ULTRA HIGH MODULUS AND HIGH STRENGTH POLYPYROMELLITIMIDE COPOLYMER FILM OBTAINED BY USING SWOLLEN DRAWING OF PAA

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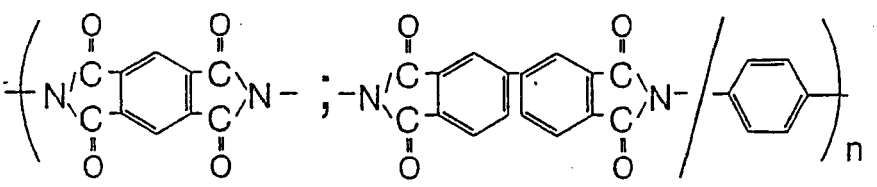
Abstract

For improving the molecular orientation and the tensile, mechanical properties of rigid-rod PI(PMDA/PDA), the precursor copoly(amic-acid) film consisting of PMDA/PDA and BPDA/PDA was uniaxially stretched by using swollen drawing. The tensile mechanical properties, WAXD patterns, orientation factors, and density changes of these PI films were measured. The main results were as follows: 1) The molecular orientation of the copolyimides were enhanced at lower draw ratio as compared with PI(PMDA/PDA) homopolymer, 2) The tensile mechanical properties of these copolyimide films were significantly improved as the film thickness became thinner, 3) There was an optimum composition for PMDA/BPDA ratio in the copolymers with respect to degree of molecular orientation of rigid-rod PMDA molecules. 4) The maximum modulus of 163.2GPa with tensile strength of 2.6GPa was obtained for PI(PMDA;2BPDA/PDA) copolymer. The swollen state of PAA films was an important factor for the chain orientation of the copolymers.

INTRODUCTION

The tensile modulus of wholly rigid-rod polyimide, PI(PMDA/PDA) has been calculated to be above 500 GPa(1). For improving the molecular orientation and the tensile , mechanical properties of rigid-rod polyimides, various drawing techniques such as the hot or the solution drawing of PAA or PI, the cold drawing of PAA have been studied(2-7).



(a) (b)

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)

Figure 1. Chemical structure and composition of PIs studied.

In 1987, we obtained the high strength and high modulus polyimide films of BPDA/PDA by means of the thermal imidization after cold drawing of PAA films(4). Furthermore, we successfully developed the polyimide/polyimide molecular composite film with the improving toughness of PI(BPDA/PDA) films(5). Tayama extended this technique for preparation of high modulus fibers of polyimide-benzobisthiazole(6). More recently, US researchers systematically investigated the high-performance fuluorinated polyimide fibers by using a dry-jet wet spinning method (7). However, it is not yet succeeded to draw out the great potential on mechanical properties for PI(PMDA/PDA) as compared with poly(p-phenylenebenzobisthiazole), and poly(p-phenylene benzobisoxazole) (8).

In this paper, we will discuss the chain rigidity in PAA chain molecules in respect to the molecular orientation and the improving of the tensile, mechanical properties of various PI(PMDA, BPDA/PDA) copolymers by using the swollen drawing of PAA films.

EXPERIMENTAL

Materials and Film drawing process

Figure 1 listed the structure and composition of PI(PMDA;BPDA/PDA) copolyimides studied. A strip film of PAA on the drawing machine was put into ethyleneglycol(EG) swelling bath for 5 min. at 35℃-55℃, and then stretched up to around 300%. The PAA film rinsed in 2-propanol, followed drying in air oven at 50℃ was thermally imidized by stepwise heating as followed: 250℃, 2 hours + 400℃, 1 hour + 450℃, 1 min. in vacuum oven(10).

RESULTS AND DISCUSSION

The swelling behavior

Table 1. Effect of thickness on the swelling of 50wt%PMDA Copoly-2 PAA film in EG for 5 min.

Thickness	Swelling Temperature							
(μ m)	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C
50	×	×	×	×	○	○	○	△
20	×	○	○	△	△	△	–	–

Table 1 shows the swelling behavior for the films of Copoly 2, PAA(PMDA;BPDA/PDA) (50wt%PMDA) with 20 and 50 μ m. When PAA film was dipped in EG bath, the change in dimension of the film was observed at early few minuets. As the film become thinner, the desired

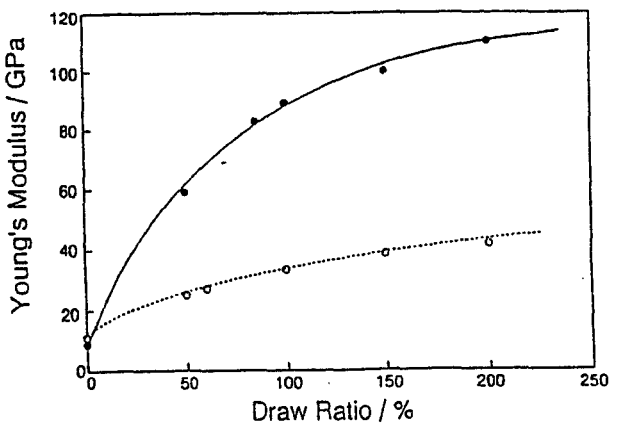


Figure 2. Dependence of Young's modulus on draw ratio for 50wt%PMDA Copoly-2 (●) and PI(PMDA/PDA)/PI(BPDA/PDA) blend (○).

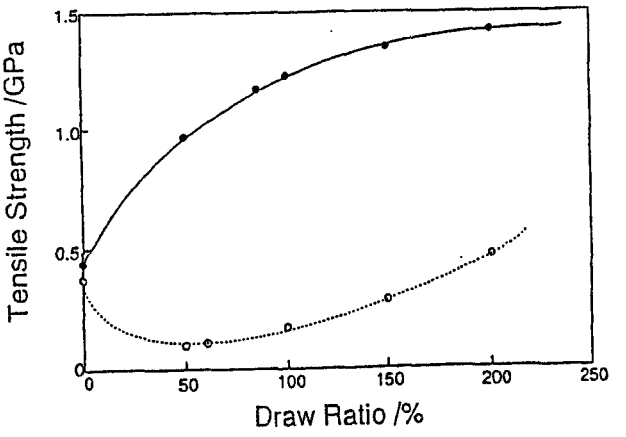


Figure 3. Dependence of tensile strength on draw ratio for 50wt%PMDA Copoly-2 (●) and PI(PMDA/PDA)/PI(BPDA/PDA) blend (○).

temperature (the windows for swollen drawing) shift to lower, suggesting more the restriction and nonuniformity of swelling for the thicker films. It was also found that PAA specimens of these copolymers mostly contain 200-300wt% EG under the swelling, indicating in higher amount of solvent with the increasing of PMDA unit. Figure 2, and 3 showed the tensile modulie and the ultimate tensile strengths for PI(PMDA/PDA)/PI(BPDA/PDA),(1:1) blend and the corresponding copolymer, Copoly-2(50wt%PMDA) on draw ratio, respectively. The tensile modulus for Copoly-2 film was considerably increased, reaching more than 100GPa at 150% drawing, whiie the modulus for the (1:1)blend was slightly increased up to only 40GPa at 200% drawing. As shown in Figure 3, the tensile properties for both films were very much difference in proportion to the modulie. The tensile strengths of the blend film were mostly lower than that of undrawn film. And furthermore, the films are very fragile. It was suggested that the swelling behavior of the blend films were not uniform in not only microscopic but also macroscopic, resulting from the difference on solubility between PMDA/PDA and BPDA/PDA molecule. The film thickness becomes thinner as 20 μ m, the swelling temperatures shifts to lower temperatures from 45℃ to 30℃ as shown in Table 1. The tensile modulie of the drawn Copoly-2 films markedly increased with improving the tensile strength, when the film thickness becomes thinner. It gives a sign that the thinner PAA film has also a better swollen state than that of thicker PAA to align polymer chains to the drawing direction(10).

The tensile mechanical properties of the copolyimides

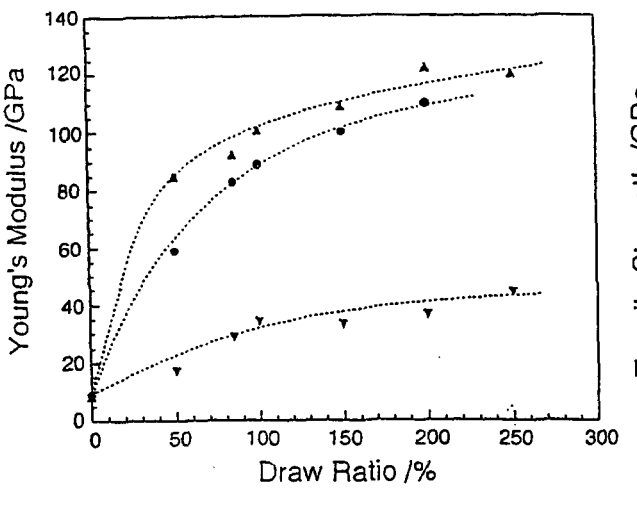


Figure 4. Dependence of Young's modulus on draw ratio for 66wt%PMDA Copoly-1 (▼), 50wt%PMDA Copoly-2 (●), and 33wt%PMDA Copoly-4 (▲).

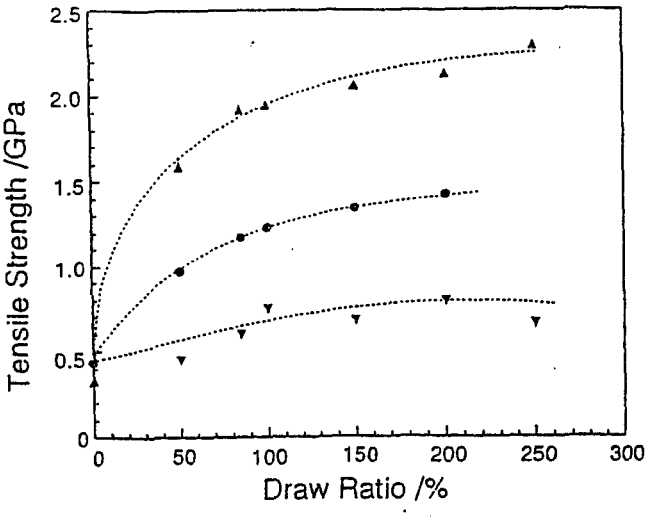


Figure 5. Dependence of tensile strength on draw ratio for 66wt%PMDA Copoly-1 (▼), 50wt%PMDA Copoly-2 (●), and 33wt%PMDA Copoly-4 (▲).

Now, let's see the effect of flexible biphenyltype imide, BPDA/PDA structure for molecular orientation of PMDA/PDA units in the copolyimides. When the flexible BPDA units increase in the copolymers, Young's modulie become higher for all of draw ratio, as shown in Figure 4. The modulie for the Copoly-4 which contains only 33% rigid-rod PMDA units are beyond 120Gpa in contrast to very low values of modulie for Copoly-1. And furthermore, when BPDA unit increase in the copolyimides, a slop of the curve on modulus rises steeply at lower draw ratio. These characteristic results reveal a fact that the rigid-rod pyromellitimide molecules preferentially align to the drawing direction with flexible biphenyldiimide molecules linked. As you see in Figure 5, the tensile strength for Copoly-1, Copoly-2, and Copoly-4 are well in proportion to the changes of Young's modulie. It is noted that the tensile strength for Copoly-4 increases steeply at only 50% drawing, and finally

reached a value of 2.2 GPa at 250% drawing. It means that these copolyimides posses the highly oriented structures without macroscopic defects in the film. On the other hand, mechanical properties of 66%PMDA Copoly-1 were not improved by drawing, suggesting the less orientation of PMDA units to the drawing direction.

Although the modulie for these copolymers such as Copoly-3, Copoly-4, and Copoly-5, were not much difference on PMDA contents, the absolute value of the tensile strengths for these copolymers are considerably difference. In the case of 33%PMDA Copoly-4, the tensile strength attained to very high value of 2,3 GP even only 50% drawing, getting to a exceedingly high value of more than 2,6 GP at 300% drawing. Whereas the tensile properties for 25%PMDA Copoly-5 became really low in comparison to Copoly-4. These results were not clearly understood, so far. However, it might be thought that the rigid-rod PMDA/PDA moieties in 40%PMDA Copoly-3 may still be enough concentration of PMDA/PDA to aggregate by themselves, resulting in the formation of some crystal-like structures which is expected to work as a weak and a stress concentrating portion in the films.

Table 2. Summarized data of WAXD intensity and Young's modulus for the copolyimides.

Samples	PMDA contents	E^{1*}	WAXD^{2*}		
	%	GPa	I_a (11°)	I_b (14°)	I_c (22°)
Copoly- 1	66	32.9	—	18572	3479
Copoly- 2	50	100.0	—	56983	46586
Copoly- 4	33	108.8	98945	64894	38743

E1*: Young's modulus (draw ratio 150%), WAXD2*: Transmission (draw ratio 150%), I_a, I_b and I_c: Intensity

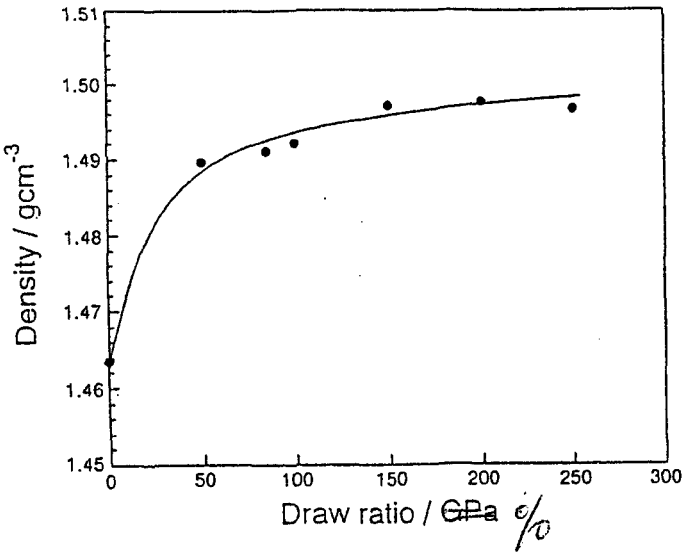


Figure 6. The changes of density for 33wt%PMDA Copoly-4 on draw ratio.

Table 2 summarized the data of WAXD intensities and Young's modulie for these copolyimides. Intensity of Ib PMDA(14°) exhibits the highest value for Copoly-4. It means that PMDA/PDA molecules preferentially align to the drawing direction. This is consistent with the results of the tensile mechanical properties for these copolyimide films in Figure 4, 5. The changes of density for the 33%PMDA Copoly-4 films in Figure 6 are very large at relatively lower draw ratio, following the results of the tensile behavior as shown in Figure 5. The changes of orientation factors which was measured by FT-IR and Fluorescense Spectroscopy of the dye-containing PAA(11) are also the same tendencies for the molecular orientation of PMDA/PDA units in the copolymer. Therefore, it can be

concluded that the rigid-rod pyromellitimide molecules preferentially orient to the drawing direction, when the flexible biphenyl type imide structures closed and surrounded around rigid-rod pyromellitimide molecules as the stage of PAA. Because of the increasing of a chance of the reorientation due to the increase in flexibility without crystallization for PMDA/PDA units in the copolymers, The flexible BPDA/PDA molecules seems to be well workable for orientation of PI(PMDA;BPDA/PDA) copolymers under the swollen drawing of precursor PAA films.

CONCLUSIONS

The tensile mechanical properties of uniaxialy drawn PI(PMDA; BPDA/PDA) copolyimide films were significantly improved as the film thickness became thinner. There was an optimum point for PMDA/BPDA ratio with respect to degree of the molecular orientation of rigid-rod PMDA molecules in the copolymers. The maximum modulus of 163.2GPa with tensile strength of2.6GPa was obtained for PI(PMDA;2BPDA/PDA) copolymer at 200% drawing. It was found that the swollen state of PAA films is a very important factor for the chain orientation of the rigid-rod PI(PMDA/PDA) molecules.

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