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Abstract

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AUTOHESION OF POLYETHYLENE UNDER HIGH PRESSURE

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The autohesion of polymers is substantially affected by the structure and mobility of their chains. In this respect amorphous polymers have been studied best of all ([1–5]), and only recently has the study of polymers with an ordered structure begun ([6–9]).

It is of interest to investigate the influence of the degree of molecular order on the autohesion process of a crystalline polymer, and also to establish the effect of external factors influencing the mobility of polymer chains: temperature and especially high pressure. For the studies, high-pressure polyethylene (PE-1) and low-pressure polyethylene (PE-2) were used; they have different branching (PE-1—3.3 $CH_3/100\,CH_2$ and PE-2 0.8 $CH_3/100\,CH_2$) and, consequently, different degrees of molecular order.

Autohesion was studied by pressing, under specified conditions, two specimens in a cylindrical press mold and subsequently tearing them apart in a tensile-testing machine in a direction perpendicular to the slip surface. The tear-off stress served as a measure of the autohesion of polyethylene under the specified pressing conditions. Pressing was carried out at pressures up to 6000 kg/cm^2 and temperatures up to 240° according to the following procedure: two polyethylene specimens 10 mm in diameter and 5 mm thick, with a thin ring of fluoroplastic-4 between them (to prevent slipping of the edges of the pellets), were placed in a cold press mold, the specified pressure was applied, and after this the temperature was raised to the specified value. At this temperature the specimens were held for 15 min. After the press mold was cooled, the pressure was released, the specimens were removed from the press mold and tested for tear-off in special clamps at a tear-off rate of 18 mm per minute. The scatter of the data in repeated tests did not exceed ±10%.

In Fig. 1 (I) the data are presented for polyethylene PE-1 and in Fig. 1 (II) for polyethylene PE-2, which has a more regular structure than polyethylene PE-1. Examination of the curves in Fig. 1 shows that the dependence of tear-

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Figure 2. Dependence of the autohesion of polyethylenes PE-1 and PE-2 on pressure: melting of PE-2 (1), PE-1 (3), onset of autohesion of PE-2 (2), PE-1 (4). Figure 3. Thermograms of molten polyethylene PE-1 at different pressures

Figure 2: Figure 2. Dependence of the autohesion of polyethylenes PE-1 and PE-2 on pressure: melting of PE-2 (1), PE-1 (3), onset of autohesion of PE-2 (2), PE-1 (4). Figure 3. Thermograms of molten polyethylene PE-1 at different pressures

off stress on pressure, for each temperature, has two clearly delimited regions: the region of partial slip of the specimens and the region in which autohesion rapidly reaches the value of the cohesive strength of the material. Figure 2 shows the regions of partial autohesion for both types of polyethylene. Here curves 2 and 4 correspond to the onset of autohesion (cf. Fig. 1), while curves 1 and 3 correspond to the transition into the region of complete fusion of the specimens, when the tear-off stress reaches the cohesive strength.

It is seen from Fig. 2 that the region of partial autohesion for the more regular polyethylene lies above that for the less regular polymer. Both regions expand noticeably with increasing pressure; at the same time curves 3 and 4, which bound the region of partial fusion for the less regular polyethylene, show a noticeable tendency toward a decrease in the pressure dependence. The region of partial autohesion is located within the region of the beginning and end of melting of polyethylene. This is confirmed by the melting thermograms of polyethylene PE-1 under···

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different pressures. Indeed, the regions of the beginning and end of melting for this polymer sample, placed in Fig. 3, are close to curves 3 and 4 in Fig. 2.

Thus, the effect of external pressure on the autohesion of polyethylene is manifested primarily in an increase in its melting temperature; moreover, with an increase in external pressure the melting interval also broadens. The presence of a broad melting interval is well known for all crystalline polymers and is usually associated with the range of sizes of secondary structures. It was es-

tablished earlier ([10]) that a more branched polymer has a broader distribution of crystallites by size and, consequently, a broader melting interval. It may be assumed that in the region of partial autohesion of polyethylene there occurs a recrystallization process, accompanied by melting of the smaller crystalline formations and growth of the larger ones ([11]). As a result of recrystallization near the boundary of separation of two specimens, new secondary formations arise with disappearance of the boundary of separation. It may be assumed that the appearance of the autohesion region is experimental evidence for the opinion expressed earlier ([11]) that recrystallization takes place through true melting of the smaller crystallites.

Near the region of complete melting of polyethylene, the autohesive bond rapidly reaches the value of cohesive strength.

As indicated above, when external pressure is applied there is a shift of the autohesion region to higher temperatures and its broadening (Fig. 2). At the same time, with increasing pressure the shift of the initial melting temperature decreases, which is especially noticeable for less ordered polyethylene. It should be assumed that the presence of structural defects associated with the greater branching of this polyethylene makes repacking and the increase of its density with increasing pressure more difficult.

Determination of the autohesion of polyethylene under pressure can serve as a simple and convenient method for estimating the degree of its branching.

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