Effects of equal biaxial stretching on the electric properties of polyimide films

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(Revised 15 May 1985)

The influence of thermal treatment and stretching on properties of poly(4,4′-oxydiphenylene pyromellitimide) films has been studied by mechanical, thermally stimulated current (t.s.c.) and dielectric measurements. Equal biaxial stretching of the films was achieved by the bubble-inflation technique. Thermal treatment at high temperatures may affect the onset temperature of the conduction loss of the samples in dielectric measurements. In addition to the improvement of tensile strength due to molecular orientation, the effect of stretching is to help further imidization of the residual reactive groups and the decrease of structural defects. An equally biaxially stretched PI film of average-area draw ratio 1.70 is a good insulating material of low dissipation factor and high stability of dielectric properties in the temperature range from −120°C to 220°C.

(Keywords: poly(4,4′-oxydiphenylene pyromellitimide); biaxial stretching; dielectric properties; thermally stimulated current)

INTRODUCTION

Poly(4,4′-oxydiphenylene pyromellitimide) (PI) film has been found to be very useful as a heat-resistant insulating material. Usually a two-step method is used for its preparation. First, a film of the corresponding polyamic acid is prepared by solution cast, which is then converted to polyimide film at high temperature. The commercial PI film (Kapton) exhibits obvious anisotropy[1,2] and is believed to be stretched during its processing. It has been reported that uniaxial stretching can greatly increase the modulus and tensile strength in the stretching direction[1,3]. However, no results about the influence of stretching on electric properties have been published. In this work the effect of equal biaxial stretching on the properties of PI films has been studied.

EXPERIMENTAL

Four film samples were used in this work. The original films (sample PI-1) were solution cast and then imidized in a heating process, the highest temperature of which was about 300°C. Their thickness was 30 μm. Sample PI-2 was obtained from PI-1 films under equal biaxial stretching by means of the bubble-inflation technique at a temperature above 260°C. The PI-2 films were kept at 320°C for 10 min after stretching. The average-area draw ratio was about 1.70. Sample PI-3 was treated under the same thermal conditions as sample PI-2, but was not stretched. A Du Pont Kapton film (PI-4) of thickness 50 μm was used for comparison.

A t.s.c. apparatus, type KH-1, produced in the Institute of Chemistry, Academia Sinica, was used to measure the thermally stimulated discharge current of the samples. The poling temperature, time and field were 214°C, 10 min and 20 kV/cm, respectively. The dielectric spectra were studied with a Dielectric Loss Measuring Set type TRS-10 made by Ando Electric Co., Ltd. The frequency used was 1 kHz. The heating rate for both t.s.c. and dielectric measurements was 3°C/min. All the film specimens were metallized before measurements.

RESULTS AND DISCUSSION

The tensile behaviour of the four samples at room temperature is given in *Table 1*. The strength and elongation of sample PI-3 are almost the same as those of the original sample PI-1. The stretched sample PI-2 shows improved strength and lower elongation, which are very close to the data for the Kapton films (PI-4). These results indicate that further thermal treatment of sample PI-1 does not affect its mechanical properties, but a stretching of low draw ratio can obviously improve its mechanical strength due to molecular orientation.

The temperature dependence of dielectric constant ε' and loss tangent $\tan\delta$ of the four samples are given in *Figures 1* and *2*. The results for PI-4 are similar to those reported in the literature[4–6]. The dielectric constant increases with temperature in the region below 0°C, and a corresponding γ loss peak can be observed at −50°C. It has been attributed to the relaxation movement of segments related to the residual reactive groups[4,6] and can be used, to some extent, to characterize the degree of unimidization of PI samples. There is a decrease in ε' above room temperature, whose origin is not clear. Sample PI-4 shows a very low and diffuse loss peak at about 110°C. In the high-temperature region a rapid

Table 1 Mechanical properties of PI samples

Sample		PI-1	PI-2	PI-3	PI-4
Strength (10^8 Pa)	Longitudinal	1.55	1.80	1.45	2.00
	Transverse	1.45		1.30	1.57
Elongation (%)	Longitudinal	95	80	90	55
	Transverse	113		110	70

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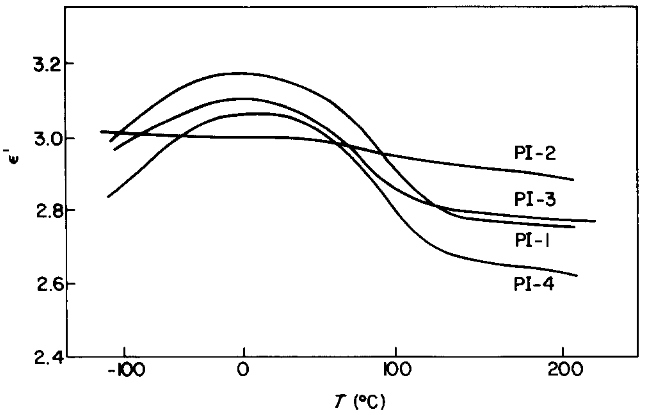

Figure 1 Temperature dependence of ε' at 10^3 Hz for polyimide samples

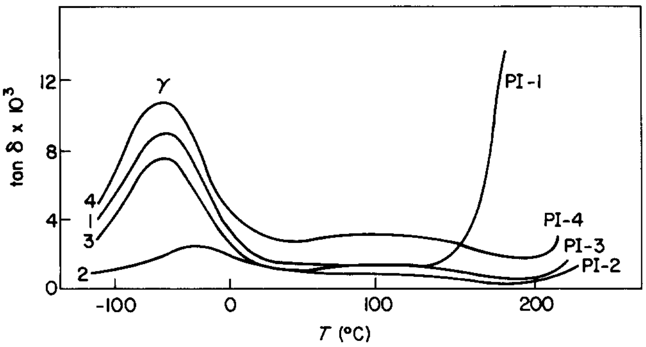

Figure 2 Temperature dependence of $\tan\delta$ at 10^3 Hz for polyimide samples

increase of dielectric loss can be observed and its onset temperature is about 200°C.

The dielectric constant of sample PI-1 is slightly larger than that of PI-4, but their temperature dependence is quite similar. Sample PI-1 exhibits a lower γ-peak, and no β-peak can be detected. The distinct difference between samples PI-1 and PI-4 is that the onset temperature of loss increase at high temperatures decreases to about 140°C for PI-1. As ε' varies smoothly in this temperature region, so the abrupt increase in $\tan\delta$ should be related to the effect of conduction within the samples. For a dielectric material the earlier appearance of a large dissipation factor is obviously undesirable for high-temperature applications.

Below 130°C the dielectric constant value for PI-3, which has been annealed at 320°C, is a little less than that for PI-1. Also, taking into account the lower γ-peak for PI-3, we may suppose that imidization occurs within sample PI-1 under high-temperature treatment. At the same time, the onset temperature of the large conduction dissipation factor moves from about 140°C to more than 200°C, which is almost the same value as for sample PI-4.

For the stretched sample PI-2, apart from the shift of the conduction-loss increase to higher temperature, its γ-peak is much lower but occurs at a higher temperature (-30°C). This may imply that the orientation of molecular chains during stretching will be beneficial to the further reaction of the residual reactive groups. The main characteristics of PI-2 are its low dissipation factor and its highly stable dielectric properties. As shown in *Figures 1* and *2*, the loss tangent is equal to or less than 2×10^{-3} and the maximum relative difference in ε' is 4.5% in a wide temperature range from -120°C to 220°C.

The decrease of ε' at temperatures around 80°C was first reported by Amborski[4] for Kapton films, but no explanation has been given. To clarify the origin of this decrease in ε', a repeat measurement of a PI-1 specimen has been designed. In this case, after the first run to about 135°C, the specimen was cooled to room temperature within the specimen chamber in the atmosphere of dry nitrogen. The second run gives an almost constant ε' value in the same temperature range (*Figure 3*). This phenomenon of decreasing ε' is, therefore, supposed to be the result of deabsorption of water in the specimen. It was supported by the fact that the performance of the specimen recovered when it was exposed to ambient atmosphere for 30 days (*Figure 3*). No change in ε' temperature-dependence has been found for sample PI-2 on repeating the same measurements. This implies that the high stability of dielectric properties of stretched PI-2 specimens is not only the result of the higher degree of imidization itself, but also the related low water absorption.

Figure 4 shows the t.s.c. spectra of some of the samples. Sample PI-1 exhibits three peaks labelled α', β' and γ'; they occur at temperatures 155°C, 120°C and 80°C, respectively. Similarly, three peaks have been found for PI-4 (*Figure 5*), but they occur at higher temperatures. In

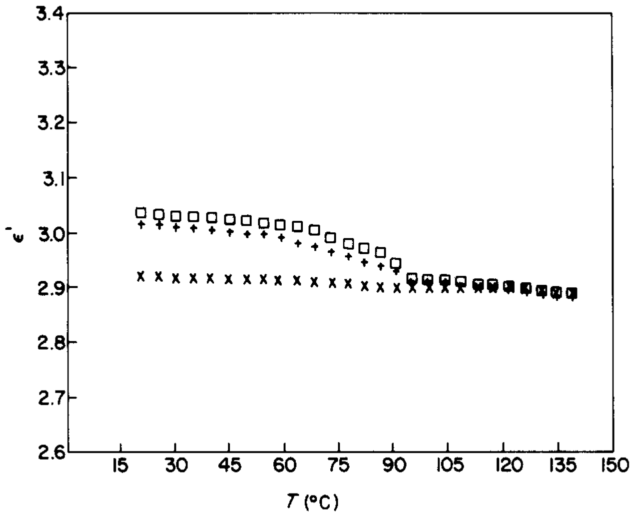

Figure 3 Repeat measurements for sample PI-1: □, first run; ×, second run, dry specimen; +, third run, specimen exposed to ambient atmosphere for 30 days

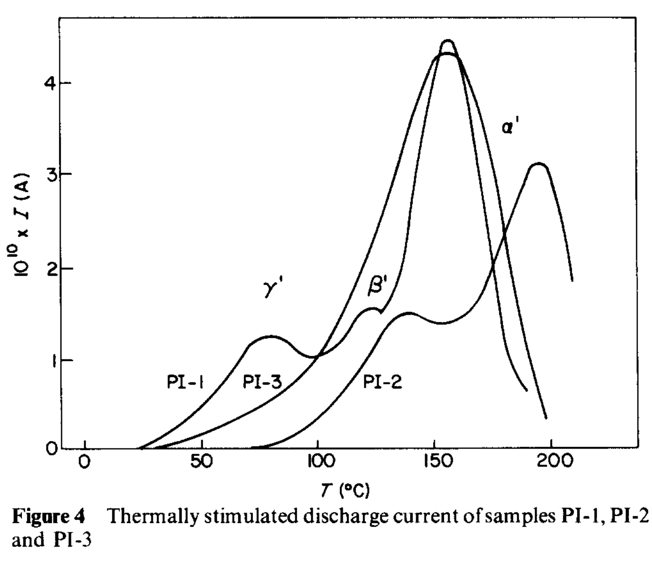

Figure 4 Thermally stimulated discharge current of samples PI-1, PI-2 and PI-3

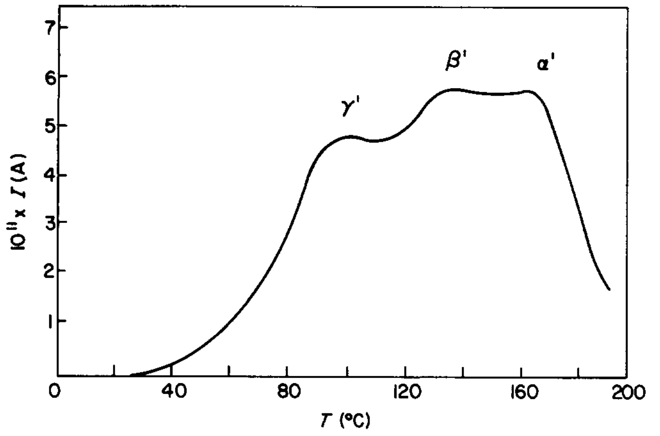

Figure 5 Thermally stimulated discharge current of PI-4

the literature two peaks in current were usually reported for Kapton films in the temperature range from 0°C to 200°C[7–9]. The peak at the lower temperature has been attributed to the orientational dipole polarization of the residual reactive groups and is related to the degree of imidization of the samples. The high-temperature t.s.c. peak is considered to be the result of a space-charge effect. The temperatures at which the peaks occur reported by Tanaka *et al.*[7] are more consistent with ours. Their 'space-charge peak' is very broad, extending from 100°C to 200°C, and the temperature at which its maximum occurs is 173°C. It is probably the case that the α' and β' peaks of PI-1 both correspond to the space-charge peak in the work of Tanaka *et al.*

The space-charge effect in the t.s.c. spectrum for PI-3 is similar to that for PI-1, but the α' and β' peaks combine with each other to give a broad space-charge current peak with the maximum occurring at 145°C. There is no individual γ' peak for PI-3, but a small t.s.c. current can still be detected in the corresponding temperature range. As has been shown before, samples PI-1 and PI-3 are quite different in their conduction behaviour at high temperature (*Figure 2*), so their similar space-charge current should be mainly the result of detrapping charges injected from the electrodes during polarization.

For stretched sample PI-2 no current has been detected in the temperature range of the γ' peak, so the t.s.c. data also imply that the reaction of residual reactive groups become easier when molecules are well oriented. The α' peak of PI-2 is lower than that for PI-1 and PI-3, and a shift of about 30°C to a higher temperature is observed. This means that stretching will help to decrease structural defects within the PI films and hence depress the injection of electrons and the space-charge phenomenon in the t.s.c. spectrum.

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