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L. P. VASILEVSKAYA, N. F. BAKEEV, L. G. LAGUN, P. V. KOZLOV,

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L. P. VASILEVSKAYA, N. F. BAKEEV, L. G. LAGUN, P. V. KOZLOV,
Academician V. A. KARGIN

THE EFFECT OF SMALL ADDITIONS OF SURFACE-ACTIVE SUBSTANCES ON THE PROPERTIES OF CRYSTALLINE POLYMERS

The mechanical properties of crystalline polymers are determined to a substantial degree by the structure of the polymeric materials. The size and morphology of crystalline structures, the degree of crystallinity, and the defectiveness of crystalline polymers are of decisive importance in determining their deformation, strength, and other mechanical characteristics.

In this connection, problems of regulating the structure of polymeric materials in the course of processing and forming articles based on them, with the aim of obtaining materials with optimal mechanical properties, acquire great importance. Effective methods influencing the crystallization of polymers and the character of the structures themselves are the well-known techniques of heat treatment of crystallizing polymers, chemical modification (grafting) [1–3], introduction of heterogeneous nuclei [4–6], and, to a lesser extent, plasticization [7].

However, the introduction of surface-active substances into crystallizing polymers opens up yet another possibility for influencing the crystallization process of polymeric materials. The present investigation is devoted to elucidating this effect of small additions of surface-active substances on the structure and properties of crystalline polymers.

The object of the investigation chosen was the readily crystallizing polyhexamethylene adipamide (nylon-66), widely used in industry, with molecular weight 30,000 and melting point 262°, and, as surface-active substances, various dyes: 1,4-dihydroxyanthraquinone (1), 1,4-dimesidinoanthraquinone (2), 4-(4-chlorophenyl-amino)-N-methyl-1,9-anthrapyridone (3).

The crystallization processes were studied in films obtained from solutions and from the melt. The samples for investigation were prepared as follows. Dyes were added to a melt of polyhexamethylene adipamide or to its 5% solution in formic acid in ratios to the polymer of 1 : 100 and 1 : 1000. After homogeneous mixing of the polyamide with the surface-active substance had been achieved, the samples, in the case of the polyamide melt, preliminarily heated to 280°, were crystallized by cooling at a rate of 4–5° per min to room temperature. In

Figure 2 and Figure 3: plots of stress versus deformation and linear growth rate of spherulitic structures

Figure 1: Figure 2 and Figure 3: plots of stress versus deformation and linear growth rate of spherulitic structures

the case where the surface-active substances were introduced through solution, the samples were prepared in the form of films by complete evaporation of the solvent and subsequent crystallization under conditions identical with those for the melt.

Optical studies of the samples obtained showed a sharp change in the sizes of the polymer spherulites upon introduction of the additives. The effect has the same character both in the case of solutions and in the case of the melt.

Figure 1 presents the structure of films of the pure polymer and of films containing additives 1, 2, and 3. Introduction of dye 2 in a ratio of 1 : 100 leads to the formation of a fine-spherulitic structure, whereas introduction of dye 1, on the contrary, leads to the formation of a coarse-spherulitic structure. The effect of dye 3 differs depending on the concentration; at a ratio of 1 : 100 a coarse-spherulitic structure is formed, while at a ratio of 1 : 1000 a fine-spherulitic structure is formed.

Electron-microscopic studies showed that no changes occur in the fine structure of the specimens.

Figure 2 presents the results of dynamometric tests of the polymer films obtained. As can be seen from the figure, the specimens studied are characterized by the known dependence of deformation-strength properties on the size of the spherulites ([8]). Thus, for example, specimens with a fine-spherulitic structure (polyamide with dyes 2, 3, ratio 1 : 1000) possess high deformability and strength, whereas specimens with a coarse-spherulitic structure (polyamide with dyes 1, 3, ratio 1 : 100) undergo brittle rupture at slight deformation.

Fig. 2. Dependence of stress on deformation for pure polyamide and for polyamide with surface-active substances 2, 3 (*I, III, IV*) and 1 and 3 (*II, V*)

Fig. 3. Linear growth rate of spherulitic structures. **1** –pure polyamide, **2** – polyamide with surface-active substance 1

Thus, from the data of optical and mechanical studies it is evident that the introduction of small additions of surface-active substances leads to a substantial change in the structure of crystalline polyamide and, as a result, to a change in its mechanical properties.

What, then, accounts for the change in the sizes of the crystalline structures of the polymer when small amounts of surface-active substances are introduced into it? As is known, the crystallization rate of polymers, as of low-molecular-weight compounds, is determined by the number of crystallization centers (nu-

Figure 1

Figure 2: Figure 1

clei) formed per unit time and by the linear growth rate of the crystals. The ratio of the rates of these two processes determines the sizes of the crystalline structures.

In order to clarify the nature of the influence of small additions of surface-active substances introduced into the polymer on the crystallization process, measurements were made of the linear growth rate of polyamide spherulites—both pure and with dye—on an MKU-1 micro-cinema apparatus. The films for this purpose were obtained from a melt heated to 295° in a stream of nitrogen, and crystallization was carried out under isothermal conditions at $240 \pm 0.5°$ on a heating stage thermostated with an accuracy of up to 0.5°.

Figure 3 presents the results of measuring the linear growth rate of spherulites in the case of pure polyamide and of polymer with additions of dye 1 in the ratio 1 : 100. As can be seen, the introduction of surface-active additions into polyamide leads to a decrease in the linear crystallization rate owing to a lowering of the surface energy at the spherulite–melt boundary. A similar decrease in surface energy at the growing boundary

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Fig. 1. *a* —initial polyamide; *b* —polyamide with surfactant 1, 1:100; *c* —polyamide with surfactant 2, 1:100; *d* —polyamide with surfactant 3, 1:100; *e* —polyamide with surfactant 3, 1:100, 600×.

of the crystal, as is well known (^{9}), leads to a decrease in the rate of its growth.

Thus, the results of measuring the linear growth rate undoubtedly indicate that the additives introduced into polyamide exert an influence characteristic of surface-active substances. Along with this effect, one should expect that a decrease in the surface energy at the crystal–melt boundary should be accompanied by a sharp increase in the rate of nucleation as a result of a decrease in the critical size of nuclei. Indeed, as is seen in the example of polyamide with additives 2 and 3 (Fig. 1, ,), the introduction of surface-active substances leads to the formation of a fine-spherulitic structure. This is the result of an increase in the nucleation rate under conditions of an increase in the total rate, which is what is actually observed.

Finally, the very curious effect of an increase in the size of spherulitic structures at a higher content of surface-active substances (dyes 1 and 3) is apparently associated with the screening influence of the introduced additives of surface-active substances (^{9}).

Thus, the introduction of very small amounts of homogeneously distributed additives of surface-active substances (0.1%) leads to a sharp change in the crystallization rate, in the size of the spherulitic structures formed, and, as a result, in the mechanical properties of polymeric materials.

Moscow State University
named after M. V. Lomonosov

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