

## Young's Modulus and Secondary Mechanical Dispersions in Polypyromellitimide

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### Synopsis

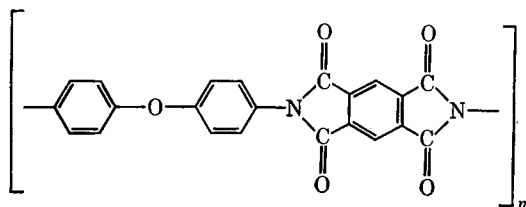
Dynamic mechanical properties were determined in polypyromellitimide at acoustic frequencies over a wide temperature range (80–750°K). Two distinct secondary relaxation effects were found: one ( $\beta'$ ) at lower temperature, characterized by a loss maximum at 250°K, and another ( $\beta$ ) at higher temperatures with a loss maximum at 400°K. The lower temperature peak is shifted towards higher temperature with increasing frequency following an Arrhenius-type equation (apparent activation energy: 15 kcal/mole); the relaxation strength increases with water content and becomes practically zero when samples dried under vacuum at 200°C are examined. The  $\beta'$  relaxation process is thus attributed to the presence of adsorbed water molecules. The higher-temperature ( $\beta$ ) dispersion, which persists even after dehydration, on the basis of some results obtained for other polymers containing *p*-oxyphenylene rings in the backbone, is tentatively attributed to torsional oscillations of aromatic rings along the chain.

Among the various new plastics proposed for high-temperature applications, the polypyromellitimides, products of polycondensation of pyromellitic dianhydride and an aromatic diamine, proved very satisfactory.

The presence along the backbone of aromatic and heterocyclic rings connected by thermally stable bonds assures them exceptional resistance to thermal degradation, dimensional stability, and mechanical strength up to temperatures which are extraordinarily high for a plastic. In addition, these materials exhibit a combination of properties which is very hard to find in other polymers, such as a high elastic modulus, extremely high glass transition temperatures, with good resilience and ductility, which can be retained even at the lowest temperatures.

For the molecular interpretation of the unusual behavior of polypyromellitimide resins, the investigation of the dielectric and mechanical relaxation effects in a wide range of frequencies and temperatures is of great interest.

Of the polypyromellitimides, the one which has been extensively investigated and attracted most interest is that obtained by the polycondensation between pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.



As we shall discuss only this particular product, it will be henceforth designated simply polyimide and denoted by PI.

The dielectric properties (dielectric constant and loss factor) of polyimide were investigated by Amborski.<sup>1</sup> Measurements were carried out on films 1–5 mils thick (Du Pont H-Film), at temperatures varying from about 200 to about 500°K, at frequencies from 10<sup>2</sup> to 10<sup>5</sup> cps. Amborski found a loss maximum below room temperature (about 243°K at 10<sup>4</sup> Hz) which shifts towards lower temperatures with decreasing test frequency. With regard to the frequency of the loss maximum against temperature, an Arrhenius-type plot was obtained with an apparent activation energy of 15 kcal/mole. No clear explanation was given of the molecular mechanism responsible for the observed dielectric dispersion.

Mechanical loss measurements were made on polyimide by Ikeda<sup>2</sup> at temperatures from about 90 to about 470°K, by means of a torsion pendulum in free oscillation at 1 cps. Two different samples were examined: one was machined from a molded specimen, with a crystallinity index of about 25% and complete absence of orientation; the other was in the form of a film, with a crystallinity index of about 13%. In the latter, x-ray examination revealed a uniplanar structure with diffraction planes, spaced from 4 to 5 Å, parallel to the plane of the film.

While for the molded sample a single loss peak at about 190°K was found, for the film two distinct loss maxima were observed, one at low temperature (corresponding to the dispersion found in the molded specimen) and another at high temperature (353°K), missing in the molded specimen.

While no explanation was given for the low-temperature dispersion, the high-temperature relaxation effect found only in the film was associated with the molecular order existing in it and attributed to an interplanar slippage, a process analogous to that found in graphite.

Recent investigations of the dynamic mechanical properties of polyimide, made by Bernier and Kline at audio-frequencies<sup>3</sup> with a longitudinal apparatus, using circular rods, at frequencies of the order of 10<sup>4</sup> cps, indicated the existence of a prominent relaxation associated with adsorbed water which is characterized by a loss maximum at about 230°K. Above 550°K the onset of a major relaxation process is observed, with a probable loss maximum at 675°K which has been attributed to large-scale backbone-chain motion. In the temperature range between room temperature and 550°K numerous minor peaks are observed, whose interpretation is not so clear.

### Experimental

The experimental data reported to date in the literature regarding the mechanical and dielectric dispersions of polyimide show some discrepancies and do not permit one to get a clear idea of the molecular relaxation processes occurring in this polymer at temperatures below its glass transition point; thus it seems useful to get additional data, in an attempt to draw some conclusions.

To this aim, we examined some samples of polyimide (du Pont's Vespel), making measurements of the Young's modulus and of the damping factor over a wide temperature range, at acoustic frequencies.

Measurements were carried out by use of a resonance electrostatic apparatus<sup>4</sup> on samples in the form of circular plates (about 3 mm thick, 36 mm in diameter) vibrating on their lowest flexural symmetrical modes.

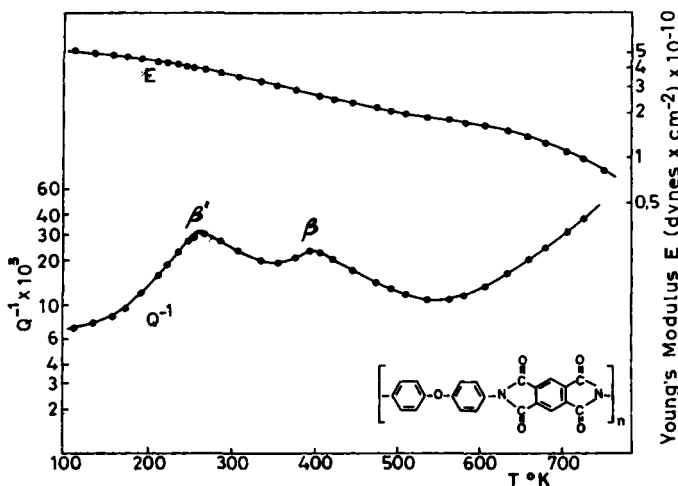


Fig. 1. Young's modulus  $E$  and damping factor  $Q^{-1}$  as functions of temperature for poly(pyromellitimide) ( $f \sim 15$  kHz).

The use of circular plates has the advantage over samples of other shapes that, with a given frequency and a given vibromotive force, larger amplitudes of vibration can be obtained. In addition, it is possible to avoid additional losses due to friction with the support, simply laying the sample on three small pins whose points enter in three small holes made along a modal circle. Measurements were made under vacuum ( $\sim 1$  mm Hg).

In Figure 1 the Young's modulus  $E$  and the damping factor (reciprocal of the resonance coefficient)  $Q^{-1}$  have been plotted as functions of temperature between 80 and 750°K. At the lowest temperature reached in the measurements, the Young's modulus is  $\sim 5.3 \times 10^{10}$  dynes/cm<sup>2</sup>. With increasing temperature,  $E$  decreases steadily over the whole temperature range examined, without showing either abrupt changes or marked relaxations.

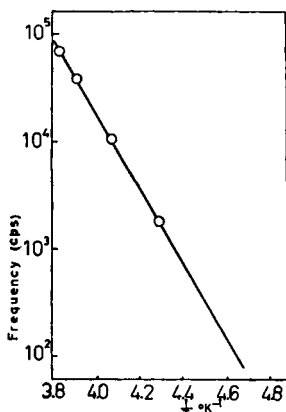


Fig. 2. Frequency dependence of the maximum damping temperatures for the  $\beta'$  process in poly(pyromellitimide).

The plot of damping factor versus temperature in the temperature range between 100 and 550°K shows two loss maxima: one ( $\beta'$ ) located below room temperature (250°K), and another ( $\beta$ ) at higher temperature (400°K). The heights of the peaks are comparable ( $\sim 20 \times 10^{-3}$ ).

These loss maxima are to be attributed to two distinct mechanical relaxation effects: they are in fact both frequency-dependent and shift towards higher temperature with increasing test frequency at different rates. The corresponding relaxations of the elastic modulus are, however, very small and hardly perceptible.

On making measurements, using samples of the same material with different dimensions and vibrating also on the second mode of vibration, in addition to the first, it could be possible to follow the shifts of the damping maxima with frequency. For the low-temperature dispersion the location of the damping peak at various frequencies could be very well determined. Plots in this case of the logarithm of the frequency  $f$  against the reciprocal absolute temperatures of the damping maxima show that the experimental points fall with good approximation on a straight line (Fig. 2). This indicates that, at least in the temperature range explored, the variation with temperature of the relaxation time  $\tau$ , of the considered process follows an Arrhenius-type equation:

$$\tau = \tau_0 e^{\Delta E^*/RT}$$

where  $\tau_0$  is the high-temperature limiting value for the relaxation time and  $\Delta E^*$  is the apparent activation energy of the relaxation process. The value of  $\Delta E^*$ , calculated from the slope of the straight line, is 15.7 kcal/mole.

For the higher-temperature ( $\beta$ ) dispersion, the shift of the corresponding loss maximum with frequency could not be followed very well, because of the tendency of the maximum itself to flatten with increasing frequency; nevertheless, from the average of numerous experimental measurements a

value for the apparent activation energy around 20–25 kcal/mole could be calculated.

At temperatures above 550°K a nearly exponential increase of the loss is observed with increasing temperature.

### Discussion of Results

The elastic modulus of polyimide at room temperature is rather high,  $3.5 \times 10^{10}$  dynes/cm<sup>2</sup>, and comparable with that of polystyrene. This is quite reasonable, owing to the limited flexibility of the chain, the polar character of the polymer and the lack of aliphatic side chains, whose presence would favor elastic deformations and decrease the modulus.

In the temperature range explored by us, no transitions and no important relaxations of the elastic modulus exist in polyimide; thus the regular small lowering of  $E$  with increasing temperature (about 0.21%/°C) can be associated essentially with the thermal expansion of the material. These results are quite understandable on the basis of the structure of the polymer, taking also into account the fact that it exhibits a very high glass transition temperature (over 1000°K).

Of the two relaxation effects found by us in the loss versus temperature curve at acoustic frequencies, it is that located at low temperature ( $\beta'$ ) the one which seems to correspond to the mechanical relaxation effect found by Ikeda at 190°K (1 cps) and by Bernier and Kline at 230°K (9500 cps) and to dielectric dispersion found by Amborski in the same material.

In particular, by comparing the mechanical with the dielectric data for this dispersion, it can be observed that, for each given temperature, the dielectric loss peak is located at a higher frequency than the corresponding mechanical one. This fact is not unusual and can be reasonably explained by considering that, while in dielectric measurements only the polar groups are affected by the applied field, in mechanical measurements larger portions of the macromolecule may be involved in the relaxation and this involves a longer "macroscopic" relaxation time.

For this dispersion no explanation was given either by Ikeda or by Amborski, but it was attributed to absorbed water molecules by Bernier and Kline. To confirm this suggestion, a sample of the material was annealed for 48 hr at 200°C under vacuum.

As during the annealing treatment there was a weight loss of the order of 1%, to ascertain the nature of the low molecular weight substance lost by evaporation, the infrared spectrum of the sample submitted to the thermal treatment was compared with that of the as-received sample.

The two spectra are practically the same, except for some small differences in the 3500 cm<sup>-1</sup> region. In this region, the original sample shows a large, poorly resolved zone, in which three maxima are detectable, at 3600, 3555, and 3485 cm<sup>-1</sup>; in the annealed sample the relative intensities of the two higher frequency peaks are much lower (Fig. 3).

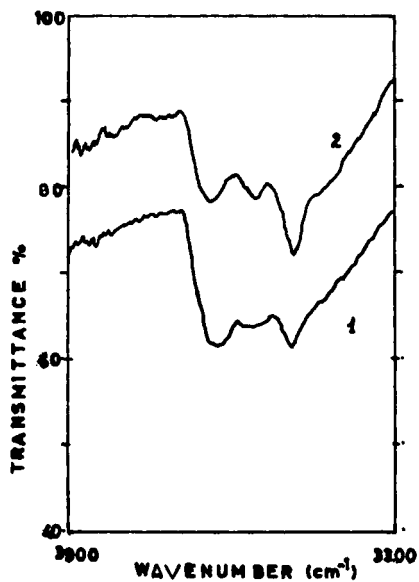


Fig. 3. Infrared spectra for samples of polypyromellitimide (Du Pont Vespel): (1) before dehydration; (2) after dehydration.

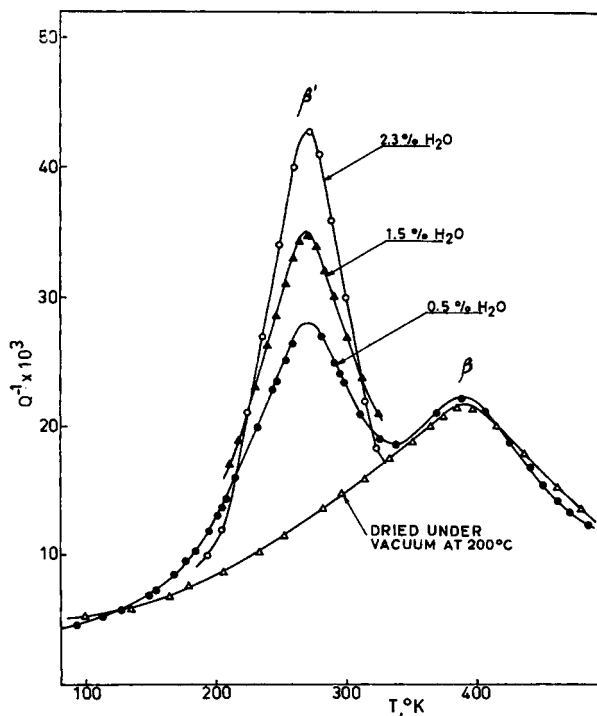


Fig. 4. Damping factor as function of temperature for polypyromellitimide with different water contents.

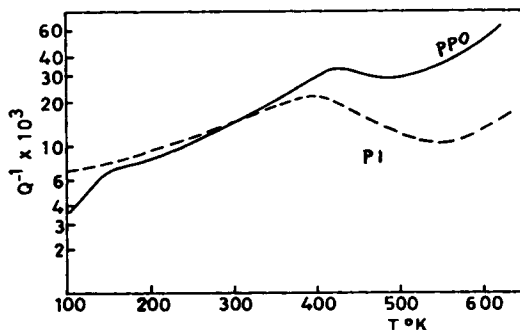


Fig. 5. Damping factor  $Q^{-1}$  as function of temperature: (—) dried polypyromellitimide; (—) poly(*p*-phenylene oxide).

The  $3485\text{ cm}^{-1}$  peak, whose intensity does not vary appreciably with the thermal treatment, may be attributed to the combination band of stretching modes of C=O bonds ( $1777 + 1714 = 3491$ ). As concerns the  $3630$  and  $3555\text{ cm}^{-1}$  bands, these could be attributed to the presence of adsorbed water molecules and associated with free and hydrogen-bonded —OH stretching modes.

On the basis of the latter results, it was deduced that the sample submitted to the thermal treatment lost water as compared with the as-received specimen.

Repeating measurements of the mechanical damping in the annealed sample it was found that while the low-temperature peak disappeared the high-temperature maximum remained practically unchanged.

It can be concluded, thus, that the  $\beta'$  dispersion found in polyimide is due to adsorbed water molecules, in accordance with the interpretation already given by Bernier and Kline. Experimental measurements made on the same material with different water contents (obtained by immersion of the annealed sample in boiling water for different lengths of time) confirmed the above conclusions (Fig. 4).

Considering the nature of polyimide, which is devoid of branchings and flexible side chains, the high-temperature viscoelastic dispersion ( $\beta$ ), may be due to local relaxation modes of the backbone.

It has been in fact demonstrated<sup>4,5</sup> that, in general, in all glassy polymers, independent of the presence of side chains, the molecular segments of the backbone execute vibrational motions about local equilibrium conformations. Some of these modes of lower frequencies and higher amplitudes, due to the resistance opposed by the surrounding medium, experience strong damping, losing their vibrational character and resulting in relaxation type motions, which, in favorable cases, can be indicated by dielectric or mechanical dispersions or through NMR absorption measurements.

The polymers in which viscoelastic dispersions associable with local relaxation modes of the backbone have been found are rather few, either because the amplitude of such motions in some cases are too small to give

place to mechanical relaxations, or because their effects are masked, on the relaxation map, by other processes which produce more important effects, such as motions of side chains or the excitation of micro-Brownian movements. Nevertheless, from the data published till now, it has been found that in general the temperatures at which the local mode relaxations of the main chain can be observed are generally below the glass transition temperature, the relaxation times are intermediate between those (very long) of the micro-Brownian motions and those (generally very brief) due to motions of the side chains, the dispersions band of the relaxation time is very broad, and the apparent activation energy is of the order of 10–20 kcal/mole.

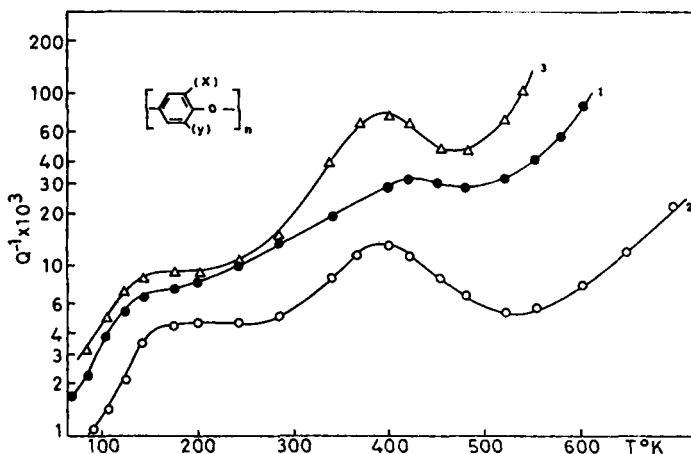


Fig. 6. Damping factor  $Q^{-1}$  as function of temperature, in some poly(phenylene oxides) ( $f \sim 7$  kHz): (1) poly(1,4-phenylene oxide); (2) poly(2-methyl-1,4-phenylene oxide); (3) poly(2-methyl-6-chloro-1,4-phenylene oxide).

As all these requirements seem to be satisfied by the  $\beta$ -process of polyimide, it seems reasonable to advance the hypothesis that such a dispersion is due to torsional oscillations of some groups, in particular  $p$ -oxyphenylene groups.

The latter suggestion is supported by the fact that a relaxation effect with characteristics very similar to that shown by the  $\beta$ -process of polyimide (i.e., temperature range of the dispersion, maximum damping temperature, height of the loss maximum, value of the apparent activation energy) is exhibited by poly- $p$ -phenylene oxide) and by many other ring-substituted poly( $p$ -phenylene oxides)<sup>6-8</sup> (Figs. 5 and 6).

As concerns, finally, the steady increase of the damping with increasing temperatures, at temperatures above 550°K, even if we agree with the suggestion made by Bernier and Kline that large-scale backbone-chain motions, including the anhydride segments, may occur in this temperature range, however we think that one should be very cautious in interpreting



the experimental results in this particular temperature range, in which the polymer starts to decompose.

Thanks are due to Dr. G. Masetti for the interpretation and useful discussions of infrared spectra.

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