The Interaction of a Cationic Silane Coupling Agent with Mica

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Synopsis

Carbon analysis was used as a method for measuring the quantity of a cationic vinyl benzyl silane (CVBS) adsorbed onto the surface of mica. The results obtained indicate that CVBS can be applied from aqueous solution over a wide pH range with best treatment in neutral and acidic media. The amount adsorbed depends on the concentration of the treating solution in the lower concentration range while in the higher range, the adsorption is less dependent on concentration. The relationship, silane adsorption vs. time of treatment, shows a steplike dependence. It is suggested that each step corresponds to a monolayer coverage. The data indicate that CVBS on mica is a highly ordered and closely packed multilayer phase with the silane molecules oriented normal to the surface. The multilayer adsorption of silane onto silane in this system may be compared in some respects to polymer crystal growth.

INTRODUCTION

In composite materials, coupling agents are often used in order to improve adhesion between the polymer binder and the inorganic substrate. The use of such agents generally results in an improvement in properties in the dry state. However, the most pronounced effects are found in property retention noted after exposure to moisture.

Most of the previous work involving the study of coupling agents on inorganic surfaces has been conducted with silanes on glass.[1] Silanes are the most widely used coupling agents and glass the most common reinforcement material. It is generally held that a covalent bond is formed between the hydrolyzed silane and the glass surface,[2-4] although in the past other theories have been proposed considering hydrogen bonding[5] or Van der Waals forces[6] as the main interaction. Plueddemann[7] has suggested a dynamic equilibrium process, which envisages the continual breaking and reforming of bonds at the silane/mineral interface in the presence of water. This model has been supported by Raman spectroscopy.[8] Such a process allows for stress relaxation at the interface without disrupting the overall bond between the polymer and the inorganic substrate. A model incorporating stress relaxation is necessary since the composite material is subject to considerable shrinkage stresses when cooled from high temperature due to the different coefficients of expansion of the polymer and inorganic material.

Silane molecules form multilayer films on glass fibers.[9] The interactions of the molecules, in this multilayer phase, with the mineral substrate are dependent
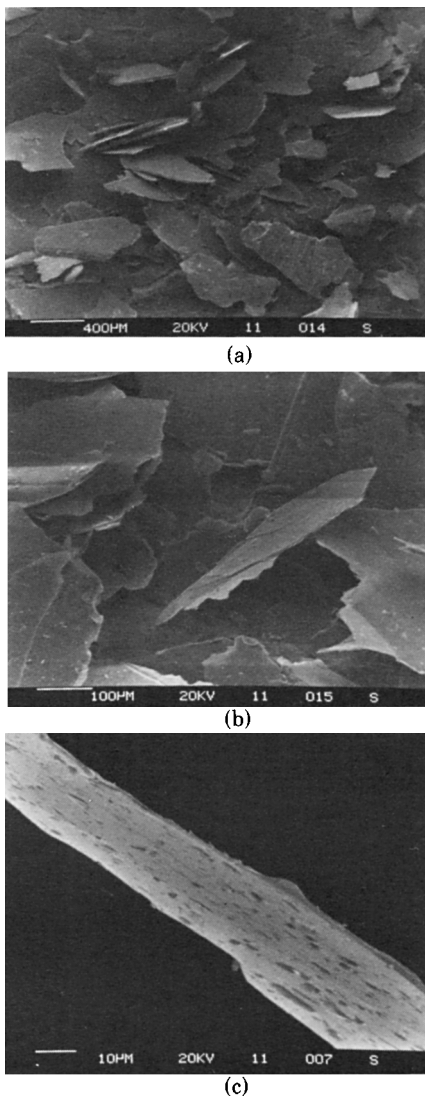
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Fig. 1. Sequence of enlargements of a particular mica flake in order to obtain a position appropriate for measuring its thickness.

on their distance from the surface.[10,11] The orientation of the silane molecules within a particular layer is critical to their performance as a coupling aid. The preferred orientation is considered to be with the organic functionality of the silane molecules extending away from the surface.[12]

Several studies have been carried out on the orientation of silanes on inorganic surfaces. Hydrolyzed γ-aminopropyltriethoxy silane applied from an aqueous solution at neutral pH has been suggested to interact with the glass surface through the amino groups in addition to the silanol groups. Under these conditions, it has therefore a tendency to lie parallel to the surface.[13] Methacryl functional silane has been shown by Fourier transform infrared spectroscopy to be oriented in a head to head position.[9] Lee[14] indicated, by contact angle measurements, that reactive functional groups of organosilanes are generally

TABLE I
Characterization of Mica 60 HK (Suzorite Mica)

	Screen analysis				Flake diameter (μm)	Flake thickness (μm)	Surface area (m^2·g^{-1})
+35	−35 + 48	−48 + 65	−65 + 100	−100			
Nil	19%	33%	30%	18%	394	12.5	0.612

positioned horizontally on the glass surface. Bascom[15] studied polysiloxane films containing chlorocarbon or fluorocarbon groups on stainless steel and glass. The films behaved, with respect to contact angle measurements, like well-oriented monolayers with the silane chains extending away from the surface.

It is evident that the nature of the silane interphase in a polymer composite is complex; such factors as the orientation of the silane molecules and their distance from the mineral surface are important considerations. In this work it will be shown that the adsorption of individual monolayers of silane on mica (a silicate material like glass) may be detected and controlled. This allows the possibility of examining the adsorption phenomenon directly or very close to the mineral surface.

For this study, a cationic vinyl benzyl silane (CVBS) was chosen since it is a widely used general purpose silane "compatible" with most thermoplastics. Mica was selected since it has been shown to be capable of imparting high degrees of reinforcement to polymeric systems[16–18] and has significant potential due especially to its low cost and high Young's modulus. Studies have shown that coupling agents added to mica improve the properties of the composite.[19,20] It is evident that an understanding of the interaction of coupling agents with mica will be required in the development of this rapidly emerging material.

The purpose of this study is to examine the importance of basic parameters (pH, initial silane concentration, and the time of treatment) affecting the adsorption of a cationic vinyl benzyl silane onto mica. Results were obtained which give an indication of the orientation of the silane molecule.

EXPERIMENTAL

Mica

The mica used was of the Phlogopite variety supplied by Marietta Resources International Ltd. (trade name Suzorite mica). The flakes obtained from Marietta had been delaminated by fluid energy to yield a relatively high aspect ratio (diameter/thickness) material. In these experiments the 60 HK mica was used, a designation whereby the value 60 corresponds to the average mesh size of the flakes and HK refers to its classification as being highly delaminated.

The mica itself is amber brown in color with well-defined cleavage planes. A scanning electron micrograph (SEM) of a typical flake is shown in Figure 1(b). The mica was characterized for screen size distribution, diameter, thickness, and surface area. The sieving was carried out using the Tyler Canadian Standard Sieve Series. The average maximum diameter was obtained by light microscopy using a calibrated eyepiece, and 50 measured diameters were used in calculating the average. The average surface area of the flakes was measured by the BET method using argon gas as the adsorbate.

TABLE II
Typical Data Obtained from Carbon Analysis

Time of silane treatment (s)	CHN sample weight (mg)	Peak height (cm)	% C	Corrected % carbon	g silane adsorbed/g mica $\times 10^3$
0			0.043	0.000	0.0
205	8.39	6.1	0.076	0.033	0.7
585	8.24	7.4	0.096	0.053	1.1
3885	9.87	9.7	0.110	0.066	1.3
9185	10.20	18.3	0.210	0.160	3.3
11,110	7.57	14.3	0.220	0.170	3.4

A technique was developed to measure the thickness of the flakes by SEM. A flake, which was in an upright position, was located on the grid. This was then oriented appropriately and adjusted until the upper face of the mica flake was no longer apparent. In this way reproducible values of the thickness could be obtained. A sequence of enlargements illustrating this process is shown in Figure 1. Twenty measured thickness values were used in calculating the average. The data for the characterization of the mica sample are compiled in Table I.

Silane Coupling Agent

A cationic vinyl benzyl silane (CVBS) was obtained from Dow Corning Inc. (tradename Z-6032). Its molecular formula is $(CH_3O)_3SiCH_2CH_2CH_2NH$—$CH_2CH_2NHCH_2(C_6H_4)CH$=$CH_2 \cdot HCl$ and it is designated as N-β-(N-vinyl benzyl amino) ethyl-γ-aminopropyl trimethoxy silane monohydrogen chloride.

In a typical experiment the silane was hydrolyzed for about 15 min in twice distilled water whose pH had been adjusted to the required value with acetic acid or sodium hydroxide. Time zero was taken in all experiments as the moment when mica flakes were added to the hydrolyzed silane. The suspension was continuously agitated, and aliquots were taken by syringe at appropriate intervals. The water of these aliquots was removed by aspiration on a buchner filter.
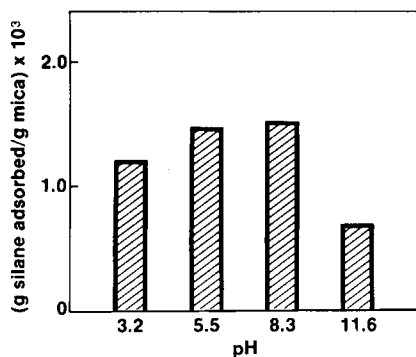

Fig. 2. Effect of pH on the adsorption of CVBS onto mica. The initial quantity of silane in the treating solution was 0.5% (g silane/g mica), or 0.025% (g silane/g H_2O).
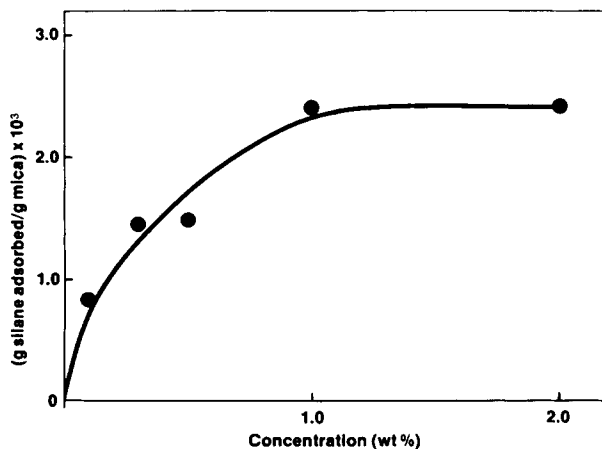
Fig. 3. Effect of the initial silane solution concentration on the adsorption of CVBS onto mica. A concentration value of 1.0% in terms of g silane/g mica as shown in this figure, corresponds to a value of 0.050% in terms of g silane/g H_2O.

The sample was washed with twice distilled water and dried briefly at approximately 140°C to complete the condensation process.

In all experiments the initial concentration of the silane in solution was calculated as the weight percent of silane on mica.

Silane Analysis

The amount of CVBS adsorbed onto the mica was measured by carbon analysis. The instrument used was the F and M Model 185 Carbon Hydrogen Nitrogen Analyzer (CHN). The sample was completely burnt, and the gases of combustion separated on a gas chromatographic column. Quantitative analysis of these gases were obtained by a thermal conductivity detector.
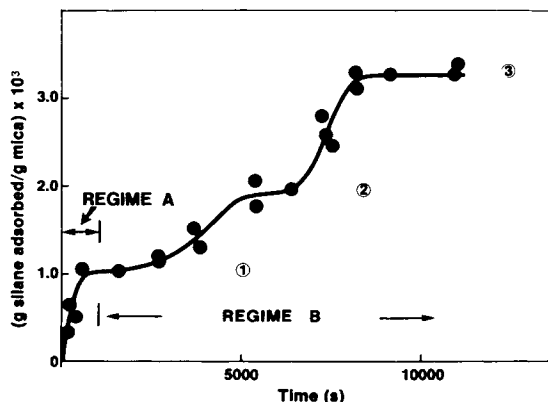

Fig. 4. Effect of the time of treatment on the adsorption of CVBS onto mica at pH 3.2. The initial quantity of silane in the treating solution was 0.5% (g silane/g mica), or 0.025% (g silane/g H_2O).
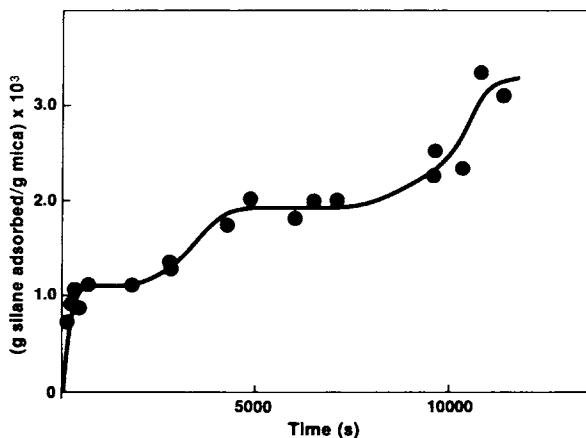
Fig. 5. Effect of the time of treatment on the adsorption of CVBS onto mica at pH 5.5. The initial quantity of silane in the treating solution was 0.5% (g silane/g mica), or 0.025% (g silane/g H_2O).

RESULTS

Table II shows typical data obtained from carbon analysis. By relating the height of the carbon peak on the CHN chromatogram to a calibration curve, a value is obtained for the percent carbon of a particular sample. From blank tests, a small quantity of carbon was found to be present in the mica before treatment. This quantity was subtracted from the total measured percent carbon, and the resulting value could therefore be related directly to the increase in carbon content due to the silane treatment. The quantity of silane was obtained by multiplying the corrected value for the carbon content by the ratio of the molecular weight of the hydrolyzed silane to the weight of carbon per mole of silane. The average error encountered was $\pm 0.8 \times 10^{-4}$ g silane/g mica.

Effect of pH

The effect of pH on the silane treatment is shown in Figure 2, where the quantity of silane adsorbed per gram of mica is plotted vs. the solution pH. The mica samples were treated with a 0.5% silane solution (g silane/g mica) for 45 min. The results indicate that CVBS can adsorb onto mica over a large pH range with the most efficient treatment occurring in neutral and acidic media and relatively poor treatment occurring at a pH of 11.6. Plueddemann has recently indicated that CVBS applied well from water to glass fiber over a wide range of pH values.[21]

Effect of Concentration

The effect of initial silane concentration is shown in Figure 3. These experiments were carried out at a pH of 5.5 with a treatment time of 45 min. Concentrations were calculated as a weight percent of silane on mica. The amount of silane adsorbed onto mica increases with the initial concentration of silane in the treating solution. The dependence decreases at higher concentrations.
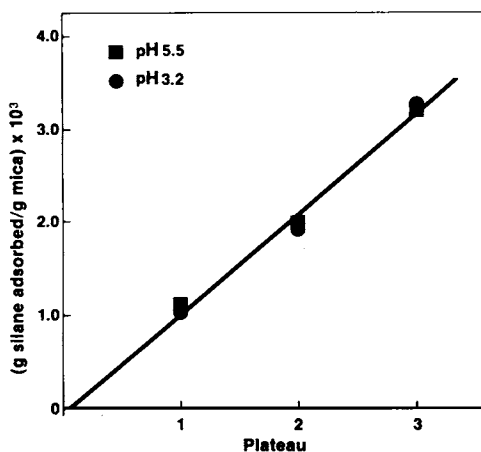
Fig. 6. Correlation of successive plateaus with the quantity of CVBS adsorbed: (■) plateau values obtained from Fig. 4, pH 5.5; (●) plateau values obtained from Fig. 5, pH 3.2.

Effect of Time of Treatment

In Figure 4 results are given showing the effect of time of treatment on the adsorption of CVBS onto mica at a pH of 3.2. The concentration of CVBS used was 0.5%. The data illustrate that silane is adsorbed in a step-wise fashion yielding three distinct plateaus. It should also be noted that there is no induction period at low values of time; silane adsorption onto mica starts immediately from time zero.

The most widely used pH range for the surface treatment of inorganic materials with silane/water solutions is 3–6. A comparable time-dependent experiment was therefore carried out at a pH of 5.5 and the results are shown in Figure 5. A similar steplike curve was obtained with the plateaus occurring at the same values as when the pH was 3.2. Before reaching the second plateaus, both Figures 4 and 5 show similar behavior; however, the induction period preceding the rise to the third plateau is longer at a pH of 5.5.

The plateau values from Figures 4 and 5 are plotted in Figure 6. It can be seen that the quantity of silane adsorbed is equal for each of the observed steps.

DISCUSSION

The observed dependence of silane adsorption on the time of treatment is of significant interest. It was observed that the silane molecules were adsorbed onto the mica flakes in a steplike fashion with each step equivalent with respect to the quantity of silane adsorbed. From Figure 6 the average number of molecules adsorbed at each plateau was calculated. Using these data and the measured surface area of the mica flakes (Table I), the area per molecule per plateau was calculated at 0.33 nm^2. The regularity of the amount adsorbed per step and the area occupied per molecule strongly suggest that each plateau observed in the time dependence curves corresponds to the adsorption of a monolayer of silane on the flake surface.
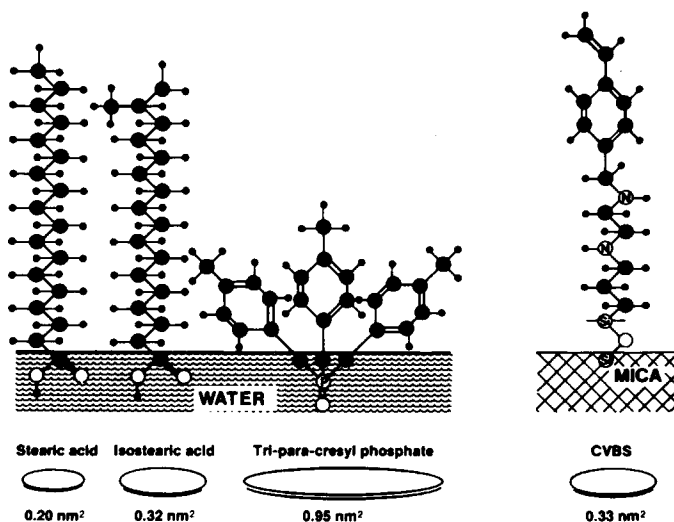
Fig. 7. Comparison of the area occupied by a CVBS molecule with classical examples[22] of molecules oriented normal to a surface: (O) oxygen; ((N)) nitrogen; ((Si)) silicon; (●) carbon; (•) hydrogen; ((P)) phosphorus.

The area occupied per molecule (0.33 nm^2) is relatively small. The small surface area occupied indicates that, outside of the silanol groups, CVBS tends not to interact with the mica surface and that it is, in fact, oriented normal to the surface. Figure 7 shows other systems which are considered as classical examples of molecules oriented normal to a surface. It can be seen that the area occupied by CVBS is comparable to these examples. The large surface area occupied by a branched molecule is also shown for comparison purposes. The equal quantity of silane adsorbed per step (Fig. 6) indicates that the second and third monolayers are oriented in a similar fashion to the first monolayer.

The fact that there is no induction period at low values of time differentiates the adsorption process in the region up to the first plateau (regime A, Fig. 4) from the rest of the curve (regime B). This observation is also consistent with a monolayer adsorption phenomenon. Regime A represents the very favorable and rapid interaction of silane with the mica surface while regime B represents the onset of multilayer adsorption of silane onto silane. It is well known that a CVBS molecule has a greater affinity for a silicate surface than for itself.[23]

The appearance of plateau regions in regime B indicate that a particular monolayer of CVBS is completed much more rapidly than the initiation of the next adsorbed layer. Such a process is illustrated schematically in Figure 8 where propagation in direction a is much faster than that in direction b. An analogy to this process is found in polymer crystallization phenomena known as regime I crystallization; once a surface nucleation act has been accomplished on the crystal surface, a particular growth strip or layer is quickly completed before a new nucleation act occurs.[24] It may be that the highly oriented nature of CVBS on mica allows the multilayer adsorption phenomenon shown in regime B to be compared with crystal growth behavior. The data obtained appear to be consistent with a model incorporating a slow quasinucleation step, which results in the plateaus shown in Figures 4 and 5. This is followed by rapid growth until the particular silane monolayer is completed.
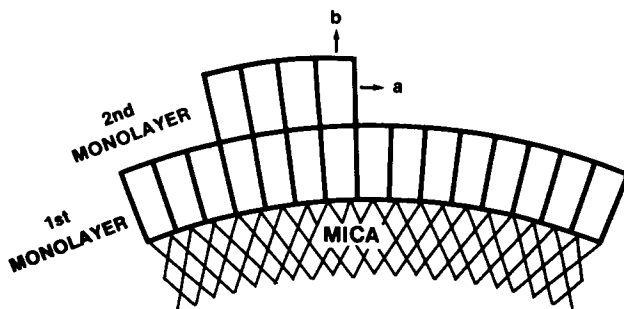
Fig. 8. Schematic illustrating that particular monolayers of CVBS on mica are completed before the next layer is started. Each rectangle represents a molecule of CVBS. Growth in direction a is much faster than in direction b.

What are the technical implications of this study? This paper has indicated the role of critical parameters on the treatment of mica with a cationic vinyl benzyl silane and introduced a precise and rapid method of analyzing that treatment. As well, the results indicate that the adsorption of individual monolayers of silane onto mica can be controlled right down to the first layer. This latter point may be of commercial interest especially if only the first layer is required for property improvement.

CONCLUSIONS

The adsorption of CVBS onto mica is sensitive to pH, concentration of treating solution and time of treatment. Furthermore, it is suggested that CVBS on mica is a highly ordered and closely packed multilayer phase with silane molecules oriented normal to the mica surface. The multilayer adsorption of silane onto silane can be compared in some respects to polymer crystal growth.

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