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ELECTRON-MICROSCOPIC STUDY OF INTERDIFFUSION IN POLYMER SYSTEMS

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The phenomena of self-diffusion and interdiffusion play a major role in the processing and application of polymers (ˆ1, ˆ2). However, despite the great practical importance of self-diffusion and interdiffusion of polymers, there are comparatively few works devoted to the direct study of these processes (3-7).

In the present work, the interdiffusion of polymers was studied by means of electron microscopy. The investigation consisted in the following: the polymers selected for the work were welded together in pairs, i.e., brought into contact for a certain time at a temperature ensuring intensive thermal motion of the molecular chains or their segments; then, from the resulting two-layer specimen, a section was prepared with an ultramicrotome in a direction perpendicular to the contact plane. This section was subjected to direct observation in an electron microscope.

Two pairs were chosen for the work: polymethyl methacrylate (PMMA)—polyvinyl chloride (PVC) and polybutyl methacrylate (PBMA)—polyvinyl chloride. The polymers composing these pairs are in the glassy state at room temperature, which facilitates obtaining sections from them on an ultramicrotome; PVC, owing to the presence of chlorine atoms in its molecule, has the ability to scatter electrons to a much greater extent than PMMA and PBMA; finally, as experience showed, these polymers are capable of being welded to one another.

Specimens for obtaining ultrathin sections were prepared by hot-air welding, a method widely used for welding thermoplastics when it is necessary to obtain a narrow weld seam. The hot-air temperature in the experiments was 160-170 and 210-220°. The temperature 160-170° lies somewhat above the flow temperature of PVC (150-160°). At 210-220° no noticeable structuring of PVC occurs during its short-term heating, and all three polymers are in the viscous-flow state. The temperature of the hot air used for welding was controlled with an ordinary thermocouple. Ultrathin sections from the specimens were obtained with an LKB-3314 ultramicrotome. The thickness of the sections, judging from their coloration in reflected light, was approximately 600-1000 Å. The sections obtained were studied with an EMI-D2 electrostatic electron microscope. Some of the electron micrographs obtained are shown in Fig. 1.

In order to determine more accurately the width of the blurred zone, that is, the depth of penetration of one polymer into the other, microphotometry of the obtained photographs was carried out in a direction perpendicular to the contact boundary with an MF-4 recording microphotometer.

Results of experiments with the PMMA-PVC system. As can be seen from Fig. 1a, which shows an electron micrograph of the contact zone of PMMA and PVC specimens welded at a temperature of 160-170°, the interphase boundary is somewhat blurred, evidently as a result of mutual diffusion of the chains of both polymers. Microphotometry gave an average width of the blurred zone equal to 1000-1300 Å, which is considerably greater than the resolving power of the electron microscope for sections of the thickness used.

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Fig. 1. Electron micrographs of transverse sections of two-layer polymer specimens.
a –PMMA–PVC, welding temperature 160–170°; *b* –PMMA–PVC, temperature 210–170°; *v* –the same, with a dark band along the interphase boundary; *g* –PBMA–PVC, welding temperature 210–220°.

Fig. 1b shows that at a welding temperature of 210-220° the boundary becomes more diffuse. According to the data obtained by microphotometry of the photographs, the width of the diffuse zone in this case reached up to 3000 Å. It is quite obvious that an increase in the blurring of the polymer contact zone can occur only because, as the temperature rises, the intensity of molecular motion increases and therefore the depth of interpenetration of the chains of one polymer into the other increases. It should be noted here that, with this method of producing a welded joint, as the temperature of the hot air (and consequently of the surface layer of the polymers) increases, the time of contact of the softened polymers also increases, since the specimens cool more slowly. Therefore, in this case the effect caused by the temperature increase is joined by an effect due to the increased duration of contact.

In some cases the contact boundary of PMMA and PVC welded at 210-220° has a somewhat different appearance, shown in Fig. 1b. In the photograph, on going from PMMA to PVC, in addition to the gradual increase in the density of the section in the contact zone, a dark band is visible, separating the two polymers and running along the entire interphase boundary, interrupted only in those places where, for one reason or another, contact between the two polymers is absent. The presence of this band indicates that the polymer system in the zone where diffusion has occurred scatters electrons even somewhat more strongly than PVC. The same was also evident from the diagram obtained by microphotometry of the corresponding photograph. Such a phenomenon may be explained by the fact that in the zone of interpenetration of the polymers, for steric reasons, the packing density of the molecular chains increases, which also leads to greater electron scattering. It is significant that the dark band is located almost entirely in PMMA. This indicates that, apparently, densification of the material in the contact zone occurs at the expense of one-sided diffusion of PVC into PMMA. The fact that the diffusion capacity of PVC is higher than that of PMMA is in good agreement with the lower flow temperature of the former polymer and the absence in its molecule of bulky side substituents. An explanation of the appearance of the dark band by destruction of PVC is evidently excluded, since in that case it should have been located in PVC.

Results of experiments with the PBMA–PVC system. Attempts to weld PBMA with PVC at a temperature of 160-170° did not give positive results—the adhesive joint obtained was too weak. Better results were given by welding at 210-220°—in this case the joint was sufficiently strong. An electron microphotograph of the contact zone of PBMA–PVC welded at 210-220° is shown in Fig. 1g. If this microphotograph is compared with a similar microphotograph obtained for PMMA and PVC (Fig. 1b), it can be seen that the blurring of the contact zone in Fig. 1g occurs to a considerably smaller degree. Microphotometry in this case gave a width of the diffuse zone of only 1000 Å.

Thus, it may be concluded that the depth of interdiffusion of PBMA and PVC is considerably less than in the case of PMMA and PVC, despite the fact that the flow temperature of PBMA is lower than the softening temperature of PMMA. This circumstance should be explained, on the one hand, by the lower compatibility of PBMA with PVC because of the low polarity of PBMA. On the other hand, the poor diffusion in this case is, of course, also explained by the presence in the molecules of polybutyl methacrylate of bulky side substituents —butyl groups.

In conclusion, we note that electron-microscopic investigations have established the possibility of interpenetration of macromolecules to a relatively great depth, on the order of hundreds and thousands of angstroms (hundredths and tenths of a micron). This is, in general, in fairly good agreement with the data obtained by Krotova (5-7) by observation in ordinary and ultraviolet light. Considering that the interpenetration of polymer molecules already by tens

angstroms can increase the adhesive strength many times over (1); the data obtained by us once again confirm the role of diffusion phenomena in the formation of adhesive bonds between polymers.

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