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THE INFLUENCE OF HIGH PRESSURES ON THE SELF-ADHESION (AUTOGHESION) OF HIGH POLYMERS

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The phenomena of self-adhesion of high polymers constitute one of the practically very important and little-studied characteristics of these materials. A number of works ([1–4]) have studied the self-adhesion of rubber-like polymers, while there are very few works concerning the self-adhesion of thermoplastics. However, the important role of self-adhesion phenomena in the processes of forming articles from powdered and granulated thermoplastics is beyond doubt.

In the present work, the influence of temperature and pressure on the self-adhesion of several powdered thermoplastics was investigated. The conditions for the formation of a transparent specimen during pressing of a powdered material in a cylindrical heated mold were studied. A specimen 10 mm in diameter and 4–5 mm high was pressed, with the pressing temperature and pressure varied over a wide range.

The following pressing regime for the specimens was adopted: a weighed portion of polymer was placed in a cold mold and the specified pressure was applied to it; after this, the temperature of the mold was raised to the specified value, and at this temperature the specimen was held for 15 min. After the mold had been cooled to 50–60°, the pressure was released, the specimen was removed from the mold, and the transparency of the specimen for visible light was assessed visually.

In the case where pressing a powdered thermoplastic yields a transparent specimen, partial or complete coalescence of the material grains takes place, with disappearance of the boundaries between them. At the same time, the strength of the transparent specimen may still not reach the cohesive strength of the material, as is sometimes assumed ([5]). Figure 1 shows the change in thickness of transparent polyvinyl chloride specimens during annealing at a temperature of 100° for 15 min. The curve was recorded with the aid of dynamometer scales, which in this case were used as a thickness gauge.

The specimens were pressed at different temperatures. The pressure was 400 kg/cm^2, and the pressing duration was 15 min. It follows from Fig. 1 that spec-

Fig. 1. Change in the thickness of transparent polyvinyl chloride specimens during annealing

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Fig. 2. Region of formation of transparent polyvinyl chloride specimens

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imens pressed at temperatures up to 130° change their dimensions appreciably during annealing. In doing so, they lose transparency and turn white.

Specimens pressed at higher temperatures are stable during annealing, retaining their dimensions and transparency.

Thus, at temperatures up to 130° only partial coalescence of the polymer grains takes place, and only at higher pressing temperatures does the strength of the specimens reach the cohesive strength of the material. In the case where opaque specimens are obtained during pressing of the polymer powder, self-adhesion of the grains does not occur.

Figure 2 gives the P–T curve for polyvinyl chloride, bounding the region of temperatures and pressures at which transparent specimens are formed. It follows from these data that self-adhesion of polyvinyl chloride begins at temperatures 5–10° above its glass-transition temperature. In this case, the boundary separating the regions of formation of opaque and transparent specimens lies in the range 100–150 kg/cm^2.

Fig. 1. Change in the thickness of transparent polyvinyl chloride specimens during annealing

Fig. 2. Region of formation of transparent polyvinyl chloride specimens

Thus, at one and the same temperature, as the pressing pressure is increased, opaque specimens are first formed, up to pressures bounded by the lower curve. This region corresponds to an increase in the total area of contact between the grains of the material with increasing pressure, which is a necessary condition for the onset of self-adhesion. Further

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Fig. 4. Regions of formation of transparent specimens: a —polyvinyl chloride (Tg = 80°), b —block polystyrene (Tg = 80°), c —polymethyl methacrylate ST-1 (Tg = 115°)

Figure 4: Fig. 4. Regions of formation of transparent specimens: a —polyvinyl chloride (Tg = 80°), b —block polystyrene (Tg = 80°), c —polymethyl methacrylate ST-1 (Tg = 115°)

temperature is raised.
a —pressure 1100 kg/cm^2,
b —pressure 2400 kg/cm^2

Fig. 4. Regions of formation of transparent specimens:
a —polyvinyl chloride ($T_g = 80^\circ$),
b —block polystyrene ($T_g = 80^\circ$),
c —polymethyl methacrylate ST-1 ($T_g = 115^\circ$)

increase in pressure leads to the formation of transparent specimens, i.e., to the disappearance of the boundaries between the grains of the material owing to complete or partial coalescence. As already indicated above, complete coalescence for polyvinyl chloride at the adopted holding time takes place at temperatures exceeding T_g by 50°, i.e., at temperatures above 130°.

The upper branch of the curve limits the pressing pressures above which only opaque specimens are again formed, i.e., at these pressures the self-adhesion of the material does not appear. The existence of the upper branch should be explained by the increasing rigidity of the polyvinyl chloride polymer chain, which becomes appreciable at pressures exceeding 1000 kg/cm^2. In this case the glass-transition temperature of the polymer rises, approaching the pressing temperature, which limits self-adhesion and leads to the formation of opaque specimens.

This situation is illustrated by the data presented in Fig. 3. In this experiment the plunger of the compression mold was connected to an indicator showing the change in volume of the polymer powder placed in the mold as the temperature of the mold was raised at a rate of 1° per minute. Before heating of the mold was begun, a pressure corresponding to one of the values on the upper branch of the curve was applied to the material and was kept constant throughout the experiment. In this case one could expect that a sharp change in the volume of the material would occur in the region of the polymer' s T_g, owing to its being forced into the clearances of the compression mold. It follows from Fig. 3 that, for pressures of 1100 kg/cm^2 and 2400 kg/cm^2, a sharp change in volume was observed at temperatures of 100 and 115°, respectively, which closely coincides with the course of the upper branch of the curve in Fig. 2 for these pressures.

The above-mentioned dependence of the glass-transition temperature of polyvinyl chloride on pressure was also observed for a number of other polymers. Figure 4 gives the *P*—*T* curves for polyvinyl chloride, polystyrene, and polymethyl methacrylate.

These dependences can be observed more clearly when, according to the regime indicated above, two polymer specimens cut from sheet are pressed together. In this case a monolithic transparent specimen is obtained only at pressures bounded by the upper and lower curves.

CITED LITERATURE

[1] S. S. Voiutskii, B. V. Shtark, DAN, **90**, 573 (1953). [2] B. V. Deryagin, N. A. Krotova, *Adhesion*, Publishing House of the Academy of Sciences of the USSR, 1949. [3] B. V. Deryagin, S. K. Zherebkov, A. M. Medvedeva, DAN, **111**, 1267 (1956). [4] S. S. Voiutskii, A. I. Shapovalova, A. P. Pisarenko, DAN, **105**, 1000 (1955). [5] H. P. Meissner, E. W. Merrill, *Mod. Plastics*, **26**, 104 (1949).

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