WAXD Analysis of High Strength and High Modulus Copolyimide : PI(PMDA ; BPDA/PDA)

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ABSTRACT

WAXD analysis of copolyimide PI(PMDA ; BPDA/PDA) film with the 1 : 2 composition (= PMDA : BPDA in molar ratio), which showed the maximum value of σ = 2.63 GPa and E = 163.2 GPA, respectively, confirmed the following conclusion ; (1) The rod-like PMDA component was successfully drawn up to over 150% with the aid of drawing orientation of the semi rod-like BPDA component. (2) In addition to the aid of an orientation of molecular chains, the high strength and high modulus of the copolyimide film was favored mainly by the formation of ordered structures of the PMDA and BPDA component, respectively. (3) The effective improvement of Young's modulus of the copolyimide film was achieved mainly by a rapid formation of the intramolecular order at the initial elongation up to 40 ~ 50 %.

INTRODUCTION

Poly(p-phenylene pyromellitimide) PI(PMDA/PDA) is fully rodlike polymer with a theoretical high modulus of ca. 505 GPa1). However, this attractive polymer is too brittle and fragile for application so that it is practically useless.

Recently, Masuda et al. 2,3) have improved these disadvantages by synthesizing copolyimides from pyromellitic dianhydride (PMDA) and 3,3', 4,4'-biphenyl tetracarboxylic dianhydride (BPDA) with p- phenylene-diamine (PDA). Mechanical properties of these copolyimides with various compositions were examined to obtain the following results; (1) The orientation of the copolyimides films depends on the state of swollen copoly(amic acids) (PAAs) in solvents. (2) Regarding the effect of semi-rodlike BPDA content in the units, the maximum values of tensile modulus and strength of PI films are 163.2GPA and 2.63GPA, respectively, for 1 : 2 copolymer of PI(PMDA ; BPDA/PDA) (= PMDA33%). (3) The introduction of the semi-rigid BPDA/ PDA molecules into rigid PMDA/PDA polymer chain units could improve the tensile, mechanical properties of fully rod PI(PMDA/PDA) films. The dependence of Young's modulus on draw ratio for the copolyimides used is shown in Fig.1.

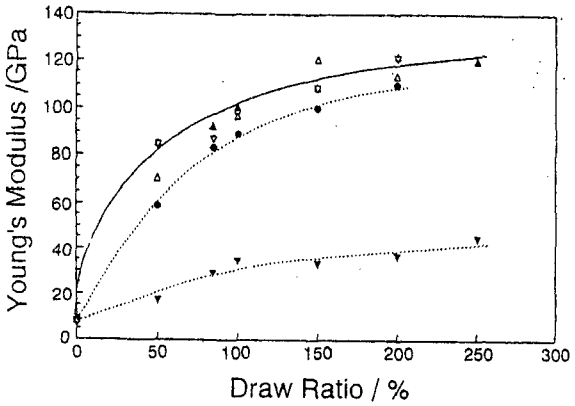
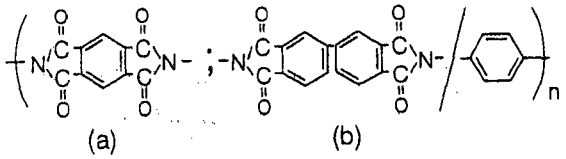


Fig.1 Dependence of Young's modulus on draw ratio for drawn PI copolymer films; Copoly-1 (▼),Copoly-2 (●),Copoly-3 (△),Copoly-4 (▲) and Copoly-5 (▽).



PI(PMDA/PDA)	a:b=1:0	(100% PMDA)
Copoly-1	a:b=2:1	(66% PMDA)
Copoly-2	a:b=1:1	(50% PMDA)
Copoly-3	a:b=2:3	(40% PMDA)
Copoly-4	a:b=1:2	(33% PMDA)
Copoly-5	a:b=1:3	(25% PMDA)
PI(BPDA/PDA)	a:b=0:1	(0% PMDA)

Fig.2 Composition of polyimide copolymers.

This paper describes the morphological study of the PI(PMDA ; BPDA/PDA) film by wide angle X-ray diffraction (WAXD) to elucidate the relation between the excellent mechanical characteristics and molecular aggregation.

EXPERIMENTAL

PAA films were uniaxially drawn in ethylene glycol. Details of the preparation of the copolyimide films with thickness of ca. 25 μ m was previously reported 2,3). The composition of the copolyimides used here is shown in Fig. 2.

WAXD measurements in both transmission and reflection modes were conducted in the $\theta/2\theta$ method over 4 – 36° using a Mac Science diffractometer MXP^{18A} with Cu Kα (λ = 1.54 A) as radiation source operated at 40 kV, 100 mA. The transmission diffractometer was used with 0.5° divergence and scattering slits, 0.3 mm receiving slit to record the transmission patterns using step-scanning with 0.05° steps and 120 sec count time per step. The reflection diffractometer was operated with 1° divergence and scattering slits, 0.6 mm receiving slit to obtain the reflection patterns using step-scanning with 0.02° steps and 4 sec count time per step.

The intensity of the X-ray diffraction was corrected to the background run and then normalized for the irradiated volume of films. A least – square peak deconvolution procedure using 4) was applied to the WAXD data in order to obtain the intensity and full width at half maximum (FWHM) of diffraction peaks.

Apparent sizes (L) of ordered regions along certain diffraction planes were caluculated by using Scherrer equation 5)

$$L = K\lambda / B\cos\theta$$

where B is FWHM and K is a geometry-dependent constant, which is assumed to be 0.9.

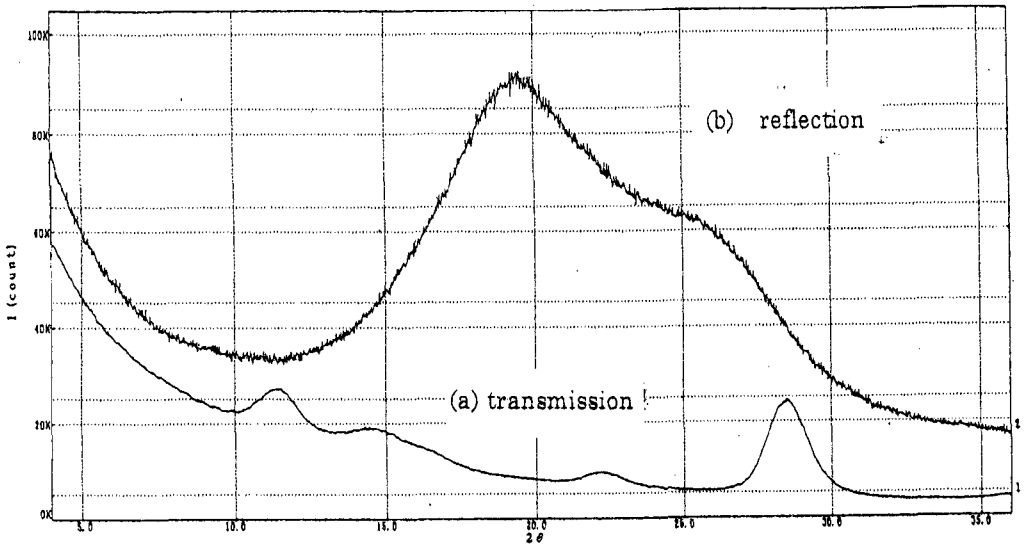


Fig.3 WAXD patterns of Copoly－4 drawn 50 % ;

RESULTS AND DISCUSSION

Fig. 3 shows the WAXD patterns of Copoly-4 film drawn 50% obtained with the transmission (a) and the reflection (b) geometry, respectively. The reflection pattern has two broad peaks at 19.4° and 25.7° 2θ, indicating no sign of any intermolecular order. In contrast, the transmission patterns exhibits four relatively sharp peaks ; The 11.5° peak can be indexed as the (004) peak of PI(BPDA/PDA). The 14.5° and 22.3° peaks can be indexed as the (002) and (003) peaks of PI(PMDA/PDA), respectively 6). The 28.5° 2θ peak is fairly strong because both the (004) peak of PI(PMDA/PDA) and the (0010) peak of PI(BPDA/PDA) can overlap just at the position. Copoly-4 film therefore can be considered to have a highly ordered smectic crystal order comprised of two kinds of monomer repeat layers, with the polymer chains aligned parallel to the film surface.

Fig.4 gives the dependence of peak intensity for the (004) peak of PI(PMDA/PDA) and (002) peak of PI(BPDA/PDA) on draw ratio in Copoly-4. It is surprizing that PMDA component can be easily drawn up to over 150 % with the aid of drawing orientation of BPDA component.

Fig.5 shows the dependence of the apparent size of respective intramolecular order along the (004) plane for PMDA and (002) plane for BPDA component on draw ratio in Copoly - 4. The size along the (002) plane of BPDA rapidly increases by 25 % elongation and remains almost constant up to 50 % untill it shows a small increase at 150 %. On the other hand, the one along the (004) plane of PMDA component also increases rapidly up to 40 % elongation, but it decreases slightly by the drawing followed.

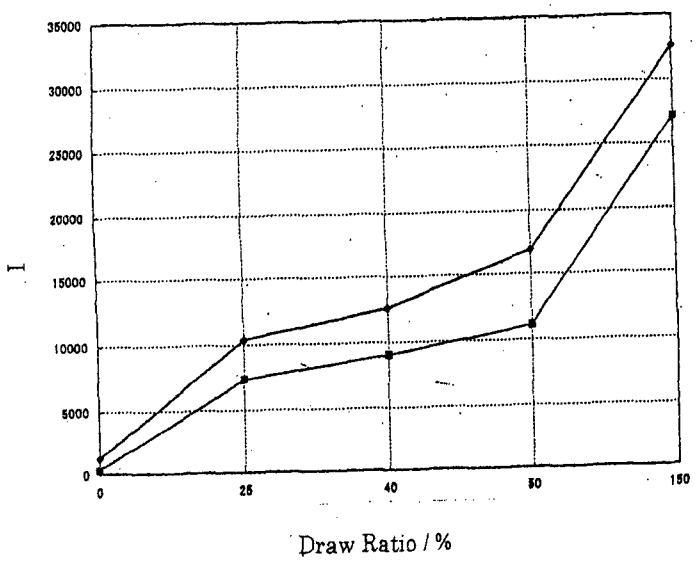


Fig.4 Dependence of peak intensity on draw ratio in Copoly – 4 : (■) (004) for PMDA, (◆) (002) for BPDA

The comparison of the behavior of Young's modulus in Fig.1 and that of morphological factors in Fig.4,5 confirms the conclusion that an effective improvement of Young's modulus of Copoly-4 film has been achieved mainly by the rapid formation of intramolecular order at initial elongation up to 40 ~ 50 %.

Fig.6 illustrates the dependence of the apparent size of intramolecular order along the (004) plane for PMDA component and (002) plane for BPDA component on PMDA content for copolyimide films drawn 50 %. Among these copolyimide films the maximum size for the (002) plane is given by Copoly - 4 (PMDA 33 %) and that for the (004) by Copoly – 3 (PMDA 40 %), respectively. This may explain

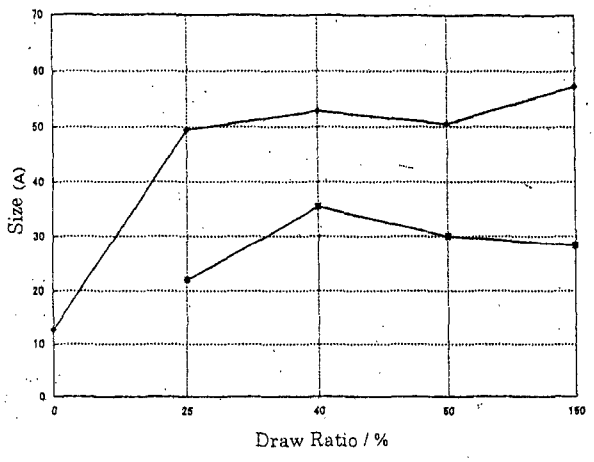


Fig.5 Dependence of size of intramolecular order on draw ratio in Copoly – 4 : (■) (004) for PMDA, (◆) (002) for BPDA

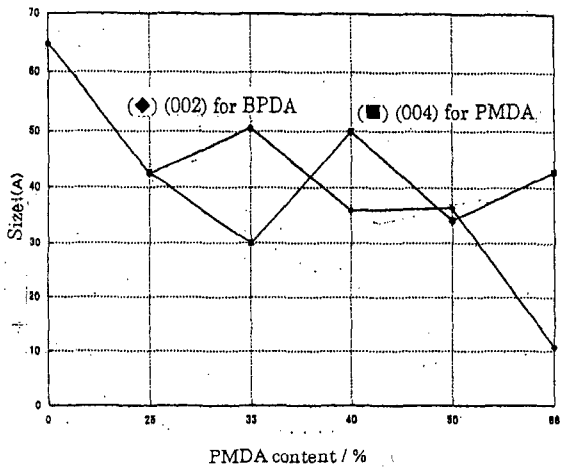


Fig.6 Dependence of size of intramolecular order on PMDA content for films drawn 50 % :

the similar excellent behavior of Young's modulus on draw ratio in Fig.1. In their analysis of dimensionally stable copolyimide PI(PMDA;BPDA/PDA) , Chung et al. 7) reported that the 30/70 (= PMDA/BPDA in molar ratio) copolyimide was the candidate for the low level stress buffer in interlayer dielectrics.

Fig.7 gives the dependence of reflection peak intensity at ca. 19° on draw ratio in Copoly – 4. The peak intensity rapidly increases beyond 40 % elongation, meaning a rapid orientation of PI chains to the direction parrallel to drawing direction.

Fig.8 shows the dependence of the apparent size of intermolecular order on PMDA content for copolyimide films drawn 50 %. The size seems to be almost constant for these copolyimide films, regardless of PMDA contents.

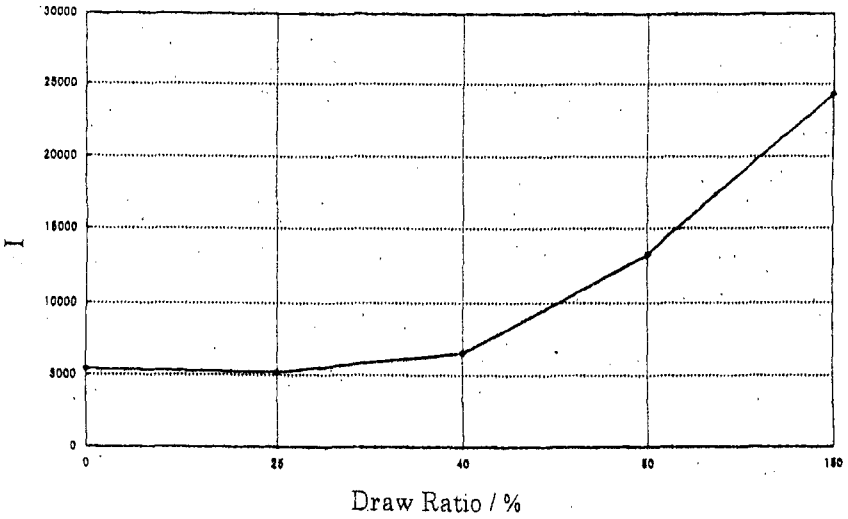


Fig.7 Dependence of intensity of intermolecular peak on draw ratio in Copoly-4

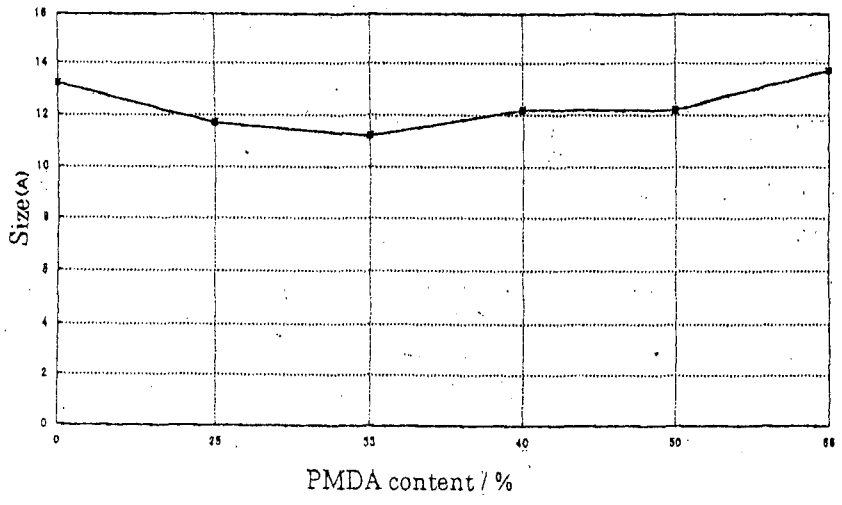


Fig.8 Dependence of size of intermolecular order on PMDA content for films drawn 50 %

The results obtained from Fig.7 and 8 indicate that high modulus of copolyimide films cannot be attained alone by the orientation of PI chains and that some intramolecular order for PI(PMDA/PDA) and PI(BPDA/PDA) must be formed in the films.

SUMMARY

(1) PMDA component can be easily drawn up to over 150 % with the aid of drawing orientation of BPDA component.

(2) The size of an intramolecular order along the (002) plane of BPDA rapidly increases by 25 % elongation and remains almost constant up to 50 % until it shows a small increase at 150 %. On the other hand, the one along the (004) plane of PMDA component also increases rapidly up to 40 % elongation, but it decreases slightly by the drawing followed.

(3) An effective improvement of Young's modulus of Copoly-4 film has been achieved mainly by the rapid formation of an intramolecular order at the initial elongation up to 40 ~ 50 %.

(4) The maximum size of an intramolecular order for the (002) plane is given by Copoly-4 (PMDA 33 %) and that for the (004) by Copoly-3 (PMDA 40 %), respectively. This may explain their remarkable behavior of Young's modulus on a draw ratio.

(5) High modulus of copolyimide films cannot be attained alone by the orientation of PI chains. Some intramolecular order for PI(PMDA/PDA) and PI(BPDA/PDA) must be formed, respectively, in the films.

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