

Further Studies on the Moisture-Related Properties of Hydrolyzed Poly(ethylene Terephthalate)

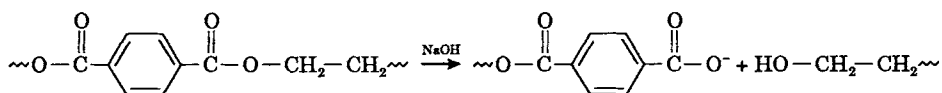
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Synopsis

Contact angle measurements with water indicate that the hydrophilicity of poly(ethylene terephthalate) (PET) film decreased in the order PET treated with aqueous sodium hydroxide > untreated PET > PET treated with methanolic sodium methoxide. When the sodium-methoxide-treated polyester was hydrolyzed with caustic soda, its contact angle fell, indicating that the methyl ester groups formed during the sodium methoxide reaction by a base-catalyzed ester interchange had been the cause of the high contact angles. Thus it appears that carboxyl groups at the surface of hydrolyzed PET play an important role in determining its hydrophilicity. It appears from adsorption experiments that there is a marked increase in the surface area of PET fibers on treatment with aqueous sodium hydroxide. The increase is attributed to the presence of the pits produced by the hydrolysis. It is suggested the higher surface area leads to increased numbers of hydrophilic groups on the fiber surface causing the greater wettability observed in the caustic hydrolyzed samples.

INTRODUCTION

Poly(ethylene terephthalate), or PET, is hydrolyzed with aqueous sodium hydroxide in a topochemical manner.¹



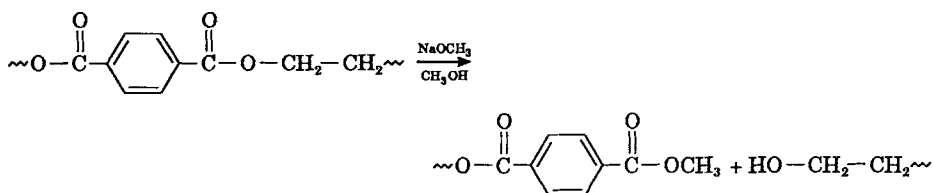
In a previous communication² we suggested that there were at least three factors that may contribute to the hydrophilicity of PET hydrolyzed in this manner, namely, increased surface roughness, possible increase in the number of hydrophilic groups (i.e., hydroxyl and carboxyl groups) on the fiber surface caused by chain scission, and increased accessibility of hydrophilic groups.

Latta³ stated that the hydrophilic properties of caustic-treated PET arose from the presence of hydroxyl and carboxyl groups on the fiber surface and that the more important ones appeared to be the former. He based this on a study in which caustic-treated PET had been acetylated with acetic anhydride. The product was tested for wettability, wicking, and soil release and was found to have reverted to performance that was at best as poor as the original non-caustic-treated fabric in each test. Latta further stated that it was unclear whether the hydroxyl groups were more important because their interaction with water was more significant than that of the carboxyl groups or simply

that they were present in much greater numbers. However, the molar water contents of a hydroxyl group and a carboxyl group do not differ greatly until the relative humidity (RH) of the ambient atmosphere increases above 70%.⁴ At 100% RH the molar water contents of these groups are 2 and 1.3, respectively. While Krevelen⁴ does not give values for carboxylate ions at higher RHs, at 70% RH the molar water content is already 4.2. Also other work^{1,5} indicates that there is not a large discrepancy between the number of hydroxyl and carboxyl groups in PET hydrolyzed with caustic soda.

To further analyze the hydrophilicity of caustic-treated PET, we have now determined the effect of blocking the carboxyl groups on the wettability of the hydrolyzed product and also the change in surface area of the fibers after the treatment.

To block the carboxyl groups, the polymer was hydrolyzed with a methanolic solution of sodium methoxide. In this reaction a base-catalyzed ester interchange occurs.⁶



It appears from the work of Gum and Goddard⁷ that Tergitol NP-10, a nonionic surfactant, will form a monolayer on the surface of PET and thus can be used to obtain a measure of surface area.

MATERIALS

The PET substrates consisted of a semi-dull Dacron 56T heat-set filament fabric (Testfabrics, Inc., Middlesex, New Jersey) and 2-mil thick Mylar D film (Polymer Products Division of E. I. DuPont de Nemours). Tergitol NP-10 was obtained from the Chemicals and Plastics Division of Union Carbide Corporation. It is a nonylphenol ethoxylate with, on average, 10 ethylene oxide units.⁷ Reagent grade, Type I water was obtained from a Millipore Milli-Q system.

PROCEDURES

Fabric Cleaning. The fabric was extracted for 3 h in a Soxhlet using trichlorotrifluoroethane as the solvent.

Fabric and Film Hydrolyses. The hydrolyses were carried out with 2.8 *M* aqueous sodium hydroxide at 60°C or with 0.22 *M* sodium methoxide in methanol at 60°C in the manner described previously.² Final washes in all cases were made with reagent grade water.

Adsorption Isotherms. The fabric, cut into 1 × 1 cm pieces, was immersed in a solution of Tergitol NP-10 (2 g sample to 100 g of solution) and shaken for 24 h at 21°C.

Concentrations of solutions, before and after the adsorption experiments, were determined by measuring the UV absorbance at 273 nm⁷ with a Beckman DB-G grating spectrophotometer.

Contact Angles. Measurements were made on the films at 21°C and 65% RH with a Kernco contact meter within 1 min of drop applications. Fifty determinations were made on each sample.

Scanning Electron Microscopy. The procedure has been described previously.⁸

RESULTS AND DISCUSSION

Weight Loss and Contact Angles

The PET film lost weight rapidly when treated with methanolic sodium methoxide (Table I). After a 6-h treatment the sample had become fragile and cockled on drying. Products treated for 3 h or less did not pucker.

The contact angle formed by water on the sodium-methoxide-treated substrates increased progressively with reaction time indicating the polymer surface had become more hydrophobic (Table I). This contrasts with the behavior reported previously when it was noted that the contact angle of water on the same film hydrolyzed with aqueous sodium hydroxide decreased, indicating that the sample had increased in hydrophilicity.² Thus it appears that base-catalyzed ester interchange had occurred when the PET was reacted with sodium methoxide and methyl ester groups had been formed.

To confirm that methyl esters had formed at the ends of the polymer chains after the reaction with sodium methoxide, the treated films were subsequently hydrolyzed with aqueous sodium hydroxide for 20 min at 60°C. Since this reaction occurs topochemically, it was hypothesized that it would remove the methyl groups and render the products more hydrophilic. In fact, this did occur (Table II). It will be observed that with little weight loss the samples became markedly hydrophilic. The contact angles were similar to those expected if the films had been hydrolyzed to equivalent weight loss with aqueous sodium hydroxide without the intervening reaction with methanolic sodium methoxide.

TABLE I
Weight Loss and Contact Angles of PET Film Treated with a
Methanolic Solution of Sodium Methoxide

Code number	Treatment ^a	Weight loss (%)	Contact angle ^b (deg)
1	None	—	71.2 ± 0.30
2	Methanol/6 h	0.61	70.9 ± 0.30
3	Sodium methoxide/methanol 1 h	13.9	71.7 ± 0.38
4	Sodium methoxide/methanol 2 h	25.9	73.3 ± 0.40
5	Sodium methoxide/methanol 3 h	45.0	74.4 ± 0.45
6	Sodium methoxide/methanol 6 h	83.6	76.6 ± 1.37

^a All treatments at 60°C.

^b Average and standard error.

TABLE II
Weight Loss and Contact Angles of PET Film Treated with a Methanolic Solution of Sodium Methoxide and Then Hydrolyzed with Aqueous Sodium Hydroxide for 20 min at 60°C

Sample code ^a	Weight loss ^b (%)	Contact angle ^c (deg)
1	0.81	69.1 ± 0.26
2	0.99	70.4 ± 0.66
3	2.11	61.2 ± 1.34
4	2.46	59.8 ± 0.82
5	3.12	57.6 ± 1.62

^a Sample treatment given in Table I, which also gives the weight loss suffered and contact angle of the sodium-methoxide-treated products.

^b Induced by hydrolysis with aqueous sodium hydroxide.

^c Average and standard error.

For example, when the same film was hydrolyzed with aqueous sodium hydroxide to weight losses of 14.5, 25.3, and 30.9%, the contact angles of the products were 65, 59.8, and 61.5°, respectively.² Thus it appears that the hydrophilicity of polyester surfaces is markedly affected by the availability of carboxyl groups.

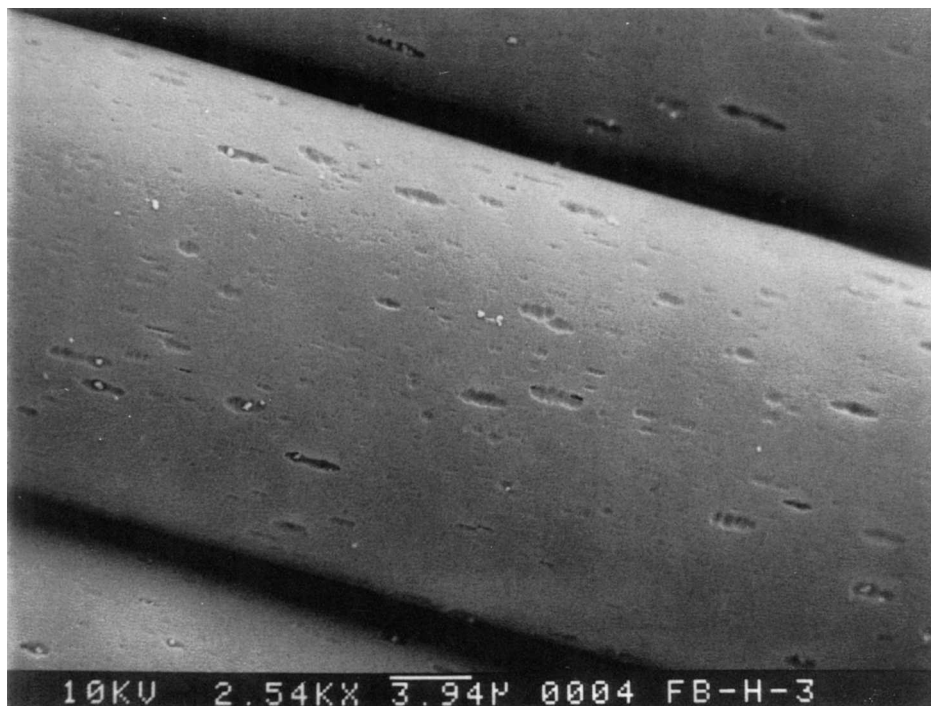


Fig. 1. PET fibers treated for 3 h with an aqueous solution of sodium hydroxide (weight loss = 6.4%).

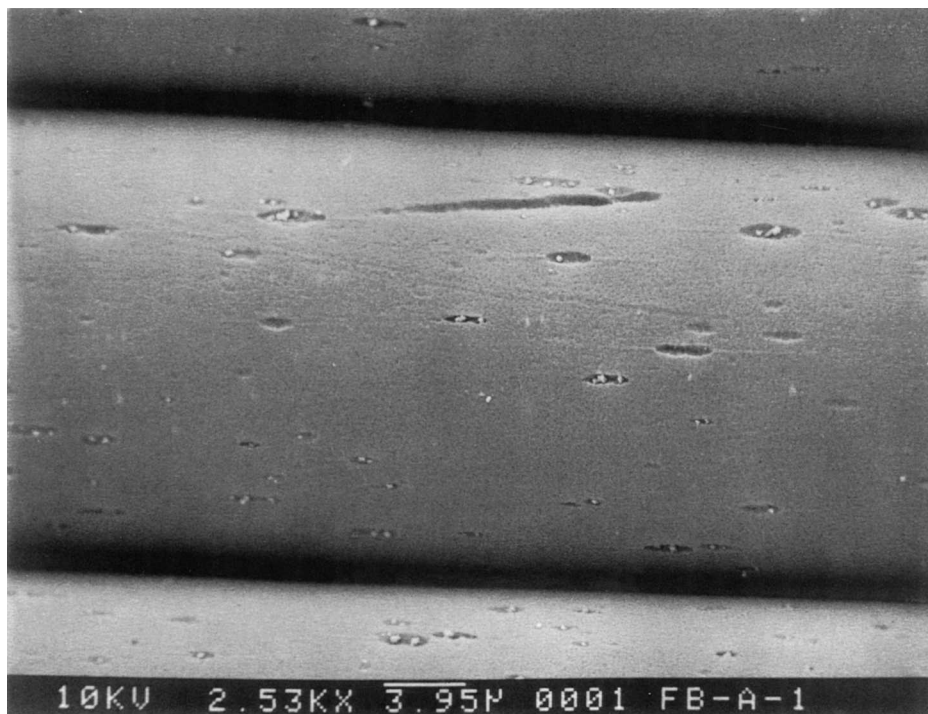


Fig. 2. PET fibers treated for 25 min with a methanolic solution of sodium methoxide (weight loss = 5.8%).

Scanning Electron Microscopy

Fibers treated with the methanolic solution of sodium methoxide had the same pitted surface features as fibers treated with aqueous sodium hydroxide (cf. Figs. 1 and 2). In contrast film treated with methanolic sodium methoxide appeared to have cracks (Fig. 3) rather than the pits observed previously² with aqueous sodium hydroxide hydrolysis. When the sodium-methoxide-treated sample was hydrolyzed with aqueous sodium hydroxide, the surface features of the product (Fig. 4) became similar to those of film hydrolyzed with aqueous sodium hydroxide without the intervening sodium methoxide reaction. Whether the different surface features of the sodium-methoxide-treated and caustic-treated films affected appreciably their contact angles is not known, but it is likely that the presence of the methyl groups on the sodium-methoxide-treated film had the more significant effect.

Adsorption Isotherms

To obtain an indication of the change in surface area of the PET after hydrolysis, adsorption isotherms were obtained of Tergitol surfactant using fibrous PET as the adsorbent. The treated samples had similar weight losses, namely, 6.4% for the caustic-treated and 5.8% for the sodium-methoxide-treated polyester. In all three cases the shape of the adsorption isotherms were similar (Fig. 5). It has been suggested that the limiting amount of this surfactant

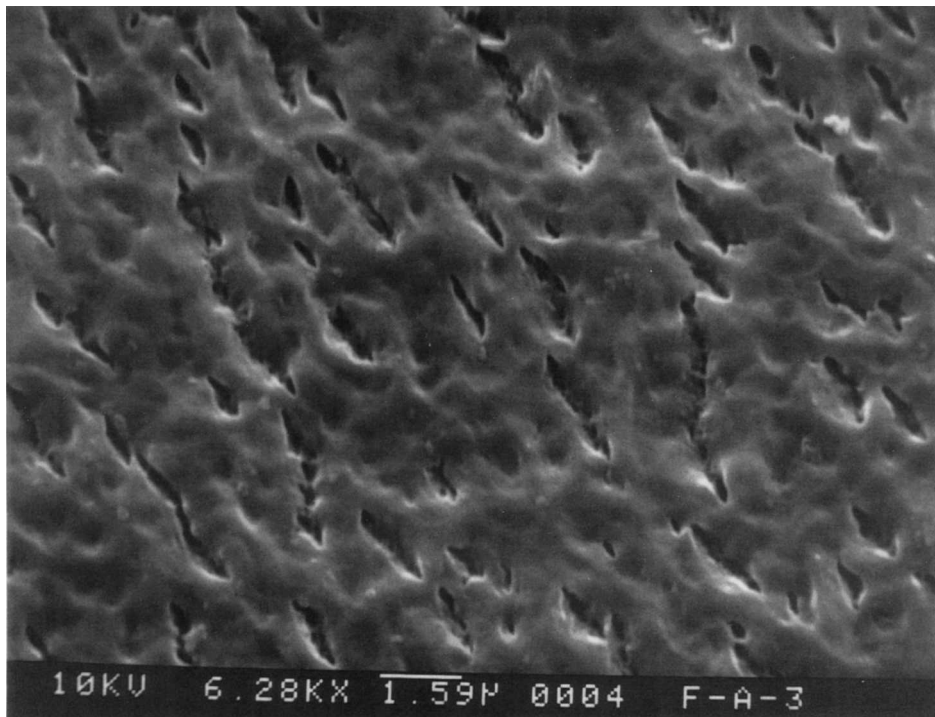


Fig. 3. PET film treated for 3 h with a methanolic solution of sodium methoxide (weight loss = 45%).

corresponds to monolayer formation on the PET substrate.⁷ It appears then that any difference in the functional groups present on the two treated polyester substrates did not markedly affect the amount of surfactant adsorbed. It will be observed also that the limiting amount of surfactant present on the hydrolyzed products is about 1.75 times higher than that of the untreated PET, indicating a large increase in surface area after the treatments. The radius of the fibers, measured microscopically, does not appear to change by more than 5% after comparable weight losses brought about by caustic hydrolysis.⁹ Thus the increased surface area obtained by the hydrolyses is attributed to the surface pitting that occurs during the reaction. The higher surface area could result in the presence of a larger number of hydrophilic groups on the surface of the hydrolyzed samples.

CONCLUSIONS

First, from our contact angle experiments, it appears that the presence of carboxyl groups as well as hydroxyl groups has an important influence on the hydrophilicity of PET surfaces. Second, it can be deduced from the adsorption experiments that the pitting of the PET caused by hydrolysis with aqueous sodium hydroxide leads to a marked increase in surface area. This increase leads to greater accessibility of carboxyl and hydroxyl groups to water and thus

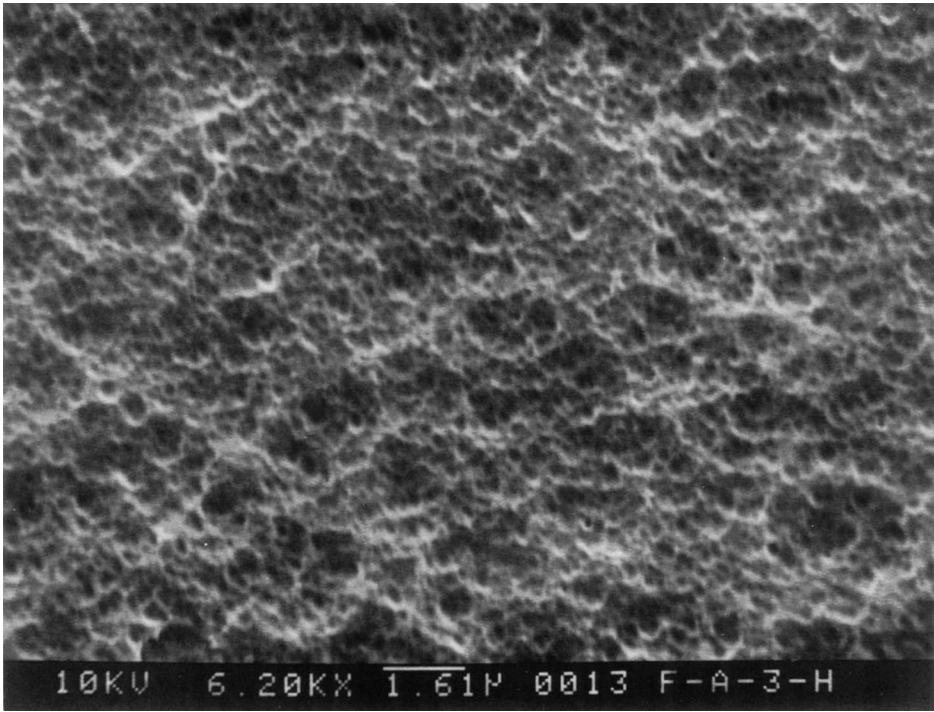


Fig. 4. Sodium-methoxide-treated PET film hydrolyzed for 20 min with aqueous sodium hydroxide (weight loss = 3.12%).

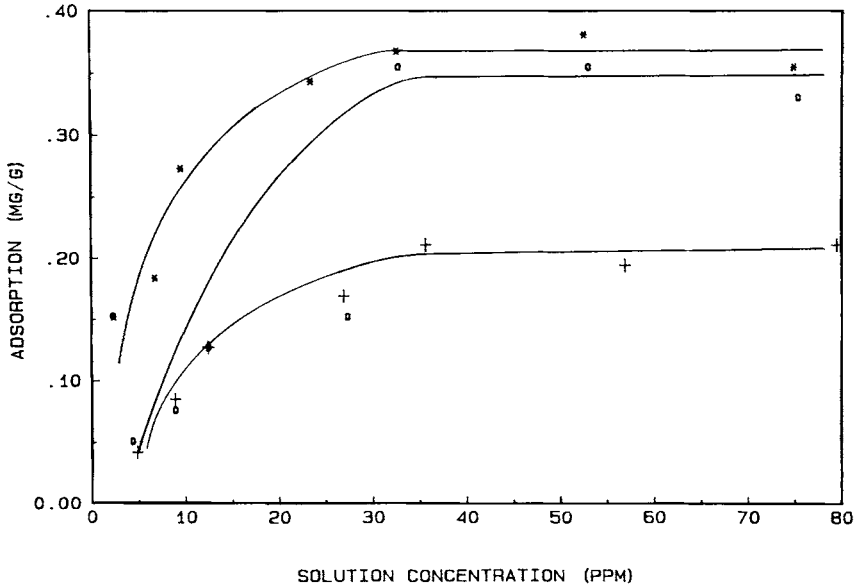


Fig. 5. Adsorption of Tergitol NP-10 by PET fibers: + + - starting sample; - * - hydrolyzed with aqueous sodium hydroxide for 3 h (weight loss = 6.4%); - o - hydrolyzed with methanolic sodium methoxide for 25 min (weight loss = 5.8%).

increase the hydrophilicity of the hydrolyzed polymer. The number of carboxyl and hydroxyl groups to be expected at the surface of PET fibers due to their presence at chain ends would be augmented by the chain scission that occurs on hydrolysis.

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