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THERMAL EXPANSION OF AROMATIC POLYAMIDEIMIDE COMPOSITE FILMS REINFORCED WITH AROMATIC POLYAMIDE FIBERS

YOSHIHIRO OHMIYA and HIROTARO KAMBE

Institute for Composite Materials, Faculty of Technology, Gunma University, 1-5-1 Tenjincho, Kiriu 376 (Japan)

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ABSTRACT

Aromatic polyamideimide (PAI) films were reinforced by aromatic polyamide fibers as a unidirectionally oriented composite (Type I) and bidirectionally oriented laminate composite (Type II). The thermal expansion of the composite films was investigated with respect to the direction of fiber orientation. The thermal expansion behavior was anisotropic in the unidirectionally reinforced composite films, and considerably isotropic in the bidirectionally reinforced composite film. The thermal expansion coefficients based on thermoelastic models are calculated and compared with experimental data.

INTRODUCTION

In a composite of plastics with continuous fibers, fibers are generally oriented unidirectionally. A unidirectionally reinforced composite exhibits, however, a strong anisotropy in its properties at practical applications. For the purpose of producing a more isotropic composite, it is more common to use the reinforcements as laminar crossed fibers or as a cloth.

Thermally stable flexible films of an aromatic polyamideimide (PAI) are obtained by casting from a solution in a polar solvent. The fairly flexible composite films of PAI are obtained with a soft fiber reinforcement. An aromatic polyamide (PA) fiber may be used as a flexible reinforcement without loss of thermal stability of PAI composite films. The mechanical properties of this type of PAI composite films were investigated by Ohmiya and Kambe [1] with respect to the direction of fiber orientation. For unidirectionally reinforced films, the most remarkable effect of the reinforcement fibers on mechanical properties was observed at the fiber direction. The elastic modulus and fracture stress of specimens having fiber orientations other than fiber direction were lowered significantly. By bidirectional reinforcements is solved the anisotropy problem, but the strength at the fiber directions is depressed markedly by the effects of the fibers having other orientations.

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As an evaluation of the thermal stability, thermal expansions of the composites were measured. The thermal expansion behavior of a composite of an epoxy resin reinforced with a PA fiber was investigated by Strife and Prewo [2]. We studied thermal expansion behavior of PAI composite films reinforced with PA fibers in consideration of the anisotropy. By the theory of Schapery [3], the thermal expansion coefficient of a unidirectional composite could be derived from thermoelastic properties of the components. The results were compared with the present experimental data.

EXPERIMENTAL

Materials

An aromatic polyamideimide (PAI) varnish produced experimentally by the Film Laboratory of Toray Co., was kindly supplied for use as our material. Dimethylacetamide used as a solvent in varnish was also used as a diluent.

A commercial fiber of an aromatic polyamide, Kevlar 49, was obtained from E.I. DuPont de Nemours, Co. in the form of 195 denier yarn, and was used as a reinforcement.

Reinforcement textures

Two types of composite film with different reinforcement textures were prepared as shown in Table 1. Type I composite film was produced with a unidirectional reinforcement of Kevlar yarns. Type II composite was produced with bidirectional reinforcement of laminar perpendicularly crossed Kevlar yarns.

Casting films

PAI composite films were prepared as follows. First, the fiber reinforcements were fixed on a glass plate. For both composite films, the Kevlar

TABLE 1

Sample composite films

Type	Reinforcement	Fiber density (Yarns/cm)	Volume fraction of fibers (%)
I	Unidirectional yarns	10	5 ± 1
II	Bidirectionally layered crossed yarns	Longitudinal 10 Transverse 10	10 ± 2

yarns were wound around the glass plate at a definite separation of ca. 1 mm. Along the edge of the glass plate, the fibers were fixed with an adhesive. The fiber reinforcements were dipped in the PAI varnish together with the glass plate and dried in vacuum overnight. After leaving in air for several hours, the resulting film was heated at 140°C for 3 h under an ambient pressure. The film was removed from the glass plate and heated at 250°C in vacuum for 3 h to get a sample film.

Composite film sample

By these procedures, the obtained composite films exhibited a considerable flexibility and an enhanced strength compared with the original PAI film. The volume fractions of the reinforcements in the composite films were evaluted from the density of the film, as shown in Table 1.

Measuring method of thermal expansion coefficient

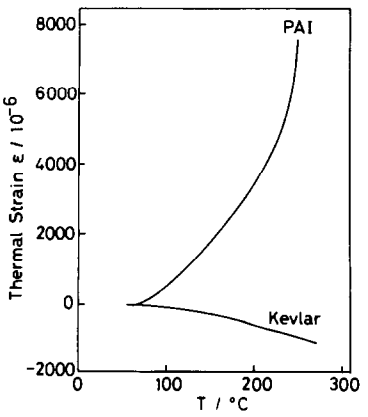
The thermal expansion coefficient of the composite films was measured with a thermomechanical analyzer system (TMS-2) from Perkin-Elmer Co., Ltd. at a temperature range of 30–250°C in nitrogen atmosphere. The specimens had an initial length of 7.75 mm and a width of 1 mm. The change of length was measured on heating and cooling at a rate of 2.5°C min^{-1}.

RESULTS AND DISCUSSION

Thermal expansion behavior during the heating process

In Fig. 1 are shown the dilation curves for Kevlar 49 fibers and a PAI homogeneous film from 50 to 250°C. The thermal expansion curve of Kevlar 49 fibers shows a negative slope, i.e. shrinkage, controlled by the existence of highly crystallized and the highly oriented Kevlar 49 fibers. The thermal expansion curve of PAI film indicates a positive slope, and especially above 250°C it shows the most rapidly increasing slope corresponding to its glass transition [4].

The dilation curves for uniaxially reinforced Type I composite at the different fiber orientation angles θ are shown in Fig. 2. The thermal expansion curve of Type I composite at $\theta = 0°$ showing a negative slope is due to Kevlar 49 fibers. The thermal expansion is enhanced with increasing θ, and above $\theta = 67.5°$ in particular shows similar behavior. The thermal expansion coefficient at a specific temperature was defined as the slope of the tangent to the $\Delta L/L$ vs. T curve, while the average value of the thermal



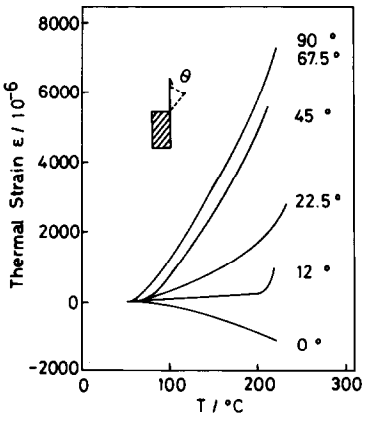


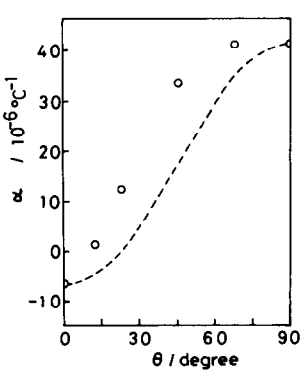
Fig. 1. Dilation curves for Kevlar 49 fibers and a PAI film from 50 to 250°C.

Fig. 2. Dilation curves for Type I composite in the directions defined by θ in the figure from 50 to 250°C.

expansion coefficient over a temperature range was calculated by the equation:

$$\alpha = \frac{\Delta L}{L_0 \Delta T} \tag{1}$$

The values of α calculated from eqn. (1) over the 100–150°C temperature range were plotted in Fig. 3. The thermal expansion coefficient of unidirectional composite may be calculated as a function of direction angle of the



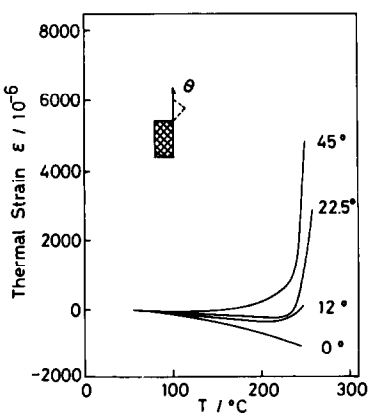


Fig. 3. Average thermal expansion coefficients for Type I composite over the 100–150°C temperature range. The dotted curve is a plot of eqn. (2) for the experimental values.

Fig. 4. Dilation curves for Type II composite in the directions defined by θ in the figure from 50 to 250°C.

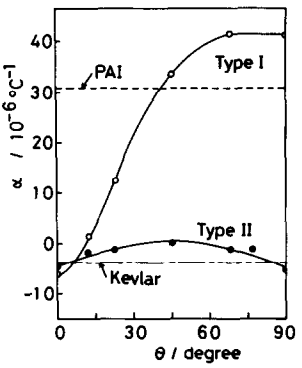


Fig. 5. Average thermal expansion coefficients for Kevlar 49 fibers, a PAI film, Type I and Type II composites over the 100–150°C temperature range.

fiber orientation from the equation [2]:

$$\alpha_\theta = \alpha_L \cos^2 \theta + \alpha_T \sin^2 \theta \quad (2)$$

where α_L and α_T are the α values at the longitudinal and the transverse directions, respectively. The measured values of α and those calculated from eqn. (2) using the average measured values of α_L and α_T are compared in Fig. 3. In the low angle range, the measured values of α increase slightly with increasing θ, but in the high angle range, the measured values of α do not change markedly with increasing θ.

Figure 4 shows the dilation curves for Type II bidirectionally reinforced laminate composite at various fiber orientation angles. This composite is constituted from two unidirectional plates orthogonally oriented at $\theta = 0$ and 90° and show thermal expansion curves symmetrically situated around a curve at $\theta = 45°$. At $\theta = 0$, 12 and 22.5°, curves indicate a negative thermal expansion at a lower temperature range. Above 250°C, a sudden positive slope of the dilation curves also appeared due to the glass transition.

Average values of α of Kevlar fibers, PAI film, Type I and Type II composite calculated from eqn. (1) over the 100–150°C temperature range, are plotted in Fig. 5. The α value of Type I unidirectional composites exhibits a high degree of anisotropy for in-plane thermal expansion, and above $\theta = 45°$ it shows a greater thermal expansion than for the PAI homogeneous film. This behavior can be explained by the fact that the matrix is restricted by Kevlar fibers. The restricted matrix expands in excess for transverse direction [5]. The α value of bidirectional composites exhibits an isotropic character for in-plane thermal expansion. This behavior is enhanced by two orthogonally oriented unidirectional reinforcements.

Thermoelastic models for thermal expansion of unidirectional composite

The linear thermal expansion coefficient of a unidirectional composite is predicted by thermoelastic properties of the component [3]. In a fiber

TABLE 2

Thermal expansion coefficients at 100°C for Type I composite film at 0 and 90° to the fiber direction

α_L	−6.45	8.56
α_T	41.3	37.4

direction, the α value of a unidirectional composite may be predicted by the equation:

$$\alpha_L = \frac{E_m \alpha_m V_m + E_f \alpha_f V_f}{E_m V_m + E_f V_f} \tag{3}$$

where E, α and V are the elastic modulus, thermal expansion coefficient and volume fraction, respectively. The suffixes m and f show the respective components of matrix and fiber. The experimentally determined value of α_L and that calculated from eqn. (3) at 100°C are listed in Table 2. The measured value is much less than the calculated one. For the longitudinal coefficient of thermal expansion of unidirectional Kevlar/epoxy composites, Strife and Prewo [2] suggest that the axial fiber expansion coefficient would be more negative than that predicted by eqn. (3). In the negative thermal expansion fiber, the coefficient of thermal expansion of the unidirectional composite has not been represented by eqn. (3).

For the transverse coefficient of thermal expansion of unidirectional composites, Schapery derived the following equation [3]:

$$\alpha_T = (1 + \nu_m)\alpha_m V_m + (1 + \nu_f)\alpha_f V_f - \alpha_T \nu_c \tag{4}$$

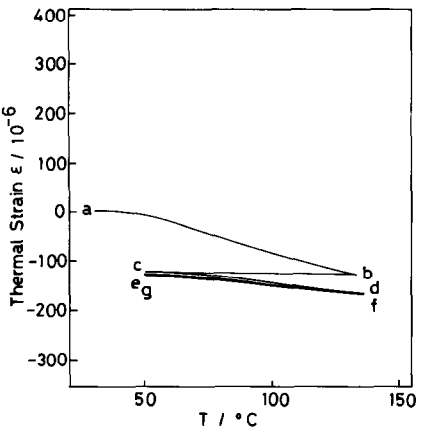
where ν is Poisson's ratio and c means the composite in bulk. The calculated value of α_T at 100°C using the fiber transversal coefficient of thermal expansion is compared with the experimental value in Table 2. Poisson's ratio of the composite, ν_c, is expressed by the component ratio:

$$\nu_c = \nu_m V_m + \nu_f V_f \tag{5}$$

It is shown that calculated values of thermal expansion are in close agreement with those measured. In the transverse direction, this agreement may be explained by a series model of the composite. The total thermal expansion can be expressed by the sum of the thermal expansion of fiber and matrix components in series.

Thermal expansion behavior during the heating and cooling cycles

In Figs. 6 and 7 the dilation curves of Type I composite film at $\theta = 0$ and 90° are presented during the heating and cooling cycles over the 30–140°C temperature range. At $\theta = 0°$, a large negative slope observed in the thermal expansion curve at the first heating (a → b) is controlled by Kevlar fibers.



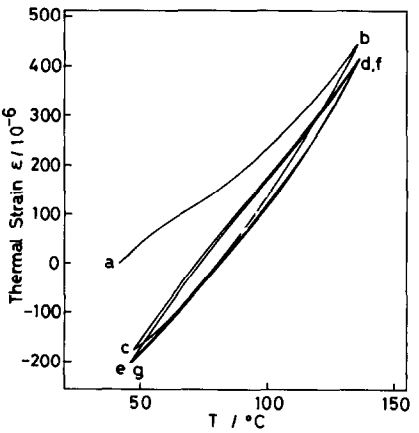


Fig. 6. Dilation curve of Type I at $\theta = 0°$ during the heating and cooling cycles over the 30–140°C temperature range.

Fig. 7. Dilation curve of Type I at $\theta = 90°$ during the heating and cooling cycles over the 30–140°C temperature range.

During the cooling process (b → c) the thermal expansion curve was not reproduced, and after the second cycle (c → d → e → f → g) the thermal expansion curves show a very small hysteresis loop. At $\theta = 90°$, after the first heating cycle, the thermal expansion curve of Type I composite was smaller than that of the original sample. This behavior may be explained by liberation of residual stresses which are restricted by long fibers [6]. After the second cycle (c → d, etc.) the thermal expansion curves showed a reversible hysteresis loop.

CONCLUSIONS

In the PAI composites with unidirectional PA fiber reinforcements, significant anisotropy was observed by the effects of the reinforcement fibers. At $\theta = 0$, in particular, considerable negative expansion was observed, and at $\theta = 90°$, on the contrary, remarkable positive expansion was observed. These facts indicate the effects of long fibers.

The thermal expansion coefficients at $\theta = 0°$ are not in agreement between calculated and measured values. The negative thermal expansion of the fiber could not be predicted by thermoelastic properties of the components.

By bidirectional reinforcements, the anisotropy problem of the composite is solved. Considerable isotropy was observed by the effects of crossed reinforcement fibers.

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