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Abstract

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ON THE QUESTION OF THE CRYSTALLIZATION OF LOW-MOLECULAR-WEIGHT SUBSTANCES FROM SOLUTIONS IN HIGH POLYMERS

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When low-molecular-weight substances are dissolved in polymers, supersaturated solutions are readily formed that possess anomalously high stability. The crystallization of low-molecular-weight substances from supersaturated polymer solutions occurs predominantly at the polymer–gas interface, in contrast to typical solutions in liquids. In technology this phenomenon is designated by the term blooming. The blooming of dissolved substances is a highly undesirable phenomenon ([1]). Despite the considerable amount of data published on this question, the cause of blooming has not yet been elucidated.

In the present work an attempt has been made to clarify the causes of this phenomenon on the basis of the experimental material obtained. The system sulfur–polybutadiene (SKB-30) was chosen as the object of study. To determine the relative amount of sulfur crystallized on the surface of the polybutadiene, a method using labeled sulfur S^{35}, proposed by Auerbach and Gaiman ([2]), was employed.

As the basic dosage, corresponding to the supersaturation limit ([3]), the ratio of 2 g of sulfur per 100 g of polybutadiene was used. Mixing was carried out on laboratory rolls. The specimens studied, 26 mm in diameter and 2 mm thick, were pressed in cellophane in a press for 60 min at 100°. The cellophane was removed from one of the planes of the specimen before the measurements were begun. The activity of the specimens was measured from the side not covered with cellophane, using an end-window counter.

A study of the kinetics of blooming showed that already one day after the surface of the specimen was freed from cellophane, a considerable increase in the activity of the specimen was observed (Fig. 1). This is explained by the crystallization of sulfur on the surface and its migration from the bulk to the surface, owing to the appearance of a concentration gradient.

Determinations of the activity of specimens covered with cellophane, carried out at various time intervals after pressing, showed that in this case no increase in the

Fig. 1

Figure 1: Fig. 1

activity of the specimens occurs. During prolonged storage of the specimens in the covered state, the intensity of blooming decreases (Fig. 1,) and ultimately the specimen loses the ability to bloom (Fig. 1,), i.e., equilibrium is attained through crystallization in the bulk. In crystallization on the surface, equilibrium is reached after 18–20 days for specimens 2 mm thick. It should be noted that crystallization begins practically immediately after removal of the cellophane, and the time required to reach equilibrium is determined by the rate of diffusion of sulfur from the plate. With plates 1 mm thick, equilibrium is reached after 10–12 days.

In the absence of a free surface, equilibrium is not reached even after 60 days, i.e., the rate of crystallization in the bulk is considerably lower than the rate of crystallization on the surface. Apparently, crystallization in the bulk is associated with overcoming certain obstacles that are absent during crystallization on the surface.

It is known that the crystallization process consists of two stages: the formation of nuclei and their subsequent growth. A study of the dependence of the intensity of blooming on the concentration of the supersaturated solution shows that the difficulties encountered in crystallization in the bulk are associated mainly with the stage of formation of crystallization nuclei. As can be seen from the data presented in Figs. 2 and 3, the intensity of blooming at first increases with increasing solution concentration, and then decreases. The absence of blooming at high sulfur concentrations (6 g and more per 100 g of polymer) indicates that, in this case, rapid crystallization is taking place in the bulk. At high supersaturations, the rate of both stages of the crystallization process increases. However, if the obstacles to crystallization in the bulk were associated with the stage of crystal growth, then after the concentration of dissolved sulfur had decreased to small degrees of supersaturation the crystallization rate would have had to decrease, and the solution would have remained supersaturated for a long time.

Fig. 1. Dependence of the activity of polybutadiene samples on time after removal of the protective cellophane layer. Duration of storage of the samples after pressing, in days: a –1, b –60, v –135.

Therefore, the rapid establishment of equilibrium at high supersaturations shows that the principal difficulties are encountered in the formation of crystallization nuclei. Attempts to initiate crystallization in the bulk by introducing fillers—carbon black, chalk, $BaSO_4$, Sb_2S_5—gave no positive result. Only when powdered metallic selenium is introduced into the mixture is it possible to initiate crystallization in the bulk, as evidenced by the absence of blooming.

Metallic selenium is insoluble in rubber. Selenium is isomorphous with sulfur

Fig. 2

Figure 2: Fig. 2

Fig. 3. Effect of concentration on the blooming of sulfur from polybutadiene. I_0 –initial activity, I_p^{p} –equilibrium activity of the sample

Figure 3: Fig. 3. Effect of concentration on the blooming of sulfur from polybutadiene. I_0 –initial activity, I_p^{p} –equilibrium activity of the sample

and readily forms mixed crystals with it. Introducing it into the mixture is equivalent to introducing crystallization nuclei into the solution. This experiment confirms the conclusion drawn above.

Fig. 2. Change in activity with time as a function of sulfur dosage (in g per 100 g): *a* –0.5; *b* –1.2; *v* –6.0; *g* –1.5; *d* –4.0; *e* –2.0.

The formation of crystallization centers occurs as a result of fluctuations in the concentration of the dissolved substance. Initially, microregions with an amorphous structure arise ([4]), which, as a result of molecular rearrangement, are transformed into centers for further development of the crystal. The presence of solvent molecules in such microregions hinders the formation of crystalline nuclei. Obviously, the time required for removal of solvent molecules from the microregion in which the nucleus is forming will depend on the self-diffusion coefficient of the solvent molecule. On the other hand,

the probability of the occurrence of a concentration-fluctuation zone and the time of its existence depend on the degree of supersaturation of the solution and on the diffusion coefficient of the dissolved substance in the given solvent.

In the case of low-molecular solvents, the difference between the value of the diffusion coefficient of the dissolved substance and the self-diffusion coefficient of the solvent is usually small. However, in the case of polymer solutions of low-molecular substances it is quite substantial: for example, for rubbers the self-diffusion coefficient at 20° is of the order of 10^{-11} cm^2/sec. (5), while the diffusion coefficients of low-molecular substances in rubber are of the order of 10^{-8} cm^2/sec. (6). Such a large difference in the quantities characterizing molecular mobility makes it possible to assume that, at one and the same degree of supersaturation, the probability of formation of crystallization centers in the bulk in the case of a polymer solvent is considerably smaller than in the case of low-molecular solvents. During crystallization on the surface, the mobility of the solvent molecule is not a limiting factor, and therefore the probability of formation of crystallization centers on the surface is considerably greater than in the bulk of the polymer.

Fig. 3. Effect of concentration on the blooming of sulfur from polybutadiene. I_0 –initial activity, I_p^{p} –equilibrium activity of the sample

Structuring and crystallization of the polymer cause a sharp decrease in the mobility of its molecules. Under these conditions the probability of crystallization in the bulk must decrease considerably. And indeed, in crystalline polycaprolactam, crystallization of the monomer proceeds rapidly in the presence of a free surface, while in its absence decomposition of the supersaturated solution does not occur even over several years. Table 1 gives data on blooming and crystallization in the bulk for SKB vulcanizates with different density of the spatial network.

Table 1

Sample No.	Free sulfur, %	Equilibrium modulus, kg/cm^2	Crystallization in the presence of a free surface	Crystallization in the absence of a free surface
1	1.48	10.1	Intensive blooming after 3 days	Many crystals in the bulk after 10 days
2	1.51	19.2	Intensive blooming after 7 days	Crystals do not form in the bulk within 1 year

An increase in the mobility of polymer molecules through plasticization of the latter by low-molecular liquid substances should increase the probability of crystallization in the bulk. And indeed, it is known that in oil-extended rubbers sulfur blooming does not occur (2).

The examples presented confirm the correctness of the conclusion drawn that the difficulties encountered during crystallization in the bulk are due to the low mobility of the solvent molecules.

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