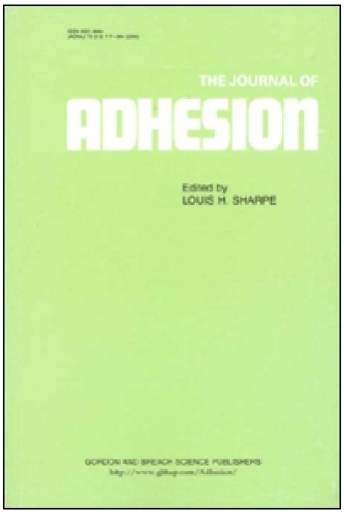

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Diffuse Reflectance Fourier Transform Infrared Spectroscopic Study of Chemical Bonding and Hydrothermal Stability of an Aminosilane on Metal Oxide Surfaces

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Fourier transform infrared spectroscopy was used to study the metal oxide/silane interface. Structures of γ-aminopropyldimethylethoxysilane (γ-APDMES) coupling agent on the surface of metal oxide powders are proposed. The structures depend on the surface characteristics of the substrate. The amine group of the silane molecule forms a hydrogen bond with the silica surface. The enhanced intensity of the amine band around 1600 cm^{-1} indicates that the amine group forms a complex on the titanium dioxide and aluminum oxide surfaces, as well as a hydrogen bond. By using the diffuse reflectance infrared technique, the Al-O-Si and Ti-O-Si antisymmetric frequencies are detected at 963 and 950 cm^{-1}, respectively, which agree favorably with the calculated frequencies. When the treated metal oxide powders are immersed in 80°C water, the rate of silane desorption increased in the following order of substrate; SiO_2, TiO_2 and Al_2O_3.

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INTRODUCTION

The surface composition of glass fibers and the surface treatment can affect the adhesion of a polymeric matrix to the fiber surface. Heat treatment, additives, etching and surface leaching are often used to imporove the durability, hardness, chemical resistance and adhesion. Chemical analysis of the surface is essential to understand the nature of these effects.

In fiber-reinforced plastic technology, glass fibers or other types of fillers are used as reinforcements or as extenders for polymeric materials. Since glass fibers are composites of various metal oxides, it is essential to elucidate the role of these metal oxides on the structure of the silanes. With different types of oxides present in glass fibers, silane coupling agents can react differently toward these metal oxides. Each oxide has its own intrinsic characteristics such as surface isoelectric point.[1] Aminosilane has been widely used in fiber-reinforced plastics. Extensive research on its molecular structure reveals that this compound can form many structures depending on the pH of the treating solution and also the drying conditions.[2] Hence, the structure of the aminosilane may be especially vulnerable to the microheterogeneity of the surface. The key to good mechanical performance and efficient processing of composite systems lies in the properties of the filler/resin interface.

In this paper, we will characterize the surface of treated metal oxides using transmission and diffuse reflectance Fourier transform infrared spectroscopy. Three model metal oxides are used in an attempt to improve our understanding of the bonding of the aminosilane with different substrates and with different domains if microheterogeneity exists in glass fibers. Immersion tests will show what type of surface will be more hydrolytically stable in hot water. The results will provide a mechanistic understanding of how the surface of reinforcements and an aminosilane interact. In order to obtain information about the hydrothermal stability of the interfacial bonds, we have chosen monoalkoxy silane. This choice will minimize complication caused by the lateral siloxane bonds which can be formed using trialkoxy silanes.

Infrared spectroscopy is widely used to study the molecular structure and chemical composition of surfaces.[3,4] The classical infrared transmission method provides both qualitative and quantitative information about the surface species[5] and has been extensively employed. With the development of Fourier transform infrared spectroscopy (FT-IR) and improvements in signal-to-noise ratio, several infrared techniques have been successfully used. Among them is the diffuse reflectance technique which is very useful for powdery samples and fibers. The diffuse reflectance technique was developed many years ago.[6,7] The diffusely reflected radiation is collected by a mirror and transmitted to the detector. The basic principles of this technique were developed by Kubelka and Munk.[6] A sample is placed in a sample pan and the spectrum is ratioed with a pure KBr spectrum. The intensity unit is in general expressed as the Kubelka-Munk unit which can be obtained by the following relationship:

$$f(R\infty) = (1-R)^2/2R$$

where $R\infty$ is the absolute reflectance of the material.

The spectral information depends on the particle size and the scattering coefficient. Qualitative information can easily be obtained. Quantative information is ambiguous at high concentrations[8] similar to the transmission technique. In order to perform an accurate spectral subtraction, Kubelka-Munk units of components to be subtracted must be low.[9] The sample may be diluted with KCl or KBr powder. Some of the advantages in using the diffuse reflectance technique are that it requires no sample preparation so the unperturbed structure of the surface species can be studied. The conventional sample preparation method, where KBr powder is ground with the sample and pressed into a pellet, can be avoided in the diffuse reflectance technique. It is not a requirement to mix the sample with KBr powder with this new technique. Another advantage of the diffuse reflectance technique includes enhanced surface selectivity. Though the spectral information is not localized only in the vicinity of the surface as is the case for X-ray photoelectron spectroscopy, the bulk contribution to the diffuse reflectance spectrum is apparently reduced. Therefore, it is easier to observe surface species with diffuse reflectance spectroscopy than with the transmission technique.

EXPERIMENTAL

Aluminum oxide (Al_2O_0), titanium dioxide (TiO_2), and silicon dioxide (SiO_2) with a specific surface area of 130, 100 and 50 m^2/g, respectively, were kindly supplied by Mr. Lierson of Degussa, Inc. Gamma-aminopropyldimethylethoxysilane (γ-APDMES) was purchased from

Petrarch Systems Inc. and used as received. One per cent and 0.2% by weight of γ-APDMES was hydrolyzed in deionized, distilled water for 40 min. Metal oxide powder was immersed in the solution for 15 min. The sample was centrifuged and the solution decanted. The treated powder was dried in air at room temperature for one day and heated at 80°C for one day. Immersion tests were made by placing the treated powder in distilled water at 80°C. The powder was removed from the water at various intervals for infrared analysis.

The amount of γ-APDMES was calibrated by transmission infrared technique. Gamma-APDMES was allowed to hyrdolyze by absorbing moisture from air for three weeks. The surface of the sample was scratched on several occasions to ensure complete exposure to moist air. The dried sample was carefully weighed with a Perkin Elmer microbalance with the accuracy of 0.1 μg. The weighed sample was ground with KBr powder and compressed into a pellet for infrared analysis.

A Fourier transform infrared spectrophotometer (Digilab FTS-20E) was used at a resolution of 4cm^{-1}. The spectrometer was constantly purged with dry nitrogen. A liquid nitrogen-cooled Mercury Cadmium Telluride (MCT) detector was used for high sensitivity data collection. A Digilab DRA-100 diffuse reflectance accessory with hemispherical mirrors was placed in the sample chamber and used to collect the diffusely scattered light from the sample. To improve the signal-to-noise ratio, a long scanning period of 600 scans was utilized whenever necessary, but in many instances 200 scans was sufficient.

The calibration of powders was done by carefully weighing the powder with a microbalance. The weighed powders were ground with approximately 200 mg of KBr powder and pressed into a pellet. The transmission infrared technique was used to monitor the intensity of the intrinsic peaks due to the sample *versus* the weight in milligrams. For the desorption study, determination of the surface coupling agent was done in two steps. First, the transmission spectrum of the silane-treated oxide powder was obtained prior to the desorption study, followed by measurement of the diffuse reflectance spectrum of the identical sample. No spectral comparison between the transmission and diffuse reflectance spectra was made. However, the silane concentration determined by the transmission technique was used as the reference, starting concentration for the diffuse reflectance spectrum. Since diffuse reflectance spectrum is quantitative at very low concentrations, such as the case in this study, comparison between the diffuse reflectance spectra at various immersion times is reasonable. By this method, one can take advantage of the quantitative nature of the transmission technique and the surface sensitive diffuse reflectance technique enabling us to determine concentration changes at very low surface coverages.

Isopropyltriisostearoyltitanate (KR-TTS) (kindly supplied by Mr. S. Monte, Kenrich Petrochemical Inc.) was used to treat the silica. The coupling agent solution was prepared from 0.5% by weight of ethanol. The sample powder was mixed in the solution for 30 min. After centrifugation, the excess ethanol was decanted and the sample was dried in vacuum at room temperature. The samples were examined by the diffuse reflectance infrared technique.

Preparation of samples for the diffuse reflectance spectroscopy was done by simply mixing the sample with KBr powder. No grinding was applied during the preparation. The single beam spectrum of the sample was ratioed with the single beam spectrum of pure KBr powder. The spectra are plotted in Kubelka-Munk units.

RESULTS

We have chosen SiO_2, TiO_2 and Al_2O_3 as substrates because the isoelectric point of these fumed powders covers a wide pH range. Therefore, a surface charge effect may be observed. Another reason for choosing TiO_2 and Al_2O_3 is the transparency of the infrared absorption in wide spectral ranges of interest. The aminosilane used has major absorption bands from 1600 to 900 cm^{-1}. The region around 1600 cm^{-1} yields information concerning the amine group. The band around 1000 cm^{-1} is informative about the siloxane bond and perhaps the interfacial metal-O-Si bond. The band at 1080 cm^{-1} is due to the Si-O-Si stretching mode of silica. This region overlaps with the Si-O-Si stretching mode of the silane coupling agent itself. Titanium dioxide has a strong absorbance at 700 cm^{-1} whereas aluminum oxide has a strong band at 830 cm^{-1}, and these bands do not overlap with useful bands of the aminosilane. Though the OH bending modes of silanol and other metal hydroxide groups do exist in the region of 1600–900 cm^{-1}, these modes are weak in intensity, and broad, thus difficult to observe. Nevertheless, we took a precaution to avoid the possible interference by these modes by employing the metal oxide powders, which were immersed in distilled, deionized water, as reference.

Figure 1C shows the spectrum of the treated silica powder (Figure 1A) minus the untreated powder (Figure 1B). The difference spectrum

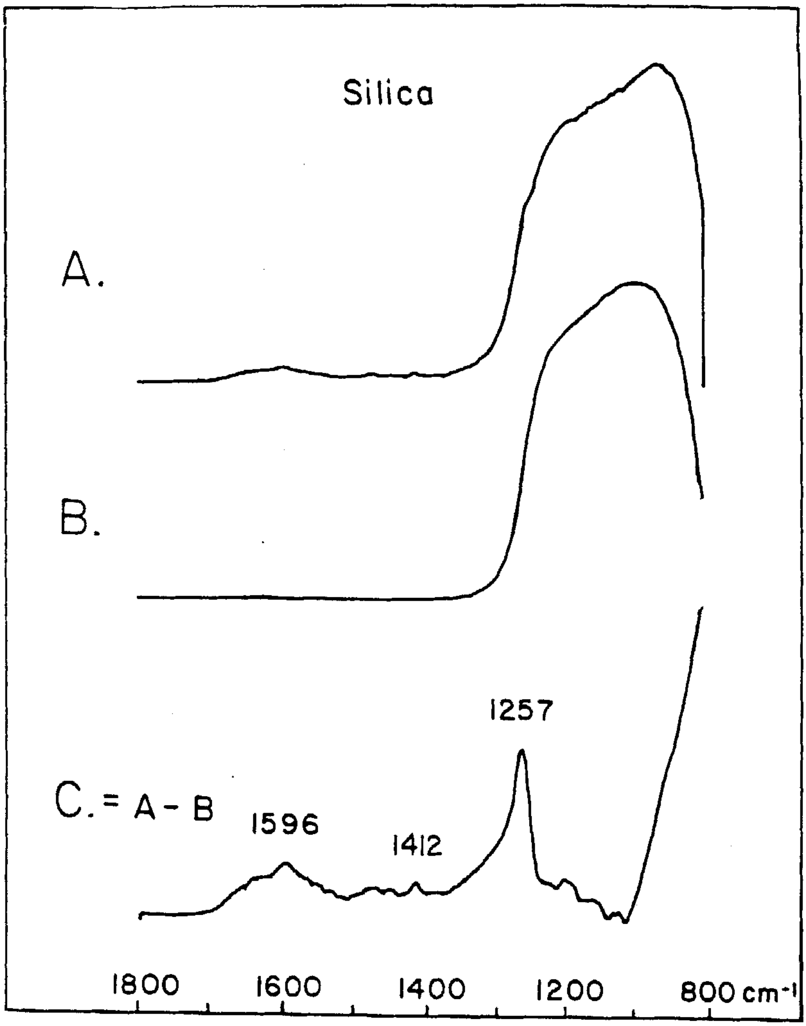

FIGURE 1 Diffuse reflectance infrared spectra of A) treated silicon dioxide with 1% γ-APDMES by weight; B) untreated silicon dioxide, and C) the difference spectrum (A-B).

reveals information about the surface treatment and the possible chemical changes that may occur. In the difference spectrum, the band at 1596 cm is assigned to the NH deformation mode of the silane coupling agent molecule. A weak band at 1412 cm^{-1} and a strong band

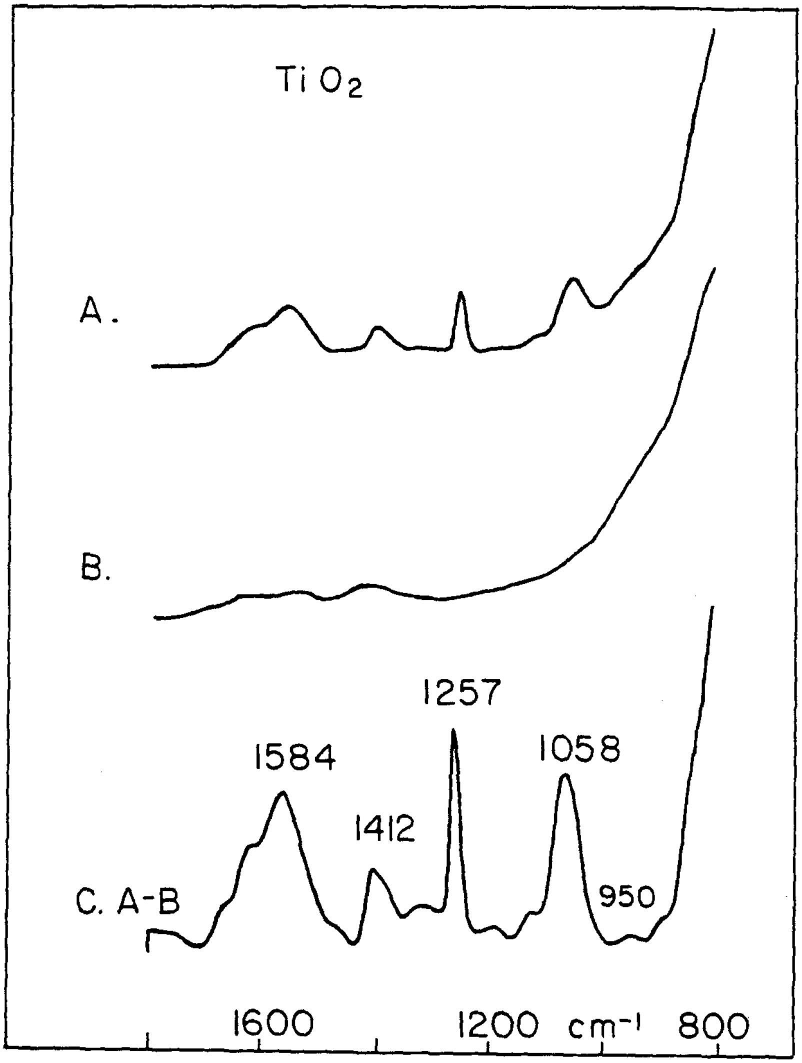

FIGURE 2 The difference spectrum (C) of treated titanium dioxide (A) and untreated titanium dioxide (B) reveals the structure of γ-APDMES adsorbed onto the surface.

at 1257 cm^{-1} are due to the antisymmetric and symmetric deformation modes of the $SiCH_3$ group, respectively.

Figure 2A is the spectrum of titanium dioxide treated with γ-APDMES from cyclohexane. Figure 2C is the difference spectrum

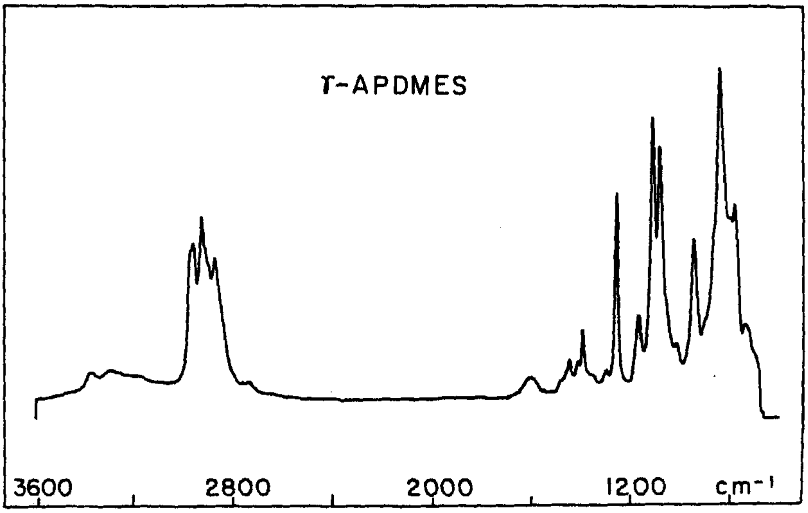

FIGURE 3 FT-IR transmission spectrum of neat γ-APDMES between KBr plates.

of the treated titanium dioxide minus the untreated sample. The NH_2 band is noticeable. The frequency of the NH_2 deformation band of the treated titanium dioxide sample shifted downward from 1596 cm^{-1}, in the case of silica, to 1584 cm^{-1}. The intensity of this band is also enhanced when compared with the neat γ-APDMES spectrum (Figure 3) and the difference spectrum of γ-APDMES on silica (Figure 1C).

The band at 1058 cm^{-1} is assigned to the Si-O-Si antisymmetric stretching mode of the γ-APDMES hydrolyzate dimer.[10,11] Only the very weak residual silanol group of the silane is observed. Hydrogen bonded silanol group of γ-APDMES shows a band around 840 cm^{-1}. Therefore, a new band at 950 cm is attributed to the interfacial bond. Neither the bulk silane nor TiO_2 show measurable modes in the vicinity of 950 cm^{-1}. Some γ-APDMES molecules may condense to form dimers while some of the remaining molecules may form chemical bonds to the titanium dioxide surface. With the presence of the 950 cm^{-1} band and the lower intensity of the dimer peak without appreciable residual silanol, the band at 950 cm^{-1} is tentatively assigned to the surface bonding of TiO_2 and silane coupling agent (the Ti-O-Si bond).

To ascertain the assignment of the 950 cm band, a titanate coupling agent (KR-TTS) was adsorbed on the surface of silica with a specific

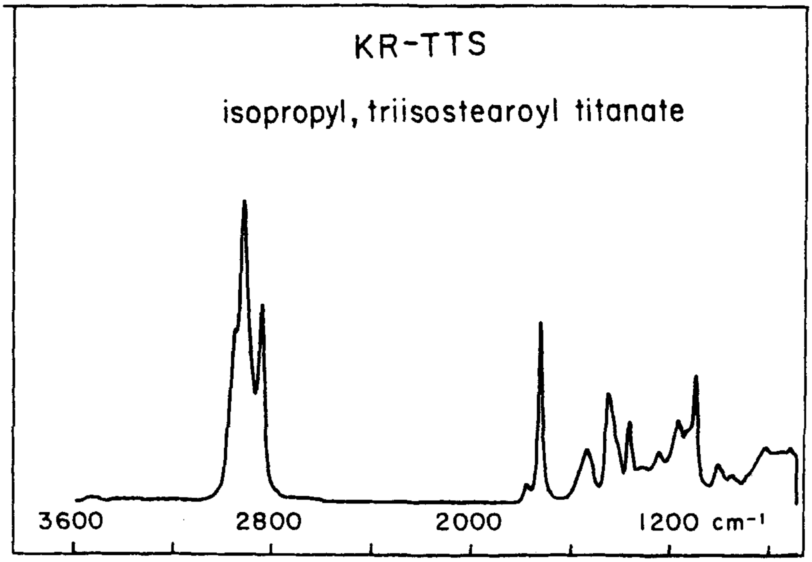

FIGURE 4 Spectrum of neat KR-TTS titanate coupling agent.

area of 380 m^2/g. Both silane-treated TiO_2 and titanate-treated SiO_2 potentially possess Ti-O-Si interfacial[2] bonds. Thus, the use of this second system should result in the interfacial bond in the vicinity of 950 cm^{-1} if this band is in fact due to the Ti-O-Si bond. Figure 4 shows the spectrum of the neat titanate coupling agent. No bands were observed around 950 cm^{-1}. When the untreated silica (Figure 5B) is subtracted from the titanate-treated sample (Figure 5A), the difference spectrum (Figure 5C) reveals an appearance of a peak at 950 cm^{-1}. This observation supports the assignment of the 950 cm^{-1} band as mentioned above.

Figures 6A and 6B are the spectra of γ-APDMES treated and distilled water-wetted aluminium oxide, respectively. The difference spectrum of the silane-treated sample (Figure 6C) shows a band at 1575 cm^{-1}. This band can be assigned to the NH_2 deformation mode. The frequency of this band is now at 1575 cm^{-1} as compared to 1596 cm^{-1} for silicon dioxide and 1584 cm^{-1} for titanium dioxide. The band at 1058 cm^{-1}, which was assigned to the γ-APDMES dimer, can be seen along with a new band at 963 cm^{-1}. Thus, we tentatively assign the band at 963 cm^{-1} to the interfacial Al-O-Si stretching mode.

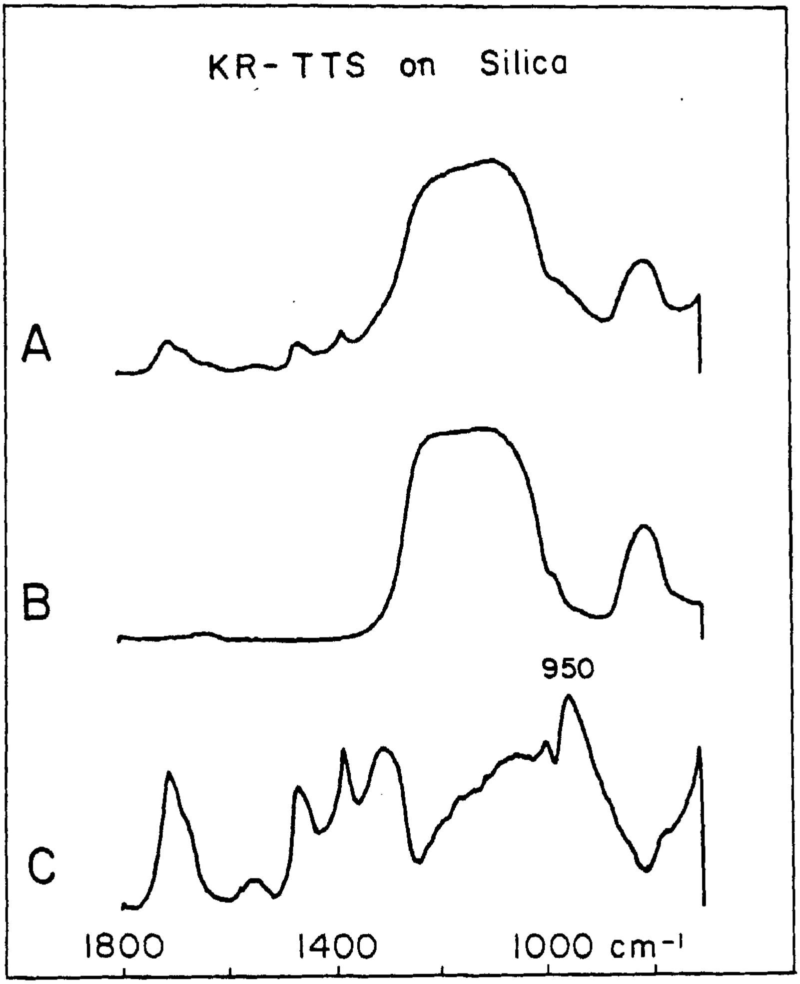

FIGURE 5 Diffuse reflectance spectrum of A) KR-TTS treated silicon dioxide; B) untreated silicon dioxide and C) the difference spectrum (A-B) showing a new peak at 950 cm^{-1}.

In order to investigate the hydrothermal stability of γ-APDMES on oxide surfaces, the samples treated with 1% γ-APDMES by weight were immersed in distilled water at 80°C. It was observed that the aluminum oxide sample sank immediately in the hot water, whereas slight difficulty was experienced with the titanium dioxide sample, which required more than 20 min before immersion. The treated silicon

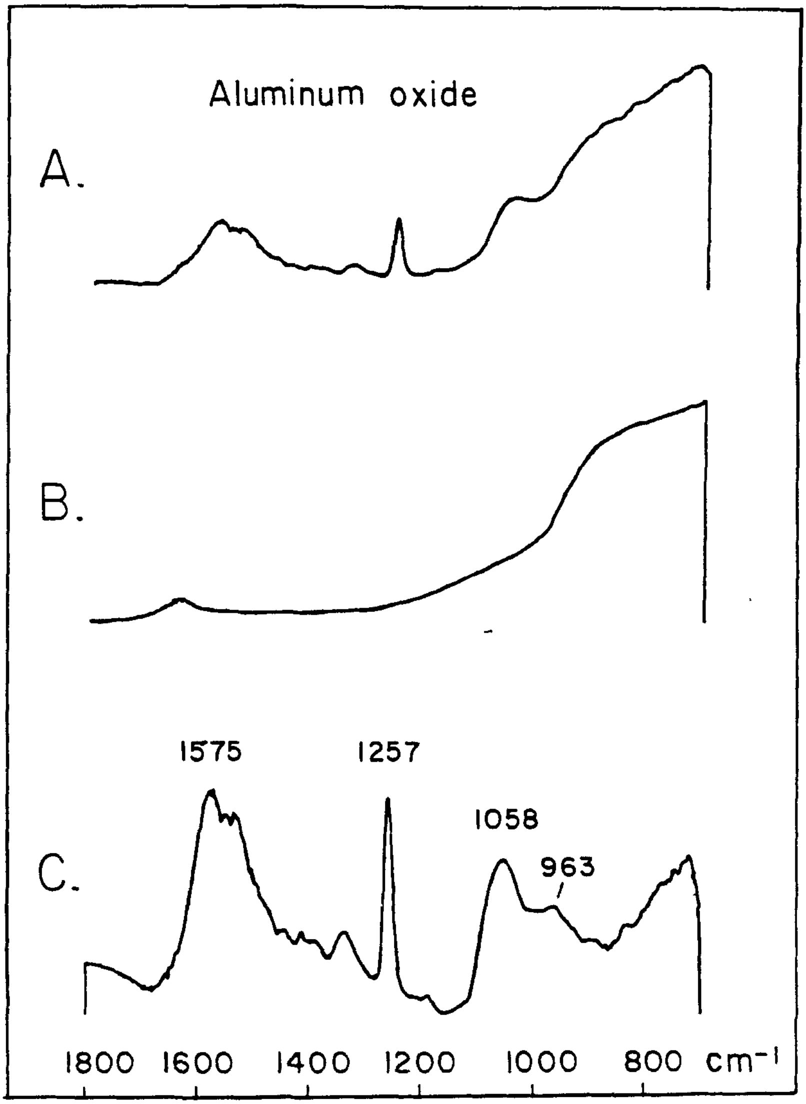

FIGURE 6 Diffuse reflectance infrared spectra of A) γ-APDMES treated aluminum oxide; B) untreated aluminum oxide and C) the difference spectrum.

dioxide, however, did not immerse even when vigorous agitation was applied. Figure 7 shows the spectra of titanium dioxide treated with

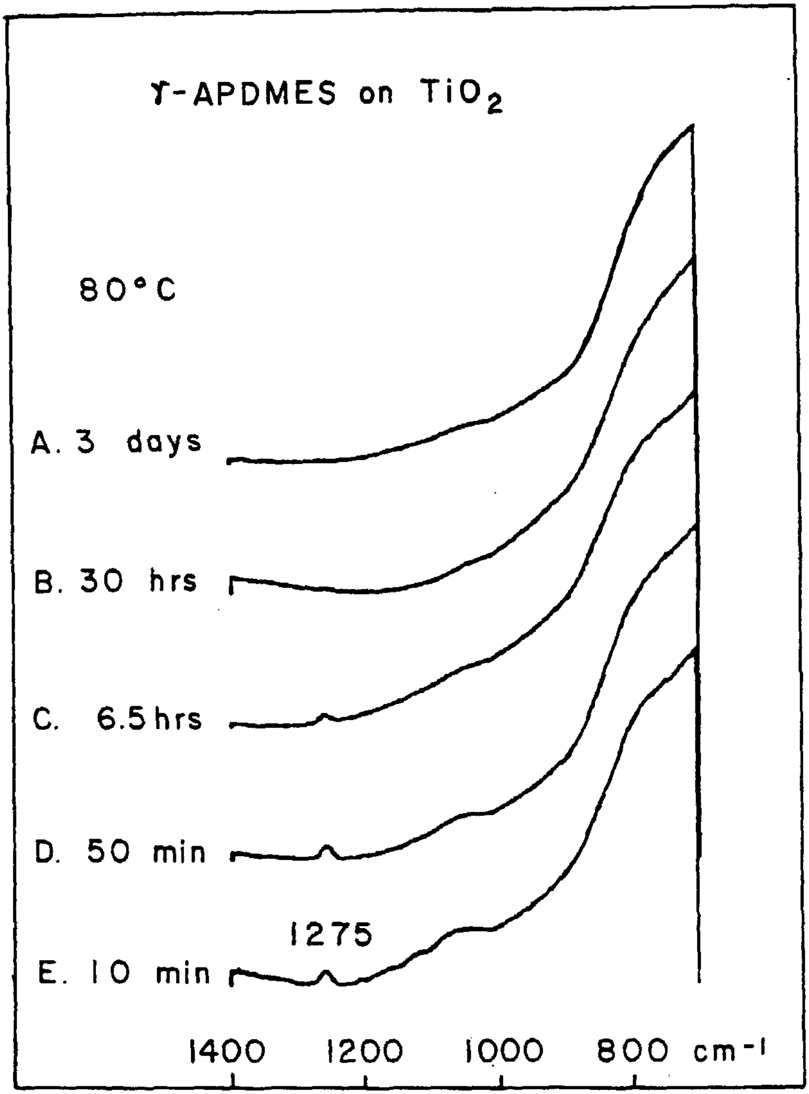

FIGURE 7 Spectra of titanium dioxide treated with γ-APDMES. γ-APDMES desorbs as a function of immersion time.

γ-APDMES immersed in 80°C water as a function of immersion time. The amount of γ-APDMES present per milligram of oxide powder is plotted against the weight of the powders in Figure 8. It can be

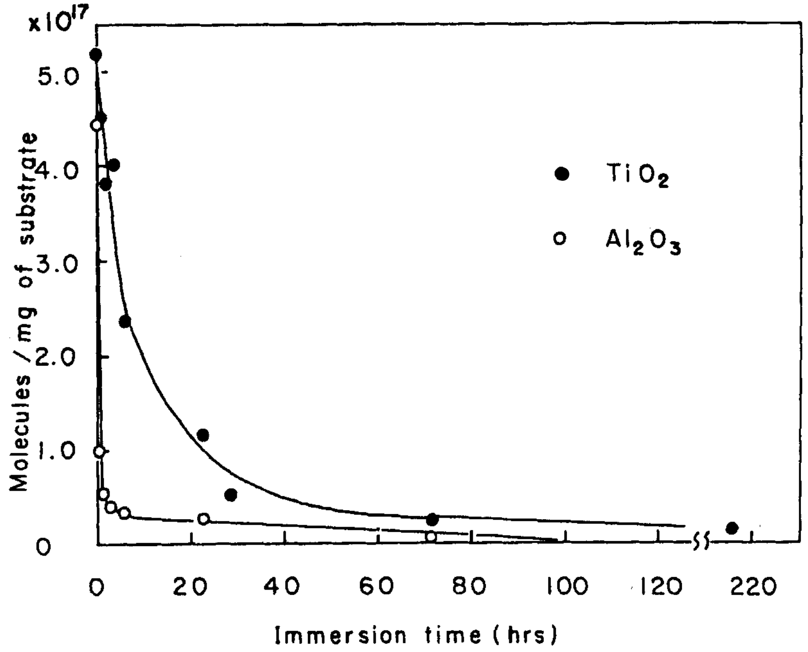

FIGURE 8 Desorption curve of γ-APDMES. The number of γ-APDMES molecules remaining on the powder per milligram of powder is plotted as a function of immersion time.

seen that the silane on the aluminum oxide desorbs at a much faster rate than on the titanium dioxide sample.

The stability of the interfacial bond between silane coupling agent and metal oxide surface is an important factor in the hydrothermal stability of composite materials. Water can hydrolyze the oxane bond and sever the interfacial linkage. In order to study the hydrothermal stability of the silane at low coverages, metal oxide powders were treated with 0.2% by weight of γ-APDMES. The amount of the silane adsorbed on the metal oxides before the immersion test was calculated using the transmission infrared technique. The samples that were recovered from the immersion test were all examined by the diffuse reflectance technique. The amount of the silane present on the powder sample can be calculated by relating the diffuse reflectance spectrum with the transmission spectrum of the sample before the immersion test.

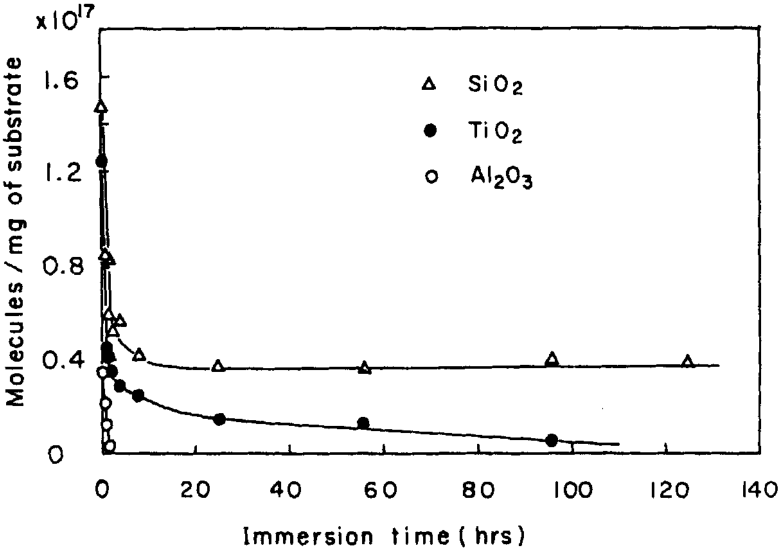

FIGURE 9 Desorption curve of γ-APDMES at low coverages on silicon dioxide, titanium dioxide and aluminum oxide powders.

The silane-treated powders were again immersed in distilled water at 80°C. All three samples easily sank in water, unlike the previous samples with higher surface coverages. The curves in Figure 9 show the comparison of the desorption of the silane from three different metal oxides. It can be seen that aluminium oxide loses the silane molecules at the fastest rate, whereas silicon dioxide maintains the silane molecules the longest.

In order to differentiate the role of the amine and silanol groups in the hydrolytic stability, the desorption of *n*-propylamine was examined with titanium dioxide as substrate. This is the system where only the amine part undergoes possible chemical interaction with the surface. Figure 10 shows the spectra of the sample obtained after various immersion times in 80°C water. The amine band shifts from 1600 cm^{-1} in the neat sample to 1575 cm^{-1} when it is on the titanium dioxide surface. The enhanced intensity at 1757 cm^{-1} band is also noticeable. After the sample was evacuated at room temperature for 12 h, *n*-propylamine still remains on the surface. It is likely that the amine interacts with titanium dioxide surface *via* hydrogen bonding and perhaps complexing with titanium atom which results in the enhanced

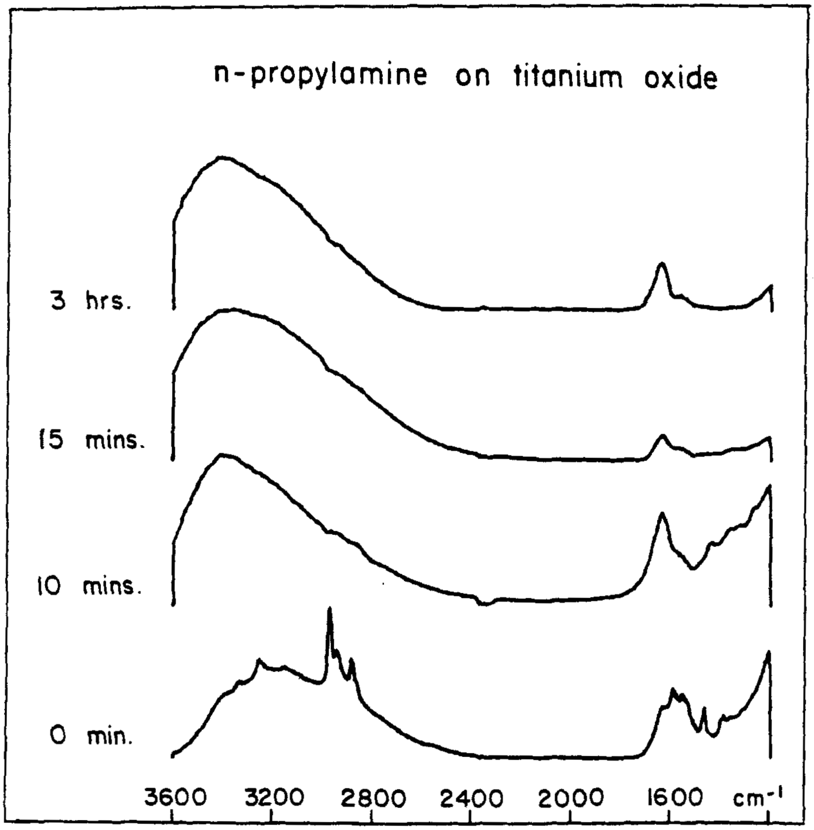

FIGURE 10 Spectra of *n*-propylamine treated titanium dioxide as a function of immersion time in 80°C water. Most of the *n*-propylamine desorbs within 10 min.

intensity. By observing the CH band around 2930 cm^{-1} which is due to the propyl chain, it can be observed that *n*-propylamine desorbs almost completely within 10 min of immersion time. The rapid desorption of *n*-propylamine may be due to the absence of covalent bonding between the surface of titanium dioxide and *n*-propylamine. It further indicates that coordination and/or hydrogen bonding of amine play little role in desorption resistance.

It was also observed that γ-APDMES does not adsorb very strongly onto the aluminium oxide surface when compared with titanium dioxide and silicon dioxide. The small amount of adsorption may be influenced by the surface isoelectric point (IEP) of aluminium oxide which is 9.1[1].

The surface of aluminium oxide in silane solution is near neutral and there is no strong interaction of silane to the aluminum oxide surface. However, silicon dioxide, which has an IEP = 2.2[1], is more negatively charged in the silane solution. Strong interaction of the amine group of the silane molecule may exist with silica. Therefore, a higher adsorption of silane is observed with the silica sample. Also, interaction of both the silanol and the amine groups with the silica surface will result in a bridge structure exposing the propyl chain of the silane. This explains why the aminosilane on silica forms hydrophobic surface.

DISCUSSION

The frequency of the interfacial Ti-O-Si and Al-O-Si bonds were calculated using a simple harmonic oscillator model[10]. Admittedly, the model is crude yet a trend of frequency shift and general region of the interfacial frequency can be determined. The calculated antisymmetric stretching frequencies of the interfacial Ti-O-Si and Al-O-Si bonds are 921 and 960 cm^{-1}. The frequency range and the direction of the frequency shift from the titanium dioxide sample to the aluminum oxide sample favorably agree.

Great care must be taken to carry out such a experiment since the difference spectrum of an aluminium oxide without silane treatment shows a band in this frequency range when the spectra of as received sample and the sample wetted with distilled water are subtracted. As described previously, we attempted to avoid this problem by employing the distilled water-wetted sample as reference.

When the silane-treated TiO_2 and Al_2O_3 samples are rinsed with tetrahydrofuran (THF), the dimers which are not chemically bonded to the surface can be washed away. The reduction in intensity of the 1058 cm^{-1} band has been observed as a consequence of the dimer desorption. It was noted that not all dimers desorb upon THF wash, probably due to the amine groups that are interacting directly with the surface.

The surface charge may have an influence on the orientation of the silane molecule adsorbed on the surface. The degree of surface charge can be determined by the isoelectric point (IEP). IEP is determined by the pH at which the surface will be neutral. Silicon dioxide, titanium dioxide, and aluminum oxide have IEP of 2.2, 6.0 and 9.1, respectively[1]. A cationic silane such as γ-APDMES can have an interaction with the surface through the amine group at the end of the propyl chain.

In the difference spectra of treated powders, the positions of an amine deformation are different. The spectrum of the treated aluminum oxide sample (Figure 6C) shows a band at 1575 cm^{-1} along with an enhanced intensity. The enhanced intensity indicates that the amine group interacts with the surface. It should be noted that an unheated sample usually shows the amine deformation band at 1575 cm^{-1} due to the amine-bicarbonate salt. Since the sample has been heat treated and the characteristic bicarbonate band at 1330 cm^{-1} is absent, the amine-bicarbonate salt is out of consideration. Illustrated in Figure 2C is the amine deformation frequency of the treated titanium dioxide sample at 1584 cm^{-1}. The enhanced intensity of the amine deformation band is also observed as in the case of treated aluminum oxide. Due to the very broad, multiple bands of the strongly hydrogen bonded amine groups, additional frequency shifts upon complexation were difficult to observe.

The possibility of amine coördinating with metal atom cannot be excluded. The enhancement in intensity of the amine deformation band around 1600 cm^{-1} indicates that amine interacts with the surface. Complexation of amine to metal such as titanium atom was found possible[14]. When *n*-propylamine was adsorbed on titanium dioxide, an enhanced intensity of the amine deformation band was observed. When the sample was evacuated for 12 h at room temperature, *n*-propylamine could not be removed from the surface. It can be concluded that amine interacts with the surface and also influences the adsorption characteristics.

Immersion tests show that desorption of silane is more rapid in the case of aluminum oxide than titanium dioxide. The treated silicon dioxide maintains the coupling agent for the longest period during the immersion tests. The major causes can be considered. First, the hydrophilicity of the treated aluminium oxide surface helps water to interact quickly with the silane. However, the equilibrium of water penetration into the silane layers may be reached very quickly since the thickness of the silane is at most a few molecular layers. Second, the hydrothermal stability of various M-O-Si bonds, where M designates the metal atom, may be different. For practical applications in composite technology, the composition of glass fibers may be important in designing hydrothermally stable materials. The contribution of different amounts of metal oxide changes the IEP of the material and, therefore, can change the conformation of the silane molecules at the interface.

CONCLUSIONS

Diffuse reflectance FT-IR spectroscopy was used to study the structure of γ-APDMES on metal oxide surfaces. It was found that the structure of silane depends on the substrate. The enhancement in intensity of the amine band around 1600 cm^{-1} indicates that the amine group can coordinate with the metal oxide surface. Diffuse reflectance spectra show a band around 950 cm^{-1} for the interfacial Ti-O-Si bond and around 963 cm^{-1} for the interfacial Al-O-Si bond. Immersion experiments show different hydrophobicity of the 1% silane-treated metal oxide surfaces. The treated aluminium oxide immerses easily in water and loses the coupling agent at a faster rate than the treated titanium dioxide and silicon dioxide. The surface isoelectric point could be an important factor in determining the orientation of the silane, especially the silane layers in the immediate vicinity of the oxide surfaces.

Acknowledgement

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