Xiaohui Yu (于晓慧)High modulus and high strength polyimide obtained by uniaxially stretching a thermoplastic polyimide film

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Abstract: A thermoplastic amorphous polyimide film was subjected to isothermal uniaxially stretched with variations of following stretching parameters: stretching velocity, stretching temperature and stretching ratio. The effects of drawing conditions on the orientation and crystallinity of films were investigated by optical birefringence and XRD. The mechanical properties, coefficient of thermal expansion, optical properties, and water absorption of the stretched films were characterized. Regardless of the stretching temperature, above or below the glass transition temperature, room-temperature strength in the stretch direction of drawn films was greatly improved. Compared with the unstretched film, tensile modulus and strength of stretched films increased about two times, which were 7.8 GPa and 390 MPa, respectively. The coefficients of thermal expansion in tensile direction declined markedly from 50 to 8 ppm/℃, even they were negative after being stretched at 200°C. The transparency of drawn films also enhanced and the color changed into yellowish from brown. Furthermore, the thickness of stretched film reduced to 20% at the furthest compared to that of unstretched film. To sum up, uniaxially stretching of thermoplastic polyimide potentially can be used as the high modulus and high strength of ultra thin film or fiber.

Key words: uniaxially stretching; polyimide film; high strength

Introduction

Polyimide (PI) films are especially important among many industrial PI products. They are widely used in the field of microelectronic industry and aircraft parts owing to their considerable thermal stability, high specific strength, high dimensional accuracy and high tolerance against radiation [1,2]. There are many methods to fabricate the polyimide films, such as casting, stretching, depositing and spraying. Stretching can reduce alignment of molecular chains in the stretching direction and promote the crystallization of the PIs during the drawing processes. The stretched films exhibited higher transparency, better surface finish quality and low permeability. The heat resistance and cold resistance of the films are also improved. The thickness of the films reduced clearly and the acreage increased. Generally speaking, the use value of the film increased and the cost reduced. Thus, the stretching method is very important to enhance their dimensional stability, stiffness, strength, transparency and electrical properties of polyimide films [3].

Studies on structural changes of the polyimides during stretching are not only of academic interest but also important for industry because of the researches on structure control to enhance the products performance [4]. When NASA successfully deployed the inflatable antenna experiment from the Space Shuttle, the importance of lightweight, high strength and dimensional stability was brought to the forefront. Both industry and NASA recognized that the ultra thin film can reduce the burthen for mechanical deployment and costly for in-orbit construction [5,6]. Now, Langley Research Center (LaRC)-developed thin polymeric films have been proposed for use in several space applications. Polyimide films are different with those thermoplastic polymers such as poly (ethylene terephthalate) film, which aren't easily stretched at near Tg owing to their rigid structures and strong interaction between polyimide chains [7]. To our knowledge, commercial polyimide films are mostly biaxially oriented by stretching the soluble amic acid precursor [8,9]. However, the simultaneous solvent outgassing and high temperature curing reaction during the stretching process are difficult to treat. The

other potentially simpler alternative is to stretch the fully imidized polyimide film [10]. Unquestionably, it requires the polyimide must be thermoplastical [11].

The present work concerns stretch orientation of PMDA-BABB polyimide film [12], but the solid content controlled to 25 wt%. This work aims at uniaxial stretching the fully imidized film (by using the SHIMADZU AG-I tensile apparatus fixed with an air-circulating oven) with variations of following stretching parameters: stretching velocity (Vst), stretching temperature (Tst) and stretching ratio (λst). Structural studies on polyimides in the drawing process have been reported by many investigators, in this report, the focus is on studying the effects of stretching on tensile properties, optical properties, coefficients of thermal expansion and the degree of orientation and the structure evolution.

Experimental

Materials

N,N-Dimethylacetamide (DMAc) and toluene were vacuum-distilled after drying over calcium hydride. Pyromellitic dianhydride (PMDA, m.p.285 °C) was purchased from Beijing Jiaohua Company, which was dried in a vacuum at 150 °C for 4 h. 1, 3-Bis (3-aminophenoxy-4'-benzoyl) Benzene (BABB) was synthesized in laboratory.

Characterization

Tensile test was performed on drawn thin film specimen (ca. 40×3×x mm3) on a SHIMADZU AG-I tensile apparatus at room temperature with a crossed speed of 8 mm/min. Dynamic mechanical analysis (DMA) was performed on thin film specimen (ca. 30×4×x mm3) on a TA instrument DMA Q800 at a heating rate of 5 °C min-1 and at a load frequency of 1 Hz under air atmosphere. Ultraviolet-Visible (UV-vis) spectra of the films were recorded on a UV-vis 2501 spectrometer. The coefficient of thermal expansion was measured with drawn thin film specimen (ca. 15×4×x mm3) by using the METTLER TOLEDO TMA/SDTA 841^e. The equilibrium water uptake was determined by the weight difference of vacuum-dried film specimens before and after immersion in deionized water at 20 °C for 24 hours. The orientation degree of the films was characterized with a Rigaku Wide-angle X-ray diffractometer (D/max rA, using Cu Ka radiation at wavelength λ=1.541E). The 2θ scan data were collected at 0.05° intervals over ranges of 10–60° and scan speed was 0.5° (2θ)/min. SAXS was performed using the same instrument over the ranges of 0.5–6° and scan speed was 0.2° (2θ)/min. All the properties of polymers were measured with films.

Preparation of the undrawn and drawn polyimide films

The undrawn films were prepared via the two-step solution polymerization and thermal imidization process, but the content of solid controlled to 25 wt% and the thickness of obtained films controlled at about 70 μm.

The high performance drawn polyimide films were obtained with uniaxially isothermal drawing by using the SHIMADZU AG-I tensile apparatus on the undrawn polyimide film strips. The tensile apparatus equipped with a hot air-circulating oven, the effective length of stretched part was fixed to 10 mm, and the width of the film was about 20-40 mm. The stretching parameters were as follows: The stretching velocity (Vst) was 4mm/min, 8mm/min and 12mm/min. Stretching temperatures (Tst) were 200° C and 235 °C. Stretching ratio (λst) was 1, 1.5, 2, 2.5 at 200 °C and 2, 5, 10, 15 at 235 °C. The stretching ratio was controlled by the tensile test. The drawn films maintained 10 minutes at the processing temperatures and then quenched to room temperature.

Results and discussions

Effects of stretching velocities

Firstly we chose the appropriate stretching velocity to reduce the burden of the experiments and studied the effects of stretching velocities on the mechanical properties of the drawn films. The films were uniaxially stretched with different stretching velocities at 235°C and with the stretching ratio of 10. The mechanical properties of stretched films in stretch direction (SD) were listed in Table 1. The results show that the smaller Vst brought the higher modulus but lower strain and stress, and the bigger Vst brought a little lower modulus but higher strain. The mesne Vst of 8 mm/min brought the excellent tensile properties, shown in Table 1. The lower Vst cost too much time to fabricate one sample, and the

higher Vst made the films easier splitted during the stretching processes. As a result, the appropriate Vst of 8 mm/min was used in the stretching processes and tests.

Table 1 The room-temperature (RT) tensile data of drawn films (Tst-235, λst-10)

V_{st}[mm/min]	Tensile Modulus[GPa]	Max Stress[MPa]	Strain[%]
4	5.1	223.7	8.5
8	4.9	258.0	17.5
12	4.9	250.1	13.0

Mechanical properties of drawn films

Mechanical properties of drawn films were examined by means of SHIMADZU AG-I tensile tester. The tensile data in stretch direction are summarized in Table 2. Regardless of the stretch temperature above or below Tg, the mechanical properties of all drawn films were improve a lot (The original tensile data was same as the paper [12]: 2.7GPa, 109.3MPa, 156.2%). The tensile modulus and max strength of the drawn films were in the range of 7.2-7.8 GPa and 329-386 MPa after being stretched at 200 °C. The highest modulus was nearly 3 times of the undrawn film and the strength was more than 3 times. The original films still possessed of excellent mechanical properties at the high temperature of 200 °C, the modulus was 2.2 GPa. The tensile data of drawn films stretched above Tg were nearly or more than 2 times comparing with the undrawn film, the modulus were in the range of 3.6-4.9 GPa, and the max strength were 146-258MPa. As might have been expected, a higher modulus was obtained with the larger λ_{st} and lower Tst, especially when the Tst was below Tg. In fact, the modulus in the stretch direction correlated fairly well with the λst that had been achieved, so modulus seems to reflect in a general way the degree of chain alignment. All the drawn films exhibited outstanding mechanical properties, it suggested that stretch produce the orientation, thus the molecular chains arrayed regularly and the degree of crystallization was enhanced. All the tensile data showed a trend of first increase and then decrease with the increased λ_{st}, which reached the maximum at the λst was 1.5 and 10, respectively. It indicated that the chain relaxation is in competition with chain orientation occurring during the stretch processes, along with the increase of λ_{st}, the relaxation possesses dominant degree, and then the mechanical properties would decline. The mechanical properties in transverse direction (TD) were also studied, and the representative results are also listed in Table 2. The results showed that the drawn films also had excellent tensile modulus (1.6 GPa) and strength (90 MPa) in TD.

Table 2. The tensile data of drawn films (Tst-200, 235)

λ_{st} 200	Tensile Modulus[GPa]		Max Strength[MPa]		Strain [%]	λ_{st} 235	Modulus [Gpa]	Max Strength[Mpa]	Strain [%]
	200°C	RT	200°C	RT	RT		RT	RT	RT
1.0	2.2	7.3	51.0	356.5	7.0	2	3.6	146.8	18.3
1.5	2.1	7.8	48.9	385.7	6.8	5	4.6	238.3	20.1
2.0	2.1	7.7	47.4	363.5	6.3	10	4.9	258.0	17.5
2.5	2.2	7.3	47.9	329.2	5.9	15	4.5	220.3	14.7
						$10_{(TD)}$	1.6	90.5	9.6

Orientation degree of drawn films

To evaluate the degree of orientation of these stretched films and study how the structures affect the mechanical properties, the aggregation structures of the drawn films were studied. Stretch induced orientation or crystallization, this can be proved by the results of the Wide Angle X-ray diffraction (XRD) and Small Angle X-ray Scattering dispersions (SAXS) of the drawn films. The XRD and SAXS of the drawn films performed at 200 °C are shown in Figure 1 and Figure 2. The XRD of the drawn films stretched at 235 °C is shown in Figure 3. Figure 1 showed that the stretched films performed at 200 °C were also amorphous, but the peak at 2θ of 45° disappeared and the intensity of peak at 2θ of 20° increased and the peak became narrow. Especially, the PI-200-1.5 had the highest intensity, indicating it has compact molecular conformation, so this film had the highest modulus and strength. Figure 2 also showed that the peak at 1.04 disappeared and another peak's degree enhanced, suggesting that the

stretched films had higher degrees of orientation. The average length of the ordered regions can be calculated according to Bragg's equation ($d=\lambda/2\sin\theta$). Where θ is the X-ray diffraction angle and λ=1.54E. The calculated d values are listed in Table 3. All films had lower d value, suggesting the degree of orientation improved. And the film of PI-200-1.5 had the lowest, indicating it has the greatest degree of orientation, thus it had the best mechanical properties. Although property improvements obtained by stretching that do not crystallize, orientation can be helpful. It supposed that the molecular chains occur physical crosslinks at lower Tst (200 °C<Tg), preventing relaxation during the stretching process and allowing a greater degree of orientation to be produced. Figure 3 showed that all drawn films stretched at 235 °C were crystalline after stretched and the degrees of crystallization were enhanced with the increase of the λ_{st}. The results suggested that the drawn films stretched at 235 °C would have higher tensile data comparing to the undrawn film. The tensile data of PIs-235 were lower than PIs-200, it was supposed that the molecular chains moved easily at higher temperature (>Tg), thus stretch induced crystallization easier than lower temperature (200 °C). But also the relaxation occurs easier, so the drawn films stretched above Tg exhibited lower tensile data than that of films performed at 200 °C, but also higher than undrawn films.

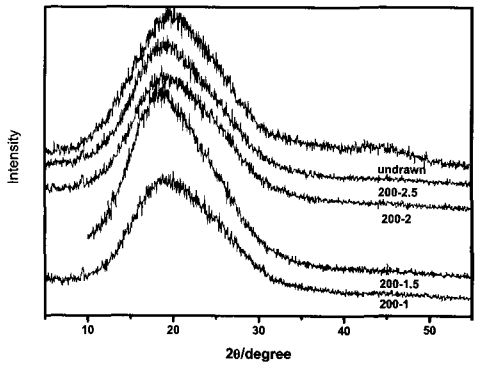

Fig.1 The WAXD of drawn films (Tst-200)

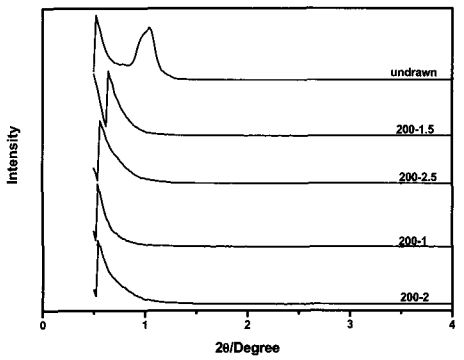

Fig.2 The SAXS of drawn films (Tst-200)

Table 3 The properties of the drawn films

Tst [°C]	λ_{st}	2θ [°]	D [Å]	E'[a] [GPa]	E'[b] [GPa]	UV [%]	λ_0 [nm]	CTE [ppm*k^{-1}]	R[c] [%]	W[d] [%]
200	1	0.54	163.40	7.9	1.5	84.5	372.0	-1.6	62.3	1.1
	1.5	0.64	137.87	7.3	1.5	85.7	377	-2.7	60.0	1.1
	2	0.54	163.40	8.2	1.6	85.3	377.5	-2.1	59.7	1.2
	2.5	0.56	157.56	8.3	1.6	84.4	381.0	-2.1	57.2	1.1
235	2	--	--	4.3	1.6	88.6	374.0	18.0	63.2	1.5
	5	--	--	4.4	1.8	88.5	376.0	17.3	65.2	1.0
	10	--	--	4.8	1.6	88.7	365.5	8.8	68.1	0.7
	15	--	--	4.4	1.7	87.5	369.0	8.0	69.0	1.3
RT	0	0.52/1.04	169.68/84.84	2.7		83.5	410.0	50.2		0.6

E'[a]:Storage modulus in stretch direction
E'[b]:Storage modulus in transverse direction
R[c]:The reduced percent of the thickness
W[d]:The water absorption of films

Dynamic properties of drawn films

Dynamic properties of drawn films in stretch direction were examined on a TA instrument DMA Q800. The storage modulus (E'[a]) data are listed in Table 3, and the representative curves of stretched films which performed at 235 °C are displayed in Figure 4. All the tests stopped automatically around the Tg without breaking owing to the shrinkage of the drawn films. The E'[a] of all the stretched films were accord with tensile modulus, and they were about 1-3 times of that of undrawn films. The E'[a] of the films stretched below Tg were the highest among those stretched films, it was nearly 3 times of

undrawn film (2.70). The trend of the E'a with λ_{st} was similar to that of the tensile modulus. The E'a of all stretched films declined rapidly at Tg (drop of E' at Tg $>10^3$), suggesting that the stretched films exhibit excellent thermoplasticity. The tanδ of stretched films were lower than undrawn film's (tanδ, 2.9), but they were also very high compared with common polyimide films. It indicated that the stretched films also maybe useful as materials for shock absorption and sound insulation. The dynamic properties of drawn films in transverse direction were also examined, and the data (E'^b) are listed in Table 3. The results suggested that the drawn films also had excellent dynamic properties, and the data were accord with the tensile modulus in TD.

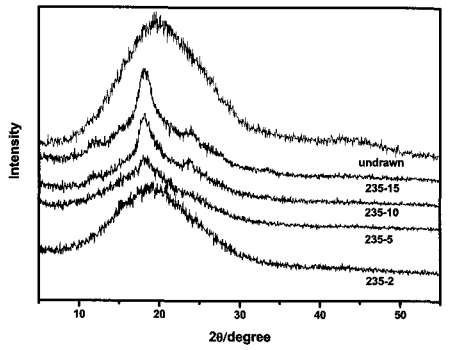

Fig.3 The WAXD of drawn films (Tst-235)

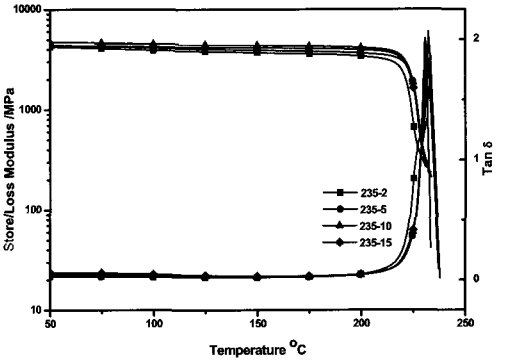

Fig.4 DMA curves of drawn films (Tst-235, SD)

Optical properties of drawn films

The optical properties of the drawn and original films were studied using UV-vis 2501 spectrometer. The optical data are summarized in Table 3. After uniaxial stretch above Tg, all the stretched films became to yellowish transparent from yellow transparent and they exhibited higher transparency (89%) than undrawn film (83%), also the λ_0 became lower from 410 nm to 365 nm. The color of the drawn films performed below Tg were still yellow transparent or semitransparent and the transparence declined from 87% to 84%, and the λ_0 reduced from 410 nm to 372 nm. All drawn films showed higher transparence and lower λ_0 after being stretched, indicating that the stretched films are useful as transparent windows or solar films. And the original film could be used to fabricate the ultra thin film with high strength and transparence.

Thermo mechanical analysis of drawn films

Thermal expansion coefficients (CTE) in stretch direction and transverse direction of the films were measured by using the TA instruments METTLER TOLEDO TMA/SDTA 841^e. The average CTE data between 50 °C to 100 °C are shown in Table 3. In stretch direction, the films of PIs-200 shrinked all the time and began to shrink fleetly above 180 °C, and the shrinkage reached the maximum length of the machine allowed around the 220 °C. Most of the films of PIs-235 elongated before 155 °C and then began to shrink, and some films shrank at 100 °C. The CTE of PIs-200 were negative about 2 ppm*k-1 in the range of 50 °C to 100 °C, and the CTEs were about -19 ppm*k-1 in the range of 50 °C to 150 °C, indicating that the films stretched at 200 °C maybe useful as materials of shrink films, owing to remarkable shrinkage at high temperature. The films stretched above Tg exhibited the plus CTE but much lower than undrawn film. And some CTEs of PIs-235 were so close to that of Cu (18ppm*k-1) and some were close to that of Si (5ppm*k-1), suggesting that these films can be used in field of microelectronic industry such as Flexible Printed Circuit Board (FPC) and Flexible Copper Clad Lamination (FCCL). The CTEs in transverse direction were increased to about 70-77 ppm*K-1. These results indicating that the CTE can be reduced by stretching method.

Other properties of drawn films

The thicknesses of the films were measured with micrometer, and the data are listed in Table 3. The thickness of the drawn films reduced more than 60% and the thinnest film was about 9 um by recorded, suggesting that this original film can be used to fabricate the ultra thin film. The water absorption was also studied and the data show that the water absorption was increased with the attenuation of the films.

Conclusions

Fully imidized polyimide film of PMDA-BABB was successfully stretch-oriented uniaxially. Uniaxial stretching improved modulus by factors of 2.7 to 4.9, 7.9 GPa in the stretch direction at Tst of 200 °C and 235 °C respectively. Also films stretched at 200 °C and 235 °C gave up to triplicate and twofold improvements in stiffness. All the drawn films had higher transparency (89%) and lower λ_0 (365nm) The CTEs decreased to 8 ppm*k-1 and -2 ppm*k-1 between 50 °C~100 °C with the Tst of 235 °C and 200 °C. These results indicated that the drawn films with high modulus and strength could be used as the transparent windows, solar films, Flexible Printed Circuit Board (FPC) and Flexible Copper Clad Lamination (FCCL). The results of this study clearly demonstrated that polyimides can be stretch oriented and sometimes accompanied by strain-induced crystallization to improve their properties, such as mechanical properties, optical properties, crystallization (or the degree of the orientation), thermal expansion coefficients. A novel kind of ultra thin film or fiber may be obtained by uniaxial stretch the fully imidized polyimide PMDA-BABB.

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(continuing fromp136) The observed small ΔE' was thought to be attributed that the increase of the number of extreme rigid structures of repeating unit: phenyl group of BAFL -PMDA- phenyl group of BAFL caused the increase of T_g up to the high temperature region (> 400 °C) that caused oxidation degradation.Fig.3 showed TGA curves of PIs(PMDA/p-ODA;BAFL). T_{d5} and residual weight at 800 °C increased with increasing BAFL content. If these residual weight at 800 °C depended on the number of aromatic rings in the PI films, these observed TGA results were found to be confirmed by increasing the content of BAFL (aromatic rings content of PI(PMDA/p-ODA) and PI(PMDA/BAFL) are theoretically 62.9.% and 67.9.%, respectively) [3].

The effect of the incorporation of BAFL on the thermal stability of the cured resins is now under considerations and will be discussed in the presentation on the day.

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