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Fig. 1

Figure 1: Fig. 1

Abstract

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ACCELERATION OF THE CRYSTALLIZATION PROCESS OF POLYETHYLENE TEREPHTHALATE UNDER THE INFLUENCE OF MECHANICAL ACTIONS

(Presented by Academician V. A. Kargin, 30 XII 1962)

The aim of the present work was to study the structural changes occurring in crystallizing polymers under the influence of periodically acting forces, and the mechanical properties of polymeric materials caused by these changes over a wide temperature range. Polyethylene terephthalate was chosen as the object of study—a crystallizing polymer with a high glass-transition temperature ($T_c = 80^\circ$) and melting point ($T_\mathrm{m} = 265^\circ$). The use of such a polymer with sufficiently flexible chains opens broad possibilities for forming a variety of structures and, consequently, for regulating the mechanical properties of materials obtained on its basis. In addition, the high glass-transition temperature of polyethylene terephthalate facilitates the possibility of fixing structural changes in it.

Fig. 1. Dependence of deformation on temperature for polyethylene terephthalate heated for 1 hour at 80° (1), and deformed at a frequency of 140 cycles/min for 1 hour at 80° (2)

The thermomechanical properties were studied, and the preliminary treatment of polyethylene terephthalate specimens was carried out, on the Aleksandrov-Gaev frequency apparatus (^{1}). The study was conducted at 140 cycles/min in the temperature interval from 20 to 230°. The rate of temperature increase during thermomechanical tests was 1°/min; the holding time of the specimen at the measurement temperature was 10 min; the maximum load was 0.7 kg/cm^2. Flat granules of quenched polyethylene terephthalate with an area of 29-30 mm^2 and a thickness of 2.0-2.2 mm were used as the initial specimens. The X-ray diffraction pattern obtained from such a granule shows a diffuse halo, indicating the amorphous nature of the initial specimens. It is analogous to the X-ray diffraction pattern in Fig. 2a (in the inset). The density of amorphous polyethylene terephthalate, determined by the gradient-tube method (^{2}), is 1.337 g/cm^3 at

Fig. 3. Dependence of deformation on temperature for polyethylene terephthalate heated for 1 hour at 95° (1), deformed at a frequency of 140 osc/min for 1 hour at 95° (2).

Figure 2: Fig. 3. Dependence of deformation on temperature for polyethylene terephthalate heated for 1 hour at 95° (1), deformed at a frequency of 140 osc/min for 1 hour at 95° (2).

20°. From the amorphous granules, specimens were prepared for further thermomechanical and X-ray structural investigation. For this purpose, one series of amorphous granules was subjected only to heat treatment at 80, 95, or 110° for 1 hour, while another series, during the same time—

To the article by A. A. Frolova and P. V. Kozlov, p. 1390

Fig. 2. X-ray diffraction patterns of polyethylene terephthalate heated for 1 hour at 95° (a), and deformed at a rate of 140 rpm for 1 hour at 95° (b)

To the article by A. P. Dybana, L. P. Demkiva, and M. S. Avgustinovich, p. 1453

Fig. 3. Section of the uterine wall of a rat kept on a sucrose diet. 15 days of pregnancy. Free arrangement of blastocysts in the uterine lumen. Absence of decidual changes in the endometrium. Hematoxylin-eosin. 160×

was subjected, at the same temperatures, to vibrational compressive deformation by a force varying according to a sinusoidal law with a specified amplitude.

X-ray structural study of samples prepared at 80° showed that, after preliminary thermal and thermomechanical treatment, the X-ray pattern is one and the same. It is analogous to the pattern for the initial amorphous polymer in Fig. 2a. In accordance with the radiographic data are the results of density determination, which in both cases was 1.338 g/cm^3.

The results of thermomechanical tests of polyethylene terephthalate samples preliminarily treated at 80° are presented in Fig. 1. The character of the dependence of deformation on temperature for a sample subjected only to thermal treatment is expressed by curve 1. Exactly the same dependence was observed for unheated amorphous samples.

Fig. 3. Dependence of deformation on temperature for polyethylene terephthalate heated for 1 hour at 95° (1), deformed at a frequency of 140 osc/min for 1 hour at 95° (2).

It is evident from the figure that at a temperature of 70° polyethylene terephthalate passes from the glassy into the highly elastic state. However, with a further increase in temperature, hardening of the sample occurs and its deformability drops sharply. This is associated, as the X-ray study showed, with crystallization of the polymer. (A similar phenomenon was previously established for a number of other polymers (3-6).) Only in the temperature interval 190-230°,

Fig. 4

Figure 3: Fig. 4

i.e., in the region where melting of the crystals begins, does polyethylene terephthalate exhibit the ability to flow.

Preliminary thermomechanical treatment basically does not change the character of the thermomechanical curve in comparison with a sample subjected only to heat treatment at the same temperature (curve 2 in Fig. 1). It is seen that, under the given conditions, such treatment also does not noticeably affect the structure of the polymer or the packing density of its chains. However, the magnitudes of the polymer deformations change, as does the glass-transition temperature, which shifts toward higher temperatures. A sharp difference in X-ray structural characteristics, thermomechanical properties, and density values is observed for samples subjected to thermal and thermomechanical action at 95°. Thus, on the radiograph (Fig. 2a, inset, p. 1353) obtained for thermally treated polyethylene terephthalate, no obvious changes are detected in comparison with the initial amorphous polymer. Only the density value, 1.343 g/cm^3, indicates a certain increase in the packing density of the polymer molecules. The X-ray pattern of the sample subjected to thermomechanical action looks quite different (Fig. 2b). The appearance of diffraction rings on the radiograph in this case indicates the emergence of crystalline order in the polyethylene terephthalate. The density value also changed substantially; it is 1.358 g/cm^3.

An equally sharp difference is also observed in the character of the thermomechanical

curves for the heated sample and the sample subjected to thermomechanical action (Fig. 3). In the first case (curve 1) the character of the dependence of deformation on temperature remains basically the same as for the amorphous polymer. Only the magnitude of the deformation is somewhat reduced. In the second case (curve 2 in Fig. 3), over a wide temperature interval polyethylene terephthalate practically shows no deformation, right up to the melting temperature of the crystals.

Fig. 4. Dependence of deformation on temperature for polyethylene terephthalate heated for 1 hour at 110° (1), and deformed at a frequency of 140 oscillations/min for 1 hour at 110° (2)

When the X-ray structural data obtained, the thermomechanical properties, and the density values are compared, it is clearly seen that the imposition of a mechanical field noticeably accelerates the course of crystallization processes in polyethylene terephthalate. Such an acceleration of the process of structural transformations under the influence of mechanical periodically acting forces has recently also been found for another crystallizing polymer—polycarbonate (^{6}).

X-ray structural investigation of polyethylene terephthalate samples subjected to thermal and thermomechanical treatment at 110° showed that in both cases the character of the X-ray pattern is the same. The appearance of diffraction rings, similar to those shown in Fig. 2b, indicates crystallization of the polymer. The density of the polymer in both cases of sample treatment increased to 1.37 g/cm^3. The character of the thermomechanical curves is also completely the same (Fig. 4). The samples do not exhibit any deformation over a wide temperature interval, and the viscous-flow state sets in only when the crystals melt.

Consequently, in this case, under the specified regime of polymer treatment, the imposition of a mechanical field does not visibly change the structure of the polymer in comparison with the structure that arose as a result of thermal action.

Thus, in the present work it has been experimentally established that thermomechanical treatment of crystallizing polymers leads to a substantial acceleration of crystallization processes in comparison with their thermal treatment. This must undoubtedly be taken into account in the use of materials and products made of crystallizing polymers.

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