

DYNAMIC THERMOMECHANOMETRY OF AROMATIC POLYMERS

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Abstract - The significance of mechanical measurements for the evaluation of thermal stability of polymers is discussed. The dynamic mechanical measurement conducted thermoanalytically is called dynamic thermomechanometry. This technique was applied to evaluate thermal stability of aromatic polymers. The formation of supermolecular structure in amorphous region of aromatic polymers due to their rigid and planar ring structures was confirmed by small angle X-ray scattering technique. By dynamic thermomechanometry, a few molecular relaxations were found in glassy state of aromatic polymers above room temperature. The transition temperature found at the highest temperature depends on the superstructure of the polymers. The thermal shrinkage of the cold-stretched films of these polymers measured by thermomechanical analysis gave us more easily the molecular relaxations at high temperature range. Aromatic polymers reinforced by straight carbon fibers were also used as the samples for the determination of molecular relaxations. The degradation of the aromatic polymer sample in NO₂ atmosphere could be followed by dynamic thermomechanometry.

INTRODUCTION

Thermal stability of polymers is usually evaluated by thermoanalytical techniques. The degradation of polymers is most conveniently measured by thermogravimetry (TG) as a weight change of the sample at a uniform heating rate. Decomposition temperature is determined by the temperature exhibiting the initiation of weight decrease. At a practical application, the polymers are not to be used up to the decomposition temperature. Much below this temperature, the polymer loses its characteristic viscoelastic properties and simultaneously its feasibility for practical uses.

The mechanical properties of polymers are measured by several means. The tensile properties such as the fracture strength and ultimate elongation of the polymer films or fibers are often utilized to estimate the thermal stability of polymers. The retention of the properties at room temperature up to higher temperatures is the most convenient way of evaluation of the stability of the polymers (1). From the experimental difficulties belonging to these measurements, it is common to measure tensile properties at a constant temperature. The isothermal measurements could be repeated at high temperatures, but it is not possible to conduct the measurement at a uniform heating rate, i.e. as a thermal analysis.

Instead of these measurements, we can apply the so-called thermomechanical analysis (TMA) for this purpose. TMA techniques are usually carried out by the indentation of a loaded needle into polymers, but many other modes of deformation, such as extension, torsion, flexure, etc. may be used for TMA (2). TMA is most usefully applied to determine the softening temperature of the polymer. This phenomenon is related to the glass transition of the amorphous polymers or the melting of crystalline region of the crystalline polymers. By using TMA, we can estimate the retention of mechanical properties of the polymers.

Dynamic mechanical measurements are also applied to evaluate the thermal stability of polymers. Tensile or torsional vibrations of the solid films are most convenient to measure the viscoelastic properties of the polymer at a high temperature. Besides the glass transition, we can obtain several molecular relaxations due to subsidiary movements of the polymer chain elements. If the method is conducted thermoanalytically, it is called dynamic thermomechanometry (2).

Many thermally stable polymers have been synthesized during these twenty years. Among them, polymers involving aromatic or heterocyclic rings in its main chain gave us the most practically useful polymers such as aromatic polyamides, polyimides, polyamideimides, polybenzimidazoles, polyphenylene oxides, polyxylylenes, polysulfones, polyquinoxalines, etc. Due to the existence of rigid and planar aromatic or heterocyclic rings in their chains, the aroma-

tic polymers show a strong intermolecular interaction. They exhibit a high glass transition temperature and also a high decomposition temperature, which are evaluated by TMA and TG thermoanalytically.

In the present paper, we would like to present some experimental results from our laboratory on the dynamic mechanical properties of several aromatic polymers by using dynamic thermo-mechanometry. Details of experimental techniques and conditions are not described here and requested to be referred to original papers.

RESULTS AND DISCUSSION

Superstructure of aromatic polymers

The molecular interaction of rigid and planar aromatic or heterocyclic rings of the chain was confirmed by the existence of supermolecular structure in the amorphous state of aromatic polymers. By using the small angle X-ray scattering technique (SAXS), we have found such a superstructure for aromatic polyimide and polyamideimide (3). By the increase of initial heating temperature for the imidization of the precursor polyamic acid films, the long-range order was found in X-ray reflexes at a small angle for aromatic polyimide samples, as shown in Fig. 1. Similar effects were found in Fig. 2 for aromatic polyamideimide annealed at various temperatures. By increasing the temperature of thermal treatment, the small angle reflex was strengthened.

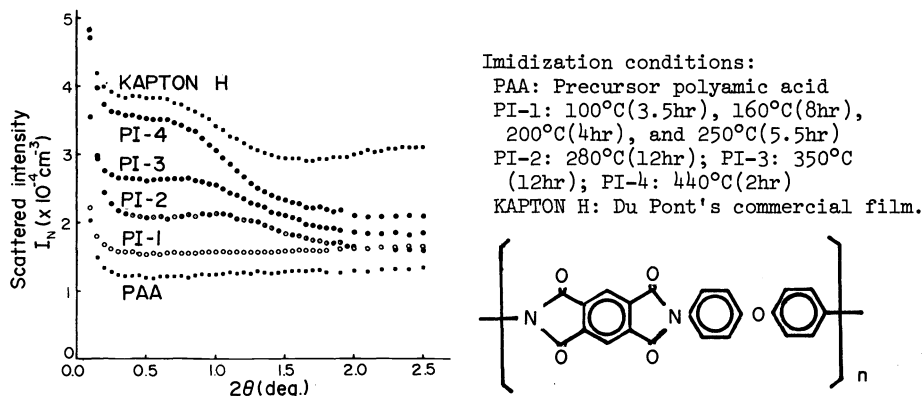


Fig. 1. Small angle X-ray scattering of aromatic polyimide (3).

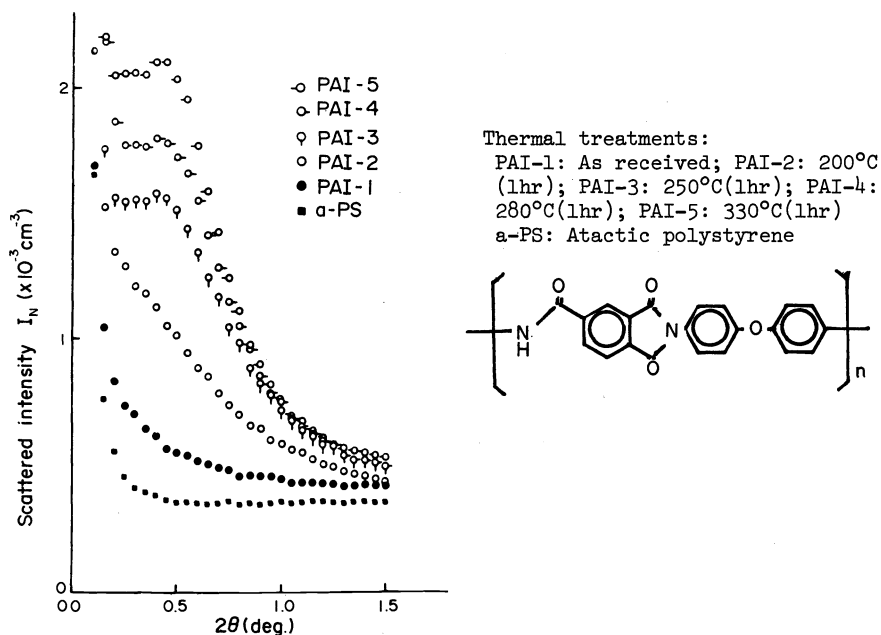


Fig. 2. Small angle X-ray scattering of aromatic polyamideimide (3).

Dynamic mechanical properties

The dynamic measurements of viscoelastic properties of aromatic polymers were conducted by tensile oscillations with a Rheovibron instrument and also by torsional oscillations with an inverse torsional pendulum. We first measured the torsional oscillations and found a few mechanical loss peaks above room temperature, particularly a new broad loss peak around 350°C for an aromatic polyimide sample. The last peak was magnified by cold-stretching of the sample film and disappeared after annealing (4), as shown in Fig. 3. Similar mechanical losses were also observed by Gillham (5) and Wrasidlo (6) for the same polyimide samples, independently. They did not notice, however, the effect of stretching on this peak. Gillham has assigned the peak to the glass transition of the polymer and the disappearance of the peak was explained by the chemical change of the polymer after thermal treatment.

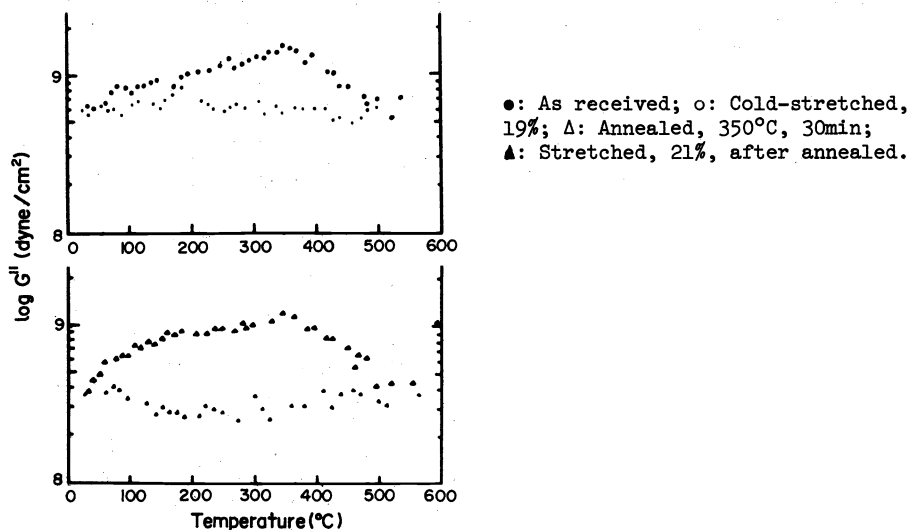


Fig. 3. Temperature dependence of dynamic loss modulus of aromatic polyimide KAPTON H films (4).

The effect of stretching on aromatic polyimide film was investigated by thermal shrinkage of cold-drawn films with thermomechanical analysis (TMA)(7). Stretched samples with different degrees of drawing by 10 - 40% showed a significant shrinkage over a broad range of temperature 50 - 500°C. By taking temperature derivatives of these curves, we observed only one shrinkage process for 12.5% stretched sample, but two and three different processes were found for 30% and 40% stretched samples, respectively, as shown in Fig. 4. These peaks are quite well corresponding to molecular relaxations obtained by dynamic measurements.

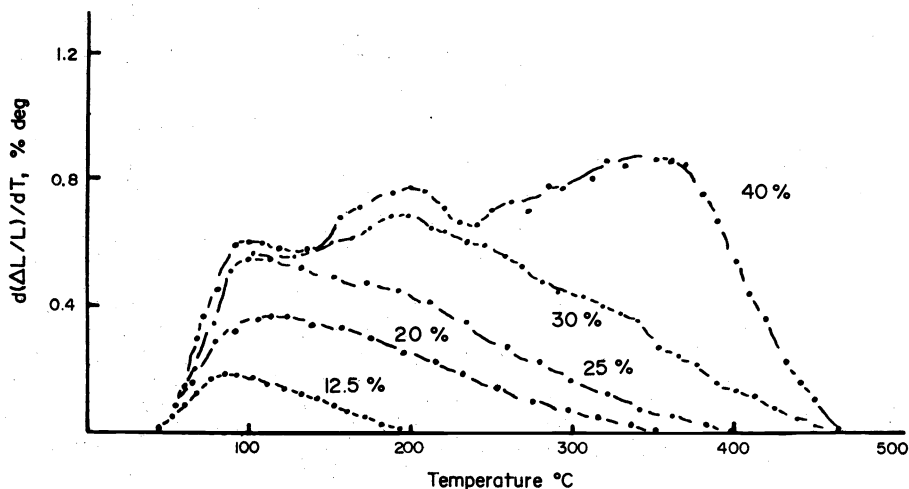


Fig. 4. Temperature derivative curves of thermal shrinkage of aromatic polyimide films with various percentages of stretching (7)

Temperature dependence of dynamic loss modulus of stretched aromatic polyamideimide shows a significant increase of loss peak around 250°C as the degree of stretching, as shown in Fig. 5 (8). The effect of stretching on this loss peak is quite similar to that observed for polyimide sample, as seen in Fig. 3.

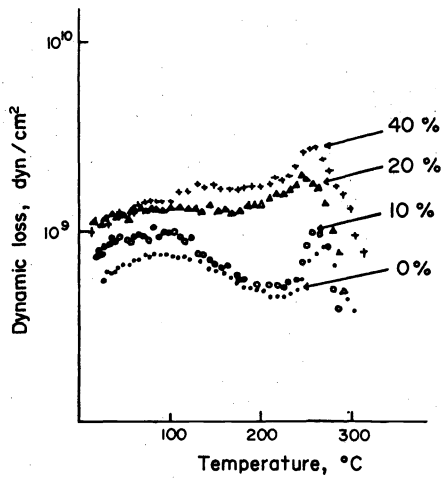


Fig. 5. Temperature dependence of dynamic loss modulus of aromatic polyamideimide films with various percentage of stretching.

The peak temperature of the loss observed around 350°C for aromatic polyimide was dependent on initial imidization temperature of polyamic acid (9), as shown in Fig. 6. As mentioned in the last section, the formation of superstructure in its amorphous phase gave a higher temperature for the loss peak. Corresponding shifts of loss peak temperature were found for thermally treated aromatic polyamideimide films, as in Fig. 7 (9).

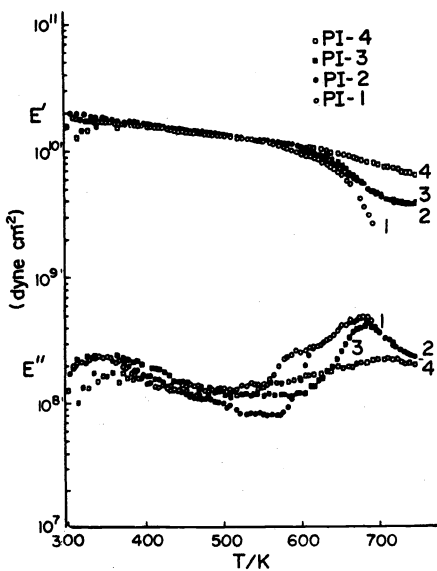


Fig. 6. Dynamic mechanical properties of aromatic polyimide films with various initial imidization temperatures. Samples are the same as those in Fig. 1 (9).

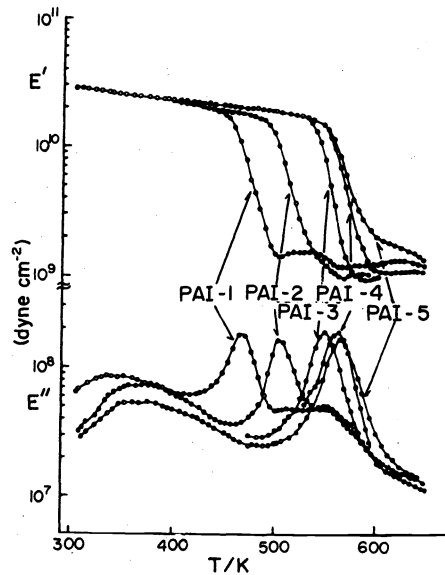


Fig. 7. Dynamic mechanical properties of aromatic polyamideimide films thermally treated at various temperatures. Samples are the same as those in Fig. 2 (9).

Reinforced plastics

The measurements of tensile oscillation properties of aromatic polyimide and polyamideimide samples were compared with torsional oscillation properties of carbon-fiber reinforced samples, by using a similar analysis as that of torsional braid analysis (TBA) developed by Gillham. As shown in Figs. 8 and 9, the similar loss peaks were obtained by both techniques as for the bulk film of the same samples (10).

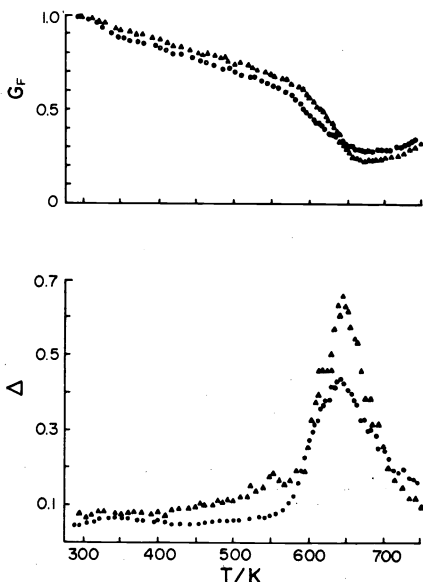


Fig. 8. Dynamic torsional properties of aromatic polyimide composites with carbon fiber yarns (10).
 Δ, \blacktriangle : Untreated fiber, 3.7°C/min; o, ●: Treated by nitric acid, 1.5°C/min.

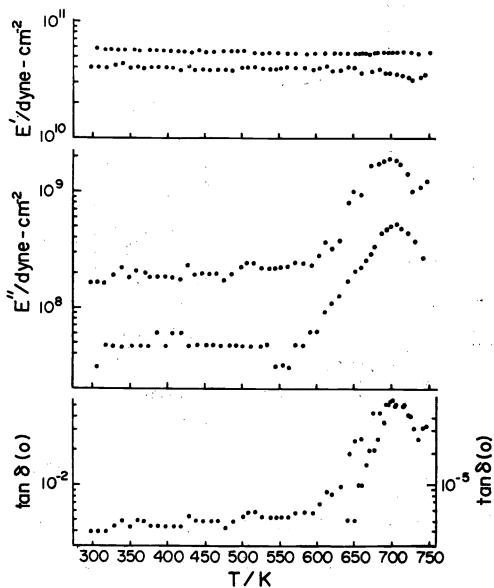


Fig. 9. Dynamic tensile properties of aromatic polyimide films reinforced by carbon fibers, 3.5 Hz, 3°C/min, in air (10).
 ●: Untreated; o: Treated by nitric acid.

The flexural vibrations of the reinforced polymers were also measured by using Du Pont Dynamic Mechanical Analyzer (11). The glass fabric reinforced polyamideimide and a polyamideimide composite sandwiched by two steel plates gave similar loss peaks, as shown in Figs. 10 and 11.

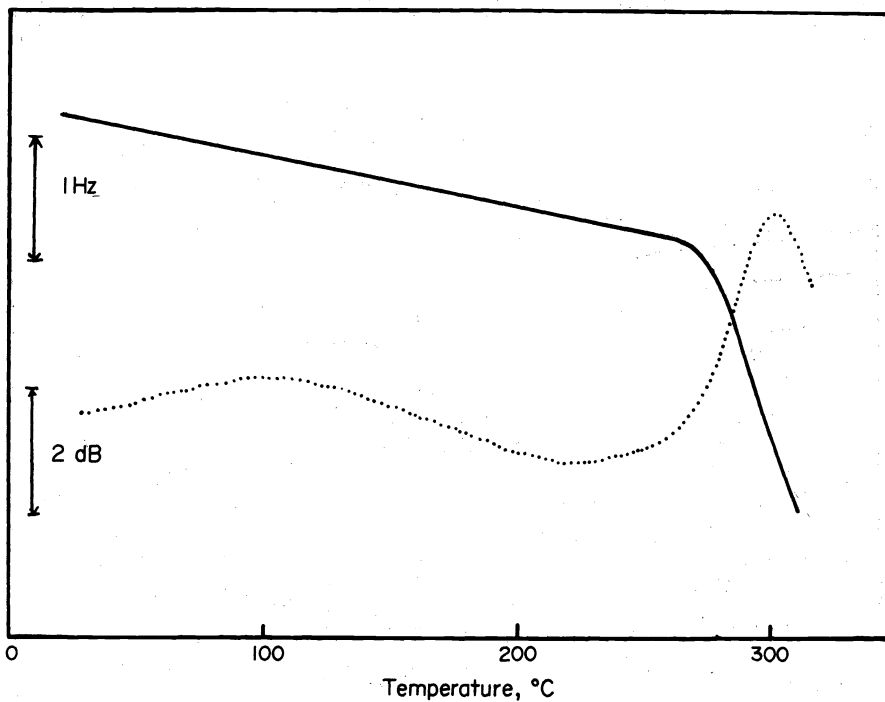


Fig. 10. Dynamic flexural properties of aromatic polyamideimide composites reinforced by glass fabric (11).

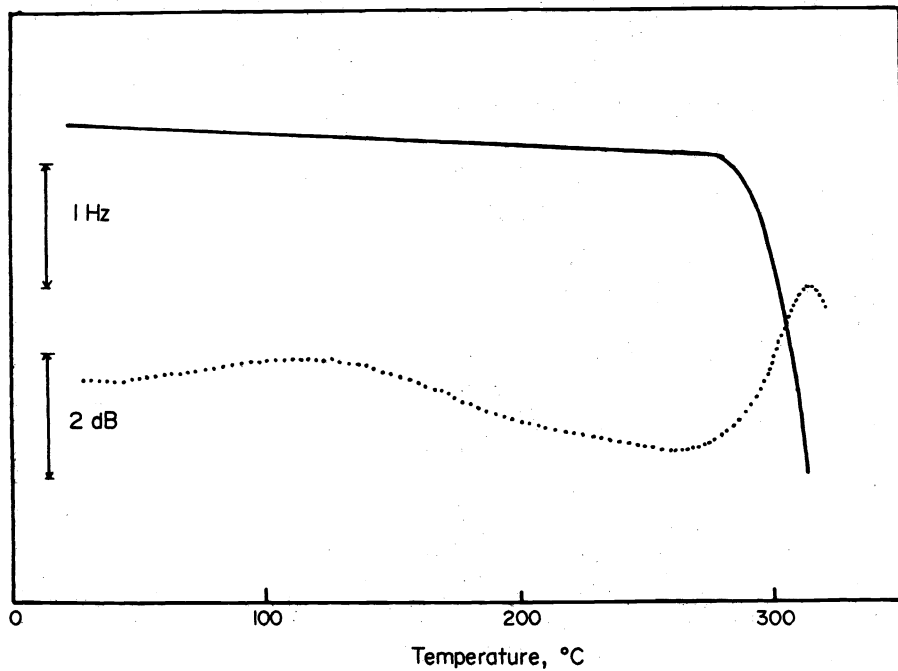
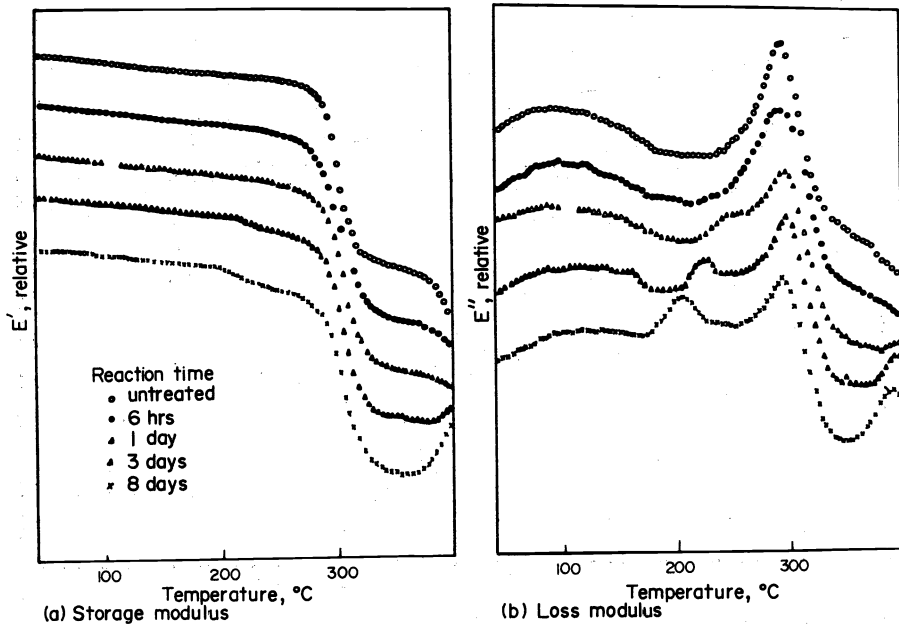


Fig. 11. Dynamic flexural properties of aromatic polyamideimide composite sandwiched between steel plates (11).

Degradation of polyamideimide in NO_2 atmosphere

The tensile oscillation properties of polyamideimide films were measured in the course of degradation in NO_2 atmosphere (12). The degradation started from the surface of the sample film and gave some lower molecular degradation products occluded in the degraded surface layers. The degraded films showed a new loss peak below the main loss peak as revealed in tensile oscillation properties in Fig. 12. The new peak was disappeared by the thermal treatment (in Fig. 13), surface scraping (in Fig. 14), and solvent extraction.



(a) Storage modulus (b) Loss modulus
Fig. 12. Dynamic tensile properties of aromatic polyamideimide films degraded in NO_2 atmosphere at 50°C , 100mmHg (12).

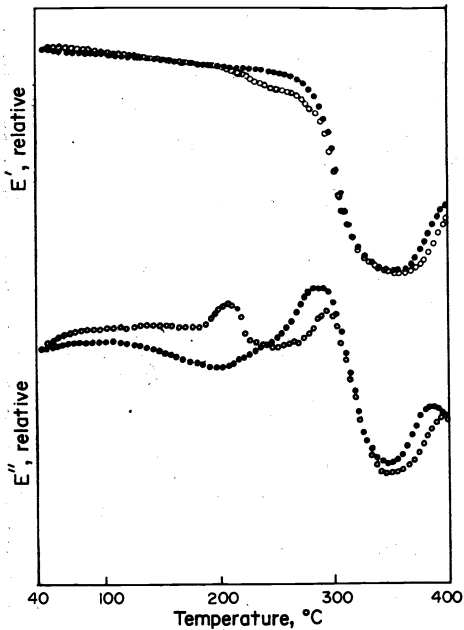


Fig. 13. Effect of thermal treatment on dynamic tensile properties of aromatic polyamideimide films degraded in NO_2 atmosphere at 50°C , 100mmHg. o: Degraded film; ●: Treated at 305°C .

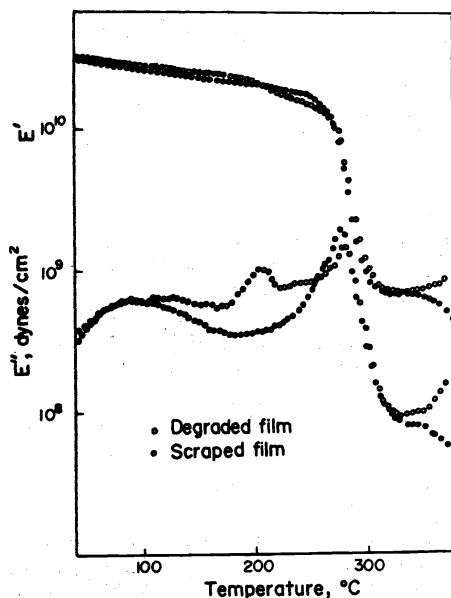


Fig. 14. Effect of surface scraping on dynamic tensile properties of aromatic polyamideimide films degraded in NO_2 atmosphere at 50°C , 100mmHg (12).

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