

Sonic-Velocity Measurements as a Suitable Tool for the Observation of Structural Changes in Polymeric Materials

G. Hinrichsen, S. M. Sadat-Darbandi, and A. Al-Irobaidi

Technical University of Berlin, Institute of Nonmetallic Materials, Polymer Physics, Englische Str. 20, D-1000 Berlin 12, Federal Republic of Germany

Summary

The sonic velocity of preoriented PET fibres as a function of temperature was measured in dependence on the degree of orientation, stress applied to the fibres, and heating rate. The results reflect the structural and orientation changes which take place in the range of and above the glass transition temperature.

Introduction

The state of orientation of amorphous and semicrystalline polymers can be determined for example by measurements of X-ray scattering, birefringence, IR dichroism, and fluorescence polarization. A relatively simple technique for characterizing the orientation of polymeric fibres and films is the measurement of sonic velocity which can give considerable insight into the nature of molecular orientation within the one or the two phases. The mechanism of sound propagation in uniaxially oriented polymeric samples has been described extensively by Moseley (1), Ward (2,3,4), and Samuels (5). The advantage of the sonic velocity technique consists in the high testing rate which allows the investigation of the time dependence of processes, for example of structural changes during deformation or heating procedures. The practicability of this measurement technique will be proven in the present short communication for instance on structural changes of preoriented high-speed poly(ethyleneterephthalate-) (PET-) fibres, which occur during a heating procedure under applied stress.

Experimental

Seven PET fibres (fibres A - G) were produced by a high-speed spinning process with winding velocities between 1450 and 3800 m/min, which result in values of birefringence between 11.7 and 59.2 and densities between 1.335 and 1.342 g/cm³ (nearly amorphous). In this paper we concentrate the investigations on the fibre sample with the highest value of velocity, birefringence, and density. Analogous investigations have been carried out on fibres A - F, the results of which will be published elsewhere.

The measuring arrangement is shown schematically in Fig. 1. The loudspeaker, two receivers (transducers), the tubular heating chamber, and the guide roller were mounted on an optical bench. The used sound wavelength was about 0.5 m, the stress applied to the fibres was varied between 2.3 and 128 MPa, and the heating rate was changed from 0.2 to 50 K min⁻¹. The fibre was supported by the edges of the two receivers and the guide roller. The propagation time of the sound impulse between the two receivers was registered by a transient recorder (R. Maurer TM 509) and transformed into the sonic-velocity values by a computer (HP 85) using a special program.

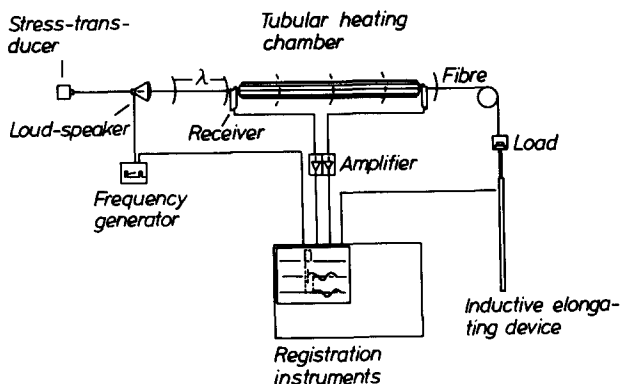


Figure 1. Schematic drawing of the measuring arrangement.

Evaluation

Within the polymeric fibres (representing a viscoelastic body) a longitudinal (extensional) wave propagates which is described by (6)

$$E(\omega) = \rho v^2 / (1 + (\beta v / \omega)^2) \quad (1)$$

with ρ density

v (phase) velocity of the wave

β damping factor

ω (angular) frequency

For sufficiently high frequencies $\omega^2 \gg (\beta v)^2$ equ. (1) can be reduced to equ. (2) which is well known for elastic bodies

$$E = \rho v^2 \quad (2)$$

Simple physical considerations suggest that the sonic velocity is orientation depending since the mechanism of propagation occurs as well along the polymer chains (intramolecular bond stretching) as across the chains (van der Waals' bonds; other chain-chain-interactions).

Moseley (1) proposed a semi-empirical treatment leading to

$$\frac{1}{v^2} = \frac{1 - \langle \cos^2 \theta \rangle}{v_{\perp}^2} + \frac{\langle \cos^2 \theta \rangle}{v_{\parallel}^2} \quad (3)$$

where v , v_{\perp} , and v_{\parallel} represent the sonic velocity for the sample having an average orientation characterized by $\langle \cos^2 \theta \rangle$, θ being the angle between chain direction and fibre axis (perpendicular orientation: $\theta = 90^\circ$; parallel orientation: $\theta = 0^\circ$).

If the case of a randomly oriented specimen is considered, i.e. $\langle \cos^2 \theta \rangle = 1/3$, then equ. (3) becomes

$$\frac{1}{v_{\parallel}^2} = \frac{2}{3v_{\perp}^2} + \frac{1}{3v_{\parallel}^2} \quad (4)$$

where v_{\perp} is the sonic velocity of an isotropic (unoriented) sample which can be obtained experimentally. Since v_{\parallel}^2 is considerably greater than v_{\perp}^2 equ. (3) can be transformed, if $\langle \cos^2 \theta \rangle$ is not too high, into

$$\langle \cos^2 \theta \rangle = 1 - \frac{2v_u^2}{3v^2} \quad (5)$$

Equ. (5) combines the measured sonic velocity with the average molecular orientation value $\langle \cos^2 \theta \rangle$. Thus, by measuring the velocity v Hermans' orientation function f can be calculated

$$f = 1/2 (3 \langle \cos^2 \theta \rangle - 1) = 1 - \frac{v_u^2}{v^2} \quad (6)$$

The sonic technique suffers from the difficulty that only an average molecular orientation of the whole sample is obtained. Samuels (5) extended the sonic modulus equations to a two-phase-system by use of a mixing rule involving bulk compressibilities. His final result is expressed by

$$\frac{1}{v^2} = \alpha \frac{1 - \langle \cos^2 \theta_c \rangle}{v_{1,c}^2} + (1 - \alpha) \frac{1 - \langle \cos^2 \theta_{am} \rangle}{v_{1,am}^2} \quad (7)$$

where the subscripts c and am stand for the crystalline and the amorphous phase, resp. and α means the volume crystallinity. Equ. (7) proves that the sonic velocity (and the elastic modulus) of an oriented semicrystalline polymer is influenced by both the degree of crystallinity and the average molecular orientation within the crystalline and amorphous regions.

Results and discussion

Fig. 2 shows as an example the sonic velocity and the strain of a pre-oriented PET fibre during a heating and cooling cycle (heating and cooling rate 1 K min^{-1}); the applied fibre tension was 11.6 MPa. The sonic velocity decreases with increasing temperature due to rising motion of the chain segments and reaches its (local) minimum at about $66 \text{ }^\circ\text{C}$. As well known the

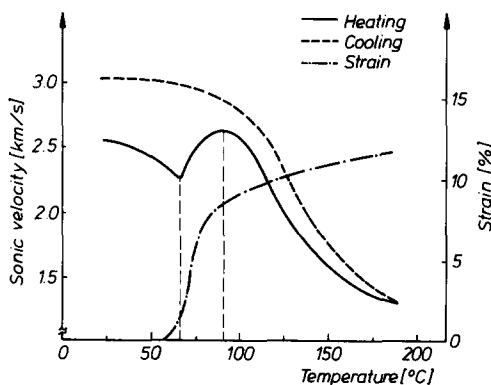


Figure 2. Sonic velocity and strain in dependence on temperature during a heating and cooling cycle (heating and cooling rate 1 K min^{-1}).

Characterization of the PET fibre (fibre G): Spinning velocity 3800 m/min ; $\bar{M}_w = 45 \text{ 000 g/mole}$; density 1.342 g/cm^3 ; birefringence $61 \cdot 10^{-3}$.

The applied stress during the measurement was kept constant at 11.6 MPa.

glass transition temperature of PET is observed at this temperature. At higher temperature the sonic velocity passes through a maximum at about 90 °C and decreases again and more rapidly with increasing temperature. Exceeding the glass transition temperature there are two effects: On the one hand the fibre is extended for some percent by the applied stress, a process which presumably gives rise to a small increase in molecular orientation; on the other hand the so-called (cold-)crystallization starts which is connected with an increase in the degree of crystallinity. The temperature interval of this crystallization is affected by the degree of preorientation: Unoriented samples have a crystallization maximum at about 115 °C which shifts towards 85 - 90 °C for highly oriented specimens (like the investigated fibre) (7). This crystallization can be proven by density measurements. Fibres which have been heated up to 150 °C and immediately cooled down to room temperature have a density of about 1.39 g cm⁻³ (degree of crystallinity of about 45 %).

If the fibre is cooled down after heating up to 180 °C the course of the sonic velocity as a function of temperature will be influenced in a remarkable manner as can be seen from Fig. 2. In this case, firstly, the glass transition at about 60 - 70 °C can only be observed in form of a break in the shape of the curve and, secondly, the sonic velocity at room temperature remains at a higher level than in the beginning. As could be proven by additional investigations the heating and cooling curves would coincide if the fibres were annealed and crystallized before the sonic measurements under stress at sufficiently high temperature.

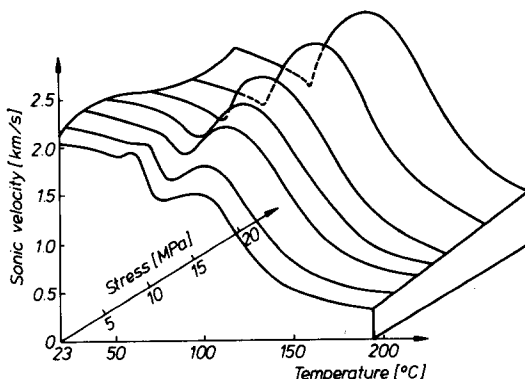


Figure 3. Three-dimensional representation of the sonic velocity as a function of temperature and applied stress (fibre G; heating rate 1 K min⁻¹).

The dependence of sonic velocity both on temperature and applied stress can be gathered from Fig. 3. The shapes of the curves are similar to each other. With increasing stress (at constant temperature) above 50 °C the sonic velocity grows whereas the deformation and crystallization maximum at about 90 °C appears more markedly.

Fig. 4 represents some typical v-T-curves for different heating rates between 0.2 and 50 K min⁻¹. The minimum in the range at about 70 °C shifts with increasing heating rate to higher temperatures, while the maximum at about 90 °C remains nearly unaffected by the heating rate. Against that, above the glass transition temperature the absolute values of the sonic

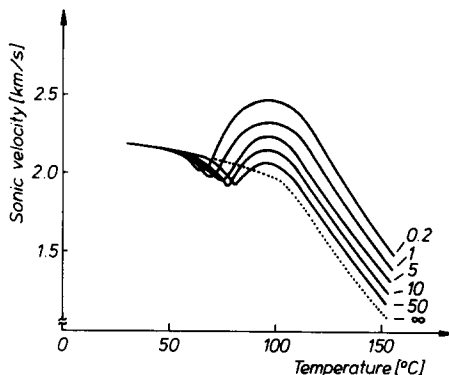


Figure 4. Sonic velocity as a function of temperature at different heating rates (fibre G; applied stress 11.6 MPa; heating rates in $[\text{K min}^{-1}]$).

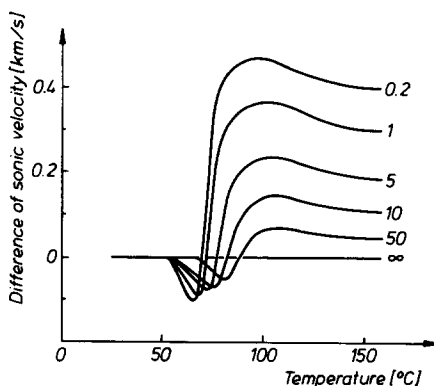


Figure 5. Difference of sonic velocity as a function of temperature at different heating rates (fibre G; applied stress 11.6 MPa; heating rates in $[\text{K min}^{-1}]$).

velocity become the greater the less the heating rate. This observation is supposed to be connected with the difference in the crystallization behaviour during the heating process: The crystallization is known to be a kinetic, i.e. time-consuming process. If the sample is heated slowly the crystallization will proceed to a higher degree above the glass temperature and this leads to a higher sonic velocity in correspondence with equ. (7).

It is an idea which suggests itself to calculate an imaginary curve of sonic velocity by extrapolation to the heating rate at infinity. (This curve may represent the course of the sonic velocity without crystallization and lengthening effects.) In doing this and calculating the respective differences of sonic velocity between the measured and the extrapolated curve, the results plotted in Fig. 5 are obtained. In agreement with the explanations made before the difference of the sonic velocity above the glass transition temperature increases with decreasing heating rate.

Measurements of sonic velocity analogous to those shown in Fig. 4 were carried out under various stresses between 5.8 and 58 MPa. Fig. 6 represents

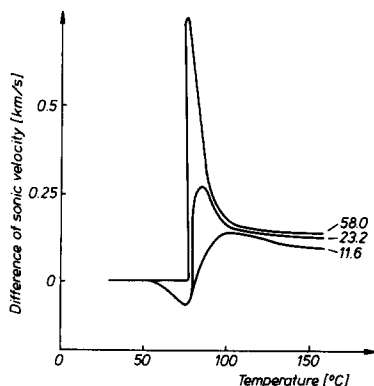


Figure 6. Difference of sonic velocity as a function of temperature at different applied stresses (fibre G; heating rate 10 K min^{-1} ; applied stresses in $[\text{MPa}]$).

the differences of sonic velocity between the measured and the extrapolated curve in dependence on temperature at constant heating rate of 10 K min^{-1} . In the temperature interval just above the glass transition the applied stress influences the difference of sonic velocity as follows: With increasing stress the maximum becomes drastically higher and shifts to slightly lower temperatures. Thus, crystallization proceeds the more dramatically the higher the applied stress. Nevertheless, in the discussion of the results shown in Figs. 5 and 6 it must not be overlooked the fact that above the glass temperature an extension of the fibres takes place which depends both on heating rate and applied stress. The measured differences of sonic velocity may therefore be caused by a superposition of these two effects (extension and crystallization). Additional studies are necessary in order to separate these two effects.

The results shortly reported in this paper prove that the measurement of sonic velocity represents a suitable technique to investigate the structural and orientation changes of amorphous or semicrystalline polymers during heating (and cooling) processes under stress.

Acknowledgement

We thank HOECHST Co. for providing the investigated fibres and the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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Accepted December 7, 1984