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Academician V. A. KARGIN, T. I. SOGOLOVA, T. K. SHAPOSHNIKOVA

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Abstract

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REGULATION OF THE SUPRAMOLECULAR STRUCTURE OF POLYMERS BY INTRODUCING ARTIFICIAL NUCLEI OF CRYSTALLIZATION

It is known that the spherulites that arise upon cooling a polymer melt are formed on nuclei originating from fluctuation inhomogeneities existing in the melt. The higher the temperature of the melt and the time of holding it at a given temperature, the fewer crystallization nuclei are preserved in it and the larger the spherulites formed upon cooling. Upon repeated melting and subsequent cooling, spherulites form in the same places where they were before, i.e., on the same nuclei. However, some of the nuclei disappear upon repeated melting, and therefore each successive melting and cooling leads to a decrease in the number of spherulites and an increase in their size ([1,2]).

In works of recent years it has been shown that the mechanical properties of polymers depend on their supramolecular structure, including the size of the spherulites, if they are obtained under identical conditions. Regulation of the sizes of spherulites, and consequently also of mechanical properties, can be carried out by the thermal regime used in preparing specimens (melt temperature, duration of residence in the molten state, cooling regime, etc.) ([2–8]).

In essence, this amounts to regulating the number of nuclei on which the formation of supramolecular structures proceeds. It could therefore be supposed that the introduction of artificial crystallization nuclei would be an effective method for regulating the supramolecular structure and, consequently, the mechanical properties of polymers.

In connection with this, exploratory studies were carried out whose purpose was to determine the possibility of regulating the supramolecular structure of polymers by introducing artificial crystallization nuclei into them.

As nucleating agents, organic substances introduced in small amounts were used, with melting temperatures higher than that of the polymer under study, insoluble in it and not chemically interacting with it. The initial object of investigation was polypropylene—a readily crystallizing polymer for which the formation of a large number of different supramolecular structures is characteristic ([9,10]). The nucleating agents were introduced into a solution of polypropylene in xylene. Films were obtained by evaporating the solvent on a microscope slide; they

were then melted and slowly cooled to room temperature. The films obtained (20-50 μ thick) were separated from the glass and subjected to mechanical tests.

A large number of studies were carried out, and a number of substances were found that are artificial nuclei of crystallization of polypropylene. Thus, it was found that indigo is an active nucleating agent in polypropylene; on its crystalline particles, growth of polypropylene spherulites proceeds (Fig. 1*a*, see insert p. 1129).

The use of other substances as nuclei of structure formation showed that the shape of the particles of the nucleating agent has a substantial influence on the supramolecular structure of the polymer. When artificial nuclei whose particles have an anisodiametric

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Fig. 1. Microphotographs of the structure of polypropylene films:
a –film obtained by evaporating a solution of polypropylene containing 0.5% indigo in xylene at 140°, then melted at 210° and cooled to 20° over the course of 1 hour;
b –powdered isotactic polystyrene was introduced into polypropylene at 210°; the formed film was cooled to 20° over the course of 1 hour.

Fig. 2. Microphotographs of the structure of polypropylene films containing alizarin, obtained from the melt at 210° and cooled to 20° over the course of 1 hour:
a –general structure of a polypropylene film containing alizarin crystals;
b –an individual spherulitic band grown on a needle-like alizarin crystal.

Fig. 3. Microstructure of polypropylene films obtained by evaporating a solution at 140°, melted at 190° and cooled to 20° over the course of 1 hour:
a –initial polypropylene;
b –polypropylene with 1% indigo.

shape, characteristic structures in the form of spherulitic bands are formed in polypropylene. For example, when alizarin is introduced into polypropylene, the structures shown in Fig. 2*a*, *b* arise in it (see insert, p. 1129). As can be seen from the figure, amizarin crystallizes in the form of needle-like crystals, on which the spherulitic bands of polypropylene grow.

In addition, we have shown that crystalline polymers whose melting temperature is higher than that of the polymer in which the supramolecular structure is to be specified can serve as artificial nuclei of crystallization. As an example, experiments may be cited in which dispersed isotactic polystyrene was introduced in small amounts into polypropylene.

As shown in Fig. 1*b*, particles of isotactic polystyrene dispersed in polypropylene are nuclei of structure formation. It should be noted that polypropylene films with 1% polystyrene, prepared from the melt at 210°, have a fine-spherulitic

Fig. 4

Figure 1: Fig. 4

structure, whereas films of the original polypropylene, obtained under the same conditions, consist of large spherulites. In polypropylene films containing 1% polystyrene and prepared at 260° (at this temperature both polystyrene and polypropylene melt), the particles of molten polystyrene in the form of droplets "melt out" of the film and do not exert a nucleating action.

This example clearly shows that only solid particles dispersed in the polymer mass, which have not melted, serve as artificial nuclei of structure formation.

The introduction of 1% indigo into polypropylene made it possible to obtain films consisting of small spherulites under those conditions in which, from polypropylene solution without a nucleating agent, films are obtained that consist of large spherulites with distinct boundaries between them (Fig. 3*a*, *b*).

Upon melting and subsequent slow cooling of such specimens, the structure of the films containing 1% indigo remains unchanged (the same as in Fig. 3*b*), whereas the structure of films containing no nucleating agent coarsens and becomes more defective. The same occurs after two and three successive remeltings.

Fig. 4. Curves of the dependence of stress on deformation for polypropylene films (at 20°) obtained by evaporating the solvent at 140°, melted at 190° and cooled to 20° over 1 hour: **1** —original polypropylene; **2** —polypropylene with 1% indigo

Figure 4 presents the dependence of stress on deformation for films of the original polypropylene and polypropylene containing 1% indigo. As can be seen from the figure, films containing indigo have a considerably greater elongation at break than films of the original polypropylene obtained under the same conditions (the specimens were melted at 190° and cooled to 20° over 1 hour). The nucleating action of solid particles was also found in a number of other crystallizing polymers—polyethylene, polyamides, polyformaldehyde, polyethylene terephthalate, crystallizing rubbers—when various high-melting organic substances were introduced into them.

Thus, we have shown that the formation of spherulitic structures proceeds by a nucleation mechanism, and that artificial nuclei of crystallization may be particles of substances dispersed in the polymer that have a higher melting temperature than the polymer. The influence of these particles is reduced to the fact that they remain unchanged in the polymer melt and, upon cooling of the melt, serve as centers at which crystallization of the polymers begins, with the formation of a spherulitic or other supramolecular structure.

Since the number of these centers can be specified by the quantity of introduced particles,

particles, it becomes possible to regulate the process of crystallization and structure formation. The presence of artificially introduced nuclei creates conditions for obtaining uniformly crystallized polymers with a supramolecular structure that provides the required set of mechanical properties. Supramolecular structures obtained on artificially introduced nuclei are more resistant to thermal and other effects.

By varying the quantity of introduced nuclei, and their size and shape, it is possible to obtain polymer samples with different supramolecular structures, resistant to thermal effects.

Regulation of the supramolecular structure of polymers by introducing artificial nuclei makes it possible to obtain, from one and the same polymer, materials with different mechanical properties.

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named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.