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### **A Review of Contemporary Views of Theories of Adhesion**

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# A Review of Contemporary Views of Theories of Adhesion†

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The once distinct and independent theories of adhesion have been losing their isolation and converging. Ideas of the effects of surface roughness, once dismissed as irrelevant except in the case of textiles, have been revised; albeit on a smaller scale as details of surfaces have been revealed by sophisticated techniques. Electrostatic interactions across an interface have been more deeply explored and their significance recognised and expounded. Diffusion of groupings and chain segments within a polymer have been related to the possibilities of interaction with a variety of surfaces. Perhaps most important, theories of adsorption have been extended in depth. The precise nature of the molecular interactions have been recognised and quantified. In doing this the contribution of diffusion and elastoplastic phenomena have been integrated. These developments are collated and analysed to present the present understanding of the concepts.

**KEY WORDS** Adsorption interactions; diffusion mechanisms; electrostatic interactions; mechanical interlocking; review, theories of adhesion.

## INTRODUCTION

The need for a deep understanding of the basis of adhesion was recognised over sixty years ago when, in 1922, the First Report of the Adhesives Research Committee<sup>1</sup> stated, "Finally it may be added, there is still no generally acceptable explanation of the action by which glues etc. cause surfaces to stick together. It is

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obviously necessary to investigate the nature of adhesion, be it physical or chemical. This problem which has such an important bearing upon many branches of industry, is constantly before the Committee”.

The first stages along the path towards understanding were taken by McBain<sup>2</sup> who, in the Second Report of that Committee, first drew a distinction between joints of two categories; one involving a mechanical type of mere embedding and the other with a specific type of true adhesion.

Over the intervening years, a number of theories have been advanced to account for and explain the observed phenomena. These have been of varying depths of sophistication and development. Frequently particular theories have suffered from the enthusiasm of their protagonists who have been inclined to promote their own view as a universal panacea. Although the shortcoming of this misconception were recognised at quite an early date<sup>3,4</sup> it has only quite slowly been eroded. Only in comparatively recent years has it been freely possible to consider which theories and mechanisms are appropriate for each particular example of adhesion and to begin to resolve the way in which the contribution of different mechanisms might be combined to provide a further understanding of observed phenomena.

So, in this paper I shall review some of the areas where deeper understanding has been achieved and finally try to bring these together into a coherent whole.

### **Mechanical interlocking**

This concept, which suggests that the interlocking of the adhesive with the irregularities of the adherend surface is the basis of adhesion, has immediate and intuitive appeal. However, the fact that strong adhesive bonds can and are achieved between surfaces as smooth as optical glass flats demonstrates that it cannot be of general application. The results for the bond strengths of maple wood samples of different roughness were clear evidence for its apparent fallacy.<sup>5</sup>

Nevertheless, the classic work of Wake and Borroff<sup>6</sup> on the adhesion of rubber to textiles for material woven from spun staple of natural origin proved that the most important factor governing

TABLE I  
Maplewood samples, bonded,  
side grain, with unreaformal-  
dehyde resin at  $5 \text{ lb f in}^{-2}$  pres-  
sure and tested in shear

Surface	Shear strength
Planed	$3120 \text{ lb f in}^{-2}$
Sanded	$2360 \text{ lb f in}^{-2}$
Sawn	$2690 \text{ lb f in}^{-2}$
Combed	$2400 \text{ lb f in}^{-2}$

the bond strength was the penetration of fibre ends from the spun yarn into the rubber. These fibre ends are broken off when the textile and the rubber are separated and the strength of the bond depends upon the number of them originally present. The specific interaction between the rubber and the surface of the fibre is only of indirect importance, as it will determine the length of fibre end which must be embedded before the interfacial shear strength exceeds the tensile strength of the fibre. Moreover, if the spun staple natural fibre was replaced by continuous filament of synthetic origin then the bond strength was very considerably reduced. Various special treatments and finishes had to be introduced to enhance the specific interaction between the surface of the textile and the fibre in order to achieve a satisfactory bond.

Another well established example where mechanical interlocking makes a significant contribution towards the bond strength is in the electroless plating of certain plastics with metal. The most commonly used base is either high impact polystyrene or ABS, both of which consist of a continuous phase of glassy polymer with an elastomer dispersed within it. The process of plating involves an etching step which results in the oxidation and removal of the rubbery material to leave a highly reticulate and porous surface following which the metal (usually copper) is deposited. Electron micrographs of sections show quite clearly the penetration and interlocking of the metal within the plastic to a depth of up to  $10 \mu\text{m}$ . A similar procedure is used for plating polyalkenes but here the etching produces less well defined attack at grain boundaries and various surface defects. Here a very extensive study by Perrers and Pettett<sup>7</sup> showed that there were two mechanisms involved and

interacting; a mechanical interlocking and an interaction depending upon the surface chemistry of the polymer.

These were all special cases and out of the main stream of structural adhesion technology and for this reason it was, at one stage, fashionable to dismiss mechanical interlocking as insignificant and irrelevant. The change began with Packham's<sup>8</sup> work on the adhesion of polyethylene to aluminium. He studied the behaviour of polyethylene which was sintered on to the surface of aluminium which had been treated in various way but particularly which had been anodised in acid electrolytes. It was already well known that the oxide film produced comprised a dense barrier layer of compact oxide immediately adjacent to the metal, surmounted by a layer of hexagonal oxide cells each with a circular pore at its centre. The size and relative number of these pores could be controlled by the conditions and duration of anodising. The diameters ranged from 120 Å to 330 Å. Measurements of bond strength showed a direct correlation with the size and concentration of these pores in the oxide. Electron micrographs of polymer surfaces which had been separated from the metal oxide revealed clusters of tufts. These clusters were about 1 μm deep and 500–2000 Å in diameter and corresponded to groups of tufts. Thus a mechanical component was clearly indicated as contributing to this adhesion.

More recently, Venables<sup>9</sup> and his team have studied the detailed morphology of the surfaces of aluminium and titanium which have been treated for adhesive bonding by the established etching processes. Sophisticated surface analytical techniques have revealed that these surfaces are both extremely rough and porous on a microscopic scale. Their evidence indicates that there is mechanical interlocking of the polymer of the adhesive which gives much stronger bonds than if the surface had been smooth. Indeed the bond only fails when the polymer itself fails by visco-elastic deformation. In contrast, when the oxide lacks the roughness and porosity and the bond depends for its strength solely on chemical forces across the interface, then separation will occur quite cleanly at the boundary at much lower levels of stress. They have gone on to show that when bond strengths deteriorate as they are exposed to a hostile environment, the cause is a change in the chemistry and morphology of the oxide layer. Aluminium oxide is converted to

hydroxide which is itself weaker and is only poorly bonded to the underlying metal. Similar results have been indicated for titanium.

Thus clear and conclusive evidence has been provided for a mechanical component in the adhesion mechanism for structural adhesives as used in the aerospace industries.

The fundamental explanation for this mechanical contribution to the total strength of adhesive bonds lies in the existence of a zone between the two materials—adherend and adhesive—wherein both are present. This zone depends upon the interpenetration of the one material into the roughness of the other. Its depth will be governed by the extent of this roughness and the completeness of penetration. In order to separate the two, energy will have to be expended and work done in order to deform and draw the material of lower compliance. This is always provided that the surface features of the roughness of the more rigid material are strong enough to withstand the force and do not themselves fracture. It is this energy which is reflected as extra bond strength.

### **Adsorption interactions**

Any ideal solid material has a mechanical strength of cohesion which depends upon the various forces of attraction between the fundamental particles of which it comprises. The nature of these forces of attraction are varied but include ionic attractions, covalent bonds, hydrogen bonds and van der Waals' forces of several types. Which are the most important in any particular case depends upon the chemistry of the material but the van der Waals' forces are universally present, whichever of the others may also be involved. This strength will be modified and reduced in all real structures (except in a very specialised instances) by various flaws and imperfections in the structure and especially in the immediate surface layers.

It has been recognised for a long time that all the forces which provide cohesive strength in a uniform solid may also be available to provide adhesive strength across the interface in a joint between two materials.<sup>10</sup> The common feature of these forces is that all of them are only effective over distances which are comparatively short on an atomic scale, at most a few tens of angstrom units. So if they

are to be invoked across an interface between two materials, it is a necessary first requirement that they must be in the closest and most intimate contact.

It is from this requirement that all the concern for wetting and spreading springs.

This concept of the origin of forces of adhesion also links the whole of this science with the main stream of physical chemistry in two ways. First of all, there are all the classical studies of the adsorption of gases and, to a lesser extent, liquids on solids. While the detailed mathematics and theories associated with the names *inter alia* of Langmuir and Brunauer may have little immediate correlation with, for instance, the interaction of an epoxy adhesive system with a prepared metal surface, yet the fundamental ideas of interaction between two sets of different molecules are common to both. The considerations of physical and chemical adsorption have direct parallels in our exposition of the fundamentals of adhesion. Secondly, all that part of surface science which considers the energy relationships of interfaces and the origins of surface tension and energy is of direct and immediate relevance.

The magnitude of the attraction arising from the entirely universal dispersion forces is, at first sight, unexpectedly high. For two perfectly plane parallel plates when the centres of molecules comprising the surface layers in each plate are separated by  $10 \text{ \AA}$ , the attractive force is about  $10^8$ – $10^{10}$  dynes  $\text{cm}^{-2}$  and if the separation is increased to  $100 \text{ \AA}$  the force is reduced to  $10^5$ – $10^7$  dynes  $\text{cm}^{-2}$ .<sup>11</sup> The magnitude of these forces depends upon the material and is greater between two metals and is about an order of magnitude less between two dielectrics. So there is a potential source of strength here considerably greater than is normally achieved in real adhesive joints and their involvement in adhesion has been extensively considered.

The relationships involved can be seen to originate in Dupré's equation<sup>12</sup> for the reversible thermodynamic work of adhesion  $W_A$  to separate two phases which are originally in intimate contact to give two clean surfaces. This gives the relationship:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12}$$

when  $\gamma_1$ ,  $\gamma_2$  are the surface free energies of the two phases and  $\gamma_{12}$  is the interfacial free energy between them.

Good and Girifalco<sup>13</sup> estimated this interfacial free energy by considering the ratio of this free energy of adhesion to the geometric mean of the free energies of cohesion of the two pure phases:

$$(\gamma_1 + \gamma_2 - \gamma_{12})/2(\gamma_1\gamma_2)^{1/2} = \Phi$$

They showed that in the simplest cases  $\Phi$  is approximately unity. So

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1\gamma_2)^{1/2}$$

and

$$W_A = 2(\gamma_1\gamma_2)^{1/2}$$

Fowkes<sup>14</sup> proposed that this work of adhesion was the result of contributions from a variety of interactions across the interface. These may include dispersion forces, hydrogen bonds, dipole/dipole and dipole/induced forces, acid/base interactions and in addition perhaps covalent bonds. Further he suggested that these contributions might be combined by a simple addition, thus

$$W_A = W_A^d + W_A^h + W_A^x + W_A^i + W_A^{ab}$$

and similarly the surface free energy (and the work of cohesion) could be expressed in terms of contributions from the various interactions

$$\gamma = \gamma^d + \gamma^h + \gamma^x + \gamma^i + \gamma^{ab}$$

where the superscripts represent *d*—dispersion forces, *h*—hydrogen bonding, *x*—dipole/dipole interactions, *i*—induced dipole/dipole interactions, *ab*—acid/base interactions.

These relationships were often contracted to

$$W_A^d = W_A^d + W_A^p$$

where the superscript *p* represented all the polar, non-dispersion forces involved.

Considerable success was achieved by correlations where only dispersion forces were relevant by using the Good and Girifalco relationship. However, this success led to the introduction of similar proposals to write

$$W_A^p = 2(\gamma_1^p\gamma_2^p)^{1/2}$$

which are not justified in terms of the original derivation and the



terms of the approximation which put  $\Phi = 1$ , although they led to useful results in some cases.

More recently, as the fallacies of this type of extension have become recognised, considerable attention has been directed towards the nature and relative significance of the other, non-dispersion interactions.

The first discussion of this was due to Bolger and Michaels<sup>15</sup> who, considering the case of (acidic) polar polymers and (basic) metallic oxides, suggested that the only forces other than dispersion forces which needed to be invoked were hydrogen bonds. These could best be treated using the Bronstead proton definition and theories of acid/base relationships, which gave satisfactory results for these particular examples of adhesion.

Then it was recognised<sup>16</sup> that this sort of treatment might be extended to a wider field by use of the Lewis acid/base definitions and theories which consider electron donor/acceptor interactions.

This most recent consideration<sup>17</sup> was based on the work of Drago<sup>18</sup> on the enthalpies (heats of reaction,  $\Delta H$ ) of acid/base pair reactions. He correlated experimental values with theoretical ones calculated on the basis of four constants, two for the acid and two for the base. The results demonstrated that the dipole interactions did not contribute measurably to the enthalpies of molecular interaction. This conclusion initially appeared to conflict with earlier work on intermolecular forces due to Keesom<sup>19</sup> and Debye<sup>20</sup>, until the differences are recognised between the situation in gases, with which the latter worked, where intermolecular distances are considerable and interactions principally involve only two molecules, and the situation in condensed phases where molecules are close and dipole interactions are minimised by multiple nearest neighbours.

Thus the work of adhesion is now to be considered as effectively arising from two components; the dispersion forces and the polar forces to be considered as acid/base interactions. Fowkes and his co-workers<sup>21</sup> have prepared series of polymers of controlled acidity or basicity by copolymerisation of ethylene with either acrylic acid or vinyl acetate. For each of these series of solids they have estimated the acid-base contribution to the work of adhesion for a series of liquids of known basicity or acidity by measurement of contact angles. In each case a set of smooth curves was obtained

relating the acid/base contribution to the work of adhesion with the degree of acidity or basicity. In addition, for an acidic liquid there was nothing but dispersion force interaction with the acidic polymers and similarly for a basic liquid with the basic polymers.

Adsorption studies of the interaction of polymers in solution in different solvents with inorganic solids confirmed this to be a triangular competition. It involved the dispersion force and acid/base interactions between polymer and solid, between polymer and solvent and between solvent and solid. The differences in dispersion forces cancel out and it is the acid/base competition which controls the adsorption behaviour.<sup>22</sup>

Direct effects upon adhesion can be illustrated by comparison of the adhesion of cast films of basic polymethyl methacrylate on an acidic glass (less than 0.1% alkali metal oxides) and on a basic glass (20% alkali metal oxide). It was difficult to remove the film from the acidic glass but it was quite easy to peel it away from the basic glass.<sup>17</sup>

A survey of the practical use of adhesives indicates that acid/base (electron donor/acceptor) interactions have been utilised largely by empirical, trial and error methods. There is some hope that, for the future, these results may be more directly achieved by consideration of the acid/base characteristics of the substrates and of the polymers used in the adhesives.

So far this discussion has involved only the secondary interaction (van der Waals) forces in the form of dispersion forces, electron pair interactions and dipole interactions (even if these last have been shown to be generally negligible). While, as was shown at the beginning, these secondary interactions are more than adequate to provide high bond strengths, yet there are instances where primary covalent bonding is believed to be involved. This is particularly the case where techniques have been developed to increase the durability of bonds and their resistance to deterioration in hostile environments.

Direct and positive evidence for this mechanism is somewhat sparse but there is considerable indirect evidence. The use of primers or coupling agents, particularly silane compounds, is now extensive especially for the manufacture of glass-fibre reinforced composites. The film of silane is itself polymerised and there is now clear evidence from Laser-Raman<sup>23</sup> spectroscopy and Secondary

Ion Mass Spectroscopy<sup>24</sup> that there are —Si—O—X— groups in the surface (where X represents the surface material) held by covalent bonds. It is believed that it is these covalent bonds which confer upon the interface the resistance to hydrolytic attack under wet conditions which is the particular object of the use of these primers. Indirect evidence also arises from studies where it has been shown by thermodynamic techniques that secondary interactions are insufficient to account for the observed properties of strength and durability.<sup>25</sup>

Direct evidence also arises from introducing quite small amounts (0.001–0.1 mole fraction) of reactive functional groups into the adhesive which often greatly increases the adhesive bond strength.<sup>26</sup> For a number of cases a relationship of the form

$$\sigma_c = \sigma_0 + kC^n$$

applies where  $\sigma_c$  is the adhesive strength when the concentration of functional group in the adhesive is  $C$ , and  $k$  and  $n$  are constants, and usually  $n$  is in the range 0.6–1.0.

Moreover, the effectiveness of functional groups in increasing adhesion shows considerable specificity with the adherend. Thus particular functional groups may be selected for particular adherends where they may give rise to chemical bonding across the interface. For example, carboxyl groups (introduced by copolymerisation with acrylic, methacrylic or maleic acid) will promote adhesion to metals.

### Electrostatic forces in adhesion

Derjaguin and his co-workers<sup>27</sup> developed an explanation for the observed behaviour of pressure-sensitive tapes based upon the development of an electric double layer in the interface. The separation of the adherends and breaking of the bond was accompanied by the drawing apart of the two components of the double layer and the work of adhesion was identified with the electrical energy stored in the capacitor system. The agreement which they reported between theoretical and experimental results appears to ignore the energy which, particularly in peeling tests, is dissipated in the viscous and visco-elastic deformation of the adherents.

The only attempt made in the West directly to develop this

approach used direct tension tests rather than peeling and reported great difficulty in measuring the charge densities and obtained considerably lower values.<sup>28</sup>

The adhesion of thin, vacuum-deposited metal films on polymer substrates has been considered in terms of electrostatic interactions. The experimental facts are that<sup>29</sup> the force needed to remove, by scratching, a thin film of metal from a polymer surface increased with the elapsed time. Suggestions that this might be due to slow oxidation processes leading to the formation of chemical bonds between the metal and the insulator were discounted by the observation that this phenomenon occurred in the case of gold as well as with base metals. Moreover, if a metal film was deposited on a polymer, allowed to age to develop strength and was then exposed to a "glow" discharge, the bond strength dropped almost to zero. It was inferred, reasonably, that this demonstrated clearly the electrostatic origin of the adhesion.

The Russian workers had argued that electron transfer had occurred from the metal to the polymer to equalise their Fermi energy levels. Weaver suggests<sup>29</sup> that this is improbable since it would require an excess energy of about 3 eV to overcome the potential energy barrier at the interface. Instead he postulated positive hole injection with the electron moving from polymer to metal. The nature of the charge-carrying bodies in the polymer is not clear. In any case, the process would be expected to be slow because of the relatively small number of conduction electrons in an insulator like the polymer, and they are likely to be in situations where their mobility is low. Thus a quite slow development of adhesion would be expected—just as is observed. Moreover, the final charge concentration might well depend upon the number of available electrons rather than their energy levels and no relationship would exist between the work function of the metal and the adhesive forces developed.

If one turns from the consideration of adhesion between plane surfaces to the adhesion of fine particles then there is clear evidence that electrostatic forces are significant. This has been demonstrated particularly by experiments<sup>30</sup> with gold particles and has been suggested as important in the retention of pollen on the stamen in flowers and its removal by bees.<sup>31</sup>

More recently, Derjaguin<sup>32</sup> has continued the discussion of the

relative importance of electrostatic forces as compared with the forces of molecular attraction. The particular point which arises is that so long as the distance between the plates of a condenser is small compared with their area then the mechanical force of attraction between them is independent of their distance apart, while the forces of molecular interaction are inversely proportional to the cube of the distance. Thus, while at close distances the electrostatic forces may be small compared to the molecular interactions, as the separation is increased so the relative significance of the forces changes and the electrostatic become more important. So, when the process of breaking adhesive bonds is considered, the electrostatic forces contribute a not insignificant proportion to the total energy involved.

### **Diffusion mechanisms in adhesion**

The classical work suggesting that diffusion is an important phenomenon in some instances of adhesion is due to Voyutskii.<sup>33</sup> Fundamentally, it involves the simple concept that if two polymers are in close contact at temperatures above their glass transition temperatures, then the long chain molecules, or at least segments of them, will interdiffuse. This is undoubtedly true in the examples of the adhesion of a polymer to itself. So when adhesives in solution are applied to two surfaces and the solvent is allowed to evaporate before the two are brought together, it is a diffusion process which is responsible for the combination and eventual disappearance of the interface between the adhesive surfaces.

From this original concept Vasenin<sup>34</sup> developed a series of theoretical relationships derived initially from the theories of mixing and inter-diffusion of liquids. For the autohesion of a polymer to itself, he gave an expression for the force required for peeling separation which was directly proportional to the rate of separation and to the one quarter root of the time of contact, as well as inversely proportional to the two-thirds root of the molecular weight. A number of series of experimental results have been shown to be in accord with these relationships.<sup>35,36</sup> All this approach was criticised by Anand<sup>37</sup> who suggested that the change with time was due to a slow increase in the true area of contact by

rheological processes not involving diffusion. To this Voyutskii<sup>38</sup> replied with qualitative evidence and interpretation.

Much of the evidence in this area is indirect and deductive and only part is direct. However, a number of workers have now studied the interfacial structure by methods which include optical and electron microscopy, radiothermoluminescence, UV luminescence, paramagnetic probe and Fourier Transform, internal reflection IR spectroscopy.<sup>39</sup> Microscopy shows, in some instances, the interface as a band in which the density varies gradually from one phase to the other over a zone which ranges from 10 Å to 1000 Å thick.

The variations of peeling strength with the temperature of bonding of pairs of polymers shows quite sharp increases at temperatures which correspond with changes of the mode of failure from interfacial to cohesive. These changes can reasonably be attributed to the incidence of effective interdiffusion between the adherends.<sup>33</sup>

An alternative approach to this is by consideration of free volume within the polymer systems. Campion<sup>40</sup> developed this for the case of rubbers and particularly considered the free spaces which inevitably occur close to the chains because of their geometry. He was able to correlate the autohesive properties of rubbers with the cross sectional area of holes available for diffusion.

The usual technique for joining polycarbonates or polysulphones is that known as "solvent bonding".<sup>41</sup> One or both surfaces are treated with a suitable solvent and after a short time the two surfaces are brought together under pressure. This produces a good bond and the original interface cannot be detected, although there is a zone in which the polymer has undergone some structural alteration. Here it appears that inter-diffusion has occurred within this bond zone but that is only possible when the solvent has loosened the chains and allowed some mobility. Thus it appears certain that for mutually compatible polymers of similar solubility parameter and at temperatures above their glass transition points then mutual interdiffusion is a prime mechanism of adhesive bonding.

A similar mechanism is involved when a coherent film is formed from a polymer latex. As the dispersing agent is lost there is a phase inversion and the polymer particles which were originally the disperse phase now become the continuous phase. At this stage the

long chain polymer molecules begin a process of interdiffusion which entirely eliminates the particle boundaries.

It has been suggested that the mechanism whereby an adhesive penetrates into the fine structure of a metal oxide is one of diffusion of the polymer into the interstices of the oxide.

## CONCLUSION

It is now quite clear that none of the accounts of the mechanism of adhesion has any reasonable claim to covering all the situations; none is a panacea. It is necessary to make this assertion because, certainly in the past, protagonists have been over-enthusiastic in their support of, and claims for, their particular theory to the exclusion of alternative explanations. Also, more recently, it has been suggested that there is not an accepted explanation of adhesion because people have not recognised the multi-component nature of the problem.

Undoubtedly, in every case where two phases are brought together there will be dispersion forces acting between them tending to hold them together. How far these ubiquitous forces will be sufficient for practical bonding will depend upon the extent and intimacy of the contact, but they will inevitably contribute to the total interactions.

Supplementary to these there are the specific interactions which have been considered under the adsorption headings. It now appears that the dipole interactions which had been postulated are insignificant compared with those arising from electron donor/acceptor interactions. These interactions are primarily considered in the Lewis view of acid/base behaviour and encompass hydrogen bonds. Clearly these are electrostatic forces and there is a convergence of this approach with that of Derjaguin and his co-workers in the strictly electrostatic theory of adhesion. There appears to be a need for a fuller exploration of this relationship between the two methods of consideration.

If we turn to the mechanical component of adhesion it is evident that, other things being equal, a surface which is rough and porous on a sufficiently small scale will result in stronger bonds than one which is relatively smooth. There is even some indication that the

precise morphology of the structure of the roughness has some effect upon the bonding behaviour. It is necessary that the surface, rough or smooth, is properly wetted by the adhesive, probably for two reasons. First of all there must be proper intimate contact between the surfaces of the two phases so that the dispersion and electron interaction forces can be effective. Secondly, the interstices of the roughness must be penetrated so that advantage may be taken of the mechanical effect. At the extreme, the mechanism whereby this penetration is achieved is one of diffusion, so there is a relationship here with the fundamental concepts originated by Voyutskii even in circumstances remote from the areas which he was considering.

So we begin to see that an adhesive bond achieves its strength from the combination of a variety of sources; the adsorption interactions including dispersion forces, acid/base electron donor/acceptor forces and chemical bonds, all of which may be described as electrostatic; mechanical interpenetrations which depend upon topography and flow and diffusion and, in the case of two polymers, interdiffusion of polymer segments. For these various mechanisms, the relative importance and the proper way in which they should be combined will vary from one example to another, but none should be excluded without very careful consideration and exploration. The whole is, usually, greater than the sum of the parts.

## References

1. *First Report of the Adhesives Research Committee HMSO*, London 1922.
2. J. W. McBain and D. G. Hopkins (i) *Second Report of the Adhesives Research Committee HMSO*, London 1926; (ii) *J. Phys. Chem.* **29**, 88 (1925).
3. R. M. Vasenin, *Adhesives Age* **8** (5), 21 and (6), 30 (1965).
4. K. W. Allen in *Aspects of Adhesion* **5**, D. J. Alner Ed. (Univ. of London Press Ltd., London, 1969), Chap. 1, p. 23.
5. J. W. Maxwell, *Trans. Am. Soc. Mech. Eng.* **67**, 104 (1945).
6. E. M. Borroff and W. C. Wake, *Trans. Inst. Rubber Industry* **25**, 199 and 210 (1949).
7. L. E. Perrins and K. Pettett, *Plastics and Polymers* **39**, 391 (1971).
8. D. E. Packham in *Aspects of Adhesion* **7**, D. J. Alner and K. W. Allen, Eds. (Transcripta Books, London, 1973), p. 51.
9. J. D. Venables (i) in *Adhesion* **7**, K. W. Allen, Ed. (Applied Science Publishers, London, 1983), Chap. 4; (ii) *J. Materials Sci.* **19**, 2431 (1984).
10. W. C. Wake, *Adhesion and the Formulation of Adhesives 2nd Ed.* (Applied Science Publishers, London, 1982), p. 9.



11. J. R. Huntsberger in *Treatise on Adhesion and Adhesives Vol. 1*, R. L. Patrick, Ed. (Edward Arnold Ltd., London, 1966), Chap. 4, p. 121.
12. A. Dupré, *Théorie mécanique de la chaleur* (Paris 1869).
13. (i) L. A. Girifalco and R. J. Good, *J. Phys. Chem.* **61**, 904 (1957); (ii) R. J. Good in *Aspects of Adhesion 7*, D. J. Alner and K. W. Allen, Eds. (Transcripta Books, London, 1973), p. 182.
14. F. M. Fowkes, (i) in *Contact Angle, Wettability and Adhesion, Advances in Chemistry 43*, (Am. Chem. Soc., Washington, D. C., 1964), p. 99; (ii) *J. Adhesion 4*, 155 (1972).
15. J. C. Bolger and A. S. Michaels in *Interface Conversion for Polymer Coatings*, P. Weiss and G. D. Cheevers Eds. (Elsevier, New York, 1968), Chap. 1.
16. K. L. Mittal, *Pure and Applied Chem.* **52**, 1295 (1980).
17. F. M. Fowkes, *Physicochemical Aspects of Polymer Surfaces*, Vol. 2 K. L. Mittal, Ed. (Plenum, New York and London, 1985), p. 583.
18. (i) R. S. Drago, G. C. Vogel and T. E. Needham, *J. Am. Chem. Soc.* **93**, 6014 (1971); (ii) R. S. Drago, L. B. Parr and C. S. Chamberlain, *J. Am. Chem. Soc.* **99**, 3203, (1977).
19. W. H. Keesom, *Physik Zeit.* **22**, 129 and 643 (1921).
20. P. Debye, *ibid* **21**, 178 (1920); **22**, 302 (1921).
21. F. M. Fowkes and S. Maruchi in *Organic Coatings and Plastics Chemistry Preprints*, **37**, 65 (1977) (Am. Chem. Soc.)
22. F. M. Fowkes and M. A. Mostafa, *Ind. Eng. Chem. Prod. Res & D.* **17**, 3 (1978).
23. J. L. Koenig and P. T. K. Shih, *J. Colloid & Interface Sci.* **36**, 247 (1971).
24. M. Gettings and A. J. Kinloch, (i) *J. Material Sci.* **12**, 2511, (1977); (ii) *Surface Interf. Analysis 1*, 189, (1980).
25. K. W. Allen, L. Greenwood and W. C. Wake, *J. Adhesion 16*, 127, (1983).
26. S. Wu, *Polymer Interface and Adhesion* (Dekker, New York, 1982), p. 420.
27. (i) B. V. Derjaguin, *et al.*, *Proc. 2nd Int. Congr. Surface Activity Div. VI(c)*, BP 595 (1957). (ii) B. V. Derjaguin and V. P. Smilga in *Adhesion: Fundamentals and Practice* (McLaren, London, 1969), p. 152. (iii) B. V. Derjaguin *Research 8*, 70 and 365 (1955).
28. S. M. Skinner, R. L. Savage and J. E. Rutzler, *J. App. Phys.* **24**, 438, (1953).
29. C. Weaver (i) in *Adhesion: Fundamentals and Practice* (McLaren, London, 1969), p. 46. (ii) in *Aspects of Adhesion 5*, D. J. Alner, Ed. (Univ. of London Press Ltd., 1969), p. 262.
30. H. Krupp (i) *J. Adhesion 4*, 83 (1972) and **5**, 269, (1973). (ii) in *Aspects of Adhesion 8*, K. W. Allen, Ed. (Transcripta Books, London, 1975), p. 187.
31. Sir James Beaumont, Private communication.
32. B. V. Derjaguin and Yu P. Toporov in *Physicochemical Aspects of Polymer Surfaces*, K. L. Mittal, Ed. (Plenum, New York and London, 1983), p. 605.
33. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers*, translated by S. Kaganoff and edited by V. Vakula (Interscience, New York, 1963).
34. R. M. Vasenin (i) *RAPRA Translations* 1005, 1006, 1010, 1075, R. J. Moseley (1960-63), (ii) *Adhesives Age 8*, (5) 21 and (6) 30 (1965).
35. J. D. Skewis, *Rubber Chem. Tech.* **39**, (2), 217 (1966).
36. W. G. Forbes and L. A. McLeod, *Trans. Inst. Rubber Ind.* **34**, 154, (1958).
37. J. N. Anand, *J. Adhesion 1*, 31 (1969); **2**, 23 (1970); **5**, 265 (1973).
38. S. S. Voyutskii, *ibid.* **3**, 69 (1971).
39. N. H. Sung, *Polymer Eng. Sci.* **19**, 810, (1979).
40. R. P. Campion (i) *J. Adhesion 7*, 1 (1975); (ii) in *Adhesion 1*, K. W. Allen, Ed., (Applied Science Publishers, London, 1977), Chap. 5.

41. W. V. Titow in *Adhesion* 2, K. W. Allen, Ed. (Applied Science Publishers, London, 1978), Chap. 12.

In addition to the above particular references four general sources have been used considerably:

A. J. Kinloch, *J. Materials Science* **15**, 2141 (1980) and **17**, 617 (1982).

W. C. Wake (i) *Adhesion and the Formulation of Adhesives*, 2nd Ed. (Applied Science Publishers, London, 1982) (ii) *Polymer* **19**, 291, (1978).

Souheng Wu, *Polymer Interface and Adhesion* (Dekker, New York and Basel, 1982).