THE MECHANICAL PROPERTIES OF HIGH YOUNG'S MODULAR AND THIN POLYIMIDE FILM

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Abstracts .. Recently, high young's modulus and thinness of the base films have been required for the long play VTR tape. And also high heat-resistance have been required for perpendicular magnetic recording tape. Under these circumstances, new higher performance films than PET, Which is used popularly as the base films, have been developed actively.

In this study, we prepared high Young's modular and thin polyimide film by drawing of swollen Polyamic Acid (PAA) film which consisted of BPDA and PPD. And we will report on the mechanical properties of the drawn polyimide film.

INTRODUCTION

We show the structure of the polyimide used in this study on Fig.1. This polyimide consists of 3,3', 4,4'- biphenyl-tetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PPD) and has an extra high young's modulus in the commercially available polyimide. This polyimide, also, has high thermal properties such as the higher glass transition point above 400°C. The processing route of the drawn polyimide film is shown in Fig.2. The PAA film which is the precursor of the polyimide film was swollen, and drawn with consecutively bi-axial, and finally imidized with heat to the polyimide film. The thickness of films prepared by this process was 6 ~ 13 µm. We have evaluated this film by measuring the mechanical properties, ie, tensile strength and young's modulus. And also

UPILEX-S $T_g > 400^\circ\text{C}$

Fig.1 The structure of the polyimide.

we measured the crystallinity and molecular orientation by the Wide Angle X-ray Diffraction (WAXD) and by Optical Birefringence Analyzer (OBA).

Fig. 2 Processing of drawn polyimide Film

EXPERIMENT

PAA FILM

We prepared the PAA film by casting on the glass or mirror-polished stainless steel belt from BPDA-PPD polyamicacid varnish. The drying was proceeded at 140 °C ,5 ~10min. and the peeled PAA film contained 30 ~36 wt% DMAC(solvent) residue and 20 ~40% imide-linkage. And the mechanical properties of the PAA film was slightly decreased during the storage in the atmosphere, because of the hydrolysis of amic-acid linkage.

Therefore we used the PAA film within 7 ~ 10days after casting, and the tensile elongation of PAA film was 50 ~70%.

Swelling

The PAA film was dipped and swollen in various solvents. For this object, the cosolvent that is a mixture of good solvent and poor solvent for PAA film was most effective. In this step, swelling time was important because of the decrease of orientation and the poor solvent was necessary to avoid the solution of PAA film. For good solvent, we used Dimethyl acetamide, Dimethyl sulfoxide(DMSO), N-methyl pyrrolidon and 1.3 Dimethyl-2-imidazoliginon. And for poor solvent, we used methanol, ethanol, isopropanol, ethyleneglycol(EG), water, acetone and benzene.

We defined the swollen ratio as follows.

$$D.Sw.(\%) = (W_t - W_o) \times 100\% / W_o$$

where W_o presents the weight of PAA Film before treating and W_t presents the weight of swollen PAA film.

Swelling condition should be also decided from the tensile properties of the swollen PAA film. The swollen PAA film should have the high elongation and modulus. From these point of view, we determined the swelling conditions as follows and the tensile properties of swollen PAA film was shown on Fig.3.

SWELLING CONDITIONS(standard)

Solvent (ratio): DMSO/EG (7/3)

Temperature : 50 °C

Time : 10 min.

D.Sw. : 30 %

Fig.3 The tensile properties of swollen PAA film

Drawing

The swollen PAA film was drawn by "VISTRON"(simultaneous bi-axial drawing equipments, IWAMOTO WORKS, Japan) at 40°C. Several types of bi-axial deformation were studied.

1. Uniaxial with free width.
2. Consecutive bi-axial.
3. Simultaneous bi-axial.

After drawing, the film was dipped into isopropyl alcohol for 1 min. at 40°C and then dried for 2 min. at 100°C. This step was very important to avoid the large shrinkage caused by solvent removing and imidizing on the latter step. In this study, we compared the only draw ratio of this step.

Heat Imidization

The drawn PAA FILM was fixed to the stenter and heat imidized in the curing oven for 20 min. The curing temperature was stepwise increased from R.T to 450°C. To keep a flatness and high tensile properties, it was necessary to stretch uniaxially during the cooling period from 450 °C. We used the uniaxial-drawable stenter and stretched less than 10% for machine direction.

RESULTS AND DISCUSSION

As described before, we used some kinds of drawing type. Typical characteristic of each type is as follows.

We present MD as the machine direction of PAA film and TD as transverse direction.

Uniaxial Draving with Free Width

Necking for width was very large and caused fibrillation during heat imidization. Consecutive Biaxial Drawing with Fixed Width

At first, the swollen film was drawn for MD axial with fixed width, then drawn for TD axial with fixed width (TD).

To avoid the fibrillation, it was necessary to have the draw ratio TD more than 10%.

$$\text{Draw Ratio}(\%) = \left(\frac{\text{Length of Drawn F.}}{\text{Length of Swollen F.}} \right) \times 100\%$$

The Draw Ratio of MD was 40 ~ 80%.

In this study, we discuss for this type and this process had given the highest mechanical properties.

Simultaneous Biaxial Drawing

We could get the draw ratio of 75% for each direction.

Although the difference of mechanical properties for MD/TD was decreased, we could not get the high Modulus.

Properties of drawn film

In this study, the conditions of swelling and imidizing and the drawing type of consecutive Biaxial Drawing with fixed width were fixed, and only draw ratio of MD was changed from 0% to 63%, and draw ratio of TD was fixed to 10%. The thickness of films prepared by this processing route were 6 μm to 13 μm .

Fig.4 shows the dependence of Young's modulus on draw ratios of MD. With increasing draw ratio of MD, Young's modulus of MD remarkably increased from 6.8GPa to 34.8GPa, and Young's modulus of TD slightly decreased to 5.0GPa. And in the case that draw ratio of MD was 63%, the total Young's modulus of MD and TD was attained to about 40GPa. On the other hand, the total Young's modulus of un-drawn film was 13.6GPa.

Fig.4 The dependence of Young's modulus on draw ratio

Fig.5 The dependence of tensile strength on draw ratio

Fig.5 shows the dependence of tensile strength on draw ratios of MD. With increasing draw ratio of MD, tensile strength of MD also increased from 0.41GPa to 0.99GPa, and tensile strength of TD also decreased to 0.19GPa.

With increasing draw ratio of MD, Elongation at break of MD remarkably decreased from 52% to 4%, and elongation at break of TD slightly decreased.

Fig.6 shows the Wide Angle X-ray Diffraction(WAXD) photographs of un-drawn and drawn polyimide films. The WAXD photographs of drawn films suggest the molecular orientation and crystallization for the direction of MD drawing. The mechanical properties of MD and TD seems to be influenced by this molecular orientation and crystallization.

Table 1 shows the birefringence measured by KS-OBA. Higher draw ratio gave high retardation and birefringence and caused the difference of orientation between MD and TD.

Table 2 shows the crystallinity measured by X-ray diffraction. Although the consecutive Biaxial Drawn film gave slightly high crystallinity, we think the difference was not evident. And we suppose the influence of orientation is larger than crystallinity.

Table 1 Birefringence of Drawn Film

Sample	Retardation	Δn
un-drawn	114.3 nm	0.0057
drawn(MD 40% $\times$ TD 10%)	4779.6 nm	0.3983
drawn(MD 63% $\times$ TD 10%)	4209.0 nm	0.4209
drawn(simultaneous 50% $\times$ 50%)	482.0 nm	0.0536

Table 2 Crystallinity of Drawn Film

Sample	Crystallinity
un-drawn	12%
concecutive drawn(MD 63% $\times$ TD 10%)	15%
simultaneous drawn(50% $\times$ 50%)	11%

CONCLUSION

High Young's modular and thin polyimide films were prepared by drawing of swollen PAA films. It was confirmed that the drawn polyimide film with draw ratio of MD 63% and of TD 10% had very high Young's modulus, $E_{MD} = 35\text{GPa}$ and $E_{TD} = 5\text{GPa}$ and $E_{Total} = 40\text{GPa}$.

REFERENCES

- [1] S.Numata et al., Polymer Preprints, Japan, "Thermal Expansion Coefficient and Moduli of Uniaxalliy Stretched Polyimide Film" Vol. 37, pp.2393,1988.
- [2] I.Mita et al., Polymer Preprints, Japan, "The Mechanical Properties of Aromatic Polyimide Stretched at High Temperature" Vol. 38, pp. 437,1989.
- [3] I.Mita et al., Polymer Preprints, Japan, "High Strengthening of Polyimide Films by Hot Drawing" Vol.39, pp.2409-2411,1990.
- [4] I.Mita et al., Polymer Preprints, Japan, "Effect of Drawing Method on High Modulus/High Strength of PI Film" Vol. 39, pp.2412-2414,1990.

Fig.6 The WAXD photographs of undrawn and drawn polyimide films.