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 surfaces[1]. 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.

chemical bonding?

Langmuir?

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 important[7]. Kinloch[8] 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 Pettett[9] 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 coworkers[12] 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. Haines[15] 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]

Voyutskii[17] and Vasenin[18] 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 $MJ^{1/2}/m^{3/2}$) and unplasticised PVC (19.4 $MJ^{1/2}/m^{3/2}$). However, adsorption of one polymer onto

what - the numbers mean!

CHAPTER - 1

INTRODUCTION

Uses of synthetic polymers are increasing day by day and is expected to be doubled in volume by the end of this century, if raw materials are available. In recognition of the growth potential of the polymer industries together with the problem of high raw materials cost due to sharp rise of feed stocks prices which are mostly derived from petroleum oil and the uncertainties in availability of sufficient petroleum feed stocks in near future, interest has now increased in the use of natural, regenerable polymers and intermediates. In particular, low-cost extenders for synthetic plastics and rubber, and total replacements, wherever possible, for certain types of synthetic polymers used in plastics and rubber industries may be mentioned.

Cellulosics have played a major role in the development of polymer industries, and still retain a not unimportant place. When considering natural polymers, however, starch-chemically similar to cellulose - is often overlooked. Starch is produced by all plants and a large quantity of this is harvested annually throughout the world which is used mainly as a food stuff with certain other conventional applications in paper, textile, adhesives, thickeners etc. During the last fifteen years or so, concerted efforts have been made to widen its applications to newer fields, particularly for use in the polymer industry[1].

Apart from its cheapness, advantages have been taken of the occurrence of starch in nature in relatively pure form, its amorphous nature and functionality (containing - OH groups which can be used as sites for various chemical modification) and its biodegradability for specific applications. Elegant chemistry has been applied to convert the starch structure into derivatives, following, for example, the xanthate route familiar with cellulosics. Another approach was its oxidation by periodic acid to starch dialdehyde. Some of the resultant products showed promise as reinforcing fillers for rubber or as components of film-forming compounds for cast films.

Comparison of the economics of starch as a filler for polymer materials with other conventional fillers is not simple. Fillers are bought by weight and used by volume, so that specific gravity is a critical consideration. In this respect, dry maize starch (specific gravity, 1.24) is twice as effective as chalk (Sp. Gr., 2.7) and significantly more efficient than common reinforcing carbon black (Sp. Gr., 1.8).

But the costs of mixing vary from virtually zero (e.g. with PVC, normally hot compounded, so that the addition of filler only requires stirring) to substantial extra expense where special masterbatches are needed. The low surface area of starch enables very high masterbatch loading (upto 100 per cent by weight) to be achieved, and the energy required for dispersion is minimal[2].

Regarding the cost of chemical modification of starch, if necessary, to improve compatibility between the hydrophilic starch structure and the hydrophobic synthetic polymers including elastomers, it may not always be necessary to modify chemically the whole bulk of the starch phase ; only the hydroxyl groups at the interface need attention, since it has been recognized that the dominance of the starch/polymer interface determines the properties of composites[3]. Simple chemical treatment to create a hydrophobic surface on the starch grains demands less than 0.25 per cent by weight of reagent[2]. It has also become apparent that the narrow particle size distribution of the natural starches causes far less viscosity increase in polymer melts and plastisols than did equivalent volumes of traditional mineral fillers.

In certain cases, however, bulk modification of starch is recommended where the dispersion of surface modified starch into the matrix polymer is poor or imparts inferior properties to the composites.

1.1 Source, Composition and Chemical Structure of Starch

Next to cellulose, starch is the most abundant natural polymer (carbohydrate), and occurs in most plants. Starch is synthesized and stored by plants in the form of small particles, the starch granules. The starch type and its contents, however, vary depending on the source type (Table 1.1).

Most starches are composed of two structurally differing polysaccharides, the linear amylose and the branched amylopectin. Both are polymers of D-glucose, and are uniformly distributed throughout the starch granules[4]. In common starch, the amylose constitutes about 20 - 30 per cent of the starch weight but it varies over a wide range depending on the starch type (Table 1.1).

The noncarbohydrate components found in commercial starch amount normally to no more than 1 per cent of starch dry weight. They include fatty acids, proteins, [illegible]

[illegible] materials [illegible] produc[illegible]

mylose, the linear component of common starch, [illegible]

mopolymer of D-Glucose. [illegible] is a ho[illegible]