

MORPHOLOGY AND PROPERTIES OF SEGMENTED BLOCK COPOLY (ETHER ESTER)S FIBERS MADE BY GEL-DRAWING

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ABSTRACT

The segmented block copoly(ether ester)s were swollen by tetrahydrofuran (THF) at 60°C and formed fibers by gel-drawing. The morphology and properties of these fibers were investigated by optical and electron microscopes, X-ray diffraction, DSC and an Instron test machine. The band structure morphology was observed in the gel-drawing fibers. The molecular chains were highly oriented as proved by X-ray diffraction data. The results indicated that the gel-drawing fibers have much better mechanical properties than those obtained otherwise. The tensile strength and elastic modulus were found to be 280 MPa and 802 MPa, respectively. The mechanism of the gel-drawing process was also discussed.

INTRODUCTION

In recent years it has attracted considerable interests to get ultra-highly oriented materials. Some effective processing methods have been developed. The method of the gel spinning/hot drawing has been investigated by Pennings et al.^[1-3]. It is interesting to note that this method essentially amounts to the stretching of the entanglement network formed a semi-dilute solution of ultra high molecular weight polyethylene and finally leads to the formation of highly oriented and highly crystalline fibrillar structure. The segmented block copoly(ether ester)s, "HYTREL", based on polybutylene terephthalate (PBT) as the hard segments and polyoxytetramethylene (PTMO) as the soft segments, are typical examples of thermoplastic elastomers. The hard segments are capable of undergoing intermolecular association or crystallization to form physically crosslinked network structures.

Yanai^[4] has studied the effect of swelling on the stress-strain relationships of crystallizable crosslinking elastomer. It indicated that the drawing stress of the swollen sample is lower than that of the unswollen sample. We have investigated the swelling behavior of segmented block copoly(ether ester)s with a set of organic solvents at different temperatures. The fibers drawn from gel of PBT-PTMO were obtained and the morphology and mechanical properties of the fibers of the PBT-PTMO made by gel-drawing are reported.

EXPERIMENTAL

1. Material and sample preparation

PBT-PTMO with a 0.72 weight fraction of the hard segments and an average degree of

polymerization of 14 for the soft segments, was used in our investigation. The plates of thickness 0.4 mm were prepared by melt pressing the granular PBT-PTMO at a temperature of 30°C above the melting point of the polymer and under the pressure of 100 Pa in nitrogen atmosphere. Subsequently the plates were cooled in ice water. The fine ribbon samples (0.4 × 0.4 × 60 mm) were obtained by cutting the plates with a steel knife.

The ribbon samples are immersed in the swelling agent THF at 60°C and drawn to fibers with a maximum drawing ratio of $\lambda = 20$ after the swelling reached an equilibrium. Finally the solvent was eliminated from the fibers in vacuum at certain temperature while the length was fixed.

2, *Wide and small angle X-ray diffraction*

Wide and small angle diffractive patterns were recorded on photographic plates using Kiessig camera with pinhole collimation. Ni filtered Cu-K α radiation was obtained from a Philips PW 1730 generator operated at 35 mA and 40 Kv. The distances between the sample and the film were 40 cm for SAXS and 7 cm for WAXD. The long space was evaluated from the position of the peak applying Bragg's law.

3, *Tensile properties*

An Instron 1122 equipment was used to measure the stress-strain behavior at room temperature. All the calculations of the stress were based on the initial cross-sectional area. Some selected samples were subjected to cyclic deformation.

4, *Optical and electron microscope*

The morphology of the fibers was observed using a Zeiss polarizing microscope. More detail supermolecular structure of the fiber surface was investigated by a Philips EM-400 transmission electron microscope using an ion etching and surface replica technique with platinum/carbon.

5, *Other measurements*

The thermal properties and crystallinity of the fibers were measured by DSC with a DSC-2 (Perkin-Elmer Co.) under dry nitrogen atmosphere in unsealed aluminium pans. All enthalpies and temperatures refer to indium as standard. During the measurements the samples were wound on an aluminium plate to keep the tension.

The measurements of macroscopic density of the fibers were performed using a conventional density gradient column prepared from heptane/tetrachloromethane mixtures. The measurements were carried out at 25°C.

RESULTS AND DISCUSSION

1, *Drawing behavior of the gel*

We have studied the swelling behavior of PBT-PTMO with some organic solvents, which includes dibutylether, 1,4 dioxane and tetrahydrofuran at different temperatures. These solvents are known for their high capability of dissolving poly(tetramethylene oxide) that formed soft segments in our sample. In addition, They do not act as solvents for poly (butylene terephthalate) i. e. hard segments, at least in the crystalline state of the polymer. We selected THF as the solvent for this work.

Fig. 1 shows the swelling curves where the percentage increase in volume fraction of the samples swollen in THF at 20°C and 60°C, respectively, are plotted against time. It indicates that the swelling degree of the sample increases with increasing temperature.

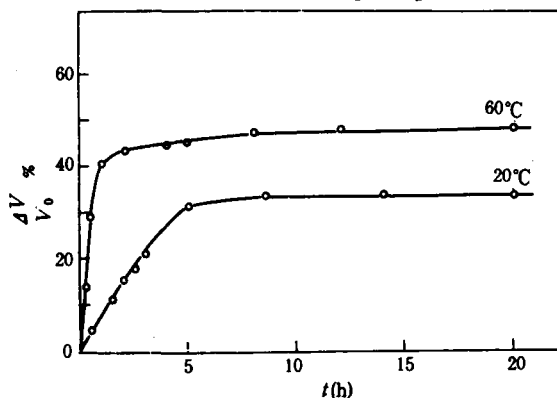


Fig. 1 The swelling curves of segmented copoly(ether-ester)s in THF at different temperatures.

An equilibrium extent of swelling reaches 48% in volume fraction at 60°C. At the same time it has been proved that the decrease in the crystallinity of the swollen samples is within the limits of the experimental errors. It indicates that the "crosslinking stability" has been sufficient in this material to retain the integrity of the lamellar network to a large extent.

Fig. 2 shows the stress-strain curves of PBT-PTMO swollen in THF at different temperatures and with unswollen sample for comparison.

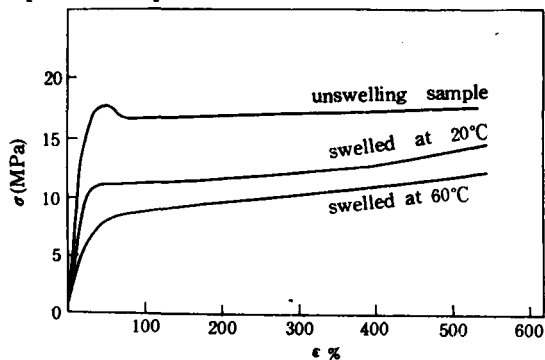


Fig. 2 Stress-strain behavior of segmented copoly(ether-ester)s swollen in THF at different temperatures and with unswollen sample for comparison.

From this figure it can be seen that the drawing behavior is very different for three samples. The stress-strain curve of unswollen sample shows a typical tensile character of the crystalline polymers. It exhibits a high yield stress and with a "necking". However, the swollen samples do not yield and there are no "necking" observed. Especially for the sample swollen at 60°C the stress-strain curve exhibits a typical tensile character of amorphous polymers and the tensile stress is much lower than that of the unswollen sample. The swollen sample, therefore, is easier to be drawn to higher drawing ratio than that of the unswollen sample at the same condition. This is due to the presence of fewer intermolecular entanglements at swollen state than that at unswollen state resulting in considerably higher molecular mobilities during drawing and therefore a higher drawability of the sample.

2. Morphology of gel-drawing fibers

The morphological structures of the fibers were investigated by optical and electron microscopes as well as small and wide angle X-ray diffractions. Fig. 3 is an optical micrograph of the morphology of the gel-drawing fiber of PBT-PTMO. It can be seen from the photo that the

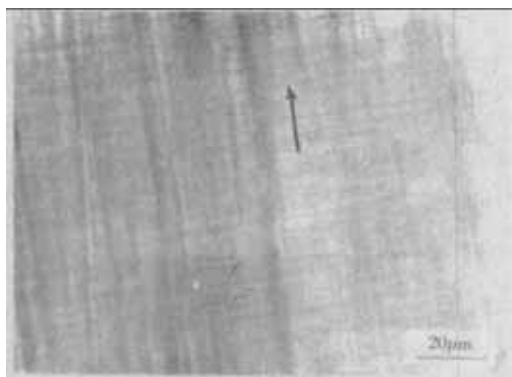


Fig. 3 Optical micrograph of the morphology of sample D (crossed polarizers).

morphology of the fiber is composed of many bands arranged in parallel with each other in the direction perpendicular to the drawing direction. The band structure as seen in a polarized light microscope exhibits alternating bright and dark bands under crossed polarizers. It is interesting to point out here that such morphology is very similar to those of Kevlar fiber^[5] and the film precipitated from the nematic solution of PPTA under shearing^[6]. It has been demonstrated that the morphology of the band structure is only an optical effect of the periodical structure of these materials^[5,7]. For PPTA film the remorphology of this periodical structure is composed of the zigzag fibrils highly oriented along the shearing direction^[7]. But in the case of the PBT-PTMO the band structure is different from that of PPTA, it may be an optical effect of another periodical structure of the oriented fibrils.

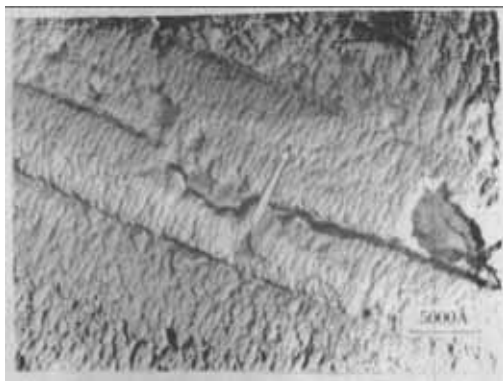


Fig. 4 Transmission electron micrograph of a replica surface of sample D etched by Argon plasma.

Fig. 4 is an electron micrograph of the surface replica of the fiber etched by Argon plasma. From this photo, it has been shown that the morphology of the gel-drawing fiber consists of the highly oriented fibrils along the fiber axis. It is interesting to note that the fibrils are made of many

"nodule structures". The dimension of these "nodules" is about $200\text{\AA}$, corresponding to the value of the long space of the fiber obtained by SAXS.

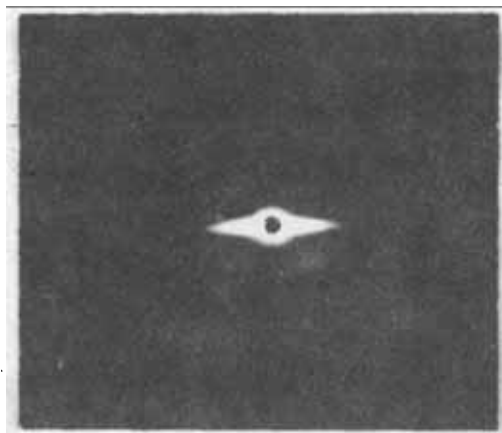


Fig. 5 Small angle X-ray scattering pattern of sample D

Fig. 5 is a pattern of SAXS of the gel-drawing fibers. It is a four point scattering pattern and indicates that the molecular chains are grouped in fibrils oriented parallel to the fiber axis and the molecular chain orientation is different in neighbouring fibrils. The long spacing calculated from Fig. 5 applying Bragg's law is $110\text{\AA}$.

The orientation of the gel-drawing fibers was investigated by wide angle X-ray diffraction. Fig. 6 shows four WAXD fiber diagrams for different fibers treated at different condition. From the intensity distribution of the equatorial reflections the degree of the orientation of the chains in the crystalline regions of the fibers can be determined. It has been found that the degree of the chain orientation in the crystalline regions of the fibers is not much different for all samples, except the fiber treated at 200°C by extension. It indicates that the chain orientation process in the crystalline regions has essentially finished during the drawing. The treatment, therefore, only increases the degree of the orientation of the chain in amorphous region and the crystallinity of the fibers. It can be proved by the change of the density of the fibers as list in Table 1. Fig. 7 is a DSC diagrams of the gel-drawing fibers, the untreated fiber appears a crystallization peak before melting, and the crystallization peak disappears when the fibers are treated. From Table 1 it can be seen that the crystallinity and the orientation degree of the fibers increase with the increasing temperature of treatment under extension.

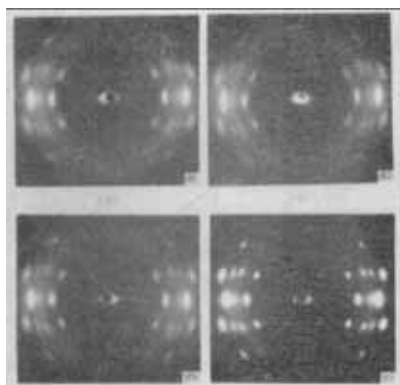


Fig. 6 Wide angle X-ray diffraction patterns of the fiber of segmented copoly(ether ester)s by gel-drawing.

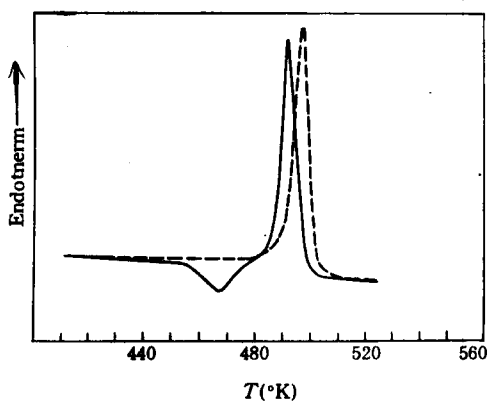


Fig. 7 DSC diagrams of gel-drawing fibers.

----- sample E. — sample B.

Table 1 Character of gel-drawing fibers

Samples	Treated conditions	T_m (°C)	d_m (g/cm)	ΔH (J/g)	W_c
A	Fiber drawn from unswelling sample	221	1.303	39.34	0.28
B	Gel-drawing fiber untreated	219	1.304	39.34	0.28
C	Gel-drawing fiber 60°C extension	222	1.307	39.34	0.28
D	Gel-drawing fiber 100°C extension	224	1.312	40.75	0.29
E	Gel-drawing fiber 200°C extension	225	1.324	44.96	0.32

3, Tensile properties of gel-drawing fibers

All tensile measurements were performed using Instron 1122 type equipment at room temperature. In all cases the effective length of the samples was 30 mm and the strain rate corresponding to a cross head speed was 10 mm/min.

As is well known the tensile strength and initial modulus depend on the conditions at which the fibers are formed. The corresponding data for gel-drawing fibers treated at different conditions are also shown in Table 2. From these data it can be seen that the tensile strength and initial modulus increase with increasing temperature of the heat treatment. This is due to the fact that the molecular chains have become more highly oriented during gel-drawing, as proved by WAXD pattern of the gel-drawing fibers.

Table 2 Mechanical properties of the fibers

Samples	σ (MPa)	ϵ (%)	E (MPa)
A	188	67	445
B	265	47	648
C	238	48	673
D	280	40	802
E	276	45	804

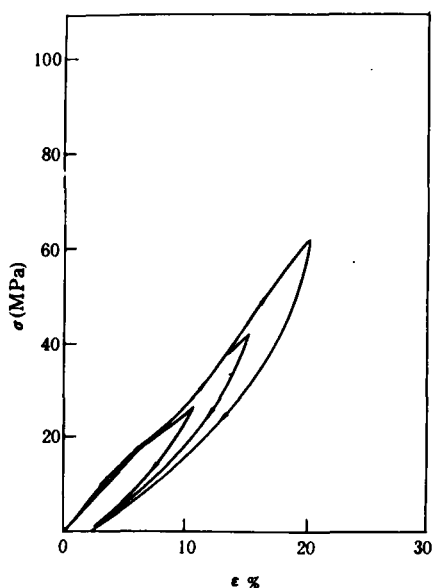


Fig. 8 Stress-strain behavior of the sample D, upon load cycling on the same sample.

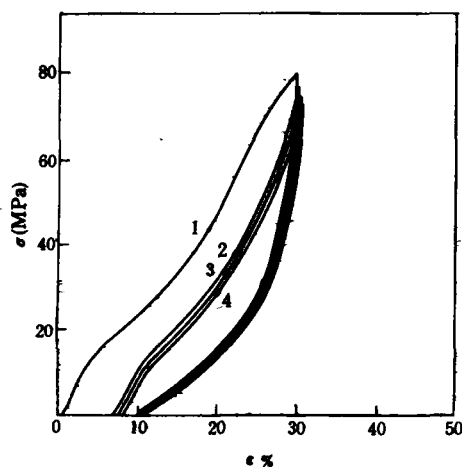


Fig. 9 Stress-strain curves for four cycle loading of sample D to 30% elongation.

Fig. 8 shows the stress-strain hysteresis of the fibers, where the same specimen was subjected to repeated load cycles. It can be seen that the deformation is reversible, even the strain is larger than 20% for gel-drawing fibers. A substantial strain hardening was observed. It has been demonstrated^[8] that the residual strain of the fiber is due to the distortion of the crystalline region.

Fig. 9 shows typical loading cycles of the fiber for 30% elongation. It is interesting to note that the tensile stress is decreased after each cycle, but the stress-strain curve of each cycle is the same in manner. The residual deformation reaches a constant value after the second cycle. Such tensile property of the gel-drawing fiber is very similar to that of the hard-elastic fibers^[9]. Therefore, when a dynamic cyclic loading condition is applied, the material properties will reach rapidly to an equilibrium state.

4, Mechanism of the gel-drawing process

The segmented block copoly(ether ester)s are thermoplastic elastomers physically crosslinked through crystalline hard segments. The amorphous region consists of the noncrystalline hard segments and soft segments, they are the crosslinking chain segments of random structure. The mobility of the entangled chain segments is enhanced as a result of interaction between the solvent and soft segment during swelling. The intermolecular segments will be disentangled and extended under the act of the swelling force. Thus, all molecular segments highly oriented along the stress direction during drawing as shown in Fig. 10. So we suggest that the gel-drawing process of polymers is a way to obtain the high strength and high modulus fibers.

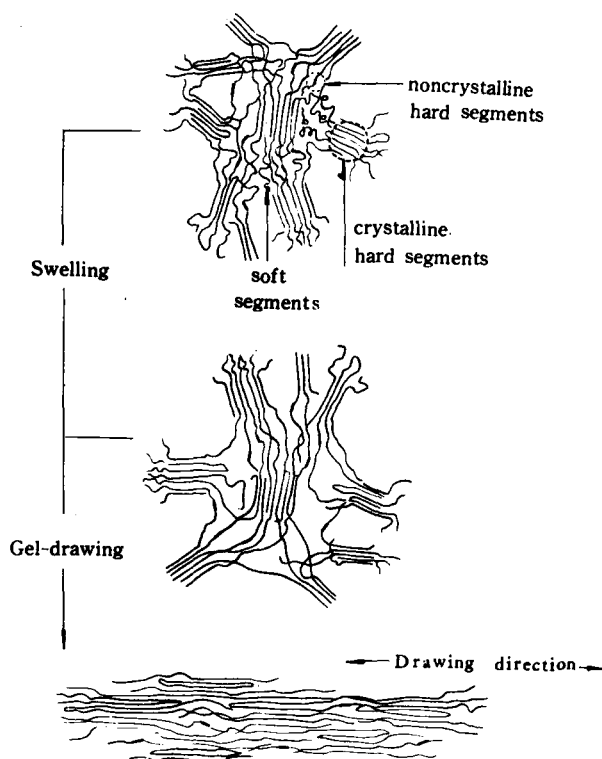


Fig. 10 Schematic representation of gel-drawing mechanism

Keywords:

Morphological structure; Mechanical property; gel-drawing fiber; segmented block copolyetherester.

REFERENCES

- [1] Smook J. and Pennings A.J., *Polymer Bull.*, **1983**, 9, 75.
- [2] Kalb B. and Pennings A.J., *J.Mater.Sci.*, **1980**, 15, 2584.
- [3] Smook J., Flinterman M. and Pennings A.J., *Polym. Bull.*, **1980**, 2, 2775.
- [4] Yanai H.S., *J.Polym.Sci.-part C*, **1968**, (23), 205.
- [5] Simmens S.C. and Hearle J.W.S., *J.Polym.Sci.-phys.*, **1980**, 18, 871.
- [6] 陈寿载、龙程奋, 高分子通讯 (*Polymer Communications*) **1979**, 240.
- [7] 陈寿载、龙程奋、蔡丽英, 高分子通讯 (*Polymer Communications*) **1981**, 424.
- [8] Cannon S.L.; Statton W.O. and Hearle J.W.S., *Polym. Eng.Sci.*, **1975**, 15, 633.
- [9] Cannon S.L.; McKenna G.B. and Statton W.O., *J.Polym.Sci.-rev.*, **1976**, 11, 209.