SHORT COMMUNICATIONS

Thermal Expansion Behavior of Various Aromatic Polyimides

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(Received January 25, 1985)

KEY WORDS Thermal Expansion / Low Thermal Expansion / Polyimide /
Film / Aromatic / Diamine / Dianhydride / Shrinkage / Polyamic Acid /
Varnish /

Polyimides, recognized as very high performance plastics due to their excellent heat resistance and toughness,¹ are used as insulation films in electric and electronics applications, such as substrates for flexible printed circuits,² and insulation layers for semiconductor devices.³ There are various kinds of polyimides^{1,4–6} and their properties are discussed in numerous reports.^{7–12}

The thermal expansion behavior of polyimides, however, has received little attention. In fact, it has long been believed that polymers, including polyimides, have high thermal expansion coefficients compared with metals and ceramics. In the present study, the authors show that some aromatic polyimides actually have very low thermal expansion coefficients.

EXPERIMENTAL

Samples

A polyamic acid varnish was prepared by reacting an aromatic diamine with an aromatic dianhydride (Table I) in *N*-methyl-2-pyrrolidone at room temperature. The varnish was coated onto a glass plate and dried at 100°C for 1 h. The resulting film was stripped off and cured at 200°C for 1 h and at 400°C for 1 h in nitrogen gas. This gave a polyimide film.

Its thermal expansion was found to depend on whether curing shrinkage was unhindered (free cure), or prevented by fixing the film on an iron frame in one direction (unifix cure) or in two directions at right angles (bifix cure).

The sample number of the polyimide is expressed by a letter for diamine and a number for dianhydride in Table I. For example, No. A1 indicates a polyimide from *p*-PDA and PMDA.

Coefficient of Thermal Expansion

A film 5 mm wide, 65 mm long (between chucks) and 20 to 100 μm thick was used as the sample. It was mounted on a thermal mechanical analyzer (TMA 1500, Shinku Riko K.K.) and the change in length was measured at a heating rate of 5°C min⁻¹ in air. Since the thermal expansion coefficient was dependent on temperature, the average value between 50 and 250°C was used as a representative value.

Table I. Materials

$\left(R_1 - \text{N} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} R_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N} \right)_n$			
	$-R_1-$		$-R_2-$
A		(<i>p</i> -PDA)	1 (PMDA)
D		(DATP)	2 (BPDA)
F		(DDS)	3 (BTDA)

RESULTS AND DISCUSSION

Figures 1 and 2 show the thermal expansion behavior of two polyimides under different

curing conditions. Figure 1 shows the behavior for polyimide No. A3 obtained from *p*-PDA and BTDA. There were dimensional changes of 0.9% for free-cured film and 0.5% for bifix-

Figure 1. Thermal expansion behavior for No. A3: 1, bifix cure; 2, free cure.

Figure 3. Thermal expansion behavior for No. D1: 1, bifix cure; 2, free cure.

Figure 2. Thermal expansion behavior for No. F3: 1, bifix cure; 2, free cure.

Figure 4. Thermal expansion behavior for No. A2: 1, bifix cure; 2, free cure; 3, UFX-X; 4, UFX-Y.

cured film when the temperature was raised from 50 to 250°C. Thus, the thermal expansion coefficients of No. A3 were about $5 \times 10^{-5} \text{ K}^{-1}$ for the free-cured film and about $3 \times 10^{-5} \text{ K}^{-1}$ for the bifix-cured film. Figure 2 shows the behavior of polyimide No. F3 obtained from DDS and BTDA. In this case, the films obtained by free and bifix cures had the same thermal expansion coefficient, $6 \times 10^{-5} \text{ K}^{-1}$. Thus, the thermal expansion coefficient of polyimide was usually from 3 to $6 \times 10^{-5} \text{ K}^{-1}$ and changed depending on the curing shrinkage conditions.

Figure 3 shows the thermal expansion behavior of polyimide No. D1 obtained from DATP and PMDA. The film had a dimensional change of about 0.2% (free cure) or about 0.1% (bifix cure) in the temperature range of 50 to 250°C. The thermal expansion coefficients of the films were about $1 \times 10^{-5} \text{ K}^{-1}$ (free cure) and about $0.6 \times 10^{-5} \text{ K}^{-1}$ (bifix cure).

Figure 4 also shows thermal expansion behavior. For the polyimide No. A2, the dimensional change with the bifix cure was 0.1% or less, while that by the free cure was as much as 0.4% in the range of 50 to 250°C. Using this polyimide, prevention of curing shrinkage on only one axis was also studied. In the prevented direction (UFX-X) the thermal expansion coefficient was found to become smaller

and the dimensional change was almost 0% up to about 250°C. But, perpendicular to the prevented direction (UFX-Y), the behavior was almost the same as that for the free cure. The shrinkage of free-cured film at the time of imidization was about 10% but the resulting effect on this polyimide was the same as that obtained by stretching a conventional polymer film as much as about 10 times of its original length.

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