Physical Chemistry

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1957-01-01T00:00:00+00:00

SovietRxiv

Abstract

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On the Mechanism of Welding Organic Glasses

(Presented by Academician V. A. Kargin, April 18, 1957)

Until recently, the nature of the phenomena underlying such a practically important process as the welding of organic glasses remained unclear. Proceeding from the fairly widespread opinion that adhesion phenomena are determined by the action of molecular forces alone (^{(1,2)}), one might try to reduce the welding of organic glasses to the softening of the contacting surfaces of the high polymer and the consequent increase in the true contact surface. However, as has been shown (^{(3,4)}), the action of intermolecular forces alone is quite insufficient to provide any more or less appreciable bonding strength between two specimens of a high polymer, even when brought into the closest contact.

Nor can the electrical theory of adhesion proposed by Deryagin and Krotova (^{(3,5)}) be used to explain the mechanism of glass welding, since in this case the phenomenon is one of autohesion (self-adhesion), and the formation of a double electric layer is unlikely.

The phenomenon of welding organic glasses is most simply explained from the standpoint of the diffusion mechanism of autohesion (^{(6-10)}).

The present communication gives some experimental data confirming that the welding of glasses is reduced to the diffusion of chain molecules, or of portions of them, from one specimen into another. The work was carried out on industrial organic glass—polymethyl methacrylate—both unplasticized and plasticized, containing 6% dibutyl phthalate.

Two rectangular plates of organic glass with smooth milled end faces were placed between two plates of heat-insulating material; the ends to be welded were pressed against each other by a force directed along the plane of the plates, and the contact region was heated by means of narrow electric resistance heaters embedded in the plates. The welding device made it possible to vary the pressing force over a fairly wide range. The presence of the plates in the welding device prevented noticeable deformation of the specimens, which softened in the contact region as a result of heating. After the specified temperature was reached, which took 15-20 min, the specimens were held in this position for a definite time (the welding time) and then cooled without being removed from the device.

In some cases the welded specimens obtained in this way were subjected to additional heat treatment. Heat treatment of welded specimens is used in practice

Fig. 1

Figure 1: Fig. 1

to eliminate residual stresses in organic glass and to reduce deformation in the region of the seam.

The welded specimens were tested in tension in a direction normal to the plane of contact, using dynamometers customarily employed for this purpose. As a rule, rupture of the welded specimens occurred along the plane of the original contact.

It is significant that, when the specimens were loaded up to the breaking load, observations in polarized light did not reveal any nonuniformities in the distribution of stresses in the plane of the welded seam. On this basis it may be considered that the obtained values of breaking resistance are a quantitative characteristic of autohesive strength. It should be noted, however, that the autohesive strength ( ) found in this way is determined not only by the diffusion of macromolecules or of their segments during welding. Diffusion takes place, of course,

Fig. 1. Dependence of the autohesive strength of plasticized polymethyl methacrylate specimens on pressure during welding:
1 –welding temperature (125^{ }); 2 –(135^{ }); 3 –(150^{ }); 4 –(160^{ }); 5 –(190^{ })

both at the end of the period of heating of the specimens and at the beginning of the period of cooling; however, since the conditions of heating and cooling were always identical, diffusion during these periods cannot have had a substantial effect on the general regularities established by us.

Figure 1 shows the dependence of the autohesive strength of plasticized polymethyl methacrylate specimens on pressure at various welding temperatures. The welding time was 15 min. The general character of the curves in Fig. 1 is similar to that of analogous curves for polyisobutylene ((^7)). The autohesive strength increases with increasing pressure, tending toward a certain limit. The higher the temperature, the smaller the increase in strength with increasing pressure. This is explained by the fact that, as the material softens, the pressure required to achieve complete contact of the surfaces being welded decreases. The fact that the maximum adhesive strength in the case of polymethyl methacrylate occurs at considerably higher pressures than in the case of polyisobutylene indicates that, in welding rigid organic glasses, complete contact of the surfaces is achieved with considerably greater difficulty.

Since for most of the temperatures tested the maximum value of autohesive strength is reached, at a comparatively short welding time (15 min.), already at a pressure of (20 kg/cm^2), all further welding experiments were carried out at this pressure.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Figure 2 shows the dependence of the autohesive strength of plasticized polymethyl methacrylate specimens on the welding time at various temperatures.

The form of the curves shown in Fig. 2 corresponds to that of analogous curves for polyisobutylene ((^{7,8})). The fact that, even at zero welding time, the curves do not begin from zero is, of course,

because diffusion to some extent has time to occur also in the process of bringing the temperature up to the welding temperature.

At welding temperatures of 135-190° the maximum autohesive strength is established in a comparatively short period of time—10-15 min. It is interesting that, at a temperature of 190°, the limit of autohesive strength approximately corresponds to the cohesive strength of the material (700 kg/cm^2).

Fig. 2. Dependence of the autohesive strength of specimens of plasticized polymethyl methacrylate on the duration of welding:
1 —welding temperature 125°; 2 —135°; 3 —150°; 4 —160°; 5 —190°

The data obtained in experiments to determine the dependence of the autohesive strength of plasticized and unplasticized polymethyl methacrylate on the welding temperature are presented in Fig. 3. In these

Fig. 3. Dependence of autohesive strength on welding temperature: 1 —unplasticized polymethyl methacrylate, 2 —plasticized polymethyl methacrylate, 3 —the same, but the welded specimens were subjected to additional heat treatment

experiments the welding duration was 15 min. After welding, some of the specimens of plasticized polymethyl methacrylate were subjected to heat treatment at 135° for 60 min.

As can be seen, in the case of unplasticized polymethyl methacrylate the autohesive strength reaches its limit at 150°. This limit, equal to approximately 500 kg/cm^2, does not change in the range of welding temperatures from 150 to 180°. However, at a temperature somewhat above 180° the curve again rises sharply upward, and the autohesive strength reaches 700 kg/cm^2—the value corresponding to the cohesive strength of the material.

in the weld zone. The slight decrease in strength at a welding temperature above (210^{ }) is probably due to thermal destruction of the material.

The two-stage character of the autohesive strength-temperature curve can be explained by the fact that in the temperature interval (150—180^{ }) polymethyl methacrylate is in the highly elastic state. In such a state, diffusion is possible only for individual sections of molecular chains, but not for whole macromolecules, which accounts for values of autohesive strength lower than the values of cohesive strength. The course of the curve in the temperature interval (150 –180^{ }), almost parallel to the abscissa axis, indicates the constancy of the mechanism of autohesion in the zone of the highly elastic state.

At temperatures above (180^{ }) the high polymer passes into a viscous-flow state, in which displacement of individual macromolecules with respect to one another becomes possible. Diffusion of the molecules as a whole leads to the fact that, in the contact zone under these conditions, the structure of the high polymer is completely restored. As a result, the material becomes monolithic, and tensile tests give values equal to the cohesive strength. The disappearance of material inhomogeneity in the weld zone is also indicated by the fact that in this case fracture of the specimen often occurs not at the welding site.

However, the restoration of the polymer structure in the weld zone at high temperatures may also be promoted by the scission and recombination of high-polymer molecules occurring under these conditions. The enormous significance of such phenomena in the flow of network high polymers under the action of large forces was recently shown by Sogolova and Kargin ((^{11})).

The curve for plasticized polymethyl methacrylate has the same character, but is shifted to the left, since the plasticizer lowers the transition temperatures of the high polymer both to the highly elastic and to the viscous-flow state.

The curve for specimens of the plasticized high polymer that underwent subsequent heat treatment at welding temperatures above (135^{ }) merges with the curve for the same untreated specimens. At lower welding temperatures, however, in the case of heat treatment the adhesive strength is significantly higher. This is also quite understandable: at a welding temperature below (135^{ }), relatively prolonged heat treatment at (135^{ }) leads to the fact that individual sections of macromolecules belonging to one specimen penetrate more deeply into the volume of the other polymethyl methacrylate specimen and thereby promote an increase in autohesive strength. At welding temperatures above (135^{ }), heat treatment at (135^{ }) is already ineffective.

All-Union Scientific Research
Institute of Aviation Materials

Received
10 IV 1957

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