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EFFECT ON ADHESION OF THE PHYSICAL STATE OF POLYMERS

(Presented by Academician S. S. Medvedev, February 22, 1963)

According to the diffusion theory of adhesion, the strength of the bond between two compatible polymers should depend on the physical state in which the polymers brought into contact were found during formation of the adhesive joint (^{1}).

When polymers that are in the glassy state or that contain a large amount of crystalline phase are brought into contact, adhesion is practically impossible. This is explained by the fact that under such conditions diffusion cannot take place. If, however, at the beginning of contact one of the polymers (the adhesive) is in a highly elastic or viscous-flow state, while the other (the substrate) is in a glassy or crystalline state, adhesion is quite possible, since the molecules of the adhesive can diffuse into the substrate and thus form a sufficiently strong adhesive bond. If bundles and other supramolecular structures are present in the adhesive, diffusion of these structures is also quite possible, as is the diffusional transfer of portions of macromolecules from bundles of the adhesive to bundles of the substrate. According to the diffusion theory, the greatest adhesion should be observed when both polymers forming the adhesive joint are in a highly elastic or viscous-flow state. Under such conditions the difference between adhesive and substrate disappears, and if the polymers are capable of being fully, or at least partially, compatible, one should already speak of mutual diffusion of the polymers. In this case, in the viscous-flow state, molecules or bundles acquire the ability to move within the polymer, and crosslinking is possible as a result of the diffusion of various structural elements as a whole. It is clear that in this case the crosslinking of polymers over the same time will be much more complete, and the adhesive bond much stronger.

The ideas set forth concerning the influence of the physical state of polymers on their adhesion to one another arose mainly on the basis of general considerations and indirect evidence. In the present communication, experimental data are presented that confirm the correctness of these views.

Fig. 1. Dependence of peel resistance of polyethylene joints with elastomers on the time of their formation at room temperature. 1 —SKS-30ARM-15; 2 —SKB-35; 3 —SKS-30; 4 —SKN-18; 5 —SKN-26; 6 —SKN-40

Figure 1: Fig. 1. Dependence of peel resistance of polyethylene joints with elastomers on the time of their formation at room temperature. 1 —SKS-30ARM-15; 2 —SKB-35; 3 —SKS-30; 4 —SKN-18; 5 —SKN-26; 6 —SKN-40

Figure 1 presents the dependence of the resistance to delamination of joints of various elastomers with polyethylene on the contact time at room temperature. In all cases, delamination was adhesive in character, and the surface of the elements of the joint after delamination remained smooth. As can be seen, the curves in Fig. 1 relating to the nonpolar polymers SKS-30ARM-15, SKB-35, SKS-30, and to the weakly polar copolymer SKN-18 resemble parabolas in their form. Proceeding from the usual ideas about the structure and properties of elastomer molecules, as well as about the role of the plasticizer present in the polymer (polymer SKS-30ARM-15), one may conclude that the adhesive strength increases the faster, the greater the mobility of the molecular chains in the polymers. At the same time, as follows from comparison of the shapes of the curves for polar butadiene–acrylonitrile copolymers, a decrease in mobility due to an increase in the molecule of acrylonitrile residues should ultimately lead to the obtainment of of polymers incapable of exhibiting adhesion to polyethylene at ordinary temperature.

According to the diffusion theory of adhesion, the ability of macromolecules or other structural elements to diffuse does not always lead to the formation of a strong adhesive bond. The adhesion of polymers to one another also depends on the compatibility (mutual solubility) of the polymers ([2,3]). As can be seen in Fig. 1, the elastomers used in the work, in order of decreasing absolute value of the strength of their adhesive bond with polyethylene, regardless of contact time, are arranged as follows:

$$\text{SKB} > \text{SKS-30} > \text{SKN-18} >> \text{SKN-26} > \text{SKN-40}.$$

This sequence fully corresponds to the decrease in the compatibility of the elastomers with polyethylene, a measure of which, in a first approximation, may be the difference between the values of the cohesive-energy densities of the polymers. Indeed, if the cohesive-energy density ([4]) for polyethylene is 7.7, then for SKB, SKS-30, SKN-18, SKN-26, and SKN-40 it is respectively 8.35; 8.48; 9.3; 9.5; and 9.83 $(\text{cal/cm}^3)^{1/2}$. The exceptionally high adhesion of SKS-30ARM-15, several times greater than the adhesion to polyethylene of the copolymer SKS-30, is explained by the presence in SKS-30ARM-15 of a plasticizer, which promotes the destruction of supermolecular structures and facilitates the diffusion of molecules and other structural elements.

Fig. 2. Dependence of peel resistance of polyethylene joints with elastomers on the time of their formation at 120-123° C. 1 –SKB-35; 2 –SKN-18; 3 –SKN-26; 4 –SKN-40

Figure 2: Fig. 2. Dependence of peel resistance of polyethylene joints with elastomers on the time of their formation at 120–123° C. 1 –SKB-35; 2 –SKN-18; 3 –SKN-26; 4 –SKN-40

Fig. 1. Dependence of the peel resistance of polyethylene joints with elastomers on the time of their formation at room temperature.
1 –SKS-30ARM-15; 2 –SKB-35; 3 –SKS-30; 4 –SKN-18; 5 –SKN-26; 6 –SKN-40.

Fig. 2. Dependence of the peel resistance of polyethylene joints with elastomers on the time of their formation at a temperature of 120–123° C.
1 –SKB-35; 2 –SKN-18; 3 –SKN-26; 4 –SKN-40.

Figure 2 presents the dependence of the peel resistance of adhesive joints of some elastomers with polyethylene on contact time at 120-123°. Destruction of the joints in this case also had an adhesive character, with the exception of SKB bonds with polyethylene, during the peeling of which cohesive failure was observed (the corresponding part of the curve in Fig. 2 is indicated by a dotted line). As follows from Fig. 2, raising the temperature of formation of the adhesive joints to 120–123° leads to an extremely sharp increase in adhesion. This, evidently, should be explained not only by an increase in the intensity of diffusion processes with temperature, but also by melting of the crystalline phase of polyethylene and by the breakdown of supermolecular structures into smaller primary elements possessing greater diffusion capacity.

Mathematical processing of the curves expressing the dependence of the delamination resistance P on the time τ shows that all of them are described by the parabolic equation $P = K\tau^a$, where K is a coefficient whose value is the greater, the better the compatibility of the polymers and the higher the contact temperature, and a is a coefficient that depends little on the nature of the polymers and the conditions of formation of the adhesive joint. It is significant that the parabolic dependence of polymer adhesion on contact time agrees well with the similar dependence found by Vasenin on the basis of theoretical premises (^{5}). The character of the curves in Fig. 2 can be explained only by the fact that the basis of adhesion in the cases under consideration is bulk interdiffusion of polymers. Indeed, if in the case of contact formation at ordinary temperature the increase in adhesion with increasing contact time can be explained at least partly by an increase in the true contact area, then in the case of temperatures on the order of 120–123° such an explanation is excluded. At the indicated temperature not only the elastomer but also polyethylene is in a viscoelastic state, and the pressures that were applied in obtaining the joints are, of course, quite sufficient to ensure complete contact for both polymers in a minimal time. It is also impossible to explain the increase in adhesion in this case from the standpoint of adsorption concepts, since nonpolar polyethylene is practically devoid of active centers, and it is difficult to assume under such conditions the existence of two-dimensional diffusion leading to a gradual coincidence of the active centers of the adhesive and the substrate.

The identical order of arrangement of the curves in Figs. 1 and 2 confirms the importance of compatibility for the adhesion of polymer to polymer. However, when considering the curves in Fig. 2, the question arises as to how to explain such high adhesion of polar butadiene–acrylonitrile copolymers to nonpolar polyethylene at a contact temperature of 120–123°. It seems to us that adhesion in this case may be due to diffusion of nonpolar segments of the elastomer molecules into the nonpolar polyethylene and, conversely, diffusion of nonpolar polyethylene molecules into the nonpolar segments of the elastomer, i.e., at the expense of a process that may conventionally be called local diffusion or local dissolution ([1]). The possibility of local diffusion, from our point of view, is explained by the fact that the microstructure of any polar elastomer is heterogeneous. In a system consisting of polar and nonpolar groups connected into flexible chains, microphase separation will always occur, similar to that which takes place in mechanical mixtures of incompatible polymers. In this process the polar groups of the polymer, as well as the nonpolar segments of its chains, will tend to form separate regions more or less delimited from one another. However, because the polar and nonpolar segments of the chains are connected with one another by primary valence forces, such microphase separation can never lead to macrophase separation.

The microheterogeneity of polar polymers also provides the possibility of local diffusion when they are in contact with nonpolar polymers. Such local diffusion is especially probable in the case when the diffusing elements are hydrocarbon chains of the nonpolar polymer, since in a polar polymer the volume of nonpolar segments usually predominates over the volume of polar groups and, consequently, the "external phase" of such a system, as a rule, is the nonpolar hydrocarbon part of the polymer. This also explains the well-known fact that nonpolar elastomers exhibit rather high adhesion to polar high-molecular-weight substrates, whereas polar elastomers exhibit almost no adhesion to nonpolar substrates ([1]). This also explains the increase in adhesion observed in the present work when polyethylene is brought into the viscoelastic state.

The considered process of local dissolution or local diffu-

···upon adhesion of a polymer to a polymer is all the more probable since, according to Patrikeev' s calculations ([6]), penetration of the adhesive molecules into the substrate by only a few angstroms is sufficient for the adhesive strength to increase manyfold.

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