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BASE HYDROLYSIS OF POLY(ETHYLENE TEREPHTHALATE) IN METHANOLIC AND AQUEOUS SOLUTIONS

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ABSTRACT

Hydrolysis of poly(ethylene terephthalate) fibers (intrinsic viscosity: 0.819 dL/g) using methanolic sodium methoxide was compared to that using aqueous sodium hydroxide. Weight and tenacity loss occurred more rapidly with methanolic NaOCH₃. After the methanolic NaOCH₃ treatment, the surface appeared far rougher, much of which was due to low molecular weight material present on the fibers. Intrinsic viscosity measurements indicated virtually no difference between the two treatments in the small amount of chain cleavage obtained at a given weight loss. Fiber density increased after the reaction with methanolic NaOCH₃, probably due to the presence of the methyl ester end groups formed during the ester interchange reaction, while fiber density was essentially unaffected by treatment in aqueous NaOH. Density decreased after the methanolic NaOCH₃-treated fiber was hydrolyzed with aqueous NaOH. Thermal analysis revealed a small increase in the melting temperature after methanolic NaOCH₃ treatment. The shoulder present in the melting region of this sample was markedly affected by chloroform extraction of low molecular weight products resulting from the reaction. While hydrolysis using methanolic NaOCH₃ was more severe than that using aqueous NaOH, both reactions appeared to be confined to the fiber surface.

INTRODUCTION

As described in a comprehensive review of the literature [1], it is well established that alkaline hydrolysis of poly(ethylene terephthalate) (PET) fibers using aqueous sodium hydroxide is confined to their surfaces, removing successive layers of the polymer as the reaction progresses. In an investigation by Namboori and Haith [2] of the hydrolysis of PET using various bases in nonaqueous media as well as hydrolysis using aqueous NaOH, it was demonstrated that weight loss was more rapid with methanolic sodium methoxide than with aqueous NaOH. Since there was no change in the specific viscosity of the samples treated in methanolic NaOCH₃ and because the fibers retained their circular cross section, it was concluded that the reaction was confined predominantly to the fiber surface. However, the tenacity of their sample decreased with increasing weight loss; at approximately 15% weight loss, it had already decreased by 28%. It might be expected that a decrease in tenacity would be reflected in a reduction in degree of polymerization. Unfortunately, neither the viscosity nor the tenacity of the aqueous NaOH-treated fibers was measured for comparison. Yet in a previous study by Namboori [3], the tenacity of aqueous NaOH-treated PET fibers decreased by only 8.5% after a weight loss of 27%. The much larger decrease in tenacity after the methanolic NaOCH₃ treatment may be inconsistent with the conclusion that the reaction occurred primarily at the fiber surface, particularly in light of the fact that the tenacity of the aqueous NaOH-treated samples was not considered.

When PET is hydrolyzed with methanolic NaOCH₃, a base-catalyzed ester interchange reaction occurs. Ester interchange reactions are of interest for PET tire cord yarn. A large amount of heat is generated in tire cord during use. Thus it is necessary that the properties of the fibers remain unaffected by heat. PET thermally degrades via hydrolysis [4], the rate of which increases as the number of carboxylic acid end groups increases due to the hydrolysis itself; the reaction is said to be autocatalytic [5]. Watanabe and Takata [6] found a relationship between the number of carboxylic acid end groups in the starting PET tire cord and its strength retention after being embedded in rubber and heat treated. They attributed strength loss to hydrolysis and aminolysis which occurred due to the presence of moisture and amines in the rubber. It has been claimed [7, 8] that PET with reduced carboxylic end group content is more resistant to high-temperature hydrolysis and less susceptible to thermal damage after treating the PET with methylstearilydiammonium chloride and *N,N'*-bis(1,6-diisopropylphenyl) carbodiimide [7], and with various ethyleneurea compounds [8].

The objective of the present study was to further analyze the hydrolysis of PET with methanolic NaOCH₃ compared to that with aqueous NaOH, specifically in terms of the location of attack and the effects on tensile and thermal properties.

EXPERIMENTAL

Materials

Bright PET yarn was provided by Hoechst Celanese, Charlotte, North Carolina. All chemicals used were of reagent grade.

Procedures

Alkaline Hydrolysis. All hydrolyses were carried out in sealed flasks at 21°C ($\pm 2^\circ\text{C}$) with mild mechanical agitation. Yarn samples were treated in 2.5 M aqueous NaOH and 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. Other yarn samples were treated in 0.22 M methanolic NaOCH₃ solution in a 20 ratio of weight/volume (g/L). In this instance a control sample was prepared by treating the yarn in methanol for 16 hours. The hydrolysis termination and sample rinsing were performed in the manner described previously [9]. After drying, portions of the products were Soxhlet extracted with chloroform for 8 hours and then allowed to come to constant weight at 21°C and 65% relative humidity.

Scanning Electron Microscopy. Samples were mounted on standard specimen stubs with silver paint and then coated with gold. Photomicrographs were taken using an International Scientific Instruments Model DS 130 Microscope operating in the secondary mode at an accelerating voltage of 10 kV.

Fiber Tensile Strength. Breaking load was measured using a table model Instron Universal Testing Machine with a 2.54-cm gauge length at 2 cm/min constant rate of elongation at 65% relative humidity and 21°C. Results are the average of 25 tests.

Tex. Three 1 meter lengths of the untreated yarn were conditioned at 21°C and 65% relative humidity and weighed. 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. Tex of the treated fibers was calculated using percentage weight loss.

Intrinsic Viscosity. Relative viscosities were measured in a 4% (w/v) solution of phenol/1,1,2,2-tetrachloroethane (3/2 v/v) at 25°C ($\pm 0.1^\circ\text{C}$). Intrinsic viscosities were calculated using a one-point method according to Billmeyer's Eq. (3) [10]:

$$[\eta] = 0.25 \frac{\eta_{sp}}{c} + 0.75 \frac{\ln \eta_r}{c}$$

where $[\eta]$, η_{sp} , η_r , and c are intrinsic viscosity, specific viscosity, relative viscosity, and solution concentration, respectively.

Density. Measurements were made at 21°C ($\pm 2^\circ\text{C}$) in a density gradient column prepared with carbon tetrachloride and *n*-heptane.

Differential Thermal Analysis. Measurements were run using approximately 3 mg of sample in a nitrogen atmosphere at a heating rate of 10°C/min on a Mettler TA 2000M Thermal Analysis System.

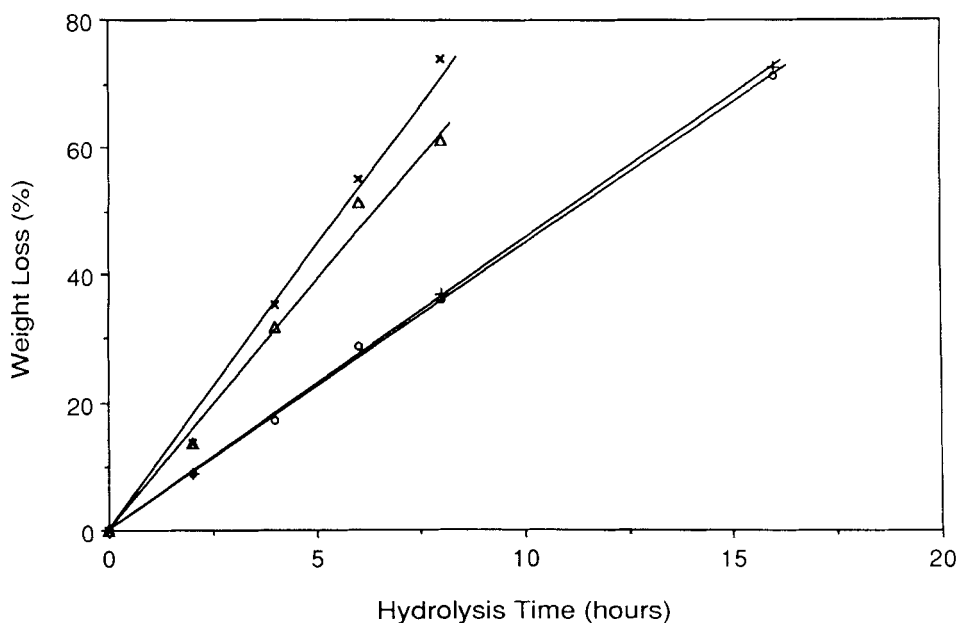


FIG. 1. Weight loss/hydrolysis time relations for PET: (O) aqueous NaOH hydrolysis, (+) aqueous NaOH after CHCl_3 extraction, (Δ) methanolic NaOCH_3 hydrolysis, (\times) methanolic NaOCH_3 after CHCl_3 extraction.

RESULTS AND DISCUSSION

Weight Loss

After treatment in methanolic NaOCH_3 , debris was visible on most of the samples as will be described in the Scanning Electron Microscopy Section. The debris was presumed to be low molecular weight material which had not dissolved in the reagent solution or which had precipitated during the rinsing part of the hydrolysis procedure. Therefore, the samples were extracted with CHCl_3 to remove products which would distort weight loss and intrinsic viscosity data. As the hydrolysis proceeded, progressively higher weight losses after extraction were observed on the methanolic NaOCH_3 samples, indicating increased production of low molecular weight material with time. The weight loss/hydrolysis time relation (Fig. 1) remained linear nonetheless. Although there was no visible detritus on the aqueous NaOH-treated samples, several of these samples were also extracted. Extraction had virtually no effect on the weight loss of the aqueous NaOH-treated samples; nearly all the low molecular weight material resulting from this treatment must have gone into solution and been rinsed away. Similarly, Collins and Zeronian [11] found an increase in weight loss after extraction of PET hydrolyzed in methanolic NaOH but virtually no change in weight after extraction of aqueous NaOH hydrolyzed PET products.

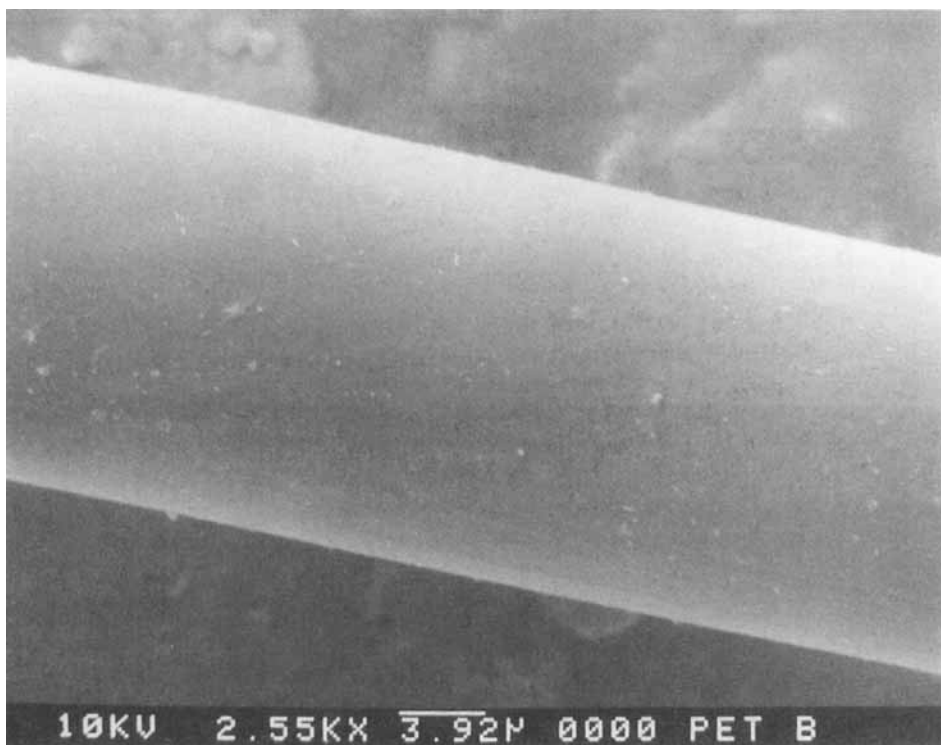


FIG. 2. SEM of untreated PET.

Scanning Electron Microscopy

Compared to the smooth untreated fibers (Fig. 2), PET treated with aqueous NaOH exhibited a slightly roughened surface before and after extraction in CHCl_3 (Fig. 3). Treatment in methanolic NaOCH_3 resulted in a great deal more roughening and a large amount of irregularly shaped debris on the fiber surface (Fig. 4A). Most of this debris was removed by extraction, although the surface remained rough (Fig. 4B). The surface appearance is another indication of the greater severity of the methanolic NaOCH_3 attack compared to the aqueous NaOH reaction. The retention of the circular cross-sectional shape after both treatments might indicate that hydrolysis using methanolic NaOCH_3 occurs primarily at the fiber surface.

Fiber Tensile Properties

Tenacities were determined before extraction for the aqueous NaOH-treated samples and after extraction for the methanolic NaOCH_3 -treated samples, although the methanolic NaOCH_3 -treated fibers had essentially equal breaking loads before and after extraction. The low molecular weight species present before extraction resulted in a greater tex value than after extraction since tex, by definition, is the

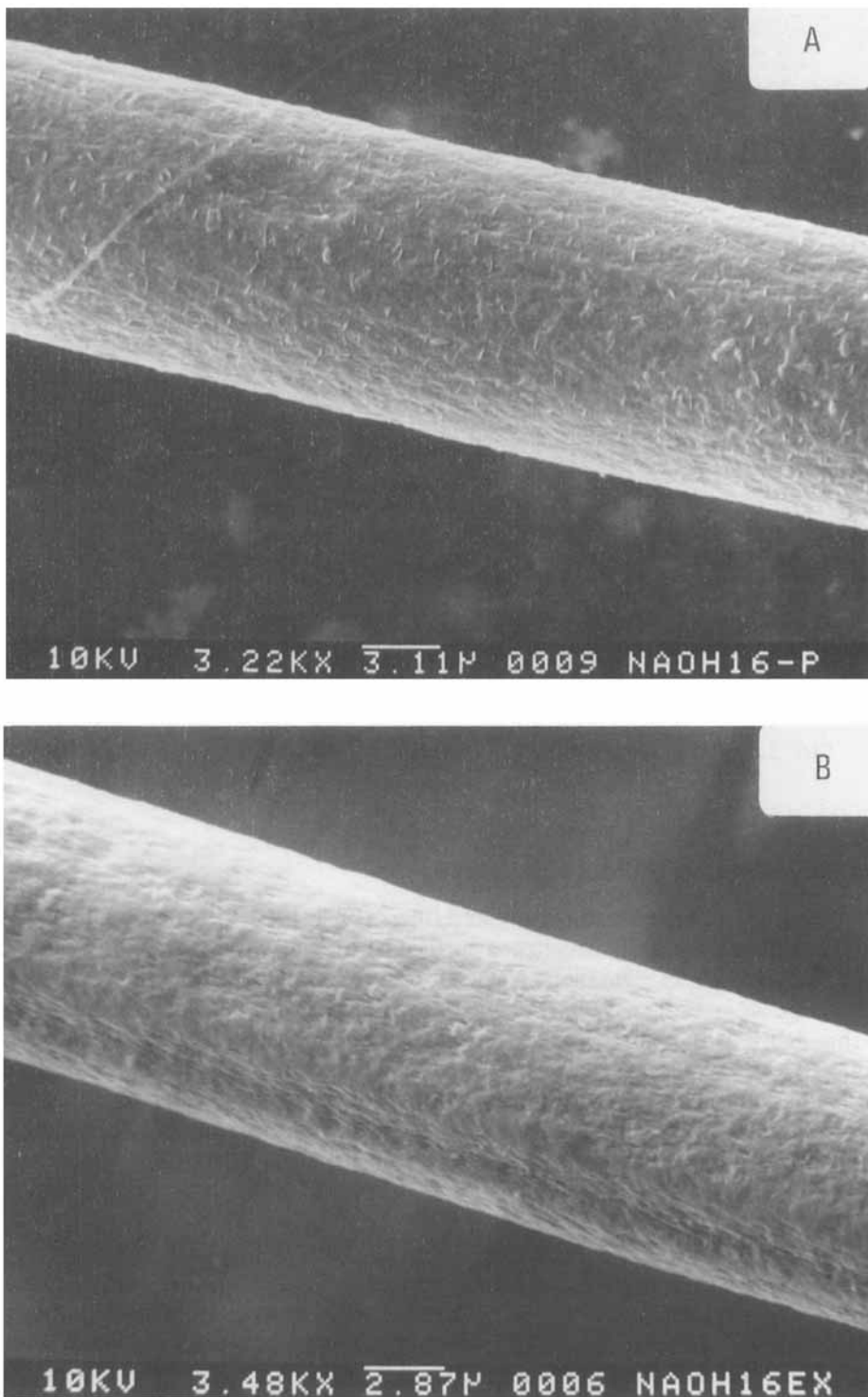


FIG. 3. SEM of PET hydrolyzed in aqueous NaOH for 16 hours: (A) before extraction, (B) after extraction.

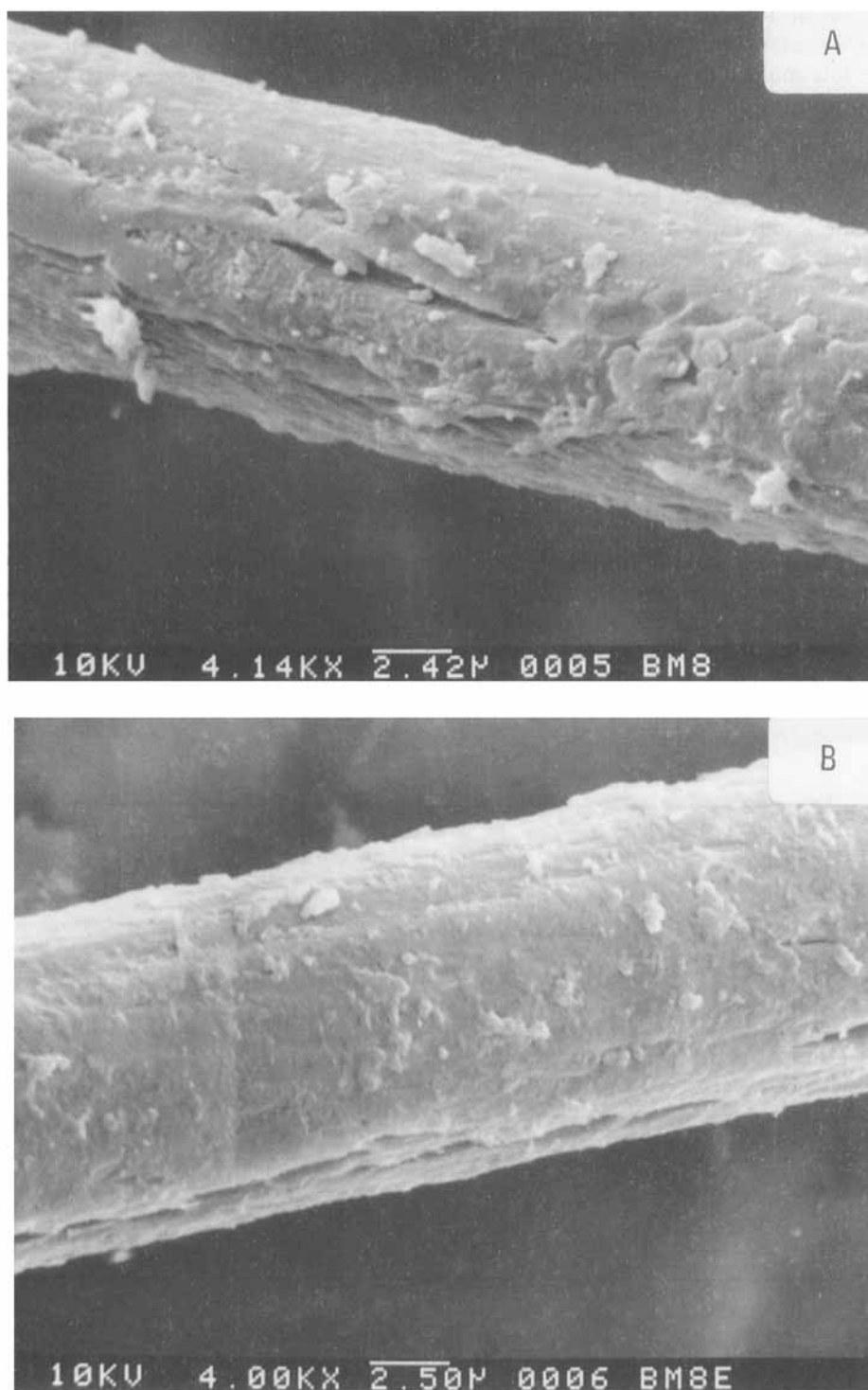


FIG. 4. SEM of PET hydrolyzed in methanolic NaOCH_3 for 8 hours: (A) before extraction, (B) after extraction.

weight of 1000 m length of the product. As a consequence, this greater tex value made the tenacity before extraction less than the tenacity after extraction. However, the low molecular weight material removed by extraction is considered to be non-load bearing since the breaking load of the fiber was unaffected. Thus the tenacity is best measured after extraction in the case of the methanolic NaOCH_3 -treated fibers.

The tenacity of both sets of samples decreased with increasing hydrolysis time (Table 2 and Fig. 5). A 23.9% drop in tenacity was observed for the methanolic NaOCH_3 -treated fibers which had suffered a weight loss of 13.6% while only a 9.4% tenacity decrease was obtained for the fibers treated in aqueous NaOH to a weight loss of 17.2%. Thus the fall in tenacity initially was greater for the products treated in methanolic NaOCH_3 . When a weight loss of approximately 70% was achieved, the tenacities of products treated with either reagent were similar. These results support a difference in the severity of attack depending on the reagent used for hydrolysis.

Intrinsic Viscosity

As a measure of the degree of polymerization (DP), intrinsic viscosity (IV) measurements were made on aqueous NaOH and methanolic NaOCH_3 -treated samples of similar weight loss (Tables 1 and 2). The IV decreased slightly with weight loss, but to the same extent for both treatments, indicating no difference in the degree of chain cleavage between the two treatments. Normally a loss in strength achieved by hydrolysis would result in a significant drop in the DP or IV of the

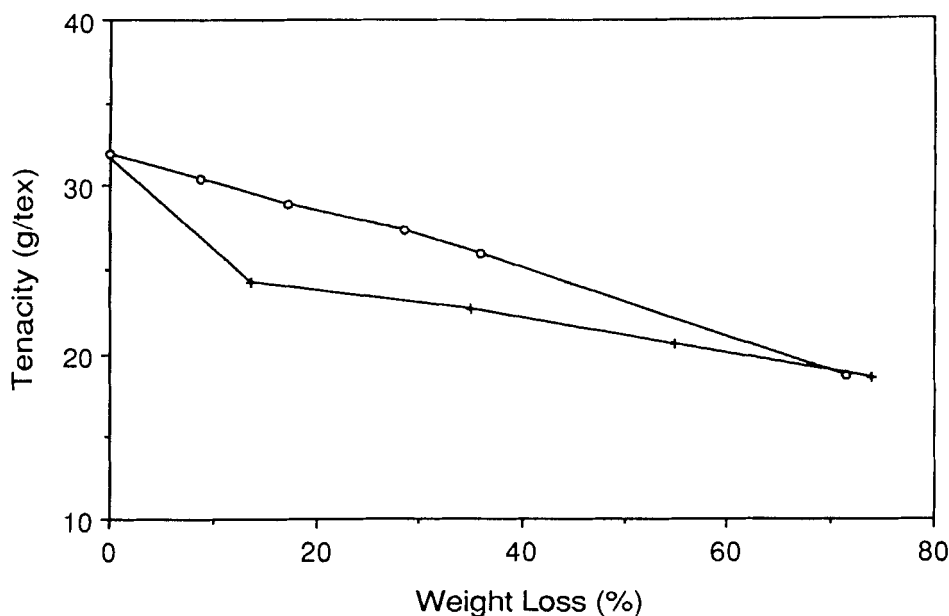


FIG. 5. Effect of weight loss on tenacity of hydrolyzed PET: (○) aqueous NaOH (hydrolyzed fiber not extracted), (+) methanolic NaOCH_3 (hydrolyzed fiber extracted).

TABLE 1. Weight Loss of Hydrolyzed and Extracted PET Samples

Hydrolysis time, hours	Total weight loss, %	
	Before extraction	After extraction
2.5 M Aqueous NaOH:		
0	0.0	0.0
2	8.8	8.9
4	17.2	—
6	28.6	—
8	36.1	36.9
16	71.5	72.7
0.22 M Methanolic NaOCH ₃ :		
Control	-0.3	-0.1
2	13.6	13.6
4	31.7	35.1
6	51.2	54.9
8	61.1	74.0

TABLE 2. Selected Properties of Hydrolyzed PET Samples^a

Hydrolysis time, hours	Tenacity, ^b g/tex	[η], ^c dL/g	Density, ^d g/cm ³
2.5 M Aqueous NaOH			
0	31.9 (0.5)	0.819	1.372
2	30.4 (0.4)	—	—
4	28.9 (0.6)	—	—
6	27.3 (0.4)	—	—
8	25.9 (0.5)	0.822	1.371
16	18.7 (0.8)	0.800	1.370
0.22 M Methanolic NaOCH ₃			
Control	31.8 (0.5)	0.853	1.370
2	24.2 (0.4)	—	1.376
4	22.7 (0.8)	0.813	1.378
6	20.5 (0.3)	—	1.381
8	18.6 (0.4)	0.799	1.387

^aStandard error in parentheses.

^bTenacity of fibers treated in aqueous NaOH was measured before extraction in CHCl₃, and those treated in methanolic NaOCH₃ were measured after extraction.

^cAll intrinsic viscosity measurements were made after extraction in CHCl₃.

^dAll density measurements were made before extraction in CHCl₃.

product. In light of this, the lower tenacity of the methanolic NaOCH_3 -treated fibers when compared to the aqueous NaOH -treated samples is probably due to the greater surface roughness of the former samples. Rupture initiates at the weakest region in a material which is likely to be at the type of the deep craters present on the surface of the methanolic NaOCH_3 -treated fibers (Fig. 4).

Density

While the density of the aqueous NaOH -treated samples remained essentially constant, the density of the methanolic NaOCH_3 -treated samples increased with hydrolysis time (Table 2). The initial deduction from the density of the two sets of samples might be that there is a difference in the mechanisms of the two treatments. However, the IV and tensile data indicate that the methanolic NaOCH_3 does not penetrate the fiber to a significant extent. Therefore the increase in density is most likely due to a more dense surface. It is feasible that the reaction with methanolic NaOCH_3 occurs at the periphery, rendering it less porous (and, therefore, more dense) possibly due in part to the relatively large methyl ester groups occupying former voids and/or to the presence of the methyl ester groups rendering the surface more swellable in methanol, thus closing voids.

To determine if the surface was made more dense by treatment in methanolic NaOCH_3 , surface layers were removed by subsequent hydrolysis in aqueous NaOH , and the density was remeasured (Table 3). After an additional weight loss of 8.0% due to aqueous NaOH hydrolysis, the density of the sample treated for 2 hours in methanolic NaOCH_3 decreased from 1.376 to 1.374 g/cm^3 . When the weight loss due to the subsequent aqueous NaOH hydrolysis reached 14.2%, the density had decreased to 1.373 g/cm^3 , which was close to that of the control sample. Consider-

TABLE 3. Weight Loss and Density of Samples Treated in Methanolic NaOCH_3 and Subsequently Hydrolyzed in Aqueous NaOH

Sample	Weight loss after NaOH hydrolysis, % ^a	Total weight loss, % ^b	Density, g/cm^3
Control	—	—	1.372
NaOCH_3 , 2 hours	—	13.6	1.376
NaOCH_3 , 2 hours, and NaOH , 2 hours	8.0	20.5	1.374
NaOCH_3 , 2 hours, and NaOH , 3 hours	14.2	25.9	1.373
NaOCH_3 , 8 hours	—	61.1	1.387
NaOCH_3 , 8 hours, and NaOH , 3 hours	29.1	72.4	1.381
NaOCH_3 , 8 hours, and NaOH , 6 hours	67.4	87.3	1.380

^aBased on weight after treatment in methanolic NaOCH_3 .

^bBased on weight of the starting sample.

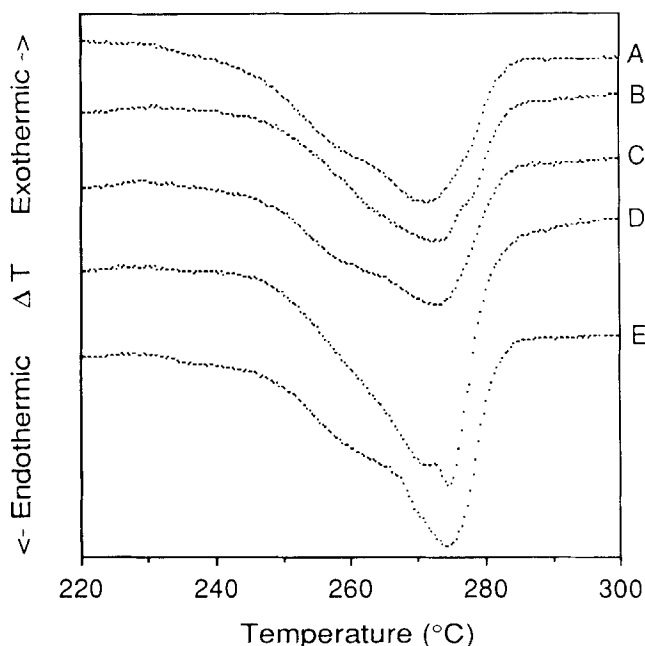


FIG. 6. Melting endotherms of various samples: (A) untreated, (B) methanol control, (C) aqueous NaOH 16 hours treatment, (D) methanolic NaOCH₃ 8 hours treatment, (E) methanolic NaOCH₃ 8 hours treatment and then extracted.

ing the sample treated for 8 hours in methanolic NaOCH₃, the density of which increased to 1.387 g/cm³, aqueous NaOH hydrolysis to an additional weight loss of 67.4% decreased the density to 1.380 g/cm³. These data indicate that treatment in methanolic NaOCH₃ renders the surface layers more dense than the remainder of the fiber.

Differential Thermal Analysis

The melting behavior of PET was unaffected by treatment in methanol alone or aqueous NaOH (Fig. 6). After hydrolysis with methanolic NaOCH₃, the melting temperature increased slightly and the shape of the melting peak changed appreciably. The sample treated for 8 hours in methanolic NaOCH₃ before extraction showed a well-defined shoulder on the low temperature side of the melting peak, which may be indicative of two crystal types present in these fibers. It is speculated that a different, lower temperature melting crystal type is formed at the fiber periphery either in the form of oligomers or material which is rich in methyl ester groups as discussed in the previous section of this paper. After extraction, the position and shape of the shoulder shifted, yet it remained better defined than in the case of the aqueous NaOH-treated samples. Again, two crystal types may be present, possibly due to the interaction of the fibers with CHCl₃, the removal of oligomers, or a combination of these two effects.

Despite the differences in the shapes of the melting peaks, the methyl ester groups formed during the methanolic NaOCH_3 hydrolysis did not have a significant effect on the thermal degradation endotherm and therefore is not presented in Fig. 6. Neither the onset of degradation nor the position of the zenith was affected by any of the treatments given to the PET. Since the reaction with methanolic NaOCH_3 is confined to the fiber periphery, it is likely that the number of methyl ester groups formed during the ester interchange is insufficient to markedly affect the thermal degradation of PET. It is also feasible that the degradation conditions, namely absence of oxygen and moisture, are not conducive to differentiating differences in the fibers subjected to the two hydrolyses.

CONCLUSIONS

Hydrolysis of PET fibers using aqueous NaOH differs from that using methanolic NaOCH_3 in terms of the severity of attack at the surface and the effect on the fine structure. Whereas aqueous NaOH can be used to remove layers without affecting the remaining fiber, the results of this study suggest that methanolic NaOCH_3 leaves the fiber with a roughened exterior of increased density which may be due to a high concentration of methyl ester groups in this region. Also, the melting behavior is affected somewhat differently by the two reactions.

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