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Abstract

Full Text

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THE INFLUENCE OF THE DEGREE OF MOLECULAR ORDERING OF CRYSTALLIZING POLYMERS IN THE MELT ON THE VISCOELASTIC PROPERTIES OF MELTS

(Presented by Academician V. A. Kargin, July 1, 1963)

At the present time much attention is being devoted to the study of the relationship between the character of secondary molecular structures of polymers and their properties in the solid state. Polymer melts (1–3), in this respect, have been studied hardly at all.

It should be assumed that the formation of secondary molecular structures in polymer melts must change the mobility of molecular chains, i.e., must be reflected primarily in the viscoelastic properties of the melts. In the present work we studied the influence of high pressures on the coalescence (autohesion) and crystallization of polymer melts—processes in which the mobility of polymer chains plays a determining role.

Powdered or granulated polymer was charged into a cylindrical heated press mold, heated above the melting temperature, and subjected to pressure. After holding at specified temperatures and pressure, the sample was cooled under pressure to room temperature and removed from the press mold. The samples obtained in this way were subjected to heat treatment (annealing), during which their X-ray study and dimensional measurements were carried out. Below, using polytetrafluoroethylene (PTFE) as an example, we present the results obtained by us.

Fig. 1. Dependence of the relative change in the height of PTFE samples on pressure

For the study we used PTFE of an ordinary industrial grade, both in the form

Fig. 2. Dependence of the molecular ordering of polytetrafluoroethylene on pressure

Figure 2: Fig. 2. Dependence of the molecular ordering of polytetrafluoroethylene on pressure

of a finely dispersed powder and in the form of granules obtained by grinding a monolithic sample. The polymer charged into the press mold was heated without pressure to 330°, then the specified pressure was applied and the temperature of the press mold was raised to 380°. Holding at 380° and at the specified pressure was 1 hour; annealing of the samples was carried out at 330° for 3 hours. A series of samples was obtained, prepared at pressures from 300 kg/cm^2 to 2000 kg/cm^2. Figure 1 shows the change in sample height after annealing as a function of the magnitude of the pressure used. Figure 2 gives the curve of the dependence of integral intensities on pressure for these same samples before annealing.

As is seen from Fig. 1, annealing of the samples leads to an increase in sample height, which is greater the higher the pressing pressure used. The change in the dimensions of the samples upon annealing is associated with relaxation of nonequilibrium deformation processes arising during the pressing of powdered or granulated material. The effect of the change in sample dimensions is even more pronounced in samples obtained from granules. As a result of annealing a series of samples obtained at different pressures from granules, only the sample prepared at a pressure of 1300 kg/cm^2 remained intact; samples obtained at higher pressures broke apart into the separate granules from which they had been formed.

It follows from Fig. 2 that external pressure promotes crystallization of PTFE up to pressures of the order of 1300 kg/cm^2. At higher pressures there is inhibition of the crystallization process and, thus, the curve

dependence of the degree of molecular ordering on external pressure passes through a maximum. High external pressure retards not only the relaxation processes occurring during the formation of a powdered or granulated polymer, but also hinders the molecular rearrangements that take place during crystallization.

The study of a number of other crystallizing polymers (polytrifluorochloroethylene, polyethylene terephthalate, polyformaldehyde, etc.), carried out by the method described above, showed that the features of the viscoelastic state under the action of high pressures, characteristic of PTFCE, also occur for melts of these polymers. Thus it has been established that the behavior of melts of crystallizing polymers under the action of high pressures is, in general outline, analogous to the behavior of linear amorphous polymers under pressure, which has been studied in considerable detail previously (4-7).

Fig. 2. Dependence of the molecular ordering of polytetrafluoroethylene on pressure

For the case of linear amorphous polymers, a number of independent methods established that high external pressure lowers the mobility of molecular chains, hindering molecular rearrangements and increasing the time of relaxation processes. A change in the rigidity of polymer chains by plasticization, by the introduction of polar groups into the chain, and by crosslinking (7), as well as an increase in the degree of molecular ordering (8), sharply changes the response of polymers to external pressure.

PTFCE has very flexible and regularly built molecules; in the condensed state it is distinguished by a high degree of packing and crystallinity. The high ordering of PTFCE is retained even at temperatures above the melting point, which determines the pressure dependence of the autohesion of the powdered material that we observe. At the same time, external pressure, by increasing the rigidity of the bundles, also retards crystallization processes. Thus, the viscoelastic properties of PTFCE in the melt are determined by the mobility not of individual molecules, but of highly ordered secondary molecular formations (9).

Similar data obtained by us for a number of other crystalline polymers allow us to conclude that the features of the viscoelastic properties of crystallizing polymers at temperatures above the melting point depend substantially on the character of the secondary structures of these polymers in the melt. Further investigations in this direction will be of great importance for substantiating polymer-processing processes.

N. A. Yartseva took part in carrying out the experimental part of the work.

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