

Surface Area of Aqueous Sodium Hydroxide Hydrolyzed High-Speed Spun Poly(ethylene terephthalate) Fibers

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SYNOPSIS

The specific surface area (SSA) of delustered undrawn and drawn high-speed spun PET fibers hydrolyzed in aqueous NaOH was measured using three methods: (1) geometric, based on fiber diameter; (2) gas adsorption using N₂ and the BET equation; and (3) adsorption of a nonionic surfactant. Increasing the spinning speed had little effect on the SSA of the untreated fibers, while drawing resulted in considerably larger SSA. For the hydrolyzed fibers, both adsorption methods resulted in larger SSAs than that predicted geometrically due to surface pitting. After hydrolysis, the higher spinning speed resulted in a greater increase in SSA over the untreated sample, whereas the increase in SSA was less for the drawn fibers compared to the undrawn. The kinetics of hydrolysis are also discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well established that hydrolysis of poly(ethylene terephthalate) (PET) fibers using aqueous sodium hydroxide is confined to the polymer surface, thereby removing successive layers as the reaction progresses.¹ Part of the basis for this conclusion is that the fibers' cross-sectional shape does not change after hydrolysis. For round fibers, a decrease in radius can be measured.² Although the overall cross-sectional shape does not change, pits develop on the surface, the size of which increase with weight loss for PET fibers to which TiO₂ has been added as a delusterant.¹ It is believed that the areas immediately surrounding the TiO₂ particles are of relatively lower orientation and crystallinity such that hydrolysis occurs preferentially at these sites.³ At high weight loss, the entire fiber surface is roughened by pits and craters.²

The change in surface area of hydrolyzed PET fibers has received little attention in the literature. Typically, the geometric surface area, i.e., surface area based on diameter or linear density, has been

considered;^{4,5} surface pitting is ignored. However, the presence of these pits on the hydrolyzed fiber obviously affects the surface area per unit weight, or specific surface area (SSA), such that the true surface area must be greater than the one calculated geometrically.

Zeronian et al.⁶ followed the adsorption of a non-ionic surfactant onto the surface of PET fabric to measure changes in SSA before and after hydrolysis. An increase in SSA was found due to treatment in either aqueous NaOH or methanolic sodium methoxide. The SSA of PET hydrolyzed to 6% weight loss by either reagent increased by approximately 75%, while the radius of aqueous NaOH-hydrolyzed PET fibers of similar weight loss decreased by only approximately 5%.² Thus, the SSA of hydrolyzed PET fibers appears to be a sensitive measure of the microscopic topographical changes which occur and are manifested as weight loss. The focus of the study by Zeronian and co-workers,⁶ however, was wettability; changes in SSA due to hydrolysis were not studied in detail.

Another method to measure SSA utilizes gas adsorption and the Brunauer, Emmett, and Teller (BET) equation. The BET method has been used very little for measuring the SSA of fibers. Gozdz and Weigmann⁷ showed good agreement between three methods of measuring SSA of untreated PET

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fibers: (1) BET using krypton as the adsorbate, (2) inverse gas chromatography employing adsorption of *n*-decane, and (3) geometric calculations based on fiber length, mass, and density.

Knowledge of actual SSA may be useful in evaluating the effects of spinning speed and drawing on the SSA of hydrolyzed high-speed spun PET fibers. Such fibers have been the focus of many recent studies⁸⁻¹¹ in attempts to discern their fine structure in relation to many processing parameters including spinning speed. Fibers spun using the high-speed method are sometimes subjected to a drawing step, influencing their fine structure and surface area. Since both fine structure and starting geometric area of the PET fiber surface have been found to affect the rate at which weight loss occurs in hydrolysis,^{2,4} surface area measurements of high-speed spun PET fibers after hydrolysis in aqueous NaOH might help to elucidate these fibers' fine structure. As pitting occurs preferentially in less ordered regions of the fiber surface, it may be possible to correlate changes in surface area with spinning speed before and after drawing.

Additionally, kinetic studies of hydrolysis may be furthered by including actual SSA measurements in the analyses. Kinetic studies of aqueous NaOH hydrolysis of PET fibers have been based on weight loss,¹² change in NaOH concentration throughout the reaction,¹³ and/or geometric surface area.^{4,5,14}

EXPERIMENTAL

Materials

High-speed spun delustered PET yarns were provided by Hoechst Celanese, Charlotte, NC. A total of four samples were studied; two of the yarns were spun at either 1615 or 3329 m/min and left undrawn, while the other two yarns were counterparts which had been subsequently drawn. The sample codes and spinning and drawing conditions are given in Table I. Union Carbide of South Charleston, WV, supplied the Tergitol NP-10, a nonylphenol ethoxylate non-ionic surfactant. All chemicals used were of reagent grade. Type I water, obtained from a Millipore Milli-Q system, was used to prepare the Tergitol NP-10 solutions.

Procedures

Alkaline Hydrolysis

All hydrolyses were carried out in sealed flasks at 21°C ($\pm 2^\circ\text{C}$) with mild mechanical agitation. Yarn

Table I Sample Codes and Spinning and Drawing Conditions of Untreated PET Fibers

Sample Code	Spinning Speed (m/min)	Draw Ratio
Undrawn		
U1	1615	—
U2	3329	—
Drawn		
D1	1615	2.44
D2	3329	1.88

samples were treated in a 2.5M aqueous NaOH, 0.1% (w/w) cetyltrimethylammonium bromide (CTAB) solution in a 2.5 ratio of weight/volume (g/L) for various lengths of time. CTAB was used to increase the rate of the reaction. The hydrolysis was terminated by rinsing the yarns in fresh NaOH solution to remove terephthalic acid which was found to precipitate onto the fiber surface when placed directly in water. Terephthalic acid absorbs in the same region of the UV spectrum as does Tergitol, obscuring SSA measurements made by that method. The fresh NaOH rinsing was followed by rinsing in distilled water, neutralizing in 1% HCl for 2 min, and rinsing again in distilled water until neutral to litmus paper. The samples were blotted with filter paper to remove excess water and allowed to air-dry in a constant temperature and humidity (CTH) room at 21°C ($\pm 2^\circ\text{C}$) and 65% relative humidity.

Weight Loss

Percentage weight loss was determined after the hydrolyzed samples had been conditioned to constant weight in the CTH room and was calculated based on the conditioned weight of the untreated samples.

Tex

Three 1 m lengths of the untreated yarn were conditioned in the CTH room before weighing. The average weight was divided by the average number of fibers in the yarn and multiplied by 1000 to obtain the tex of the untreated fiber. The tex of the hydrolyzed fibers was calculated using percentage weight loss.

Geometric Specific Surface Area (SSA_G)

To measure fiber diameter, fibers were immersed in glycerol and viewed at 400 \times using a Nikon binocular light microscope fitted with a calibrated eyepiece.

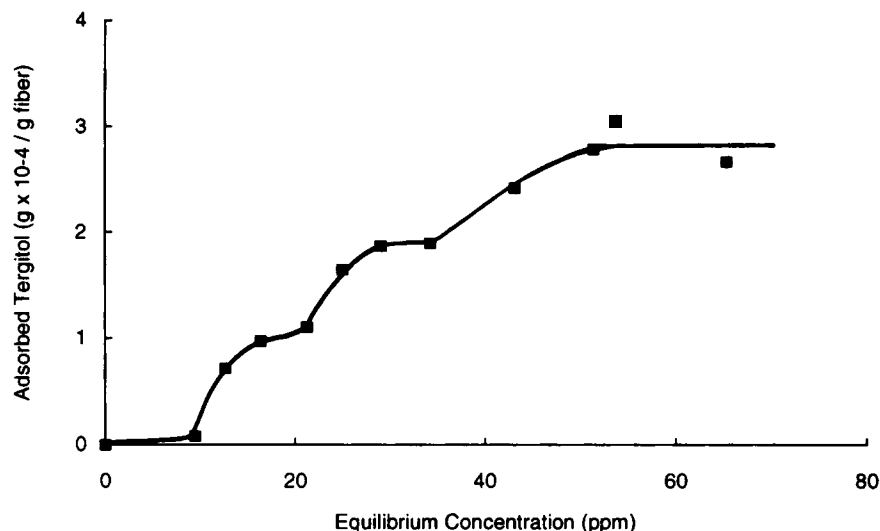


Figure 1 Adsorption isotherm of Tergitol NP-10 on untreated PET fiber U2.

SSA_G was then calculated, assuming that the surface area of fiber ends was negligible, as

$$SSA_G = \frac{\pi d}{\text{tex}} \quad (1)$$

where d is the fiber diameter in m and tex is the fiber linear density in g/1000 m. d is the average of 10 fibers. SSA_G is the mean from two sample portions. The coefficient of variation for all SSA_G data averaged 3.2%.

BET Specific Surface Area (SSA_B)

Nitrogen gas adsorption was measured on a Micromeritics Gemini 2360 Surface Area Analyzer equipped with a data acquisition station which calculated SSA_B using the BET equation¹⁵ to obtain the amount of nitrogen adsorbed at monolayer formation:

$$\frac{x}{n(1-x)} = \frac{1}{cn_m} + \frac{(c-1)x}{cn_m} \quad (2)$$

where x is the partial pressure of nitrogen; n , the number of moles of nitrogen adsorbed at x ; n_m , the number of moles of nitrogen adsorbed at monolayer coverage; and c , a constant. For type II adsorption isotherms (typical of physical adsorption), eq. (2) is linear in the range of $x = 0.05$ to 0.30 with the y -intercept equal to $1/cn_m$ and the slope equal to $(c-1)/cn_m$. From the slope and the intercept, n_m can be determined, which allows calculation of SSA_B (Ref. 15):

$$SSA_B = \frac{n_m N_A \sigma^0}{m} \quad (3)$$

where N_A is Avogadro's number; σ^0 , the area occupied by one nitrogen molecule; and m , the mass of the fiber. σ^0 of nitrogen is equal to $16.2 \times 10^{-20} \text{ m}^2/\text{molecule}$.¹⁶ SSA_B is an average of two determinations, with a mean coefficient of variation of 5.6%.

Tergitol Specific Surface Area (SSA_T)

Untreated fibers to be used in Tergitol SSA measurements were first cleaned by Soxhlet extraction in trichlorotrifluoroethane for 3 h. To determine surfactant adsorption, fibers were cut to lengths of approximately 2.5 cm and immersed in an aqueous solution of Tergitol NP-10 in a ratio of 2 g of fiber to 100 g of solution. The fibers were shaken in the solution for 24 h at 21°C. A Hitachi U-2000 spectrophotometer was used to determine the concentrations of the solutions, before and after adsorption, by measuring the UV absorbance at 274.2 nm using cuvettes with a 100 mm path length. SSA_T was calculated as

$$SSA_T = \frac{X N_A A}{MW} \quad (4)$$

where X is the amount of Tergitol adsorbed per weight of fiber in g/g; N_A , Avogadro's number; A , the surface area of the Tergitol molecule in m^2 ; and MW , the molecular weight of one Tergitol molecule. X is the mean of two determinations measured at a starting concentration of approximately 60 ppm. At

Table II Weight Loss and Specific Surface Area of NaOH-hydrolyzed PET Fibers

Sample	Hydrolysis Time Hours	Weight Loss (%)	Specific Surface Area ^a (m ² /g)		
			Geometric	BET	Tergitol
U1	Untreated	—	0.115	0.155	0.106
	1.0	5.0	0.120	0.193	0.179
	7.5	33.5	0.149	0.207	0.168
	11.0	56.9	0.146	0.292	0.261
U2	Untreated	—	0.114	0.152	0.114
	2.0	5.9	0.116	0.208	0.222
	9.5	30.1	0.131	0.250	0.372
	19.0	53.8	0.174	0.343	0.352
D1	Untreated	—	0.161	0.181	0.177
	15.0	6.0	0.165	0.208	0.210
	81.0	28.7	0.188	0.235	0.228
	168.0	54.9	0.269	0.303	0.261
D2	Untreated	—	0.163	0.172	0.194
	18.0	5.1	0.168	0.232	0.273
	110.0	32.8	0.194	0.268	0.364
	220.0	51.1	0.233	0.327	0.433

this concentration, the adsorption had leveled out and was assumed to be Langmuirian (Fig. 1), i.e., a monolayer of Tergitol molecules had formed on the fiber surface. As discussed later, A was calculated to be 43.9×10^{-20} m²/molecule. MW is equal to 682 g/mol.¹⁷ The same samples as those used in the SSA_B measurements were utilized. The mean coefficient of variation of the SSA_T data was 5.9%.

RESULTS AND DISCUSSION

SSA was measured on the untreated fibers, and after three weight losses, approximately 5, 30, and 55% (Table II). In this manner, changes in SSA could be observed at the initial onset of pitting, at a moderate level of pitting, and at more severe pitting.

Evaluation of BET and Tergitol SSA Methods

To examine the validity of the BET data obtained in this study using N₂ as the adsorbate, the SSA of several samples was compared to measurements made by Micromeritics of Norcross, GA, using krypton as the adsorbate (Table III). For solids of low surface area (< 1.0 m²/g), it has been reported¹⁸ that Kr is the adsorbate of choice. With low surface area solids, the amount of gas contained in voids

can be significant compared to the amount of gas adsorbed on the substrate. Using an adsorbate with a low vapor pressure, such as Kr, reduces errors arising from gas trapped in voids. At monolayer coverage, less Kr will be present in voids than when N₂ is used. However, the amount of Kr adsorbed by the solid will be less than the amount of N₂ adsorbed by the solid by a factor equal to the ratio of their cross-sectional areas.¹⁸ For N₂, the cross-sectional area is 16.2×10^{-20} m²/molecule, while Micromeritics used 21.0×10^{-20} m²/molecule for the area of Kr, making the ratio of their areas equal to 0.77. There is some disagreement as to the actual cross-sectional area of the Kr molecule. Values range from

Table III Comparison of BET Data using N₂ and Kr

Sample	Weight Loss (%)	SSA _B (m ² /g)	
		N ₂	Kr
U1	Untreated	0.155	0.133
	5.0	0.193	0.139
	56.9	0.292	0.215
D1	54.9	0.303	0.279

$19.2 \times 10^{-20} \text{ m}^2/\text{molecule}$ to $21.4 \times 10^{-20} \text{ m}^2/\text{molecule}$.¹⁹ It has been suggested that the SSA measured using Kr be calibrated against that using N₂, although this is in direct conflict with the reason for using Kr at all. Without such calibration, it is reported that the Kr SSA may be approximately 20% in error.¹⁹ This is approximately the difference between the N₂ and Kr SSA data obtained in this study (Table III). Determining SSA using Kr is further complicated by its very slow adsorption-desorption kinetics. However, both gases indicated similar trends, and the differences were relatively small on an absolute scale. Thus, it is concluded that the BET data obtained using N₂ can be used to draw general conclusions.

Calculation of SSA_T requires knowledge of the area occupied by each Tergitol molecule at monolayer coverage [eq. (4)]. Gum and Goddard²⁰ calculated the area occupied by one Tergitol molecule based on the geometric SSA of their polyester fibers and the amount of Tergitol adsorbed at equilibrium using the equation

$$A = \frac{\text{SSA}_G \text{ MW}}{XN_A} \quad (5)$$

where SSA_G of the fibers used by Gum and Goddard was equal to $0.14 \text{ m}^2/\text{g}$ and the other variables are as defined in the Experimental section. Using this equation, Gum and Goddard found $A = 63 \times 10^{-20} \text{ m}^2/\text{molecule}$, which is close to the area that they calculated using the Gibbs equation ($59 \times 10^{-20} \text{ m}^2/\text{molecule}$). The implication is that the Tergitol molecule is adsorbed onto the fiber surface in an end-to-end configuration.

However, when A was calculated using eq. (5) and the SSA_G of the untreated fibers in this study, the mean was $43.5 \times 10^{-20} \text{ m}^2/\text{molecule}$ (Table IV). Additionally, if the BET data were taken as the true SSA of the fibers, the area actually occupied by each adsorbed Tergitol molecule can be calculated by substituting SSA_B for SSA_G in eq. (5):

$$A' = \frac{\text{SSA}_B \text{ MW}}{XN_A} \quad (6)$$

where A' is the area in $\text{m}^2/\text{molecule}$ occupied by Tergitol based on SSA_B data, and the other variables are as previously defined. The mean A' (Table IV) is seen to be $44.3 \times 10^{-20} \text{ m}^2/\text{molecule}$, which nearly equals that obtained by applying eq. (5) to the SSA_G

Table IV Area Occupied by Tergitol Molecule, Calculated Using SSA_G or SSA_B Data

Sample	Weight Loss (%)	A ^a (m ² /Molecule × 10 ²⁰)	A' ^b (m ² /Molecule × 10 ²⁰)
U1	Untreated	47.9	79.4
	5.0		45.9
	33.5		52.5
	56.9		47.6
U2	Untreated	43.8	57.1
	5.9		39.9
	30.1		28.6
	53.8		41.5
D1	Untreated	42.4	43.5
	6.0		42.3
	28.7		44.0
	54.9		49.4
D2	Untreated	40.0	37.6
	5.1		36.2
	32.8		31.4
	51.1		32.3
Mean		43.5	44.3
Standard error		1.66	3.03

^a Calculated using eq. (5).

^b Calculated using eq. (6).

of the untreated fibers. Thus, the SSA_T data in Table II were calculated using $A = 43.9 \times 10^{-20} \text{ m}^2/\text{molecule}$ (the mean of 43.5×10^{-20} and $44.3 \times 10^{-20} \text{ m}^2/\text{molecule}$).

The validity of using a value of $43.9 \times 10^{-20} \text{ m}^2/\text{molecule}$ for the area of a Tergitol molecule should be addressed. The $43.9 \times 10^{-20} \text{ m}^2/\text{molecule}$ is roughly twice the $20.5 \times 10^{-20} \text{ m}^2/\text{molecule}$, the cross-sectional area of typical surfactants.¹⁵ The factor of 2 difference could be due to the Tergitol NP-10 being branched, as indicated by the manufacturer¹⁷ and typical of polyoxyethylene alkylphenol surfactants.²¹ Thus, it is hypothesized that in this work the Tergitol molecule did not adsorb in an end-to-end monolayer configuration but, rather, in a vertically oriented monolayer. These results concur with the expected behavior of a nonionic surfactant with a nonpolar adsorbent, such as PET. The Tergitol molecule is in an end-to-end configuration when the concentration of surfactant in solution is low. As the concentration increases, the hydrophilic head of the Tergitol molecule is easily displaced due to the hydrophobicity of the PET surface. As the critical micelle concentration is approached, the Tergitol molecules aggregate, resulting in a large increase in adsorption. The final adsorption state is with the Tergitol molecules oriented vertically or in a hemimicelle configuration.²²

Further evidence of the vertical as opposed to parallel orientation of the Tergitol molecule is given

by the adsorption isotherm of Tergitol on untreated U2 fibers (Fig. 1). It is clear that the adsorption does not take the shape of a normal one-step Langmuir isotherm as reported by Gum and Goddard.²⁰ Rather, the adsorption is multistep, corresponding to changes in orientation of the Tergitol molecule with respect to the fiber surface. The expected changes in orientation at each step, as described by Clunie and Ingram,²² are from parallel to parallel with heads displaced to vertical.

As hydrolysis proceeds, carboxyl and hydroxyl groups appear on the fiber surface, and it becomes relatively hydrophilic.^{23,24} However, this did not appear to markedly change the adsorption of the Tergitol molecules as indicated by a comparison of SSA_B and SSA_T values in Table II.

Effect of Hydrolysis on SSA

It is likely that SSA_G is conservative even for the untreated fibers due to deviations from the assumed circular geometry to which the BET and Tergitol methods are sensitive. As the samples were hydrolyzed, SSA generally increased with increasing weight loss, regardless of the method determining SSA (Table II). For SSA_G , this is as expected since the diameter decreases and the density remains constant with weight loss,²⁵ decreasing the linear density and increasing SSA due to its definition. The BET and Tergitol methods generally resulted

Table V Percent Increase in SSA per Percent Weight Loss of Hydrolyzed Samples over Untreated Samples

Sample	SSA Method	Percent Increase in SSA/Percent Weight Loss		
		Approximate Weight Loss (%)		
		5	30	55
U1	Geometric	0.86	0.88	0.47
	BET	4.80	1.00	1.55
	Tergitol	13.78	1.75	2.57
U2	Geometric	2.34	0.50	0.98
	BET	6.24	2.14	2.34
	Tergitol	16.05	7.52	3.88
D1	Geometric	0.42	0.59	1.22
	BET	2.48	1.04	1.23
	Tergitol	3.10	1.00	0.87
D2	Geometric	0.61	0.58	0.84
	BET	6.84	1.70	1.76
	Tergitol	7.98	2.67	2.40

in greater SSA values after hydrolysis compared to those of the SSA determined geometrically (Table II). This is probably due to the pitting which contributes to an increase in SSA yet is ignored in diameter measurements but not in gas or surfactant adsorption measurements.

When the data in Table II are calculated as percent increase in SSA per percent weight loss of the hydrolyzed samples over the untreated samples (Table V), it is apparent that for each sample the increase in SSA_B and SSA_T is greatest at the initial weight loss. Thus, the initial onset of pitting appears to be particularly significant in increasing SSA. As weight loss continues, pits become larger and more numerous,^{2,25} but the relative changes in SSA are not as great as when the smooth, round untreated fiber first incurs pitting.

Effects of Drawing and Spinning Speed on SSA

Regardless of the method used to measure SSA, drawing the untreated fibers resulted in greater SSA, while increasing the spinning speed had little effect (Table II). For the hydrolyzed samples, the difference between SSA_G and SSA_B or SSA_T of the undrawn fibers was generally greater than for the drawn fibers (Table VI). Since the SSA of the untreated drawn fibers was greater than that of the untreated undrawn fibers (Table II), it appears that once hydrolysis and pitting begin, pits, as reflected by weight loss, will have a relatively smaller effect on fibers of initially greater SSA.

The percent increase in SSA per percent weight loss over the untreated values was generally greater at the higher spinning speed (Table V). In general, increasing the spinning speed appeared to have a

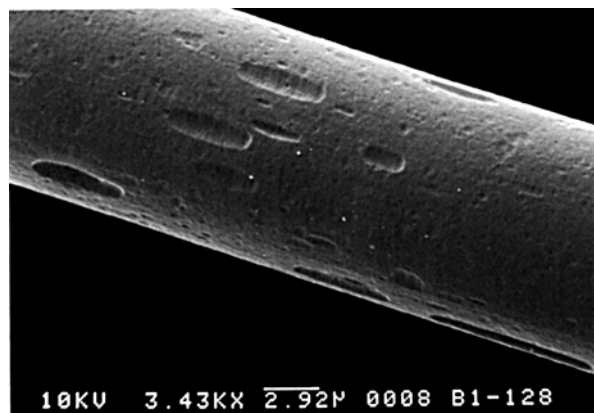


Figure 2 Scanning electron micrograph of PET fiber D1 hydrolyzed in aqueous NaOH to a weight loss of 44.2%.

larger effect on the SSA when measured using the BET or Tergitol methods as opposed to the geometric method. Thus, when pitting is considered, at a given weight loss, pits are contributing an increasingly greater proportion of the surface area of hydrolyzed fibers as spinning speed increases. A possible explanation might be the following: The NaOH preferentially attacks amorphous, unoriented regions such as those surrounding TiO_2 particles, forming pits there. This occurs to some extent at both spinning speeds. Once the pitting on the fibers spun at the slower speed has been initiated, it proceeds easily due to the low orientation and crystallinity. The pits become larger, while the unpitted surface is relatively smooth (Fig. 2). As spinning speed increases, orientation and crystallinity increase somewhat.²⁵ Pitting is initiated because of the presence of TiO_2 , but it is relatively more difficult

Table VI Increase in SSA_B or SSA_T over SSA_G

Sample	SSA Method	Increase in SSA_B or SSA_T over SSA_G (%)			
		Approximate Weight Loss (%)			
		Untreated	5	30	55
U1	BET	34.8	60.8	38.9	100.0
	Tergitol	-7.8	49.2	12.8	78.8
U2	BET	33.3	79.3	90.8	97.1
	Tergitol	0.0	91.4	184.0	102.3
D1	BET	12.4	26.1	25.0	12.6
	Tergitol	9.9	27.3	21.3	-3.1
D2	BET	5.5	38.1	38.1	40.3
	Tergitol	19.0	62.5	87.6	85.8

for the pits to increase in size due to the greater orientation and crystallinity. Therefore, hydrolysis of the higher-speed spun fibers results in a surface with smaller pits and more surface roughening (Fig. 3). The increased surface roughening is believed to be responsible for the greater increase in SSA of the hydrolyzed fibers spun at the higher speed.

Kinetics

Hydrolysis rate equations have been derived in terms of weight loss, hydrolysis time, concentration of the hydroxyl ion, and surface area.^{5,14} Kallay et al.,¹⁴ assuming that hydrolysis occurred at the PET fiber surface, presented the following rate equation:

$$\frac{dn}{dt} = -kAc^h \quad (7)$$

where n is the amount of undissolved PET; t , the time; k , the reaction constant; c , the concentration of the reaction solution; and h , the reaction order. They found that their data were best represented by a first-order reaction.

Others, assuming that the reaction occurs at the surface of cylindrical fibers of constant density and that the fibers remain cylindrical during hydrolysis, have proposed relations between the initial fiber radius and rate of weight loss²⁶ or between the initial and hydrolyzed fiber radii and fractional weight loss.² Their relations hold for a given concentration of reagent solution and an excess of the reagent.

In all cases, workers have assumed that the fiber surface is perfectly smooth and the fiber is cylindrical in shape. Generally, the correlations that they have obtained between theoretical values and em-

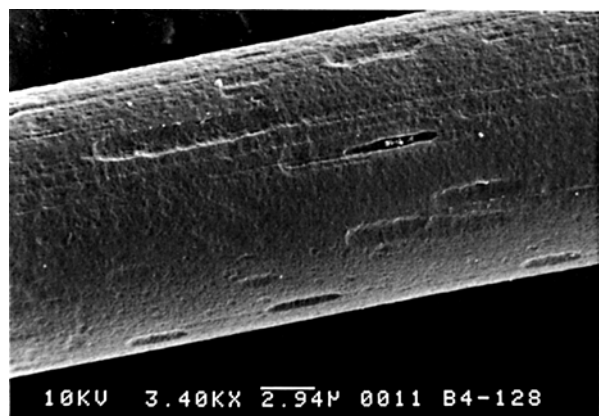


Figure 3 Scanning electron micrograph of PET fiber D2 hydrolyzed in aqueous NaOH to a weight loss of 34.3%.

pirical data have been excellent. As we have seen that the fibers become increasingly pitted and the discrepancy between geometrical SSA and BET or Tergitol SSA increases on hydrolysis, it appears that the reaction of PET and aqueous NaOH is more complex than initially assumed. It seems that the portion of SSA contributed by the pits is increasing more rapidly, due to their depths increasing, than that of the nonpitted part of the fiber. Thus, the fiber diameter decreases relatively slowly in comparison to the weight loss.

CONCLUSIONS

Differences exist among geometric, gas adsorption, and surfactant adsorption methods of measuring the SSA of untreated and hydrolyzed high-speed spun PET fibers. The gas and surfactant adsorption methods result in the same general trends. The SSA of hydrolyzed fibers measured using gas or surfactant adsorption is greater than SSA measurements based on fiber diameter due to surface pitting. The spinning speed and drawing affect the increase in SSA per percent weight loss differently.

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