as cellulose to about 93 mL for particles such as Super-Slurper. The absorption capacity observed over 10 swelling and redrying cycles was reproducible to within 0.5%. The dry weight measured at the end of these 10 cycles was within 0.02% of the initial dry weight, which means that the loss of particles was insignificant despite rather rough handling during the multiple cycles of swelling and redrying.

Since the cohesive strength of these composites is provided entirely by the entangled network of PTFE microfibers, the force required to rupture samples of non-water-swellaible (or poorly water-swellaible) composites in the wet state is about the same as that in the dry state. The tensile strengths of the water-swellaible samples, however, decrease with swelling. This observation is consistent with expectation, since tensile strength is measured in terms of force required to effect rupture per unit area of the rupture plane, and the number of fibers, which provides the tensile strength, per unit cross section decreases with swelling. As explained in the Experimental section, the tensile strength of these composite films increases with the weight fraction of PTFE in the composition, and also with the magnitude of work done on the composition during the preparative procedure.

The void space (i.e., porosity) is usually somewhat less for films with high % PTFE. Moreover, the capacity to absorb liquid per gram of entrapped particles may also be less in films with very high % PTFE, owing to the extra restraining force of the PTFE microfiber network, especially for films made from particles that can swell enormously such as Super-Slurper. Such films absorb about 110 g of water per gram of S-S in composite films that contain 15% PTFE (Film 19, Table I), but absorb only about 40 g of water

per gram of S-S in films that contain 43% PTFE (Film 20, Table I). This does not appear to be as critical for composite films made from particles that have much less swelling capacity. Thus, Sephadex absorbed 2.5, 2.9, and 2.0 g of water per gram of particles in films that contained 15, 40, and 60% PTFE, respectively (Films 15, 16, and 17, Table I).

In view of the magnitude of the apparent nonreversible expansion of the PTFE microfiber network [Figs. 1(B) and 1(C)] caused by particles that swell only about twofold in water, one might suspect that the physical integrity of such composites would be destroyed when the particle component is a material such as Super-Slurper, which can swell more than 90-fold. This is not the case, however, as evidenced by the before-and-after photograph (Fig. 2) taken after 5 swelling-and-redrying cycles. At its maximal swollen state, the composite is a hard transparent gel that can support > 1 psi in compression without rupture or loss of water. When the gel is dried at ambient room conditions, however, it becomes rigid and cardboardlike in appearance. Apparently the restraining microfibers become embedded in the soft par-



Fig. 2. Photograph of Super-Slurper enmeshed in PTFE composite membrane, showing a sample (bottom) that was dried at ambient room conditions and an equivalent sample (top) originally of the same dimensions that was swelled to equilibrium in excess water.

ticles at maximal swelling, and then compress along with the shrinking enmeshed particles during subsequent desiccation at ambient room conditions to form ultimately the rigid cardboard-like structure relatively free of void space as shown in Figures 3(A) and 3(B), which are SEM photomicrographs of the top surface and fractured edge views, respectively, of the formerly swollen sample (Fig. 2). When the gel is freeze dried in vacuum, however, the fully expanded microfibrillar network is preserved, and the dried product consists of mostly void space as noted in Figure 4(A) and 4(B), which are SEM photomicrographs of the top surface and fractured edge views of the swollen sample (Fig. 2) after it was freeze dried.⁷ Unlike the sample dried at ambient room conditions, which is dense and rigid [Fig. 3(B)], the freeze-dried material [Fig. 3(C)] is feather light and extremely soft.

The absorption capacity of the Super-Slurper-PTFE composite is a function of the mole fraction of the carboxylic acid groups of the starch-hydrolyzed polyacrylonitrile component converted to the salt form. The acid form of the particulate was used to make the composite membrane, in which form it absorbs only about 2 g of water per gram of composite (Film 21, Table I). After the acidic component was reconverted to its salt form by neutralization with aqueous NaOH, its absorption capacity increased to >90 g of water per gram of composite (Film 19, Table I). This capacity decreased monotonically, however, with each repeated swelling and drying cycle, presumably owing to ion exchange with water. After five cycles,

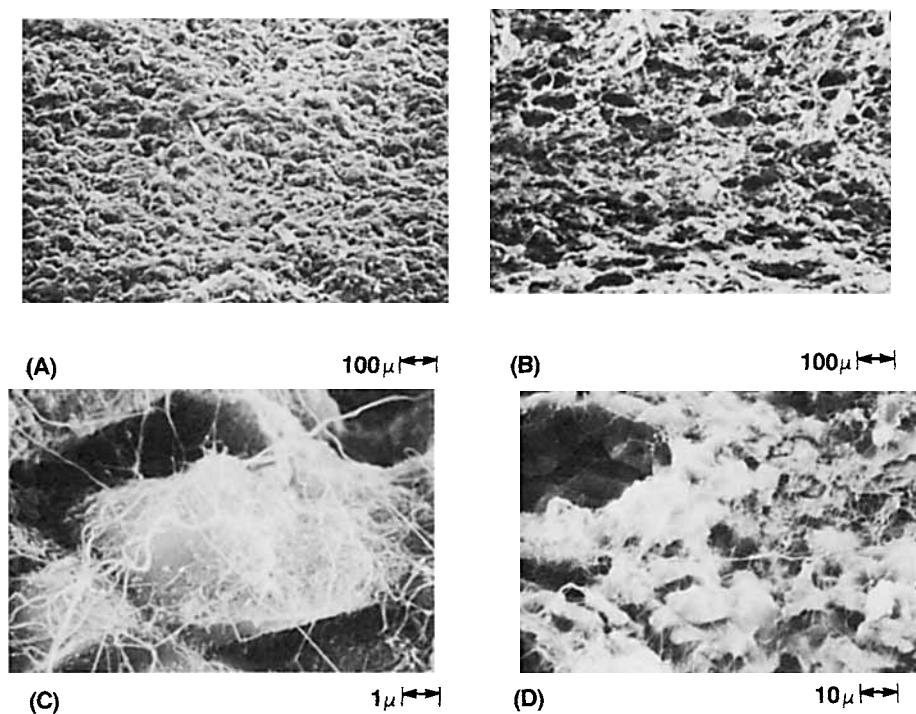


Fig. 3. SEM photomicrographs of the dried sample (bottom of Fig. 2). (A) Top surface viewed at a 45° angle from the horizontal plane. (B) Freeze fractured edge viewed at a 0° angle. (D) Tenfold enlargement of "B". (C) Tenfold enlargement of "A."

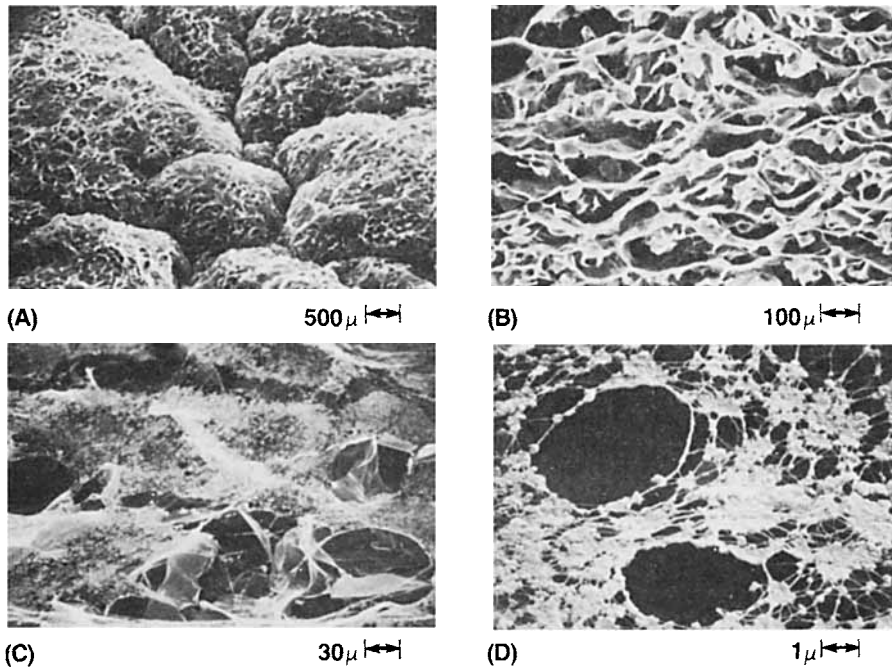


Fig. 4. SEM photomicrographs of a sample (top of Fig. 2) that was freeze dried after equilibrium swelling in excess water. (A) Top surface viewed at a 45° angle from the horizontal plane. (B) Freeze-fractured edge viewed at a 0° angle from the horizontal plane. (C) threefold magnification of "B". (D) thirtyfold magnification of "C."

equilibrium swelling was attained at only 44 g of absorbed water per gram of composite (Fig. 2). When the sample was acidified with dilute HCl, the volume of the gel decreased sharply such that it now contained only about 2 g of water per gram of composite. When this sample was reneutralized with base, it again absorbed about 90 g of water per gram of composite.

The absorption capacity of Super-Slurper is also affected adversely by association with inorganic particulates such as kaolin. Thus, composite films made from equal-weight mixtures of S-S (33%) and kaolin (33%) absorb only 7 g of water per gram of S-S (Films 24 and 25, Table I); whereas in composite films restrained by about the same amount of PTFE, but in the absence of kaolin, the absorption capacity is about 37 g of water per gram of S-S (Film 20, Table I). Actually, the absorption capacity of composite films made from Super-Slurper-kaolin mixtures enmeshed in the same %PTFE increase linearly with %S-S when kaolin is in excess, but exponentially with %S-S when S-S is in excess (Fig. 5).

Liquid Absorption Studies

Time studies of liquid absorption by 10 samples taken from the same microporous composite film were carried out simultaneously to test the reproducibility of the kinetics of liquid uptake to the state of equilibrium swelling, and also the reproducibility of liquid capacity at the swelling equilibrium state. The data obtained in these studies are summarized in

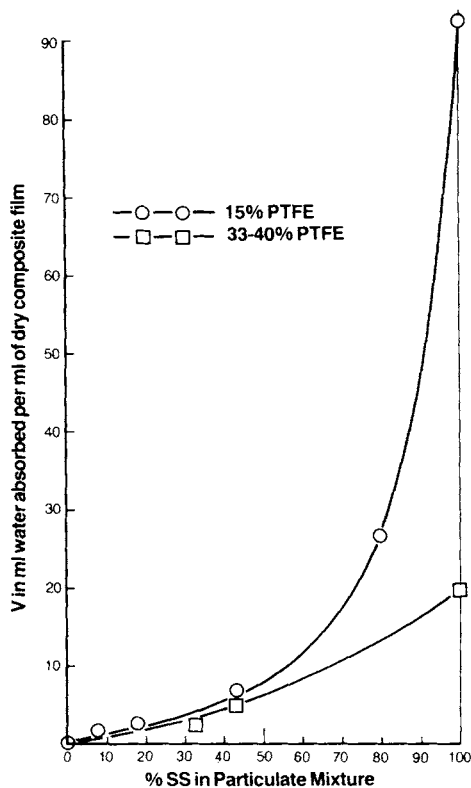


Fig. 5. Absorptivity of Super-Slurper/kaolin mixtures enmeshed in PTFE, in mL of absorbed water per gram of composite, as a function of percent SS in the SS/kaolin mixture.

Table II. The volume (V) of liquid absorbed per gram of composite was a continuous function of the cumulative time (t) that the microporous composite sample was in surface contact with the liquid (Figs. 6, 7, and 8). The plot of V as a function of t for each of the 10 replicate time studies is within the narrow band between the upper and lower bounds of the data collected in a given scan interval (indicated by vertical bars in Figs. 6 and 7); these curves, however, did not always parallel uniformly the line through the corresponding averaged data points (indicated as closed circles in Figs. 6, 7, and 8).

The best reproducibility was evidenced in the data for uptake of organic liquids by composites that contained organic-liquid-swelling particulates (Fig. 7). In these studies, the range of the data collected in a given scan interval was within 0.01 of the averaged data point recorded in Figure 7 as a closed circle.

The worst reproducibility was exhibited before equilibrium swelling was established, especially in the case of water-swelling microporous films (Figs. 6 and 8). The range in the data for liquid absorption by 10 samples of the same film in a given scan interval was maximal at about 50% of saturation, but this range narrowed considerably when the samples attained the state of near saturation (Fig. 8). This difference in rate of water uptake before saturation is believed to reflect differences in surface chemistry of

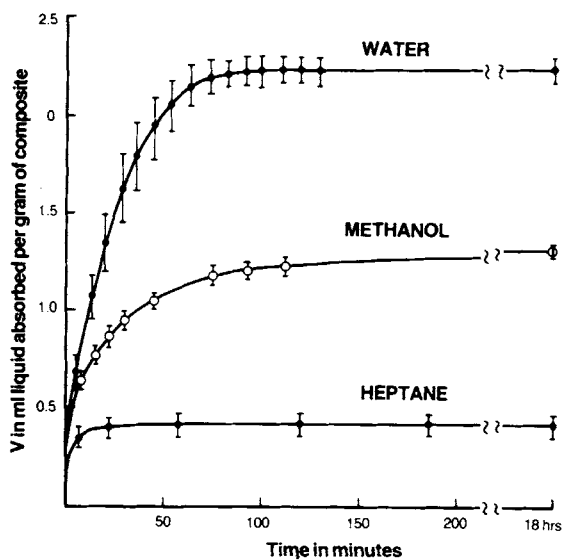


Fig. 6. Kinetics of liquid absorptions in 10 replicates using samples cut from the same microporous composite sheet that consisted of Sephadex microspheres enmeshed in PTFE (ca. 20% by weight; Fig. 1).

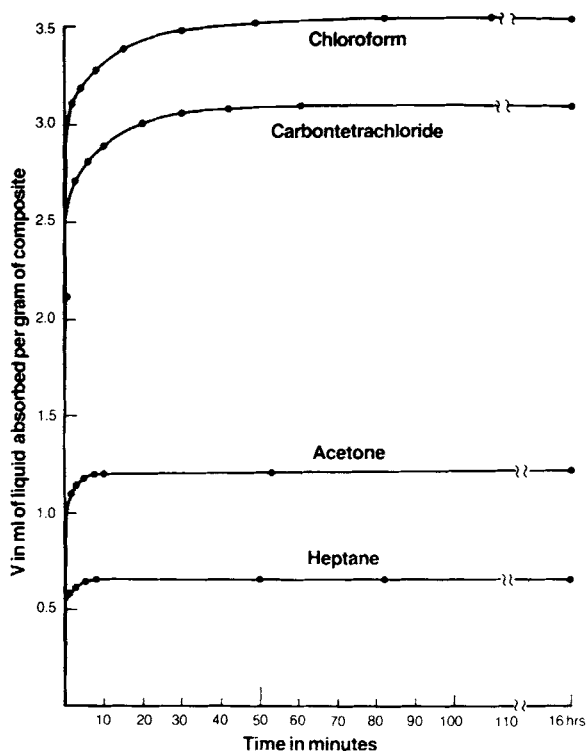


Fig. 7. Kinetics of liquid absorptions in 10 replicates using samples cut from the same microporous composite sheet that consisted of poly(styrene-co-divinylbenzene) microspheres enmeshed in PTFE (ca. 20% by weight).

the particles, which affects markedly the rate of water permeation of microporous membranes as reported and discussed elsewhere.⁸⁻¹⁰

In support of this point of view are the results obtained in the set of time studies of water uptake by 10 samples taken from the same microporous film made from comminuted ($<5\mu$) poly(acrylamide) (Bio-Gel P-6). This material is not swelled measurably by methanol. Thus, the volume of methanol absorbed per gram of composite was only 0.16 ± 0.02 mL (Fig. 8), which corresponds within experimental error to the void space of this particular sample. The amount of methanol adsorbed on the surface of the entrapped particulates, however, can have a marked effect subsequently on the rate that the sample absorbs water to attain saturation. Thus, the rate of water uptake during the first 20 minutes of subsequent contact with water was 0.153 mL/min per gram of composite for the sample that was removed from methanol, damp dried between paper towels, and then allowed to dry for only one additional minute at ambient room conditions (V as a function of t is indicated in Fig. 8 by the upper bound of the absorption data collected at scan times $t < 40$ minutes). The initial rate of water uptake exhibited by the other 9 film samples decreased monotonically with time allowed for the sample to dry at ambient room conditions, so that it was only 0.112 mL per minute for the sample that was allowed the longest time (15 minutes)

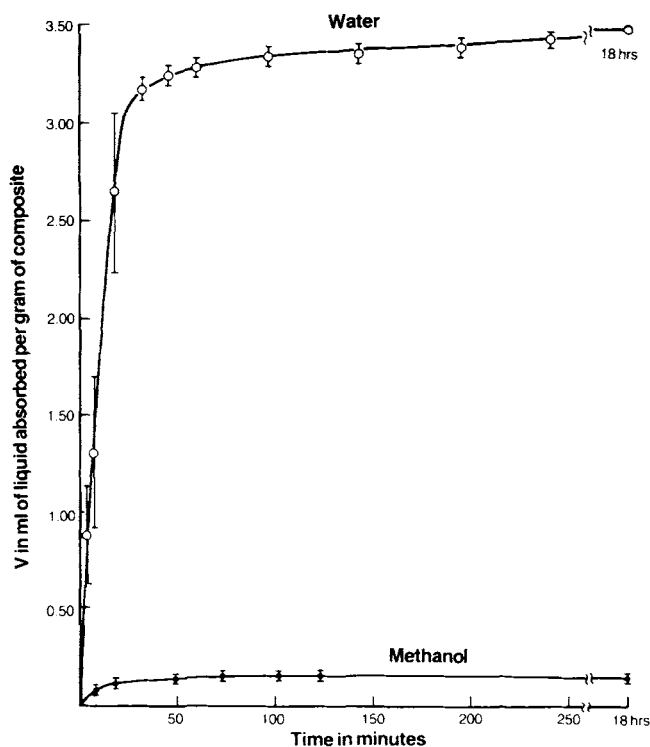


Fig. 8. Kinetics of liquid absorptions in 10 replicates using samples cut from the same microporous composite sheet that consisted of comminuted cross-linked poly(acrylamide) enmeshed in PTFE (ca. 20% by weight).

(V as a function of t is indicated in Fig. 8 by the lower bound of the absorption data recorded at scan times $t < 40$ min.). After the 10 samples became virtually saturated with water (i.e., for scan times $t > 50$ minutes), the absorption data was randomly distributed about the average data point (indicated by a closed circle) independent of the time allowed for drying between-time studies, showing that the amount of residual adsorbed methanol had no effect on the capacity for water absorption at swelling equilibrium ($V = 3.39 \pm 0.02$ mL/g of composite), despite that it had a significant effect on the rate of water uptake before attaining swelling equilibrium.

The time studies of liquid absorption by microporous composite membranes made from hydrophilic nonswellable particles, such as kaolin or calcium carbonate, show that the samples were saturated within two minutes after contact with the liquid (Table II). The absorption patterns for these time studies were similar in form to those shown for absorption of heptane by the microporous membranes made from cross-linked poly(styrene) ($V = 0.65 \pm 0.02$; Fig. 7) and also from cross-linked dextran ($V = 0.40 \pm 0.04$; Fig. 6), and for absorption of methanol by the composite film made from poly(acrylamide) ($V = 0.16 \pm 0.02$; Fig. 8) all of which neared saturation within 10 min. The volume of heptane absorbed by the poly(styrene) composite film corresponds well with the porosity determined on the basis of water content at the end point of the preparative procedure (Table II). It is believed, therefore, that the volume of heptane and methanol absorbed by the above three composite films corresponds to the porosity of that film, which depends on the preparative procedure as described in the Experimental section.

When the membranes were made from swellable particles, however, 0.5 to 2 h was required to attain virtual saturation (Table II) depending primarily upon the surface to volume ratio of the particles, but mitigated somewhat by the surface state of the particles component as described above. The longer times to saturation (Fig. 6) were exhibited by membranes made from larger particles (40 to 80 μ), and the shorter times (Fig. 7) were exhibited by membranes made from smaller particles (1 - 10 μ).

Reproducibility of Swelling and Drying Cycles

After the small amount of soluble components, and the edge particles (visible along the plane of freeze fracture in Fig. 1), are removed by continuous agitation in warm water for 24 h, followed by subsequent sequential extraction in acetone and toluene, the dry weight of that composite sample is reproducible thereafter to within 0.2%, even after 100 swelling and re-drying cycles. This reproducibility verifies that the number of enmeshed nonsoluble particulates lost because of the vigorous handling during the numerous repeated swelling and drying cycles is insignificant.

The difference in weight after drying to equilibrium in air at 20°C and 50% RH, and the weight after subsequent drying for an additional hour at 100°C in a vacuum oven, represents the weight of adsorbed water vapor, which is 0.04 to 0.06 g per gram of composite made from particles such as cross-linked dextrans and poly(acrylamide). The reproducibility of this difference in 10 successive cycles using the same sample was within the limits

of experimental error exhibited by 10 samples cut from the same composite sheet. This is not surprising in view of the results observed by Fowkes et al.,⁵ who compared absorption of organic vapors by powdered organic polymer with the corresponding absorption by samples of the same particulates enmeshed in PTFE composites, which were made in our laboratory. They reported comparable accuracy and reproducibility for the two methods for measuring absorption by particulate polymer. The time to attain equilibrium using the thin sheets of enmeshed particles, however, was much shorter. Moreover, handling the particles in membrane form was much more convenient, and the physical integrity permitted multiple cyclic reuse of the same sample, which minimized sampling and personal errors.

The amount of liquid absorbed, at equilibrium swelling in excess liquid per gram of microporous composite, is also reproducible to within 0.2% provided that the particulate matter does not undergo chemical modification during one or more of the swelling-drying cycles. An example of change in absorptivity caused by chemical modification was observed with composites made from cross-linked dextrans. When such composite membranes are allowed to remain in water for several days, a significant amount of biodegradation occurs, which produces water- and/or methanol-soluble products. When such biodegraded samples were swelled subsequently in methanol for 1.5 h to apparent equilibrium, the absorptive capacity was only 89% of that observed for methanol before biodegradation was allowed to occur. This decrease in absorptive capacity was accompanied by an unusual 2.4% decrease in dry weight, owing primarily to extraction of soluble degradation products. When the sample was reswelled in methanol for 24 h, the capacity for methanol increased slowly from 1.21 ± 0.04 mL/g of composite at apparent equilibrium, established at $t = 1.5$ h, to 1.31 ± 0.04 mL/g established at $t = 24$ h. This slow monotonic increase was attributed to chemical modification, presumably acetal and/or ether formation. The decrease in dry weight over this cycle was only 0.6% owing to weight loss by extraction of low-molecular weight products and compensating weight gained as a result of binding methanol by ether and/or acetal formation. As a result of this apparent modification, the absorptivity with respect to heptane was also modified considerably; before the chemical modification, the cross-linked dextran particulate composite absorbed only 0.41 ± 0.06 mL of heptane per gram of composite (i.e., only enough to fill the void spaces of the composite). After the chemical modification, the absorptivity for heptane was 1.31 ± 0.04 mL/g of composite, which is clearly the result of particles swelling. The absorptive capacity for water also was changed markedly; before biodegradation and further modification in methanol, the membrane absorbed 2.25 ± 0.06 mL of water per gram of composite, but after this chemical modification it was only 1.57 ± 0.05 .

Conclusions and Potential Applications

The results reported in this and earlier publications¹⁻⁶ show that particles enmeshed in PTFE microfiber membranes represent a convenient form in which to study liquid and/or gas absorption by polymeric materials. The open-cell structure affords unimpeded uniform access of the fluid to the

entrapped particulates, so that the rate of fluid uptake is controlled primarily by the surface-to-volume ratio of the particles. The inert PTFE microfiber network that physically restrains the particles provides the tough physical integrity of the composition, which enables one to handle such films even roughly without measurable loss of entrapped particles.

Composite membranes, made in this laboratory using non-cross-linked particulate polymer, were used by Fowkes to monitor absorption of organic vapors at a given temperature and partial pressure in his studies of acid-base complexes of polymers.⁵ The reproducibility of the data in these studies was excellent because loss of entrapped polymer by solvent extraction was not a factor. This is not the case, however, when one is monitoring liquid uptake by composite membranes in large excess of liquid. Under these conditions non-cross-linked polymer could be dissolved completely leaving only the chemically inert network of PTFE microfibers. In such studies, therefore, the choice of entrapped particles must of necessity be limited to cross-linked polymers. In fact, good reproducibility cannot be attained until all extraneous components, such as added surfactants and loose particles located along the edges of the composite samples [Fig. 1(C)] have been removed by extraction and agitation in a suitable liquid. Thereafter, the reproducibility is as good as that reported for adsorption of organic vapors.³⁻⁵

In this publication our data for liquid uptake, V , is given in milliliters absorbed per gram of composite. Since the weight fraction $(1-x)$ of chemically inert component PTFE, and the void space, V_0 , unique to the composite sample, are measurable quantities, the volume of liquid v absorbed per gram of entrapped particulate polymer can be calculated for each sample directly from the respective observed V (i.e., $v = (V - V_0)/x$). It is obvious, therefore, that these composite membranes may afford a convenient means for studying swelling of cross-linked polymer and relating it to the molecular structure of the polymer and that of the swelling liquid. The results of such studies will be reported in subsequent publications.

It is also obvious that these composite membranes may have potential in many specialty applications that require selective removal of liquids and/or solutes. For example, it was reported by Cussler et al.¹¹ that water-swelling particles can be used *per se* to concentrate aqueous solutions of protein products of fermentation or aqueous colloidal suspensions. Since the protein solutes (or colloids) are not absorbed, they remain in the filtrate after the mixture of gelled particles and solution are separated by filtration. This sort of separation can be carried out more conveniently when the water-absorbent particulate matter is enmeshed in a PTFE microfiber network. Such a composite membrane has considerable physical integrity even in its swollen state at water saturation (Fig. 2). Consequently, the water-swollen particles entrapped in the PTFE microfiber network can be separated conveniently from the aqueous concentrate with minimal occlusion of solute or suspensoid.

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