

Poly(ethylene Terephthalate). II. Electron Microscopic Studies

K. G. MAYHAN, W. J. JAMES, and WOUTER BOSCH, *Departments of Chemical Engineering and Chemistry, University of Missouri, Rolla, Missouri*

Synopsis

Electron micrographs were made from replicas taken from the natural, argon-etched, and fractured surfaces, respectively, of the polymer before and after progressive stages of crystallization. The natural surface protrusions were identified as axialities and became more defined as the crystallization progressed. The argon-etched surfaces of highly crystallized polymer did reveal the crystalline nature of the polymer, but replicas of the slightly crystalline material gave patterns which cannot be quantitatively described at this time. It is thought that heat effects and/or interactions with the argon ions had an effect on the polymer surfaces. Replicas of the fractured amorphous samples revealed a typical conchoidal fracture, whereas those of the fractured surfaces of the highly crystalline samples gave tangible evidence that this polymer crystallized in a characteristic spherulitic manner.

Electron micrographs were made from poly(ethylene terephthalate) (PET) after various stages of crystallization in silicone oil. It was desired to obtain micrographs of the amorphous polymer, at the beginning of crystallization, and after appreciable crystallization had taken place. Micrographs were made of the polymer surface in its natural condition, after etching with argon ions, and of the surface resulting from fracturing the polymer normal to the machine direction.

The electron micrographs were obtained with a Philips Metalix Type 11980 electron microscope. Parlodion-chromium-shadowed carbon replicas were chosen for this work because they were relatively simple to prepare and also provided adequate detail. When the replicas are examined in the microscope the electrons pass more readily through the shaded areas than through areas which have been shadowed and therefore produce correspondingly denser images on photographic film. The contours of the original surfaces can be deduced from the shadows in the micrographs. Indentations on the replica surfaces produce internal shadows and correspond to protrusions on the original surface.

Natural Surface

Special treatment of the polymer surfaces was not required for this phase of the work. The natural surface of the cast amorphous PET before any

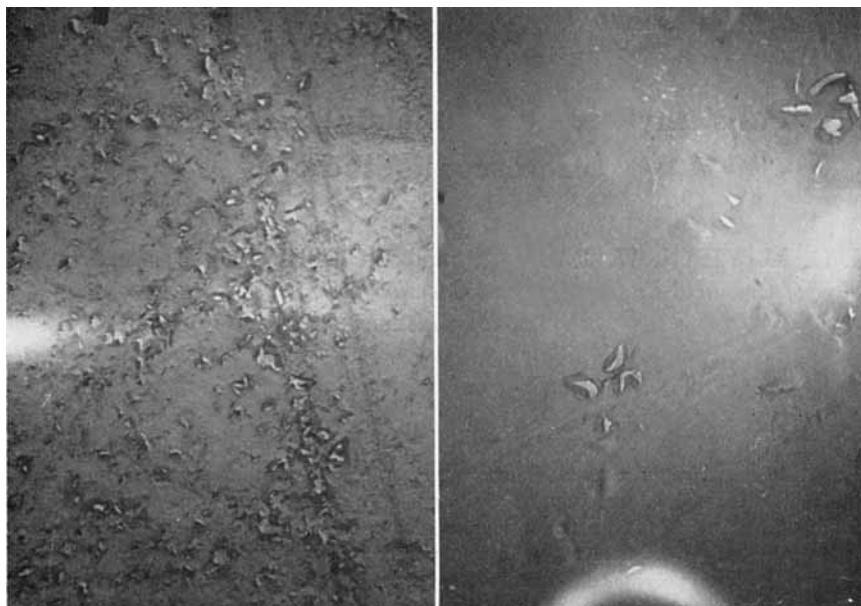


Fig. 1 (left). Amorphous PET, normal surface. 12,500 \times .

Fig. 2 (right). Normal surface of PET after 10% weight of crystallization; polymer crystallized at 100.0 $^{\circ}$ C. 12,500 \times .

treatment is shown in Figure 1. This micrograph reveals that the surface is composed of numerous shallow craters and minor protrusions. Some of the protrusions appear as though they could be the result of ruptures in the surface. The slightly diagonal lines running through the center (top to bottom) are thought to be imperfections in the surface of the casting drum.

A series of replicas was made of the polymer surfaces at different stages of the primary crystallization process. At this point the polymer has passed through the relaxation period and the initial crystallization patterns should be well established. Figure 2 shows a much smoother surface than was obtained for the amorphous samples. Practically all of the craters have disappeared, which indicates that the polymer has undergone a rearrangement or "hole-filling" process. The appearance of an entirely different type of surface protrusion is noted in this series. Replicas were then taken from samples which had been crystallized to a point representing the beginning of a secondary crystallization period, as shown in Figures 3 and 4 (112.5 and 119.5 $^{\circ}$ C., respectively). These micrographs show that the new protrusions are more pronounced and in many cases are arranged to form odd geometric patterns. A number of replicas were also examined from samples representing different stages of crystallization along both the primary and secondary processes. The overall surfaces remain smooth except for a number of fine ridges which occur regularly over most of the polymer. When the entire series of micrographs is shuffled and arranged

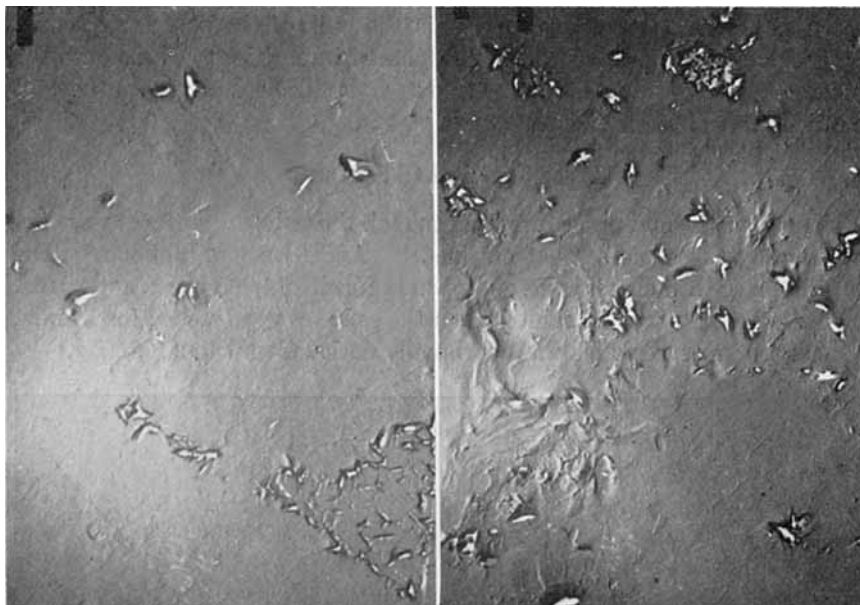


Fig. 3 (left). Normal surface of PET after 10% weight of crystallization; polymer crystallized at 112.5°C. 12,500 \times .

Fig. 4 (right). Normal surface of PET after 31% weight of crystallization; polymer crystallized at 119.5°C. 12,500 \times .

in a random order, it is not possible in most cases to distinguish the more crystalline samples from those possessing less crystallinity. For this reason no attempt was made to extract quantitative information from this series.

Recently, Bassett et al.¹ described the crystallization of polyethylene from xylene in concentrations up to 50%. The resulting lamellar crystallization products were found to be much more compact than single crystals grown from dilute solutions. These compact objects were referred to as axialites or hedrites, as outlined by Geil.² Axialites have been interpreted as being intermediates between single crystals and spherulites. There is a close similarity between the axialites reported by the above authors and the protrusions shown in Figures 3 and 4. It appears reasonable to assume that axialites grown from concentrated solutions begin to approach the environment prevailing in a bulk polymer. If axialites were free to grow on or near the surface of a bulk polymer they should then be even more compact. Although it is difficult to visualize the surface of a bulk polymer on a molecular level, it is nevertheless probable that a number of molecule chain ends would protrude from the surface at varying angles and that the population density of subsequent crystallization sites would vary over the surface. Under the proper conditions perhaps the chain segments and ends form small bundles of crystallites which in some characteristic manner resemble axialites. Another possibility is that during the initial stages of crystalli-

zation sufficient stresses develop within the bulk of the polymer to cause some of the low molecular weight products or impurities to exude onto the surface. These products are then free to crystallize readily, since they are relatively free of steric effects.

Argon Ion-Etched Surfaces

The apparatus and procedure used to etch the polymer surfaces were approximately the same as that outlined by Anderson and Holland.³ The glow discharge attachment was equipped to furnish 14,000 v. a.c. and 25 ma. Consistent results were obtained when the samples were etched for 15 min. at an argon pressure which was continually varied from 1 to 2 mm. Hg.

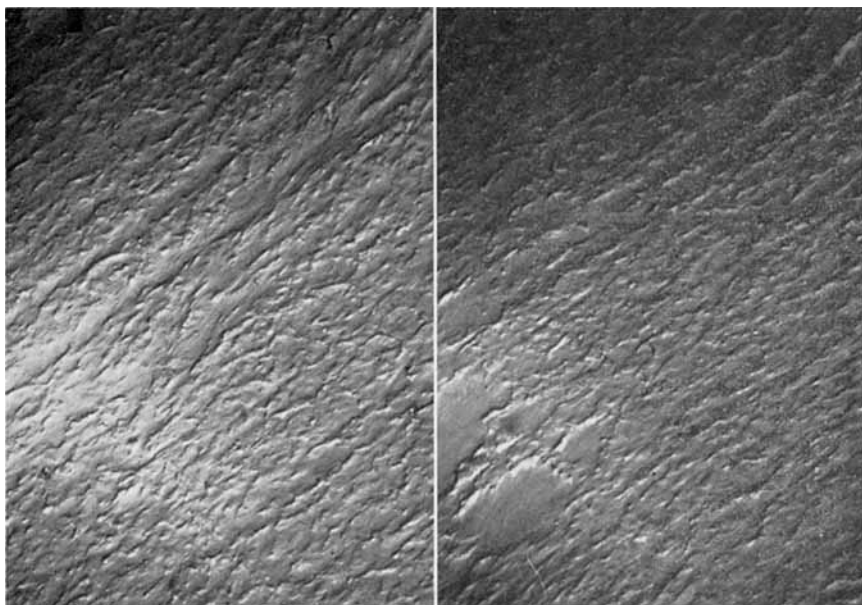


Fig. 5 (left). Argon-etched surface of PET after 31% weight of crystallization; polymer crystallized at 119.5°C. 12,500 \times .

Fig. 6 (right). Different area of same specimen as in Fig. 5.

The same samples used to make the micrographs for the normal surfaces were etched with argon ions and replicas were then taken from these surfaces. Figures 5 and 6 show the etched surface of the sample crystallized at 119.6°C. These micrographs reveal elongated fibrils with some degree of ordering. This is somewhat surprising, since a completely random pattern was expected. Some of the fibrils appear to be twisted in a helical or ropelike configuration and extend over appreciable molecular distances. Anderson and Holland pointed out that the true etching mechanism is not fully understood and that no definite conclusions can be drawn as to why such rope-shaped units are exposed during the etching of a synthetic polymer. Although the structural significance of their origin may not be

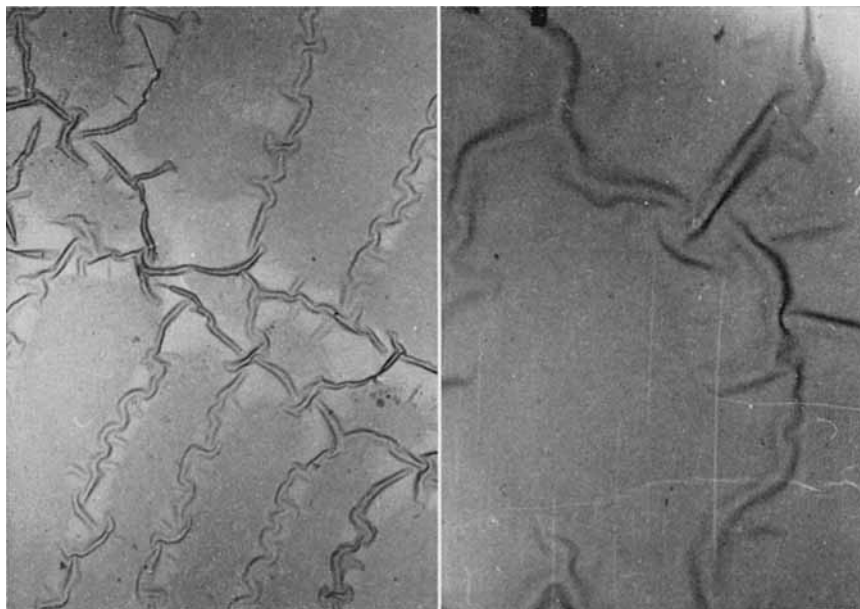


Fig. 7 (left). Argon-etched surface of PET after 10% weight of crystallization; polymer crystallized at 100.0°C. 5,000 \times .

Fig. 8 (right). Argon-etched surface of PET after 10% weight of crystallization. 12,500 \times .

known, the etch units may well have some relationship to the chain folding observed in single crystals. Patterns similar to those shown in Figures 5 and 6 were reported by Scott⁴ for orientation split samples of PET that had been partially degraded with *n*-propylamine prior to taking surface replicas. It could not be definitely established that the bumps observed were crystallites; however, the authors did not find this granularity in amorphous specimens.

The etch patterns obtained from samples representing the beginning of the first crystallization zone are strikingly different as shown in Figures 7 and 8. The unusual regularity and geometry of these patterns cannot be fully explained. Several separate replicas were made from different samples on different days, which tends to rule out the possibility that these effects are the result of the techniques employed. It cannot be stated with any degree of certainty that these etch patterns represent the true nature at this stage in the crystallization process. However, since the polymer is only slightly crystalline, there is a possibility that impingement of the argon ions on the polymer surface causes unusual effects, such as localized heating, which show up on the replicas.

Fractured Surfaces

Since the polymer films were thin it was necessary to use a composite of 15 strips in order to have an adequate replica surface after fracturing. The strips of polymer were held firmly between two machined Bakelite blocks

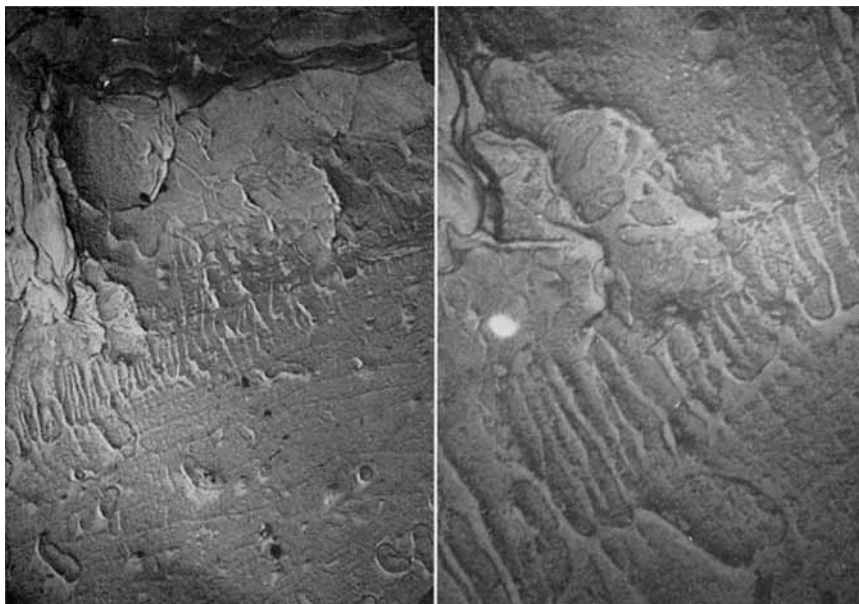


Fig. 9 (left). Fracture surface of amorphous PET. 5,000 \times .
Fig. 10 (right). Fracture surface of amorphous PET. 12,500 \times .



Fig. 11 (left). Fracture surface of PET after 43% weight of crystallization; polymer crystallized at 200°C. 5,000 \times .
Fig. 12 (right). Fracture surface of PET after 43% weight of crystallization; polymer crystallized at 200°C. 12,500 \times .

and immersed in liquid nitrogen for several minutes to embrittle the samples. After removal from the liquid nitrogen the samples were fractured as close to the blocks as possible. The assembly was allowed to warm to room temperature in a desiccator before making replicas. Samples of the amorphous polymer and of the polymer which was crystallized at 200°C. were fractured perpendicular to the machine direction. These extremes were selected in order to show the maximum differences in structure.

Electron micrographs of the amorphous fracture are presented in Figures 9 and 10. The replicas reveal the expected conchoidal fracture which is typical of an amorphous material. The difference in the appearance of

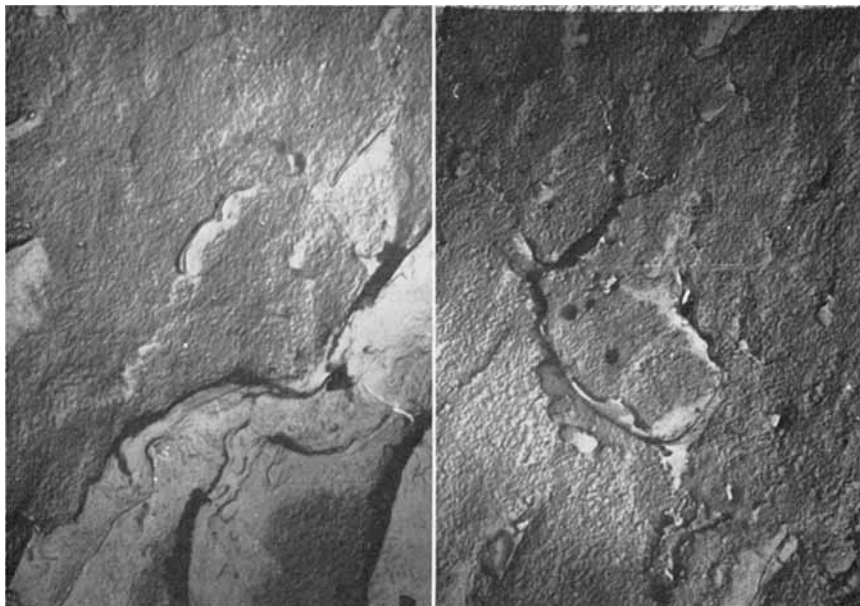


Fig. 13 (left). Different area of same specimen as in Fig. 12.

Fig. 14 (right). Different area of same specimen as in Fig. 12.

various parts of the fracture raises the interesting speculation that perhaps these could be the result of localized short-range orientation between segments of chains that develop during the initial quenching of the polymer.

Electron micrographs of the crystalline fracture are shown in Figures 11-14. Referring to Figure 11, the structure located near the center of the lower third appears to be the central portion of a large spherulite which is oriented at a slight angle to the surface. The structures on both sides are thought to be spherulites whose lamella are more or less normal to the fracture surface. A closer look at this area (Fig. 12) reveals the presence of small spherulites parallel to the fracture. Several other parts of spherulites can also be seen in the upper part of this micrograph and small spherulites can also be seen in the interstices between the large spherulites.

Figures 13 and 14 show enlarged sections of the lower portion of Figure 11. These areas appear to be composed of growths whose lamellae run parallel to the surface, which may be an indication of chain folding. The fact that PET is capable of chain folding has recently been proven by Hirai.⁵ He has grown single crystals of PET from dilute solutions of diphenyl ether and dimethyl phthalate. The single crystals were parallelepipeds and were thickened by spiral growths with screw dislocations at their centers. The platelets making up the crystals had a thickness of 100 Å and a width of 300 Å. The habit of the crystals was strongly dependent upon crystallization conditions, which in the bulk polymer may also control the degree of chain folding.

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Résumé

Des micrographies électroniques ont été faites au départ des répliques prises sur des surfaces d'un polymère, naturelles, traitées au moyen d'argon, et brisées, et cela avant et après les étapes successives de la cristallisation. Les aspérités naturelles de la surface sont des axialites et deviennent plus prononcées quand la cristallisation progresse. Les surfaces traitées à l'argon d'un polymère hautement cristallin montrent la nature cristalline d'un polymère, mais les répliques d'un matériau faiblement cristallin fournissent des diagrammes qui ne peuvent pas être interprétés quantitativement en ce moment. On croit que des effets thermiques et/ou des interactions avec les ions d'argon exercent un effet sur les surfaces du polymère. Les répliques des échantillons amorphes fracturés montrent une brisure typique conchoïde alors que celle des surfaces brisées d'échantillons hautement cristallins montrent que ce polymère cristallise de manière à former des sphérolites caractéristiques.

Zusammenfassung

Elektronenmikroskopische Replikaufnahmen wurden von der natürlichen, Argon-geätzten bzw. Bruchoberfläche des Polymeren vor und nach fortschreitenden Kristallisationsstadien des Polymeren gemacht. Die natürlichen Oberflächenausbuchtungen wurden als axial identifiziert und zeigten sich beim Kristallisationsfortschreiten als besser definiert. Die Argon-geätzten Oberflächen eines hochgradig kristallisierten Polymeren liessen die kristalline Natur des Polymeren erkennen, Replikas des schwachkristallinen Materials lieferten jedoch Bilder, welche derzeit noch nicht quantitativ beschrieben werden können. Es wird angenommen, dass Hitzeeffekte und Wechselwirkung mit den Argonionen einen Einfluss auf die Polymeroberfläche besitzen. Replikas der amorphen Bruchproben zeigten einen typisch muscheligen Bruch, während diejenigen der Bruchoberflächen von hochgradig kristallinen Proben die charakteristische sphärolithische Kristallisation dieses Polymeren erkennen liessen.

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