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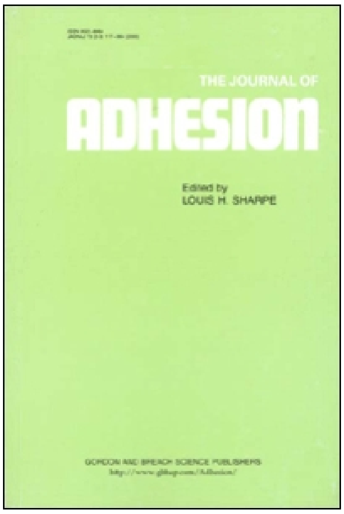

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Some Comments on the Series of Papers "Interfacial Contact and Bonding in Autohesion"

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Note

Some Comments on the Series of Papers "Interfacial Contact and Bonding in Autohesion"

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In articles by Anand and coworkers which were published in the *Journal of Adhesion*[1] some critical comments were made about the diffusion theory of autohesion which we developed, and an attempt was made to explain autohesion of polymers by molecular forces acting at the boundary between the surfaces brought into contact. In these articles the process of forming an adhesive joint is divided into two stages: (1) formation of contact as the result of polymer flow; (2) establishment of molecular interaction between the surfaces brought into contact.

The idea of the need of the first stage to ensure good autohesion or adhesion is rather trivial. It is well known that any theory of adhesion considers as necessary initially the formation of a firm contact between the substrate and the adhesive, and then some kind of interaction or another between them. We note in passing that the question of establishment of contact in autohesion or adhesion as the result of polymer flow was considered in detail, before the work of Anand *et al.*, in the work of many investigators, among them, in that of Gul' *et al.*[2]

As concerns the second stage of autohesion, we have never denied that the action of molecular forces lies at the base of this phenomenon. This is indicated, for example, on pages 16–17 and 145 of the American edition of the author's monograph.[3] We have only shown that, in the autohesion of polymers with flexible molecules whose segments are capable of thermal motion, interdiffusion of molecules or segments can take place, which will lead to an increase in molecular contact area and, of course, because of this, to an increase in the strength of the adhesive junction.

Indirect proofs of the presence of diffusion of macromolecules or segments of them in the formation of an autohesive or an adhesive joint between completely or partially compatible polymers, present in a highly elastic or viscous flowing state, are given in the monograph cited.[3] In particular, the increase in strength of an autohesive joint with increase in contact time or temperature is well explained by the diffusion theory of autohesion. The objection that the rise in strength of an adhesive joint with increase in contact time or temperature can be explained by a simple increase in contact area of the elastomers is unsound.

First, all who have worked with transparent films of elastomers, for example mirror-smooth films of polyisobutylene, know well that when such films are carefully doubled, so that the presence of very fine air bubbles at the boundary is excluded, the doubled film so obtained has the same optical density as the original one. This can be the case only upon complete contact (coalescence) of the surfaces of the two original films. Meanwhile, it has already been shown in Ref. 3 that the autohesive strength of films so doubled rises considerably with time. The latter phenomenon, of course, can be explained only by an interdiffusion of macromolecules or segments of them which is taking place.

Second, in the work of Korenevskaya *et al.*[4] it was shown quantitatively that the shear resistance of an autohesive joint of two films of SKN-40 butadiene–acrylonitrile copolymer, for example, continues to grow with time even after attainment of the maximum equilibrium value of completeness of contact, as established using the improved Mekhau method. Figure 1 shows this graphically.

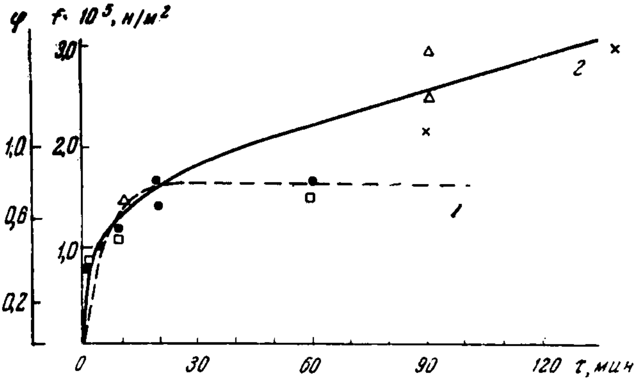

FIGURE 1 Dependence of completeness of contact, ϕ, and of shear resistance, f, on contact time, τ, for autohesion of SKN-40 copolymer.
(1) Completeness of contact. ϕ; (2) shear resistance, f.

Third, the adhesive joints used both in our work and also in that of the other workers were always prepared using pressures which ensured complete contact of the elastomers, which can be judged from arrival at the straight-line portion of the adhesion-pressure curve upon contact.

At present, however, direct proofs of the diffusion of macromolecules or their segments in the autohesion of compatible or partially compatible polymers have been obtained, which, apparently, were unknown to the authors of reference 1.

1) Radiometric studies carried out by Bueche and coworkers in the U.S.A.[5] and by Bresler *et al.* in the U.S.S.R.[6] have demonstrated the presence of macromolecule diffusion in the case of compatible polymers, the diffusion coefficients being of the order of 10^{-11} to 10^{-14} cm^2/sec. The diffusion rate calculated from these data is completely adequate for the formation of a strong autohesive or adhesive bond between the polymer layers after a few seconds.

2) In the work of Krotova and Morozova[7,8], where microscopic observations were made under ordinary ultraviolet light, using luminescence analysis, it was established that in the case of well compatible polymers the zone of interfacial boundary dissolution due to diffusion may attain 10 microns. Unfortunately, the work of Krotova and Morozova[7,8], which established without doubt the dissolution of an interfacial boundary of nonpolar polymers with very flexible molecules as a result of interdiffusion, cannot give information on what takes place in the contact zone of polar polymers or polymers which differ greatly in polarity. In these last two cases, dissolution of the interfacial boundary can be so small that it is impossible to detect with the aid of the usual microscope.

3) In very recent times, dissolution of boundaries between compatible or partially compatible polymers has been demonstrated using the electron microscope,[9] whose resolving power is two orders of magnitude greater than that of a light microscope. Thereupon, photometry of the photographs obtained showed a gradual change in optical density of the contact zone upon transition from one polymer to another, which can be explained only by polymer interdiffusion.

In Figures 2 and 3 we show electron photomicrographs of transverse sections of two-layer samples prepared at 210–220° from two pairs of polymers: poly(methyl methacrylate)–poly(vinyl chloride); and poly(butyl methacrylate)–poly(vinyl chloride). In Figure 4 we give curves obtained by photometry of the same electron photomicrographs in the direction perpendicular to the interfacial boundary. First, as may be seen from Figures 2 and 3, there are no voids between the two polymers, which would have indicated absence of complete contact. Second, it is clearly apparent that the dissolution of the contact zone as a result of diffusion is far greater in the case of the first pair of polymers, since poly(methyl methacrylate) is better compatible with the polar poly(vinyl chloride) than the less polar poly(butyl methacrylate). The same follows from Figure 4. However, it must be noted that poorly compatible, or even completely thermodynamically incompatible polymers can give a rather strong adhesive bond under definite conditions, due to so-called local compatibility of the polymers, the nature of which we considered in detail in Ref. 10.

4) Finally, both we[11] and, independently, Iyengar *et al.*[12] have established a direct dependence of polymer adhesion on the so-called β parameter proposed by Gee in 1946 to characterize compatibility.[13] The less the

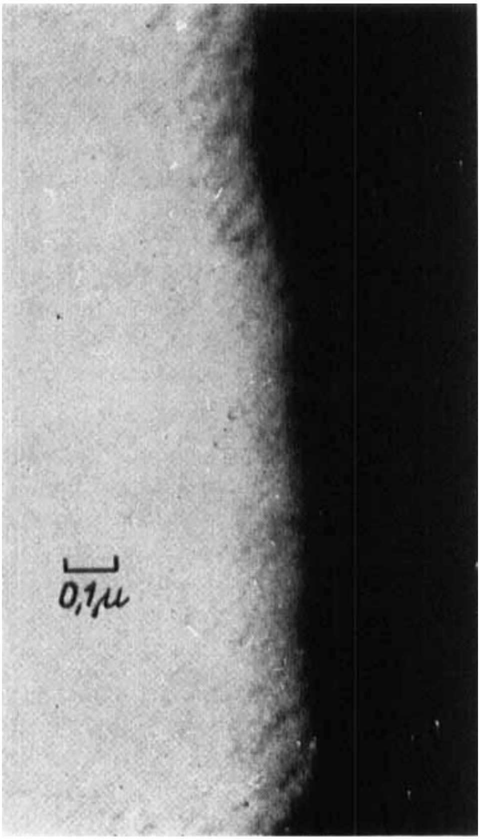

FIGURE 2 Electron photomicrograph of transverse section of film of poly(methyl methacrylate) and poly(vinyl chloride), doubled at 210–220°.

FIGURE 3 Electron photomicrograph of transverse section of film of poly(butyl methacrylate) and poly(vinyl chloride), doubled at 210–220°.

compatibility parameter, β, the better the polymers blend and the higher the adhesion. This is clearly evident from Figure 5, which has been borrowed from one of our articles.[11] Obviously, when $\beta = 0$, that is, when autohesion is taking place, compatibility should be greatest. And actually, at low values of β the adhesion is maximum and failure of the adhesive joint bears a cohesive character (this section is shown on the curve by a dotted line). Hence, the important conclusion follows that if adhesion correlates with the compatibility parameter, then the polymers at the interfacial boundary should blend; that is, interdiffusion of one polymer into the other should be observed, since in this case compatibility can be attained only as the result of interdiffusion of macromolecules or segments of them. If there were no such dependence, polymer adhesion would depend on other thermodynamic

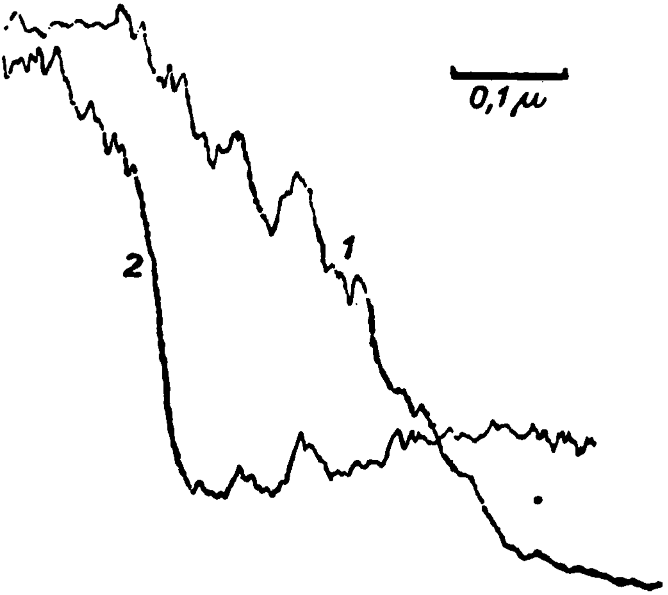

FIGURE 4 Photometry curves of electron photomicrographs shown in Figure 2 (curve 1) and in Figure 3 (curve 2).

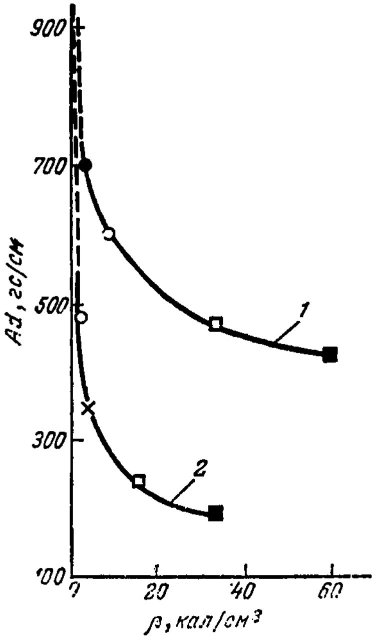

FIGURE 5 (Curve 1) Dependence of strength of adhesive joint, Ad, of polyisobutylene with various polymers on value of compatibility parameter, β: ●) poly(vinyl chloride); ○) poly(ethylene terephthalate); □) a polyamide; ■) hydrocellulose. (Curve 2) Same, for adhesive joints with NBR-40 butadiene-acrylonitrile polymer.

parameters, for example, on wetting—which is not the case, according to our observations.

Naturally, the proofs given in points (1)–(4) are simultaneously a proof of the diffusion mechanism for the origin of an autohesive bond between polymers, since autohesion is only a special case of adhesion. We have given a more or less complete examination of the experimental results of the works cited above in a review article.[14]

It is significant that, in recent years, as a result of the work of Vasenin[15-17] and of Voyutskii, Vasenin, *et al.*[18], the diffusion theory of autohesion, which initially had a qualitative character, has now received a quantitative foundation.

There are still other proofs of the correctness of the diffusion theory of polymer autohesion, on which we need not dwell here.

In conclusion, we note that concepts of the diffusion nature of the autohesive bond are not just held by Voyutskii *et al.*, as the impression is gained on reading the work of Anand,[1] but also by a number of other researchers, both Russian and foreign. Among these, in the Soviet Union, are B. V. Deryagin, N. A. Krotova, V. A. Kargin, B. A. Dogadkin, V. N. Kuleznev, S. B. Ratner, V. G. Épshtein, and many others. Abroad, similar views are held by Mark[19], Scott,[20], Forbes and McLeod,[21], Thirion[22], Skewis[23], Boenig and his coworkers[24], and others. It must be said that Josefowitz and Mark[19] first indicated the role of diffusion phenomena at the boundary of two layers of polymer which have been brought into contact.

From all that has been said, the conclusion follows that when polymers are in a highly elastic or viscous state (and under these conditions only polymer autohesion or adhesion is possible), diffusion phenomena always take place at their point of contact, and these lead, as it were, to a "sewing together" of the two layers of polymer (or polymers) and to the formation of an intermediate transition layer consisting of the interwoven molecules. This layer can have a relatively large thickness (of the order of microns) in the case of compatible polymers or can consist of only a few Angstroms in the case of poorly compatible or incompatible polymers. However, in spite of the low thickness of this transition layer, it can sharply increase the adhesive bond strength. As G. A. Patrikeev showed,[3] upon an interpenetration of macromolecules by 10 to 20 Å in all, a relative increase in molecular contact area takes place, and, consequently, a 5- to 9-fold increase in adhesion.

From all that has been said above, one can see that the arguments of Anand and his coworkers[1], which disregard the reality of the existence of a transition layer formed as a result of interdiffusion of molecules or segments in autohesion and which are based only on the action of molecular forces at the point of initial contact, lose all meaning. Thus, attempts to deny the role of diffusion phenomena in forming adhesive joints, or even more in forming autohesive joints, are without any foundation.

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