

Alkaline Hydrolysis of Polyester Fibers - Structural Effects

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ABSTRACT

Partially oriented and fully drawn poly(ethylene terephthalate) (PET) fibers were treated with aqueous solution of 10% sodium hydroxide at 30°C. The weight loss ,density ,diameters and birefringence of fibers were measured. X-ray diffraction studies were carried out and SEM photomicrographs of fibers were obtained. Both yarn types showed progressive weight loss and reduction of diameters with increasing time of alkaline treatment. There were no changes in orientation and crystallinity of fibers.

Surface morphology differed between partially oriented and fully drawn fibers. It is concluded that the reaction occurs preferentially in the region of low structural order on the surface of fibers.

INTRODUCTION

In the production of polyester fabric ,alkaline treatment has been used for about 30 years as a procedure for improving physical properties of fabrics. This type of finishing process leads to controlled degradation of fabric with better wettability ,air - permeability ,wicking and also a silk like appearance.

It is well known that the reaction between an aqueous solution of sodium hydroxide and polyester is a hydrolysis reaction and it takes place at the fiber surfaces and not in the fiber interior [1-8]. According to McIntyre [9] highly ionized compounds such as sodium hydroxide cannot diffuse in to the nonpolar polyester. Thus the diameter of individual fibers decreases gradually during hydrolysis. Treatment of fabrics with sodium hydroxide leads to the decrease of fiber diameter and exposure of the new surfaces and hence the fabric properties will change [8].

The kinetics of the reaction between polyester and aqueous sodium hydroxide have been studied by Latta [4]. Based on the results of works by Zeronian et al. [8] ,Latta [4] has suggested that the reaction does not preferentially occur in either region of low order or of high order of fibers. In the presence of an excess of sodium hydroxide ,in a wide range of temperatures ,the relation between

weight loss and time of the treatment was found to be linear [4,5]. Datye and Palan [5] examined the effect of alkaline on filaments of PET ,CDP (cationic dyeable PET) and EDP (easy dyeable PET). The rate of hydrolysis of these three types of polyesters at 97°C with 1 N NaOH has been reported to be in the following order :PET < EDP < CDP.

Also it was found [5] that the weight loss depends upon the specific area or thickness of fibers. After a specific time the amount of weight loss depends upon temperature ,alkaline concentration ,specific area of fiber ,previous history of fibers (textured or flat yarn) ,presence of delustrant and construction of fabrics.

Among these factors the effects of physical structure of fibers on weight loss have not fully been investigated. Hence the purpose of this work is to re-examine the caustic reduction processes on the oriented and crystalline PET filaments.

EXPERIMENTAL

Materials

The filament yarns used in this work have been specified in Table 1. PET fibers in forms of the filament yarn were obtained from Polyacryl Iran Co., a producer of polyester fibers. The sodium

hydroxide and acetic acid used were of analytical reagent grade. Distilled water was used for treatments and for washing the samples.

Table 1: Characteristics of yarns

Yarn	No. of filament	Nominal yarn denier
Partially Oriented Yarn (POY)	34	256
Fully Drawn Yarn (FDY)	34	155

Methods of Treatment

The yarns were cut by scissors to prepare short pieces approximately 5 cm in length and samples were weighed before immersion in beakers containing 200 cc, 10% aqueous NaOH at room temperature 28°C. The beakers were kept in a constant temperature bath at 30°C. At the end of the designated time the yarns were removed and rinsed with distilled water several times and dried at room temperature for several days. The samples were weighed and weight - loss calculated using equation (1).

$$\% \text{ Weight loss} = W.L = ((W1-W2)/W1) \times 100 \quad (1)$$

Where W1 is the weight of samples before treatment and W2 is the weight of samples after treatment. Experience has shown that both yarns (POY and FDY) do not shrink measurably in 30°C in the aqueous solution of sodium hydroxide.

Characterization of Fibers

Density: The density of fibers were determined using a density gradient column, thermostated at 24°C. Solution of calcium nitrate in water was used to obtain linear density variation in the column.

Scanning electron microscopy (SEM): A JEOL microscope was used to obtain photomicrographs of fiber surface. Coating was done with gold in a vacuum evaporator.

X-ray: X-ray diffraction studies were carried out using Philips X-R Diffractometers. Cu, K α radiation with wave length = 1/5418 Å filtered by nickel, was used. Samples were scanned at 2°/min, between

2 θ =10° to 2 θ =36° and the chart speed was set at 2 cm/min.

Birefringence: Refractive indices were measured by the Becke Line method using a polarizing microscope (Carl Zeiss Jena). These indices were also measured by the shearing method using an interference microscope (Carl Zeiss Jena Interfac).

Determination of fiber diameters: Fiber diameters were measured by a light microscope equipped with a graduated eye piece.

RESULTS AND DISCUSSION

Table 2 shows the density, diameter and weight loss of the fibers treated with an aqueous solution of 10% sodium hydroxide.

Table 2: Characteristics of the fibers treated with 10% sodium hydroxide

Treatment time (h)	Density g/cm		Diameter (μ m)		% Weight loss	
	POY	FDY	POY	FDY	POY	FDY
0	1.343	1.374	29.0	22.6	0.0	0.0
2	1.343	1.374	29.0	22.6	0.648	0.602
6	1.343	1.374	29.0	22.5	1.481	0.864
20	1.343	1.374	28.4	22.3	4.207	2.438
40	1.343	1.374	27.6	22.1	9.262	4.576
50	1.343	1.374	26.8	21.7	14.787	7.565
100	1.343	1.374	25.0	21.0	25.619	13.546

As the time of hydrolysis increased from 2 h to 100 h, weight loss of FDY samples increased from 0.60% to 13.5%, while the weight loss of POY samples increased from 0.65% to 25.6%. For both samples, the weight loss time relation was found to be linear. The regression equation has approximately zero intercept for both samples and slopes of 0.261 and 0.1235 for POY and FDY samples, respectively (Figure 1). The correlation coefficient (R²) was 0.988 for both regression equations.

The density of the samples after degradation remained constant, which is in agreement with previously reported results for drawn fibers [2,5].

The POY yarns were spun at the take up speed of approximately 3000 m/min. The fibers can be visualized as amorphous oriented PET. FDY yarns are obtained by drawing the POY filaments with a draw ratio of 1.6 at a temperature slightly above glass transition temperature. This process of

drawing caused the short lengths of molecules to move and form more stable intermolecular bonds i.e. ,the crystallinity increased.This stable molecular arrangement will not be easily accessible in the reaction with NaOH.

The crystallinity of PET fibers can be calculated from the density measurements.The density of 100% crystalline and amorphous PET has been reported by Hsieh and Mo [10] 1.457 gr/cm³ and 1.336 gr/cm³, respectively.If these values are used then the volume fraction of crystallinity can be calculated by equation (2).

$$\% \text{ crystallinity} = ((d-1.336)/0.121) \times 100 \quad (2)$$

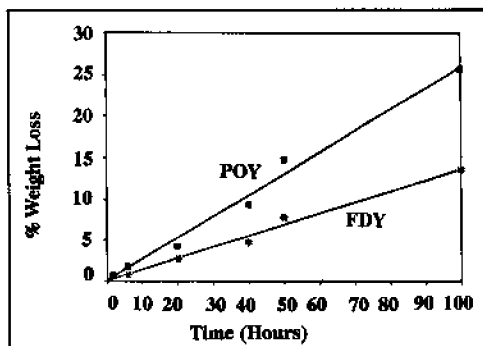


Figure 1:Weight Loss - Time Relation

Where d is the density of the sample of unknown crystallinity.

Then the % crystallinity of POY samples will be 5.8% and that of FDY samples will be 31.4% which remained unchanged during the progress of hydrolysis.

The x-ray diffraction patterns from the samples treated for 100 hours with sodium hydroxide and from the original samples are shown in Figures 2a to 2d.The POY fibers show no sign of crystallinity while those of FDY had peaks at about $2\theta = 18.5^\circ$ and $2\theta = 25$ degrees ,indicating partially crystalline order.Upon hydrolysis no changes are observed in the x-ray diffraction patterns.These results are in accordance with the results of density measurements i.e. ,the internal fiber morphology is not changed upon hydrolysis.

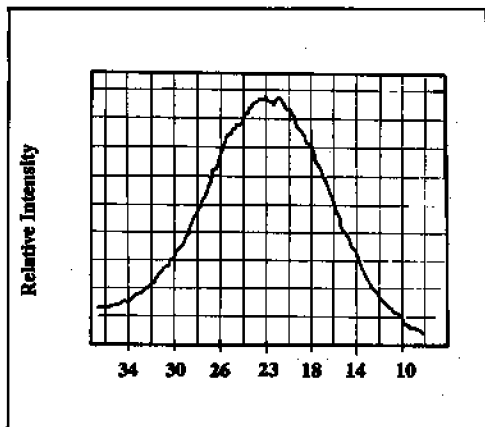
The values of the parallel ($n_{||}$),perpendicular

(n_{\perp}) refractive indices and birefringence (Δn) of samples are shown in Table 3.As expected ,the birefringence and parallel refractive index ($n_{||}$) of drawn fibers (FDY) are greater than those for (POY) fibers indicating higher molecular orientation.In drawn fibers a good agreement exists between the results of interference technique and the Becke Line method ,which indicates that there are no skin effects.Treatment with NaOH does not affect the molecular orientation for both POY and FDY samples.

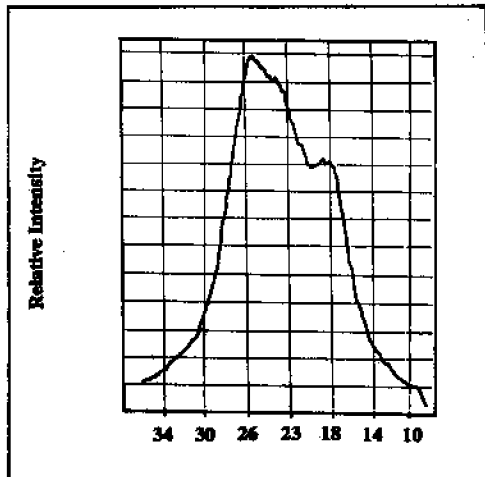
SEM photomicrographs from POY and FDY samples are shown in Figures 3a to 3d.The surface of untreated samples are smooth except those defects and imperfections presumably left from the extrusion process.Surface roughness ,probably produced by delustrant particles and oligomers is distributed on the surface of both POY and FDY untreated samples (Figures 3a and 3c).In hydrolysis of PET ,cavities are formed on the surface of both POY and FDY samples.This finding is in accordance with what was found for drawn fibers by Latta [5] and Ellison et al. [2].The pits on the surface of POY fibers are more or less round while on the FDY fibers they are elliptical and elongated in the direction of the fiber axes.

Figure 1 shows that the rate of weight loss for crystalline and partially oriented fibers is different.Also ,results of the density ,x-ray and birefringence measurements indicate no changes occurred in the internal structure of the fibers.Hence ,it has to be assumed that on the surface of fibers ,the region of low structural order were attacked more rapidly than the ordered region.After removal of the regions of low order a skin with a different physical structure will remain.Ellison et al. [2] ,investigating physical properties of polyester fibers treated by alkaline hydrolysis indicated:"Treatment with aqueous sodium hydroxide appears to leave the polyester fiber surface more resistance to abrasion damage".

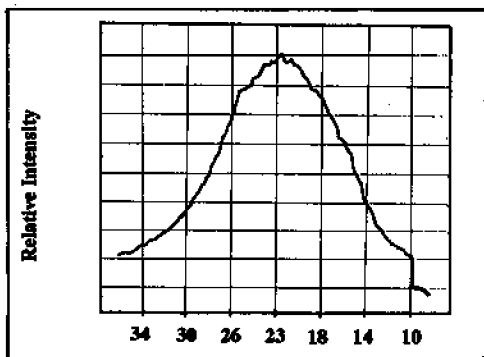
The elliptical elongated pits on the surface of FDY fibers are the results of crystalline and amorphous orientation or elongation of the accessible regions.



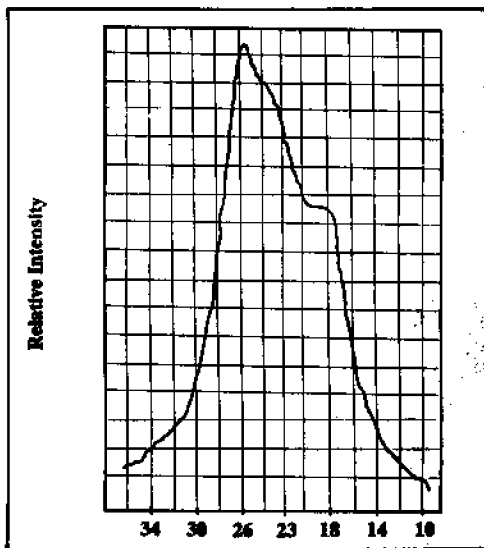
a-Untreated POY



b-Untreated FDY



c-100 hr treated POY

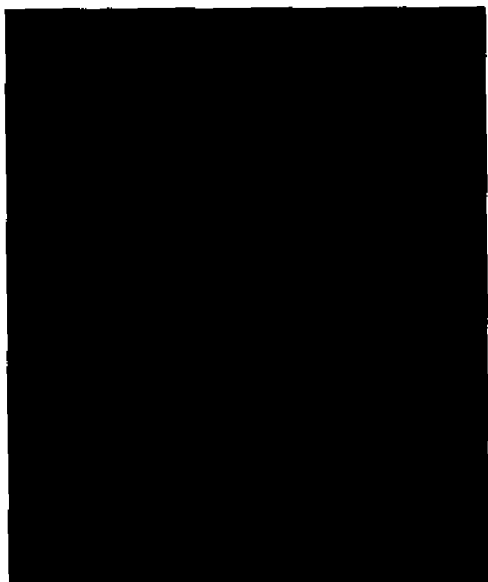


d-100 hr treated FDY

Figure 2: X-ray diffraction curves

Table 3: Refractive indices and birefringence of fibers

Materials	Becke Line			Interference		
	n_{\parallel}	n_{\perp}	Δn	n_{\parallel}	n_{\perp}	Δn
POY Untreated	1.602	1.568	0.034	1.605	1.568	0.034
POY 100h In 10% NaOH	1.600	1.568	0.032	1.600	1.568	0.032
FDY Untreated	1.707	1.535	0.172	1.707	1.535	0.172
FDY 100h In 10% NaOH	1.707	1.535	0.172	1.707	1.535	0.172



a-FDY Untreated



c-POY Untreated



b-FDY Treated 100 hr



d-POY Treated for 100 hr

Figure 3:SEM photomicrographs

CONCLUSION

When PET fibers in the forms of partially oriented (POY) having less than 6% crystallinity and fully drawn (FDY) having 31% crystallinity, are treated with aqueous solution of 10% sodium hydroxide, the rate of weight loss of POY was found to be greater than that of FDY samples. In both fibers the attack was limited to the surfaces. No changes in crystallinity and orientation were detected. These observations indicate that the attack of alkaline to the surface of fibers is preferential.

Under scanning electron microscopy, both treated fibers (POY and FDY) show etchings, ditches, cuts and holes with increasing weight loss. The pits on the surface of POY fibers are more or less round while on the FDY fibers they are elongated in the direction of fiber axis.

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