Soviet-era science, translated into English

Reports of the Academy of Sciences of the USSR

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1965

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Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Volume 162, No. 5

PHYSICAL CHEMISTRY

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ON THE QUESTION OF ARTIFICIAL NUCLEI OF CRYSTALLIZATION FOR CRYSTALLIZING POLYMERS

Recently, in a number of works it has been noted that regulation of the supramolecular structure is possible not only by changing the temperature and time conditions of melting and crystallization of the polymer when obtaining specimens from solution or melt, but also by introducing artificial nuclei of polymer crystallization. In these works it was shown that substances chemically noninteracting with the polymer and having a melting temperature above the melting temperature of the polymer can serve as artificial nuclei of crystallization ([1]-[5]).

It seemed to us essential to use, as artificial nuclei of crystallization, salts of organic acids whose melting temperature is above the melting temperature of the polymers under study.

For these investigations crystalline polymers were used: low- and high-density polyethylene, polypropylene, and polyamide. A systematic and more detailed study of the influence of artificial crystallization nuclei on the supramolecular structure of the polymer was carried out on polypropylene and low-density polyethylene.

Artificial nuclei of crystallization were introduced during rolling of the polymer for 1.5 min at a temperature 5-10° below the melting temperature of the polymer. It was found that, for a more homogeneous distribution of the artificial crystallization nuclei, it is expedient to carry out the rolling process in two stages. In stage I, the required amount of artificial crystallization nuclei was introduced into a portion of the polymer, and in stage II the remaining portion of the polymer was added to the mixture obtained by rolling. Both stages were approximately the same in duration—45 sec.

The criterion for the action of various salts as artificial crystallization nuclei was the change in the supramolecular structure of the polymers, as well as the change in their mechanical characteristics—strength and deformability. Optical investigations were carried out using an MIN-8 polarizing microscope; the change

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Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

in strength and deformability was measured on a pendulum-type dynamometer (6).

As a result of the investigations we carried out, it was found that most salts of heavy metals of organic acids are artificial nuclei of crystallization for polymers. The optimum amount of artificial crystallization nuclei effectively influencing the change in the supramolecular structure of polymers was found (0.15–0.2% relative to the weight of the polymer). As an example, Fig. 1 presents microphotographs of specimens of polypropylene and polyamide containing and not containing artificial crystallization nuclei.

It is evident from Fig. 1 that the size of supramolecular formations of the spherulitic type decreases significantly upon introduction of artificial crystallization nuclei—bismuth salicylate, titanium oxalate, and lead acetate. Other salts produced an analogous effect.

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Fig. 1. Microphotographs of samples of polypropylene (*a, b, v, g*) and polyamide (*d, e*)—initial samples (*a* and *d*) and samples containing artificial crystallization nuclei: titanium oxalate (*b*), bismuth salicylate (*v*), lead acetate (*g, e*)

In addition, experiments were carried out with samples of low- and high-density polyethylene, as a result of which it was found that copper naphthenate,

Fig. 2. Dependence of stress on deformation for polypropylene: original (*1*) and containing bismuth salicylate (*2*), titanium oxalate (*3*), cadmium benzoate (*4*), lead acetate (*5*) at 50°.

Fig. 3. Dependence of stress on deformation for low-density polyethylene: original (*1*) and containing copper naphthenate (*2*), bismuth salicylate (*3*), titanium oxalate (*4*), lead acetate (*5*), lead palmitate (*6*) at 50°.

titanium oxalate, bismuth salicylate, cobalt naphthenate, lead palmitate, lead acetate, lead benzoate, zinc acetate also influence changes in supramolecular formations of the spherulitic type in these polymers.

Fig. 4

Figure 3: Fig. 4

Fig. 4. Dependence of deformation on temperature at different frequencies of force action for low-density polyethylene: original (*a*) and containing copper naphthenate (*b*) and bismuth salicylate (*c*). *1* $-\omega_1$, *2* $-\omega_2$, *3* $-\omega_3$, *4* $-\omega_4$.

It seemed essential to us to follow the change in the strength and deformability of polymer specimens containing and not containing artificial crystallization nuclei. For this purpose, specimens in the form of films 110 μ thick were subjected to tensile deformation on a dynamometer.

Figures 2 and 3 present tensile curves for specimens of polypropylene and low-density polyethylene containing and not containing artificial crystallization nuclei. From these figures it is evident that the introduction of artificial crystallization nuclei leads to an increase in the strength and deformability of the polymer, and also to an increase in the value of the recrystallization stress of the specimens.

It was of interest to follow the behavior of polymer specimens containing and not containing artificial crystallization nuclei over a wide temperature interval under conditions of dynamic action of forces. For these experiments the Aleksandrov-Gaev apparatus (7) was used. The tests were carried out at different frequencies of force action (the frequencies $\omega_1 < \omega_2 < \omega_3 < \omega_4$ are respectively equal to 1; 10; 100; 1000 oscillations per minute), in the temperature interval from -90 to $+110°$.

Figure 4 gives graphs of the dependence of deformation (in arbitrary units) for specimens of low-density polyethylene, containing and not containing artificial crystallization nuclei, on temperature at different frequencies of action of a sinusoidal force with constant amplitude.

From Fig. 4 it is evident that the transition region, which for the initial low-density polyethylene lies between $-60°$ and $+100°$, is preserved in almost the same temperature interval for polyethylene containing artificial crystallization nuclei, but the dependence of the deformation of the polymer specimen on the frequency under conditions of dynamic action of the force is reduced, as is its deformability.

In work (8) the behavior of polyethylene and polypropylene was studied over a wide temperature interval under conditions of dynamic action of forces. Comparing the results of our experiments with the results of work (8), it may be said that the introduction of artificial crystallization nuclei promotes the formation of more ordered systems. Apparently, this phenomenon occurs because of the deeper crystallization of the polymer, which proceeds readily in the presence of artificial crystallization nuclei; this is manifested in a decrease in the deformability of the specimen at all the investigated frequencies of action of the force amplitude.

As a result of the investigations carried out, it became clear that by introducing salts of heavy metals of organic acids as artificial crystallization nuclei it is possible to regulate the supramolecular structure of crystalline polymers and to exert a substantial influence on the strength and deformability of crystallizing polymers.

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Received
11 I 1965

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