THE STRENGTH PROPERTIES OF ACICULAR SINGLE CRYSTALS OF POLYOXYMETHYLENE

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The strength properties of acicular formations of polyoxymethylene, obtained by the directed polymerization of trioxane "whiskers," have been studied. It has been found that the acicular single crystals obtained in this process exhibit a high strength.

At the present time, the chief method for the production of highly oriented polymeric materials exhibiting high strength is by the stretching of polymers. By a suitable choice of temperature-dynamic conditions of stretching, it has been possible to achieve extremely high values for the strength of polymers—about 300 kg/mm² at room temperature and 500-600 kg/mm² at the temperature of liquid nitrogen for polymers such as polyvinyl alcohol and polyformaldehyde (polyoxymethylene) [1]. Methods of obtaining oriented polymers other than by stretching are also of considerable interest, however. In orientational stretching it is necessary to "straighten" and "disentangle" chain molecules, which were in different, generally twisted, states in the original nonoriented polymer. It is possible that a further increase in the strength of polymers (the theoretical strength has been estimated as 1500-2500 kg/mm² [2, 3] so that the strength reserves are far from exhausted) which is naturally associated with further increase in the order in the arrangement of the molecules throughout the volume of the polymer ensuring uniformity of the loading of the molecules, by the stretching method alone will become difficult.

Methods in which it is not necessary to overcome the original disorder of the chain molecules, and in which it is possible to obtain immediately a polymeric material with completely straight chain molecules arranged in parallel fashion, are therefore of interest. We are speaking of the method of directed polymerization, of which one of the most effective forms is the polymerization of the monomer in the solid crystalline phase.* If polymerization is initiated in a crystal of the monomer, the polymer chains grow in definite crystallographic directions and form a polymer crystal in which, in contrast to the polymer crystals which are grown in dilute solutions and which contain molecules folded on one another (folded conformation of the molecules) [6], the molecules are straight along the entire length and are arranged parallel to one another [7, 8].

The study of the strength of acicular polymer crystals of this kind (polyoxymethylene, obtained by the polymerization of trioxane) has shown that it is possible to obtain materials with extremely high strength, i.e., 350 kg/mm² (at room temperature) [9]. In all cases up to the present, however, the monomer has consisted of a polycrystalline block, and the small polymer needles formed after radiation polymerization [7, 9] have been separated from the rest of the polymer mass.

This method has recently been extended to the interesting case where the monomer was taken in the form of "prepared" acicular single crystals of trioxane, grown in the gaseous phase of the monomer; these "whiskers" are formations with a length of several centimeters and a cross section of several tens of micrometers. The familiar high degree of perfection of the structure of "whiskers" of substances with low

*Other methods of directed polymerization exist—polymerization of the monomer from the gaseous phase on to an oriented support [4] and polymerization in the liquid with an applied field (for example, electrostatic) [5]. We shall not consider these methods.

molecular weight [10-12] and the original fibrous form made the attempt to convert these into "polymer whiskers" particularly attractive. We were able to do this by a combined catalytic-radiation method of polymerization [13]. A polymer "jacket" was first created in the surface region of the monomer "whisker" by placing it in an atmosphere containing a catalyst (BF₃ or SnCl₄), after which the "whiskers" were irradiated in a γ source and the polymerization was carried out by heating the "whiskers" to a temperature close to the melting point of the trioxane crystals. The initial polymer "jacket" was necessary in order to prevent the volatilization of trioxane and to make it possible for the polymerization to take place along the middle of the "whisker." As a result we obtained "prepared" polymer needles (Fig. 1). X-ray diffraction study of the structure of these materials showed that they are single crystals of polyoxymethylene with chain molecules directed preferentially along the axis of the polymer needle. In addition to the high degree of perfection of the crystal lattice, the polymer "whiskers" were found to contain defects of the pore type, which are scattered throughout the volume of the "whiskers" and are apparently associated both with the catalytic stage of the polymerization and with the incomplete conversion of the monomer into the polymer in the radiation polymerization.*

*The structural data for the acicular polyoxymethylene formations obtained will be given in detail in a separate paper, to be published in the Journal "Vysokomolekulyarnye Soedineniya."