

The Role of Diffusion Phenomena in Polymer-to-Polymer Adhesion

S. S. VOYUTSKII and V. L. VAKULA, *Lomonosov's Institute of Fine
Chemical Technology, Moscow, U.S.S.R.*

In considering the materials used as adhesives it is easy to note that almost all of them are high polymers. Thermoplastic and thermosetting resins, natural resins, cellulose derivatives, proteins, and rubbers are known to be used for bonding. It is important that only high molecular substances with their long-chain molecules have pronounced adhesive properties.

Only such inorganic compounds as cements and solders can be considered as nonpolymeric adhesives. However, the bond formation with cements and solders takes place in accordance with completely specific mechanism (fusion of crystals, welding) which has little in common with the formation of the usual adhesive bond and can only conventionally be considered as bonding. As far as bonding with sodium silicate is concerned, it is established at present that sodium silicate can be considered as an inorganic high molecular substance.¹

The present paper is a discussion of the mechanism of specific adhesion of polymers to each other. This case of adhesion is of great practical importance. The production of tires, confection of rubber products, production of rubber wear by glueing, as well as bonding and welding of plastics, and sizing of paper are all based on polymer-to-polymer adhesion. The technology of most of the aviation materials and of the artificial leather is also entirely based on the process of polymer-to-polymer bonding. Finally, bonding with polymers is widely used in wood processing and plywood manufacture, civil engineering, during the assembly of airplanes, and in a good number of other branches of engineering. Polymer-to-metal adhesion is not discussed here because of a special character of polymer-metal bond, which is probably chemical in most cases. The adhesion of polymers to inorganic glass is not considered here either though glass represents inorganic polymer and the authors of the present paper have some grounds to believe that the mechanism of polymer-to-glass adhesion in some cases is similar to that of polymer-to-polymer adhesion.

Attempts at theoretical generalization of the results obtained were made by the first investigators of bonding.²⁻⁶ However, the importance of the earlier investigations in the development of a theoretical approach to the bonding of polymers is depreciated by the fact that in most cases bonding of surfaces (wood, metal, glass, etc.) has been studied by means of the layer of

liquids or solids whose nature is quite different from all the typical polymers. Also in these investigations in testing bond strength little attention was paid to the type of failure though determination of the type of separation is one of the fundamentals for correct evaluation of adhesion. Finally, earlier authors attempted to relate adhesion to wetting and incorrectly approached the bonding as a thermodynamically reversible phenomenon.

Remarkable progress in the physical chemistry of adhesion has been made only during the last few years. These years mark the appearance of the adsorption and electric theories of polymer adhesion. The adsorption theory considers adhesion as a purely surface process which is analogous to the adsorption and accounts for the formation of a strong bond between adhesive and adherend through intermolecular forces.

The role that adsorption plays in adhesion was already pointed out by Bancroft back in 1926.² However a complete adsorption theory for the case of polymer-to-polymer adhesion was developed by McLaren and co-workers.⁷⁻¹¹

According to McLaren the formation of adhesive bond can be divided into two stages. The first stage consists of the migration of large polymer molecules from the solution to the surface of the adherend as a result of micro-Brownian motion. As a consequence polar groups of macromolecules of the adhesive approach the polar groups of the adherend. Through pressure and lowering of viscosity during heating, the chain segments can approach the surface very closely even in the absence of a solvent. The second stage of adhesion consists of the sorption process. When distance between molecules of adhesive and adherend becomes less than 5 Å, intermolecular forces come into play. This includes the whole "force spectrum" starting with dispersion forces (about 10^2 cal./mole) up to hydrogen bonding with energies in the range of 10^4 cal./mole. The bonds formed can be represented by the dipole-dipole bonds (cellulose-polyvinyl chloride), dipole-induced dipole bonds (cellulose-polystyrene), and hydrogen bonding (cellulose-polyvinyl alcohol).

In spite of the broad circulation of the adsorption theory of adhesion^{12,13} it has the following flaws concerning its application for polymers:

1. As shown by Deryagin and Krotova^{14,15} the peeling work of the adhesive film can reach values as high as 10^4 – 10^6 ergs/cm.², but the work required to overcome molecular forces does not exceed 10^2 – 10^3 ergs/cm.². In other words, the real work of adhesion is several magnitudes higher than that expected from molecular forces. The attempts at explaining this by attributing it to the expenditure of work of film deformation when peeling failed.

2. As established by Deryagin and Krotova,¹⁴ adhesion depends upon the peeling rate of the adhesive film while the work required to overcome the molecular forces must not depend on the separation rate of the molecules.

3. Adsorption theory cannot account for the high adhesion between non-polar polymers. However, it is known that such nonpolar polymers as polyisobutylene, natural rubber, and gutta-percha show good adhesion to a number of adherends.

4. As will be shown later, the fact that too high polarity of the polymer tends to decrease adhesion to very polar adherend contradicts the adsorption theory. If adhesion were determined only by adsorption it would increase in this case.

5. Finally, as is known, the adhesion of polymers containing double bond decreases abruptly even at slight vulcanization and vanishes completely when the molecular weight M_c between two network junctions approaches 5000. If adhesion were determined by adsorption this phenomenon would be inexplicable because such a long segment would of course have sufficient mobility in order to have its active groups approached to active centers of the adherend.

To account for these facts, for which the adsorption theory offers no explanation, the electric theory of adhesion was suggested by Deryagin and Krotova.^{14,15}

In accordance with this theory the adhesive-adherend system is identified with a condenser, the plates of which are the double electric layer that arises when contacting two different substances. When peeling of the bonded sample occurs it may be pictured as the separation of the plates of the condenser; the difference in potential then develops up to a certain limit where discharge occurs. On rapid peeling, the charges do not have time to leak, and the high initial charge density is preserved until gas discharge occurs. This, then, is the basis for the high values of adhesion since the action of the attraction forces of opposite charges is overcome at relatively great distances. When slow separation takes place the adhesion is decreased naturally as a result of partial removal of charges from the surfaces formed; the dependence of the value of adhesion upon the peeling rate is a proof for such a mechanism. Indication that electric phenomena may take place during the peeling of polymer bonded samples is given by the following: electrization of the surfaces formed, presence of the electrical discharge and electronic emission in some cases, and decrease of adhesion on irradiation of bonded sample by x-ray, gamma rays, etc.

It should be noted that the viewpoint according to which adhesion is caused by purely electrical phenomena is at present shared by other investigators.¹⁶

However, the electric theory alone cannot provide an explanation for polymer-to-polymer adhesion. First, the phenomena of the surface electrization, gas discharge, electronic emission, etc., are not detectable in many cases of separation of adhered polymer pairs. In other cases these phenomena are only observed under special conditions, though given pairs of polymers form a strong bond even if no electrical phenomenon is observed during the process of peeling. Secondly, when polymers are dielectrics, it is difficult to admit that considerable quantities of electrons can be transferred from one polymer to the other thus creating a large enough contact potential between adhesive and adherend. Thirdly, it is known that the more similar the nature of high polymers, the higher their adhesion. If the whole phenomenon could be reduced to the formation of a

double electric layer, the opposite relationship should be observed because the more similar phases brought into contact, the lower the contact potential difference.

Fourthly, if adhesion arose solely from the formation of double electric layer, adhesion between carbon black loaded polymers would be impossible since such systems are good conductors. However it is common knowledge that such systems show good adhesion not only to each other but also to metals.

Finally, this theory also cannot explain the decrease of adhesion on vulcanization of rubbers since the presence of a small quantity of sulfur in adhesive should not greatly influence the contact potential.

It is the authors' opinion therefore that the electric theory of the polymer-to-polymer adhesion is only applicable in cases when polymers are incompatible or insoluble in each other. If both polymers are compatible it is necessary to distinguish between two cases—adhesion of nonpolar and that of polar polymers. When a bond forms between nonpolar polymers, the electrical mechanism is not acceptable since such polymers could not be electron donors. It is the present authors' opinion that adhesion in this case is caused by the interlacing of the surface macromolecules due to their mutual diffusion. Upon formation of bonds between polar polymers the double electric layers can arise; but if the polymer molecules or any of their portions are capable of intense thermal motion "sewing together" of both layers will also occur as a result of diffusion. As the time of contact increases, the importance of the first mechanism will of course gradually decrease but that of the second will increase due to disappearance of the contact surfaces and increasing penetration depth of the macromolecules of the adhesive into the adherence. Morozova and Krotova experimentally investigated the relative importance of electrical and diffusion processes in the adhesion of polymers and came to similar conclusions.¹⁷

In accordance with the views of Voyutskii et al.¹⁸⁻²¹ adhesion of polymers to each other as well as their autohesion is, in many cases, reduced to the diffusion of chainlike molecules and as a result leads to the formation of a strong bond between adhesive and adherend. The possibility of self-diffusion of polymers and the diffusion of one polymer into another does not cause any doubts²² at present if both polymers are not in glassy or crystalline state. Also, the diffusion nature of autohesion causing the confection of nonvulcanized rubber articles,²³ welding of thermoplastics,²⁴ the production of articles from molding powders,²⁵ and the film production from the dispersion of polymers²⁶ was proved by a number of works²⁷⁻³⁴ and hence there is no necessity to dwell upon this matter.

The difference between adhesion and autohesion is that the latter is accompanied by the diffusion of identical molecules, i.e., by self-diffusion, while in the former the diffusion of two different types of macromolecules occurs. The essential peculiarity of the diffusion theory of adhesion, in which it differs from the other theories, lies in the fact that it involves the

most characteristic properties of polymeric substances: their chainlike structure, the flexibility of their molecules, and the ability of the latter for micro-Brownian motion.

It is worthwhile to note that as a rule adhesive molecules have the ability to diffuse. However, if the adhesive is applied in solution, and the adherend is capable of swelling or dissolving in this solution, a remarkable diffusion of the molecules of adherend into the adhesive may occur. Both processes lead to the disappearance of the boundary between the phases and to the formation of a bond presenting a gradual transition from one polymer to the other. Hence, adhesion, according to the diffusion theory, essentially presents a volume phenomenon.

Because the diffusion theory provides for the formation of a sturdy transition layer between the adhesive and adherend, unlike the adsorption theory it easily explains the lack of agreement between the peeling work and the work required to overcome the molecular forces between the adhesive and the adherend. The diffusion theory also explains the rate dependence of the adhesion work on the basis of the interpretation for the rate dependence of the tensile strength of polymers.

It is quite obvious that the diffusion of molecules of one polymer into another is nothing but solubility. Voyutskii was the first to point out the value of mutual solubility of polymer for their adhesion.³⁵ He suggested using polymer-to-polymer adhesion as a criterion for their compatibility. Later Deryagin et al.³⁶ also emphasized the relationship between compatibility and adhesion and suggested judging adhesion by compatibility data.

Mutual solubility of the components is important for their adhesion and in the first approximation is determined by the polarity of polymers;³⁷ it is also in good agreement with the known empirical de Bruyne's rule, according to which adhesion is strong only when both polymers are either polar or nonpolar and is made more difficult in the case of polar plus nonpolar polymer. The usual objection to the diffusion explanation of adhesion of elastomer to high molecular but rather dense and stiff adherend such as cellophane³⁸ comes down to the fact that the molecules of adhesive cannot penetrate into such a adherend. However, it is necessary to keep in mind that the penetration of the molecules of adhesive into the adherend to a negligible depth (of the order of 10 Å) is sufficient to increase manifold the adhesion strength. This is supported by Patrikeev's elementary calculations.³⁹ Such a small depth of penetration presents difficulties in the direct experimental proof of the presence of the diffusion phenomena during adhesion. Nevertheless, under definite conditions when polymers have sufficiently high diffusibility, Morozova and Krotova¹⁷ established the presence of diffusion during adhesion with the aid of microscopic investigation.

In addition to general considerations that confirm the correctness of the diffusion theory of adhesion there are a series of experimental data and observations in favor of it. Only some of these will be gone into.

The Effect of Contact Time of Adhesive and Adherend

Little attention has so far been paid to the influence of contact time between adhesive and adherend. But this dependence is one of the most substantial proofs of the diffusion theory of adhesion. Figure 1 shows a typical curve characterizing the adhesion of butadiene-acrylonitrile copolymer containing 38% nitrile to the cellophane eluted from glycerol (plasticizer) as a function of time from the moment of bonding sample to the moment of its peeling.¹⁹ As can be seen, at first the adhesion between high molecular adhesive and polymeric adherend rapidly increases with contact time and then increases progressively slower approaching finally a certain

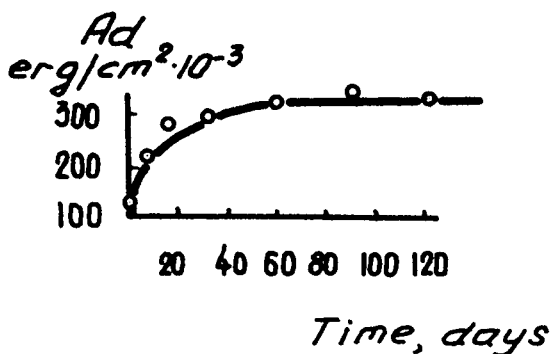


Fig. 1. Adhesion Ad of butadiene-acrylonitrile copolymer containing 38% nitrile to cellophane vs. time from the moment of the preparation of the bonded sample to the moment of its peeling.

limiting value. The increase in adhesion as a result of the removal of the air from the surface of adherend raising the real contact area is impossible in this case because the bonded samples were prepared by the application of adhesive solution to the adherend. Analogous results were obtained by Forbes and MacLeod²³ during the investigation of the adhesion of different elastomers pressed together under low pressure at varying times. This excludes the possibility of explaining the increase in adhesion as a result of evaporation of the remaining solvent.

Neither adsorption nor electrical theory can provide the satisfactory interpretation of the increasing adhesion strength with the time represented in Figure 1, and only the diffusion theory easily explains such a dependence by the slow penetration of the macromolecules of adhesive into the adherend.

The Effect of Bonding Temperature or Thermal Treatment of the Glue Bond

In Figure 2 a typical curve is given showing the characteristic dependence of adhesion upon the temperature to which the bonded samples of cellophane with butadiene-acrylonitrile copolymer were heated.¹⁹ The samples

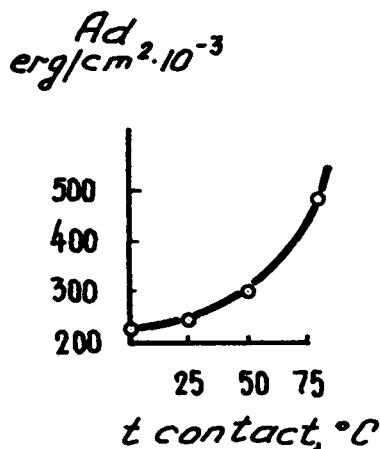


Fig. 2. Adhesion of butadiene-acrylonitrile copolymer containing 38% nitrile vs. temperature of thermal treatment of the bonded sample.

tested were prepared by pouring the adhesive solution on cellophane and drying the assembly near 0°C .; before peeling, the bonded samples were heated at different temperatures for 40 min. As can be seen, throughout the temperature investigated adhesion increased on heating without approaching a limiting value.

Another example of temperature dependence of adhesion is represented in Figure 3.⁴⁰ In this case, polyamide in the form of film was used as an adherend and the fractions of butadiene-acrylonitrile copolymer with 42% nitrile in molecule was used as an adhesive. These fractions were obtained by fractional precipitation. The bonded samples were prepared by bringing the adhesive and film adherend into contact followed by rolling and heating for 30 min. at the proper temperatures. In Figure 3 as well as in the other figures the solid curves correspond to adhesive failure; dashed curves correspond to cohesive failure. As can be seen, the character of the curves in Figures 2 and 3 in general coincides.

Increasing the adhesion on heating of the bonded samples cannot be attributed to an increase in true contact area or to the evaporation or remaining solvent since the increase in adhesion is observed for the bonded samples prepared from the copolymer solution (for which the area of real contact should be maximum) as well as for those prepared by bringing into contact the adherend and the film of adhesive without the solvent.

The stronger adhesion with the increase in temperature of the thermal treatment cannot be explained by either the electric or the adsorption theory. If the former theory were correct the strength of adherence would not depend upon the thermal treatment of the adhesive bond because the influence of temperature on the contact potential should be reversible. If the latter theory were correct the adhesion should not depend upon the heating because the application of adhesive solution would ensure com-

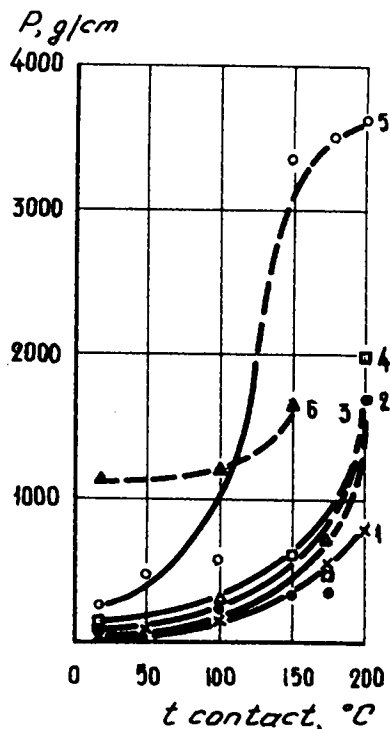


Fig. 3. Peeling strength P of the bonded samples of polyamide with different fractions of butadiene-acrylonitrile copolymer with 42% nitrile vs. temperature of thermal treatment of the bonded samples. (1) Fraction of molecular weight 550,000; (2) fraction of molecular weight 524,000; (3) molecular weight 378,000; (4) molecular weight 266,000; (5) molecular weight 100,000; (6) molecular weight 20,000.

plete orientation of the segments capable of diffusing close to the surface of the adherend already during the preparation of the bonded sample. On the contrary, the diffusion theory easily explains the reason for increased adhesion through the increased thermal motion of macromolecules or their segments and through the increase of their diffusive penetration into the adherend with the rise of temperature.

The Effect of the Molecular Weight of the Adhesive

If the diffusion theory is correct, the value of the molecular weight and the shape of macromolecules involved must affect adhesion since both of these factors affect the rate of diffusion. It also holds true that in the case of the correctness of the adsorption or electric theories these factors should not have any large effect upon adhesion itself.

Experiments have shown that adhesion is actually dependent upon the molecular weight. Figure 4 represents adhesion of the fractions of butadiene-acrylonitrile copolymers with varying polarity to polyamide as a function of the molecular weight of these fractions. The bonded samples

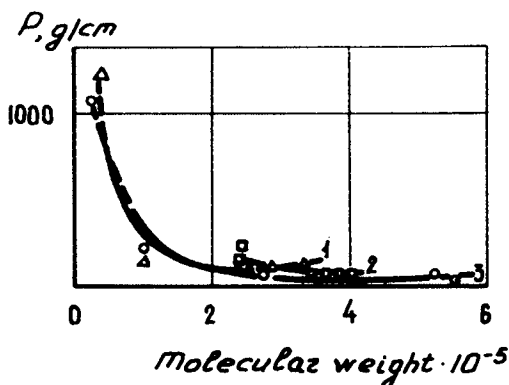


Fig. 4. Peeling strength P of the bonded samples of polyamide with various fractions of different butadiene-acrylonitrile copolymers vs. their molecular weights. (1) Copolymer with 20% nitrile; (2) copolymer with 32% nitrile; (3) copolymer with 49% nitrile.

were prepared by the rolling of adherend with adhesive film at 20°C. From Figure 4 it follows that adhesion of nitrile rubbers to polyamide first drops with increasing molecular weight, and then becomes constant. At room temperature the adhesion of fractions of nitrile rubbers with molecular weight of more than 300,000–350,000 is very small and depends very little on the polarity of polymer.

The independence of adhesion upon molecular weight after its definite limiting value was observed with completely different polymers by other authors.^{7,9,41} From the diffusion viewpoint such a phenomenon should be explained in the same way as in the case of autohesion.³¹ Apparently when the molecular weight is low and the size of the macromolecule is commensurable with the segment length, the number of free ends (i.e., end segments) is relatively great, and consequently the probability of their diffusion into an adherend is also great. In keeping with purely steric reasons, the probability of the diffusion of the end segments of macromolecules into a bulk polymer is more than that of the middle segments. Therefore under these conditions the adhesion will be determined almost completely by the diffusion of the free ends of the macromolecules. As the molecular weight increases, the relative proportion of end and middle segments changes abruptly in favor of the latter, thus decreasing adhesion. Finally, at some definite value of molecular weight, the number of ends of macromolecules becomes so small in comparison with the total number of segments in the macromolecule that the participation of the former in diffusion becomes imperceptible. Hence, at high molecular weights adhesion will be determined mainly by the diffusion of middle segments, and insofar as the size of the segment does not depend on the length of the macromolecule, adhesion ceases to be dependent on the molecular weight of the polymer.

Such an approach is supported by the fact that Bueche et al.²² could measure the rate of self-diffusion in polybutyl acrylates only for the

samples of a molecular weight below 300,000. Also, it is of importance that Bueche²² noted the special role of chain ends in phenomena related to the flow and self-diffusion in the bulk polymer. He believed that chain ends serve to loosen the structure of the polymer.

This approach also coincides with Douglas and McCall's conclusions which were made after investigation of the self-diffusion in paraffins.⁴² According to these authors the elementary process of self-diffusion mainly represents the transition of the stretched molecules parallel to its axis.

Another explanation of the independence of adhesion upon molecular weight (if the latter surpasses some known value) is the fact that diffusion is practically absent for polymers with sufficiently high molecular weight. The low adhesion observed is completely determined by the molecular forces at the contact line.

From the data under consideration it could be concluded that adhesion is higher, the lower the molecular weight of the polymer. This conclusion is quite understandable on the basis of the diffusion theory: when the size of the molecules decreases their ability to diffuse increases and consequently adhesion must increase. However, since with decreasing molecular weight of polymeric adhesives their cohesive strength falls, polymers of medium molecular weight must obviously have optimum bonding ability; they are able to provide good adhesion and at the same time a sufficiently high cohesive strength of adhesive.

With the influence of molecular weight of the polymer on its adhesive properties the question of the influence of the polydispersity of adhesive is closely related. Obviously the lower the molecular fraction in polymer, the higher its adhesion. Insofar as the polydispersity of commercial polymers usually changes from batch to batch in sufficiently wide range it is becoming perfectly clear why different authors quite differently evaluate the adhesive properties of one and the same polymer. Polydispersity of the commercial polymers also explains why the adhesion of such polymers is always higher than that of high molecular fractions separated from them.

The Effect of the Polarity of Adhesive

Experiment shows that at room temperature the adhesion of the polar polymers to the polar adherend slightly depends upon the content of polar groups in these polymers. Such a conclusion can be drawn from Figure 4, for example.

It is seen more clearly in Figure 5, which represents data characterizing the adhesion of butadiene-acrylonitrile copolymers to polyamide vs. the content of polar acrylonitrile groups.⁴⁰ In order to exclude the influence of molecular weight on adhesion, an assumed fraction of molecular weight of 320,000 was chosen for polymers of different polarity (in this region of molecular weight, as one can see from Fig. 4, its change has very little influence on the values of measured adhesion). The values of adhesion of copolymers to polyamide were taken from the curves characterizing the

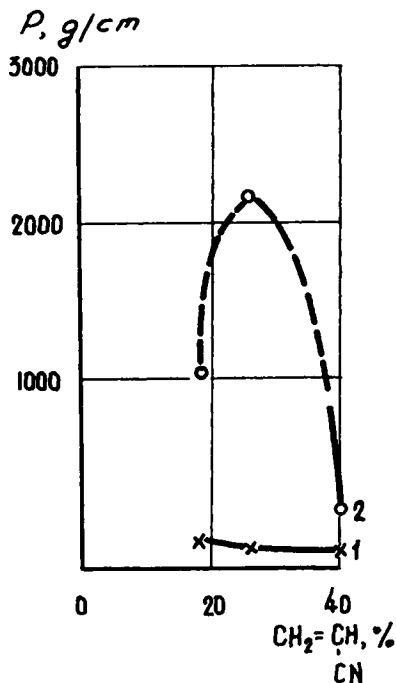


Fig. 5. Peeling strength P of the bonded samples of polyamide with the fractions of butadiene-acrylonitrile copolymers of molecular weight 320,000 vs. the content of nitrile in the copolymers. (1) Nonheated bonded samples and (2) bonded samples heated at 150°C . during 30 min.

dependence of adhesion of different fractions on molecular weight at contact temperature 20 and 150°C .

From the basis of both Figures 4 and 5, it follows that at room contact temperature adhesion of copolymers to polar adherend depends to a small degree on the content of polar groups in the copolymer. However, at contact temperature 150°C . adhesion depends on polarity to a great extent. The copolymer with about 40% acrylonitrile shows minimum adhesion in this case. Bonded samples of less polar rubber have cohesive failure and reasonably high peeling strength. This proves their much higher adhesion to polyamide.

On the basis of these data the following conclusion can be drawn: The adhesion of polar polymer to polar adherend decreases with increasing polarity and the less the polarity of a polymer, the greater its adhesion with an increase in the contact temperature. This was also discovered in other works.^{41,43,44}

The reason for the lower adhesion of high polar nitrile rubber can be sought in poor compatibility of such a polymer with polyamide or in the fact that the diffusion of this polymer into adherend becomes difficult because of the low flexibility of their molecules and of the presence between

them of intermolecular forces of considerable value. However, the determination of the swelling of various butadiene-acrylonitrile copolymers in caprolactam as well as the comparison of the values of specific cohesive energies of these copolymers show that the copolymer containing a maximum amount of nitrile should have the best compatibility.⁴⁰ Hence, both the higher adhesion of low nitrile content copolymers to high polar polyamide and the higher increase in their adhesion with increasing contact temperature would be explained from a purely kinetic viewpoint by the greater intensity of micro-Brownian motion of their chains and by the fact that the increase of flexibility of molecular chains and the destruction of intermolecular links take place with increasing temperature more rapidly for these adhesives than for the more polar copolymer.

The fact that low polar butadiene-acrylonitrile copolymers show higher adhesion to polyamide as compared to a copolymer of high polarity can serve as a good proof of the diffusion theory of adhesion. The adsorption theory cannot explain such a phenomenon—according to it, the adhesive strength can only increase with the decrease of the difference between polarity of adhesive and adherend.

It should be noted that the decrease of adhesion with increasing polarity of a polymer cannot always be observed. For instance, MacLaren established^{7,9} that with increasing chlorine content in chlorinated polyethylene the strength of adherence of polymer to cellophane at first increased and then started falling. MacLaren also observed that moderate content of polar groups—chlorine, carboxyl, carbonyl, and hydroxyl—in macromolecules may improve adhesion of polymer to cellophane. This phenomenon may be ascribed to the fact that at moderate polarity of polymer the increase of adhesion due to better solubility overshadows the decrease of adhesion because of the deterioration of the diffusibility of adhesive.

Adhesion of polymer elastomers to nonpolar adherend is very characteristic. Adhesion of individual fractions of butadiene-acrylonitrile co-

TABLE I
Adhesion of Fractions of Butadiene-Acrylonitrile Rubbers
to Polyisobutylene at Various Contact Temperatures
(g./cm.)

Nitrile in copoly- mer, %	Mol. wt. of fractions	Contact temperature, °C.					
		20	50	100	150	175	200
20	334,000	80	100	70	60	50	60
	25,000	35	50	35	50	50	80
32	408,000	65	80	130	140	120	110
	238,000	75	75	100	85	60	60
42	550,000	65	50	70	90	80	50
	100,000	70	50	40	50	40	90

polymers to polyisobutylene at various contact temperatures is shown in Table I.⁴⁰

As can be seen from Table I, adhesion is very low and no degree of dependence could be assigned to the changes of polarity of the adhesive, its molecular weight, and the contact temperature.

Such a phenomenon can be explained by the noncompatibility of polar nitrile rubbers with nonpolar polyisobutylene. This results in the impossibility of diffusion of molecules of the adhesive into the adherend. In this case abrupt difference in the polarity of the adhesive and adherend indicates that even such a strong factor in the diffusion acceleration of macromolecules as the temperature cannot increase the adhesion.

The Effect of Structure of the Adhesive Molecule

In connection with the great influence of molecular weight on adhesion established by the present authors, and in order to find out how such factors as the presence of lateral groups in the molecules and the regularity of the chain structure can influence the adhesive properties of a polymer, it is necessary to deal with polymers of different molecular structure but with the same molecular weight. Unfortunately, such experiments, insofar as is known, were not conducted. However, a large amount of experimental data characterizing the adhesion of commercial polymers with the molecules of various structure to different high molecular adherends^{7-11,41,43} enables one to draw some conclusions which of course are not completely grounded.

It was established that the increase of butadiene in 1-2 position in the molecule of polybutadiene makes adhesion worse.⁴¹ This phenomenon can obviously be explained by the fact that the ability of a molecule to diffuse decreases with increasing number of butadiene 1,2 groups in a macromolecule due to purely steric factors based on the increase in the number of vinyl side chains. The introduction of styrene with its bulky lateral phenyl group into a macromolecule consisting of butadiene units also abruptly decreases the adhesion of copolymer to all adherends. The greater the content of styrene introduced into a molecule, the greater the decrease in adhesion.^{41,43} The exchange of styrene for methylstyrene decreases adhesion to a greater extent.^{41,43}

Hence, the presence of short lateral groups (vinyl, phenyl, methyl) in a macromolecule generally lowers its adhesion. However, if the side chains are sufficiently long they can play the part of separate chains and they will then diffuse with greater ease into the adherend than will the middle segments of the macromolecules due to steric hindrances. The correctness of this assumption is borne out by the data of MacLaren,^{7,9} who established that adhesion to cellophane increases in series of polymethyl methacrylate from poly-*n*-methacrylate to poly-*n*-butyl methacrylate. MacLaren also showed that polyisopropyl methacrylate and poly-isobutyl methacrylate have considerably poorer adhesion to cellophane than the corresponding poly-*n*-alkyl methacrylates.

This stands in good agreement with the present authors' concept of the influence of the shape of the macromolecules on adhesion.

Consideration of the temperature dependence of adhesion of butadiene-styrene and butadiene-methylstyrene copolymers⁴³ shows that in all cases the increase of temperature results in the increase in adhesion. This increase of adhesion is so great that it diminishes to a notable extent the influence of quantitative and qualitative composition of lateral groups. It leads one to the conclusion that probably the increase of contact temperature promoting the increase of mobility of the macromolecules can make short lateral groups a factor contributing to adhesion due to the increase of number of the "anchor" points. However, it should be noted that the increase in adhesion cannot only be a consequence of the quantitative increase of the mobility of molecular chains during the heating but also can be a result of qualitative changes in the mechanism of diffusion when kinetic unit taking part in diffusion becomes the molecular chain as a whole but not its separate segments.

Two conclusions may be drawn as to the effect of the structure of molecules on adhesion, which follow from the above and from the generalizations of the diffusion theory.

First, the absence of lateral groups and regular structure of molecules in general tends to increase adhesion since in this case flexibility and mobility of the molecular chains increases. However, if the polymer consists of molecules of a regular structure and is capable of crystallizing, its adhesion becomes insignificant. As an example one can take amorphous polyisobutylene (under common conditions) and crystalline polyethylene. While the former has remarkably high adhesion, polyethylene at room temperature shows none.

Secondly, three-dimensional (crosslinked) polymers are not capable of adhering. This is clear because the crosslinks connecting the main chains make their diffusion into the adherend impossible. This conclusion is confirmed by the complete absence of adhesive ability found in rubber after vulcanization.

The Effect of the Phase State of Polymers

Proceeding from the above-developed approach to the nature of adhesion it is easy to see that at the contact of two polymers the value of adhesion should primarily depend upon the phase state of polymers. In fact, at glassy state of both polymers when mobility of segments is absent, no diffusion can exist and consequently the adhesion is brought to nought. In the region of rubberlike state the middle segments and macromolecule ends take part in thermal motion. Insofar as the molecule ends diffuse easier than middle segments due to steric reasons it is obvious that in this case considerable adhesion will be observed only for polymers with sufficiently low molecular weight or for polydisperse polymers containing a sufficient amount of low molecular fractions. Finally in a flow state whole macromolecules take part in the diffusion. This eventually results

in the abrupt increase in the values of adhesion. The correctness of such an approach was shown with the welding of organic glass at various temperatures as an example.²⁴ Of course at the contact of two different polymers the situation is getting complicated by the fact that temperature regions of different phase states for both polymers brought into contact do not usually coincide.

Conclusions

When comparing the above-said concerning the influence of the duration and temperature of contact as well as the influence of the properties of polymers on the adhesion, there is no avoiding the eye-catching fact that in the case of mutually soluble polymers the factors increasing adhesion are always those promoting diffusion. It serves as a significant reason in favor of the fact that the formation of transition layer at the expense of the penetration of the adhesion into the adherend, or if the phase state of adherend allows, at the expense of mutual penetration of both polymers, lies at the basis of the adhesion of compatible polymers.

To sum up the role of the diffusion phenomena during the adhesion of polymers it should be noted that this viewpoint explains the effects observed in the technology of bonding: the use of solvent common for adhesive and adherend, the rejuvenation of the surfaces with solvent before bonding, the use of tackifiers for the promotion of adhesion, the use of graft polymers based on two polymers different in polarity for the improvement of their bonding, etc. A detailed explanation of these methods may be found in a series of recently published technical papers²⁵ and also in a monograph.²¹

References

1. Hurd, C. B., and P. C. Merz, *J. Am. Chem. Soc.*, **68**, 61 (1946).
2. Bancroft, M. B., *Applied Colloid Chemistry*, McGraw-Hill, New York, 1926, p. 81.
3. Hardy, W. B., and M. E. Nottage, *Proc. Roy. Soc. (London)*, **112**, 62 (1926); **118**, 209 (1929); *Phil. Trans. Roy. Soc. London*, **230**, 1 (1931).
4. Hardy, W. B., *Proc. Roy. Soc. (London)*, **138**, 259 (1932).
5. Nottage, M. E., *Proc. Roy. Soc. (London)*, **126**, 630 (1930).
6. McBain, J. W., and W. Lee, *J. Phys. Soc.*, **31**, 1674 (1927); **32**, 1178 (1928); *Proc. Roy. Soc. (London)*, **113**, 606 (1927); *Ind. Eng. Chem.*, **19**, 105 (1927); *J. Soc. Chem. Ind.*, **321**, 46 (1927).
7. McLaren, A. D., and C. H. Hofrichter, *Paper Trade J.*, **125**, 19, 96 (1947).
8. Hofrichter, C. H., and A. D. McLaren, *Ind. Eng. Chem.*, **40**, 329 (1948).
9. McLaren, A. D., *J. Polymer Sci.*, **3**, 652 (1948).
10. McLaren, A. D., and C. J. Seiler, *J. Polymer Sci.*, **4**, 63 (1949).
11. McLaren, A. D., in *Adhesion and Adhesives*, Wiley, New York, 1954, p. 57.
12. *Adhesion and Adhesives*, N. A. de Bruyne and R. Houwink, eds., Wiley, New York, 1951.
13. *Adhesion and Adhesives*, J. E. Rutzler and R. L. Savage, eds., Wiley, New York, 1954.
14. Deryagin, B. V., and N. A. Krotova, *Adhesion*, Academy of Science U.S.S.R., Moscow-Leningrad, 1949.

15. Deryagin, B. V., *Vestnik Akad. Nauk S.S.S.R.*, No. 7, 10 (1954).
16. Skinner, S. M., R. L. Savage, and J. E. Rutzler, *J. Appl. Phys.*, **24**, 438 (1953); S. M. Skinner, *J. Appl. Phys.*, **26**, 498, 509 (1955); S. M. Skinner, J. Gaynor and G. W. Sohl, WADC Tech. Report 56-158, Aug. 1956; S. M. Skinner, E. L. Kern and M. K. Park, WADC Tech. Report 58-9, Jan. 1958.
17. Morozova, L. P., and N. A. Krotova, *Doklady Akad. Nauk S.S.S.R.*, **115**, 747 (1957); *Rubber Chem. Technol.*, **33**, 240 (1960).
18. Voyutskii, S. S., A. I. Shapovalova, and A. P. Pisarenko, *Doklady Akad. Nauk S.S.S.R.*, **105**, 1000 (1955).
19. Voyutskii, S. S., *Vysokomolekulayrnye Soedineniya*, **1**, 230 (1959); *Rubber Chem. Technol.*, **33**, 748 (1960).
20. Voyutskii, S. S., and V. L. Vakula, *Uspehi chim.*, **28**, 701 (1959).
21. Voyutskii, S. S., *Autohesion and Adhesion of High Polymers*, Rostechizdat, Moscow, 1960.
22. Bueche, F., W. M. Cashin, and P. Debye, *J. Chem. Phys.*, **20**, 1956 (1952); F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).
23. Sbornik. "Prochnost svyazi mezhdu elementami rezino-kanevich izdelii v proizvodstve i ekspluatatsii," Goschimizdat, M-L, 1956.
24. Grishin, N. A., and S. S. Voyutskii, *Vysokomolekulayrnye Soedineniya*, **1**, 1778, 1788 (1959).
25. Igonin, L. A., Y. V. Ovchinnikov, and S. A. Arjakov, *Doklady Akad. Nauk S.S.S.R.*, **120**, 1062 (1958); S. A. Arjakov, E. E. Rylov, and B. P. Shtarkman; *Vysokomolekulayrnye Soedineniya*, **1**, 1351, 1357 (1959).
26. Voyutskii, S. S., and B. V. Shtarch, "Physicochemistry of the Processes of Film Formation from High Polymer Dispersion," Gislepprom, M., 1954.
27. Josefowitz, D., and H. Mark, *India Rubber World*, **106**, 33 (1942).
28. Scott, I. R., *Paint Technol.*, **9**, 218 (1944).
29. Voyutskii, S. S., and Y. L. Margolina, *Uspehi chim.*, **18**, 449 (1949); *Rubber Chem. Technol.*, **30**, 531 (1957).
30. Voyutskii, S. S., and V. M. Zamazii, *Doklady Akad. Nauk S.S.S.R.*, **81**, 63 (1951); *Colloid J.*, (*U.S.S.R.*), **15**, 407 (1953); *Rubber Chem. Technol.*, **30**, 544 (1957).
31. Voyutskii, S. S., and B. V. Shtarch, *Doklady Akad. Nauk S.S.S.R.*, **90**, 573 (1953); *Colloid J.*, (*U.S.S.R.*), **16**, 3 (1954); *Rubber Chem. Technol.*, **30**, 548 (1957).
32. Shapovalova, A. I., N. A. Zvetkova, and S. S. Voyutskii, "Nauchno-issledovatel'skie trudi ZNIKZ," sb. V, Gislepprom, M., 1953, p. 58.
33. Forbes, W. G., and L. A. MacLeod, *Trans. Inst. Rubber Ind.*, **34-5**, No. 4, 154 (1958).
34. Thirion, P., *Rev. gen. caoutchouc*, **35**, 441 (1958).
35. Voyutskii, S. S., *Legkaya Prom.*, No. 1, 42 (1953).
36. Deryagin, B. V., S. K. Zharebkov, and A. I. Medvedeva, *Colloid J.*, (*U.S.S.R.*), **18**, 4 (1956).
37. Alexeenko, V. I., I. U. Mishustin, and S. S. Voyutskii, *Doklady Akad. Nauk S.S.S.R.*, **95**, 93, (1954); *Colloid J.* (*U.S.S.R.*), **17**, 3 (1955).
38. Weidner, C. L., and G. L. Grocker, *Rubber Chem. Technol.*, **33**, 1323 (1960).
39. Patrikeev, G. A., in *Bond Strength between Elements of Multilayered Rubber-Fabric Articles in Manufacture and Use*, Chemical Pub. House, Moscow, 1956, p. 78; *Rubber Chem. Technol.*, **32**, 1192 (1959).
40. Vakula, V. L., Che Yun-Tsui, V. E. Gul' and S. S. Voyutskii, *Vysokomolekulayrnye Soedineniya*, **2**, 636 (1960).
41. Voyutskii, S. S., A. I. Shapovalova, and A. P. Pisarenko, *Colloid J.* (*U.S.S.R.*), **19**, 274 (1957).
42. Douglas, D. C., and D. W. McCall, *J. Phys. Chem.*, **62**, 1102 (1958).
43. Voyutskii, S. S., and V. L. Vakula, *Vysokomolekulayrnye Soedineniya*, **2**, 51 (1960).
44. Voyutskii, S. S., V. L. Vakula, N. I. Smelaya, and I. A. Tutorskii, *Vysokomolekulayrnye Soedineniya*, **3**, 1671 (1960).

Synopsis

In the present paper different views concerning polymer-to-polymer adhesion were considered and the theory suggested whereby adhesion of high polymers as well as autohesion is reduced to diffusion of chain molecules or their segments and to the formation of a sturdy bond between the adhesive and the adherend as a result. From the viewpoint of the suggested theory the influence of such factors as the duration of contact between the adhesive and the adherend, contact temperature, molecular weight of the adhesive, shape and polarity of macromolecules, and phase state of polymers was considered and explained.

Résumé

Dans cette publication on considère les différentes études concernant l'adhésion d'un polymère à un autre polymère. On propose une théorie suivant laquelle aussi bien l'adhésion de hauts polymères que leur manque d'adhésion se ramènent à la diffusion des chaînes moléculaires ou de leurs segments avec comme résultat la formation d'un lien solide entre l'élément adhésif et l'adhérent. En considérant la théorie proposée on explique l'influence de facteurs tels que le temps de contact entre l'adhésif et l'adhérent, la température de contact, le poids moléculaire de l'adhésif, la forme et la polarité des macromolécules et la phase polymérique.

Zusammenfassung

In der vorliegenden Arbeit wurden verschiedene Ansichten über die Adhäsion von Polymeren an Polymeren erörtert und es wurde eine Theorie vorgeschlagen, nach der die Adhäsion von Hochpolymeren wie auch ihre Autohesion auf die Diffusion von Kettenmolekülen oder deren Segmenten und auf die sich daraus ergebende Bildung einer starken Bindung zwischen den adhärierenden Stoffen zurückgeführt wird. Vom Standpunkt der vorgeschlagenen Theorie aus wird der Einfluss folgender Faktoren behandelt und geklärt: Kontaktdauer zwischen adhärierenden Stoffen, Kontakttemperatur, Molekulargewicht des Adhäsionsmittels, Gestalt und Polarität der Makromoleküle und Phasenzustand der Polymeren.

Received October 11, 1961