

CHAPTER I
INTRODUCTION AND REVIEW

Adhesion has been defined as the state in which two surfaces are held together by interfacial forces of attraction, owing to the interactions of molecules, atoms and ions in the two surfaces¹. These forces range in magnitude from the strong chemical bonds formed when two atoms share electrons, or when electric charges attract each other, to the comparatively weak attractive forces, known as van der Waal's interactions, which are found whenever two substances are placed in intimate contact.²⁻⁶

The interaction, i.e., adhesion, between two different materials across an interface may involve either chemical or physical bonding. Chemical bonding consists of direct interlinking between molecules of the two materials, e.g, the adhesion may result from mechanical interlocking or from the forces of physical adsorption between adhesive molecules and substrate molecules or by the penetration of adhesive molecules into the substrate by diffusion. Thus, the mechanism of adhesive action is quite different for various types of adhesives and substrates. The five main mechanisms currently in vogue are reviewed below; they are considered mainly from the viewpoint of adhesives, but many of them also apply to coatings.

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I.1 MECHANISMS OF ADHESION

I.1.1 Mechanical Theory :

The layman's view of adhesive action is usually one of mechanical interlocking of components i.e., the adhesive interlocks around the irregularities or pores of the substrate. However, when the adhesion to a rough surface is considered, other factors must be taken into account. A rough surface will have a larger potential bonding area than a smooth one. On the other hand, stress concentrations due to voids may be important⁷. Kinloch⁸ has emphasised that the energy dissipated viscoelastically and plastically during fracture may be much larger with a rough surface. Therefore, if roughness is increased by a surface treatment, the reasons for the changes in adhesion may be complex.

The mechanical view of adhesive action is well typified by the layman's approach to glueing wood. The wood is cleaned and 'roughened' with glass paper in order that the glue may penetrate irregularities of the surface and thus 'lock' into it. The electroless method of plating certain plastics with metals may be taken as a very good example of adhesion where mechanical interlocking is thought to be an essential feature of the process. In this method of plating, the metal penetrates into the polymeric material, the surface of which is etched with chromic acid, sensitised with SnCl_2 solution followed by a silver or palladium salt and then made conductive by having a Cu or Ni salt reduced on it. The materials commonly used

for this purpose are high impact polystyrene and ABS rubber. Perrins and Pettett⁹ reported a comprehensive investigation on the effects of different acids concerned in adhesion. The adhesion was assessed by measuring the peel force required to remove the metal. From the experiments it was observed that only the suitable mechanical component and the proper chemical surface taken together produce the highest bond strength. Packham^{10,11} studied the adhesion of polyethylene to aluminium carrying a porous anodic film. The peel force increased with length of pores and decreased as porosity decreased, which can be explained considering mechanical keying. Allen and coworkers¹² also noted a qualitative effect of surface roughness in bonding titanium alloys with epoxide adhesives.

Mechanical factors have also been shown to be important in adhesion to textiles and other fibrous masses^{13,14}. Adhesion to leather also appears to be governed by factors which imply a strong mechanical component. To obtain good adhesion to leather, it is necessary to roughen the surface and thus raise the fibres of the corium and for the adhesive to surround and embed them. Haines¹⁵ showed, by means of superb photomicrography, the need for a continuous film of adhesive to remain between leather adherends and the significance of surface roughness of the adherends.

In brief, adhesive joints frequently possess an important mechanical component essential for the performance of the joint but this type of component cannot suffice as the

sole mechanism whereby surfaces are joined. It must be enhanced by, just as it enhances, specific adhesion.

I.1.2 Diffusion Theory :

The interdiffusion of high polymers across an interface is possible when the polymers are at temperatures above, preferably greatly above, their glass transition temperatures. It is an important adhesive process and the basis of the self-tack of rubbers for which the term autohesion was coined by the Russians.¹⁶

Voyutskii¹⁷ and Vasenin¹⁸ in particular have been strong advocates of the diffusion mechanism. Voyutskii's experimental evidence is based mainly on autohesion experiments where substrate and adhesive are identical. In particular, he studied the bonding of rubbers at elevated temperatures and found that the joint strength increased with increased period of contact, increasing temperature, increasing pressure, decreasing molecular weight and addition of plasticiser, and decreased with crosslinking.

A fundamental feature of the theoretical treatment of diffusion is that thermodynamic compatibility must exist between the materials. With autohesion there is no problem, but the theory could not be automatically applied to adhesion of, say for example, PMMA ($18 \text{ MJ}^{1/2} / \text{m}^{3/2}$) and unplasticised PVC ($19.4 \text{ MJ}^{1/2} / \text{m}^{3/2}$). However, adsorption of one polymer onto

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the other with perhaps some adlineation of dipoles might be considered a more probable explanation for their adherence. Voyutskii performed studies based on luminescence analysis in U.V. light and showed that an interfacial zone existed between these two polymers, about $0.4 \mu\text{m}$ wide in which interdiffusion occurred but there was no interdiffusion of polybutylmethacrylate i.e., PBMA (solubility parameter $16.6 \text{ MJ}^{1/2} / \text{m}^{3/2}$) and PVC (solubility parameter $19.4 \text{ MJ}^{1/2} / \text{m}^{3/2}$).

Less fundamental in the physicists' sense but definitely relating autohesion to diffusion is Campion's¹⁹ semi-empirical use of the Kauzmann-Eyring theory of diffusion in liquids. This is a kinetic theory in which segments of the polymer move into spaces or 'holes' when random fluctuations allow holes of requisite size to form at or diffuse to sites contiguous to the segment. The hole, formed by thermal fluctuations of the surrounding polymer molecules, precedes a jump by the segment and the sum of the process over many molecules constitutes the diffusion process.

Anand and coworkers²⁰ have concluded that the kinetics of bond strength is adequately accounted for by rheological processes involved in making intimate contact without diffusion being involved. On the other hand, Bister, Borchard and Rehage²¹ have detected stages in the autohesive (i.e., diffusive) combination of rubbers during which different rate processes apply