Chemical Etching of Poly(ethylene Terephthalate) Filaments

R. S. CHAUHAN, M. V. S. RAO, and N. E. DWELTZ, *Ahmedabad Textile Industry's Research Association, Ahmedabad 380 015, India*

Synopsis

Chemical etching of poly(ethylene terephthalate) filaments with aqueous methylamine has revealed a complex stress–cracking behavior, which varied with orientation and thermal crystallization conditions. The appearance of both longitudinal and transverse cracks, can be explained on the basis of the existence of two types of domains, where the stresses are preferentially concentrated. They are explained on the basis of Prevorsek's structural model. In heat-set fibers, there exists a skin to core differentiation in the internal stress distribution. The crack pattern also varied depending on whether the fibers were heat-set in the taut or slack conditions. This chemical etching technique can prove to be a very useful tool, for the study of the internal stress distribution induced in fibers by various fabrication processes or post mechanical deformations.

INTRODUCTION

Most of the previous studies on the chemical etching of poly(ethylene terephthalate) were concerned with the nature of the degradation and the resulting physical changes. Since chemical etching or degradation is relative rather than an absolute parameter—depending upon the chemical conditions of treatment a specimen can be degraded to different extents, affecting both the crystalline and amorphous regions—a controversy persisted regarding the selective nature of the amine attack. While Farrow et al.[1] have expressed doubts about the selective nature of amine treatment for PET, many other workers[2–4] have reported that amine etching is selective enough to discriminate between the crystalline and amorphous regions. Studies based on optical and electron microscopy of chemically etched specimens of polyester have provided interesting data on the topographical feature of the specimen, as well as on the physical nature of the degradation.[2,5–7] Chu and Wilkes,[6] as well as Adams,[7] have shown that the etched samples exhibited a surface network structure, which was dependent on the mechanical and thermal history of the sample. Murray et al.[2] have concluded that the undegraded PET possesses a fibrous morphology similar to that proposed by Prevosek et al.[8] and that amine etching destroys this fibrous texture, leaving a weak granular structure which still showed some orientation. However, they were unable to offer any explanation for the curious regularity of the etched patterns.

Recent studies by Sweet and Bell[9] have revealed that transverse, as well as helical, cracks appear on the surface of polyester filaments after prolonged etching. Their hypothesis suggests that amine etching is a stress sensitive degradation process. However, the authors offered no explanation

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for the observed regularity of the pattern in the amine treated drawn and heat-set polyester filaments.

Based on experimental evidence provided by various workers, it is evident that the chemical etching of PET by amines is more a stress sensitive degradation process than a selective etching process. This characteristic nature of amine etching of poly(ethylene terephthalate) might prove very useful from the technological point of view if proper correlation between the etch patterns and the stress distribution within a polymer specimen can be established. Apart from the excellent work by Sweet and Bell,[9] no systematic attempt seems to have been made to study the relationship between the chemical degradative stress cracking behavior of polyester and the physical changes induced during the drawing and thermal crystallization processes. Extensive work in this direction has been taken up in our laboratory. In this study, the effects of orientation and thermal crystallization of PET filaments on the stress sensitive chemical degradative etch patterns have been investigated. The changes in topography at the gross structural level are presented, and the possible dependence on microstructural changes is discussed.

MATERIALS AND METHODS

Fibers

The following fibrous materials having differences in orientation and crystallinity were examined: unoriented, amorphous filaments (as-spun tow); unoriented, crystalline filaments (as-spun tow after heat-setting); oriented, moderately crystalline filaments (commercially drawn flat yarn); oriented, highly crystalline filaments (commercially drawn filaments after heat-setting); both the as-spun tow and the commercially drawn filaments were heat-set at 200°C slack (free to shrink), as well as under tension (at constant length).

While the above-mentioned samples were rapidly brought to room temperature (quenched) after heat-setting them for 5 min in an oven, a few commercially drawn samples were allowed to anneal, cool slowly to room temperature after heat-setting them for 30 min at 200°C in an air oven. The latter are referred to as annealed samples, while the rapidly cooled samples are referred to as quenched samples.

Chemical Etching

All the etching experiments were carried out at room temperature (27°C) using a 40% aqueous methylamine solution in sealed test tubes to prevent the loss of gaseous methylamine. The fiber to liquid ratio was kept high. Experiments were run without agitation. For the tow (as-spun) series, the etching time was 3.5 h and for the control commercial filament series 5.5 h. In order to monitor the reaction precisely, all the experiments were run having untreated control fiber as a monitoring specimen. The control etched fibers were observed under an optical microscope and the final (exact) reaction duration was decided, so as to get nearly the same etching effect in each experiment. The observed monitoring specimen, however, was always rejected once it was taken out for observation. All the specimens became brittle, to various extents, after treatment and care was taken while handling samples in order to avoid artifacts.

Scanning Electron Microscopy

All scanning electron microscope observations were made with a Cambridge "Stereoscan," S4-10 model. Samples were coated with a thin layer of gold produced by thermal evaporation in a vacuum coating unit to prevent charging.

X-Ray Diffraction

Wide angle x-ray diffraction patterns were obtained for a few samples before they were amine-etched, using a cylindrical camera mounted on a Philips x-ray Generator, Model PW 1720, Collimeted CuK radiation after N1 filtering, was used.

RESULTS

In almost all the cases studied, the mosaic patterns generated as a result of amine etching were always found to have the cracks running either longitudinally or nearly transverse to the fiber axis.

Figure 1 shows undrawn amorphous filaments after amine etching. These filaments are devoid of any gross morphological features. The surface presents a granular structure, indicating that uniform etching of the filaments has taken place. As has been reported by Sweet and Bell[9] this type of uniform etching is understandable because filaments in the undrawn state are almost free of internal stresses, or the internal stresses are too weak to be effective for any selective etching to take place.

The undrawn amorphous filaments, which showed no stress-cracking pattern prior to crystallization, exhibited characteristic transverse crack patterns (Figs. 2 and 3) after heat-setting. It is known that thermal crystallization of undrawn amorphous filaments leads to the development of internal stresses, and this is evident from the cracks developed.

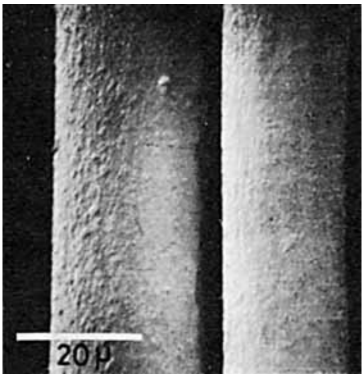

Fig. 1. Undrawn amorphous filament.

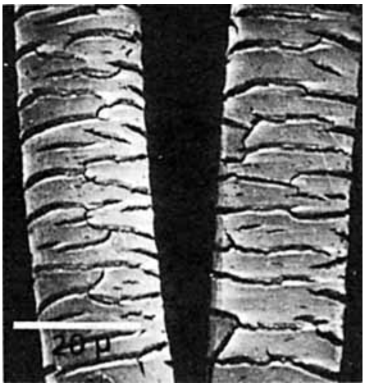

Fig. 2. Undrawn amorphous filament, slack heat-set (quenched).

The mosaic pattern in the case of filaments heat-set in the slack condition in a gaseous atmosphere and subsequently quenched shows a predominence of transverse cracks (Fig. 2). However, the cracks were found to be neither uniform nor regular. Increasing time of the amine treatment did not lead to any improvement in the uniformity or regularity of the crack pattern. Instead, the fibers disintegrated into very small fragments. On the other hand, the samples heat-set under tension in a gaseous atmosphere and later quenched showed (Fig. 3) fairly uniform transverse cracks. This regular disk type morphological structure was also observed by Murray et al.[2]

In a study of the fracture patterns of heat-set unoriented material (to be published elsewhere[10]), it was observed that under tensile strain the material ruptured in a very brittle manner in which flat-topped fractured fibers ends were obtained very similar to fractured glass fibers. This had suggested that there were zones of weakness transverse to the fiber axis and distributed along the length of the fibers. The amine etching treatment has revealed these transverse regions in a very graphic manner through the pattern of cracks.

Baker,[11] as well as Sweet and Bell[9] have shown that a combination of the degradative effect of aqueous amine and the presence of stresses in the

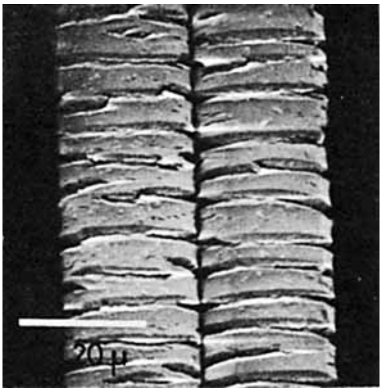

Fig. 3. Undrawn amorphous filament, tension heat-set (quenched).

polymer produces a synergestic effect which results in surface cracking of the material. From the observed etch patterns of unoriented crystallized materials it can be concluded that thermal crystallization results in the introduction of residual stress in the material. While slack heat-setting leads to a nonuniform distribution of this stress, heat-setting under tension allows the stress to be distributed fairly uniformly across the specimen. In order to verify whether these differences in the stress distribution, and subsequently in the etch pattern by slack and tension heat-setting processes, have any origin in the changes that take place at the structural level, these specimens prior to chemical etching, were subjected to x-ray diffraction analysis. The detailed work will be reported elsewhere.[12] The x-ray diffraction pattern of slack heat-set unoriented filaments showed that, though there is a slight tendency for the 100 reflection to lie in the meridion, the overall pattern indicates a fairly random distribution of crystallites. On the other hand, the diffraction pattern of tension heat-set unoriented filaments revealed that the crystallographic a-axis prefers to align along the fiber axis as indicated by the predominance of the 100 reflection on the meridian. x-ray equatorial diffraction analysis of these samples showed that the crystallographic c-axis has a slight preference to align perpendicular to the fiber axis in the case of slack heat-set materials. For tension heat-set filaments this tendency was even more pronounced. In addition, birefringence measurements indicated that tension heat-set filaments exhibit a much higher negative birefringence compared to slack heat-set unoriented filaments. Thus tension heat-setting of unoriented filaments results in the orientation of crystallites transverse to the fiber axis. Slack heat-setting, on the other hand, leads to a more random distribution of crystallites. Though the crack patterns are macroscopic in nature and cannot be directly related at present to the submicroscopic structure, the above results indicate that some relationship exists between the molecular structural changes and the crack patterns developed in the specimen.

A very different type of etch pattern is observed for the commercially drawn polyester and corresponding slack and tension heat-set filaments after amine treatment. In commercially drawn control fibers, in addition to the transverse cracks, a few longitudinal cracks parallel to the fiber axis

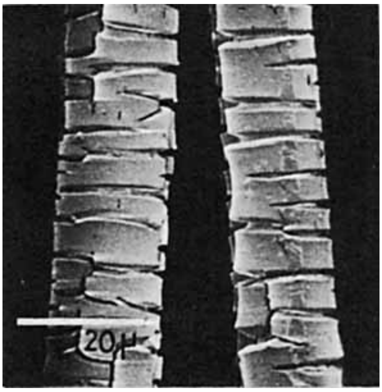

Fig. 4. Commercially drawn filament.

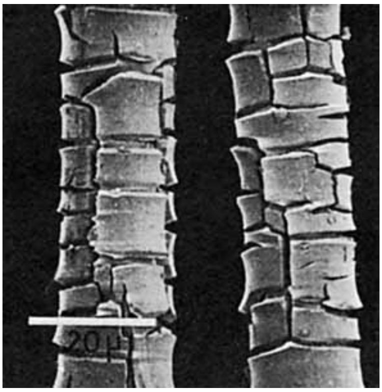

Fig. 5. Commercially drawn filament, tension heat-set (quenched).

also appeared (Fig. 4). The longitudinal cracks were found to occur at irregular intervals, and their overall distribution was also irregular. The complex nature of the pattern made it difficult to explain their origin. However, as these longitudinal cracks were not observed in the unoriented crystallized filaments, their origin may have something to do with the orientation of molecular chains during the drawing process. When these filaments were heat-set (quenched) under tension and amine etched (Fig. 5), the longitudinal cracks were found to increase in length, as well as in numbers. The transverse cracks, however, did not travel uniformly along the width of the fibers. These two types of cracks yield a random mosaic pattern in contrast to the disklike pattern observed in the case of unoriented heat-set filaments. In our earlier study (to be published elsewhere[10]) of the fracture pattern of polyester fibers, it was noted that the commercial control fibers before and after heat-setting exhibited a very typical thermoplastic fracture pattern characteristic of an oriented fibrous material. This was very different from the brittle fracture patterns of unoriented heat-set fibers described earlier. In the same manner, it has been noted in the present study that the amine etch patterns of the oriented materials are very different from those of undrawn or unoriented materials.

The complexity of the crack pattern of the tension heat-set filaments was not noticed in slack heat-set drawn filaments. The patterns show (Fig. 6) a

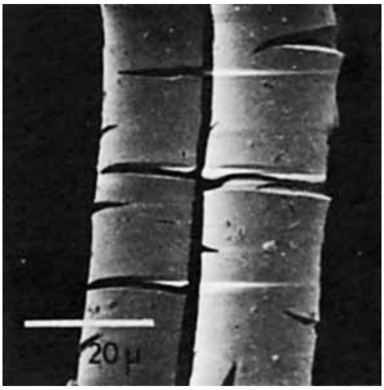

Fig. 6. Commercially drawn filament, slack heat-set (quenched).

Fig. 7. Commercially drawn filament, slack heat-set, 165°C.

more regular disk like morphological structure held together by a central core. The disk size is much larger and the cracks wider and deeper than those obtained in the case of the unoriented samples. A few longitudinal cracks were also noticed, and in some cases a few helical cracks were observed in the case of the slack set oriented filament.

The effect of heat-setting temperature on the etch pattern of slack quenched filament is shown in Figures 7 and 8. For filaments slack heat-treated at 165°C (Fig. 7) the etch pattern appeared to be similar to that observed for the tension quenched samples treated at 200°C (Fig. 5). It presents a bricklike structure with longitudinal as well as transverse cracks. However, the etch pattern for filaments heat-set at a higher temperature (230°C) was quite different (Fig. 8). The cracks were predominently transverse with short longitudinal cracks occasionally seen. When filaments are heat-set in the slack condition, the internal stresses introduced during the drawing (fabrication) processes are relieved, and the specimen contracts. However, when the heat-setting temperature is low (165°C), this shrinkage is very small, and thereby the relaxation of internal stress is incomplete, and so there is a similiarity between the patterns observed here and those before heat-setting or after tension setting. On the other hand, when the filaments are heat-set at sufficiently high temperatures, extensive shrinkage, and internal molecular chain relaxation occur, leading to a uniform

Fig. 8. Commercially drawn filament, slack heat-set, 230°C.

Fig. 9. Commercially drawn filament, tension heat-set (annealed).

regular distribution of internal stresses. This may be one of the reasons for the observed disklike pattern with only transverse cracks predominent in these high temperature (230°C) heat-set filaments (Fig. 8).

Figures 9 and 10 show the filaments which were tension- and slack-annealed, respectively, at 200°C followed by amine etching. Both the longitudinal and transverse cracks appears to be irregular and are neither wide nor deep. In most cases, the transverse cracks did not travel the full width of the fiber, in contrast to the slack quenched patterns. However, in the tension annealed filaments (Fig. 9) the overall crack pattern is much more uniform as compared to the slack annealed filaments (Fig. 10). Sweet and Bell indicated that these irregular crack patterns may arise due to molecular disorientation in the skin, as a result of heat treatment.

In order to verify this "skin-core" effect the etching experiments were repeated on the quenched and annealed samples. The etching patterns were observed at different time intervals. Figures 11, 12, and 13 show the patterns for the slack quenched fibres for different durations. The filaments etched for 3 h (Fig. 11) showed a definite crack pattern consisting only of longitudinal cracks. The depth, as well as the width of these cracks, appears to be small. As the duration of the treatment increases, the fiber surface develops deeper transverse cracks (Fig. 12) while the longitudinal cracks

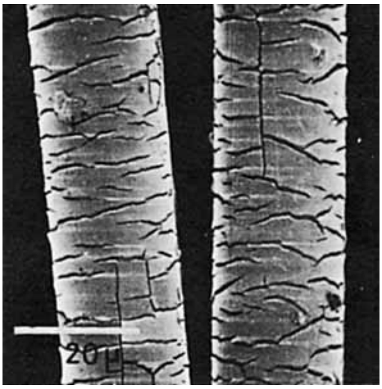

Fig. 10. Commercially drawn filament, slack heat-set (annealed).

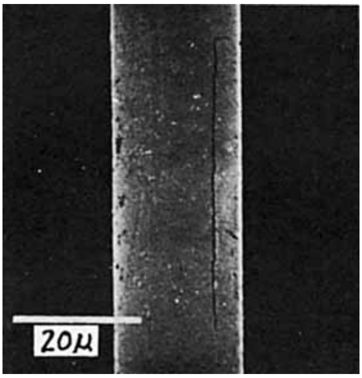

Fig. 11. Commercially drawn filament, slack heat-set (quenched), amine-treated for 3 h.

are less affected, resulting in crack pattern in which the transverse cracks dominate (Fig. 13). These differences in etch patterns with respect to time of treatment were also observed in the case of the annealed samples but only after a longer duration of treatment. Different crack patterns developed on the surface of the filament at various time intervals indicate a point variation of local residual stress, resulting probably from a nonuniform distribution of the molecular orientation. On the other hand, the appearance of uniform cracks after prolonged etching suggests that the stress distribution may be more uniform and localized in the interior layers of the filament. This type of skin to core differences in the crack patterns was observed in the untreated control filaments also, but the skin is not as resistant to the chemical attack as in the case of the annealed filaments. From these results it can be inferred that heat treatment leads to redistribution of stress in the surface and interior layers of the filament to different extents, resulting in a skin to core variation.

Mechanical Deformation

Individual polyester filaments (400 denier) were strained to three different levels of tensile strain (40, 80, and 90% of the breaking strain) by cyclic tensile extension on an Instron Tensile Tester, for a sufficient number of

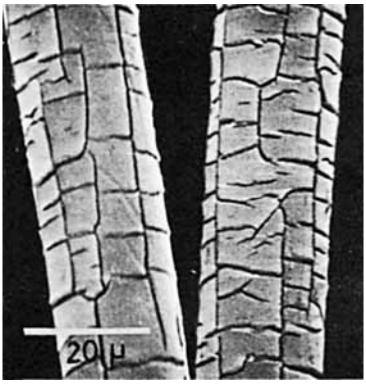

Fig. 12. Commercially drawn filament, slack heat-set (quenched), amine-treated for 4 h.

Fig. 13. Commercially drawn filament, slack heat-set (quenched), amine-treated for 5 h.

cycles until the stress strain curve stabilized to a constant shape for successive cycles. These highly stressed filaments, along with an unstressed control filament, were amine-etched under identical conditions. After amine etching they present a mosaic surface (Figures 14–17 having 0, 40, 80, and 90% extension, respectively) with a series of deep longitudinal and transverse cracks or canals with rather regular sized platelets or tiles in between making up the mosaic. As a result of cyclic tensile deformation to 40, 80, and 90% extension the depth and width of the transverse and longitudinal cracks become less with increasing strain level and also the sizes of the tiles or platelets in between get progressively reduced. The size of platelets became very regular and uniform after the specimen was strained to 90% (Fig. 17), whereas in the control sample (Fig. 14) the platelet size is rather irregular. In the case of the strained samples the platelet widths level off approximately at 6.0 μm. The average length of the platelets parallel to the fiber axis is found to reduce with increasing strain from 6.0 μm in the control (Fig. 14) to 3.4 μm in the highest stressed sample (Fig. 17). As the level of strain increases, the resistance of the material to amine etching also appears to progressively increase. In other words, it appears that as the orientation of the fiber progressively increases, the resistance of the fibre to amine etching also increases correspondingly.

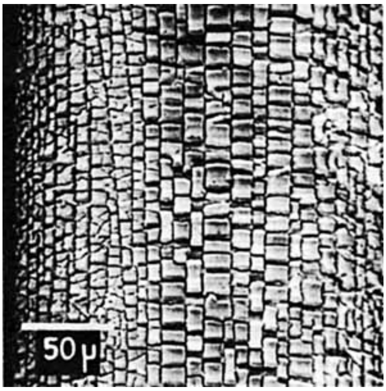

Fig. 14. Polyester monofilament, unstrained.

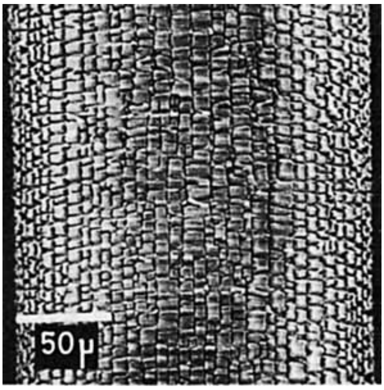

Fig. 15. Polyester monofilament, strained to 40% of the breaking strain.

In another experiment, these stressed filaments along with a control sample were plasma-etched in an air atmosphere and the corresponding weight losses were determined. The weight loss (%) of material decreases substantially, from a level of 15% for the control through 9.6 and 2.4 to 0.75% with increasing strain level or orientation for the 40%, 80%, and 90% strain levels, respectively. Thus, qualitatively, the resistance to amine etching and plasma etching appear to be closely correlated, and also promise to be useful techniques to examine the resistance of the fibres to degradation as well as to examine the extent of disorder. The geometry of the stress-cracking pattern appears to be affected by the level of the internal residual stress concentration.

DISCUSSION

After etching with a 40% aqueous methylamine solution the surfaces of poly(ethylene terephthalate) filaments exhibited a complex mosaic pattern of cracks. The morphology and geometry was found to change with varying orientation and thermal histories. This complexity in the crack geometry made if difficult to find a straight forward explanation for all the observed changes in the crack patterns. Earlier Sweet and Bell[9] explained the surface

Fig. 16. Polyester monofilament, strained to 80% of the breaking strain.

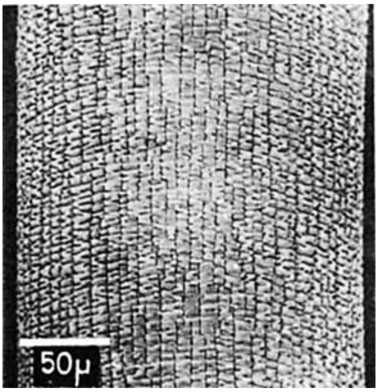

Fig. 17. Polyester monofilament, strained to 90% of the breaking strain.

cracking of PET caused by chemical degradation, on the basis of a biaxial stress field induced in the material during the drawing and annealing processes, and they believed that the resultant of the longitudinal and transverse stresses leads to a helical crack pattern.

An alternative explanation for the observed pattern can be found from Baker's work.[11] Baker creased drawn PET films, before subjecting them to amine etching, and found that etching preferentially took place along the creased portion of the film independent of whether the direction of creasing was parallel or perpendicular to the orientation axis. Baker therefore reasoned that, in drawn films certain organized volumes are produced due to the fabrication process and these volumes contained higher energy (high stress) than the neighboring regions, which rendered them more vulnerable to chemical attack and subsequent degradation.

Following Baker's and Sweet and Bell's line of reasoning, the observed transverse and longitudinal cracks might be explained on the basis of the existence of two types of domains in which the fabrication stresses are broadly concentrated to different extents, namely, high and low. It can than be postulated that the amine attacks these two types of domains at two different rates. It was also noticed in the case of oriented samples that during the initial stages of crack formation, the longitudinal cracks were found to form first followed by the transverse cracks. This difference in rate of attack of amine on these two types of domains indicated that the stress levels must be different in the two parpendicular directions. Baker had also earlier predicted the existence of two types of amorphous domains in PET based on amine etching studies.

The etch patterns obtained in our work can be explained on the basis of Prevorsek's[8] structural model.

Prevorsek's model suggested the presence of two types of amorphous domains: inter micro- or macrofibriller regions and intra micro- or macrofibriller regions. During drawing the micro- or macrofibrils slip past each other, and as a result the interfibrillar tie molecules are highly stressed, while the intrafibrillar tie chains are relatively less affected. It was also proposed by Prevorsek that near the surface the macrofibrils are frequently oriented with their wider surface area parallel to the fiber surface, and in

TABLE I
Semblance of Correlation between the Observed Etch Pattern and the Structural Modifications Due to Drawing and Heat-Setting

Sample polyester	Fabrication history	Structural modification	Experimental evidences	Observed macroscopic crack patterns
1	As-spun (undrawn) tow	Relatively Amorphous, unoriented, structureless	Birefringence very low—0.008; wide angle x-ray halo	No cracks, fiber surface etching uniform
2	As-spun slack heat-set at 200°C	Crystalline, randomly oriented	Sharp concentric rings in x-ray pattern; birefringence values vary from small negative to small positive value	Transverse cracks observed; these cracks are nonuniform and irregular across the specimen surface
3	As-spun tension heat-set at 200°C	Crystalline, transversely oriented	100 reflection observed on meridion in x-ray pattern; perpendicular orientation of crystallographic *C*-axis; high negative birefringence	Transverse cracks uniform across the fiber; regular disklike pattern; disc dimensions small
4	Commercial filament drawn at 80°C	Partially crystalline, crystalline regions oriented along fiber axis; microfibrillar structure, inter- and intrafibrillar tie molecules stressed	Oriented crystalline type, x-ray pattern; high positive birefringence	Both longitudinal and transverse cracks present number of longitudinal cracks are relatively less; irregular disclike morphology
5	Sample 4 tension heat-set at 200°C	Crystallinity increased, orientation improved; both inter- and intrafibrillar tie molecules are highly stressed; poor lateral cohesion between fibrils	Highly oriented crystalline x-ray pattern very positive birefringence; no length contraction	Large number of longitudinal and transverse cracks, laterally displaced brick or platelet mosaic pattern, brick size irregular

(*Continued*)

TABLE I (*Continued from the previous page.*)

Sample polyester	Fabrication history	Structural modification	Experimental evidences	Observed macroscopic crack patterns
6	Sample 4 slack heat-set at 200°C	Highly crystalline, high lateral order, slight disorientation of crystallites; the interfibrillar tie molecules are relaxed and the intrafibrillar tie molecules are stressed; high lateral cohesion between fibrils exists	High shrinkage; oriented crystalline, x-ray pattern; birefringence lower than sample 5	Almost no longitudinal cracks, fairly uniform and well separated transverse cracks; transverse cracks following smooth circular path; regular disklike morphology; disc dimensions large
7	Sample 4 Slack heat-set at 165°C	Crystallinity increased with respect to sample 4, orientation retained, inter- and intrafibrillar domain having stress concentration; poor lateral cohesion between fibrils	Comparatively low shrinkage; slight decrease in birefringence; oriented crystalline pattern	Both longitudinal as well as transverse cracks present; laterally displaced brick or platelet mosaic pattern, sizes irregular
8	Sample 4 Slack heat-set at 230°C	Crystallinity increased with respect to no. 6 slightly disoriented crystalline patterns; stress on the interfibrillar tie chain greatly relaxed; intrafibrillar tie chains are very highly stressed	Considerable decrease in birefringence slightly disoriented crystalline x-ray pattern and high length contraction	Longitudinal cracks are rarely observed; smooth circular and deep transverse cracks; regular disklike pattern, disk dimensions smaller than for sample no. 6

the domains between macrofibrils one often observes longitudinal cracks that separate clusters of several hundreds of microfibrils. During chemical etching, the highly stressed intermicrofibrillar matter is preferentially etched. As the etching continues, the intrafibrillar chains are attacked, and transverse cracks begin to appear. During tension annealing or quenching, where the specimen is not allowed to shrink, the interfibrillar tie molecules as well as the intrafibrillar chains are both subjected to a high level of stress due to the constraints imposed. This structure, when it is subsequently subjected to amine etching, presents a pattern having longitudinal and transverse cracks. During slack quenching, on the other hand, a considerable amount of shrinkage and chain folding occurs. This allows the interfibrillar tie molecules to relax, simultaneously putting stresses on the intrafibrillar chain molecules. This gives rise to an etch pattern that is dominated by transverse cracks. It is indeed difficult to visualize how such a simple structural model, which describes the fine structure at the angström level can predict the macroscopic crack formation in polyester. This is due largely to the fact that chemical etching is cumulative phenomenon, where the local variation in the stress levels can lead to a fairly large variation in the etch patterns within any specimen. However, it must be accepted that structural changes are still representative of the particular fabrication parameters or prehistory as well as subsequent mechanical or thermal deformations. Variations in parameters, such as temperature, time of cooling and tension during heat-setting have all been shown to produce characteristic changes in the observed crack patterns. Thus it is only logical to expect that the surface modifications taking place during these processes are somehow affecting the stress distribution and hence the crack pattern within the polymer material. Table I shows a semblance of correlation between the observed macroscopic crack pattern and the induced structural modifications due to the drawing and heat-setting processes.

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