

## SEM Studies of Cold-Rolled Spherulitic Films of Poly(tetramethylene Terephthalate)

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### Synopsis

By using the method of scanning electron microscopy, a visual study was made of the macro-deformation of spherulitic deformation during the cold rolling of poly(ethylene terephthalate) (PET) and poly(tetramethylene terephthalate) (PTMT). By rolling solution cast films to different extension ratios, it was found that the surface material (nearest the rollers) appeared to deform first by the shearing action. With higher extension, the material toward the core of the film began to deform. In all cases, the deformation process tended to flatten the spherulites yet, in general, the spherulitic boundaries were maintained. It was noted that the same general behavior was observed for both PET and PTMT.

### INTRODUCTION

Over the past several years, a number of investigations have been directed at learning how a semicrystalline spherulitic polymer deforms during a biaxial deformation,<sup>1-9</sup> one example being a cold rolling process.<sup>5-8</sup> In general, these studies have primarily focused on the measurement of the orientation of the crystalline phase by utilizing wide- and small-angle x-ray diffraction analysis.<sup>6,8</sup> While speculation has been made about the transformation of spherulitic to microfibrillar morphology, the number of studies directed specifically at the superstructure level has been limited. Those that have investigated this aspect have used small-angle light scattering (SALS) as a characterization tool; however, this method has limitations in that for biaxial deformations, the effects of birefringence can hinder the interpretation of the observed scattering.<sup>5</sup> Furthermore, it has been recently shown by direct microscopy investigations carried out in conjunction with SALS studies that the latter method only provides partial information about the actual deformation behavior of the superstructure.<sup>10,11</sup>

While the SALS method has helped elucidate the deformation behavior of the superstructure, it is desirable to investigate this directly via microscopy methods. Because all past studies have been carried out with molded materials, direct observation has not been easy due to the fact that compression molding results in a surface (replication of the mold surface) that hinders investigation by electron microscopy. Optical microscopy

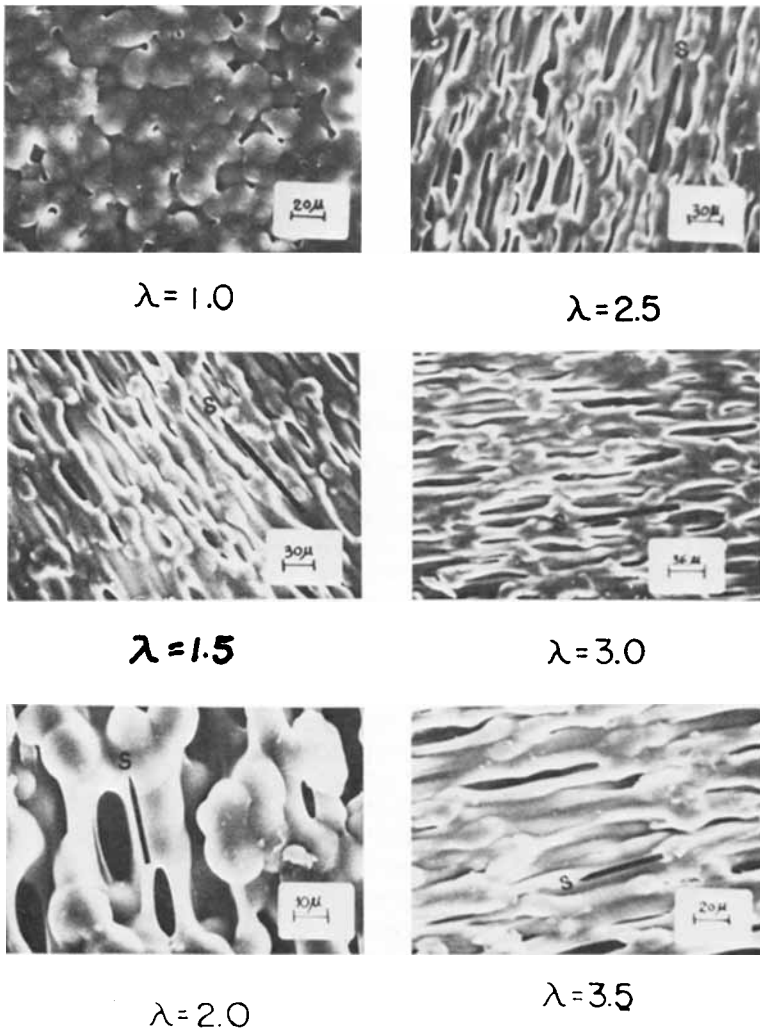


Fig. 1. Series of SEM micrographs showing how the spherulitic texture of PET deforms as a function of extension ratio. Crystallinity of the film was  $\sim 40\%$  as determined by flotation. Stretch direction is indicated by black arrow.

is also limited by the biaxial nature of the rolling deformation, the result being that the birefringence effects limit direct observation of the separate spherulites.

Recently, we have succeeded in solution casting highly spherulitic films of segmented urethanes, poly(ethylene terephthalate) (PET), and poly(tetramethylene terephthalate) (PTMT). Using scanning electron microscopy (SEM), direct study of the spherulitic structure has been carried out. This same characterizational method was also found suitable to follow the uniaxial deformation of this superstructure.<sup>10,11</sup> Figure 1a illustrates

one case of the uniaxial deformation behavior of a PET film cast from trifluoroacetic acid.<sup>11</sup> Poly(tetramethylene terephthalate) also displayed similar behavior.<sup>11</sup>

While the solution-cast films possess some interspherulitic porosity, the degree of crystallinity can be made comparable to molded materials, and therefore the general deformation behavior experienced by the cast films should be quite representative of spherulites within molded material. With this assumption as our premise, it is the intention of this paper to directly demonstrate, via SEM, how the spherulitic texture of PTMT transforms under a cold-rolling deformation. While this method has a principal deformation axis (along the rolling axes), this process should also be expected to be somewhat representative of some other biaxial deformation processes used commercially.

## EXPERIMENTAL

**Film Preparation.** Films of PTMT were solution cast from trifluoroacetic acid on a glass surface. It was noted that the casting condition of evaporation rate and temperature influenced the morphology to some degree. The PTMT material was of commercial grade (Tennite-Tennessee Eastman). The film thickness was purposely kept thin ( $\sim 2$  mils) to facilitate the microscopy studies.

**Rolling.** The cast films were cold rolled at 26°C on a motorized laboratory roller described elsewhere.<sup>5</sup>

**Electron Microscopy.** All SEM studies were carried out with a Joelco scanning electron microscope.

## RESULTS AND DISCUSSION

Figures 2a–2d show SEM micrographs of films undeformed and rolled to low extension ratios  $\lambda$ . It should be stated that the initial three-dimensional, ball-like spherulites gave a characteristic strong Maltese pattern between crossed polars in an optical microscope.

From the other micrographs in Figures 2a–2d, a number of interesting observations can be quickly noted. First, the deformation behavior results in localized yielding at very low extensions. That is, the shearing action of the rollers at the surface results in localized deformation only at the regions where the uppermost (or lowermost) spherulites within the film have contacted the roller surface (see Fig. 2b). This is particularly obvious when the sample is tilted within the SEM as is illustrated in Figure 2c, where one can clearly see the distinct flattening of the spherulitic surfaces caused by rolling; yet the underlying portions of the same spherulite, or those spherulites lying below, are not deformed at all. This nonuniform deformation behavior with respect to the thickness direction has been indicated by earlier studies on cold-rolled polyethylene,<sup>5,7,9</sup> but this SEM study directly verifies many of the earlier speculations.

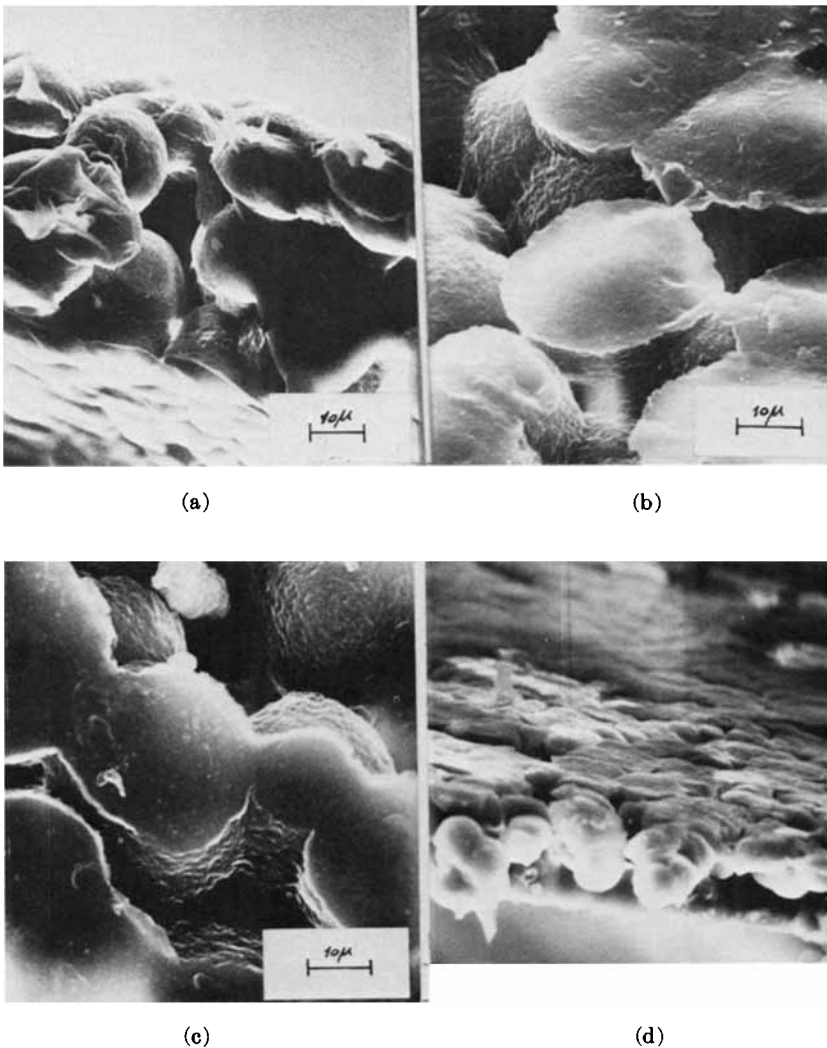


Fig. 2. SEM micrographs of PTMT spherulitic films: (a) unrolled; (b) rolled to  $\lambda = 1.1$ ; (c) as (b) but tilted view to show undeformed underlying spherulitic material; (d) tilted view of film rolled to  $\lambda = 1.15$ , showing flattening of the spherulites nearest the surfaces.

As the extension ratio increases, the degree of spherulite flattening increases until all spherulites throughout the thickness direction have displayed deformation (Figs. 3a and 3b). Although thin films were used in this investigation, one can suspect in thicker "bulk" materials that, even at extension ratios well above unity, one may well have a parabolic profile in spherulitic deformation, with the maximum deformation being greatest at the surfaces as a result of the maximum shear forces induced by the rollers.

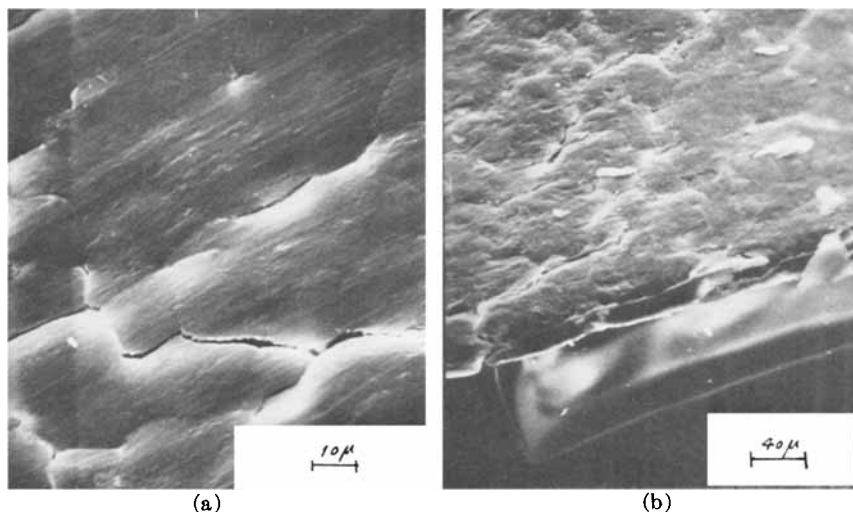


Fig. 3. SEM micrographs of cold-rolled PTMT spherulitic films: (a)  $\lambda = 1.3$ ; (b)  $\lambda = 1.8$

From Figures 2 and 3, it is clearly evident that, under rolling conditions, the spherulitic deformation is biaxial and leads to the transformation of three-dimensional spheres to that of flattened disks with some indication that the disks are partially elliptical, with the principal axis being along the roll direction. From Figure 3a, it is apparent that during the flattening process, the individual spherulites retain their individual boundaries rather than completely "coalesce" with neighboring spherulites. In some cases, a given spherulite may show partial recovery, thereby separating from its flattened neighbors (see Fig. 4). At higher extensions ( $\lambda > 2.0$ ), the spherulitic boundaries were also still obvious although a more uniform surface was evident. It was also found that upon annealing the rolled films at  $150^{\circ}\text{C}$ , some retraction occurred ( $\sim 10\text{--}15\%$ ), but the recovery was not considerable. This lack of large retraction upon annealing is in contrast to observations of our own<sup>5</sup> and others<sup>9</sup> on cold-rolled bulk samples of spherulitic polyethylene. Not having measured the recoverability of cold-rolled bulk PTMT samples, we can only speculate that this low degree of recovery of the PTMT material may be related to the fact that the spherulites in our films are less interconnected than probably occurs in bulk crystallized samples. Even so, one might still have expected more retraction of individual spherulites. Further work is clearly necessary to understand these differences and may require fine structure studies of the spherulitic entities.

While SALS and optical microscopy studies were carried out simultaneously with the SEM study given here, these latter two methods did not provide fruitful data owing to birefringence effects.

Fine structure studies have not been made of this material; however, one might first approximate the biaxial deformation behavior of a rolled

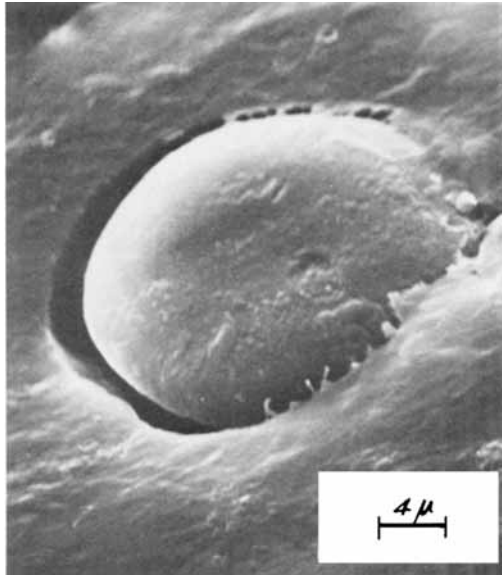


Fig. 4. SEM micrograph showing a region in a cold-rolled PTMT film where one spherulite has displayed "recovery" following an initial rolling to  $\lambda = 1.3$ .

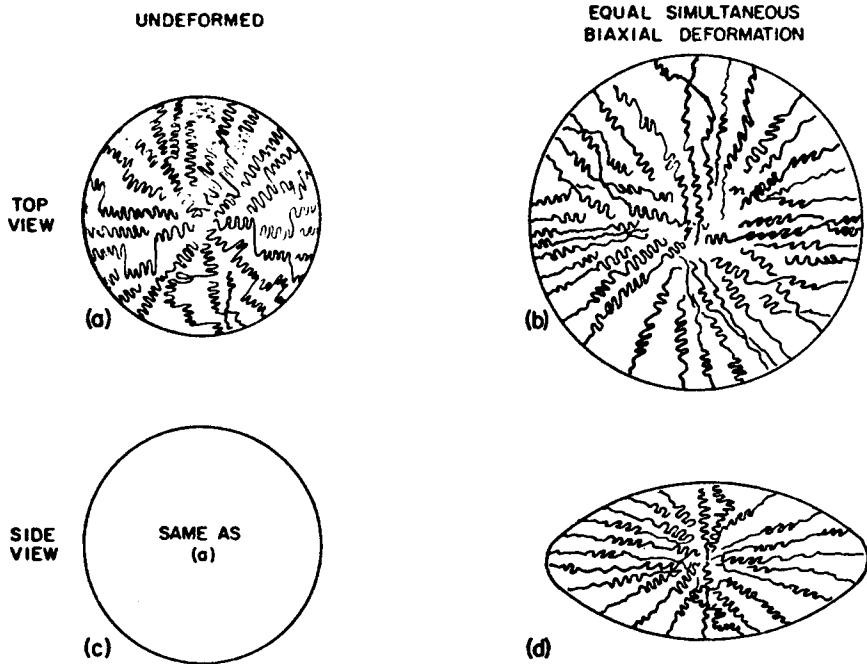


Fig. 5. Simple model illustrating how a spherulite may transform in biaxial deformation. This scheme is based on equal, simultaneous biaxial deformation as would occur in a compression experiment.

spherulite by the simple model given in Figure 5. This model, which attempts to illustrate an equal, simultaneous biaxial deformation suggests the partial unfolding or break-up of folded-chain lamellar structure which is not initially highly perfected in this material as noted by small-angle x-ray diffraction. This model is also based on the earlier rolling studies of cold-rolled polyethylene mentioned earlier. While this oversimplified model concerns the intraspherulitic material, it is obvious that the behavior of the interspherulitic regions will be very important in affecting the extensibility and final morphology.

In closing, it may be mentioned that similar rolling studies on spherulitic PET displayed quite analogous deformation behavior to that found for PTMT.

*Note added in proof:* Both quenched and annealed bulk crystallized films have since been rolled to  $\lambda \sim 2.0$  and subsequently heat treated at 150°C. Both of these films also displayed a recovery of only  $\sim 16\%$ .

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