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Specific features of the thermoelastic effect in polymers

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Abstract

An adiabatic uniaxial elastic tension in non-oriented polymers (polyethylene, polypropylene) has been found to cause a cooling that is sharper than linear (with respect to stress σ), and close to the quadratic dependence on σ. In this paper we suggest a thermodynamic derivation of the $\Delta T(\sigma)$ dependence (where ΔT is the change in temperature of an elastic body on loading) that takes into account the temperature dependence of the elastic modulus. A more general expression for $\Delta T(\sigma)$ (compared to the Kelvin expression) derived here, gives a satisfactory explanation of the observed non-linearity of $\Delta T(\sigma)$ just for polymers.

Keywords: HDPE; LDPE; Polymer; PP; Thermoelastic; Thermoelectric

1. Introduction

The process of deformation of a solid is accompanied by a change in its internal energy and a release or absorption of heat. If a solid is deformed elastically, this is termed the thermoelastic effect. Its laws have been fairly well studied for many low-molecular solids. They have also been studied for polymers [1] where the thermoelastic effect has specific features caused by a substantial difference in the interactions between atoms that are in one molecule and atoms belonging to different molecules.

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Table 1
Comparison between experimental and calculated characteristics of the non-linear thermoelastic effect in polymers

Polymer	T in K	$\rho \times 10^6$ in kg m^{-3}	$C \times 10^6$ in J m^{-3} K^{-1}	E in GPa	$\partial E/\partial T \times 10^2$ in Pa K^{-1} from Fig. 3	$\frac{1}{2C}\frac{\partial E}{\partial T}\frac{1}{E^2} \times 10^{-18}$ in Pa^{-2}	
						Calculation	Experiment (Fig. 2)
PP	293	907	1.56	2.8	−2.7	−1.1	−1.5
LDPE	293	926	2.08	0.8	−2.1	−8.0	−9.0
	268			1.5	−2.1	−2.3	−4.5
HDPE	293	955	1.80	2.0	−1.5	−1.0	−0.65
	268			2.4	−1.5	−0.7	−0.65

2. Experimental

Non-oriented amorphous-crystalline polymers, i.e. polypropylene (PP) and low- and high-density polyethylene (LDPE and HDPE) were studied. Table 1 lists the densities ρ and specific volume heat capacities C of these polymers. All the polymers studied had a spherulitic structure. The average diameter of the spherulites of ≈ 3 μm was estimated by small-angle scattering of polarized light. The thermal effects were studied on polymer samples in the form of two tightly fitted long strips, with a total cross sectional area of ≈ 10 mm^2 and with the length of the working portion being ≈ 100 mm, which were extended in a vacuum chamber at different velocities at 293 and 268 K. A junction of a differential thermocouple made of manganine–constantan wires ≈ 40 μm in diameter was placed between the strips to reduce heat removal from the sample. The other junction of the thermocouple was attached to the undeformable portion of the sample in the clamp. Temperature variations were measured with an accuracy of 0.02 K. The specific heat capacity C was determined by direct heating.

3. Results

Fig. 1 shows temperature changes in the samples ΔT as a function of conditional stress σ (load per unit cross sectional area of an undeformed sample).

In the polymers studied, an increase in stress is first accompanied by cooling, up to deformations of $\approx 5\%$ (HDPE) and $\approx 14\%$ (LDPE). Further deformation proceeds at nearly constant σ (quasi-plasticity) and cooling is superseded by heating. In PP only cooling up to the moment of rupture or neck formation at an $\approx 6\%$ deformation is observed. Quasi-plasticity and, hence, the onset of heating in the samples extended at different velocities is observed at different levels of stress. The lower the rate of tension, the lower the stress level (curves 2 and 2′, 3 and 3′ in Fig. 1).

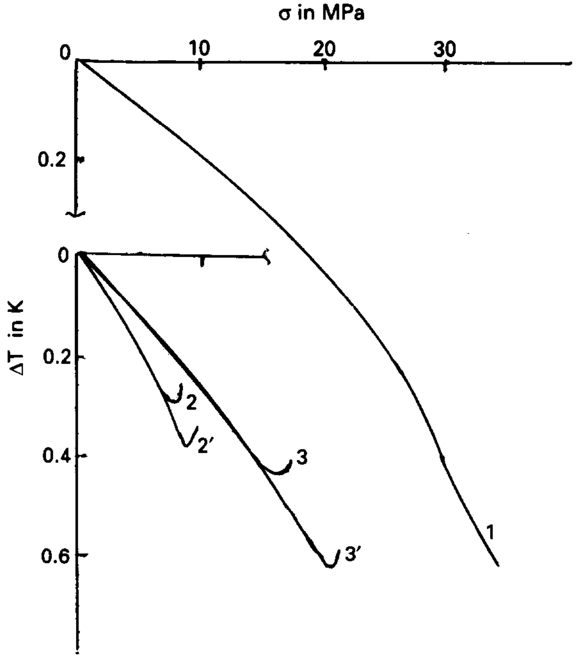

Fig. 1. Change in temperature of polymers as a function of conditional stress in adiabatic tension: 1, PP; 2 and 2′, LDPE; 3 and 3′, HDPE. Curves 1–3 were measured at a rate of extension of 7.5×10^{-4} s^{-1}, curves 2′ and 3′ at a rate of 1.3×10^{-2} s^{-1}.

As seen from the $\Delta T(\sigma)$ curve, the observed effect of cooling proves to be independent of the rate of deformation (see curves 2 and 2′ and 3 and 3′). In this work we confine ourselves to the reversible thermoelastic effect on polymer loading, i.e. to the $\Delta T(\sigma)$ dependencies in Fig. 1 up to a sample deformation of not higher than ≈4%.

It must be stressed that the $\Delta T(\sigma)$ dependence in Fig. 1 behaves non-linearly at the stage of deformation of interest. If there were an "upward" deviation from linearity, i.e. a decrease in the degree of cooling, the plasticity that leads to heat release and reduces the effect of cooling might be supposed to manifest itself earlier. But in this case the $\Delta T(\sigma)$ dependence for unloading would be different from that for loading, and this is not the case. Therefore, the observed non-linearity of $\Delta T(\sigma)$ is interesting. In order to emphasize the existence of the non-linearity of $\Delta T(\sigma)$ and to characterize this non-linearity quantitatively, the $\Delta T(\sigma)$ dependences in Fig. 1 were replotted in the $(\Delta T/T\sigma)(\sigma)$ coordinates (Fig. 2). The points in the plots of Fig. 2 correspond to $\Delta T(\sigma)$ values recalculated to the $(\Delta T/T\sigma)(\sigma)$ values.

If the $\Delta T(\sigma)$ dependence were linear (proportional), there would be a "horizontal" line in the $(\Delta T/T\sigma)(\sigma)$ coordinates (shown by a dashed line in Fig. 2); but Fig. 2 shows sloping falling $(\Delta T/T\sigma)(\sigma)$ curves close to the linear plots. The linearity of the $(\Delta T/T\sigma)(\sigma)$ dependence clearly implies that the $\Delta T(\sigma)$ dependence is quadratic.

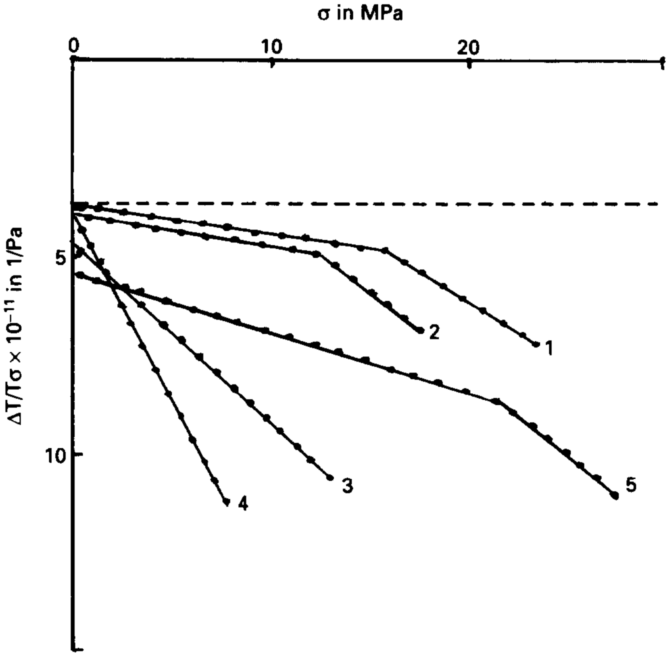

Fig. 2. $\Delta T/T\sigma$ as a function of σ: 1, HDPE at 268 K; 2, HDPE at 293 K; 3, LDPE at 268 K; 4, LDPE at 293 K; 5, PP.

The literature on the thermoelastic effect in low-molecular elastic solids (metals and their alloys) reports only a linear (proportional) temperature decrease with increasing tensile stress [2]. The quadratic temperature decrease with increasing tensile stress measured in this work can be classified as a specific feature of the thermoelastic effect peculiar to polymers. Let us try to explain this feature.

4. Thermal dynamics of uniaxial tension

The dependence of the temperature changes of a solid ΔT in its elastic adiabatic tension, on conditional stress (load per unit cross section of the sample) can be given in the general case by [3]

$$\Delta T(\sigma) = \frac{\partial T}{\partial \sigma}\sigma + \frac{\partial^2 T}{\partial \sigma^2}\frac{\sigma^2}{2} + \cdots$$

To find the coefficients in this series we use the expression for a change in the thermodynamic potential

$$\mathrm{d}H = \mathrm{d}(U - \sigma + Vp)$$

where U is the internal energy, V is the volume, p is the pressure, and λ is the degree of extension of a solid. In view of the fact that

$$\mathrm{d}U = -p\,\mathrm{d}V + \sigma\,\mathrm{d}\lambda + T\,\mathrm{d}S$$

where S is the entropy, and assuming the pressure to be constant ($p = \text{const}$) we obtain

$$\mathrm{d}H = T\,\mathrm{d}S - \lambda\,\mathrm{d}\sigma = \frac{\partial H}{\partial S}\,\mathrm{d}S + \frac{\partial H}{\partial \sigma}\,\mathrm{d}\sigma$$

Because the second combined derivatives of the thermodynamic potential are independent of the sequence of differentiation, we have

$$\frac{\partial T}{\partial \sigma} = \frac{\partial^2 H}{\partial S\,\partial \sigma} = -\frac{T\alpha}{C}$$

where $\alpha = \partial\lambda/\partial T$ is the linear thermal expansion coefficient, and $C = T(\partial S/\partial T)$ is the specific heat capacity (per unit volume) under a constant pressure and stress.

Then

$$\frac{\partial^2 T}{\partial \sigma^2} = -\frac{T}{C}\frac{\partial \alpha}{\partial \sigma} = -\frac{T}{C}\frac{\partial^2 \lambda}{\partial T\,\partial \sigma} = -\frac{T}{C}\frac{\partial E^{-1}}{\partial T} = \frac{T}{C}\frac{\partial E}{\partial T}\frac{1}{E^2}$$

where E is the adiabatic modulus of elasticity.

Finally we get

$$\Delta T(\sigma) = -\frac{T}{C}\left(\alpha\sigma - \frac{\partial E}{\partial T}\frac{\sigma^2}{2E^2}\right) \tag{1}$$

The temperature dependence of the modulus of elasticity reflects the anharmonicity of interction between structural elements of a solid.

It can be seen that expression (1) gives a quadratic dependence of the temperature change of a solid on applied stress.

In the general expression (1), the linear term (with respect to σ) corresponds to the well-known thermodynamic expression first suggested by Kelvin [2]

$$\Delta T(\sigma) = -\frac{\alpha T \sigma}{C} \tag{2}$$

Thus, the Kelvin formula proves to be the first (linear) approximation in the description of the thermoelastic effect. As follows from (1), the $\Delta T(\sigma)$ dependence is nearly linear when the coefficient $(\partial E/\partial T)(1/E^2)$ is low, and, hence, the quadratic term in expression (1) is negligibly small.

For ordinary low-molecular solids (metals and their alloys) $\Delta E/\Delta T \approx -(10^7$ to $10^8)$ Pa K^{-1} and $(\Delta E/\Delta T)(1/E^2) \approx -(10^{-15}$ to $10^{-14})$ Pa^{-1} K^{-1}. Then in the region of $\sigma < 100$ MPa which is typically employed in experimental studies of the thermoelastic effect in metals, the quadratic term in (1) is 1–2 decimal orders of magnitude lower than the linear term. This is probably the reason why the literature reports only the linear $\Delta T(\sigma)$ dependence for metals.

5. Quantitative estimates for the thermoelastic effect in polymers

As noted above, polymers differ from ordinary low-molecular solids in specific features of their molecular and supermolecular structure.

Because of their chain molecular structure, polymers have strongly differing interatomic bonds. There are strong rigid bonds (covalent) inside a molecule, and weak soft bonds (Van der Waals or hydrogen) between molecules. The supermolecular structure of amorphous-crystalline polymers exhibits a high heterogeneity because of alternating crystallites and loose amorphous-like regions.

As a consequence, the overall macroscopic moduli of elasticity (both static and dynamic) of polymeric bodies are determined by superposition of different components. Depending on the structural state of a polymeric body (for instance, the degree of its orientation), the temperature, and the type of stressed state, etc., the properties of one or another type of bond can dominate.

The characteristics of the supermolecular structure (size and shapes of crystallites and intercrystallite layers, imperfection of the structural elements) are determined by the molecular structure (molecular mass, imperfection of chain molecules), the prehistory of the polymeric body (regime of solidification, annealing, etc), and also by the temperature. These characteristics affect the mutual arrangement of molecules and, hence, the intermolecular interaction. Therefore, values such as the macroscopic modulus of elasticity, heat capacity and density can differ markedly even for one and the same polymer, see, for example, PE in Table 1.

As follows from expression (1), to analyse the thermoelastic effect we must know the adiabatic modulus of elasticity E and its temperature dependence $\Delta E/\Delta T$. To this end, the dynamic (adiabatic) modulus of elasticity was determined from the velocity of ultrasound measured by the technique of moving waves at a frequency of 35 kHz in the temperature range 210–340 K [4]. The measuring error was 5%. The results are shown in Fig. 3. It is seen that the magnitudes of E lie in the region $\approx 1-5$ GPa and decrease with temperature more or less monotonically.

It is known that the moduli of longitudinal elasticity of polymer molecules are rather high, 200–250 GPa [5]. The macroscopic moduli of elasticity of non-oriented polymers (1–5 GPa, Fig. 3) are close to the elastic moduli of polymer crystallites in the transverse directions in the axis of chain molecules [5]. Therefore, the macroscopic moduli of elasticity of the polymers studied correspond to the intermolecular interaction elasticity rather than to the skeleton elasticity of the chain molecules.

Let us use expression (1) to describe and analyse the experimental results. From (1) we obtain

$$\frac{\Delta T}{T\sigma}(\sigma) = -\frac{\alpha}{C} + \frac{1}{2C}\frac{\partial E}{\partial T}\frac{1}{E^2}\sigma \tag{3}$$

The coefficient of σ in the second term corresponds to the slopes of the curves in Fig. 2 (up to the inflections for PP and HDPE).

The magnitudes of the slopes of the curves for the polymers studied obtained from the data of Fig. 2 are listed in Table 1.

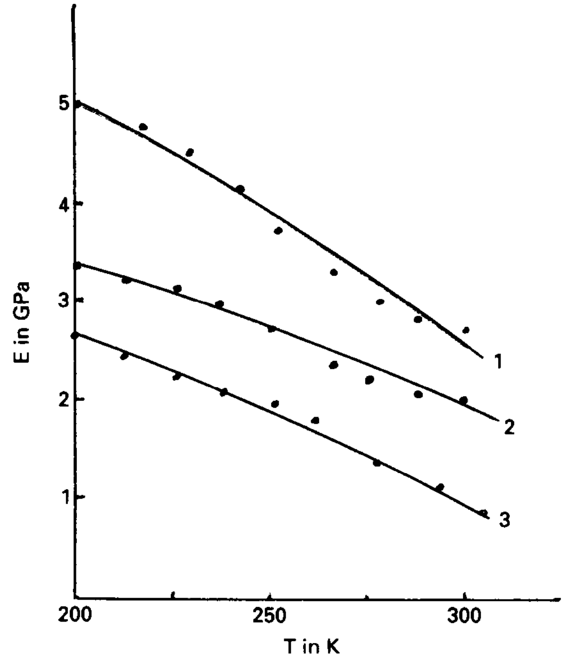

Fig. 3. Temperature dependences of the dynamic modulus of elasticity: 1, PP; 2, HDPE; 3, LDPE.

These slopes can also be calculated using the data in the table (magnitudes of *C*) and the $E(T)$ dependence in Fig. 3. The calculated values are also given in the table. We believe that the experimental and calculated magnitudes of the slopes are in reasonable agreement.

It can be seen from Fig. 2 that the slopes of the $(\Delta T/T\sigma)(\sigma)$ dependence differ markedly for different polymers, for the structural state of one and the same polymer (PE), and for different temperatures (LDPE). As the calculated slopes in the table show, these differences in the slopes can be successfully explained by variations in the modulus of elasticity, its temperature dependence, and the heat capacity which were measured independently and are also listed in the table.

Thus it can be concluded that the non-linearity of the dependence for polymers and indeed caused by a high $(\partial E/\partial T)/E^2$ ratio. The absolute magnitude of the temperature derivative $(\partial E/\partial T)$ for polymers is approximately equal to that of, for instance, metals ($\approx 10^7$ Pa K^{-1}). But because of a low modulus of elasticity *E* itself (due to soft intermolecular bonds in polymers), the relative temperature derivative $(\partial E/\partial T)/E^2$ is much higher than that for metals (by about 2–3 decimal orders of magnitude), which leads to a fairly pronounced manifestation of the quadratic $\Delta T(\sigma)$ dependence.

So far we have discussed the reversible thermoelastic effect in polymers in uniaxial tension up to the $\approx$4% deformation. However, in some cases further extension gives rise to a sharper cooling of polymers which causes inflections on the

$(\Delta T/T\sigma)(\sigma)$ dependences for PP and HDPE (Fig. 2). The thermoelastic effect proves to be different in tension and shrinkage on the portions of the dependences after the bends, i.e. reversibility is disturbed. It is still difficult to explain the observed increase in the slopes. This requires further study.

6. Conclusions

In the general case, the thermoelastic effect should be described by its dependence on stress of at least a quadratic type. For low-molecular solids with a high modulus of elasticity, the quadratic term can be neglected, and, hence, the classical linear Kelvin expression suffices.

Elastic deformation of non-oriented polymers occurs mainly at the expense of extension (compression) of weak and soft intermolecular bonds. This gives rise to a stronger influence of the anharmonicity of the intermolecular interaction on the thermoelastic effect and this leads to a fairly pronounced manifestation of the quadratic dependence of temperature changes in adiabatic tension of such solids.

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