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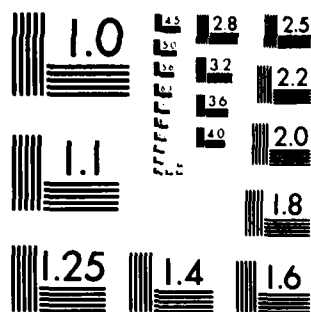| REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
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Studies of the structural gradient within the silane coupling agent interphase are reviewed. Origins of the structural variation in the silane layers are discussed in terms of the silane treating solution and variations in the substrates. The solution pH, concentration, solvent, hydrolysis time and aging time are some of the important parameters identified. Consideration is given to the following categories; the first monolayer on the substrate, the tightly chemisorbed layers near the substrate, the loosely chemisorbed layers in the middle and finally the physisorbed silanes in the

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forcement mechanism of composites and the rheology of polymer melts
is discussed. Complex formation of silanes with metallic substrates
is briefly mentioned.

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AND ITS INFLUENCE ON THE MECHANICAL

AND PHYSICAL PROPERTIES OF COMPOSITES

by

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cussed. Complex formation of silanes with metallic substrates is
briefly mentioned.

INTRODUCTION

Silane coupling agents have been used to improve interfacial adhesion at the glass fiber or particulate filler/matrix interface, reduce viscosity during processing, protect glass fibers from damage during handling, alter the catalytic effect of surfaces and improve the dispersion of particulate fillers. An excellent monography has been published on the chemistry, structure and application technology of silane coupling agents [1]. Historically, the application of coupling agents has been done by a trial-and-error basis with little fundamental understanding of the interfacial region or the structure of the applied coupling agent. The use of modern surface spectroscopic techniques has led to a remarkable improvement in the molecular understanding of the interfacial structures. It is clear that the glass/matrix interface region is not a simple layer but consists of complex structures. The importance of the interface in composite performance has been well documented [1,2].

The structural variations that exist at the glass/matrix interfacial region have been studied in recent years both qualitatively and quantitatively. Several factors influence the interfacial structures of the silane coupling agent including the pH, concentration, organofunctionality, solvent, application method, and temperature of the silane treating solution. Other factors related to the reinforcement material that influence the silane coupling agent structure are the average pH, local acid-base character, surface coverage, surface functionality and topology. Drying conditions such as thermal treatment accelerate the rate at which the predetermined

structure affected by the abovementioned factors is achieved. A summary of interfacial structural parameters and their origin is listed in Table I.

It is possible in many cases to control the interfacial structure by properly adjusting the treating conditions. The mechanical and physical properties of composites are strongly influenced by the interfacial structures. If the interfacial structure can be quantitatively linked with the mechanical and physical behavior of composites, then their performance may be predicted and controlled. The few studies that have been reported in this area indicate the usefulness of this approach.

It is possible to simulate some of the silane structures present on various surfaces without using the reinforcing materials. Unique aspects of the surface effects arise from the ability of the surface of solids to catalyze some reactions, restrict the molecular mobility and orientation, and influence the packing of silane molecules. Combined studies of the bulk simulation and surface structures are helpful to extract the specific influence of the surface of reinforcement material.

It is the purpose of this review article to discuss the structural gradient in the silane coupling agent layers on the surface of reinforcement materials. Special emphasis is placed on the role that specific silane structures have on the reinforcement mechanisms and rheological properties of the composite. Little attention has been given to the existence and the role of physisorbed silanes in the past. Those who are interested in background information on

the molecular structure of interfaces should refer to the aforementioned monographs [1,2] and recent review articles [3,4].

THE STRUCTURE OF THE PHYSISORBED SILANES

Physically adsorbed silane molecules exist in the outermost layers of the silane interphase. These silanes can be removed from the surface by washing with an organic solvent which does not cleave the siloxane linkages. Small oligomers predominate physisorbed silanes and the molecular weight is believed to be a function of the thickness across the interface. Thus, the amount of the physisorbed silane determined by an organic solvent is a function of the length of time washed. However, the majority of physisorbed silane desorbes relatively quickly.

A radioisotope-labeled aminosilane was used by Schrader et al. [5] to study the desorption of the coupling agent by hot and cold water from a glass plate. Their work was the earliest attempt to demonstrate the existence of a structural gradient in the silane interphase. The use of water as a solvent prevented the observation of the well defined physisorbed silane because the aminosilane self-catalyzes the hydrolysis of the Si-O-Si linkages. A combination of cold and hot water extractions probed the structural profile of the silane interphase. Based on the resistance to desorption, the silane layers were conveniently divided into three regions. The few layers closest to the glass surface was reported to be the most difficult to remove. Johannson et al. [6] using radioisotope-labeled methacryl-functional silane showed that a portion of the silane can

be washed away by toluene and ethyl acetate confirming the existence of physisorbed silane.

The hydrolytic stability study of various silanes with and without matrix resin using Fourier transform infrared spectroscopy by Ishida and Koenig [7] showed that some silane molecules desorbed during the polymerization with the matrix resin. These results suggested the formation of a matrix interphase consisting of physisorbed silane and matrix copolymer near the glass surface. The amount of the physisorbed silane was measured quantitatively as a function of the concentration of the silane treating solution. While the chemisorbed hydrolyzate of γ-methacryloxypropyltrimethoxysilane (γ-MPS) showed surface induced polymerization of the C=C group, the physisorbed silane showed no signs of such effects.

The following authors [8-11] used the so-called dry-blending technique to treat particulate fillers. The dry-blending method uses a silane organic solution which is sprayed onto the filler powder avoiding complete wetting and subsequent caking problem of the filler.

The first extensive attempt to study the structure of the physisorbed γ-MPS on particulate fillers was reported by Nakatsuka et al. [8] using IR and gel permeation chromatography (GPC). They reported a number of important observations including the molecular weight variation on different fillers, evaporation of the silane during drying when an alcoholic solvent was used, and desorption of the physisorbed silane by a styrene wash. They showed that the molecular weight of the γ-MPS oligomer was lower on calcium carbonate

surface than the clay sample used. Also, the molecular weight of the oligomer increased upon phospholic acid treatment of the calcium carbonate surface. Their mechanical study clearly demonstrated that calcium carbonate, a filler historically considered to be nonreinforcing in terms of strength, can reinforce a rubbery matrix when proper surface treatments are applied.

Subsequently, Ishida and Miller [9] studied the structure of physisorbed and chemisorbed silane on many particulate fillers using GPC and diffuse reflectance FT-IR. They determined that the siloxane network structure is influenced by the long-range acid-base effects of the filler surface. Fillers that had a similar slurry pH, yielded oligomeric siloxanes that had the same network structures and molecular weights as shown in Figures 1 and 2. As long as the extent of surface coverage is similar, the surface coverage determines in part the concentration and availability of the silanol for homecondensation reaction influencing the kinetics and resultant structure of siloxane networks. The fillers were classified based on a unified concept, the slurry pH.

Miller et al. [10] simulated the siloxane network structure by adjusting the pH of the silane treating solution. They were able to duplicate the siloxane structures that appeared on all fillers of interest without using the fillers. These results implied that the pH of the treating solution predetermines to some extent the structure of the silane. The combination of the solution pH and the acid-base character of the filler determines the final siloxane structure in addition to the surface coverage effects already mentioned.

An attempt to control the structure of the coupling agent on filler surfaces by mixing different silanes with γ-MPS was reported [11]. When tetraethoxysilane, vinyltrimethoxysilane and γ-aminopropyltriethoxy ilane (γ-APS) were mixed with γ-MPS in a 1:10 mole ratio, all combinations showed a remarkable increase in molecular weight of the bulk hydrolyzates upon room temperature drying. For a particular combination of γ-APS/γ-MPS, the alcoholic aqueous solution gelled relatively quickly due to the catalytic effect of the amine in γ-APS. Quite surprisingly, negligible effects were seen when the same solution was used to treat fillers and subsequently examined on the physisorbed silane molecules by GPC. This observation indicates that there is a strong driving force for cyclization of the siloxane chain on the filler surface possibly by influencing the mobility and availability of the silanol groups. These results are illustrated in Figures 3 and 4, where the molecular weights of the mixed silane with and without a filler powder were measured by GPC. Thus, the filler surface induces the formation of the physisorbed silane.

Migration of an amine functional silane was demonstrated by Sung et al. [12] using x-ray microprobe analysis. When γ-APS was used to treat an Al_2O_3 plate as an adhesion promotor for polyethylene (PE), the distribution of γ-APS as measured by the x-ray signal of the silicon atom was very narrow if the silane layers were heat treated prior to the PE application. When unheat-treated γ-APS was used, a much broader distribution with respect to the distance from the interface was obtained indicating the migration of the

physisorbed γ-APS. The spacial distribution of the silane mole-
cule with and without the heat treatment is shown in Figures 5 and
6. These results indicated that the physisorbed silane migrates
out of the substrate surface a great distance compared to the initial
thickness of the silane layers.

It has been proposed that the structure of the silane in the
treating solution strongly influences the network structure within
the silane layers [13]. This is supported by Belton et al's [14]
work using ellipsometry of γ-APS as an adhesion promotor for a
polyimide film on a silicon wafer. They observed that the thickness
of the γ-APS layer was reduced the most for the thickest silane
layers while, for a very thin layer (2.3 nm), no reduction in
thickness was observed. The reduced thickness as a function of
the original silane thickness is replotted in Figure 7. Since the
thickness variation was produced by changing the silane concentra-
tion, this structural difference must reflect the silane structure
in the solution. The desorbed silane is predominantly due to the
physisorbed silane. As described in the chemisorbed silane section
regarding Culler et al's [15] results, this portion of silane
obtained from very dilute solutions shows a great sensitivity to
thermal treatments being converted to chemisorbed silane.

Based on the above discussion, the qualitative and quantitative
nature of the physisorbed silane is better understood. The question
as to why the relative amount of the physisorbed and chemisorbed
silane varies from one substrate to another remains. Silanes with
large and flexible organofunctional groups tend to form more cyclic

structures than do silanes with smaller and more rigid substituents [16]. Many useful silanes for composite applications belong to the former category. Effects of pH on the structure of silane coupling agent has been studied by GPC using γ-MPA [9]. When silanes condense at pH ranges below 7 or above 9, the molecular weights tend to be small. If there are no surface functional groups, such as the metal hydroxide groups normally present on metal oxides, these small oligomers easily desorb. The low surface coverage tends to restrict the availability of the silanol groups for the condensation reaction causing more cage-like structures to form. It is possible that this cage-like structure incorporates the surface as a major part of the cage. Within the pH ranges described above, the amount of physisorbed silane is influenced by the surface functionality, surface coverage of the silane and the topology of the filler.

When the pH range is 7 to 9, the situation is quite different. The molecular weight of the silane is much higher and these large molecules have an open structure, a double chain ladder-like structure, that tend to form hydrogen bonding between themselves resulting in the formation of a physically crosslinked gel structure. It requires a long time for this gel to be separated and dissolve into a solvent. Thus, these gels appear to be chemisorbed, even if there are no primary bonds connecting the substrate and the silane molecules.

THE ROLE OF THE PHYSISORBED SILANE

Although the existence of the physically adsorbed silane has been known for a long time and now more detailed characteristics have been revealed, few attempts have been made to elucidate its role in the reinforcement mechanisms of composites. Fragmental information reported to date, however, indicate the unique role of the physisorbed silane at the glass/matrix interface. It is intuitively obvious that the physisorbed silane, a low molecular weight silicone oil, would have a quite different role from the chemisorbed silane which is a part of the reinforcement material. In this section, an attempt will be made to elucidate the effects of the physisorbed silane on the mechanical and rheological properties of composites.

The influence of these physisorbed silanes on the mechanical properties of composite is not known. Nevertheless, there have been a few occasions where removal of the physisorbed silane improved the flexural strength of the composite. Kokubo et al. [17] reported that extraction of the silane by methanol from a mica surface increased the flexural strength of the composite. Similarly, Graf et al. [18] observed an improved flexural strength after removal of the physisorbed silane by tetrahydrofuran (THF).

It is commonly observed [6,12,18,19,20] that there is a certain silane concentration at which optimum flexural strength is achieved. Concentrations higher than this resulted in inferior strengths. It was found that the higher the content of physisorbed silane, the lower the flexural strength for the E-glass fiber/γ-MPS/polyester

composite [18]. Many more systems have to be examined before generalizations can be made.

It is thought that the copolymer between the physisorbed silane and the matrix resin influences the mechanical behavior of the composite. Judging from the distance to which the physisorbed is capable of migrating, the thickness of the matrix interphase can be substantial. More quantitative information has been obtained by a simulation study of the interfacial material by Graf et al. [18]. They studied the copolymer of the γ-MPS hydrolyzate and poly-ester resin at various silane contents. The flexural strength of the copolymers linearly decreased as the silane content increased during the first 40% by weight silane content. This simulation study suggests that the matrix near the glass fiber, the matrix interphase, is one of the weakest portions of the composite. Naturally, organic solvent wash prior to the mixing with the matrix resin minimizes this weak matrix interphase without altering the integrity of the chemisorbed silane layers, resulting in an overall improvement in the flexural strength. Illustrated in Figure 8 is the improved flexural strength of fiber-glass reinforced polyester upon removal of the physisorbed silane by THF. The impor-tance of this data lies in its mechanistic understanding of the rein-forcing action rather than the magnitude of the improvement.

Physisorbed silane also has an important role in composite processing. A major reason why surface treatment by silane coupling agents reduces, in many cases, the viscosity of particulate-filled polymer melts is that the physisorbed silane acts as a lubricant

during processing. An additional reason includes the inhibition of the preferred interaction between the surface functional groups and the specific sites on the polymer chain.

Han et al's [21] results are consistent with the structural scheme described in the previous section. They studied the effects of surface treatments on the rheological properties of $CaCO_3$/polypropylene (PP) and glass beads/PP systems with amino-and octyl-functional silanes as coupling agents. The viscosity of the particulate-filled PP melt was reduced markedly for both silanes when $CaCO_3$ was used as depicted in Figure 9. The trends are explainable by Miller et al's work [9,10] demonstrating that the molecular weight of the silane would be low and the content of the physisorbed silane very high, since there are no surface functional groups. Therefore, the silane oligomers act as a lubricant and reduce the viscosity of the PP melt.

Little reduction in the viscosity was observed over the untreated filler when the octyl-functional silane was used on glass beads. Furthermore, the viscosity even increased when an aminosilane was used. The results are shown in Figure 10. Possible reasons are that the amount of the physisorbed silane would be much lower on glass beads than on $CaCO_3$, because the glass beads have surface functional groups, and that the molecular weight of the silane may be higher than on $CaCO_3$ since the glass beads are more neutral than $CaCO_3$. These factors may contribute to the small reduction of the viscosity. As for the aminosilanes, there may be a small number of chemical bonds or molecular entanglement with the PP, which increases the viscosity. This statement is supported by

the fact that the increment of the viscosity was higher at a
higher experimental temperature.

STRUCTURE OF THE CHEMISORBED SILANE

In addition to the physisorbed silane, it is apparent that
chemisorbed silane also exists. Within the chemisorbed silane
layers there exist structural variations depending on the treat-
ment conditions. This portion of silane may be mainly responsible
for the reinforcement mechanisms. The chemisorbed silane may not
be as easily amenable to ordinary analytical techniques as the
physisorbed portion. The molecular weight is, by definition, infi-
nite since it is a part of the solid even though there seems to
exist distinct segmental size that determine the mechanical con-
sequence of the composite. The existence of the substrate may
complicate the data collection and interpretation of the results. In
spite of all these difficulties, modern surface sensitive spectro-
scopies have made these interfacial studies much easier. As we shall
see in the following section, the wealth of information reported
now enables us to distinguish structural differences even within
the chemisorbed silanes.

It should be realized that, when the substrate surface is mole-
cularly smooth as is the case for glass fibers, the chemisorbed
silane may not be a monolayer thick but may form thick multilayers.
The first molecular layer is unique in its structure and interaction.
The organofunctional group may be attracted to form hydrogen bonds
or repelled depending on the chemical nature of the organic group

and the surface. The silanol groups of the silane molecules usually condense with the surface hydroxyl groups and the silane molecule becomes a part of the substrate. The mobility of the silane molecule within the first monolayer is, therefore, uniquely restricted by the distribution and the nature of the surface active sites. From the second layer and above, the bulk nature increases as the distance from the surface increases although the surface effects may still be felt. In this section, the existance of loosely chemically bound layers are also proposed.

Schrader [5] reported a very thin, tightly bound γ-APS layer near the substrate surface. It was difficult to desorb even by boiling water. The origin of this tenacious nature is not known, however it is believed that chemical bonding to the surface is responsible. They also reported that as much as 98% of the adsorbed silane desorbed by cold water wash. The film thickness was approximately a few hundred monolayer equivalents which corresponds to a relatively high concentration of silane treating solution. Observation of such a high content of physisorbed silane is in good agreement with the study by Culler et al. [5] on the hydrothermal stability of γ-APS on glass fibers, where they reported a strong concentration dependence on the amount of physisorbed silane as shown in Figure 11. Below 1% by weight, the amount of the chemisorbed silane suddenly increases and this portion of silane is susceptible to the thermal treatment while the silane from relatively concentrated solutions show little effect to heat treatment. It has been reported that the silanetriol content of γ-APS suddenly increased below 1% by weight [22].

These silanetriol monomers may be needed to produce the chemisorbed silane. Consequently, it can be concluded that the self-catalyzation of the amine group of γ-APS leads to oligomer formation in the silane solution prior to adsorption. These oligomers do not produce a high yield of chemisorbed silane resulting in the very high content of the physisorbed silane as observed by Schrader et al. [5] and Culler et al. [15]. This type of concentration dependence is unique to amino-functional silanes where the catalytic effects produce a high content of oligomers. However, the role of oligomers may be similar regardless of the type of organofunctionality. The low oligomer content of other neutral silanes do not produce such a dramatic effect as the aminosilanes.

A detrimental effect of the physisorbed oligomer on the wet strength retention of a Al_2O_3/γ-APS/PE joint system is seen in Figure 12. Since little chemical reaction is expected in this system, the oligomeric physisorbed silane cannot provide good hydrothermal stability while the chemically adsorbed silane can. A remarkable similarity in the shape of the curves in Figures 11 and 12 indicates the reasonableness of this statement.

In addition to the quantity of silane molecules extant on the substrate, structural information can also be obtained. Interaction of organic molecules with high-surface-area metal oxides has been the subject of long and extensive investigation and many excellent monographs have been published [23-25]. We shall mainly discuss silanes on relatively low-surface-area substrates, though one can observe many similarities among these substrates in terms of silane structures.

It is well known that more than a monolayer of silane is needed
to yield the optimum strength of a composite material. This is likely
due to the necessity of the interfacial chemical bonds, interpene-
trating network formation in the chemisorbed silane layers, and
proper orientation of the organofunctional groups. Many silanes
used in composite materials especially for the prupose of improving
the strength have reactive, polar groups as exemplified in amino-,
methacryloxy- and epoxy-functional silanes. These silanes tend to
form a bridge-like structure in the first monolayer where the silanol
groups covalently bond to the surface and the organofunctional groups
hydrogen bond with the surface active sites reducing the availabil-
ity of the reactive group for copolymer formation with the matrix
resin.

Hydrogen bonding of carbonyl-containing molecules with mineral
surfaces is well-known. As expected, the methacryloxy-functional
silane also shows evidence of hydrogen bonding with glass fibers
[26] and various particulate fillers [27]. This silane is a very
useful molecular probe for studying the interfacial structure
because of the sensitivity of the infrared carbonyl frequency to
different environments. Definition of a monolayer equivalent of
a silane on a substrate is not as straight-forward as a monolayer
film deposited on a flat surface by the Langumuir-Blagett technique.
Nonetheless, the amount of silane at which the surface property
of the substrate changes drastically from the initial inorganic
nature to the organic nature is of great technical and fundamental
importance. Monolayer equivalence may be defined as the unimole-
cular layer which consists of only uniquely interacting molecules

with the substrate surface. The molecular probe described above
provides a convenient means of determining the monolayer coverage.
An example is shown in Figure 13 where the relative intensity vari-
ation of the hydrogen bonded and free carbonyl groups as a function
of γ-MPS loadings is illustrated. Determination of surface energetics
may be useful to study the orientation of the molecule once the sur-
face coverage is determined by other means. The same silane mole-
cule may yield different values depending on the orientation of
the organofunctional groups. A typical example is that an amino-
functional silane yields contact angle data similar to the hydro-
carbons rather than the amine [28] due to the bridge-like structure
mentioned above [15,26,27].

In relation to the definition of monolayer equivalence, the
area occupied by a single molecules becomes an important quantity.
To date, only a few experimental determinations of the molecular
size of the silane on the surface of substrates have appeared in
the literature. Ishida et al. [26] have reported that γ-MPS
occupies approximately 0.48 nm^2/molecule on a E-glass fiber surface.
This is in accord with the expected molecular size when the mole-
cule is flatly adsorbed. Favis et al. [29.30] reported that the
areas of silanes and a titanate on mica were 0.24 nm^2/molecule
for γ-MPS, 0.33 nm^2/molecule for vinyl-benxyl-amino-functional
silane and 1.43 nm^2/molecule for isopropyl-tri(dioctylpyrophos-
phato)titanate. Their values are consistent with the expected
molecular size for the vertical orientation. Miller and Ishida
[31] also measured the occupied area of a γ-MPS hydrolyzate on the

surface of clay and lead oxide, and obtained the value to be 0.60

and 0.59 nm^2/molecule, respectively. Again this value is in

agreement with the flat adsorption, which is consistent with the

observation of the hydrogen bonded carbonyl groups to the surface.

The difference in orientation observed above is believed to be

due to the treatment conditions such as the concentration of the

treating solution.

The discussion of the chemisorbed silane is extended to the

silanes near the surface but beyond the first monolayer. There

seems to be tightly bound layers and loosely bound layers within

the chemisorbed multilayers which can be distinguished by the hydro-

thermal desorption studies [7,14]. Extensive siloxane networks are

statistically and chemically unfavorable for the desorption.

Thus, the shape of the desorption curve yields qualitative information

on the extent of open structure. The cyclic or caged structures

tend to isolate the segmental units and between these units little

covalent bonding exists, thus in this case hydrolytic desorption

takes place easier than the open structure.

Belton et al's [32] work seems to be consistent with the above

model of the chemisorbed silane. They studied an amino-functional

silane on a silicon wafer using the combination of chemical etching

with alkaline solution and ellipsometry. Their results are replotted

in Figure 14. The results indicate that the thicker the silane

film, the quicker the desorption. Since the thickness variation

was created by using silane treating solution with varying concen-

tration, the higher concentration solution may be said to yield more

loosely bound silane layers. The amount of physisorbed silane also has to be taken into account. The results of water wash were shown previously in Figure 7 where the thicker layers had more physisorbed silanes. Even though the physisorbed silanes are taken into account, the etching rate for the thicker silane film cannot be accounted for unless the etchability of the thicker film is easier. The γ-APS film remained the longest on the silicon wafer when treated from the most dilute solution. As it has been reported in the literature [13], this is due to the effects on the siloxane network structure by the silane structure in the treating solution. It should be emphasized that the hydrolytic stability of the individual siloxane linkage may not be affected by the specific network structure. In fact, very different silanes show similar hydrolytic stability in terms of bond cleavage by water [7]. What affects the desorption characteristics in such a dramatic fashion is the organization of the siloxane bonds or extent of three dimensional network formation. In other words, cyclic cage-like molecules have fewer bonds connecting each cage unit and this structure leads to poor overall hydrolytic stability, in spite of similar hydrolytic stability of individual siloxane bond.

Unlike exponential desorption curves reported for thick γ-APS films on substrates [5], the desorption curves of thinner films resemble that of vinyl-functional silane [7] which tend to form more open, non-cyclic structures. The lower the concentration of silane treating solution, the longer the threshhold period for quick desorption. The thicker films show almost no threshhold

periods. This indicates a more open (or extensive) siloxane network structure for the silane from lower concentrations and a more closed (or cyclic) siloxane structure for the silane from higher concentrations.

Molecular order in the silane interphase was first proposed by Ishida and Koenig [13] using vinyltrimethoxysilane as an example. They also observed a higher rate and extent of condensation of the silanol groups when adsorbed from a more dilute solution. The amount of the residual silanol increased dramatically above the concentration termed "onset of association." General tendency of the head-to-head orientation was also proposed [13] and experimental support was obtained from the study of x-ray crystallographic data of a single crystal of cyclohexylsilanetriol [33]. It should be noted that the degree of order and head-to-head adsorption vary considerably depending on the chemical structure of the organofunctional group. In general, a more flexible group tends to deviate from the trend described above. These trends may influence the structural hierarchy within the silane interphase.

Molecular order in the chemisorbed silane layers has also been reported by Favis et al. [29,30] where they studied a few silanes on phlogopite mica utilyzing carbon-hydrogen-nitrogen analyzer. They have reported that silane molecules adsorbed on a mica surface in a stepwise fashion thus there was a time lag before the next molecular layer of silane started adsorbing. Figure 15 shows some of their results where γ-MPS was hydrolyzed for 25 min and then adsorbed onto the mica surface. A stepwise adsorption scheme is

clearly seen. Two factors may be expecially significant for interpreting the observed results. First, the mica surface is molecularly smooth and it has been observed that a smooth surface allows better molecular stacking [13]. Second, the concentration of the silane solution used is approximately 0.025% by weight which is extremely low compared with the concentrations studied by many other researchers. At this concentration level, all silane molecules are isolated and adsorbed onto the surface individually.

It was also noted that when the hydrolysis time was increased to 90 min, no γ-MPS was adsorbed onto mica, whereas the cationic styryl-benxyl amino-functional silane did not show this effect over the experimental uncertainty. Since the concentration is so low that no silane molecules can associate with each other, condensation of silanol groups in such a short period of time is negligible. Thus, oligomer formation is an unlikely cause. An alternative explanation is that the methacryloxy moiety is hydrolyzed in 90 min to form methyl methacrylic acid and no longer the silanetriol of γ-MPS. Alkali catalyzed hydrolysis product has been reported [10] and indication of acid-catalyzed product has also been reported [34]. It is not surprising since methyl methacrylate can be hydrolyzed both in acidic and alkaline media.

Substrate effects on the structure and adsorption characteristics of silane is an interesting subject and essential to the understanding of the structure of the silane film. Silanes on metals have been studied extensively by Boerio et al. [34-37] and others [38,39]. Very little depth profile information has been reported. Nonetheless,

it is believed that the structure of silane on metallic substrates
follow general trends described above for the nonmetallic substrates
except for the complex formation of the organofunctional group and the
metal ions. Boerio et al. [37] reported that copper (II) ion
exists in the silane interphase using x-ray photoelectron spectro-
scopy as shown in Figure 16. Copper (II) ions show the same funda-
mental core electron energies in ESCA spectrum with copper (I) which
normally exists on the polished copper surface. However, the shape-up
satellites observed at the lower energy side are characteristic to
copper (II). Thus, they have concluded that the amine group of
γ-APS forms a complex with the copper ion after dissolution of
the surface oxide film. The etching effect of the surface oxide
films by γ-APS has also been observed on aluminum substrates.

Allen and Stevens [38] reported the infrared study of
γ-glycidoxypropyltrimethoxysilane (γ-GPS) on aluminum substrate
as a function of the amount adsorbed. A very thin silane film
lowered the OH stretching frequency indicating stronger hydrogen
bonding. They reasoned that the frequency shift was due to the
complex formation with the aluminum substrate, though only incon-
clusive evidence was shown.

Silane coupling agents are sometimes reported to inhibit cor-
rosion of metals. An amine containing silane has synonymous function
as anticorrosion agents such as benzotriazole and imidazole deriva-
tives for copper, as evidenced by the observation of complex formation
of γ-APS with copper. These anticorrosion agents are also known to
form complexes which are a necessity for their anticorrosion action.

Hence, it is reasonable to expect the anticorrosion action of
γ-APS on copper and possibly on other metals by a similar mechanism
of these azoles. Once a complex is formed, the interaction between
the amine group and the metallic ion is strong and inhibits the
availability of the organofunctional groups for copolymer formation
with the matrix resin. If the complex is known to catalyze the cure
of the matrix resin, another effect may be expected. Thus, the
metal/silane/coating interface can be quite different than those
corresponding interfaces with non-metallic substrate. The glass/silane
interface is relatively well defined as compared to the probable
diffuse boundary of the metal/silane interface. The silane/matrix
interface is diffusely defined for both glass and metal substrates.

THE ROLE OF THE CHEMISORBED SILANE

The role of the chemisorbed silane in the reinforcement mech-
anisms of composites can be discussed based on the studies by
Schrader et al. [40], Emadipour and Koenig [41], and Belton et al.
[32,42]. Schrader et al. [40] investigated the effect of silane
desorption on the joint life during hydrothermal aging. Adhesive
joints were prepared after the hydrothermal desorption of the
silane. They observed a relatively insensitive decrease of the
joint life in spite of the major desorption of the physisorbed
silane as shown in Figure 17. On the other hand, the hot water
extraction of the silane leads to a significant reduction of the joint
life indicating the importance of the chemisorbed silane. It
should be pointed out that the hot water extraction not only etches

the outer layer of the silane but also degrades the integrity of the siloxane networks which still remain on the substrate surface. Thus, the loss of network integrity has to be taken into account. If the silane layers are subjected to postcuring after the hydrothermal desorption, this effect will be minimized. This statement is supported by Emadipour and Koenig [41] as shown in Figure 18 where they measured the pull-out strength of a glass rod from an epoxy matrix. The silane layers were etched by hot water and given subsequent heat treatment prior to the preparation of the fiber pull-out samples. The interfacial shear strength after the hydrothermal treatment improved. Furthermore, the improved strengths were nearly constant regardless of the concentration of the silane treating solution in the relatively concentrated range (1-10% by weight), which is compared with the strong concentration dependency of the strength for the as prepared sample.

More direct observation was made by Belton et al. [4,32,42] using etching experiments of silicon wafer/γ-APS/polyimide system. A thin polyimide film cured on a silane treated silicon wafer was etched by an alkaline solution and the time required to etch the film was studied as a function of the thickness of the initial silane interphase. Although they did not distinguish the contribution of the chemisorbed and physisorbed silanes, the thickness range and the concentration of the silane treating solutions produce predominantly chemisorbed silanes upon heat treatment. Thus, the physisorbed component at room temperature drying has different configurations than the truly physisorbed silane which remains physisorbed even

after the heat treatment. This type of silane will provide a favorable situation for the intermixing between the silane and the polyimide precursor. Upon curing of the polymeric film, the silane is also cured to form more extensive networks than the truly physisorbed silane. Also, the availability of the organofunctional groups of this potentially chemisorbed silane may be quite different than the truly physisorbed silane. Their results are replotted in Figure 19 where the etching time is plotted as a function of the silane film thickness. As the silane thickness increased, the time required for complete removal of the polyimide film increased to a certain thickness, again showing that a monolayer silane does not yield an optimum property.

With all these observations, one can postulate the existence of loosely chemisorbed silane layers whose structure is favorable for interpenetration of the matrix resin. Only indirect observation of the existence and function of this portion of the silane have been made to date and further rigorous studies are needed to elucidate the structure.

CONCLUSION

The gradient in the silane interphase on various substrates has been discussed in terms of the chemical structure as well as the role of various portions of the silane in the reinforcement mechanisms of composite and rheological behavior of composite melts. It is proposed that silane interphase be subdivided into two clearly distinguishable regions using an organic solvent wash that does not

induce the hydrolytic scission of the siloxane bonds. These
are termed the physisorbed and chemisorbed silanes. Within the
chemisorbed silane layers, it is also proposed that this portion
of silane be again subdivided into at least two regions and possibly
three regions depending on the interaction with the substrate. The
first monolayer is uniquely interacting with the substrate surface
and the nature of the interaction is totally dependent on the com-
bination of the chemical structure of the organofunctional group
and the substrate surface. Above this first layer but very near the
surface of the substrate, there are tightly chemically adsorbed
layers. Further outer layers near the physisorbed silanes, another
structure exists where loosely bound though chemisorbed silane
dominates.

The role of the physisorbed silane on the mechanical properties
of the composite is dependent upon the mechanical properties of the
particular copolymer between the physisorbed silane and the matrix
resin. In some limited examples, these copolymers are reported to
be unfavorable with respect to the improved mechanical performance.
This silane acts as a processing aid by reducing the viscosity of
the reinforcement/polymer systems. The chemisorbed silane is
thought to be mainly responsible for the reinforcement mechanisms
through chemical bond formation along with interpenetrating network
formation.

<u>FIGURE CAPTIONS</u>

Figure 1. Gel permeation chromatograms of the physisorbed γ-MPS collected from the surface of (A) tungsten oxide (slurry pH 4.8) and (B) clay (slurry pH 4.1). Polystyrene was used as molecular weight standards.

Figure 2. Gel permeation chromatograms of the physisorbed γ-MPS collected from the surface of (A) Kaolin (slurry pH 7.1) and (B) Zinc oxide (slurry pH 7.6).

Figure 3. Gel permeation chromatograms of the bulk hydrolyzates of γ-MPS containing a second component and heated at 80°C for 85 hr. (A) no second component (B) 10 mole % tetramethoxysilane and (C) 10 mole % vinyltrimethoxysilane. The silanes were hydrolyzed in n-butanol containing small amount of water.

Figure 4. Gel permeation chromatograms of γ-MPS hydrolyzate on clay. (A) no second component (B) 10 mole % tetramethoxysilane and (C) 10 mole % vinyltrimethoxysilane. The same silane solutions, hydrolysis conditions and heating conditions as in Figure 3 were used.

Figure 5. X-ray microprobe analysis of γ-APS hydrolyzate on Al_2O_3 as a function of the distance from the substrate surface. The negative values indicate within the substrate.

Figure 6. X-ray microprobe analysis of γ-APS hydrolyzate on polyethylene as a function of the distance from the substrate surface.

Figure 7. Thickness of γ-APS films on a silicon wafer measured by ellipsometry. The difference thickness between the initial and solvent washed film is plotted against the thickness of the initial γ-APS film.

Figure 8. Flexural strength of fiber-glass reinforced polyester as a function of the amount of γ-MPS as measured by infrared band intensity. Open circle represents the composite prepared from as-treated E-glass cloth while the closed circle utilized E-glass cloth washed with tetrahydrofuran prior to the composite manufacturing.

Figure 9. Viscosity of polypropylene melt with $CaCO_3$ at 200°C. The surface of $CaCO_3$ is treated with various silanes. The polypropylene contains: (O) no filler (▲) untreated $CaCO_3$) (●) $CaCO_3$ treated with octyltrymethoxysilane and (X) $CaCO_3$ treated with γ-APS. The filler content is 30% by weight.

Figure 10. Viscosity of polypropylene melt with glass beads at 200°C. The surface of glass beads is treated with the same silane as in Figure 9. (O) no filler (▲) untreated glass beads (●) glass beads treated with octyltrimethoxysilane and (X) glass beads treated with γ-APS. The filler content is 30% by weight.

Figure 11. Amount of chemisorbed γ-APS on E-glass fibers as a function of the concentration of silane treating solutions. Water is used as a washing solvent. (O) dried at room temperature and (●) dried at 120°C for 2 hr.

Figure 12. Wet peel strength retention of polyethylene coating on Al_2O_3 whose surface is treated with γ-APS at various concentrations of aqueous solution.

Figure 13. Fourier transform infrared spectra of γ-MPS on clay with silane loadings of (A) 4 wt. % (B) 2 wt. % (C) 1 wt. % (D) 0.5 wt. % and (E) 0.2 wt. % showing the free carbonyl (1720 cm^{-1}) and the hydrogen bonded carbonyl (1700 cm^{-1}).

Figure 14. Etching time of γ-APS on a silicon wafer as a function of the initial thickness. An alkaline aqueous solution is used as an ethant. The thickness of the film is determined by ellipsometry. The γ-APS concentration is (O) 0.02 vol %, (●) 0.04 vol % and (⊖) 0.10 vol %.

Figure 15. Amount of γ-MPS adsorbed on mica surface as a function of absorption time. Each plateau corresponds approximately to monolayer equivalent when vertical adsorption is assumed.

Figure 16. X-ray photoelectron spectra of γ-APS on a copper substrate. The samples are dried at R. T. and stored (A) in a decicator until spectral examination, (B) in laboratory atmosphere for 4 days.

Figure 17. Joint life of the glass/epoxy adhesive/glass system where the glass surface is treated by a radioisotope-labeled γ-APS. The variation of surface coverage is produced by extracting the silane with cold water (in the 60-30 molecule/nm^2 range) and with hot water (in the 30-0 molecule/nm^2 range). The joint is immersed in hot water with a constant load.

Figure 18. Shear stress of a single glass rod determined by the fiber pull-out test from an epoxy matrix. The glass surface is treated with γ-APS at various concentrations. Closed circle represents the glass rod as treated and the open circle shows the silane-treated glass rod which is boiled in water for 4 hr and dried.

Figure 19. Etching time for complete film removal of polyimide against γ-APS solution concentration for different silane application techniques. The polyimide is cured on γ-APS-treated silicon wafer at 150°C for 45 min. The alkaline aqueous solution is used as an ethant. Silane is spin coated at 5000 rpm by (O) immersing a silicon wafer in the silane solution for 15 min followed by spin coating and (●) placing the silane solution on a silicon wafer followed by spin coating.

TABLE I

INTERFACIAL SILANE STRUCTURES THAT INFLUENCE
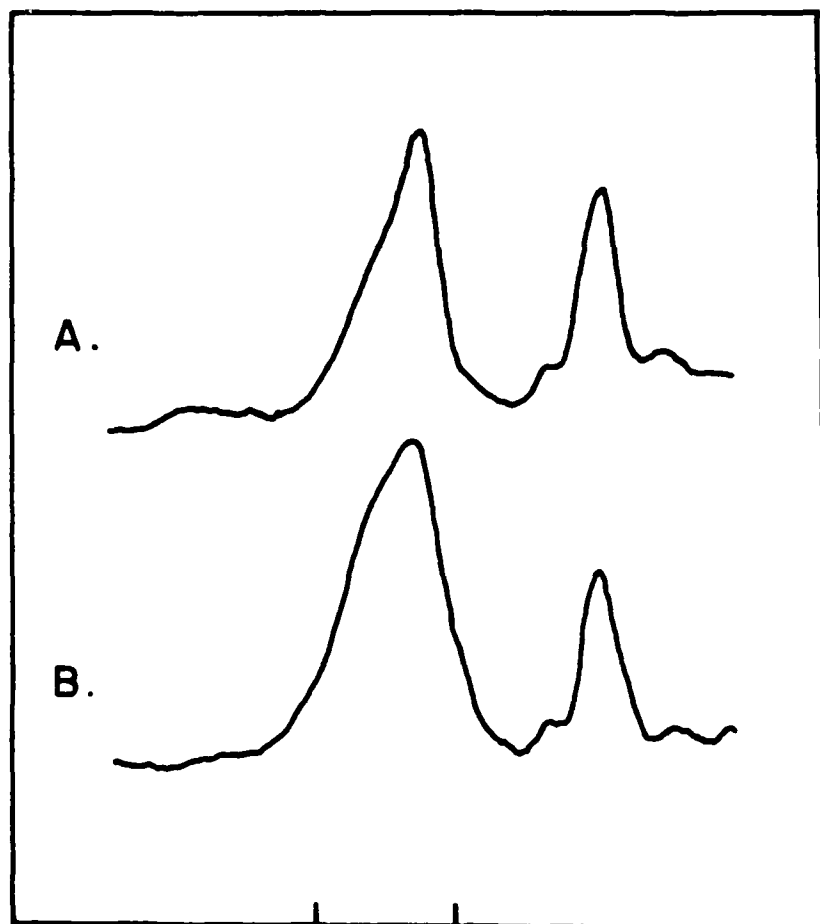
THE MECHANICAL PERFORMANCE OF COMPOSITES

FACTORS	ORIGIN
1. Degree of curing	Time, Temperature Concentration
2. Orientation	Isoelectric point of surface pH of the silane solution
3. Organization	Isolated silanetriol in the treating solution
4. Physisorbed silane	Concentration pH of the silane solution Surface functionality Isoelectric point of surface
5. Chemisorbed silane	Surface functionality pH of the silane solution
6. Thickness	Concentration Topology

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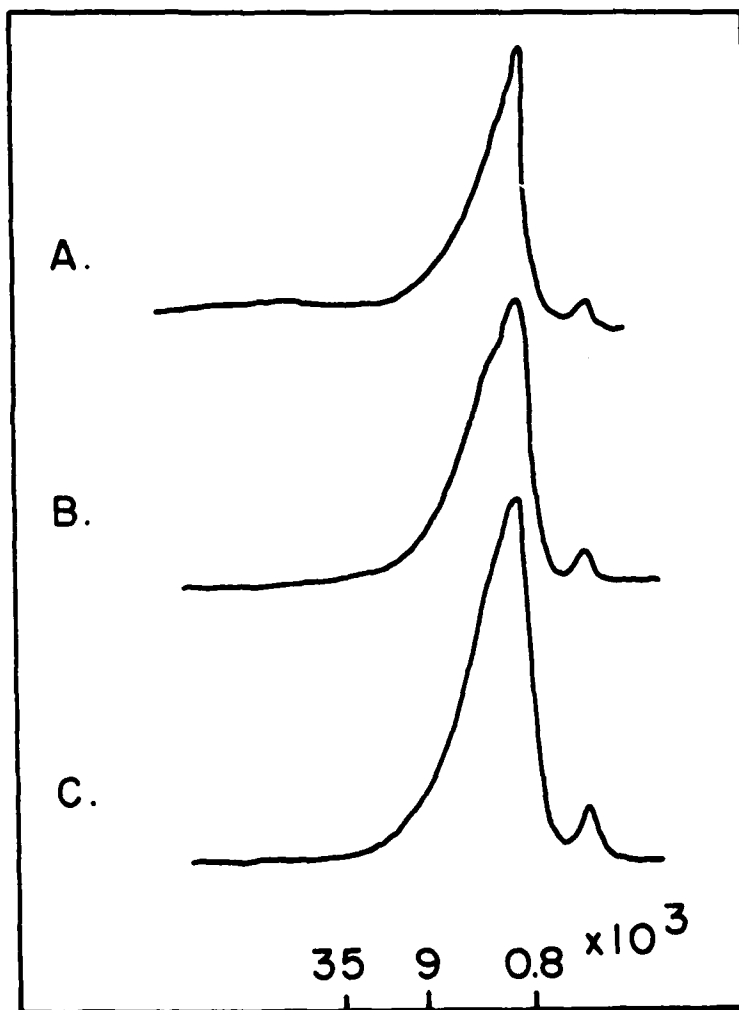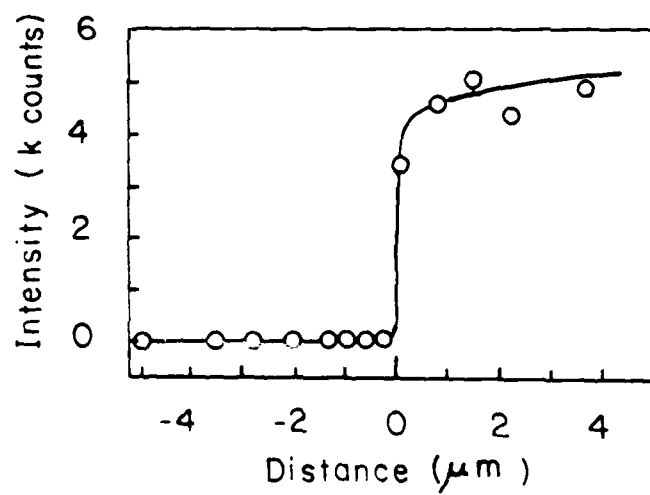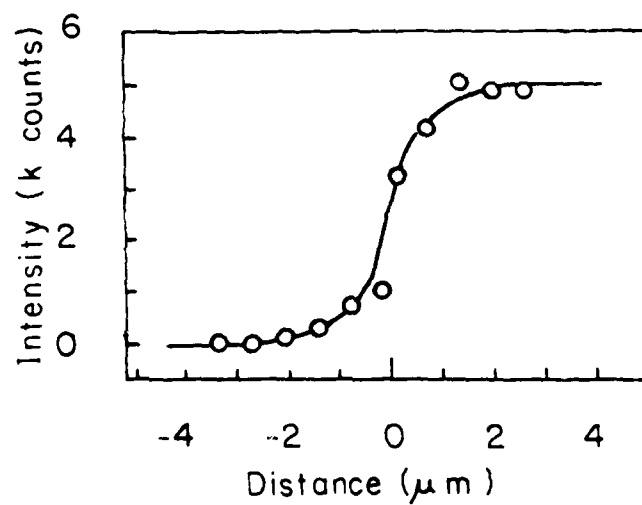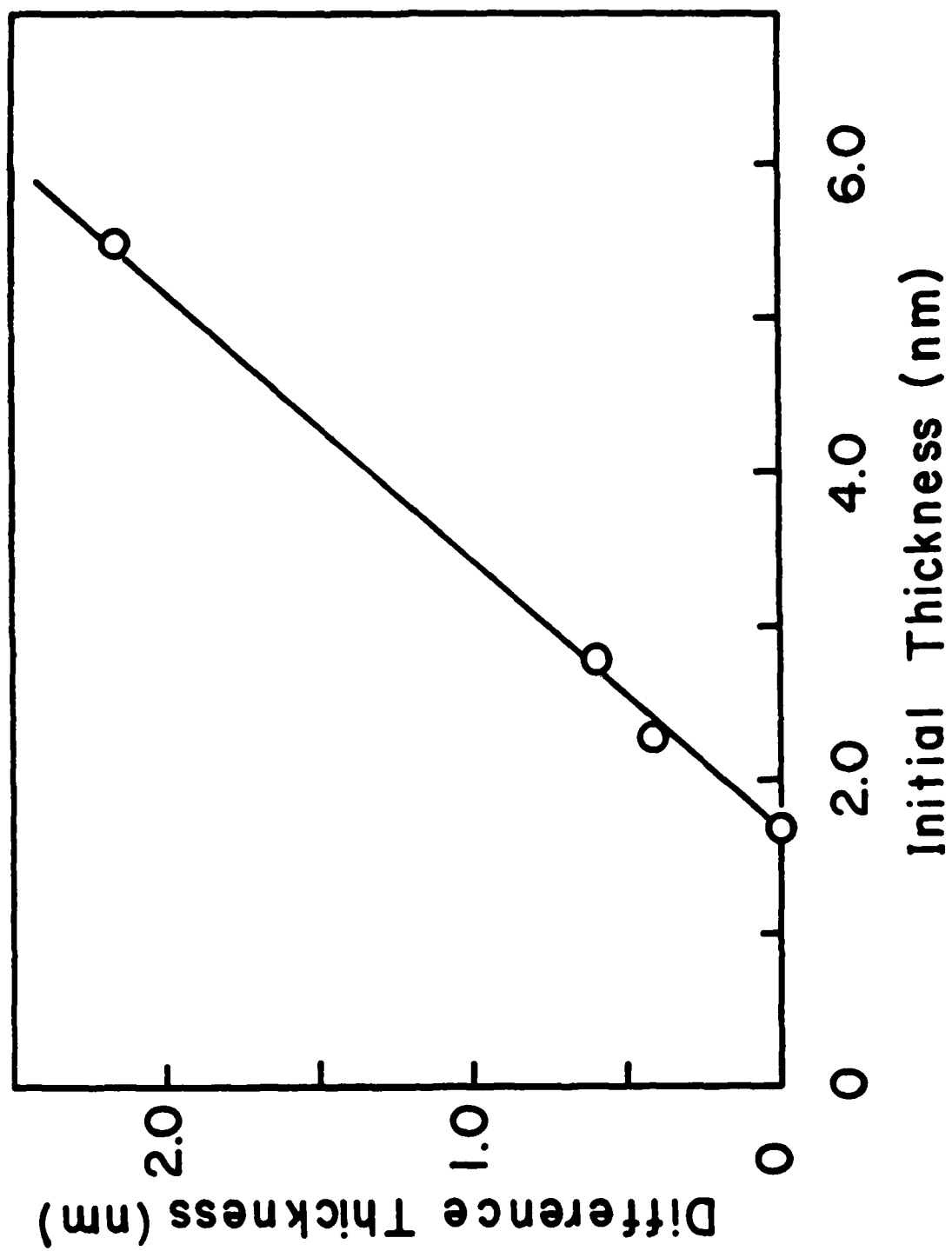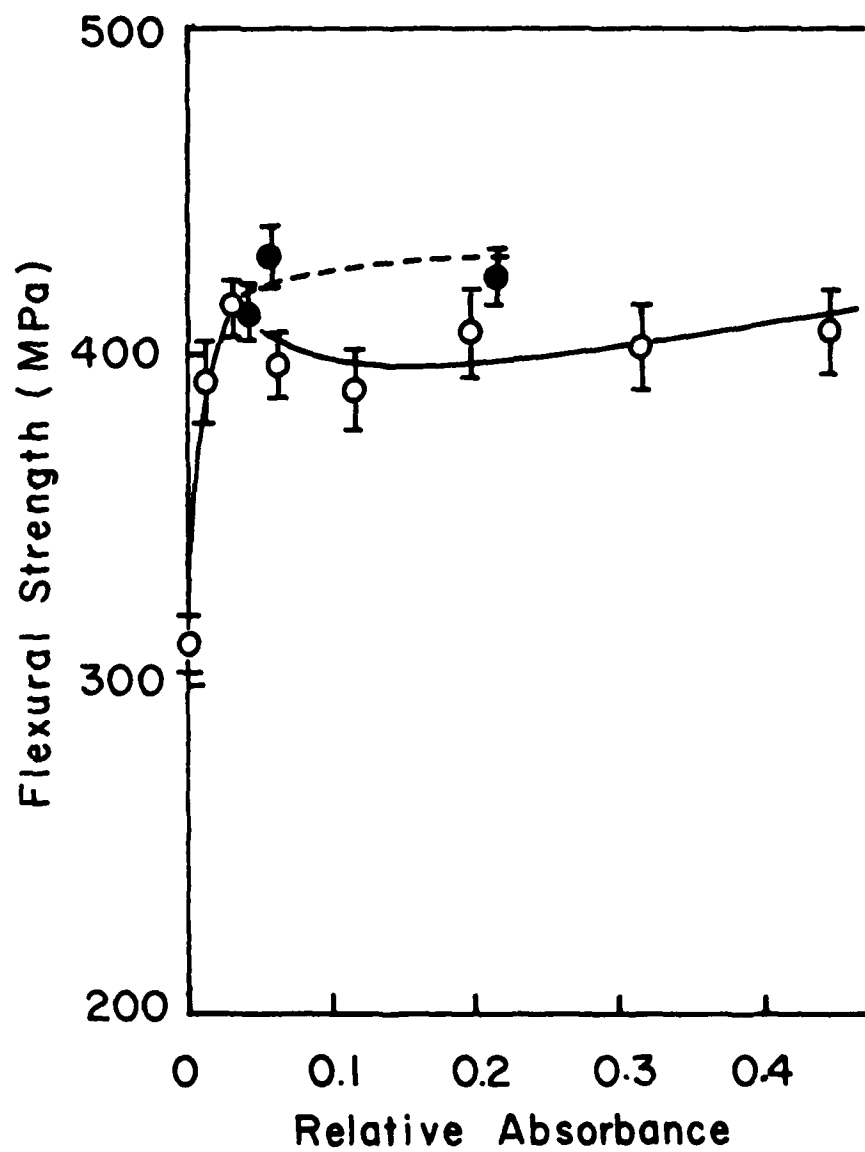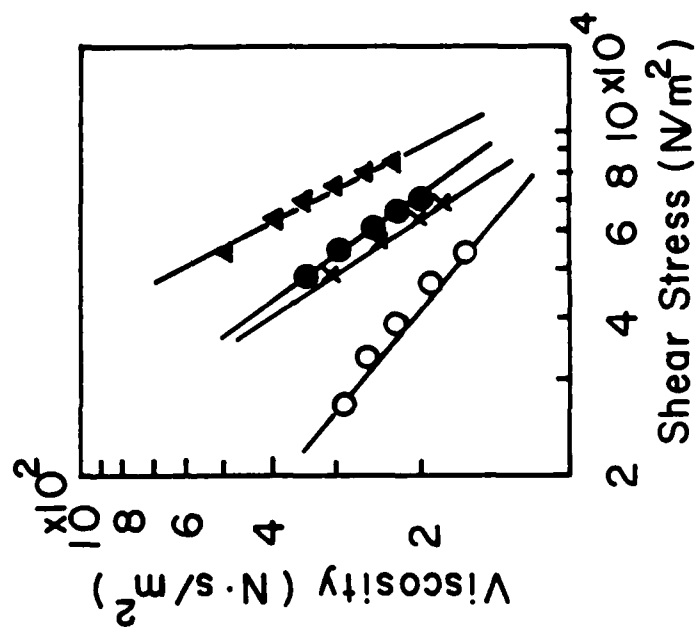
4000   800

Molecular Weight of Standards

Monomer

A.

B.

4000   800

Molecular Weight of Standards

A.

B.

C.

390 100 35 9   0.8$^{\times 10^3}$

Molecular Weight of Standards

A.

B.

C.

35   9   0.8 ×10^3

Molecular Weight of Standards

Free C=O   H-bonded C=O
1720   1700

1800   1700   1600 cm⁻¹

A.
B.
C.
D.
E.

Etching Time (min)

Film Thickness Retention (%)

mg Silane/g Mica

Adsorption Time (s)

12×10^3

Cu₂p

Shake-up satellites

A.

B.

960   940 eV

Binding Energy

Shear Stress (MPa) vs Concentration (wt %)

DAT FILM