THERMOGRAPHIC AND DILATOMETRIC STUDY OF POLYPYROMELLITIMIDE

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Abstract

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THERMOGRAPHIC AND DILATOMETRIC STUDY OF POLYPYROMELLITIMIDE

Polyimides are a new class of polymers with unusual properties ([1–3]). Thus, at room temperature films of polypyromellitimide (PM) have an elastic modulus of 30,000 kg/cm^2 and elongations at break of 100–120% ([2]). In polymers of other classes that are in the solid state, elongations at break are usually tens of times smaller.

To understand the properties of PM, along with the results of physicochemical ([3]) and physicomechanical studies ([2]), it is important to know the characteristics of the phase and aggregate state over a wide temperature range. In this connection we carried out a study of PM films subjected to different heat treatments by thermographic methods. Thermographic measurements were performed on an apparatus constructed by one of the authors for differential thermal analysis (DTA), and dilatometric measurements on an apparatus for determining the thermal expansion of films and fibers in vacuum ([4]). In both cases films 40–50 μ thick were used; the heating rates were 5°/min in the thermographic measurements and 2.5°/min in the dilatometric measurements.

Three types of films were investigated: I—initial, polyamic-acid film, obtained by drying a solution of polyamic acid in dimethylformamide at 20–40°; II—partially imidized, i.e., additionally heated at 80° for 40 min and at 130° for 15 min; III —imidized, whose heat treatment was completed by heating at 400° for 30 min.

Figure 1 presents the DTA data. For the initial film (Fig. 1a), on the first-heating curve (1) two regions of heat absorption are clearly observed, with maxima at 90 and 145°, respectively. The cooling curve (2) is shallow and has a very broad weak maximum in the region 120–180°. On repeated heating no thermal effects were observed.

During the first heating of film II (Fig. 1b, curve 1), one broad maximum of heat absorption was observed in the interval 90–160°. On cooling and repeated heating the thermal effects were absent (curves 2, 3). In film III no thermal effects were observed either in the first or in subsequent heating–cooling cycles. However, in some cases the marginal thickened pieces of film III gave clear, repeatedly reproducible thermograms with maxima and minima (Fig. 1c). On

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the heating curve (1) a maximum of heat absorption was observed at 187°; on the cooling curve (2), a minimum of heat evolution at 160°.

The presence of maxima on the DTA diagrams of films I and II during the first heating is due to the occurrence of irreversible endothermic physicochemical processes. Such processes may be removal of residual solvent (dimethylformamide, which has a boiling point of 150°) and elimination of water during the dehydrocyclization of polyamic acid. Apparently, the thermal effects are caused mainly by removal of the solvent, since dehydrocyclization, as indicated in ([3]), proceeds intensively at 200-250°. However, this question cannot be considered resolved, since so far it has not been possible to separate the two effects.

The absence of maxima on the DTA diagrams of film III, as well as of films I and II during repeated heating and cooling, indicates that in polypyromellitimide, after completion of the high-temperature transformations in the range 20-400°, no phase transitions associated with the evolution or absorption of heat occur.

Fig. 1. DTA thermograms: 1 —heating, 2 —cooling: *a* —film I (polyamic acid), *b* —film II (partially imidized), 3 —repeated heating, *v* —edge of film III (imidized), *g* —diaminodiphenyl ether.

The thermal effects that were observed at the thick edges of film III are due to the presence of unreacted diaminodiphenyl ether. The thermogram of the latter is shown in Fig. 1*g*. It is clear from it that the maximum at 187° and the minimum at 160° correspond precisely to those maxima and minima that were observed during heating and cooling of the edge of film III.

Let us consider the dilatometric data. Figure 2 shows the thermal-expansion curve of film II. It can be seen that upon reaching 90° a sharp contraction begins —the shrinkage of the film. At constant temperature the shrinkage depends linearly on the logarithm of time (Fig. 2*b*).

Fig. 2. Film II (partially imidized): *a* —thermal-expansion curve, *b* —kinetics of film shrinkage; $\theta = \text{const} = 90^{\circ}$.

Film III behaved differently from film II: heating was not accompanied by contraction (Fig. 3). Figure 3*a* shows the dilatometric curve obtained during the first heating of film III. In this case a break was observed on the curve at 150°, resembling the break in amorphous linear polymers at vitrification ([5]).

The break disappeared after several heating (to 400°)—cooling cycles. After this the thermal-expansion curve became smooth and monotonically increasing. It

Figure 3

Figure 3: Figure 3

contained no anomalous regions over the entire temperature interval investigated by us, 20–400° (Fig. 3*b*). The dilatometric data agree with the DTA results. The shrinkage of film II during heating confirms that irreversible changes occur in it—removal of solvent or dehydrocyclization, which should also be accompanied by densification.* In accordance with the DTA data, film III shows no anomalies of thermal expansion.

The appearance of a break at 150° on the dilatometric curve of this film during the first heating is not accidental, since in this same temperature region—

* Removal of solvent is always accompanied by a decrease in dimensions ([4]).

in polyimide films, a small maximum of dielectric losses is observed, independent of frequency ([1], [2]). The loss maximum and the break in the expansion curve cannot be explained by the existence of a transition of the glass-transition—softening type. This follows from control experiments of type ([5]), which indicated the absence of characteristic reversible relaxation dilatometric effects upon annealing below and above 150°. The disappearance of the break after several heating–cooling cycles indicates that film III was not yet completely stable. However, the residual effects were insignificant; therefore they were not detected by the DTA method.

Fig. 3. Film III (imidized): *a*—thermal expansion curve during the first heating; *b*—thermal expansion curve after several heating–cooling cycles

On the whole, the data presented make it possible to assert that in polypyromellitimide, after completion of the entire heat-treatment cycle and stabilization of the chemical structure, no phase or aggregate transitions occur in the temperature interval from 20 to 400°.

X-ray diffraction patterns showed that the films we studied were amorphous. However, apparently the possibility of obtaining crystalline polypyromellitimide is not excluded, since after thermal drawing of the films a sharp texture appeared.*

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* Data obtained by B. M. Ginzburg and L. A. Volkova.

Note: Figure translations are in progress. See original paper for figures.