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Effects of Annealing upon Molecular Orientation and Microwave Dielectric Anisotropy in Polyimide Films

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ABSTRACT: Molecular orientation and dielectric anisotropy of polyimide films before and after annealing for 2 h at 250°C were studied by use of the microwave method. The annealing made the dielectric constant ε' and loss ε'' decrease markedly while gave a little change in the orientation pattern and then in the direction and degree of molecular orientation in the polyimide films. On the other hand, the direction of maximal thermal shrinkage corresponded to that in which the polyimide molecules are, on an average, aligned in the maximum dielectric loss and minimum transmitted microwave intensity. The results suggest that the orientation pattern reflects the thermal shrinkage and that the decrease in ε'' due to the annealing is ascribed to an increase in crystallinity of polyimide molecules in the amorphous region but gives a bit change in orientation of macromolecules.

KEY WORDS Annealing / Polyimide / Molecular Orientation / Dielectric Anisotropy / Microwave /

Aromatic polyimide films exhibit excellent physical, electrical, and mechanical properties over a wide temperature range. Because of the good electrical properties in dielectric strength and dissipation factor over a wide range of temperature and frequency, the films are useful for heat-resistive insulating materials such as printed circuit board and electric cable. In the practical application to the electronic engineering field, the information on the thermal shrinkage and the mechanical and microwave dielectric properties is very important.

As for polyimide films, the molecular orientation has been roughly estimated from the data on the viscoelastic modulus[1,2] and the complex dielectric constant has been measured only at audio frequencies.[3,4] But, the molecular orientation affecting thermal shrinkage data and microwave dielectric data on polyimide films had not yet been reported in details in the literature.

The microwave method developed by the author[5-7] has overcome such difficulty in the time-consuming. The microwave method made it possible to determine quickly and accurately the molecular or fiber orientation and the microwave dielectric anisotropy without contact. It was applied to the paper sheets,[8-11] polymer films such as poly(ethylene terephthalate) (PET) and poly(vinylidene fluoride),[12-20] human blood vessels,[21] cow skins,[22] and nonwoven fabrics.[23] In a previous paper,[24] we reported the molecular orientation of polyimide films determined by the microwave method, and compared the results with those by the mechanical and infrared methods.

The present paper describes effects of annealing upon the molecular orientation and the microwave dielectric anisotropy in polyimide films and compares the results with the thermal shrinkage.

EXPERIMENTAL

Samples

Samples used here were commercially available polyimide Kapton 100H (Du Pont) films with 26 μm thick which were prepared by the cast method.

Measurement of Orientation Pattern

A given film is inserted into the cavity resonator system.[12,15] Polarized microwaves are incident perpendicularly to the plane of the film which is rotated at a speed of 6.0 s per turn about the axis normal to it. The transmitted microwave intensity I is detected at every 1° of rotation angle θ.[12] The angular dependence of the transmitted microwave, which is hereafter called the orientation pattern,[15] reflects the orientational distribution of molecules in the film plane. The measuring frequency F for the orientation pattern data was 4.0 GHz.

Dielectric Measurement

The dielectric constant ε' and dielectric loss ε'' at θ are expressed by the following equation for the film to which a perturbation theory is applicable for determination of complex dielectric constant.[5,15]

$$\varepsilon'(\theta) = 1 + A(c/t)[f_{10} - f_{20}(\theta)]/f_{20}(\theta) \quad (1)$$

$$\varepsilon''(\theta) = B(c/2t)\{[1/Q_2(\theta)] - [1/Q_1]\} \quad (2)$$

Here, t is the thickness of the sample, c is a parameter related to the depth of rectangular waveguide, Q_i is the Q-value defined by the ratio of the resonance frequency f_{i0} to the half-width of the resonance curve, and A and B are constants associated with the apparatus. The subscripts $i=1$ and 2 indicate the values before and after the insertion of the sample. The f_{10} and Q_1 are constants independent of θ.

The time needed for dielectric measurement was 30 s at a fixed direction. For the measurement we used a transverse electric wave of the type TE_{10L}, with L = odd integer, as the electromagnetic mode.[5,7] The sample size was 100 × 100 mm.

Measurements of Thermal Properties

The thermal shrinkage was measured as follows: Two strips of 10 mm wide, 100 mm long and 26 μm thick cut from the original film in the same direction were prepared in different directions. The strips were annealed for 2 h at 250°C. The dimensions of the strips were measured at room temperature by using an optical reading microscope. The thermal shrinkage $S(\theta)$ defined as

$$S(\theta) = -[L_2(\theta) - L_1(\theta)]/L_1(\theta) \qquad (3)$$

where L is the length of the strip at room temperature and the subscripts 1 and 2 denote before and after the annealing, respectively. The S values for the two strips cut in the same direction were averaged.

Dependence of Complex Dielectric Constant upon Transmitted Microwave Intensity

The transmitted microwave intensity $I(\theta)$ is given by[14]

$$I(\theta)/I_{10} = 1/(X+Y) \qquad (4)$$

$$X = [1 + 2t\varepsilon''(\theta)Q_1/(Bc)]^2 \qquad (5)$$

$$Y = Q_1{}^2[Acf_{10}/(\{Ac + t[\varepsilon'(\theta) - 1]\}f_{\text{obs}}) - \{Ac + t[\varepsilon'(\theta) - 1]\}f_{\text{obs}}/(Acf_{10})]^2 \qquad (6)$$

Here, I_{10} is the transmitted microwave intensity before insertion of sample and I_{10} and f_{10} are constants independent of θ.

For a sample with low ε' and ε'', the term of Y in eq 6 is negligible in comparison with the term of X. This negligibility was estimated to be reasonable from results obtained by the present measurement system. And, the X is approximately expressed by

$$X \fallingdotseq 1 + 4t\varepsilon''(\theta)Q_1/Bc \qquad (7)$$

Thus, eq 4 is given by

$$I(\theta))/I_{10} \fallingdotseq 1 - 4t\varepsilon''(\theta)Q_1/Bc \qquad (8)$$

and then

$$\{I_{10} - I(\theta)\}/I_{10} = 4t\varepsilon''(\theta)Q_1/Bc \qquad (9)$$

Since I_{10}, t, Q_{10}, B and c is unchangeable for the measurement system considered here, $I(\theta)$ increases with a decrease in the value of $\varepsilon''(\theta)$. Furthermore, eq 9 shows that the attenuation in microwaves should depend on the value of ε''.

RESULTS

Figure 1 gives the orientation patterns measured at room temperature before and after the annealing, for 2 h at 250°C, of the polyimide film of 100 mm × 100 mm size, which was obtained by cutting out of the original Kapton 100H film with 508 mm width. Here, the machine direction MD is defined as that for rolling film in the process of preparing the film. In order to discuss the orientation characteristics two parameters are introduced. One is the orientation angle β defined as the θ at which the transmitted microwave intensity I shows a minimum, and the other is the molecular orientation ratio MOR defined as the maximum-to-minimum ratio of I. These can be taken as the average direction of molecular chains and a measure of orientational anisotropy, respectively. Further, the ratio TD/MD of the transmitted microwave intensities in the transverse direction TD to the MD is described in Figure 1. Here, the MD is perpendicular to the TD. In the measurements of the orientation pattern in Figure 1 the microwave power incident to the polyimide film was adjusted so that

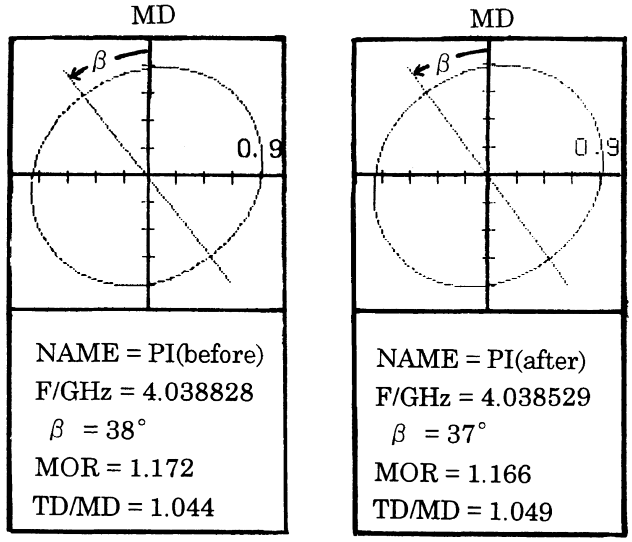

Figure 1. Orientation patterns at 4.0 GHz of Kapton 100H film at room temperature before and after the annealing for 2 h at 250°C.

the maximal value of transmitted intensities detected at different angles before the annealing should be equal to that after the annealing.

It should be noted here that, though the annealing for 2 h at 250°C gave a marked change in the thermal shrinkage described below, a little effect was seen for the orientation pattern: the change in β was from 38° to 37° and that in MOR and TD/MD was from 1.172 to 1.166 and from 1.044 to 1.049, respectively. This means that the anisotropy TD/MD in the two directions increased a little bit even though as a whole the anisotropy of the film decreased and then suggests that an anisotropic shrinkage occurred in the film plane. When the microwave power incident to the polyimide film was kept constant before and after the annealing, a change was observed in the orientation pattern even though the patterns were not shown here. That is, the transmitted microwave intensity increased obviously by annealing. This fact comes from a decrease in ε'', according to eq 8. The annealing also makes the degree of attenuation in microwaves decrease, as expressed by eq 9. Correspondingly, the value of F decreased from 4.038828 to 4.038529 GHz and then the film thickness increased slightly[23] within an error of one micrometer. These facts are worth noting.

Such non-uniformity in the polyimide film may have some effects on its thermal shrinkage. The angular dependence of thermal shrinkage S for polyimide film 1—3 (see sample No. 1—3 in Figure 3 of ref 24) illustrated in Figure 2 is markedly different from those obtained for I, ε', ε'', breaking strength and elastic modulus as described in a previous paper.[24] The β and MOR for the polyimide film 1—3 before the annealing were determined to be 39° and 1.171, respectively. The S value changes from 4.68×10^{-4} to 3.31×10^{-3} as θ changes. This means that the annealing evidently induced an anisotropic shrinkage. However, $\theta \sim 40°$ for the maximal shrinkage is consistent with the average chain directions estimated by other data[24] such as mechanical strength, infrared spectra and orientation pattern. Such a correspondence is observed for the PET film.[12] The direction of maximal shrinkage corresponds to that in which the polyimide

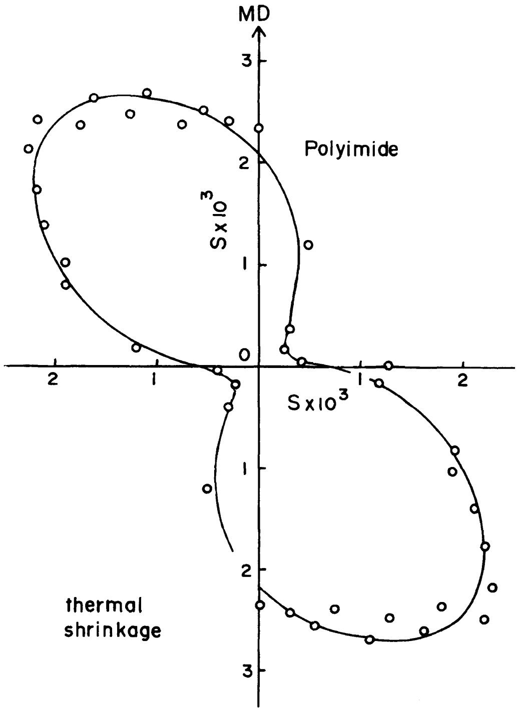

Figure 2. Angular dependence of thermal shrinkage S, for the polyimide film 1—3, measured at room temperature after annealing for 2 h at 250°C.

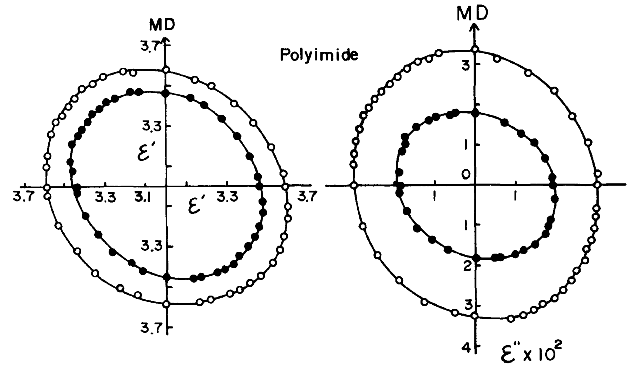

Figure 3. Angular dependences of ε' and ε'' at 4.0 GHz for the polyimide film 1—3 at room temperature before (open circles) and after (solid circles) annealing for 2 h at 250°C.

molecules are, on an average, preferentially aligned. Thus, the anisotropic thermal shrinkage closely relates to the change in the orientation pattern due to the annealing. It should be noted here that, though the annealing for 2 h at 250°C gave rise to a marked shrinkage of the film, a little effect was seen for the orientation pattern described above.

Figure 3 shows the angular dependences of ε' and ε'' at room temperature before and after the annealing, for 2 h at 250°C, of the polyimide film 1—3. It indicates that the annealing induces no substantial change in chain orientation, as pointed out above, but it results in an appreciable decrease in the ε' and ε'' by about 4% and 40%, respectively. This lowering mainly in the dielectric loss may be considered to arise from an increase in crystallinity[16] or from a frequency shift of dielectric relaxation due to annealing.[16] Though the annealing temperature is far below the glass transition temperature, the rearrangement of the molecules in the amorphous region may be induced at 250°C. Thus, such a annealing of polyimide film gives dielectric loss ε'' as a good dielectric material.

In this way the annealing gave a significant change in the dielectric properties of polyimide films.

DISCUSSION

In a previous paper,[24] the directions of the maximal mechanical breaking strength, elastic modulus, and infrared absorbance corresponded to the maximal dielectric constant and loss. The dielectric loss of polyimide at 4.0 GHz may originate from such local motions as the twisting of the main chain. Then, the largest change in dipole moment of the sample occurs in the direction of the main chain of poly(4,4′-oxydiphenyl pyromellitimide) Kapton 100H.[25,26] These facts suggest that the polyimide molecules are, on an average, aligned preferentially in the direction of β. This means that all the polyimide molecules in the Kapton films used here are not necessarily aligned in the MD. Such a behavior is similar to the results observed for the biaxially stretched PET films.[7,12] It is well known that the direction of molecular orientation is often affected by the machine conditions such as temperature and stress in the process of preparing films.

A change in the orientation pattern due to the annealing evidently suggests an occurrence of anisotropic shrinkage, and then corresponds to the result on the thermal shrinkage.

The annealing temperature, 250°C, is far below the glass transition temperature of Kapton, which is estimated to be *ca.* 410°C. Nonetheless, the annealing caused a remarkably appreciable shrinkage and an obvious change in the orientation pattern for polyimide film. Especially, a increase in the transmitted microwave intensity corresponds to the decrease in ε''. This also means that the attenuation in microwaves closely relates to the value of ε''. Such a result may be ascribed mainly to the enhancement of local motion of the chain in the amorphous region. The drastic lowering in ε'' by the annealing may be ascribed to an increase in crystallinity or a shift in relaxation. In the future, such a lowering should be made clear in detail.

REFERENCES

1. I. M. Ward, *Adv. Polym. Sci.*, **49**, 458 (1985).
2. G. Conte, L. D'Ilario, N. V. Pavel, and E. Giglio, *J. Polym. Sci., Phys. Ed.*, **14**, 1533 (1976).
3. E. Sacher, *IEEE Trans. Electr. Insul.*, **EI-13**(2), 94 (1978).
4. E. Sacher, *IEEE Trans. Electr. Insul.*, **EI-13**(2), 85 (1979).
5. S. Osaki, *J. Appl. Phys.*, **64**, 4181(1988).
6. S. Osaki, *Nature*, **347**, 132 (1990).
7. S. Osaki, *Review of Scientific Instruments*, **68**, 2518 (1997).
8. S. Osaki, *Bull. Jpn. Soc. Print. Technol.*, **23**, 19 (1985).
9. S. Osaki, *Tappi*, **70**, 105 (1987).
10. S. Osaki, *J. Appl. Polym. Sci.*, **37**, 527 (1989).
11. S. Osaki, *Sen-i Gakkaishi*, ***31***, 33 (1990).
12. S. Osaki, *Polym. J.*, **19**, 821 (1987).
13. S. Osaki and K. Uranishi, *Polymer*, **31**, 33 (1990).

14. S. Osaki, *J. Polym. Sci. Part C.*, **28**, 147 (1990).
15. S. Osaki, *J. Appl. Phys.*, **67**, 6513 (1990).
16. S. Osaki, *Polym. J.*, **25**, 1311 (1993).
17. S. Osaki, *Polymer*, **35**, 47 (1994).
18. S. Osaki, *J. Polym. Sci. Phys. Ed.*, **33**, 685 (1995).
19. S. Osaki, *Polym. J.*, **28**, 131 (1996).
20. S. Osaki, *Polym. J.*, **28**, 323 (1996).
21. K. Yamamoto, S. Osaki, S. Yamashita, and M-o. Yamada, *Cell. Mol. Biol.*, **34**, 571 (1988).
22. S. Osaki, M-o. Yamada, A. Takakusu, and K. Murakami, *Cell. Mol. Biol.*, **39**, 673 (1993).
23. S. Osaki, *Tappi.*, **72**, 171 (1989).
24. S. Osaki and K. Tashiro, to be submitted to *Macromolecules*.
25. G. Conte, L. D'Ilario, N. V. Pavel, and E. Giglio, *J. Polym. Sci.*, **B12**, 603 (1976).
26. N. Takahashi, D. Y. Yoon, and W. Parrish, *Macromolecules*, **17**, 2583 (1984).