

MORPHOLOGICAL STUDIES OF PET FILMS WITH DIFFERENT CRYSTALLIZATION RATE IN DRAWING PROCESSES*

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ABSTRACT

Morphological changes during stretching of two PET samples (S and T) with different crystallization rate have been studied by means of SALS, solvent etching and polarizing microscope techniques. Results show that under the same drawing conditions larger and more perfect rod-like and spherulitic superstructures were formed more easily in the sample with higher crystallization rate (sample S). The amount of less compact regions which may be easily attacked by the vapor of allyl amine decreases more rapidly in sample S than in sample T during stretching, and these regions are more randomly distributed in sample T especially at low elongations. The difference of the two samples in morphological changes is coincident with their difference in tensile behavior.

INTRODUCTION

It has been found that crystallization rate is a very important factor affecting the tensile behavior of polyethylene terephthalate (PET)^[1]. The difference in tensile behavior is obvious for samples of almost the same molecular weight, molecular weight distribution, density and glass transition temperature, but quite different crystallization rate. The sample of low crystallization rate always shows larger area ratio at break and lower stress during stretching in both uniaxial and biaxial experiments. This has been supposed to be the results of the influence of crystallization and orientation of the samples on their further deformation.

In this work small angle light scattering, solvent etching and polarizing microscope techniques are used to study the morphological changes of two PET samples with different crystallization rate during uniaxial and biaxial stretching.

EXPERIMENTAL

Two samples, S and T, were used, and sample S has a higher crystallization rate than sample T. Their basic characteristics have been given in [1]. Film specimens were stretched with a 2-axes stretching tester. Both uniaxial and biaxial stretchings are performed at temperatures of 90, 100 and 110°C with various strain rates. The simultaneous and sequential modes are included for biaxial stretchings. In the case of sequential biaxial stretching the film was first stretched to a draw ratio of three in one direction and then was drawn immediately in the

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second direction perpendicular to the first one. A spray device was installed in the 2-axis tester^[2], so the specimens could be quenched to low temperatures very quickly by spraying liquid nitrogen, and structural changes of the specimens after stretching could be avoided.

SALS observations were performed with a He-Ne gas laser ($\lambda=6328\text{\AA}$). The scattering patterns were recorded photographically. The effect of birefringence on scattering was minimized by means of rotating the specimen around the incident beam to a proper position.

Etching treatment of PET specimens was carried out in the atmosphere of saturated allyl amine vapor at room temperature for 15 hours.

RESULTS AND DISCUSSION

The crystal morphology of the two samples stretched under various conditions has been studied by SALS method. Figs. 1 and 2 are H_V scattering patterns of uniaxially stretched films. Fig. 1 shows that under the given conditions sample T does not give obvious H_V scattering, while a four-leaf clover pattern without intensity maximum and extended almost in the $\pm 45^\circ$ directions is observed for sample S. It means that some anisotropic rod-like structures of wavelength dimensions are formed in sample S and their orientation within the film plane is almost random. In the case of very high strain rate both samples give rather complicated scattering patterns (Fig. 2) which might be the superposition of the contributions of different scattering entities within these samples. The depressed four-leaf clover scattering pattern can be attributed to spherulitic structures, as intensity maximum is observed with increasing scattering angle. These spherulites might be deformed and oriented in the stretching

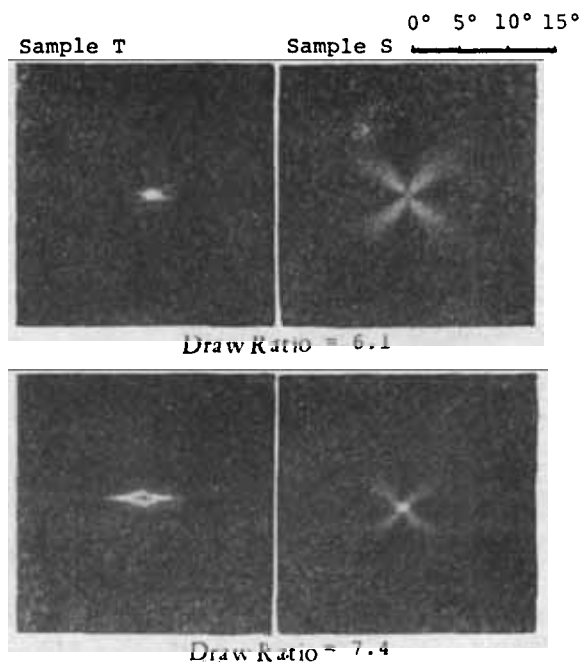


Fig. 1 SALS H_V patterns of PET samples uniaxially stretched at 110°C (strain rate 40 min^{-1}). The stretching direction is vertical.

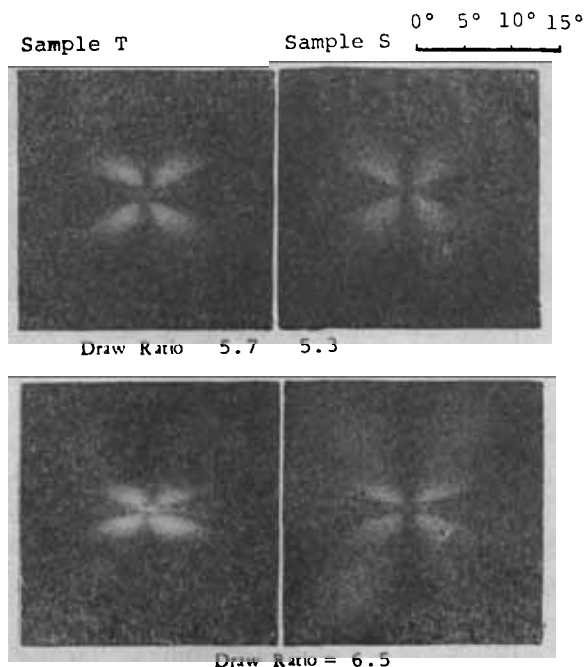


Fig. 2 SALS H_v patterns of PET samples uniaxially stretched at 110°C (strain rate 211.6 min^{-1})
The stretching direction is vertical.

direction, because their scattering patterns are more or less inclined to the direction of equator which is perpendicular to the stretching direction in this case. Besides, a group of stripe-like scattering extended almost in the direction of equator implies the existence of anisotropic rod-like structures highly oriented in the stretching direction. In the case of specimens drawn with very high draw ratio scatterings at large scattering angle and extended in the stretching direction can be observed. It is probably the contribution of some rod-like structures oriented in the direction perpendicular to the stretching direction.

Misra and Stein^[3] have shown the SALS patterns of PET films uniaxially stretched at 80°C . At low elongations scattering of rod-like structure oriented in the direction perpendicular to the stretching direction was observed. With increasing draw ratio they found scattering patterns of deformed spherulites and then highly oriented rods or fibrils. Both the spherulites and fibrils were oriented in the stretching direction. Some differences between the results of Misra and Stein and that of ours is possibly due to the fact that the film specimen of Misra and Stein could contract freely in the lateral directions during stretching, but in our experiments the film was constrained in the width direction, and only its thickness was changed with elongation.

In Fig 3, H_v scattering patterns are given for the specimens of two samples after simultaneous biaxial stretching. The scattering of sample T is too weak to be detected. The patterns of sample S are more complicated in this case, scatterings extended in different directions can be observed from different places of the same film specimen. It indicated the structural nonuniformity within these films after stretching.

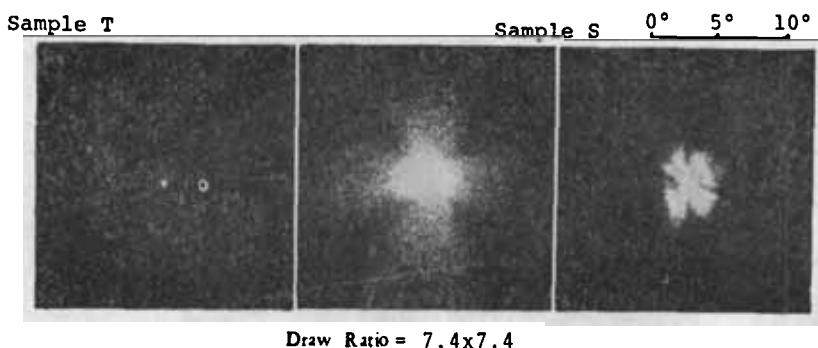


Fig. 3 SALS H_v patterns of PET samples biaxially stretched (simultaneously) at 100°C
The strain rate of both directions is 8.4 min^{-1} .

Results of sequential biaxial stretching are shown in Fig. 4. No obvious H_v scattering has been observed for sample T. The scattering pattern of sample S suggests a superposition of scatterings resulted from two groups of rod-like anisotropic structures. They are oriented in the two stretching directions respectively, and the group oriented in the second stretching direction has higher degree of orientation than the other one.

Etching is a useful technique in morphological studies. Etching agents like *n*-propyl amine, methylamine, chlorophenol and water have been used for PET samples^[4-8]. During etching treatment regions of low crystallinity and that not compactly packed are more easily to be attacked.

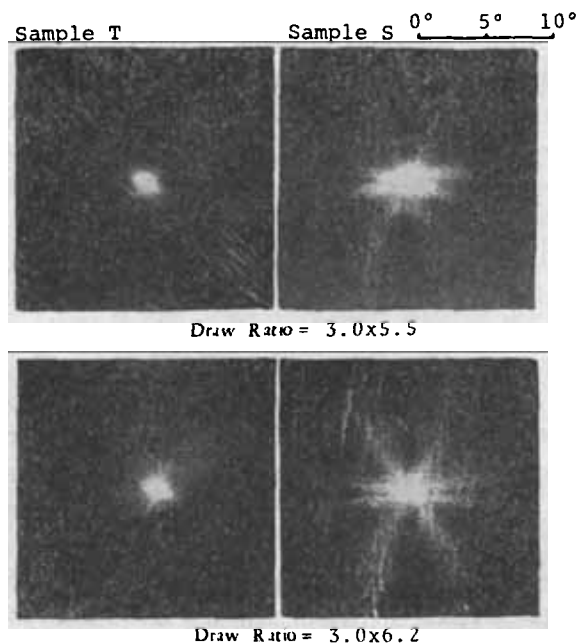


Fig. 4 SALS H_v patterns of PET samples biaxially stretched (sequentially) at 100°C
The strain rates are 22.9 and 9.9 min^{-1} for first and second stretchings respectively.
The direction of the second stretching is vertical.

Thus, it's possible to get information about the distribution of domains of different degrees of order by means of proper selecting etching agent and conditions. Fig. 5 shows micrographs of uniaxially stretched specimens treated with allyl amine. The stretching direction makes an angle of about 45° with the directions of crossed polaroids which are vertical and horizontal in Fig. 5. Dark bands of about 10–20 microns in width are observed on a bright background, and the latter is believed to be the evidence of macroscopic orientation within these drawn specimens. At higher elongation these dark bands are much narrower and almost parallel to the direction of stretching. With decreasing elongation the dark bands become wider and randomly curved without preferential orientation. It should be noted that under the same conditions specimens of sample T always gave wider and less oriented dark bands than that of sample S. It implies that T specimens remain more less oriented regions than S specimens during stretching, and their distribution is more random. These dark band regions observed under polarizing microscope are not isotropic, but are less oriented than their surroundings. As film specimens did not show obvious nonuniformity in orientation before etching, so the observed micrographs might indicate some decrease of molecular orientation in the regions attacked by allyl amine.

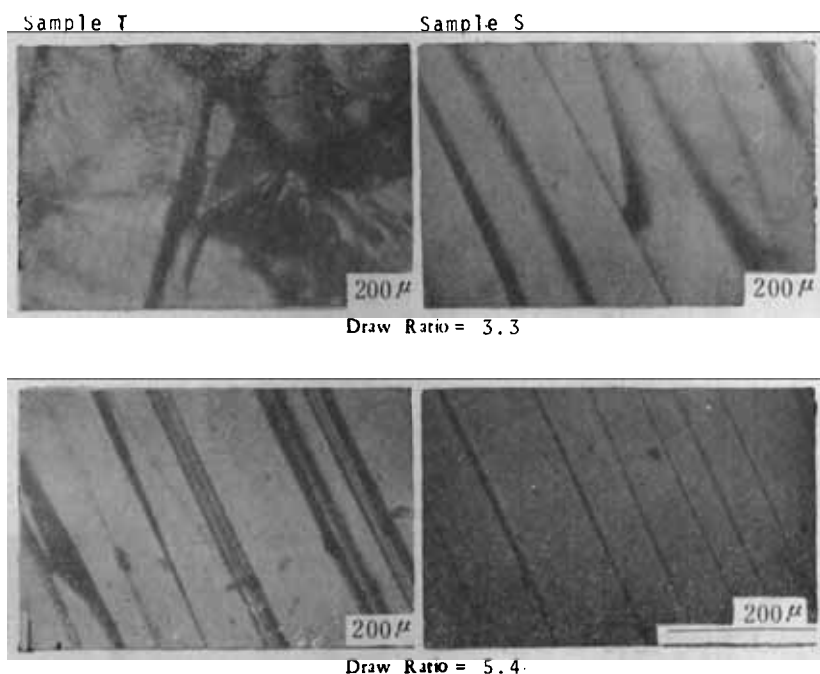


Fig. 5 Polarizing micrographs of PET samples uniaxially stretched at 100°C (strain rate 23.3 min^{-1}) and treated by the vapor of allyl amine. The stretching direction of the samples makes an angle of about 45° with the directions of polarizer and analyzer.

In the case of sequential biaxial stretching the dark bands observed after etching are very thin and sometimes become uncontinual dotted lines (Fig. 6). Baker^[6] has studied the etching of PET by *n*-propyl amine and found similar results as shown in Fig. 5 for uniaxially stretched specimens and "brick wall" structure for sequential biaxially stretched ones which is similar

to what we have obtained for specimens of lower elongation and strain rate (Fig. 7). Besides, Hinrichsen et al.^[9] have observed similar patterns for unetched specimens after biaxial sequential stretching.

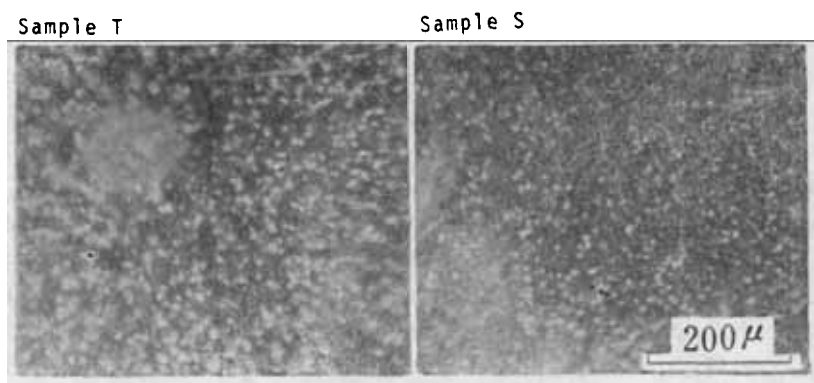


Fig. 6 Polarizing micrographs of PET samples after biaxial sequential stretching at 100°C (strain rates: 32.7 min⁻¹/9.86 min⁻¹, draw ratio 3.0/3.7) and then treated by the vapor of allyl amine. The stretching directions make an angle of about 45° with the directions of polarizer and analyzer.

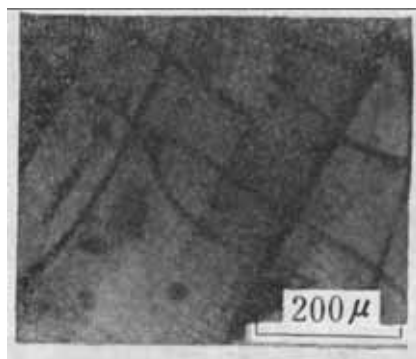


Fig. 7 Polarizing micrograph of sample T after biaxial sequential stretching at 100°C (strain rates 32.7 min⁻¹/5.15 min⁻¹, draw ratios 3.0/2.7) and then treated by the vapor of allyl amine. The stretching directions make an angle of about 45° with the directions of polarizer and analyzer.

Fig. 8 gives the micrographs of specimens after simultaneous biaxial stretching. The two stretching directions are parallel to the directions of crossed polarizers respectively. Regions attacked by allyl amine can be observed as bright spots randomly distributed on a dark background. Usually the bright spots of T specimens cover a larger area fraction than those of S specimens.

The observed differences between the morphological changes of the two samples stretched under different temperatures (90°C, 100°C and 110°C) are similar. In a previous paper^[10] we have studied the difference between the same two samples in degree of crystallization and orientation during stretching. Results of all these studies indicate that the difference in structure changes of sample S and sample T during stretching is evident. More structural

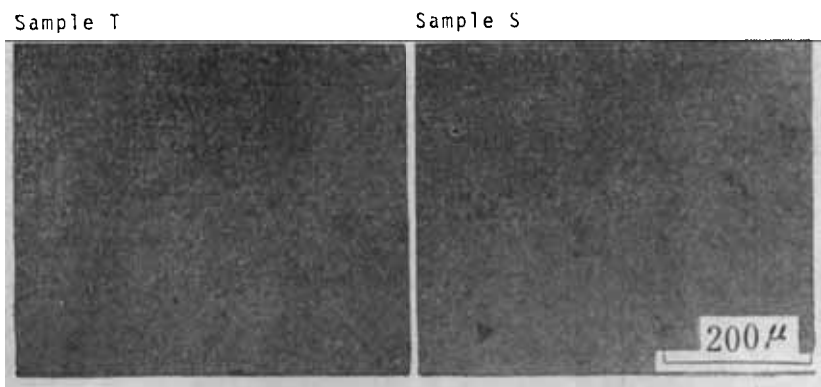


Fig. 8 Polarizing micrographs of PET samples after biaxial simultaneous stretching at 110°C (strain rate 8.38 min^{-1} , draw ratio 7.4 for both directions) and then treated by the vapor of allyl amine. The stretching directions are parallel to the directions of polarizer and analyzer.

changes are observed for sample S, which includes higher crystallinity, easier to form large crystalline superstructures, more ordering of the non-crystalline state and better molecular orientation. It can be supposed that these phenomena are just the results of the different crystallization behavior of the two samples. On the other hand, the higher ability of sample S in structure formation or ordering will be expected to reduce its deformability and to cause a high stress during deformation. Thus it seems reasonable to conclude that the crystallization rate is an important and independent factor which affects the tensile behavior of amorphous polyethylene terephthalate.

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