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Abstract

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On the Influence of the Thickness of a Polymer Film on Its Structure

Crystallization of polymeric substances in thin layers has its own particular features. It is known that near the surface of a solid body the mobility of bundles and chains decreases as a result of adsorption interaction and steric hindrance ([1,2]). There is a report that, at a certain minimum film thickness (less than 1 μ), secondary structures do not form at all ([3]).

The present work is devoted to studying the influence of layer thickness on the formation of secondary structures from polymer melts. The films for the experiments were obtained by melting the polymer between a plane-parallel glass plate and the spherical surface of a plano-convex lens of large radius of curvature under constant pressure. Such a system made it possible to obtain a wedge-shaped polymer layer with a thickness from tenths of a micron (in the ideal case, from zero) to 30–40 μ in a single sample. To improve the wettability of the glass by the polymer, the glass was first hydrophobized by treating it with dimethyldichlorosilane vapors.

The samples were subjected to the appropriate heat treatment, and then observed in polarized light with an MIN-8 microscope. The thickness of the polymer film was determined with an accuracy of up to 1 μ from the difference between the thickness of the bonded sample and the total thickness of the lens and plate. For this purpose, a measuring spring head of the IG type and a set of end plane-parallel length measures (Johansson gauge blocks) were used. The diameter of the spherulites was measured directly under the microscope or on photomicrographs using a photographed and printed, at the same magnification, scale of an object micrometer, and was then averaged arithmetically.

Gutta-percha was studied in the greatest detail. The gutta-percha was purified by dissolution in CCl_4 and, after three reprecipitations with an acetone–methanol mixture (3 : 1), was dried in vacuum at 39° for 2 days. Gutta-percha films enclosed between the surfaces of the lens and the plate were kept under pressure for 1-2 hours at temperatures of 100; 120; 145; 200 and 240°, and were then cooled to 40° (at a rate of 6-10°/min) and held at this temperature for about 3 hours.

In a film 30 μ thick, very small spherulites are obtained under all the regimes used. As the film thickness decreases, there is observed–

Fig. 1

Figure 1: Fig. 1

Fig. 3

Figure 2: Fig. 3

Fig. 1. Structure of gutta-percha in thin layers.
a —dependence of the structure on thickness (the film thickness decreases from top to bottom). In the lower part of the photograph, an optically empty region adjacent to the center of the sample is visible, where the layer thickness is about 1 μ, and a pattern of transition from large spherulites to small ones with decreasing thickness (initial melt temperature 240°); *b* —structure at a layer thickness of 1—1.5 μ and an initial melt temperature of 100—120°; *v* —principal morphological forms of gutta-percha. The main axis of a single crystal (in the center of the frame) is parallel to the polarizer axis; *g* —the same object, but the direction of the main axis of the single crystal makes an angle of 45° with the polarizer axes.

Fig. 3. Structure of isotactic polypropymene in a thin layer.

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Fig. 1

Fig. 3

the diameter of the spherulites visible in the microscope gradually increases, reaching a maximum at a certain thickness that depends on the melt temperature; the volume of a single spherulite (calculated from its visible diameter and the film thickness in the observed region) also increases. A further decrease in the thickness of the polymer layer to 5-1.5 μ is characterized by a sharp decrease in the size of the spherulites simultaneously with an increase in their number, and at thicknesses of 1-1.5 μ and an initial melt temperature above 140°, spherulites visible in the microscope do not form at all (Fig. 1a).

Figure 2 presents a series of curves for the dependence of the volumes of gutta-percha spherulites on the layer thickness for different initial melt temperatures*.

With an increase in the melt temperature, the sizes of the spherulites grow at all film thicknesses, and the maximum shifts into the region of thinner layers. If the sample was held at 100—120°, the layer thickness in the center of the sample was 1-1.5 μ, and an irregular crystalline structure formed in this region (Fig. 1b). At a higher melt temperature the layer thickness in the center of the sample was less than 1 μ, and the region near the center of the lens became optically empty, structureless (Fig. 1a).

Fig. 2. Dependence of the volumes of gutta-percha spherulites on layer thickness for different initial melt temperatures: 1 –100°, 2 –120°, 3 –145°, 4 –200°, 5 –240°

Figure 3: Fig. 2. Dependence of the volumes of gutta-percha spherulites on layer thickness for different initial melt temperatures: 1 –100°, 2 –120°, 3 –145°, 4 –200°, 5 –240°

The extremal character of the dependence of spherulite size on layer thickness can be explained as follows. It is known that the sizes of crystalline formations are determined by the competition of two factors—the rate at which active crystallization centers arise and the growth rate of crystals. Near the glass surface, because of adsorption interaction and steric hindrance, the mobility of the bundles determining the growth rate of the spherulites decreases. This decrease in mobility may lead to the fact that, at least under some crystallization conditions, far from the solid surface the spherulites will have time to grow, while on centers located near the surface structures of visible dimensions will not have time to grow.

Fig. 2. Dependence of the volumes of gutta-percha spherulites on the layer thickness for different initial melt temperatures:
1 –100°, 2 –120°, 3 –145°, 4 –200°, 5 –240°.

With a decrease in the thickness of the polymer film, the relative volume of the adsorption layer in the sample increases and the number of "living" crystallization nuclei located outside this layer decreases. As a result, a larger volume of substance corresponds to one active center and the size of the spherulites increases.

With a further decrease in the film thickness from 5 to 2 μ, the adsorption layer apparently begins to play the decisive role, which leads to a sharp decrease in the mobility of bundles and chains of polymer molecules. As a result, the rate at which active centers arise becomes the predominant factor, and a large number of spherulites appear, whose volume decreases with decreasing thickness. At a film thickness of 1-1.5 μ, the mobility of the bundles is so hindered that forma- spherulites does not occur at all, and only an inhomogeneous crystalline structure arises (Fig. 1b).

It is seen from Fig. 2 that, with an increase in the melt temperature, the region of maximum spherulite volumes shifts toward thinner layers. Evidently, as the melt temperature is increased, the adsorption layer is partially destroyed. Rapid cooling of the specimen to 40° does not allow it to recover completely.

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* These curves were constructed by calculation from an experimentally obtained graph of the dependence of the visible sizes of spherulites on the layer thickness of the sample.

As a result, the higher the melt temperature, the more readily the mobility of molecules is facilitated in thinner layers.

Under all the above-mentioned heat-treatment conditions, the following structural forms of gutta-percha were obtained (Fig. 1e, d): spherulites of two types (“plate-like” and those constructed from radially oriented fibrils) and ellipsoidal formations, which become completely dark when their axes are parallel to the axes of the polaroids and become light upon rotation by 45°. Similar formations, which are possibly single crystals, were observed by Novikova ([4], [5]).

The character of the dependence of the sizes of all three structural forms of gutta-percha on thickness is the same. At all thicknesses the largest are the fibrillar spherulites. The smallest relative sizes are exhibited by the ellipsoidal formations. The plate-like spherulites have intermediate sizes and occur, under the given conditions, more often than the other forms.

During crystallization under the conditions of our experiments, isotactic polystyrene gives a picture in many respects analogous to gutta-percha. Under a certain thermal regime, in the center of the specimen at a thickness of 1–2 μ an optically empty region is obtained; in layers about 3 μ thick, a large number of small spherulites is obtained. At a layer thickness of 5-25 μ, spherulites lying at some distance from one another and about 60 μ in diameter are obtained; their size does not change with a further increase in thickness.

In the case of crystallization of polypropylene, the regions adjoining the center of the specimen are also optically empty. In layers 2–8 μ thick, polypropylene crystallizes in the form of radially oriented fibrils (as a result of flow during preparation of the specimen), which at thicknesses greater than 8 μ form spherulitic ribbons (Fig. 3).

Thus, in our work it has been shown that the size and shape of supramolecular structures forming in polymers depend on the thickness of the specimen layer. If the thickness of the polymer film is fixed by two glass surfaces, then at a layer thickness of about 1 μ and less, supramolecular structures visible in the microscope are not formed.

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