

Hydrolysis of Resin-Coated Poly(ethylene Terephthalate) Yarns*

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Synopsis

A comparison of the resistance of resin coated and uncoated poly(ethylene terephthalate) (PET) yarns to steam exposure at 160°C shows that the coated yarn degrades more rapidly. The decrease in tensile strength upon steam exposure results from hydrolytic scission which is accelerated by acidic hydrolysis products. The resin coating on the yarn acts as a skin around the filaments, a skin which apparently does not retard steam penetration, but does trap hydrolysis products in the yarn structure. A comparison study of PET films substantiated these conclusions. Hydrolysis products in films and small bundles of monofilaments taken from yarns were measured by infrared spectroscopy.

INTRODUCTION

For the majority of its applications (clothing, home furnishing, etc.) poly(ethylene terephthalate) (PET) yarns provide excellent performance and resistance to environmental deterioration. The high tenacity and high melting point of PET have encouraged its application in demanding industrial areas such as tires and filter fabrics, where resistance to extreme conditions of temperature, especially in the presence of water, is required. However, thermal and/or hydrolytic deterioration can occur.¹⁻⁶ Hydrolytic deterioration is especially important in areas such as paper-makers' screens and felts where increasing production speeds have resulted in exposure to high temperatures. For example, PET screens are routinely evaluated by exposure to superheated steam at temperatures of up to 180°C.^{3,7-11}

Commercial PET yarns have been developed for industries such as paper making and laundries in order to minimize problems caused by the lack of dimensional stability of large, fast moving belts or sieves under high tensions and pressures. One approach involves the weaving of fabrics from multifilament PET yarns coated with a resin to enhance dimensional stability.^{7,11} In this paper, the hydrolytic sensitivity of such a coated commercial yarn is examined, and the reasons for its limited performance discussed and compared with published results.

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EXPERIMENTAL

Materials

The basic material used in all yarn experiments was a multifilament PET yarn (Diolen, Enka Glanzstoff). This industrial yarn was constructed from two highly twisted 110 tex yarns, which were twisted together to give a two-ply yarn of final size (expressed in tex, i.e., weight in g/1000 m) of 250 tex. Using the nomenclature suggested by A.S.T.M. (D 1244) the complete description of the final yarn is R250 tex. S 461 t.p.m./2Z 461 t.p.m.; 110 tex. This yarn was used in both the uncoated and coated forms. The crosslinked, acrylate coating (Fröhlich and Wolff, Hessisch Lichtenau, West Germany) gave a total linear density of 275 tex (12 wt % coating). Samples of paper making screens prepared from these coated and uncoated yarns were also examined.

For some model experiments, PET films were examined (Melinex, I.C.I., 'O' grade or Mylar, DuPont, 25 μm thickness in each case).

Hydrolysis

Yarns (as loose skeins) and small film samples were placed in a glass-lined stainless steel laboratory autoclave (350 mL volume) with 50 mL of distilled water. The sealed autoclave was then heated in a circulating air thermostat at 160°C (absolute steam pressure 6.1 atm). Pairs of coated and uncoated yarn were exposed side by side to allow direct comparison of changes in properties for identical treatments. Some large film samples and fabric strips were hydrolyzed in a commercial autoclave (American Steralizer Co.) at 120°C (absolute steam pressure 2.0 atm).

Yarns and fabric strips were also exposed to dry heat at 160°C and 120°C, respectively, in a circulating air oven.

Tensile Testing

The stress-strain properties of fabrics drawn in the warp (machine) direction (as 3 cm wide strips, including 58 warp yarns), the two-ply yarns and films (as 2 mm wide strips) were measured on an Instron Tensile Tester. All samples were tested at constant rates of extension of 50% min^{-1} for fabrics, 40% min^{-1} for yarns and 8% min^{-1} for films after being preconditioned at 55% RH and 24°C before testing. Yarns were handled and tested essentially as recommended in ASTM D885. Standard deviations (≥ 10 yarns tested) were ± 0.8 kg force and $\pm 0.8\%$ elongation.

IR Analysis of Films and Fibers

Spectra were recorded on a Beckman 4210 grating spectrophotometer fitted with a gold wiregrid polarizer in the common beam. To eliminate interference ripples which complicate quantitative measurements, film samples were inclined at the Brewster angle to the polarized IR beam, as suggested by Harrick.¹² From refractive index measurement the Brewster angle for PET is $\sim 60^\circ$.

Spectra of fibres are extremely weak, because of sample mounting problems and scatter from the fiber arrays. To minimize these problems, small bundles

of monofilaments (~20 individual fibers) taken from a single ply of each yarn were mounted in the micro-vice described previously.¹³ Spectra were then recorded on a Nicolet 7199 Fourier Transform IR spectrophotometer (FTIR), equipped with a high sensitivity mercury cadmium telluride detector. This instrument stores data in a digital form in its computer, allowing subsequent spectral manipulation (scaling, subtraction, etc.) Normally 500 scans were collected on a sample to give an acceptable signal to noise ratio.

The IR absorption at $\sim 1690\text{ cm}^{-1}$ of aromatic carboxylic acid groups expected in PET is completely masked by the intense ester absorption of the polymer. Treatment with sulfur tetrafluoride (SF_4 , Matheson) can convert carboxylic acid groups to acid fluorides, which absorb strongly at $\sim 1820\text{ cm}^{-1}$.^{14,15} Gas penetration into films and especially into the highly oriented fiber structure is slow, and treatment times of $\geq 75\text{ h}$ at 25°C were found to be necessary before plateau levels of $-\text{C}(=\text{O})\text{F}$ were reached together with a complete loss of the $-\text{OH}$ absorptions at $3600\text{--}2800\text{ cm}^{-1}$. The fact that the acid fluoride level did not increase further on extended exposure to SF_4 beyond $\sim 75\text{ h}$ implies that SF_4 does not attack the ester links in the polymer backbone. As a crosscheck on the reliability of the SF_4 treatment for the estimation of carboxylic acid end groups, the acid end groups in some film samples were determined by potentiometric titration as described previously.¹⁶

Physical Characterization

Crystallinity indices were estimated by wide-line X-ray diffraction (WAXS) on wound yarn samples in an evacuated camera as described previously.¹⁷ Yarn densities were measured by floatation in carbon tetrachloride–heptane mixtures.

Yarn and film samples were examined by scanning electron microscopy (SEM) with a Cambridge Stereoscan (Mark 2A) at a tilt angle of 45° after being vacuum coated with gold. Magnifications are indicated by micron markers on each micrograph.

RESULTS

The effects of exposure to dry heat or steam at 120°C on the tensile properties of the coated and uncoated PET fabrics (paper-making screens) are compared in Figure 1. The tensile strength of the coated fabric consistently deteriorates at a faster rate than that of the uncoated upon steam exposure. The mechanism of the hydrolysis of PET has been extensively studied.^{1–6} Our aim has been to confirm that this deterioration results from hydrolysis, and to investigate the reason for this acceleration of hydrolysis by the coating, which superficially would be expected to reduce steam access to the yarn and confer some protection.⁷

From Figure 2 it can be seen that individual coated yarns also deteriorate faster than the uncoated stock whereas dry heat has only a small effect on tensile strength. Both dry and steam heat cause marked changes in elongation at break. Some typical stress strain curves are shown in Figure 3.

The construction of the yarns and the effects of steam exposure on the construction were examined by SEM. From Figure 4, it is clear that the commercial coating of the tightly twisted two-ply yarn barely penetrates the outer filaments

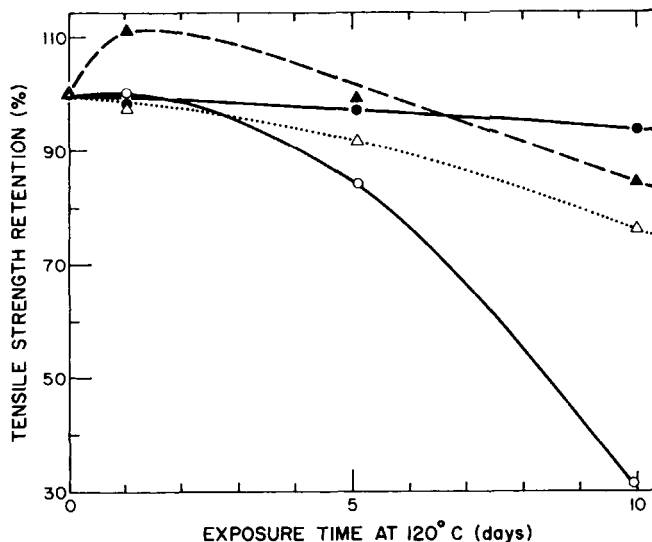


Fig. 1. Effects of exposure of 120°C on PET mesh: Closed symbols: dry heat; open symbols: in steam. (Δ, ●) Uncoated mesh; initial tensile strength = 790 kg (3-cm strip); (○, ●) coated mesh; initial tensile strength = 750 kg (3-cm strip).

of each ply and that there is little resin even between the two plies. Prolonged steam exposure (≥ 60 h at 160°C) produces yarns which fracture spontaneously in the autoclave or during gentle manipulation.¹⁰ However, at the shorter steam exposure times (of technical interest) only some slight damage to the acrylate coating on the multifilaments is seen (Figure 5).

Hydrolysis products from PET include glycol —OH and carboxylic acid end groups which have been frequently detected in film by IR spectroscopy.^{1,18} The traditional method for end group estimation in PET films and plaques is based on the measurements of the broad, relatively weak absorptions at 3542 cm^{-1} (glycol —OH, extinction coefficient $\epsilon = 154 \text{ M}^{-1}\cdot\text{cm}^{-1}$ in semicrystalline PET¹⁸) and 3256 cm^{-1} (carboxylic acid —OH, $\epsilon = 135 \text{ M}^{-1}\cdot\text{cm}^{-1}$)¹⁸. The strong car-

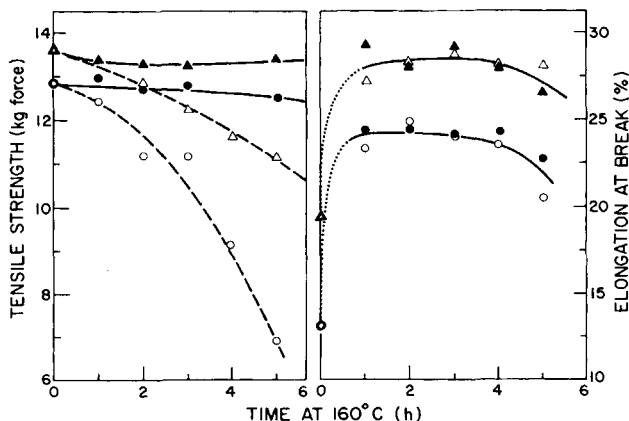


Fig. 2. Effects of exposure at 160°C in PET yarns. Closed symbols: dry heat; open symbols: in steam. (Δ, ●) Uncoated yarns; (○, ●) coated yarns.

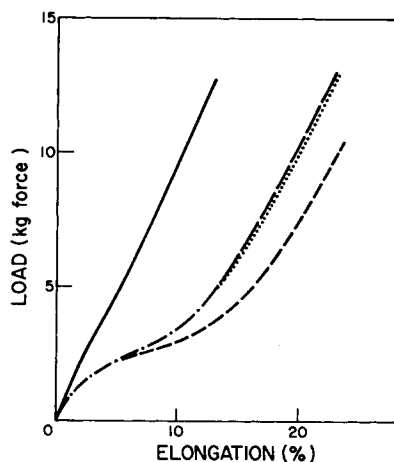


Fig. 3. Typical stress-strain curves for coated yarns exposed at 160°C: (—) control—no heat exposure; (.....) 1 h steam exposure; (---) 1 h dry heat; (- · -) 4 h steam exposure.

bonyl absorption at $\sim 1690\text{ cm}^{-1}$ of aromatic carboxylic acids is completely masked by the intense ester absorption of the polymer. Although differences in the —OH region are observed by FTIR after yarn hydrolysis (Figures 6 and 7) this spectral region is complicated by the broad absorptions of adsorbed water (centered at 3620 cm^{-1})¹⁶ and absorbed water (at $\sim 3350\text{ cm}^{-1}$); this water is ex-

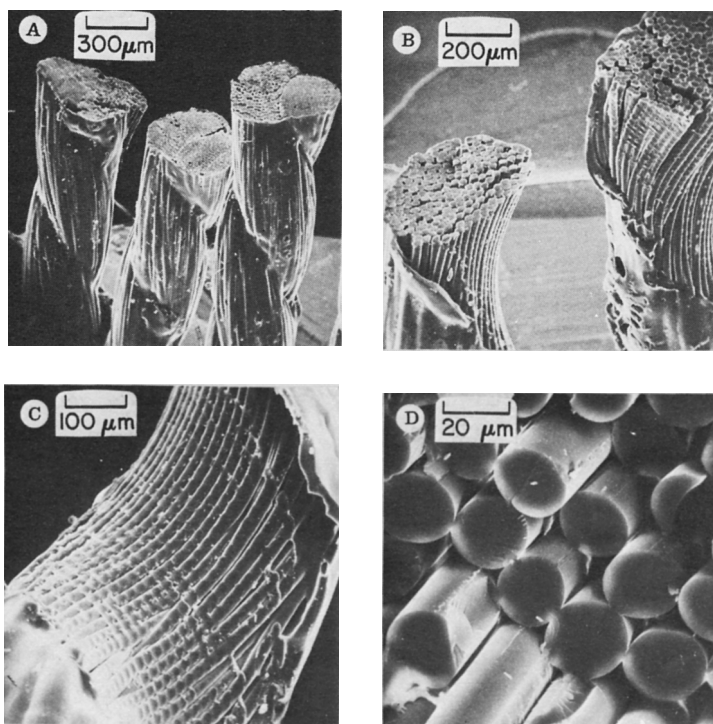


Fig. 4. SEM micrographs of coated two-ply yarn construction: (A) two-ply yarns, transverse cut by blade; (B) single ply separated from two-ply yarn; (C) detail of contact area between yarn plies after ply separation; (D) PET monofilaments within single ply.

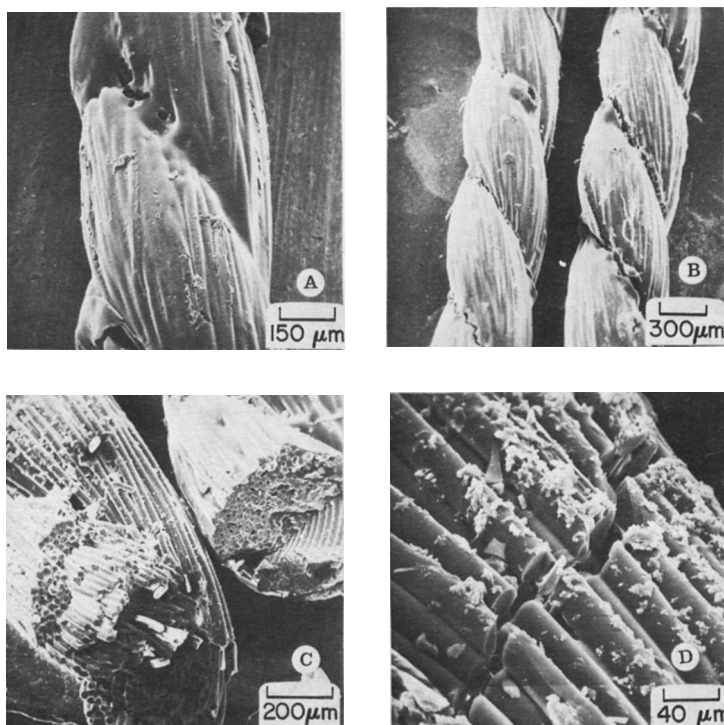


Fig. 5. SEM micrographs of steam exposed, coated, two-ply yarns: (A) before steam exposure; (B) after 25 h steam exposure at 160°C; (C) after 75 h steam exposure at 160°C; (D) detail of residual coating on C.

tremely difficult to remove from the yarn even by prolonged evacuation. The difficulty of deciding upon a realistic baseline under the absorptions also complicates quantitative measurements. Frequently prolonged immersion of PET film in D_2O has been used to convert all $-OH$ groups to $-OD$, so as to produce the $-OH$ -free background in the $3650-3100\text{ cm}^{-1}$ region.^{1,16,18} However, this method may extract out some of the low-molecular-weight products from hydrolysis. These problems can be simplified by the exposure of PET samples to gaseous SF_4 . This procedure has been used previously for the estimation of carboxylic acids and alcohols in oxidized polyolefins.^{14,15} All $-OH$ groups are fluorinated, so that the spectrum resulting after SF_4 exposure represents the basic, $-OH$ -free, polymer spectrum. In addition the acid fluoride group [$-C(=O)F$] absorbs strongly at 1820 cm^{-1} ($\epsilon = 610\text{ M}^{-1}\cdot\text{cm}^{-1}$)¹⁴ and can be used for the quantitative estimation of carboxylic acid end groups before and after hydrolysis (Figs. 6 and 7). Carboxylic acid end groups estimated from SF_4 -treated yarns are shown in Table I. Because of IR leakage between filaments producing lowered optical density values, the fiber data in Table I are based on ratios of 1820 cm^{-1} to 1610 cm^{-1} absorptions, the 1610 cm^{-1} absorption being quite insensitive to polymer orientation. The $-OH$ absorptions of the yarns (prior to SF_4 treatment) were not used quantitatively because of the complications caused by absorbed water. The validity of the SF_4 method was also checked on PET film samples (see the film hydrolysis section).

Polyester film hydrolysis is known to be catalyzed by the hydrolysis products.^{1,2,5} To investigate the extent of this effect on yarns, some yarn samples

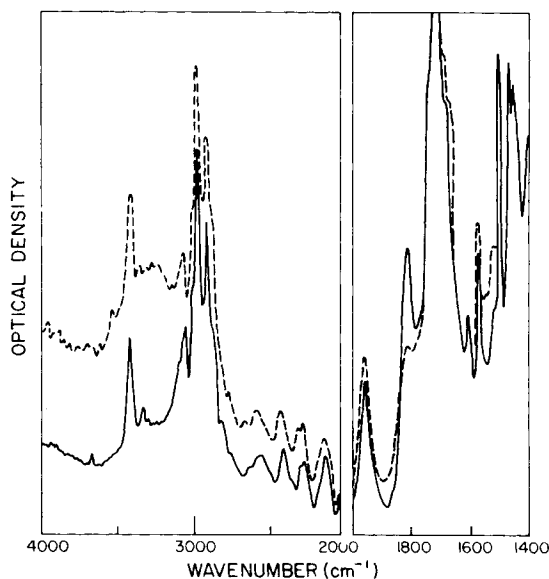


Fig. 6. FTIR spectra of PET filaments from coated yarn, no heat treatment: (---) as supplied; (—) after SF₄ treatment (75 h).

were exposed in the autoclave containing water and the model compounds benzoic acid and ethylene glycol. Changes in tensile strength for these samples are shown in Table II.

Changes in yarn crystallinity resulting from exposure to steam at 160°C were measured by WAXS. Coated and uncoated yarns showed very similar behavior. Yarns increased in crystallinity on exposure at 160°C to both dry heat and steam

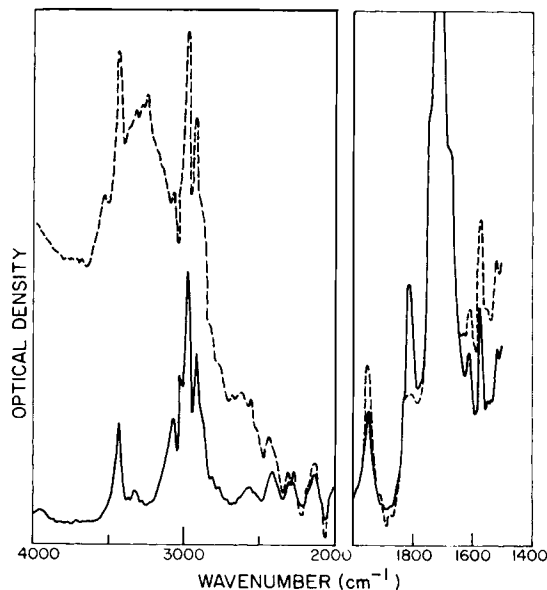


Fig. 7. FTIR spectra of PET filaments from coated yarn: (---) 4 h steam at 160°C; (—) 4 h steam at 160°C, + SF₄ treatment (75 h).

TABLE I
 PET Hydrolysis: End Groups

Hydrolysis exposure	Sample	Tensile strength	Observed end groups ^b		
			[R—OH]	[C(=O)OH]	[C(=O)—F]
None	Film ^c	—	69	27 ^d	31 ^d
None	Film ^e	1520	102	84	91
Steam, 120°, 46 h, "open"	Film ^e	920	140	101	114
Steam, 120°C, 46 h, "enclosed"	Film ^e	730	162	132	151
None	Coated yarn	12.9	—	—	9
None	Uncoated yarn	13.6	—	—	8
Steam, 160°C, 4 h	Coated yarn	9.1	—	—	17

^a Film: kg-cm⁻¹; yarns: kg/yarn.

^b At 3542 cm⁻¹, $\epsilon_{\text{OH}} = 154 \text{ M}^{-1}\cdot\text{cm}^{-1}$; at 3256 cm⁻¹, $\epsilon_{\text{COOH}} = 135 \text{ M}^{-1}\cdot\text{cm}^{-1}$; at 1820 cm⁻¹, $\epsilon_{\text{COF}} = 610 \text{ M}^{-1}\cdot\text{cm}^{-1}$.

^c Mylar.

^d Acid end groups 35 meq/kg from potentiometric titration.

^e Melinex.

heat, although the latter caused a more marked increase. Typical crystallinity index¹⁹ values were 0.28 (untreated), 0.30 (2 h dry heat), 0.36 (2 h steam heat), 0.33 (10 h dry heat), and 0.38 (10 h steam heat). Restructuring during steam exposure was also indicated by the rapid increase in the density of the uncoated yarn from 1.396 to 1.479 g·mL⁻¹ during the first hour of exposure at 160°C. Prolonged exposure resulted in no further increase. An identical behavior resulted from dry heat exposure at 160°C. Coated yarn increased in density from 1.361 to 1.452 g·mL⁻¹ during the first hour of dry or wet heat. Densities then plateaued at the higher value. In all cases very long flotation times were required before a final (i.e., nondrifting) density value could be measured. The density of the crystallite unit cell in PET is 1.4547 g·mL⁻¹.⁴ That is *smaller* than the densities observed after heat treatment. However, Miyagi and Wunderlich have observed similar results which they attribute to the selective absorption of the dense component (CCl₄) from the flotation mixture (CCl₄—heptane).⁴ Thus the observed density values are overestimations; yet the trends do imply a rapid annealing of the yarns at 160°C.

 TABLE II
 Effects of Model Products on Hydrolysis of Uncoated PET Yarns

Exposure conditions ^a	Tensile strength (kg force/yarn)
None	13.6
4 h steam	11.6
4 h steam + 10% ethylene glycol	11.4
4 h steam + 0.5% benzoic acid	7.6
4 h steam + 5% benzoic acid	3.5

^a At 160°C.

PET Film Hydrolysis

Commercial PET film was hydrolyzed under various conditions in an attempt to simulate the changes observed in yarn samples. The effects of hydrolysis on film IR spectra are shown in Figure 8. After vacuum drying, end groups were estimated from absorbances at 3542 cm^{-1} (glycol—OH), at 3290 cm^{-1} (carboxylic acid—OH), and at 1820 cm^{-1} [$-\text{C}(=\text{O})-\text{F}$ from SF_4 treatment (Fig. 9)]. End group concentrations calculated for film samples are collected in Table I. Good agreement was found between the concentrations of acid end groups measured by potentiometric titration¹⁶ and from IR measurements.

In order to maximize any effects of PET hydrolysis products on the hydrolytic process, in some experiments ($10 \times 25\text{ cm}^2$) film was arranged in the large autoclave so that one half was freely exposed to steam, whereas the other half was enclosed in a rigid sandwich comprising (in order) a Pyrex plate, PET film, PET test film, PET film, and Pyrex plate. The test film was spaced (on average) $\sim 50\text{ }\mu\text{m}$ from the two PET films adjacent to it. Thus steam could reach the surface of the sandwiched test film, but hydrolysis products from both the test film and the adjacent films could not readily distill away.

From Table I the film hydrolyzed "enclosed" shows a distinctly greater loss in tensile strength and a higher concentration of end groups than does the film area hydrolyzed in a free environment. In addition, film from the "enclosed" hydrolysis showed an obviously higher level of surface products (much greater haze and deposits) than the areas exposed in the open conditions.

The IR spectra of all hydrolyzed films indicated that restructuring of the PET occurred during steam exposure. For example, amorphous content decreased (decreased absorptions at 1612 , 1578 , 1173 , 1042 , 793 , and 632 cm^{-1}), whereas crystallinity increased (increased absorptions at 1386 , 972 , 508 , and 438 cm^{-1}) and crystallite fold content increased (988 cm^{-1} absorption).²⁰

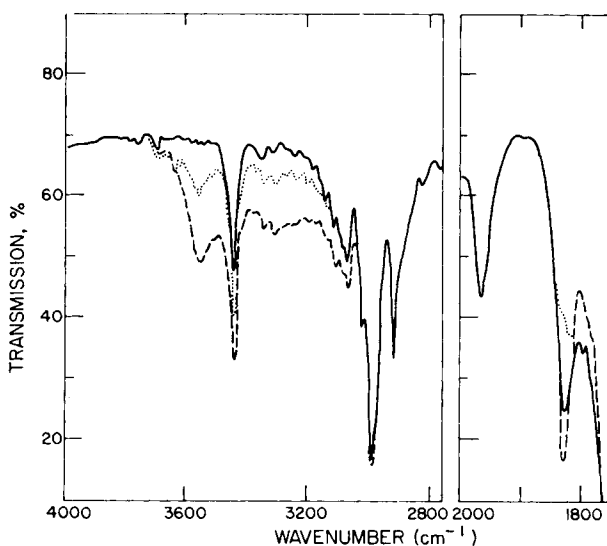


Fig. 8. IR spectra of PET films. $4000\text{--}2700\text{ cm}^{-1}$: (.....) 0 h steam; (—) 0 h steam + SF_4 treatment; (---) 87 h steam at 120°C . $2000\text{--}1700\text{ cm}^{-1}$: (.....) 0 h steam and 87 h steam at 120°C , (—) 0 h steam + SF_4 treatment; (---) 87 h steam at 120°C + SF_4 treatment.

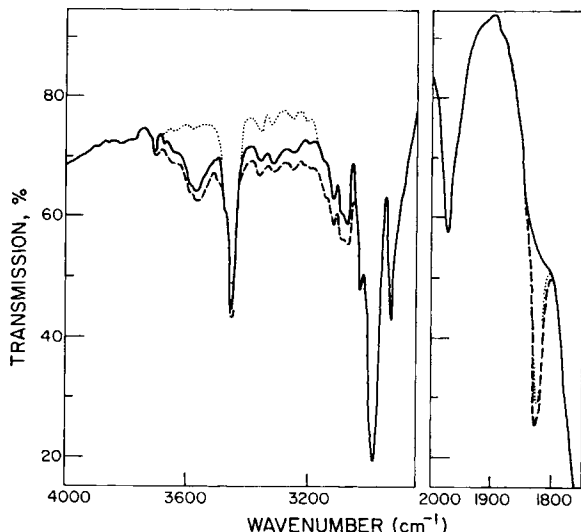


Fig. 9. IR Spectra of PET films. All samples steam exposed 46 h at 120°C, either "free" or "enclosed." 4000–2700 cm^{-1} : (—) Steam exposed "free"; (---) steam exposed "enclosed"; (.....) steam exposed "free" or "enclosed" after SF_4 treatment. 2000–1700 cm^{-1} : (—) Steam exposed "free" or "enclosed"; (---) steam exposed "enclosed" after SF_4 treatment; (.....) steam exposed "free" after SF_4 treatment.

DISCUSSION

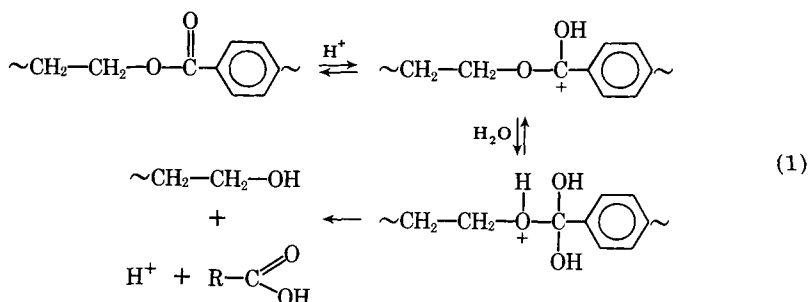
At 160°C, PET is above its glass transition temperature (T_g , 67°C for non-oriented, amorphous PET²¹) so that rapid restructuring must be expected during dry or steam heat at this temperature. This physical restructuring is clearly shown by the increases in the X-ray crystallinity index and the density (of yarn) and the IR crystallinity (of film). The changes in tensile properties observed after dry heat (Figs. 2 and 3) are consistent with the yarn having become relaxed and less oriented (typical of fiber annealing with free ends).²¹ This relaxation appears to be completed within the first hour of heat treatment to give a yarn showing the onset of a yield behavior on drawing; more prolonged dry heat causes no further change in the stress-strain behavior (Figs. 2 and 3), implying no further physical restructuring or degradation. PET has been shown to be 5000 times more resistant to oxidative deterioration and 1000 times more resistant to thermal degradation under dry heat conditions as compared to hydrolysis.⁶ Increased elongation at break has also been observed in the dry heat and steam exposure work of Hendrix⁷ and Kleinheins.⁹

Exposure to steam at 160°C initially results in changes in tensile behavior quite similar to those from dry heat (Fig. 2), and these changes again presumably result from the annealing process. On more extensive steam exposure (≥ 2 h), tensile properties deteriorate progressively. This deterioration is clearly due to hydrolytic chain cleavage, as indicated by the increases in end groups (Figs. 6 and 7; Table I), which have often been observed for PET films and plaques.¹⁻⁵

Coated PET yarns and fabrics are markedly more susceptible to steam exposure than the uncoated materials (Figs. 1 and 2).

Ravens and Ward^{1,2} and Zimmerman and Kim⁵ have shown that PET hydrolysis is catalyzed by ionized acids within the polymer (Reaction 1). Thus it

is possible that the difference between coated and uncoated PET yarns during hydrolysis is related to differing retentions of acidic products. Hydrolysis ex-



periments on model film and yarn systems are consistent with this possibility. For example, yarn hydrolysis in the presence of benzoic acid (to simulate the effects of the carboxylic acid end groups from the PET hydrolysis) is dramatically accelerated (Table II), even at quite low concentrations of benzoic acid. The presence of ethylene glycol during hydrolysis had no effect on tensile properties. Similarly film hydrolysis under (“enclosed”) conditions which reduced the loss of hydrolysis products from the polymer caused a larger deterioration in tensile properties than steam exposure of the “free” film (Table I).

The acrylate resin on the commercial yarn completely encases the two plies (Fig. 4), but does not penetrate into the inter filament spacing and has many defects (bubbles, cracks, etc.). Upon exposure of the coated yarn to steam, relatively rapid hydrolysis occurs, indicating that steam readily penetrates the coating (by diffusion or direct transport through defects). Hydrolysis of the coated yarn will then generate an atmosphere rich in hydrolysis products from the PET (linear oligomer, terephthalic acid, etc.^{3,22}), products which will be largely trapped within the yarns by the coating. The carboxylic acid products will then autocatalyze the hydrolytic cleavage.

Hendrix⁷ has also studied the effects of resin impregnation on the hydrolytic stability of PET multifilament yarns. Hendrix has also used a sealed autoclave at absolute steam pressures of up to 7.8 atm, but most of his data refer to superheated steam (at up to 180°C) at atmospheric pressure. He concluded that many of his laboratory-applied resin coatings (acrylates, urethanes, epoxies, etc.) enhanced the hydrolytic stability of PET. This apparent conflict with our results can be rationalized by considering differences between the commercial yarn which we studied and the yarns Hendrix coated in the laboratory. Our yarns were encased in a thin outer coating with some defects and little interfilament penetration (Figs. 4 and 5). In Hendrix’s case, resin penetration was complete, throughout the yarn cross section, so that during autoclaving steam penetration to the PET monofilament was presumably greatly restricted and hydrolysis retarded as compared to the uncoated yarns.

The acrylate-coated multifilament yarns are used extensively in paper-making screens because of their superior dimensional stability over uncoated filaments. However, a drawback of the coating lies in the increased rate of hydrolysis. Many other coatings (including phenol-formaldehydes, melamines, epoxy, and ureas) have been tested,¹¹ but all accelerate PET yarn hydrolysis as compared to the uncoated yarns. This acceleration of PET hydrolysis by certain coatings must occur in many applications of polyester, including filters or steam presses and

possibly also in tire cords. In some circumstances, the autocatalyzed hydrolytic scission of polyesters can be retarded by the incorporation of carboxylic acid scavengers such as carbodiimides or epoxides.^{23,24} These additives may reduce the effect of coatings on the hydrolysis sensitivity of PET yarns.

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