

The Function of Adhesion Promoters in Adhesive Bonding

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ABSTRACT

The wet strength of adhesive bonds between resins and glass or metal can be substantially improved by applying adhesion promoters to the glass or metal surface. The most widely used of these adhesion promoters are the organofunctional trialkoxysilanes $\text{RSi}(\text{OR}')_3$. Some of the more pertinent research results concerning these silanes have been reviewed in the hope of establishing how they function as finishing agents. Work at NRL and elsewhere indicates that these compounds form polysiloxane coatings on the adherend surface. These coatings consist of a strongly adsorbed polysiloxane network along with a more weakly held material consisting of small polymer molecules and unreacted silane. The polysiloxane network exposes a high density of the organofunctional group R- at the air/silane-coating interface. However, the R- groups are not closely spaced, and, in fact, there is some evidence that the coatings can be penetrated by the adhesive resin. This view of the silane coatings as polysiloxane films is more realistic than some of the previous models, but the research is still a long way from identifying the mechanisms by which these films improve adhesion wet strength. Some new approaches are offered for research into the highly complex but exceedingly important area of adhesion promoters.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

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THE FUNCTION OF ADHESION PROMOTERS IN ADHESIVE BONDING

INTRODUCTION

The adhesion of polymers to glass and metals can be significantly improved by applying to the adherend surface certain chemicals variously known as adhesion promoters, finishing agents, or coupling agents. These agents are particularly effective in improving bond strength under wet or moist conditions. Poor adhesive wet strength is a major problem in materials science, especially in connection with structural adhesives and composites in which organic resins are combined with glass, metal, boron, ceramics, and carbon.

In this report some highlights of recent research on the so-called "silane" adhesion promoters are reviewed. The intent is to develop a picture of the films that these surface-treating agents form on adherend surfaces and to determine if this picture gives any clues as to how these films impede stress corrosion by water. Meaningful research results are meager; therefore, the conclusions reached must be considered speculative.

THE TECHNOLOGY OF SILANE ADHESION PROMOTERS

Before considering the fundamental studies of silane films, it will be helpful to consider how these agents are used in technical practice and how effective they actually are. The silanes have the general formula $R-Si(OR')_3$ and are more properly called H-substituted trialkoxysilanes; the $-OR'$ groups are alkoxy functions, and the R group is referred to as the organofunctional group. Examples of these compounds are listed in the first column of Table 1.

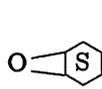
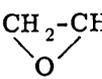
A simple illustration of the effectiveness of silane finishing agents is the ability of γ -aminopropyltrialkoxysilane to increase the bond life in water at 190° F for plates of glass bonded by a thin epoxy layer (1). A bond life of 48 days was observed when the glass plates were pretreated with the aminopropyl compound compared with 1 day when the plates were untreated. The silane film was applied by contacting the glass with a 0.5% aqueous solution of the silane for about 30 sec and then drying at room temperature.

Another example is the improvement in the wet strength of glass-fiber-resin composites (Table 1) (2). Mechanically these tests represent a more complex situation than the bonded plates, but the effect of the silanes is clearly evident. The silane is usually applied by treating the glass cloth with a water or water-alcohol solution of the silane followed by drying to give a deposit of about 1% of the cloth weight (3). More recent technical practice is to add the silane to the liquid resin (2).

The silanes are just as effective in promoting the adhesion of polymers to metals. Data for metal-resin-metal lap joint specimens are given in Table 2 (4) and for metal-powder epoxy composites in Table 3 (5). The use of the silanes to improve resin-metal adhesion is a relatively recent innovation. Previously it was believed that these agents were only useful for resin-to-glass adhesion.

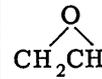
Note: This review was presented at Wayne State University on June 7, 1968.

Table 1
The Performance of Organofunctional Silanes as Adhesion Promoters for Glass-Resin Composites*

Adhesion Promoter	Flexural Strength (psi)	
	Dry	After 8-hr Water Boil
Polyester Resin		
Control	61,000	23,000
$\text{CH}_3\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	43,500	29,700
$\text{CH}_2=\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	69,000	61,000
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	87,000	79,000
Epoxy Resin		
Control	78,000	29,000
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	90,000	54,000
 $\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	101,000	66,000
 $\text{CH}_2-\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	87,000	56,000

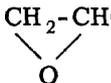
*Ref. 2.

Table 2
The Effect of Silane Adhesion Promoters on Metal-Resin Adhesion*

Resin-Metal	Adhesion Promoter	Adhesion Improvement (%)	
		Dry	After 2-hr Water Boil
Phenolic-steel	$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	60	60
Phenolic-aluminum	 $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	100	150

*Ref. 4.

Table 3
The Performance of Organofunctional Silanes as Adhesion Promoters for Aluminum-Epoxy Composites*

Adhesion Promoter	Flexural Strength (psi)	
	Initial	After 72-hr Water Boil
None	620	470
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$	1240	1310
 $-\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	1240	1200
 $\text{CH}_2-\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	1110	1030

*Ref. 5.

The silane adhesion promoters are not the final answer to protecting adherend/adhesive interfaces from water. The results in Tables 1 to 3 might suggest that they are, but the test methods used to obtain the data were not severe enough, because these methods involved either a static load or no load at all while the specimens were immersed in water. Much greater strength losses are observed when the specimens are fatigue tested; i.e., stress is applied and removed cyclically during exposure. For example, the rate at which filament-wound, glass-resin ring specimens lose their stiffness in fatigue tests is much greater in water than in dry air even though the glass filaments had been precoated with a silane adhesion promoter (6). Indeed, fatigue failure by stress corrosion is so severe as to put into serious question the reliability of military and civilian equipment in which structural adhesives or composite materials are used.

THEORIES OF ADHESION PROMOTING ACTION

Despite the large amount of practical experience with the silanes, no unambiguous mechanism has been established for their action. A number of theories have been proposed, but none is consistent with all facts. However, as working hypotheses, the theories have been useful in developing improved finishing agents. The coupling theory (Fig. 1), which is the most widely held explanation, proposes that the trialkoxysilane finishing agent chemically bonds to the glass surface through interaction of alkoxy groups with surface silanols and bonds to the adhesive by reaction of the organofunctional group with the resin molecules (2,7). The principal argument for the coupling theory is the specificity of the organofunctional groups; those agents most effective for epoxy resins have organofunctional groups capable of reacting with the epoxy groups, and those effective for polyesters have the capability of reacting with polyester molecules.

Efforts to demonstrate that chemical reaction occurs between the resin and the silane finish have not been successful. Chemical bonding with surface silanol groups has been observed in hydrocarbon solution (8) and in the gas phase (9). In both studies the evidence for chemisorption was a decrease in intensity of the surface silanol infrared adsorption band at approximately 3700 cm^{-1} (O-H stretch) when silica powder was contacted with the silane. The silane was presumed to form Si-O-Si bonds by chemically reacting with the surface silanols rather than having been simply hydrogen bonded, since the band at about 3400 cm^{-1} for H-bonded hydroxyls did not appear.

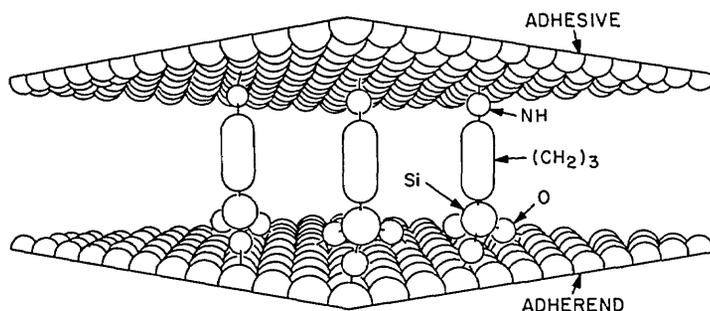


Fig. 1 - The "coupling theory" model

It is questionable if this chemisorption is essential for good bonding. The silanes are effective on metals as well as on glass, and although the trialkoxysilanes may form metallo-siloxane bonds to metal surfaces, such bonds are easily susceptible to hydrolysis (10). This fact makes it difficult to accept an explanation for improved wet strength between metal and resin that is based on the formation of easily hydrolyzed surface bonds.

In the search for explanations other than the coupling theory, various authors have suggested that the adhesion promoters (a) improve wetting of the adherend by the resin (11), (b) form a barrier to water vapor, or (c) modify the mechanical properties (i.e., strength and modulus) of the resin in the vicinity of the adhesive/adherend interface (12-14). No single explanation appears to be consistent with all of the facts, but each has its merits, and it is not unreasonable to suppose that the surface-treating agents are multifunctional.

THE STRUCTURE OF SILANE FILMS

Part of the reason that there is no convincing explanation for the action of adhesion promoters is that so little is known about the chemical and physical structure of the films they form on adherend surfaces. The existing theories are based largely on conjecture, and they ignore the ability of the trialkoxysilane to undergo hydrolysis-polymerization to three-dimensional network polymers. The reactions involved in the polymerization are given in Fig. 2. Note that for every siloxane linkage formed, one molecule of water disappears and a molecule of ethanol is generated. To this extent the silanes can serve as water scavengers. This is probably not a principal function of the finishing agent but may be important whenever the silane is applied from nonaqueous solution or is added to the adhesive resin.

The only extensive study of these hydrolysis-polymerization reactions is the work of Sprung and Guenther (15,16). They investigated the hydrolysis of methyl, ethyl, and other alkane triethoxy- and trimethoxysilanes. They found the reactions to be acid and base catalyzed and that the initial products were small, usually cyclic, polymer units. Under rather special hydrolysis conditions linear polymers predominate. The small polysiloxane fragments react further to form high-molecular-weight network polymers. No similar study has been reported for any organofunctional silanes useful as adhesion promoters. However, the author's experience has been that solutions of these silanes frequently yield highly insoluble precipitates if given sufficient time. This observation suggests that they also polymerize progressively to three-dimensional siloxane polymers.

The first clear evidence that the silane adhesion promoters produce polymer films on glass and metal surfaces was presented by Stromberg, Tutas, and Passaglia (17). They used ellipsometry to determine the thickness of the films formed by aminopropyltriethoxysilane and vinyltris(2-methoxyethoxy) silane from water and methyl ethyl ketone on glass and steel. A 1% solution of the aminopropyl compound in water produced a film of 50 to

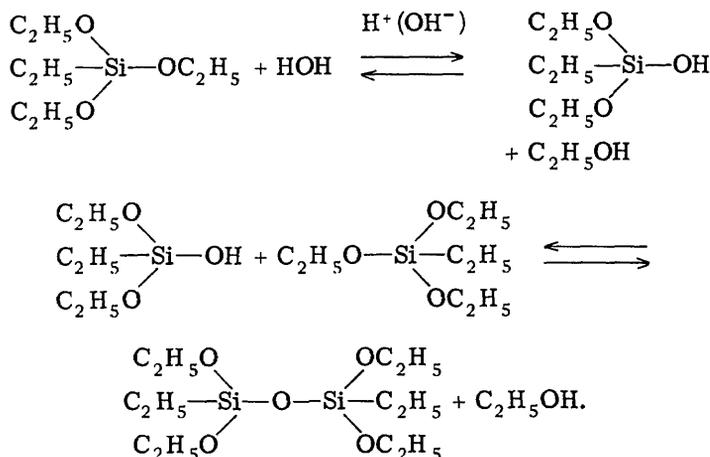


Fig. 2 - Hydrolysis-polymerization reaction

70 Å on glass within a few minutes with no further increase in thickness even after many hours. The vinyl compound adsorbed continuously and produced films as thick as 200 Å after 5 hr adsorption time. A single molecular layer of these silanes would have been less than 20 Å thick. The adsorption of more than a monolayer does not necessarily mean that the film was polymeric, but it is difficult to explain such thick-film formation otherwise. Actually, the film thicknesses determined by ellipsometry were probably underestimated, since the authors assumed the film refractive indices to be the same as that of the pure silane monomers. If the silanes adsorbed in a patchwise fashion or as an open polysiloxane structure, the actual film refractive index would be smaller than the assumed values. An overestimate in film index leads to an underestimate in film thickness (18).

Further evidence that the silane films are polymeric was obtained by Schrader, et al. (19), and Johannson, et al. (13), using C^{14} -labeled silane adhesion promoters. In both studies films were deposited on glass by evaporation from aqueous solution. This usually left a visible coating, part of which could be easily removed by rinsing with water or organic solvents. After rinsing, there remained a film, which, from its radioactivity, was determined to be thicker than a monolayer of the silane and which was more resistant to desorption than can be explained by a thick accumulation of silane monomer. Evidently, these coatings contained unhydrolyzed or partially hydrolyzed silane and small polysiloxane molecules which could be easily removed by solvent. The more tenacious material was probably high-molecular-weight siloxane network polymer which would resist removal because of low solubility in both aqueous and nonaqueous solvents (15). Another factor contributing to the desorption resistance of the polysiloxane network is that wherever a polymer segment has multiple bonds to the surface its removal requires that these bonds be broken simultaneously. This process requires a large activation energy even when the individual attachments involve weak, nonspecific dispersion forces (20).

Although most studies of silane films have been on glass surfaces, very similar films are formed on metals and metal oxides. At NRL a group of fluorocarbon- and chlorocarbon-trimethoxysilanes was investigated on steel, alumina, and gold as well as on glass and silica (21). Table 4 lists some of the properties of these films on steel. The fluorocarbon silanes were especially interesting, since their films could be isolated from solution by retraction. That is, the solution did not wet the adsorbate films so that the substrate emerged dry. Ellipsometric determinations of thickness and refractive index indicated the fluorocarbon-silane films to be hundreds of angstroms thick even after prolonged rinsing with Freon TF, a fluorocarbon solvent (Table 4a). Part of the initial film could be removed

Table 4a
The Properties of Fluorocarbon-Silicon Films on Stainless Steel

Film	d_f (Å)	n_f	γ_c (dynes/cm)	θ_{H_2O} (degrees)
Initial Film				
$CF_3(CF_2)_6CH_2OCH_2CH_2Si(OCH_2CH_3)_3^*$	401	1.34	14	112
$(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_3^\dagger$	59±9	1.3-1.5†	indeterminate	80
Rinsed Film§				
$CF_3(CH_2)_6CH_2OCH_2CH_2Si(OCH_2CH_3)_3^*$	233	1.23	14	116
$(CF_3)_2CFOCH_2CH_2CH_2Si(OCH_3)_3^\dagger$	25±4	1.3-1.5†	20	96

*0.25% solution in α -chloronaphthalene at 70°C with an acetic acid/adsorbate mole ratio of 1/10.

†0.25% solution in α -chloronaphthalene at 25°C.

‡Values were assumed in calculating the film thickness.

§Initial films were rinsed with Freon TF.

Table 4b
The Properties of the Chlorocarbon-Silicon Films on Stainless Steel*

Adsorbate	d_f (Å)	Film Properties		
		n_f	γ_c (dynes/cm)	θ_{H_2O} (degrees)
$p-C_6H_4CH_2CH_2Si(OCH_3)_3$	51-65	1.4-1.6†	47	85
$ClCH_2CH_2CH_2Si(OCH_3)_3$	233	1.35	44	84

*0.25% solution in bicyclohexyl at 70°C with an acetic acid/adsorbate mole ratio of 1/10; the film was isolated by rinsing with acetone.

†Assumed.

by the rinse, and again this material is presumed to be a monomer and low-molecular-weight polymer soluble in the fluorocarbon solvent. A point of interest here is that the low-molecular-weight adsorbate had been left on the surface as part of the adsorption process. In the studies of Schrader (19) and Johannson (13) it was at least possible that the easily desorbed, low-molecular-weight components had simply been left on the surface as the solution evaporated. This could not have been the case for the fluorocarbon-silane films of Table 4a, since they had been obtained by retraction, which left no bulk solution on the surface.

The chlorocarbon-silane films were not oleophobic to the adsorbate solution, so the metal surfaces were rinsed with acetone after exposure to remove the adhering solution. This treatment would have removed any low-molecular-weight siloxane adsorbate. The remaining films resisted further desorption and, like the fluorocarbon-siloxane films, were many times thicker than a monolayer of the unhydrolyzed adsorbate (Table 4b).

In characterizing the silane films, an essential consideration is their molecular structure. The conformation of linear polymers in adsorbed films has been the subject of considerable research (20), but little use can be made of these studies here. First of

all, the silanes form three-dimensional network polymers for which the adsorption behavior is likely to be significantly different from that of linear polymers. Furthermore, film formation by the silanes is actually a process of simultaneous polymerization and adsorption. In the solution the silane monomer undergoes hydrolysis and polymerization. On the surface, the monomer as well as the polymeric products are adsorbed and once adsorbed may undergo further polymerization. The best that can be done is to examine the film produced under a particular set of conditions in an effort to determine its structure but without much hope of identifying the process by which it formed.

Wettability measurements have proved to be a sensitive and informative means of investigating the structure of the silane films. The basis for using wettability measurements to determine the chemical constitution of surface films comes from the studies by Zisman and coworkers (22). The quantitative index of wettability is the critical surface tension γ_c . Briefly stated, surfaces rich in fluorocarbon or hydrocarbon groups have low critical surface tensions ($\gamma_c < 30$ dynes/cm), whereas surfaces containing the more polarizable groups Cl-, NH₂-, or NO₂⁻ have much higher values ($\gamma_c > 40$ dynes/cm). The major limitation in the use of wettabilities to study the chemical makeup of silane films is that the films must first be rinsed free of the low-molecular-weight adsorbate, which might dissolve into or spread onto the test drops.

Films of the silanes usually exhibit critical surface tensions characteristic of the organofunctional group present. This fact is evident from the data in Table 5; the fluorocarbon-containing films had low γ_c values characteristic of fluorocarbon-rich surfaces, and the chlorocarbon-containing films had much higher γ_c values characteristic of surfaces rich in covalent-bonded chlorine atoms. The water contact angles are also those anticipated for fluorine and chlorine-rich surfaces. An important point about these wettability data is that the critical surface tensions were all greater than would be expected for a close-packed array of the fluorocarbon or chlorocarbon group (21). Evidently, the structures of these films are such that the organofunctional groups (fluorocarbon and chlorocarbon) are far enough apart to allow exposure of portions of the siloxane network to the wetting liquids. Keep in mind that these films had been rinsed with acetone or Freon and that their "openness" may have resulted from the removal of low-molecular-weight components.

Before leaving the data in Table 5, it is worth noting that the film wettabilities for a given silane were essentially the same regardless of whether the substrate was glass or metal. Furthermore, the wettabilities of the films on different substrates were not altered by prolonged rinsing with acetone, water, or Freon beyond the initial rinse. Therefore, as far as these experiments could detect, the choice of substrate had no significant influence on film structure or on its ability to resist desorption. It is reasonable to speculate that this independence lies in the polymeric nature of the films. The film structure is determined by the hydrolysis-polymerization of the silane monomer, and these reactions are not influenced by forces emanating from the surface. Once formed the films resist desorption because of their high molecular weight (and low solubility) and not because of any specific surface attachments that may or may not have formed. There must of course be some surface bonds at the film/substrate interface. However, it was noted earlier that each polymer segment or fragment will be multiply bonded to the surface, and even if these bonds are weak—as they must be on gold—the activation energy required for desorption is much greater than is available in the desorption experiments. The statement that the substrate does not influence the polymerization is probably not entirely true. Certainly the kinetics of polymerization of silane molecules held on a surface could be different than for a free molecule in the solution, and there may be kinetic differences from one substrate to another. These effects may be important in the initial stages of film formation, but judging from the data in Table 5 any differences in the adsorption process were not discernible after 20 hr adsorption time.

The wettabilities of several silane adhesion promoter films were determined by Lee (23). His results generally support the two principal conclusions reached here about film

Table 5a
The Wettability of
 $\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{OCH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ Films*

Substrate	γ_c (dynes/cm)	$\theta_{\text{H}_2\text{O}}$ (degrees)
Stainless steel	14	116
Gold	16	118
Pyrex	14	111

*0.25% solution in α -chloronaphthalene at 70°C with an acetic acid/adsorbate mole ratio of 1/10; the film was isolated by rinsing with Freon TF.

Table 5b
The Wettability of Chlorocarbon-Silicon
Films on Various Substrates

Substrate	Wettability	
	γ_c (dynes/cm)	$\theta_{\text{H}_2\text{O}}$ (degrees)
$\text{p-ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3^*$		
Silica	44	85
Pyrex	45	85
Aluminosilicate glass (Corning 1720)	47	88
α -Alumina	44	85
Stainless steel	47	86
Gold	47	87
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3^\dagger$		
Pyrex	43	80
α -Alumina	45	81
Stainless steel	45	82

*0.25% solution in bicyclohexyl at 70°C with an acetic acid/adsorbate mole ratio of 1/10; the film was isolated by rinsing with acetone.

†0.25% solution in α -chloronaphthalene at 70°C with an acetic acid/adsorbate mole ratio of 1/10; the film was isolated by rinsing with acetone.

structure: (a) that the critical surface tensions of the films are characteristic of the organofunctional group present and (b) that although the organofunctional group may predominate at the film/air interface these groups are not close packed. A note of qualification concerning Lee's work is that the films had not been rinsed to remove low-molecular-weight components. They had been formed by deposition from water or water-isopropanol solution onto glass slides followed by drying at 60°C for 1 hr. Drying at this temperature would drive off some of the more volatile components, and as long as there was water present it would advance the polymerization of residual material. However, experience here indicates that even after this treatment there is still some acetone removable material left on the surface.

Mention should be made of another wettability study from NRL, because it gives some insight into the silane adsorption process and into the effect the hydrolysis catalyst has on film structure (24). The study was concerned with the films of ethyl- and vinyltriethoxysilane, and the results for the ethyl compound are given in Fig. 3. In these experiments the films were adsorbed on silica plates from a nonpolar solvent (α -chloronaphthalene) which had a high surface tension so that the films could be isolated by retraction. The essential conclusions were that (a) the ethyltriethoxysilane (ETES) monomer, in the absence of a catalyst, does not form strongly adsorbed films, (b) when the solution contains preformed ETES polymer as well as monomer, the resulting film presents a high density of ethyl and ethoxy groups (low γ_c) and is strongly adsorbed (no change in γ_c or θ_{H_2O} after 1 hr of continuous water rinsing), and (c) finally, from solutions containing the monomer and an organic acid or base catalyst the changes in wettability (Fig. 3) indicate that the film passes through various changes in structure with increasing adsorption time. By 20 hr the films were as strongly adsorbed as from the polymer solutions but had a much lower density of hydrocarbon groups at the air/film interface (high γ_c). These changes in γ_c with time emphasize the "process" aspect of film formation. Over many hours the film continued to "equilibrate" with the solution and not until 20 hr adsorption time was a steady-state condition reached. A number of low-molecular-weight organic acids and bases were used, and with one exception they all lead to films having γ_c values between 20 and 30 dynes/cm and water contact angles of 80 to 90 degrees.

The exceptional catalyst was n-propylamine. When this strong base was used at a ratio of at least 1 mole of amine to 4 moles of the ethylsilane, the resulting film had a γ_c of 39 dynes/cm and θ_{H_2O} of 110 degrees (Fig. 3). Nearly identical values were obtained using the vinylsilane with the propylamine catalyst. The value of 39 dynes/cm is characteristic of a weakly oleophilic surface, such as nylon, but the high water contact angle is characteristic of a hydrophobic surface, such as Teflon. A plausible explanation for this unique oleophilic-hydrophobic behavior is that the film structure is penetrated (or swelled) by the organic test liquids used to determine γ_c but is not penetrated by water test drops. Zisman and Shafrin (25) reviewed the wettabilities of over 80 polymers and adsorbed monolayers, but none of the surfaces showed the particular oleophilic-hydrophobic behavior of the amine-catalyzed films. These unusual wettability properties illustrate that previous experience with close-packed monolayers or with polymer surfaces cannot be indiscriminately extrapolated to the trialkoxysilane films.

TECHNICAL IMPLICATIONS

Although a reasonable picture of the silane film structures is beginning to develop, there is nothing in this picture that reveals the mechanisms by which they reduce the stress corrosive action of water. It is possible that the silanes act as water scavengers, but this action would not apply in aqueous systems. It would be incorrect to view the siloxane films simply as protection barriers, since they are not dense enough to block the diffusion of water molecules. Explanations based on the silanes forming covalent bonds to the adherend are inconsistent with the ability of these finishing agents to improve the wet strength of resin-to-metal adhesion, if we take account of the low water stability of Me-O-Si bonds.

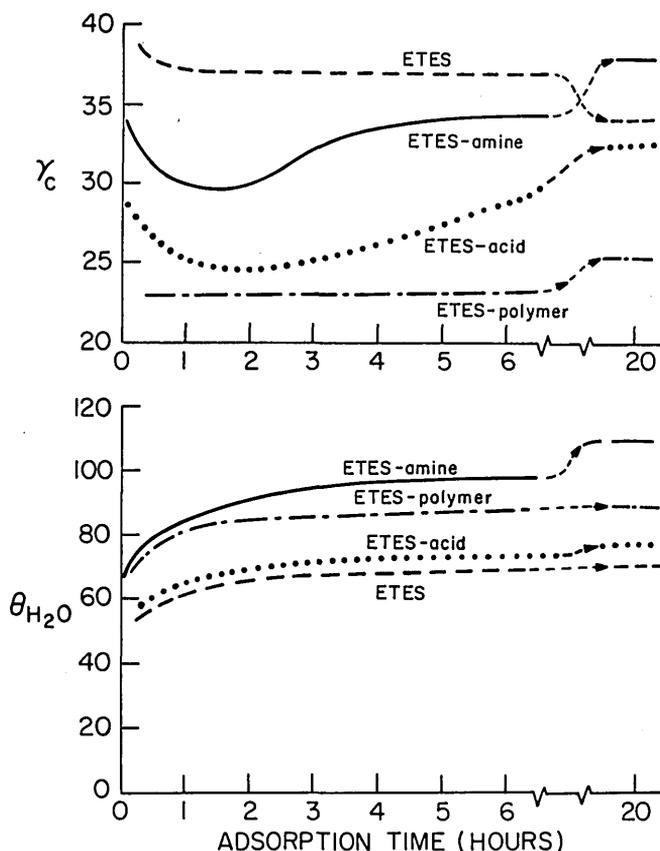


Fig. 3 - The change in critical surface tension and water contact angle with adsorption time for ethyltriethoxysilane (ETES) films on silica

Although the research results reviewed here are severely limited, it is still useful to speculate on what occurs when a liquid resin contacts a silane-treated surface. If the solubility parameter of the silane coating material is close to the solubility parameter of the resin, it is plausible that the smaller molecules of unhydrolyzed (or partially hydrolyzed) monomer and the lower-molecular-weight polysiloxane fragments are dissolved into the resin phase. Furthermore, there may be some penetration of the polysiloxane network by the liquid resin. These events are illustrated schematically in Fig. 4.

The situation illustrated in Fig. 4 is probably too complex to permit a simple relationship between the solubility parameter of the silane coatings and their ability to improve adhesion. Nonetheless, Plueddemann (26) was able to show for thermoplastic resins that, when the solubility parameters of the silane and the laminating resin were close, the wet and dry strength of the laminates were close to optimum. For thermosetting resins, the silanes with organofunctional groups capable of reacting with the resin were decidedly better than the silanes that matched the resin solubility parameter but were incapable of reacting with the resin.

Even if solution and penetration of the silane coatings does occur, it remains to be seen whether these processes are essential to the adhesion promoting action. In fact, there is some evidence that a monolayer coverage of siloxane is sufficient to give substantial (but not optimum) improvement (2,19). For example, in the work of Schrader, et al. (19), a residual monolayer of polyaminopropylsiloxane left after exhaustive water

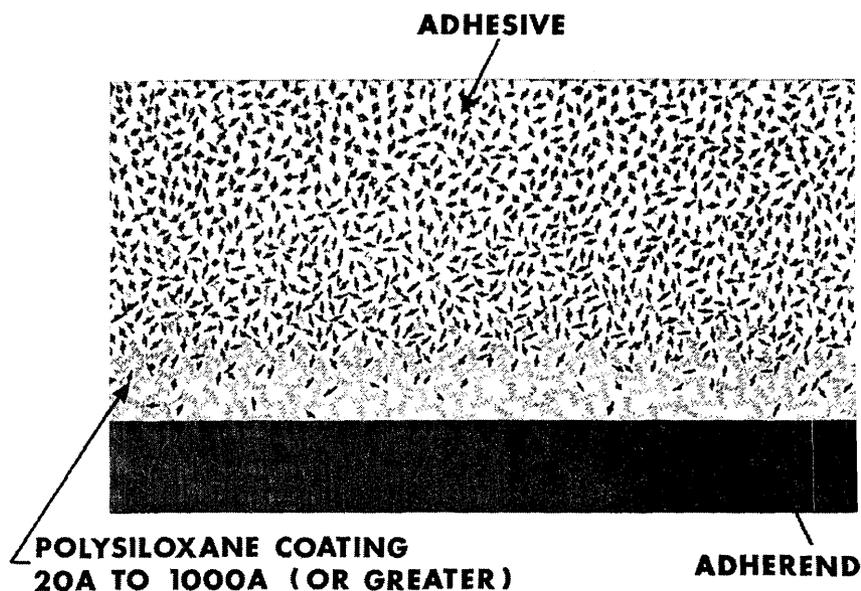


Fig. 4 - A model of the interfacial region between an adhesive resin and the silane-treated adherend surface

desorption was effective in improving the bond life between glass and epoxy held under a static load in boiling water. However, it would be seldom that the silane film is limited to a monolayer, and so in any real situation the silane coatings must be viewed as three-dimensional polysiloxane films.

New research approaches are needed to resolve the role of silane-finishing agents. One approach would be to focus on the interfacial zone where the siloxane film and adhesive resin interpenetrate. Too often the resin is viewed as a homogeneous structure, when in reality it is not. For example, electron microscopy and optical microscopy (27,28) of epoxy, phenolic, and phthalate resins reveal that they consist of micelles or granules of high-density polymer separated by narrow boundary regions of lower-molecular-weight material. How these micelles originate is not known. Possibly polymerization initiates from random points and proceeds radially. As these regions approach one another, they are unable to coalesce into a homogeneous network. Instead, the polymerization is terminated, leaving unreacted or partially reacted material at the periphery. At an interface, this low-molecular-weight material may exist as a thin, continuous film or as channels between micelles. Either way, the low-density regions offer pathways for the easy entry of water into the interfacial region. Entanglement of this low-density resin into a preformed siloxane film would increase its density and thus hinder water penetration. When the siloxane films contain reactive groups, these groups may initiate polymerization of the resin so that there is a high percentage of dense polymer at the interface. This highly speculative model is offered as a starting point for new research. It does have the merit of being consistent with present information about the nature of adhesive polymers and silane films.

Quite a different approach would be to investigate the stress corrosion process itself by a direct study of the effect of water on adhesive bonds formed without a coupling agent. This would be followed by an effort to observe how the silanes interfere with the stress corrosion process. Such a study would be an interdisciplinary problem in mechanics and surface chemistry. It would be necessary to analyze controlled crack propagation at adhesive/adherend interfaces (29,30), and if results are to be meaningful, there would have to be strict surface chemical control of specimen preparation and of the test environment.

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13. ABSTRACT <p>The wet strength of adhesive bonds between resins and glass or metal can be substantially improved by applying adhesion promoters to the glass or metal surface. The most widely used of these adhesion promoters are the organofunctional tri-alkoxysilanes RSi(OR)'_3. Some of the more pertinent research results concerning these silanes have been reviewed in the hope of establishing how they function as finishing agents. Work at NRL and elsewhere indicates that these compounds form polysiloxane coatings on the adherend surface. These coatings consist of a strongly adsorbed polysiloxane network along with a more weakly held material consisting of small polymer molecules and unreacted silane. The polysiloxane network exposes a high density of the organofunctional group R- at the air/silane-coating interface. However, the R- groups are not closely spaced, and, in fact, there is some evidence that the coatings can be penetrated by the adhesive resin. This view of the silane coatings as polysiloxane films is more realistic than some of the previous models, but the research is still a long way from identifying the mechanisms by which these films improve adhesion wet strength. Some new approaches are offered for research into the highly complex but exceedingly important area of adhesion promoters.</p>			

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