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Abstract

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ON THE QUESTION OF THE NATURE OF THE ADHESIVE BOND BETWEEN POLYMERS

The impossibility of forming a strong adhesive bond between polymers through the action of molecular forces alone has been pointed out repeatedly in the Soviet literature ([1−2]). To explain the adhesion of a polymer to a polymer, concepts are usually invoked either of mutual diffusion of molecules or of the action of electrical forces arising as a result of the formation of a double electric layer between the polymers. Recently, however, Reznikovskii and Kamenskii ([3]) have again advanced the proposition that the adhesion of a polymer to a polymer may be due purely to surface interactions—chemical or physical. Without objecting to the fact that in a number of special cases adhesive joints between polymers are formed through chemical interactions (for example, during the co-vulcanization of rubbers), we consider the authors' arguments concerning the formation of strong adhesive bonds as a result of the action of ordinary molecular forces unconvincing.

In defense of their point of view, Reznikovskii and Kamenskii present the following considerations:

1. The well-known effect of temperature and contact time on the strength of the adhesive bond between polymers, usually cited as an argument in favor of the diffusion theory, cannot serve as a criterion in choosing between this theory and notions of purely surface interaction.
2. The ability of polymers to form an adhesive bond predominantly in the viscous-flow state, when the molecules are in macrobrownian motion, argues against diffusion concepts, since, according to these authors, the principal type of molecular motion causing the formation of an adhesive joint as a result of mutual diffusion is microbrownian motion. In developing their ideas, the authors point out that vulcanization, which leads to loss of flow but at the first stage has almost no effect on the character of the microbrownian motion of the chains, practically completely deprives a rubber compound of the ability for autohesion.
3. The increase in polymer adhesion with increasing roughness of the substrate surface.

4. Finally, as an argument against a diffusion explanation of the formation of an adhesive bond between polymers, the authors of work ([3]) cite their data on the absence of an effect on adhesion of the duration of "resting" of duplicated specimens before their testing.

Let us consider the arguments presented in order.

1. The positive influence of temperature and contact time on the strength of the adhesive bond between polymers indeed cannot be regarded as unambiguous proof of the correctness of the diffusion theory. However, this trivial objection was raised as early as 1956 and in work ([4,5]) was not only considered, but also unequivocally refuted by experiments with contact of thin films of rubbers of different thickness. A relationship between adhesion and the compatibility of rubbers was also unambiguously demonstrated.

Direct evidence for the presence of self- and interdiffusion in the establishment of an adhesive bond includes the fairly well-known studies of these phenomena carried out with the aid of labeled polymers ([6,7]), as well as with ordinary and luminescence microscopes ([8–10]). Quite recently, evidence of interdiffusion during the welding of thermoplastic polymers—polymethyl methacrylate and polybutyl methacrylate with polyvinyl chloride—was obtained by electron-microscopic observations ([11]).

Indirect evidence of the role of diffusion in the formation of an adhesive joint includes, for example, the decrease in adhesion with increasing polarity of the polymers ([12]) and the decrease in autohesion when the macromolecules of the polymer are oriented perpendicular to the plane of contact ([13]). Evidence for the role of diffusion in the emergence of a bond between polymers may also be regarded as the agreement between experimental kinetic adhesion curves and calculated curves computed on the basis of diffusion concepts ([14,15]). Finally, an argument in favor of the diffusion theory is the simple consideration that two polymers completely different in chemical nature, i.e., mutually incompatible and therefore incapable of interdiffusion, never form a strong adhesive bond, regardless of the time of contact and the magnitude of the pressing pressure during duplication ([16]).

As for the opinion of the authors of the cited work concerning the significance for adhesion of the completeness of contact between polymers, this opinion is trivial. To establish a strong adhesive bond, close contact between polymers is absolutely necessary, irrespective of the adopted theory of adhesion ([1,3,17,18]). The influence of pressure, time, and temperature of contact on the magnitude of the true contact area in the case of an elastomer–substrate has been studied in detail experimentally in ([19]).

2. The considerations of Reznikovsky and Kamensky that the strength of the adhesive joint between polymers is wholly determined by flow phenomena cannot be regarded as sufficiently substantiated. Indeed, data on the influence of the duration and temperature of contact on the strength of

the adhesive joint of elastomers, contained in numerous studies carried out both by us and by other authors, were always obtained at sufficiently high pressing pressures, guaranteeing the independence of the obtained values of adhesive strength from flow. In addition, in most cases, when obtaining bonds by pressing, mirror-smooth surfaces were used as a rule, which excludes any appreciable influence of flow on adhesive strength. It should also be pointed out that the characteristic increase in the adhesion of polymers with increasing time and temperature of contact is observed even when the polymer is brought into contact with the substrate in the form of a solution in a volatile solvent (20). Clearly, under such conditions of obtaining the bond, complete contact of the polymer with the substrate is guaranteed.

It is also appropriate to note here that the opinion is erroneous that the ability of polymers to form an adhesive bond as a result of diffusion is due only to micro-Brownian motion. In works (13,21), using thermoplastics and elastomers as examples, it was convincingly shown that an adhesive bond can arise through both micro-Brownian and macro-Brownian motion, and in the latter case this bond is considerably stronger. The cited authors (3) are also mistaken in believing that vulcanization completely deprives a rubber compound of its ability for autohesion. In (22) it was shown that, at low degrees of structuring, vulcanization not only does not decrease autohesion but even increases it somewhat. Only with substantial structuring, when micro-Brownian motion is already hindered, does vulcanization lead to a sharp drop in autohesion. The dependence of polymer adhesion on the length of the segment of the molecular chain located between two network junctions of the vulcanizate has been studied in detail in (23).

3. The considerations (3) that an increase in adhesion with increasing roughness of the substrate surface supposedly contradicts the diffusion theory are based on an obvious misunderstanding. Under any mechanism of formation of the adhesive seam, including diffusion (17,18), the strength of the seam should increase with increasing roughness of the substrate. The observations of Reznikovsky and Kamensky, which showed that the peel resistance for specimens with a smooth surface of the substrate (vulcanizate) depends on the doubling time much less than for specimens with a rough surface, indicate only that flow is superimposed on diffusion.

4. The independence of adhesive strength from the "conditioning" of the doubled specimens before testing, observed by the authors, should probably be explained by the fact that, owing to the use as substrate of a vulcanizate with a sufficiently dense molecular network, diffusion of the elastomer occurs to a very slight extent and is completed already in the first minutes of contact. It should be noted that the increase in adhesion during doubling with the application of pressure, observed in (3), also ended very quickly —within several minutes.

Thus, the considerations presented in (3) as arguments in favor of explaining the bonding of polymers by the action of purely surface forces cannot be regarded as valid. Adhesion of polymers to polymer substrates can be explained with far greater success either by interpenetration of elements of molecular chains (for compatible polymers), or by the action of electrostatic forces as a result of the formation of an electrical double layer in the contact zone.

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