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Abstract

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EFFECT OF ARTIFICIAL CRYSTALLIZATION NUCLEI ON THE KINETICS OF CRYSTALLIZATION AND THE MECHANICAL PROPERTIES OF ISOTACTIC POLYSTYRENE

It was shown in ([1]) that the introduction of artificial crystallization nuclei can effectively influence the structure of crystalline polymers. This phenomenon is manifested especially clearly in the case of polymers possessing rigid chains and, consequently, slow crystallization kinetics, for example in the case of isotactic polystyrene.

The process of crystallization of isotactic polystyrene from the melt is characterized by a low rate of formation of crystallization nuclei and by a comparatively low rate of their growth ([2]). The crystallization nuclei of the initial polystyrene may be microregions with crystalline order that either were not destroyed during melting and preexist in the polymer melt, or arise fluctuationally at the crystallization temperature. Naturally, the higher the melt temperature, the fewer undestroyed ordered regions remain and, consequently, the smaller the number of crystallization nuclei preexisting in the melt ([3],[4]).

For the rate of formation of crystallization nuclei, as well as for the rate of their growth, there are temperature optima lying below T_m of the crystalline phase of the polymer; moreover, in the general case the temperatures of the maximum rate of nucleation and of the maximum rate of growth of the structures do not coincide with one another ([5]). The maximum growth rate of crystalline formations of polystyrene is observed in the temperature interval 160—175° ([2],[6]). At these temperatures the rate of formation of nuclei is very small; therefore crystallization proceeds predominantly on those nuclei that preexisted in the melt, and the structure of films crystallizing under these conditions depends to a high degree on the melt temperature.

At temperatures exceeding T_m of crystalline polystyrene by 10° and more (for example, 245°), few crystallization centers remain in the melt, and the structure of films formed during crystallization at 160° consists of individual spherulites located in an uncrystallized amorphous mass; moreover, the number of spherulites is the smaller, the higher the melt temperature (Fig. 1). Such films possess the mechanical properties of an amorphous body. The presence of well-formed spherulites located in an amorphous film does not hinder the manifestation, above T_c, of high-elastic deformation; moreover, the spherulites themselves are deformed to a very small extent. The strength of such specimens is determined by the strength of the amorphous film (Fig. 3, a), and the presence of a greater or smaller number of spherulites affects only the values of elongation at break, since in this case the spherulites essentially play the role of macroinclusions leading to fracture of the specimen before the development of high deformations.

It was of interest to determine how the introduction of artificial crystallization nuclei affects the rate of crystallization and the mechanical properties of isotactic polystyrene.

It turned out that the introduction of certain organic substances (with T_m higher than that of crystalline polystyrene) leads to rapid and deep crystallization of polystyrene even in the case of very high melt temperatures.

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Fig. 1. Microphotographs of films of the original isotactic polystyrene. Melt temperature: *a* —280°; *b* —260°; *c* —245°. Crystallization temperature 160°; crystallization time 1 hour.

Fig. 2. Microphotographs of samples of isotactic polystyrene containing 2% fluorescein (*a*), 2% indigo (*b*), 4% alizarin (*c*). Melt temperature 260°, crystallization temperature 160°. Crystallization time 1 hour.

It is known that the rate of crystallization depends on the rates of two independent stages: the formation of crystallization nuclei and their growth. The introduction of artificial crystallization nuclei reduces to zero the time required for the first stage to proceed and thereby increases the rate of crystallization.

Various organic dyes were used as artificial crystallization nuclei: fluorescein, quinacridone, indigo, and alizarin.

It turned out that substances differing in chemical nature have different activity with respect to their effect on the rate of crystallization of polystyrene.

Fig. 3. Dependence of stress on deformation of isotactic polystyrene specimens. Pressing temperature 280°, crystallization temperature 160°: *a* —original polystyrene, crystallization duration 3 h; , , , —polystyrene containing 2% indigo, crystallization duration respectively 15, 30, 45, and 60 min.

Fig. 4. Dependence of stress on deformation of isotactic polystyrene films. Pressing temperature 260°, crystallization temperature 160°. Crystallization duration 1 h: *a* —polystyrene containing 2% indigo; —polystyrene containing 4% alizarin.

Fig. 3. Dependence of stress on deformation of isotactic polystyrene specimens. Pressing temperature 280°, crystallization temperature 160°: a —original polystyrene, crystallization duration 3 h; , , , —polystyrene containing 2% indigo, crystallization duration respectively 15, 30, 45, and 60 min.

Figure 1: Fig. 3. Dependence of stress on deformation of isotactic polystyrene specimens. Pressing temperature 280°, crystallization temperature 160°: a —original polystyrene, crystallization duration 3 h; , , , —polystyrene containing 2% indigo, crystallization duration respectively 15, 30, 45, and 60 min.

Fig. 4. Dependence of stress on deformation of isotactic polystyrene films. Pressing temperature 260°, crystallization temperature 160°. Crystallization duration 1 h: a —polystyrene containing 2% indigo; —polystyrene containing 4% alizarin

Figure 2: Fig. 4. Dependence of stress on deformation of isotactic polystyrene films. Pressing temperature 260°, crystallization temperature 160°. Crystallization duration 1 h: a —polystyrene containing 2% indigo; —polystyrene containing 4% alizarin

Figure 2 presents the structure of films containing fluorescein, indigo, and alizarin, obtained from the melt at 260° with subsequent crystallization at 160°.

The introduction of 2% fluorescein does not substantially change the number of spherulites located in the amorphous polystyrene film (Fig. 2*a*; compare with Fig. 1); fluorescein is not a crystallization nucleus for polystyrene, and in Fig. 2*a* crystals and aggregates of fluorescein crystals are clearly visible, on which no growth of crystalline polystyrene formations occurs. In contrast to fluorescein, the introduction of indigo (or quinacridone) leads to rapid crystallization of polystyrene with the formation of films of fine-spherulitic structure (Fig. 2).

In the presence of alizarin, rapid, deep crystallization of polystyrene also occurs, with the formation of films whose structure consists of large joint spherulites of alizarin and polystyrene (Fig. 2). Alizarin is the only one of the crystallization nuclei listed above whose crystals dissolve in the polystyrene melt—

styrene; nevertheless, it can serve as a center of crystallization of polystyrene, since at the crystallization temperature it precipitates again from solution in polystyrene in the form of spherulites, and the rate of its crystallization from solution considerably exceeds the rate of crystallization of polystyrene. The radial fibrils of alizarin spherulites become centers of growth of crystalline polystyrene formations.

Thus, the introduction of artificial crystallization nuclei increases the rate of crystallization of polystyrene from the melt. Naturally, the acceleration of polystyrene crystallization in the presence of artificial nuclei is reflected in the mechanical properties of polystyrene.

In the presence of indigo, quinacridone, or alizarin, polystyrene films always exhibit mechanical properties typical of crystalline bodies, since at any temperature below the melting temperature of the artificial nucleus a quantity of centers sufficient for deep crystallization is retained in the polystyrene melt.*

The acceleration of polystyrene crystallization in the presence of artificial crystallization nuclei is vividly illustrated by Fig. 3, which gives the tensile curves of polystyrene films, both original and containing indigo, pressed at 280° and subjected to crystallization at 160° for various times. As can be seen from the figure, the original polystyrene, even after 3-hour crystallization, exhibits the mechanical properties of an amorphous body (curve *a*), whereas in the presence of 2% indigo even 15-minute crystallization leads to the formation of crystalline films (curve *b*).

As the duration of crystallization increases, films containing indigo lose deformability (Fig. 3, *g*, *d*), which is evidently associated with structural changes occurring under these conditions (indistinguishable in the optical microscope).

It is possible to preserve the deformability and strength of polystyrene films subjected to crystallization for 1–2 hours by introducing alizarin as the crystallization nucleus (Fig. 2 *v*). In this case, after crystallization for one hour, film deformability of 300% is retained (Fig. 4 *b*).

Thus, the introduction of artificial crystallization nuclei leads to a sharp increase in the crystallization rate of slowly crystallizing polymers. Variation of the nature and geometric form of the seed crystals makes it possible to control the mechanical properties of crystalline polymers.

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[*] It should be noted that films with the mechanical properties of a crystalline body can be obtained from the original polystyrene if the melt temperature exceeds its melting temperature by only a few degrees (for example, 230°), since under these conditions many undestroyed crystallization centers remain in the melt. However, the structure of such films changes strongly with small fluctuations of the melt temperature, which leads to structural inhomogeneity of the films and creates certain inconveniences in working with them.

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

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