The Effect of Absorbed Water on the Dynamic Mechanical Properties of Some Polyamides

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The dynamic mechanical properties of poly(hexamethylene isophthalamide) and poly(dodecamethylene terephthalamide) have been determined over a wide range of temperature at low frequencies (~ 1 c/s) by torsion pendulum measurements and at high frequencies (~ 500 c/s) by a vibrating reed technique. It has been shown that absorbed moisture leads to the appearance of an intermediate loss peak at temperatures in the range −20°C to −70°C, between the main glass/rubber transition at 120°C and a low temperature process with a peak near −150°C. Unlike other polyamides such as nylon 6-6, the main glass/rubber transition is unaffected by moisture.

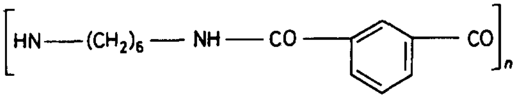
EXAMINATION of polymeric systems by dynamic mechanical methods yields information on the single or multiple transitions in modulus that occur over the temperature/frequency spectrum and corresponding loss processes which can be correlated with molecular structure. The main glass transition temperature is of practical significance as it indicates the limit of usefulness in purely amorphous systems either as rubbers or rigid glasses; in partially crystalline systems it often marks the onset with increasing temperature of improved toughness, e.g. polyethylene or polypropylene both have T_g below room temperature. Other minor transitions often exist at lower temperatures than T_g and even when these have relatively small associated changes in modulus they can sometimes be correlated with improved failure properties. e.g. polycarbonate has useful properties between T_g and its secondary transition at lower temperatures. T_g and other transitions are usually interpreted in terms of particular molecular motions of the main chain or side chain coupling. In some systems T_g can be affected by the presence of simple molecules; practically the addition of simple liquids is efficacious, modifying mechanical properties where a more flexible material is required at temperatures normally below T_g. Polyvinyl chloride exemplifies the application of this principle where large amounts of a plasticizer lower T_g. In other polymers less desirable property changes can result. In particular moisture has a pronounced effect on the mechanical properties of polyamides. Woodward and Sauer[1] have reviewed mechanical relaxation phenomena in polymers including polyamides. They report for example, addition of water to dry nylon 6-6 shifts the main glass transition (α peak in the loss spectra) to lower temperatures and in addition a further loss peak occurs at lower temperatures, typically in the range −50° to 0°C at ~ 400 c/s. Mechanical properties such as modulus are thus reduced in the presence of moisture but on the other hand the polymer becomes much tougher.

Here we report an examination of the effect of moisture on the dynamic mechanical properties of two polyamides, poly(hexamethylene isophthalamide) and poly(dodecamethylene terephthalamide), where the main chain structure includes residues from aromatic units, only polymer being predominantly amorphous and the other crystalline.

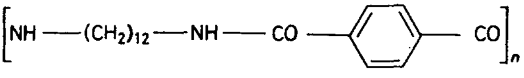
EXPERIMENTAL

Materials

Polyhexamethylene isophthalamide (6IPA) has the structure



and that of polydodecamethylene terephthalamide (12TA) is



Samples of both polymers were supplied by I.C.I. Fibres Ltd, Pontypool.

Physical properties

6IPA—The polymer used had an inherent viscosity of 0·74 dl/g determined in formic acid at 25°C; 6IPA is only crystallized with difficulty and a crystal sample formed from solution had a melting point of 210°C; the T_g of the non-crystalline polymer, determined by DTA at a heating rate of 20 deg. C/min and by low frequency torsion pendulum (~ 1 c/s), was 120°C. Osmometry and end group analysis were used to determine $\bar{M}_n$; the mean value was 13 000.

12TA—The sample examined had an inherent viscosity 1·10 dl/g measured from a ½% solution in dichloracetic acid at 25°C; the crystalline melting point determined by DTA at a heating rate of 20 deg. C/min was 292°C; the T_g of the polymer assigned from dynamic mechanical properties was 120°C by low frequency torsion pendulum (~ 1 c/s) and 140°C by vibrating reed (~ 300 c/s).

Mechanical properties

The tensile properties of the polymers at room temperature determined on injection moulded dumb-bell shaped specimens using a Hounsfield E-type tensometer are given in *Table 1*. Under the moulding conditions used 6IPA samples are clear, glassy materials, amorphous by X-ray or thermal examination whereas 12TA samples are highly crystalline.

Table 1. Tensile properties of polymers at 20°C and a strain rate of 100%/min

Polymer	*6IPA*	*12TA*
Initial modulus, kg/cm^2	32 000	26 000
Yield stress, kg/cm^2	850	730
Breaking stress, kg/cm^2	580	500
Elongation to break, %	20–80	30–50

Dynamic mechanical apparatus

The test specimens used for the study of dynamic mechanical properties were cut from injection moulded samples in the form of rectangular cross section strips, approximately 1 in. × 0·125 in. × 0·065 in. Drying of the samples was carried out above T_g at 150°C, under high vacuum (0·1 mm of mercury).

(*a*) *Low frequency torsion pendulum*—Shear moduli and the corresponding loss factor were determined using a torsion pendulum similar to that described by Nielsen[2]. The sample was enclosed in a metal envelope which could be flushed continually with dry nitrogen and mounted in a silicone oil thermostat bath controlled at the desired temperature ± 0·1 deg. C for temperatures above ambient. For low temperatures, the oil bath was replaced with a 'Dewar' filled with metal chips through which liquid nitrogen could be blown. Temperature control to ± 1 deg. C was achieved by controlling the rate of discharge of liquid nitrogen. Passage of dry nitrogen through the metal envelope prevented condensation of moisture on the sample.

The dynamic shear modulus, G', was calculated from the period τ of the torsion pendulum, its moment of inertia, I, and the sample dimensions according to the relationship

$$G' \simeq 64\pi^2 Il/cd^3 \mu\tau^2$$

where l, c and d are the length, breadth and thickness respectively, of the sample and μ is a shape factor, as described by Nielsen[2]. The loss factor was calculated from log decrement/π. The frequency of the experiments was usually of the order of 1 c/s. Experiments were carried out at intervals of constant temperature with increasing temperature; each successive temperature was maintained until constancy of the measured frequency assured thermal equilibrium.

(*b*) *Vibrating reed apparatus*—Higher frequency (of the order of 500 c/s) dynamic mechanical measurements were made on a vibrating reed apparatus based on a design by Robinson[3]. Sample temperature control was achieved by passage of an exchange gas at the desired temperature through the Dewar vessel enclosing the specimen, low temperatures being obtained by chilling the gas passing through a coil in liquid nitrogen. This method yields a dynamic Young's modulus, E from

$$E' \simeq 48\pi^2 \rho l^4 f_0^2/m^4 d^2$$

where as previously l and d refer to the length and thickness (in the plane of vibration) respectively, ρ is the density, f_0 is the measured resonant frequency and m is a constant for the mode of vibration. The loss factor was obtained from the ratio of the bandwidth of the resonance curve to the resonant frequency, f_0.

RESULTS

In *Figures 1* and *2* the results using the torsion pendulum are shown. 6IPA without special preparation shows three loss maxima; the main T_g peak (α) at 120°C and two smaller peaks at −50°C and −140°C. Similarly, 12TA shows three peaks when examined without special drying procedures; again

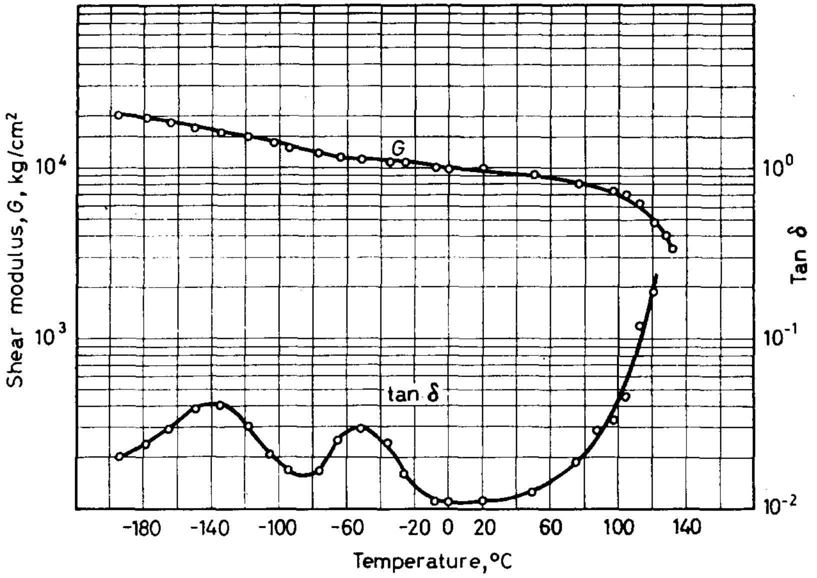


Figure 1—Polyhexamethylene isophthalamide. Variation of shear modulus with temperature determined in the torsion pendulum; sample as prepared

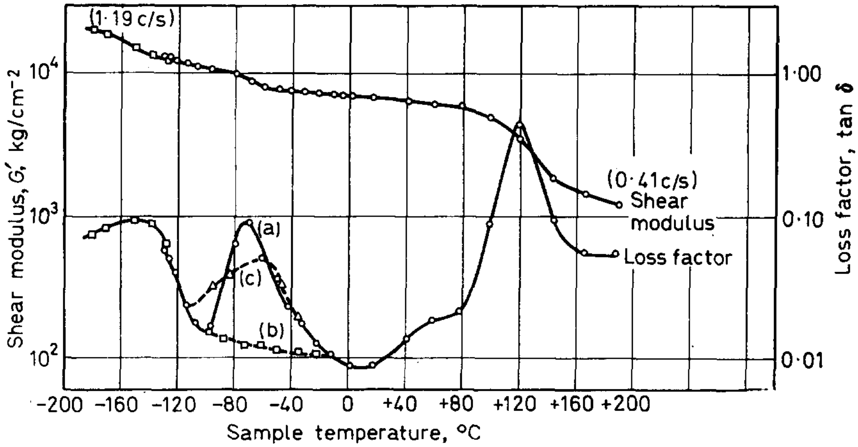


Figure 2—Polydodecamethylene terephthalamide. Variation of shear modulus and damping with temperature determined using a torsion pendulum. (a) ——— Sample as injection moulded; (b) — — — Sample as injection moulded, heated for 48 h at 130°C under high vacuum; (c) - - - - Sample as injection moulded, dried as in (b) and then held for 120 h at 98% humidity at 38°C

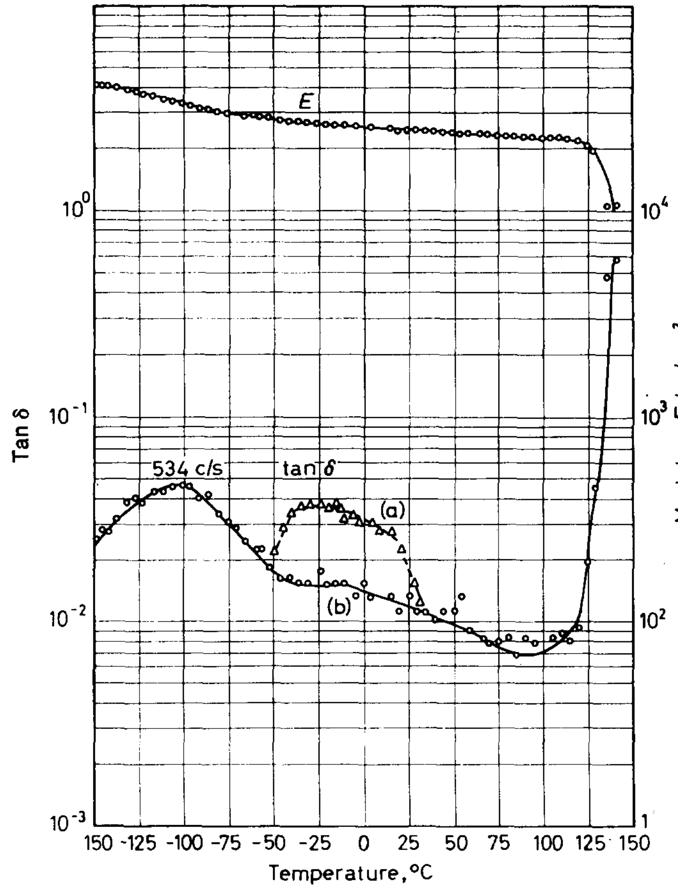


Figure 3—Polyhexamethylene isophthalamide. Variation of modulus and loss with temperature determined using a vibrating reed technique: (a) Sample as prepared; (b) Sample dried at 105°C for 48 h

the main T_g peak is about 120°C and the two minor transitions are seen as somewhat lower temperatures than 6IPA being about −70°C and −150°C.

As anticipated the vibrating reed technique gives similar data but since the frequency is higher the observed peaks occur at higher temperatures. The results are shown in *Figures 3* and *4*.

The effect of absorbed moisture is readily seen. The intermediate transition can be completely eliminated if the sample is dried but as shown in curve c of *Figure 2*, re-conditioning of the sample in a humid atmosphere restores the peak. Longer periods of treatment lead to complete re-establishment of the peak. However, no shift of the main T_g peak has been observed (possibly with T_g above 100°C any change is obscured by rapid diffusion of absorbed water) nor is a shift of the low temperature process seen. Only those parts of the curves showing any divergence have been plotted.

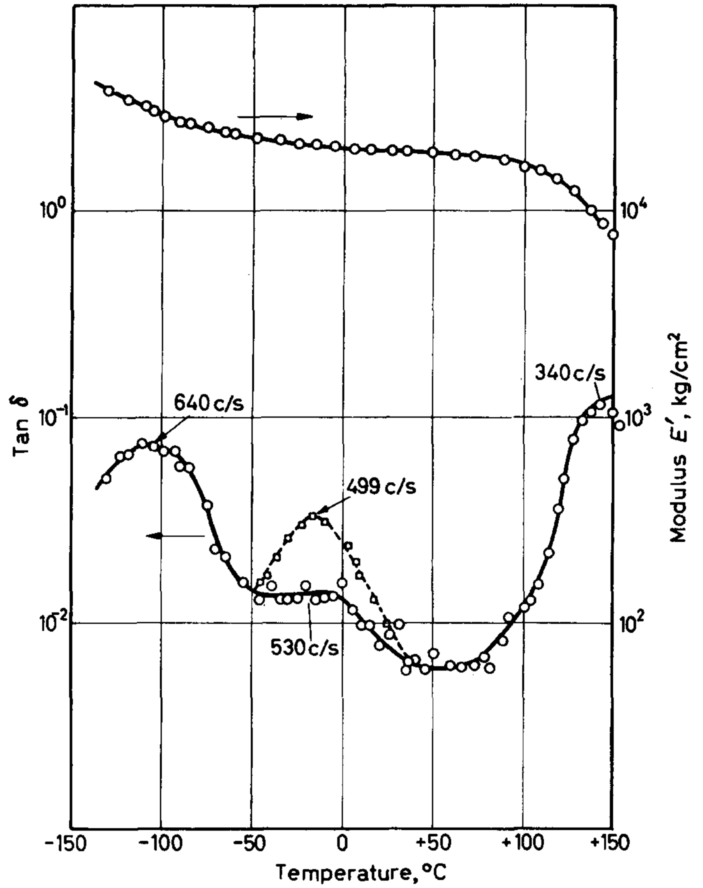


Figure 4—Polydodecamethylene terephthalamide. Variation of modulus and loss factor with temperature as measured using a vibrating reed technique: (a) — — — Sample as injection moulded; (b) ——— Sample as injection moulded, heated for ½ h at 150°C under high vacuum

DISCUSSION

Previous studies[4] of the effect of water on wholly aliphatic polyamides describe the appearance of an intermediate peak when moisture is present. In addition the main relaxation peak is seen to shift to lower temperatures unlike our results where no shift of the main peak was observed. Other workers have shown that the effect is not only induced by moisture but simple alcohols have been found[5] to lead to similar changes in the loss spectra. It has been suggested[4] that in the aliphatic polyamides the effect can be attributed to a cooperative main chain motion between the methylene units and non-bonded amide units, the hydrogen bonding between adjacent chain amide links presumably having been replaced by hydrogen bonded water molecules on each chain.

Recently, Andrews[6] has proposed that transitions in long chain molecules originate from a breakdown or association–dissociation equilibrium of dipole–dipole bonding between chains. Such a concept readily explains the observed effects in polyamides where the nature of the dipole interactions is greatly altered by the presence of hydrogen bonded water molecules.

The main relaxation process at 120°C in the partly aromatic polyamides which is higher than aliphatic polyamides with similar repeat lengths between amide links must be attributed to the aromatic in-chain substituent. No shift of this peak with adsorbed moisture has been observed unlike the aliphatic polyamides and it is concluded that the relaxation process involving the aromatic substituent does not involve cooperation with amide links either bonded or non-bonded.

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REFERENCES

[1] WOODWARD, A. E. and SAUER, J. A. *The Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M. M. LABES and A. WEISSBERGER, Vol. II, Chap. 7. Interscience: New York, 1965

[2] NIELSEN, L. E. *Rev. sci. Instrum.* 1951, **22**, 690
NIELSEN, L. E. *J. appl. Phys.* 1954, **25**, 1209

[3] ROBINSON, D. W. *J. sci. Instrum.* 1955, **32**, 2

[4] WOODWARD, A. E., CRISSMAN, J. M. and SAUER, J. A. *J. Polym. Sci.* 1960, **44**, 23

[5] ILLERS, K. H. and JACOBS, H. *Makromol. Chem.* 1960, **39**, 234

[6] ANDREWS, R. D. *J. Polym. Sci. C*, 1966, **14**, 261