Degradation Cracking of Poly(ethylene terephthalate) Filaments by Methylamine and *N*-Propylamine

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ABSTRACT: Poly(ethylene terephthalate) (PET) filaments were degraded with aqueous solutions of *n*-propylamine and methylamine. The treated materials were examined by chemical microscopy and physical and mechanical methods. After partial degradation by aqueous solutions of amines, the surfaces of the filaments cracked. Direct observations of the cracking pattern formation and the changes in the physical properties of the filaments led to an explanation for the cracking pattern formation. The cracked patterns showed the swelled and deformed structure of the filaments. This explanation of the possible mechanisms for crack formation goes further than those discussed in previous research. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1923–1931, 2000

Key words: aminolysis; poly(ethylene terephthalate); filament; etching; degradation; stress cracking

INTRODUCTION

The effects of monofunctional amines on poly(ethylene terephthalate) (PET) fibers and films were studied previously from different points of view[1–23] and recently a review article was published.[24] There are patents describing the application of amine treatments to polyester-fiber fabrics[24] to improve properties. From the industrial point of view, in the production of polyester fibers the spin finish components may produce regular crack patterns that affect the mechanical properties of the filaments.[25]

During aminolysis amines attack the electron-deficient carbonyl carbon where chain scission and amide formation occur, which results in a reduction of the molecular weight of the sample.[1,3,24] The techniques used in several studies[5,7,10,11,13,15] mainly rely on the controversial assumption that the ordered or crystalline regions are insoluble and the amines predominantly react with the noncrystalline regions.

Some reports show surface etching with a regular pattern that occurs upon amine treatments of PET fibers and films.[4,13,14,16,17,20,21] Other reports[16,20,21] suggest that amine etching of fibers is a stress-sensitive degradation process. The cause of crack formation is believed to be due to the residual stress developed during production processes and previous heat setting treatments, which is released by aminolysis.[10,16,20] Naik and Bhat[21] believe that the combination of degradation and the presence of built-in stress enhance cracking. Holmes[23] used vapor and an aqueous solution of *n*-butylamine to differentiate the different locations of attack by vapor and an aqueous solution of amine.

In the present study the problem was looked at with another viewpoint. It is believed that if the mechanism of formation of cracking patterns by amine etching is understood and the parameters involved are determined, then selecting the suitable amine treatment can produce proper surface

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Table I   Characteristics of Filament Yarns

Properties	POY	FOY
Count (dtex)	280	167
No. filaments	34	34
TiO$_2$ (%)	0.3	0.3
Density (g/mL)	1.343	1.375
Birefringence	0.0345	0.173
LRV	21	21
Spin, finish (%)	0.4	0.6
Strength (g/tex)	25.3	32.2
Breaking extension (%)	143.5	32.2

patterns, which leads to different fiber surface properties. The purpose of the present study is to report further experimental evidence indicating that the redecoration of the degraded materials is responsible for crack formation.

EXPERIMENTAL

Materials

N-Propylamine (C$_3$H$_7$—NH$_2$) in a 99.9% form, methylamine (CH$_3$—NH$_2$) in a 40% aqueous solution, sodium hydroxide, and m-cresol were laboratory reagent grade. During storage, n-propylamine possibly reacts with oxygen and absorbs water; its color changes from colorless to yellow. The n-propylamine was extracted 4 times before use. Distilled water was used for the preparation of amine solutions and washings. Dyestuff was kindly supplied by the local distributor for Ciba–Geigy.

PET fibers in the form of filament yarns were obtained from PolyAcryl Iran Co., a domestic producer of polyester fibers. The fibers were in two different structural forms: partially oriented (POY) and fully drawn (FOY) continuous filament yarns. Table I shows the properties of the yarn used in this work.

Methods

Treatments

POY and FOY filaments were separately cut into a few millimeter lengths and a special glass cell of $2 \times 10 \times 10$ mm dimensions was filled with 40% aqueous methylamine and a few sections of filaments. The samples were observed for different periods of time with an optical microscope. We

thought that the development of cracks could be directly observed by this procedure.

In other experiments 30-mL bottles were filed with amines and filaments (about 0.05 g, 1–2 cm lengths). The glass-stoppered bottles were kept at constant temperature for different periods of time. Then the filaments were rinsed and washed several times with distilled water. Care was taken to keep the filaments immersed in the water during washings and transferring. The filaments with water were placed on the microscope slides and examined under a microscope until the water evaporated.

To examine the properties of the treated filaments, samples of the filaments were treated with the amines (similar to the above) in the glass-stoppered bottles. After degradation the samples were washed in an excess of distilled water, rinsed, and dried at room temperature.

We knew from the literature[15,16,20,24] and our previous experiments[17,26,27] that n-propylamine and methylamine are both cracking agents. The rate of reaction of PET with methylamine is higher than n-propylamine.[24] Thus, the changes in the filament surfaces could be followed with methylamine in a shorter time. N-Propylamine is readily available in neat (99.9%) forms and solutions with a high concentration of amine can be made easily.

Characterizations

A Carl Zeiss Jena polarizing microscope (Jena, Germany), equipped with a calibrating eyepiece and Interfaco attachment, was used for the measurement of filament diameters and birefringence. The average diameters of the filaments were measured on more than 10 sections in the water before drying and after drying. The diameter contraction (DC%) is calculated by

$$DC\% = ((DW - DD)/DD) \times 100)$$

where DW and DD are the filament diameters before and after drying, respectively.

The crack density (number of transverse cracks in 1-cm length of filament) was calculated from the numbers of cracks in a known length of filament measured under an optical microscope.[27] A scanning electron microscope (SEM) was used to obtain photomicrographs of filament surfaces. The samples were coated with gold in a vacuum evaporator. The load elongation curves of the sin-

gle filaments were measured with a Textechno Faffegraph (Monchengladbach, Germany), which is a constant rate of elongation strength tester. The bulk densities of the filaments were determined by the flotation method using a mixture of carbon tetrachloride and benzene at 25°C. The IR spectra of the fibers in KBr disks were obtained using a Iss88 Bruker FTIR spectrophotometer. The moisture regains of the filaments were obtained by conditioning samples at 65% relative humidity and 20°C and measuring the dry and conditioned weights with a Sartirious balance equipped with a heating chamber. The weights of the conditioned samples were measured by a balance with an accuracy of 5 μg. The weight loss (WL%) was calculated by

$$\%WL = 100((W1 - W2)/W1)$$

where W1 is the weight of the sample before treatment and W2 is the weight of sample after treatment. A differential scanning calorimeter (DuPont 2000) was used for the measurement of the melting temperature. The laboratory relative viscosity (LRV) was determined at 25°C with a Cannon Fenske Viscometer using hexafloroisopropanol as a solvent.

RESULTS

Direct Observations

Degradation of the filaments by amines in a glass cell was observed by an optical microscope for different periods of time at room temperature. No cracks were observed on the filament surfaces. Figure 1(a) shows a representative photomicrograph of the surface of POY filaments in a 40% aqueous solution of methylamine after 120 min. The same filaments were washed with distilled water and dried at room temperature. Examination with a microscope revealed that the filaments had several transverse cracks. Figure 1(b) shows the same filament immersed in water and observed under the microscope.

This direct observation indicates that formation of the cracking pattern is related to the drying process and the removal of water from reacted fibers with the aqueous amine solution. No crack was observed in similar experiments when distilled neat *n*-propylamine was used.

In another experiment, after treatments with an aqueous solution of the amines, a large
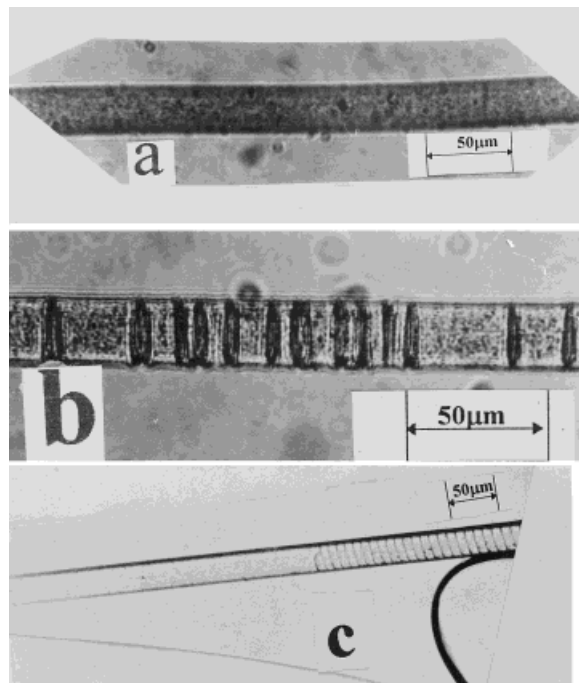

Figure 1 A representative photomicrograph of the surface of a POY filament in a 40% aqueous solution of methylamine after 120 min: (a) before drying, (b) after drying, and (c) during the removal of water.

amount of water was added to the solutions; then the filaments were transferred to a glass slide with a sufficient amount of water. The filaments were then examined under a microscope for several minutes until the water evaporated and the filaments dried. The previous finding that the crack formations accompanied the removal of water was confirmed. During the removal of water from the wet filaments, the outgrowths of cracks were observed. Figure 1(c) shows a filament in water under the microscope; in one side the water is removed and cracks appear while in the left side the water is still present and there are no cracks on the surface of the filaments.

To provide evidence of the gradual advancement of amine into the filaments, a disperse dye (Duranol Brilliant ECB 600) was added to the amine solutions. After the treatment of POY and FOY filaments with these solutions and washing and drying, the cross sections of the filaments were prepared by a hand microtome and examined under a microscope. Figure 2(a,b) shows the cross sections of POY filaments after 120 and 180 min of treatments with a 40% aqueous solution of *n*-propylamine. The width of the section in which the dye penetrated increased with the time of
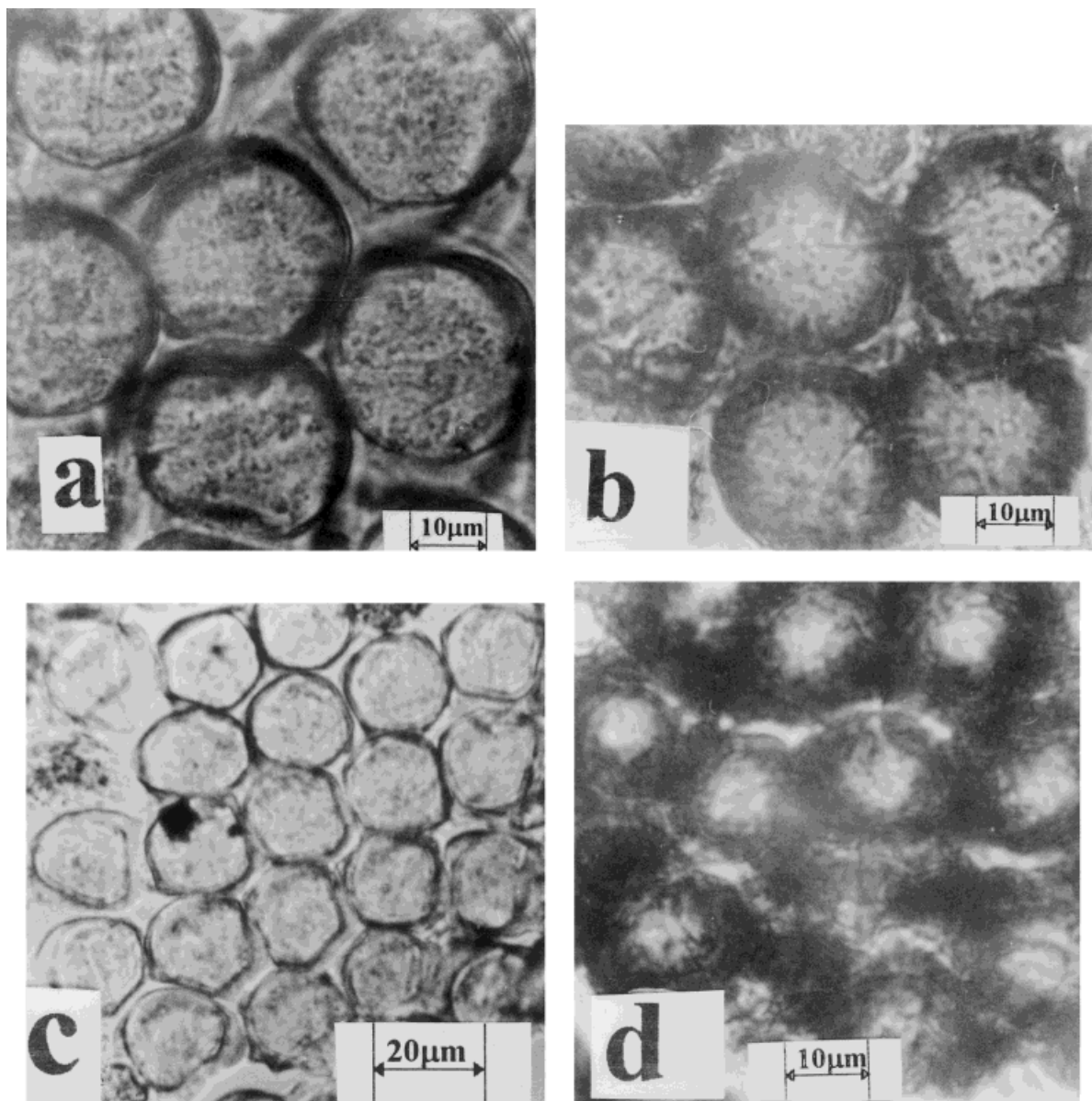
Figure 2 Cross sections of filaments after treatments with a 40% aqueous solution of *n*-propylamine and dyes: (a) POY filament after 120-min treatment, (b) POY filament after 180-min treatment, (c) FOY filament after 5-h treatment, and (d) FOY filament after 17-h treatment.

treatment. Similar results were obtained with FOY filaments, but the treatment times were longer than those for POY filaments. Figure 2(c,d) shows the cross sections of FOY filaments after 5 and 17 h of treatments with a 40% aqueous solution of *n*-propylamine and dye. The disperse dye at 30°C does not penetrate into the PET filaments and the central portion (core) remains colorless.

It is known from the literature that sodium hydroxide hydrolyzes and dissolves polyester af-

ter a relatively long time of exposure at relatively high temperature[24] and *m*-cresol dissolves polyester at the boiling temperature.[28] At room temperature for a properly selected exposure time, it seems that when amine treated fibers are exposed to any of these chemicals, only the reacted portions of the filament dissolves. The reacted shell of filaments treated with aqueous amine can be removed by *m*-cresol or an aqueous solution of 10% sodium hydroxide at room temperature. At
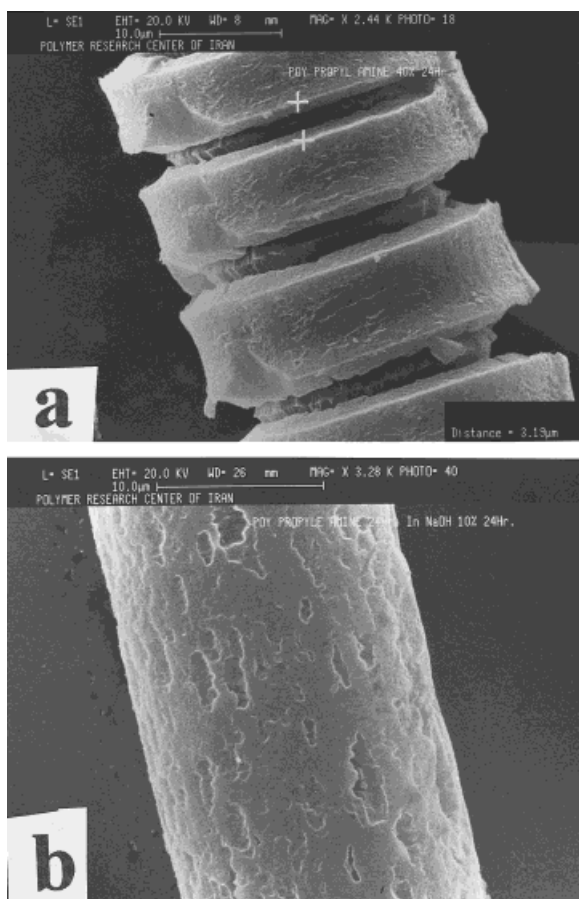
Figure 3 A representative SEM photomicrograph of a POY filament treated with a 40% aqueous propylamine solution: (a) dried sample, and (b) sample after treatment with 10% sodium hydroxide solution for 24 h at 25°C.

room temperature the POY filaments treated with aqueous n-propylamine dissolve in m-cresol after 120 min while untreated filaments remain without significant changes. Figure 3(a,b) shows a representative SEM photomicrograph of amine treated POY filaments before and after treatment with sodium hydroxide at 25°C. An aqueous solution of sodium hydroxide removed the cracked patterns and produced a roughened and pitted surface over the core. Similar results were obtained using m-cresol to solve the reacted section.

Diameter Change

Table II shows the diameter contraction (DC%) of the filaments upon drying. In aqueous solutions, the removal of water caused the filaments (POY and FOY) to contract more than 4% diametrically. This contraction of the diameter of the filaments

is due to the contraction of the reacted section (shell). In case of 99.9% (neat) n-propylamine this is for the whole filament; the diameter contracted no more than 1.8%. After 95 min the POY filaments in the neat n-propylamine were broken into pieces without any cracks, while in the aqueous solutions of amine only cracks developed on the surface of the filament after 120 min.

Change in Tensile Properties

Treatment of the filaments with the aqueous solution of the amines causes a gradual change in the stress–strain behavior. Figure 4(a) shows the stress–strain curves of the untreated POY filament, and Figure 4(b) shows the stress–strain curve of POY filaments after 60-min treatment with a 40% aqueous solution of methylamine. Even after 60 min of treatment with amine the filaments did not lose their integrity and this can be extended up to 100%; the cracked patterns formed mostly on the surface of the filaments. Figure 5(a) shows the stress–strain curves of the untreated FOY filament; Figure 5(b) shows the stress–strain curves of FOY filaments after 180-min treatment with a 40% aqueous solution of methylamine, where entire filaments were not degraded.

Change in Density

After treating the filaments with an aqueous solution of amine, washing, and drying, the samples were subjected to ultrasonic irradiation in a water

Table II Diameter Contraction (DC) of Amine Treated Filaments upon Drying

| Yarn Type	Bath	Time (min)	Temp. (°C)	DC (%)
POY	Propylamine 99.9%	15	45	1.8
POY	Propylamine 99.9%	55	45	1.4
POY	Propylamine 99.9%	95	45	1.8
POY	Propylamine 40%	120	45	4.3
POY	Propylamine 40%	180	45	5.7
POY	Propylamine 40%	240	45	7.5
FOY	Propylamine 99.9%	45	45	0.0
FOY	Propylamine 99.9%	105	45	0.9
FOY	Propylamine 99.9%	165	45	0.0
FOY	Methylamine 40%	165	30	4.0
FOY	Methylamine 40%	225	30	6.7
FOY	Methylamine 40%	285	30	16.2
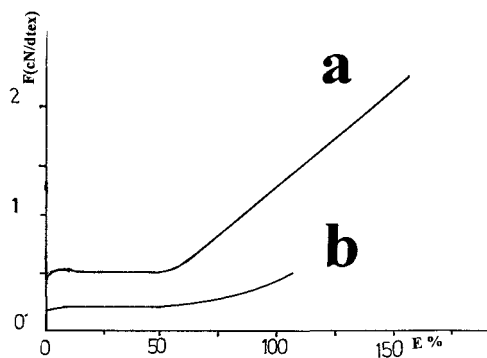
Figure 4 Stress–strain curves of POY filaments treated with a 40% aqueous solution of methylamine: (a) untreated and (b) 1-h treatment.

bath. We found that the central portion can be separated from the outer section only for the treated POY filaments. The density of the outer shell (reacted) and the central portions (nonreacted core) were determined. The results are shown in Table III. The densities of several sections of the core were similar, but the density of the powdery shell varied between 1.4 and 1.5 g/mL. For FOY samples, it was not possible to separate the shell from the core by this method. The density of the treated FOY filament also increased. This increase of density could be due to the increase of crystallinity or the removal of the low density (less ordered) regions.

The increase of the crystallinity of undrawn filaments treated with methylamine and ethylamine is reported by several authors.[2,5,6,10,21] The density of part of the reacted shell of treated samples is probably increased to the density of 100% crystalline PET (1.457,[7] 1.455,[13,22] 1.445,[14] and 1.515 g/mL[29]).

Crack Density

The amine concentration has effects on the crack density (number of cracks per unit length of filament). When using neat (99.9%) n-propylamine, no cracks were observed on the surfaces of the dried filaments. Decreasing the concentration of amine to 95% produced only a few occasional cracks on the surface of the dried treated filaments. Figure 6 shows the effect of the n-propylamine concentration on the crack density after 6 h of treatment at 40°C; the average of at least 20 measurements and 95% confidence limits are indicated. For a moderate time of aminolysis, in several cases the treatment time did not have a statistically significant effect on the crack den-

sity. Similar results were observed with methylamine and FOY samples but with different time scales.[27]

IR Spectra and Moisture Regain

To characterize the nature of the reacted portion and central core of treated filaments, IR absorption spectra of untreated filaments, treated filaments, and the core were made. The core was
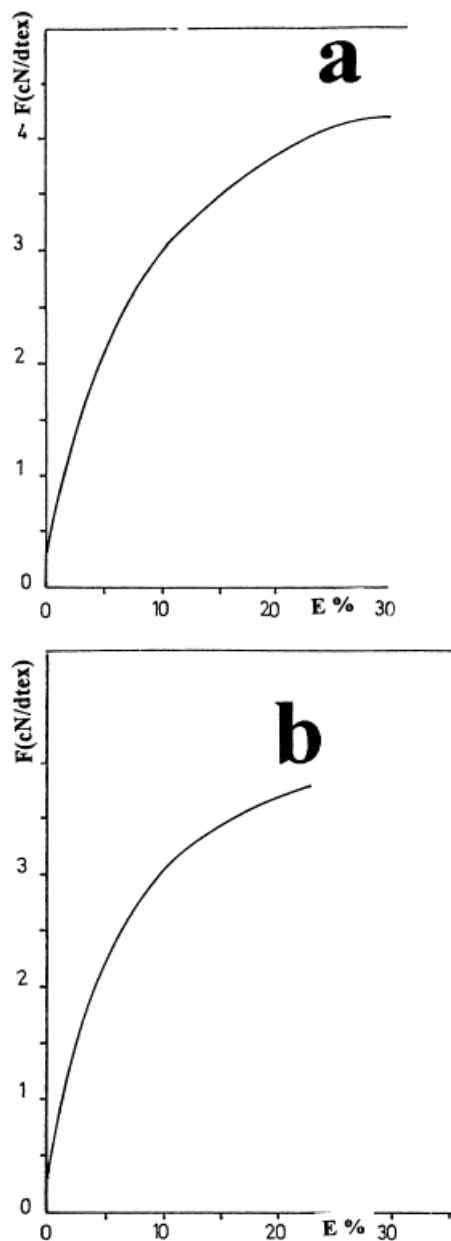

Figure 5 Stress–strain curves of FOY samples treated with a 40% aqueous solution of methylamine: (a) untreated and (b) 3-h treatment.

Table III   Density (g/mL) of Sections of Treated Filaments with 40% Aqueous Solution of Methylamine at 30°C

Samples	Treatment Time (min)	Density (g/mL)
Untreated POY filament	0	1.343
Treated POY filament (whole)	120	1.390
Outer section (reacted shell)	120	1.40–1.50
Central section (unreacted core)	120	1.340
Untreated FOY filament	0	1.375
Treated FOY filament (whole)	120	1.400

identified as PET, but there was no indication of an amide group. The treated filaments had bands at 3350, 1545, and 1630 cm^{-1} that are characteristics of N—H and C=O bending. This result indicates that the central section (core) remains intact during a moderate time of aminolysis by an aqueous solution of amines.

Table IV shows the increase of moisture regains of POY filaments with the treatment time with methylamine. The increase of moisture regains may be due to the presence of amide groups in the reacted shell.

Weight Loss, LRV, and Melting Temperatures

Weight loss, LRV, and melting temperatures of some of the samples during the treatment with an 40% aqueous solution of methylamine were measured. The results are shown in Table V. The melting temperature and LRV of the POY and

FOY samples decrease with increasing treatment time. The LRV, which is an indication of the molecular weight, decreases considerably before weight loss and the reduction of the diameter becomes significant. The decrease of the melting temperature and relative viscosity is due to the chain scission, decrease of the molecular weight, and formation of a new structure. This is in agreement with the previously reported results on the effects of amines on PET fibers.[8,14,15,19,24]

DISCUSSION

Considering the previous published work[5–8,13–21,23] and the present experimental evidence, Figure 7 exhibits the changes that could happen during aminolysis. Figure 7(a) shows the fringed-micelle structure of untreated filaments that show some degree of orientation and crystallinity.[30]

Figure 7(b) shows a part of a reacted filament in the solution; the permeated section and unreacted core of a filament are shown. During the treatment, aqueous amine penetrates gently and progressively into the filaments and reacts with the molecules, leaving short chain molecules with hydrophilic amide groups and a few longer chains linking with the central section (core). Water attracted by the hydrophilic groups opens the struc-
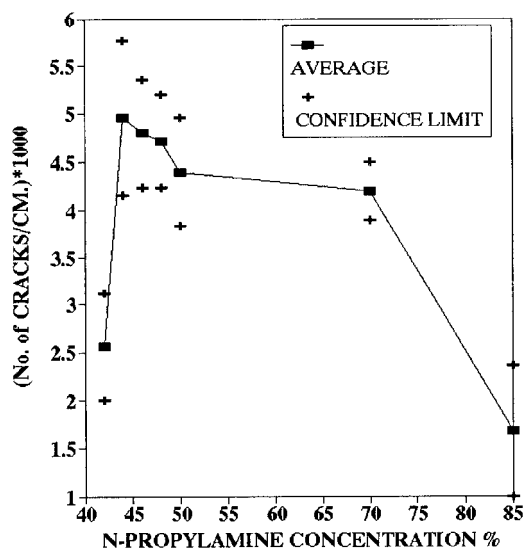

Figure 6   The effects of *n*-propylamine concentration on the crack density.

Table IV   Moisture Regain at 65% Relative Humidity and 20°C for POY Filaments Treated with 40% Aqueous Solution of Methylamine

Treatment Time (min)	Moisture Regain (%)
0	0.360
45	0.501
90	0.563
120	0.572

Table V   Melting Temperature, Weight Loss (WL), Diameter, and LRV of Filaments Treated with Aqueous Solution of 40% Methylamine

Types of Filaments	Treatment Time (min)	Melting Temp. (°C)	WL (%)	Diameter (μm)	LRV
POY	0	259.6	0	27.0	21.0
POY	30	—	0	27.0	13.5
POY	60	—	15.4	26.5	4.0
POY	120	250.0	—	—	—
POY	180	246.5	65.0	24.5	—
FOY	0	260.0	0	21.2	21.0
FOY	180	255.0	1.0	20.5−	14.1
FOY	240	250.8	10.0	20.0	2.65
FOY	270	—	—	—	1.9
FOY	300	234.8	—	19.7	1.5

ture and causes the increase of the filament diameter. There is a limited interchange of positions between the fiber molecules and water molecules.

Figure 7(c) shows a part of a filament after drying. Removal of water causes the outer regions to contract and shrink. Shortened chain molecules form a new structure and probably a few longer chains link the outer section to the central portion that remains intact. Because the fibers are long, the shell cannot shrink continuously around the core and as a result, transverse cracks on the filaments occur. For thin filaments most of the cracks were transverse while for the thick filaments longitudinal cracks were also observed.[17,20]

Sweet and Bell[16] suggest that the amine etching is a stress-sensitive degradation process. In fact, the outer section (shell) of the aqueous amine treated filaments is very stress sensitive and it cannot sustain elongation, either in the solution or after drying. It breaks into pieces upon extension. The geometry of the cracking patterns developed on the surface of treated filaments depends on the amount of shell contraction and coupling between the core and shell, among other factors.
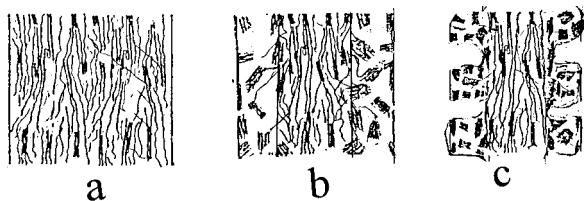
Another possible process of cracking pattern formation that can be speculated is associated with the surface tension. The reacted shell that is composed of water and reacted shortened chain molecules is soft and it tends to minimize its surface energy, which results in crack formation.

Published works show that the previous fiber history (draw ratio, heat setting, and aging) effects the cracking patterns[4,20,21,24] and at least the first stages of aminolysis is selective.[5–8,13–15,24] In the present work the differences between cracking patterns between POY and FOY samples treated with *n*-propylamine or methylamine were also observed. POY samples have a very low crystallinity, as indicated by the density measurement, and considerable orientation, as indicated by the birefringence. FOY samples have considerable crystallinity (30%) and orientation. In the moderate time of treatment for crystalline samples, the amine preferentially reacts with the less ordered region leaving aggregation of the water molecule, crystallite, and reacted and restructured chain molecules. The reacted shells of fibers with different structures have crystallites of different sizes, different molecular weight distributions, different strengths of coupling between the core and shell, and different surface tensions. This is the reason for the cracking patterns of fibers with different structures.

Figure 7   A model representing filaments during aminolysis: (a) the original filament, (b) reacted filaments while in the water, and (c) filaments after drying.

CONCLUSIONS

The physical changes taking place during the degradation period of PET filaments treated with

n-propylamine and methylamine was followed and examined by several techniques to reveal the origin and mechanism of crack formation. Several parameters were found to affect the formation of the cracking pattern. These parameters were amine concentration, drying conditions, and previous fiber history. The process of crack formation is associated with shrinkage of the reacted section of filaments upon drying and possibly the surface tension of the reacted section.

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