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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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THE EFFECT OF MECHANICAL ACTIONS ON THE RATE OF THE CRYSTALLIZATION PROCESS OF ISOTACTIC POLYSTYRENE

In recent years, owing to a complex of many valuable properties, crystallizing polymers have found wide practical application. From this point of view, the study of structural transformations in crystallizing polymers that lead to changes in their physicomechanical characteristics is of substantial interest.

In the present work, we investigated the influence of periodically acting forces on the rate of the crystallization process and the change in the structure and thermomechanical properties of crystallizing polymers under the action of these forces.

Fig. 1. Dependence of deformation on temperature for isotactic polystyrene: **1** –heated for 1 hour at 100°; **2** –deformed at a frequency of 140 oscillations/min for 1 hour at 100°

The object of study was isotactic polystyrene, obtained by stereospecific polymerization on Ziegler-type catalysts. The ability of isotactic polystyrene to crystallize readily and rapidly above the glass-transition temperature makes it possible to obtain specimens of a definite structure. This structure can easily be fixed by sharply cooling the specimen to room temperature, since it is far below the glass-transition temperature of isotactic polystyrene and relaxation processes under these conditions proceed very slowly.

To study the structural transformations taking place and the properties of isotactic polystyrene that depend on them, X-ray structural and thermomechanical methods of investigation were used. The study of the thermomechanical properties and the preliminary treatment of specimens of isotactic polystyrene were carried out on the Alexandrov-Gaev frequency apparatus (1). The investigations were performed in the temperature range from 20 to 220°, and a frequency of 140 oscillations per minute was used. The rate of temperature increase in thermomechanical tests was 1° per minute, the holding time of the specimen

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Fig. 3

Figure 2: Fig. 3

at the measurement temperature was 10 min, and the maximum load was 0.7 kg/cm^2. Before preparation of the specimens for investigation, the isotactic polystyrene was purified of possible impurities of catalyst, monomer, and atactic polystyrene. For this purpose it was washed with 0.1 *N* HCl, then boiled in acetone and methyl ethyl ketone, with repeated replacement of the mother liquor by fresh solvent. After purification, the isotactic polystyrene was washed with methanol and dried.

to constant weight at a temperature of 80°. The specimens for the study were prepared in the form of tablets 10 mm in diameter and 2.2-2.4 mm thick by pressing on a laboratory press, taking into account the conditions of true pressing ([2,3]). It was established by X-ray analysis that the prepared specimens have an amorphous structure, and their X-ray patterns are shown in Fig. 2, *a*. Subsequently, in order to obtain specimens of a definite structure, one part of the tablets of amorphized isotactic polystyrene was heated at 100, 120, and 140° for 1 hour at one of the indicated temperatures, while the other part, for the same time and at the same temperatures, was subjected to vibrational compression deformation by a force varying sinusoidally with a specified amplitude.

For determining the influence of the preliminary treatment of the polymer on its subsequent thermomechanical properties, isotactic polystyrene was subjected to thermomechanical tests over a wide temperature range. Figure 1 presents the results of these tests for specimens treated at a temperature of 100°. It is seen that, depending on the method of preliminary treatment, the course of the thermomechanical curves changes substantially. Curve 1, which expresses the dependence of deformation on temperature for a specimen subjected only to thermal action, shows that at a temperature of 100° the transition of isotactic polystyrene from the glassy to the highly elastic state begins to occur. Further increase in temperature leads to crystallization of the polymer and to a sharp decrease in its deformability as a result of hardening of the material ([4]). Only in the temperature interval 200-220°, i.e., in the region where melting of the crystals begins, does isotactic polystyrene pass into the viscous-flow state. An analogous dependence was also observed for unheated amorphous specimens. From curve 2 in Fig. 1 it is seen that preliminary thermomechanical treatment led to a considerable decrease in the magnitude of the polymer deformation, without basically changing the character of the thermomechanical curve in comparison with the specimen subjected only to thermal treatment at the same temperature.

Fig. 3. Dependence of deformation on temperature for isotactic polystyrene: 1 —heated for 1 hour at 120°; 2 —deformed at a frequency of 140 cycles/min for 1 hour at 120°.

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Fig. 4. Dependence of deformation on temperature for isotactic polystyrene: 1 —heated for 1 hour at 140°; 2 —deformed at a frequency of 140 osc/min for 1 hour at 140°.

Figure 3: Fig. 4. Dependence of deformation on temperature for isotactic polystyrene: 1 —heated for 1 hour at 140°; 2 —deformed at a frequency of 140 osc/min for 1 hour at 140°.

The X-ray structural investigation carried out on these same specimens of isotactic polystyrene showed that, in the case of thermal treatment alone, the character of the X-ray pattern did not change in comparison with the initial amorphous polymer (Fig. 2, *a*). At the same time, preliminary thermomechanical treatment led to the appearance, along with the diffuse halo, of a faint diffraction ring along its outer contour, indicating the formation of a structure of a higher order than the initial one (Fig. 2, *b*).

The further development of the crystalline structure of isotactic polystyrene under the action of deforming forces occurs at higher temperatures, when the mobility of molecular chains or secondary structural formations increases. This is clearly manifested in the character of the X-ray patterns of isotactic polystyrene specimens,

subjected to treatment at 120°. The X-ray diffraction pattern obtained for the thermally treated sample shows the diffuse halo characteristic of an amorphous polymer (Fig. 2, a), whereas preliminary thermomechanical treatment leads to a sharpening of the diffuse halo and to the appearance in the X-ray diffraction pattern (Fig. 2, c) of diffraction rings, which indicate the formation of a crystalline structure. Such a difference in the structures of the treated samples leads to a sharp difference in the thermomechanical properties of samples of isotactic polystyrene subjected only to thermal treatment at the indicated temperature, as compared with thermomechanically treated samples.

Fig. 4. Dependence of deformation on temperature for isotactic polystyrene: **1** —heated for 1 hour at 140°; **2** —deformed at a frequency of 140 osc/min for 1 hour at 140°.

As can be seen from curve 1 in Fig. 3, heating the sample at 120° did not lead to a change in the character of the dependence of deformation on temperature, in comparison with the sample heated at 100° and with the initial amorphous polymer, which shows exactly the same dependence. The thermomechanical curve has an entirely different form in the case when the sample was subjected to thermomechanical action at the same temperature and for the same time (curve 2 in Fig. 3). It is clearly seen that over a wide temperature range, up to the melting temperature of the crystals, at which the transition to the viscous-flow state begins, isotactic polystyrene is practically not deformed.

From the X-ray structural data obtained and the thermomechanical tests of isotactic polystyrene it follows quite evidently that thermomechanical actions have a substantial influence on the change in the structure of the crystallizing polymer and increase the rate of the crystallization process. Acceleration of the process of structural transformations upon application of a mechanical field has recently also been found for other crystallizing polymers—polycarbonate and polyethylene terephthalate ([5], [6]).

With a further increase in the temperature of the preliminary thermal and thermomechanical treatment under the specified experimental conditions, no difference was found either in the structure or in the thermomechanical properties of the polymer. As follows from Fig. 4, the character of the thermomechanical curves of isotactic polystyrene, both in the case of only thermal treatment and in the case of thermomechanical treatment at 140°, is completely identical. Over a wide temperature range the samples do not deform, and the viscous-flow state sets in only upon melting of the crystals. The X-ray structural data are also in agreement with the thermomechanical properties. In both cases the character of the X-ray pattern is the same. Sharp diffraction rings indicate the occurrence of a well-ordered crystalline structure (Fig. 2, e). Consequently, in this case, under the specified polymer-treatment regime, the application of a mechanical field does not noticeably change the structure of the polymer, since at the indicated temperature the crystallization rate of isotactic polystyrene is sufficiently high.

Thus, in the present work, by means of X-ray structural

and thermomechanical methods has shown that periodically acting mechanical forces lead to an increase in the rate of the crystallization process of polymers as compared with thermal action. The study of thermomechanical properties made it possible to reveal the dependence of the character of the thermomechanical curves on the type and conditions of preliminary treatment. This, undoubtedly, should be taken into account in the processing and use of materials and articles made from crystallizing polymers.

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