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A. A. FROLOVA, V. G. BRUSENTSOVA, P. V. KOZLOV,
Academician V. A. KARGIN

STUDY OF RELAXATION PHENOMENA IN CRYSTALLINE POLYCAPROAMIDE ==================================

In the preceding work (^1) certain features were established in the course of relaxation processes in a series of amorphized crystallizing polymers, which differed from one another in the degree of flexibility of their molecules and in their ability to form crystalline structures.

For precisely this reason it was of interest to investigate relaxation phenomena in a crystalline polymer with various degrees of stiffening of its structural elements.

The aim of the present work was to study the relaxation properties of polycaproamide using samples of a definite structure but of different depth of crystallization, and to attempt to establish a relation between the magnitudes of deformation and the frequency of the acting force. The choice of readily crystallizing polycaproamide as the object of investigation was due to the fact that this polymer has a high melting point and a low glass-transition temperature, lying far below room temperature. This creates favorable conditions for obtaining polymer samples of quite definite structure and of the required depth of crystallization. To study relaxation phenomena in polycaproamide, the same apparatus and the same experimental conditions were used as in work (^1); the only difference was that the investigations were carried out in the temperature interval from −30 to 220° and the rate of temperature increase in the thermomechanical tests in the present case was 2° per 1 min. The samples for the investigation were prepared in the form of tablets 10 mm in diameter and 2.3–2.4 mm thick by pressing on a laboratory press, taking into account the conditions of true pressing (^2, ^3). After pressing at 220° under a pressure of 300 kg/cm^2, the samples were cooled with liquid nitrogen to −50°. On X-ray photographs taken from these samples, diffraction rings are observed, indicating crystalline ordering. This is also confirmed by the values of the density, measured pycnometrically. It increases, in comparison with the density value for amorphous polycaproamide, to 1.145 g/cm^3. Study of the fracture surface in polarized light with crossed nicols permits the conclusion that the samples obtained have a spherulitic structure. Some of these samples were used to study the relaxation properties immediately after their preparation. Another portion was subjected to additional heat treatment in order to obtain samples with a greater depth of crystallization. For this purpose the polycaproamide samples were heated at 180° for 1 hour. The increase in the number of diffraction rings on the X-ray photographs obtained from these samples indicates the formation of a crystalline structure of a higher order than the initial one. In accordance with the X-ray data

results obtained in determining the density of the heated specimens. In this case the density increased to 1.153 g/cm^3, which indicates an increase in the degree of crystallization of the polymer. Microscopic examination of the fracture surface of specimens heated at 180° revealed, as in the initial specimens, a spherulitic structure. On these two series of polycapramide specimens with a fine-grained spherulitic structure, but with different degrees of crystallization, the relaxation properties of the crystalline polymer were studied.

Figure 1 shows the dependence of deformation on temperature for polycapramide specimens of lower degree of crystallization, for different frequencies of the applied force. It is noteworthy that the character of the thermomechanical curves depends on the frequency of the applied force. In the case where the frequency of action on the specimen is high and the relaxation time of the polymer is much greater than the time of action of the force, the polymer practically does not deform over the entire range up to the melting temperature of the crystals, at which the transition to a viscous-flow state begins (curve 1 in Fig. 1). With decreasing frequency of the applied force, the form of the thermomechanical curves changes. Curves 2 and 3 show that, at these frequencies of action, the crystallized polycapramide is already capable of appreciable deformation. On the thermomechanical curves there appeared all three regions corresponding to the three physical states of ordinary amorphous polymers—glassy, highly elastic, and viscous-flow. However, as the study of the structure of the specimens after recording the thermomechanical curves up to temperatures far exceeding the glass-transition temperature T_c of the polymer showed, diffraction rings are observed on the X-ray patterns. A further decrease in the frequency of the applied force also leads to a change in the character of the thermomechanical curve (curves 4 and 5), which in this case has the same form as the curves for polymers crystallizing during the course of the test. X-ray analysis established the crystalline structure of the specimens after deformation at these frequencies. It should be noted that, beginning at a certain temperature above T_c, the magnitudes of polymer deformation for several frequencies are practically identical and remain unchanged over a wide temperature interval. Such constancy of the deformation magnitudes can be explained by the fact that the duration of the experiment is comparatively short, and the rate of temperature increase is too high for further crystallization processes to take place that would lead to a decrease in the deformability of polycapramide. The coincidence of curves 3, 4, and 5 above T_c is due to the fact that they were obtained precisely for those frequencies at which, in the transitional region of T_c, irreversible structural changes in polymers begin to occur under the influence of mechanical actions [4-6].

Fig. 1. Dependence of deformation (arb. units) on temperature for unheated polycapramide at different frequencies of action of the force: 1 –1400, 2 –140, 3 –14, 4 –1.4, 5 –0.14 oscillations per 1 min

Figure 1

Figure 1: Figure 1

Fig. 2. Dependence of deformation (arbitrary units) on temperature for polycapramide heated at 180° for 1 hour, for different frequencies of action of the force: 1 –14, 2 –1.4, 3 –0.14 oscillations per 1 min

Figure 2: Fig. 2. Dependence of deformation (arbitrary units) on temperature for polycapramide heated at 180° for 1 hour, for different frequencies of action of the force: 1 –14, 2 –1.4, 3 –0.14 oscillations per 1 min

The study of the thermomechanical properties of polycapramide specimens of greater degree of crystallization (heated at 180°, $d = 1.153$ g/cm^3)

showed that for them, too, it is possible to observe, as a function of the frequency of action of the force, the same three types of curves (Fig. 2) as for specimens with a smaller degree of crystallization depth ($d = 1.145$ g/cm^3). Only the frequency interval in which the transition from one type of thermomechanical curve to another is found is considerably narrowed. It should be especially noted that an entirely analogous dependence of the character of the thermomechanical curves on the frequency of the acting force is also observed for a rigid-chain polymer–polycarbonate (4,1). In other words, a polymer with sufficiently flexible chains, but rigidified by crystallization, and a rigid-chain polymer reveal the same dependence of deformation on temperature, which is well explained by relaxation phenomena. In addition, the fact is of interest in itself that crystallized polycapramide is capable, above T_c, of relatively large reversible deformations, although, as has been shown by X-ray diffraction, it has a crystalline structure. This suggests that, above the glass-transition temperature, secondary structural formations take part in the deformation process, and their mobility is the smaller the greater the degree of crystallization depth of the polymer.

Fig. 2. Dependence of deformation (arb. units) on temperature for polycapramide heated at 180° for 1 hour, for different frequencies of action of the force: 1 –14, 2 –1.4, 3 –0.14 oscillations per 1 min.

When comparing the curves shown in Figs. 1 and 2, it is seen that increasing the degree of crystallization depth of polycapramide leads not only to an increase in T_c, but also to a loss of the dependence of T_c on the frequency of action of the force, which was not observed for ordinary amorphous polymers and for specimens with a smaller degree of crystallization depth (in the present case T_c is understood as the temperature at which the mobility of structural elements increases substantially and the polymer is capable of exhibiting comparatively large deformations (7)). The results obtained are conveniently interpreted on the basis of the concepts of the bundle structure of polymers, developed by V. A. Kargin, A. I. Kitaigorodskii, and G. L. Slonimskii (8). According to these

Fig. 3. Dependence of the maximum value of deformation (arb. units) on the logarithm of frequency for polycapramide: 1 —unheated, 2 —heated at 180° for 1 hour

Figure 3: Fig. 3. Dependence of the maximum value of deformation (arb. units) on the logarithm of frequency for polycapramide: 1 —unheated, 2 —heated at 180° for 1 hour

concepts, chains in crystalline and amorphous polymers exist in the form of bundles, within which, on the whole, a parallel orientation of the chains is preserved. The difference between bundles in crystalline polymers and bundles in amorphous polymers consists in the fact that, in a crystalline bundle, along with the parallel orientation of chains, there exists azimuthal order in the arrangement of the axes of chain molecules and side groups. The order within bundles may vary over wide limits, the limiting case of ordering being a bundle in a crystalline polymer. Taking into account the stepwise character of the crystallization process, it is natural to assume that, with an increase in the degree of crystallization depth, further ordering within the bundle occurs. This leads to its rigidification and to an impoverishment of the set of relaxation times, which is the cause of the increase in T_c and of its independence from the frequency of the acting force. The assumption made agrees well with the experimental data. An increase in the degree of ordering is indicated by X-ray structural···

data and density values. In this case the density increases, and additional diffraction rings appear on the X-ray patterns.

From Figs. 1 and 2 it is evident how strongly the maximum values of the polymer deformation $\varepsilon_{\mathrm{max}}$ vary as a function of the frequency ω of the acting force, increasing as it decreases. If one plots the dependence of $\varepsilon_{\mathrm{max}}$ on the logarithm of the frequency (Fig. 3), then for each of the series of polycapramide specimens of a definite depth of crystallinity a linear dependence is observed. Moreover, the greater the stiffening of the polymer as a result of crystallization, i.e., the less mobile the structural elements become, the smaller these quantities are. The points of intersection of the straight lines with the abscissa axis correspond to the logarithms of those frequencies at which, under the given conditions, the polymer is practically not deformed up to the melting temperature of the crystals. As shown in [1], the same dependence of $\varepsilon_{\mathrm{max}}$ on the logarithm of frequency also exists for amorphized crystallizing polymers.

Fig. 3. Dependence of the maximum value of deformation (arb. units) on the logarithm of frequency for polycapramide: **1** —unheated, **2** —heated at 180° for 1 hour

Thus, in the present work, using specimens of polycapramide of a definite structure but with different degrees of crystallization as an example, the relaxation properties of crystalline polymers have been studied. In the investigated range of frequencies of periodically acting forces, a dependence of the character of the

thermomechanical curves on frequency was found. It was established that the degree of crystallization of the polymer affects the width of the frequency interval in which this dependence appears. An analogy was also drawn between the properties of a polymer plasticized by an external plasticizer and polycapramide stiffened by crystallization. Study of the relaxation properties of polycapramide specimens of different degrees of crystallization made it possible to establish a linear dependence of the maximum values of polymer deformation on the logarithm of the frequency of the acting force. It was shown that stiffening of the polymer by crystallization leads to a decrease in the values of $\varepsilon_{\max}$ and, in addition, is the cause of an increase in T_c and of its independence from the frequency of action of the force. X-ray structural and thermomechanical studies of crystallized polycapramide made it possible to establish that, above T_c, secondary structural formations take part in the deformation process.

The experimental data obtained have been interpreted on the basis of concepts of the packet structure of polymers.

Moscow State University
named after M. V. Lomonosov

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