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# ADHESION PROMOTERS – ORGANO-SILANES AS PRE-TREATMENT OF SUBSTRATES SURFACE

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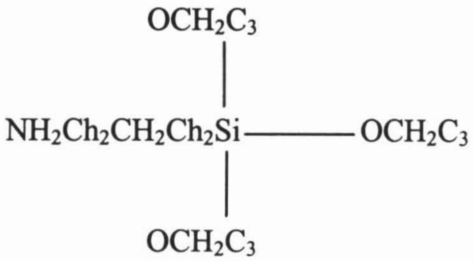
## ABSTRACT

The principle behind adhesion promoters is the enhancement of the interfacial bond strength either by reacting chemically with both the phases' or/and by altering the ctitical surface tension. These promoters which are sometimes referred to as coupling agents, form molecular bridges by reacting with free radicals and atoms between the inorganic substrate/s surface and the organic polymer matrix at the interface. These reactions can be easily achieved by selecting coupling agents bearing functional groups that can react with the polymer and the substrate. Organosilances are among the oldest adhesion promoters known and has been subjected to much study. This paper intends to introduce and discuss much of the findings and theories that has been put forward on the mechanisms of adhesion enhancement by organosilane compounds.

## INTRODUCTION

Among the oldest adhesion promoter and that has been subjected to much research is the family of organosilanes. The general formula for a silane is $R'\text{-}Si'(OR)_3$ where R' represents an organic functional group that can react with the polymer while – $(OR)_3$ is the hydrolysable alkoxy groups. A typical silane coupling agent is shown below:



$$\begin{array}{ccc} & \mathrm{OCH_2C_3} & \\ & | & \\ \mathrm{NH_2Ch_2CH_2Ch_2Si} & \text{———} & \mathrm{OCH_2C_3} \\ & | & \\ & \mathrm{OCH_2C_3} & \end{array}$$

3-aminopropyltriethoxysilane

Theories on adhesion promotion by silanes are much based on the coupling theory. Thus when in use, the silane end is hydrolysed in the presence of water and forms strong chemical bonds with the substrate, leaving the functional group to react with the polymer. The overall adhesion enhancement is due to the bridging effect of the silane molecule between the polymer and the substrate.

Silanes can be used as a primer or as additives. As a primer, the silanes are usually prehydrolysed first in an aqueous medium before application to the substrate. While as an additive, silanes are normally added into the coating system. Silanes used as additives have the property of accumulating at the substrates. The alkoxy group will react directly with the hydroxyl groups on the mineral surfaces according the the hydrolysis reaction. Other than that, silanes can also reat with surface moisture to form silanol groups, which have strong hydrogen bonding tendencies.

Other adhesion promoters employed have been reviewed by Sathyanarayana and Yaseen (1), but for more specific systems. Among them are amide/imide promoters, siloxanes, naphthenates (metallic soap), organic titanates, organophoshous enamines and zircoaluminates.

When glass fibres were used as reinforcements in organic resins, the neef for new bonding technique emerged. This was largely because the techniques employed at that time were unable to retain their bond strength during prolonged exposure to the at atmosphere. The loss of strength was much due to the debonding of the resin from the hydrophilic glass by water.

This compound contain an organic functional group, R'-and a hydrolysable alkoxy group –OR. The use of organosilane compounds as coupling agents was based on the fact that it is a hybrid compound of organic and inorganic silica and therefore is believed to have the ability to bridge a mineral surface, especially glass to an organic polymer through chemical interactions (2).

Silane compounds may be applied as a surface modifier, a primer or as adhesives. As surface modifier, the thickness may only be a monomolecular layer, although in practice this is seldom acheived. In this case, the material functions to chemically modify a surface without contributing any mechanical film properties of its own.

As a primer, it must have adequate physical and mechanical film properties. The primer may be that of hydrolysed silane or silane modified polymer. Solvent is normally used in this case to aid uniform coverage of the surface.

As an adhesive, the pure silanes are normally used as gap-filling polymers or polymer precursor to improve surface adhesion between solid adherents. The monomers may also be used in integral blends of fillers and liquid resins in the preparation of composites. The modified polymer "adhesive" in this case is termed as matrix resin.

In coating systems, silane can be deposited on the substrate's surface from solutions or can act as additives in the coating. When deposited from solution, the silane layer is normally in the form of a multi-layer film with variable orientation, depending upon conditions of deposition. It is argued that, a major portion of the deposited film can be removed by water or organic solvents leaving a small residue retained strongly on the substrate's surface. It is this last trace coupling agent on the surface that is necessary for improved adhesion (3).

When used as additives, the silane is dissolved into the resin prior to application on substrates. When in contact with the substrate, the silane will migrate towards the interfacial region to react with the absorbed moisture present at the hydrophilic surface of the substrate to produce silanol groups which bond to the surface (4).

## 2.0 GENERAL ISSUES ON ADHESION ENHANCEMENT THROUGH SILANE COUPLING AGENTS

### 2.1 *The Chemical Bonding Theory (Coupling Theory)*

In this theory the coupling agent contain within itself chemical functional groups that can react with the mineral surface at one end and with the resin at the other end (5) to form a water resistant "bridge" across the interface. In order to achieve this, the alkoxy group is first hydrolysed. The hydrolysed end will then react with the mineral or glass surface to form strong chemical bonds. The hydrolysed end of a molecule may also react with its neighbouring molecules through the of Si-O-Si bond formations to form a polymeric structure of silane film. Meanwhile, the organo functional group will react with the adhesive resin.

There has been a lot of controversial arguements raised on this theory. For example, this theory cannot explain why certain silanes are effective adhesion promoters even though they have organo functional groups that are incapable of reacting with the resin (6). Secondly, the proposed formation of the metalsiloxane bonds are easily susceptible to hydrolysis, yet organosilane compounds are successfully used as adhesion promoters (7).

Moving on to the issues regarding bonding of the hydrolysed alkoxy group to the mineral surface. The commonly proposed theory, is that, this group will form hydrogen bonds with the hydroxyl groups of the mineral surface and then condense to form strong covalent oxane bond with it. However this theory does not seem to agree with some experimental observations. For example, Plueddeman's (8), work with methacrylate functional silane, showed that when it is applid on glass, its mobility was considerable, as shown by its ready displacement by acetoxy propylsilanols.

Nevertheless, when glass surface is treated with methacrylate functional silane, it can produce a very good polyester laminate. This lead him to comment that either the oxane condensation with the glass was not necessary or even if it does takes place, then it will have to be during the curing process of the laminates. More recently, van Ooij and Sabataj (9) studied the adsorption of $\gamma$-aminopropyltrimethoxysilane on steel substrates by using TOFSIMS technique. The results show that the formation of the Fe-O-Si bond was observed when treatment was done from a silane solution of pH 8.0 but not from a silane solution of pH 10.5. The disappearanc eof the Si-O-Fe signal at pH 10.5 cannot be due to formation of thicker film, as the intensity of the $Fe^+$ peak indicates that the thickness of the deposited film at pH 10.5 was in fact lower that that at pH. 8.0. This is vital as the sampling depth of TOFSIMS is in the order of two molecular layers (10).

On the other hand, infrared analysis by White (11) have shown that silanol monomers can react with surface hydroxyls to form a chemisorbed monomer. These monomers may then condense to form complex oligomers which can also react with the surface hydroxyls.

Study by Gettings and Kinloch (12), on $\gamma$-glycidoxypropyltrimethoxy silane on mild steel was conducted using the static secondary ion mass spectroscopy method. The presence of an ionic peak in the spectrum attributed to that of $FeOSi^+$ radicals was attributed towards the formation of the Si-O-Fe bonds.

With regards to the reaction of the organofunctional group with the resin, early studies by Plueddemann shows some indirect evidences of coreaction between polymer resin and the organofunctional silane deposited on glass. For example, he compared the wt and dry adhesion strength of polyester laminates coated over glass treated with vinyl and allytricholosilane to that of ethil and propyltricholosilane (13). It was found that the adhesion strength of the laminates was much higher in the former system than the latter.

In another work, Walker (14) also found that organosilanes of the vinyl and methacrylate functional type are effective adhesion promoters for sytrenated alkyds and acrylic paints on aluminium and mild steel substrates.

A more direct approach was conducted by Ishida and Koenig (15). Here the silane interphase region of glass fibres treated with methacrylate functional silane coated with styrene-diluted polyester, was observed during curing, using the FTIR method. He found that the silane multilayer molecules polymerise completely during resin cure. From the carbonyl frequencey of the polymerised silane, he concluded that true co-polymerisation of the couping agent and the resin had taken place.

## 2.2 *The Wetting And Surface Energy Factor*

Zisman (16) concluded that good wetting of adherent by liquid resin is vital in preparing good composites. In order to obtain good wetting of the surface, the adhesive must be of low viscosity and that its surface tension must be lower than the critical surface tension of the mineral surface. Although this is true in cases where licquid adhesives is applied on to solid mineral surfaces, the hydrophilic nature of most mineral surfaces will cause the atmospheric moisture to be adsorbed on to it, causing the surface tension of the surface to be lowered. Hence poor wetting of non-polar adhesive may occur on such surfaces. However, polar adheseves may be able to adsorb or displace the water through surface chemical reaction. Therefore, it seems that for organosilane to be effective as coupling agents, the surface tension of the resulting surface must be considered. When the mineral surface is fully wetted by the silane treatment, it will now have a new surface tension value.

This value is usually defined by the nature of the deposited silane such as its orientation and the type of organofunctional group it bears.

However the critical surface tension brought about by silane treatment on mineral surface, that leads to good wetting by the resin, by itself cannot explain why some silane sare effective and why some are not. For example, Plueddemann (17) reported that in theory, a treated glass should preferably have a minimum $y_c$ value of the surface was 40.5 and 43.5 dyne/cm. On these surface, however, the adhesion of the polyester was found to be very poor.

It is therefore thought that for adhesion promotion by silane, other factors than wetting ability of resin, may be of more significant. A comparison of the reactivity to the solubility factor of silanes for polyester's adhesion on glass was conducted by Plueddemann (18). It was found that unreactive silanes do not improve the polyester's adhesion on glass, while for the reactive silanes, the performance is parallel to the silane's organofunctional reactivity rathen than its solubility to the polyester resin. For example, the methacrylate functional silane has the same solubility to polyester as the crotonate ester silane. Adhesion of the resin was found to be greatly enhances by the former thatn the latter. Therefore it seems like the reactivity of silanes in copolymerising with the resin is more important than wettability of the treated glass surface.

### 2.3 *The Surface Morphology Factor*

It has been proposed that the interfacial morphology of polymers on a substrate is important in determining the adhesion of the polymer (19).

Although there is much confusion over what type of morphology of the adjacent polymer is desired, it seems that a deformable interphase is favourable in order to accommodate the stress at the interface due to coating shrinkage during curing processes. At the same time, it is also though that silane pre-treatment on substrates can effect the morphology of the adjacent polymer coating in order to improve adhesion. However it is still uncertain whether the amount of silane deposited is sufficient to provide a low modules layer at the interface as required by the deformable layer theory.

Another theory, suggested that silane coupling agents function by "tightening up" the polymer structure at the interphase region. This is in line with work of Kumins and Roteman (20) who suggested that the resin adjacent to the interface region should have a modulus in between that of the polymer and the substrate. Gaehde (21) in his experiment, treated kaolin with vinyl, methacrylate and aminopropyl silanes and used it as a filler in polyethylene. The mode of action of these silanes were determined and their effect on the mechanical properties of the composite was compared. The vinyl silane chemically reacted with the polymer and was termed as "grafted" into the polyethylene at the interphase region, while the methacrylate and aminopropylsilane forms a homopolymer structure at the interface region. It was discovered that the strengths (both tensile and flexural) of the composite formed was higher for the methacrylate and aminopropyl silane system than the vinylsilane. This observation was attributed towards the effectiveness of methacrylate and aminopropylsilane in increasing the crystalinity of polyethylene at the interface. It was therefore concluded that the mechanical properties of kaolin filled polyethylene is more dependent on the polymer structure at the interface than on the chemical grafting.

### *2.4 The Acid-base Reactions.*

This theory is very much based upon the acid-base reaction in the adhesion theory as discussed in the earlier section. Work by Plueddemann and Stark (22) has shown that acid-base reaction may be important in aligning silane coupling agents on filler surface.

## 3.0 THEORIES OF ADHESION OF SILANES TO HYDROPHILIC SURFACES

Adhesion of silanes on to hydrophilic mineral surfaces is an important phenomenon in the enhancement of adhesion of coatings on metallic substrates like iron. The mechanisms of adhesion of silanes on hydrophilic surface was proposed by Pleuddemann (23). According to this theory, as the silanol groups reached the hydropilic surface, they will be hydrated by the surface water because of their strong hydrogen bonding capacity. These hydrated silanols will then bond to the surface hydroxyls along with the elimination of the water. However, it is not known whether this reaction is through hydrogen bonds or the oxane bond. Nevertheless, it was claimed that either reaction is reversible.

The nature of the bonds provided by the silane coupling agent on hydrophilic surface sis such that it is capable of using the hydrolytic intrusion of water as means of stress relaxation without disrupting the overall bond between polymer and the mineral surface. This reaction is reversible, and therefore in a rigid polymer system, the reactive positions are held in a position that the free silanols resulting from hydrolysis of bond have no place to go and eventually reform the original bond or make new bond with an adjacent group. Therefore as long as the interface is rigid, this bond breaking and remaking in the presence of water is reversible.

It was further argued that, if the polymer is flexible, then, water resistant bonds to hydrophilic surface cannot be formed by the silane coupling agents. This is because the intrusion of water will cause the silanol groups to retract from the surface as individual bonds. Since its reactive position can be moved by the flexible nature of the polymer, it can now no longer be available for new bond formation. A solution suggested to solve this problem is by applying a rigid primer to a silane treated surface prior to applying the flexible polymer.

## CONCLUSION

In summary, it has been recognised that water is needed for bonding of rigid polymer to mineral surfaces. This owes to the fact that water can act as mean of stress relaxation during the curing process of the polymer. In fact it has been observed that in the case of composites of graphite fibres (a non-hydrophilic surface ) in epoxy resin, translaminar cracks were observed even before stress was applied. This was due to the thermal stresses induced during cooling of the laminate (24).

In practical coating systems, low molecular weight materials are in competition with the organic polymers for adhesion to the substrates surface. These materials can form potential weak boundary layers. As such elimination as much of these materials prior to coating is very important. However, the use of silanes as coupling agents especially in rigid polymer systems has proven beneficial due to its ability to compete with these low molecular weight materials for reaction with the surfaces.

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