

In Situ Examination of Water Diffusion to the Polypropylene–Silane Interface Using FTIR-ATR

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ABSTRACT: This study investigated the effect of moisture on a model silane coupling agent modified adhesive bond. Fourier transform infrared–attenuated total reflectance (FTIR-ATR) spectroscopy was used to characterize the transport of moisture to a polypropylene-silane interphase and monitor the resulting chemical changes. The FTIR-ATR method offers the advantage of *in-situ* examination of the diffusion process, as well as the ability to characterize chemical changes that occur due to the presence of moisture. Experiments were conducted at ambient and elevated temperatures. The results of the real-time measurements demonstrated that moisture will migrate through the polypropylene to the silane interphase. The diffusion behavior was described well by a Fickian model. The apparent diffusion coefficients for water in the polypropylene-silane bilayer were on the order of the diffusion coefficients for water in polypropylene at both test temperatures. Furthermore, changes in the spectra were observed during the diffusion experiments. These changes were indicative of hydrolysis of the siloxane backbone in the silane layer while buried beneath the polypropylene film. This finding is significant as it presents direct evidence of a degradation mechanism in silane-modified adhesive bonds. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1971–1985, 1997

Key words: adhesion; adhesive bonding; polymer–silane interphase; silane coupling agents; FTIR-ATR; water diffusion; polymer composite

INTRODUCTION

Recently, the use of chemical coupling agents for adhesion improvement has received widespread attention. Specifically, silane coupling agents are often used to promote adhesion between inorganic oxides and polymers.^{1–5} The hot-wet performance of composites as well as adhesive bonds has been dramatically improved in instances where silane coupling agents have been employed. This improvement has been attributed to a number of

mechanisms and reviewed thoroughly elsewhere.^{1–5} However, very little direct information regarding the nature of the buried polymer-silane interphase, or the effect of moisture on the interphase, has been presented. A better understanding of the polymer-silane interphase and the potential interactions between moisture and silane may point to mechanisms that improve the long-term adhesion of silane-modified bonds.

Although the use of silanes generally improves the hot-wet properties of the composite or adhesive bond, there is usually some loss in mechanical performance after exposure to hot-wet conditions, which indicates the existence of interaction

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between the moisture and the bond. Reversible hydrolysis of the siloxane network has been suggested previously by Plueddemann to explain some of the effects of moisture on composite properties.¹ Boerio has proposed that silane coupling agents improve the performance of epoxy-aluminum bonds by increasing the induction period for the hydration of the underlying aluminum oxide layer.² Previous research in our laboratories has pointed to potential hydrolysis of the silane layer adjacent to the inorganic surface when exposed to hot-wet conditions.⁶⁻⁷ This hydrolysis was believed to cause significant decreases in joint performance and affect the overall durability of the bonded structure. However, since hydrolysis was detected on the failure surfaces after testing had been completed, it was difficult to ascertain when the hydrolysis had initiated. These and other previously reported results motivate a study of the behavior of the polymer-silane interface in the presence of water. Ideally, an *in-situ* investigation would be preferred so that the kinetics of any physical or chemical changes can be studied directly.

In this work, an *in-situ* method for studying the polymer-silane interphase and moisture ingress to the interface is described. The technique involves the use of attenuated total reflectance in conjunction with Fourier transform infrared spectroscopy (FTIR-ATR). This experimental method has the ability to monitor both the kinetics of moisture ingress, as well as any chemical changes occurring in the deposited silane layer. A brief background on the use of FTIR-ATR and applications for diffusion studies are discussed, and experimental results from a polymer-silane pair consisting of polypropylene (PP) and vinylbenzyl-(trimethoxysilyl)-propylethanediamine hydrochloride (acationic-styrlamine coupling agent hence denoted as CSS) are presented. The changes in the spectra that occur upon processing of the bond are evaluated. Also, the diffusion of water to the interphase and its effects are studied *in situ* at two temperatures. It is hoped that this study will provide further insight into the mechanisms for performance loss in adhesively bonded aluminum samples that had been treated using silane coupling agents.

BACKGROUND

Traditional methods for determining the rate of diffusion of liquid permeants in polymers gener-

ally employ gravimetric means. The kinetics of water uptake are often described by Fick's second law, and the diffusion can be considered to be one-dimensional in instances in which the sample thickness is much less than the length and width. The diffusion of water into polymers is usually measured by monitoring the weight change of samples exposed to moist environments as a function of time. In this case, the solution to Fick's second law is related to the weight gain through the following expression to obtain the diffusion constant:

$$\frac{M(t)}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2\pi^2Dt}{4l^2}\right] \quad (1)$$

Here, $M(t)$ represents the change in weight at any time, M_{∞} is the equilibrium uptake, l is the film half thickness, and D is the diffusion constant of the penetrant. This equation has been widely used to determine diffusion coefficients of permeants in polymers. Several excellent studies on moisture uptake of polymers and composites have been published previously⁸⁻¹¹ and have revealed the usefulness of this technique. Thus, by monitoring the weight of samples exposed to moisture, the diffusion coefficient of water can be easily obtained.

Table I lists typical values for diffusion constants and equilibrium uptakes for water at different temperatures for various polymeric and polymer composite materials. Diffusion of water in semicrystalline thermoplastic polymers is generally slower than in thermosets, as evidenced by the diffusion values for water in polyetherether ketone (PEEK) and PP as compared to epoxies. Additionally, the equilibrium uptakes in semicrystalline thermoplastics are very small, which hinders the effective use of gravimetric techniques to study the transport process.

In addition to gravimetric methods, several other experimental techniques have been evaluated for use as effective probes to study diffusion in polymers. FTIR-ATR spectroscopy has been shown to be a very effective and sensitive technique for studying molecular changes at surfaces and interfaces.¹⁶ Two distinct advantages of using an FTIR-ATR technique over other existing methods for diffusivity evaluation include the *in-situ* measurement of concentrations and the possibil-

Table I Moisture Diffusivity and Uptake Data for Various Polymers Obtained from the Literature

Polymer	Temperature (°C)	Diffusion Coefficient (cm ² /s)	Final Uptake (wt %)	Reference
Epoxy adhesives	20	1.5–3.0 × 10 ⁻⁹	3–6	8, 10, 11
	40	6–10 × 10 ⁻⁹	3–7	
Polydimethylsiloxane	25	3.5–5 × 10 ⁻⁵	6–8	8
	60	10 ⁻⁴	8–9	9
Polypropylene	65	3.8 × 10 ⁻⁸	0.235	7
Polyetheretherketone	25	4.9 × 10 ⁻⁹	0.41	14, 15
	35	8.8 × 10 ⁻⁹	0.44	
	65	2.2 × 10 ⁻⁸	0.50	
	95	3.2 × 10 ⁻⁸	0.55	
Carbon fiber/polyimide composite (K3A-polyimide)	25	≈ 1 × 10 ⁻⁹	—	13
	40	≈ 2.5 × 10 ⁻⁹	—	
	80 (75% RH)	≈ 1.5 × 10 ⁻⁸	—	
Polyetherimide	25	3 × 10 ⁻⁹	—	13
	65	2 × 10 ⁻⁸	—	
Polyacrylonitrile	25	10 ⁻¹⁰	—	12

ity of achieving small penetration depths (of the order of 0.1–0.5 μm).

The physics of ATR spectroscopy offers a unique opportunity to probe changes that occur in the region immediately next to the solid surface, including buried interfaces. Previous reflection-absorbance infrared (RAIR) spectroscopy studies on silane primers have shown that significant changes occur when the silanes are heated in air or exposed to reactive monomers.^{2–3,6–7} However, little information is available concerning the chemical changes that occur in a silane that is buried beneath a coating or adhesive layer. Therefore, an ATR study of the polymer-silane interphase should complement earlier RAIR studies of silanes.^{2–3,6–7} In this way, more insight can be gained on the chemical structure of the silane primer layer, the changes that occur upon processing, and any associated interactions with the polymer coating.

In addition to studying the chemistry at buried interfaces, FTIR-ATR has been used to study transport phenomena in polymeric systems. FTIR-ATR studies on diffusion of water through organic coatings,^{12,17} polymer-polymer interdiffusion,^{18–20} and diffusion of amine curing agents in solid epoxy resins²¹ have been reported. A unique advantage of internal reflection spectroscopy is the use of an optically dense medium—an inter-

nal reflection element (IRE)—as an optical wave guide to obtain an IR spectrum. The sample is placed in contact to the IRE surface; and above the critical angle, the IR radiation is totally reflected at the interface. When radiation is totally internally reflected, an evanescent wave is formed at the IRE/sample interface that interacts with the material. If the sample absorbs the IR, attenuation of the total reflection of the propagating beam inside the IRE will occur, yielding an IR spectrum. The amplitude of the evanescent wave decays exponentially from the surface, which means that the largest contribution to the spectrum comes from the material that is adjacent to the IRE surface. Figure 1 shows this effect schematically. In FTIR-ATR, the penetration depth is defined as the distance from the IRE surface, over which the magnitude of the penetrating electric field diminishes by a factor of 1/e and is given by the following expression:

$$d_p = \frac{\lambda}{2\pi n_2 (\sin^2 \theta - (n_2/n_1)^2)^{1/2}} \quad (2)$$

where λ is the wavelength of the radiation in vacuum, θ is the angle of incidence, and n₁ and n₂ are the refractive indices of the IRE and sample respectively.¹⁶ The absorbance measured in FTIR-

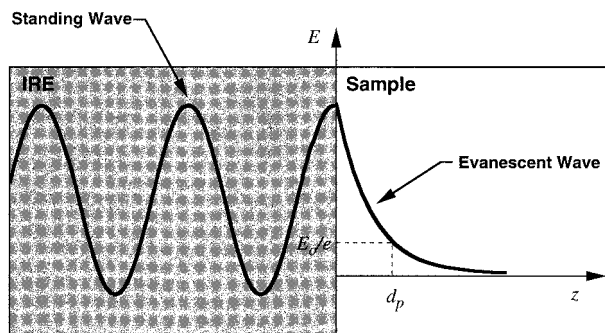


Figure 1 Schematic of the evanescent wave formed at the internal reflection element-sample interface. The depth of penetration is defined through eq. (2).

ATR spectroscopy is given by the following expression, which is analogous to the Beer-Lambert law for transmission:

$$A = \int_0^{\infty} aSC(z) \exp(-2z/d_p) dz \quad (3)$$

where z is the distance from the surface, a is the oscillator strength, $C(z)$ is the concentration, S is the cross-sectional area, and d_p is the penetration depth.¹⁶ This expression represents a weighted average of the concentration of the IR absorbing chemical species $C(z)$. Thus, the changes in concentration can be directly related to the change in absorbance measured during the experiment. Furthermore, bulk phase homogeneous chemical reactions and interactions between the species can be simultaneously monitored if the necessary bands are detectable and distinguishable. Therefore, FTIR-ATR is well suited to studying the diffusion and effects of moisture on the polymer-silane interphase *in situ*. In order to evaluate the kinetics of the diffusion process, the physics of FTIR-ATR must be incorporated with a suitable diffusion model.

Equation (3) indicates that the measured absorbance can be directly related to the concentration of the absorbing species in the vicinity of the internal reflection element. Thus, by analyzing the absorbance data using a suitable diffusion model, the diffusion coefficient can be determined. The transport of the moisture through the polypropylene and silane layers will first be modeled using a bilayer film approach. The different transport properties of the silane and polypropylene can be included using such a model. This is a reasonable approach, since the diffusion constant for water in polysiloxanes can be orders of magnitude

higher than for polypropylene, as indicated in Table I. Also, the equilibrium uptake of the silane layer may be significantly higher than that of PP. In fact, recent neutron reflectivity experiments have shown that the equilibrium moisture content in a silane-modified polyimide interphase is much higher than in the bulk polymer.²²

Analysis of the transient transport behavior in multilayered solids can be extremely complex, and the process used to obtain a solution^{7,23} will only be outlined here. The starting point for the analysis is to write the governing diffusion equation (Fick's Second Law) for each material. Here, the PP is designated as Material 1, with diffusion coefficient D_1 and equilibrium moisture uptake $c_{\infty 1}$, and the silane is designated Material 2 (D_2 , $c_{\infty 2}$). The thickness of the silane primer is α , and the thickness of the PP is l . The origin of the coordinate system lies at the interface between the silane and the PP. (Fig. 2 shows the problem geometry for each diffusion problem.) Appropriate boundary conditions are also needed. These represent the constant concentration condition at the PP-water interface and no penetration condition at the crystal surface. Two additional boundary conditions are found by applying matching conditions at the PP-silane interface.^{23,24} First, there is an equilibrium condition that must be maintained at the interface at all times. Additionally, the fluxes must be matched at the interface due to conservation of mass. The initial condition for the diffusion problem is zero concentration throughout the entire bilayer.

Problems of this type are best solved analytically using the method of Laplace transforms.²³ The use of Laplace transforms to solve partial differential equations has been widely documented in numerous texts²³⁻²⁵ and will only be outlined here. The first step is to perform a Laplace transform on the governing equations and the associated boundary conditions. This set of transformed differential equations is solved in Laplace space. Once the solutions have been obtained in Laplace space, the inverse Laplace transform is calculated to obtain the solutions in real space for each region. The solutions in real space can be determined through use of the Laplace Inversion Formula^{23,25} in order to obtain the transform. The Inversion Formula is a contour integral in complex space and is often used in conjunction with the Residue Theorem.²⁵ It has been shown⁷ that the resulting solution describing the diffusion of water through the bilayer film is expressed as

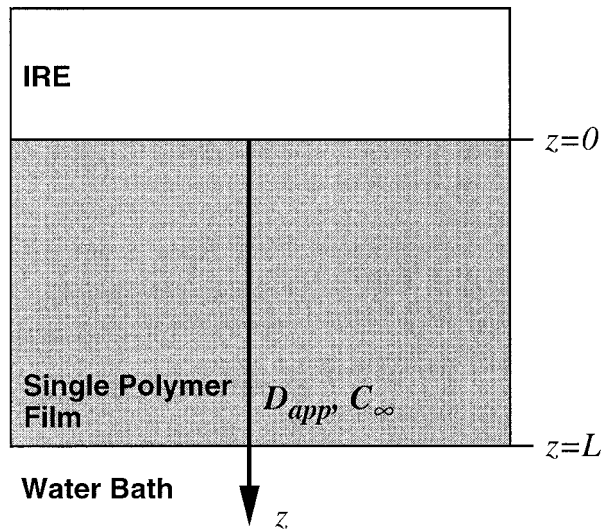
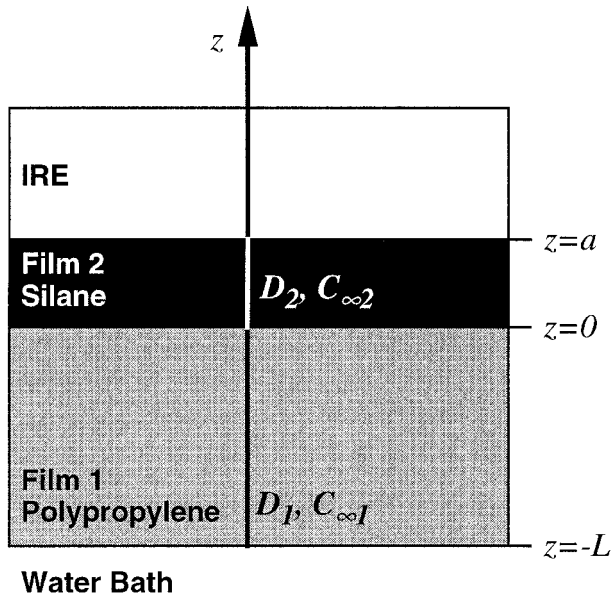


Figure 2 Geometry and coordinate system for the diffusion problems. Note the location of the origin in each case. In the bilayer problem, the silane and polymer layers are modeled independently, while they are combined in the single-film case.

$$c_1(z, t) = c_{1\infty} - 2c_{1\infty} \sum_{m=1}^{\infty} \frac{[\cos \beta_m z \cos p\beta_m a + \sigma \sin \beta_m z \sin p\beta_m a] \times \exp(-D1\beta_m^2 t)}{\beta_m [(l + \sigma pa) \sin \beta_m l \cos p\beta_m a + (pa + \sigma l) \cos \beta_m l \sin p\beta_m a]} \quad (4)$$

$$c_2(z, t) = \frac{c_{1\infty}}{k} - \frac{2c_{1\infty}}{k} \sum_{m=1}^{\infty} \frac{[\cos p\beta_m (a - z)] \exp(-D1\beta_m^2 t)}{\beta_m [(l + \sigma pa) \sin \beta_m l \cos p\beta_m a + (pa + \sigma l) \cos \beta_m l \sin p\beta_m a]} \quad (5)$$

where the β_n s are obtained by evaluating the poles of the following expression:

$$\cos \beta_m l \cos p\beta_m a - \sigma \sin l \sin p\beta_m a = 0 \quad (6)$$

with

$$p = \sqrt{\frac{D_1}{D_2}}$$

$$\sigma = \frac{1}{k} \sqrt{\frac{D_2}{D_1}}$$

The term k represents the equilibrium partition coefficient for water in polypropylene and CSS. Clearly, the solutions for the bilayer film cannot be readily manipulated in order to fit the diffusion equation using absorbance data. The solution listed in eqs. (4) through (6) requires the independent diffusion constants and problem geometry *a priori* as input in order to determine the coefficients of the infinite series. However, since the thickness of the silane layer is extremely small and transport through the polypropylene would conceptually appear to be the rate-limiting step, it may be possible to study the diffusion process using a simpler single film solution.

To this end, case studies can be performed using these solutions to provide insight into the deviation from the behavior that is predicted by the one film-diffusion solution. Using the composite bilayer solution, the concentration profile of moisture can be determined for any given geometry as a function of time. Then, the calculated concentration profile can be used in eq. (5) to model the measured absorbance that would develop with time, and these results can be compared to the single film solution. The solution to penetrant diffusion in a single film has been previously incorporated with eq. (5) to relate the change in absorbance to the Fickian diffusion process,^{12,18-21} and this approach will be used here. Essentially, the absorbance at any time can be normalized to the overall change in absorbance and fitted to an expression in which the diffusion coefficient D is

the only fitting parameter.^{8,12-14} When the film thickness is much greater than the penetration depth ($l \gg d_p$), this relationship can be expressed as

$$\frac{A_\infty - A(t)}{A_\infty - A_0} = \frac{\left\{ \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{(2n+1)^3 \pi^2 + 16 \left(\frac{L}{d_p}\right)^2 (2n+1)} \right] \times \exp\left(-\left(\frac{(2n+1)\pi}{2L}\right)^2 Dt\right) \right\}}{\left\{ \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{(2n+1)^3 \pi^2 + 16 \left(\frac{L}{d_p}\right)^2 (2n+1)} \right] \right\}} \quad (7)$$

where $A(t)$, A_0 , and A_∞ are the real-time, initial, and equilibrium absorbance, respectively; L is the film thickness; and d_p is the penetration depth of the radiation at the band of interest.^{8,21} This expression can be used to fit the simulated absorbance data calculated from the concentration profiles that are determined from eqs. (4)–(6).

For example, in the experiments that will be described in this work, the silane thickness usually was on the order of 0.5 μm , and the polymer film was about 100 μm . The diffusion constant for water in polypropylene at 65°C has been experimentally measured at approximately 3.8×10^{-8} cm^2/s .⁷ Additionally, assuming moisture diffusion behavior in a silane is reasonably close to that in a siloxane polymer, the diffusion constant should be about 1×10^{-4} cm^2/s . These values can be used to determine the β s, and the concentration profile of water in the composite bilayer at any given time can be calculated. Equation (3) can then be used to calculate the theoretical absorbance of a band due to the concentration of the water inside the whole domain, and this data can be fitted with eq. (7) to determine the error associated with using a one film-diffusion solution.

The normalized absorbance calculated from the model output is shown in Figure 3 as a function of different equilibrium concentration ratios (k values). The fits obtained from the one film solution approximation are also shown. [That is, the model data for the bilayer case was fitted using eq. (7).] Table II summarizes the apparent diffusion constants obtained when eq. (6) was used to fit the model data. For the geometry to be used in

the experiments, the deviation from the results obtained from a one-film solution is not very significant. If the equilibrium concentration of water is much greater in the silane than in the PP ($c_{2\infty} \gg c_{1\infty}$), then there appears to be a slight effect. The time needed to reach steady state is longer than in the one-film case. This makes sense physically, as more moisture is needed in the silane to achieve equilibrium, and transport through the polypropylene film is the rate-limiting step in this process. Even in this worse case, the discrepancy is small. Thus, reasonable fits should be obtained when using the one-film solution on the diffusion data for water into the PP-silane system. Due to the expected small deviations, the experimental data presented in the next section will be fitted with the one-film solution; however, it is carefully noted that the calculated diffusion constants will only be considered apparent values for the entire bilayer.

EXPERIMENTAL

Optical Constants, Depth of Penetration, and Band Selection

The value of the penetration depth is a necessary parameter for proper evaluation of the diffusivity. Therefore, the indices of refraction in the IR must be known for the polymers that are being evaluated. A method described by Harrick¹⁶ to determine the index of refraction of samples in the IR evaluates the critical angle for total internal reflection by monitoring the shape of the absorbance bands as the angle of incidence is changed. The dispersion associated with the band shape changes dramatically at the critical angle. The index of refraction of the polymer can be obtained once the critical angle has been determined. Using this method, the index of refraction in the IR region for PP was found to be approximately 1.27, and the index of refraction for CSS was found to be about 1.3. Work by Skourlis and McCullough²¹ has shown that the depth of penetration is relatively insensitive to changes in index of refraction of this magnitude. Thus, an average value of $n = 1.285$ will be used accordingly in eq. (4) to determine penetration depth at the wavelengths of interest.

For the FTIR-ATR method to provide useful information on diffusion processes, distinguishable bands for the two components of the diffusion couple must be identified. Spectra for CSS, PP,

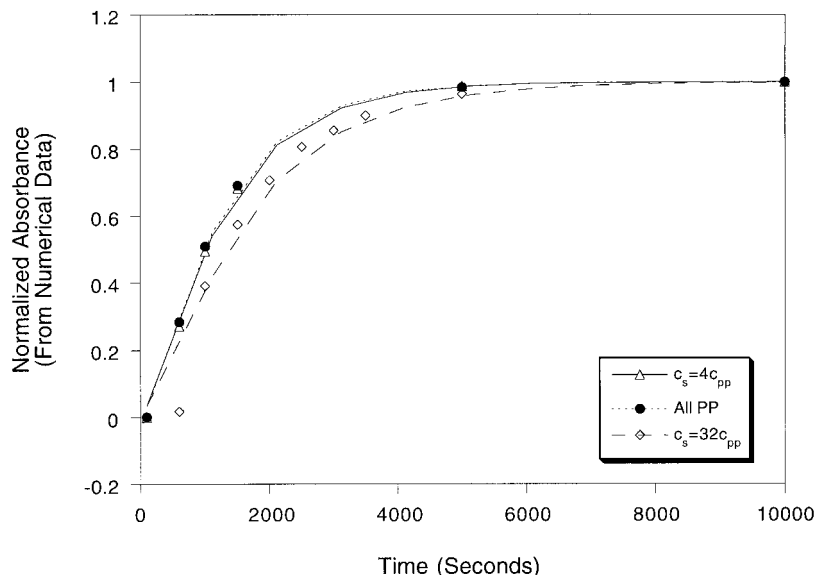


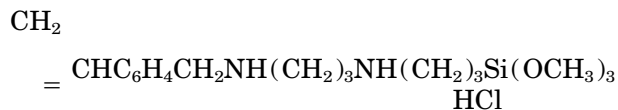
Figure 3 Change in the absorbance calculated using the concentration profiles obtained with the bilayer solution and associated fit resulting from the single-film diffusion solution. Each set of data and fit represents a different equilibrium partition of water between the two layers.

and water were evaluated for suitable peaks to monitor during the diffusion process. The OH stretching band near 3400 cm^{-1} associated with water was taken as the peak to monitor for diffusion. The peak due to the main chain CH deformation at 1458 cm^{-1} will be followed to assess the change in concentration of the polymer species during the diffusion process.

Specimen Preparation

FTIR-ATR specimens were prepared using the following method, which mirrors the bonding process previously used in our laboratory.⁶⁻⁷ The IREs in this study were composed of germanium ($n = 4.0$) or silicon ($n = 3.8$) and had a 60-degree incidence angle. Both of these IRE materials are

expected to have hydrated oxides on the surfaces.²⁶ Although differences in the specific nature of the hydrated oxides are known to produce differences in the properties of adsorbed silane films, these IREs will serve as model substrates for typical hydrated inorganic oxide surfaces. Primer solutions were composed of hydrolyzed CSS silane in a 95% methanol–5% water mixture. The chemical structure of this silane before hydrolysis is shown as follows:



To fabricate the ATR specimens, CSS primer was first solution coated onto the IRE and then dried

Table II Summary of Bilayer Diffusion Model Results

Case $c_{pp} = kc_s$ ($k =$)	Fitted Values [eq. (6)]			Compared to D_{pp} (% Error)
	D (apparent) ($\times 10^{-8}\text{ cm}^2/\text{s}$)	Error ($\times 10^{-8}\text{ cm}^2/\text{s}$)	R	
All PP ($c_s = 1$)	3.7999	0.0006	0.9997	0.038%
$k = 1$	3.6942	.0628	0.9995	2.7%
$k = \frac{1}{4}$	3.6595	.0627	0.9994	5.3%
$k = \frac{1}{32}$	2.7398	0.150	0.9813	27.9%

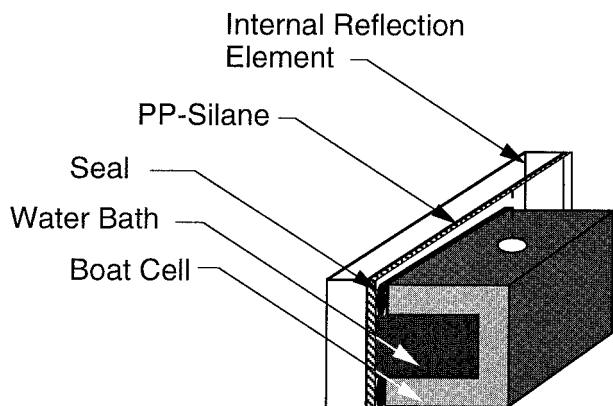


Figure 4 Schematic of the experimental set-up for the FTIR-ATR diffusion studies.

for 30 minutes at 65°C. (The deposited silane layer was estimated gravimetrically to be about 0.2–0.4 microns in thickness.) The FTIR-ATR spectrum of the hydrolyzed silane primer layer on the IRE was acquired. Next, a film of PP was pressed to the primed surface, and the assembly was heated in vacuum to 200°C, where it was held for one hour. Previous research has shown that the one-hour dwell period results in maximum bond strength between the CSS silane and the polypropylene film.^{6–7} Upon cooling, another spectrum was collected at room temperature to establish the initial state of the PP-silane bilayer and to evaluate the chemical structure of the PP-CSS interface.

To study the ingress of moisture to the interphase, the diffusion couple was completed by pressing an open boat cell onto the coated IRE and filling the cell with deionized/distilled water. (Fig. 4 schematically shows a cut-away view of the experimental set-up.) The temperature of the water was maintained using feedback-controlled heating of the IRE and boat cell assembly with internally mounted cartridge heaters. Room temperature tests were conducted at ambient conditions, and the temperature was assumed to vary little during the experiment. Diffusion of water into the PP-silane bilayer film was monitored by recording spectra in real time. The experiment was concluded at the point where no change in spectra could be detected, and this was assumed to be the equilibrium state.

RESULTS AND DISCUSSION

Initial Spectra of PP-CSS Bilayers

Figure 5 shows the two ATR spectra obtained from the CSS-PP sample. The lower spectrum rep-

resents only the CSS primer layer after being deposited on the IRE and dried for 30 minutes at 65°C. The ATR spectrum is very similar to what has been reported for other alkoxy silane coupling agents.^{2–3} After deposition, the film appears to be partially hydrolyzed, as indicated by the presence of the moderate band at 905 cm^{-1} , which can be assigned to the Si—OH vibration.^{2,4} However, the silane film appears to have condensed somewhat into a low-molecular-weight polysiloxane, as indicated by the presence of the well-characterized bands corresponding to the Si—O—Si vibrational modes.^{2–3,27} The strong peak near 1115 cm^{-1} has been assigned previously to both Si—O—Si and Si—O—C vibrational modes. Often, the two modes are very close in location and difficult to distinguish.²⁸ The presence of the shoulder at 1038 cm^{-1} , assigned to vibrations of Si—O—Si species, further indicates the presence of a siloxane.^{2–3} These observations are consistent with previous FTIR studies of silane coupling agents.

Additionally, peaks are present that correspond to the vinyl functional groups on the silane.²⁷ At elevated temperatures or in the presence of free radicals, the vinyl groups can open and cross-link to form a network polymer structure. Decreases in the intensity of these bands may indicate that such reactions have occurred. The peak at 989 cm^{-1} can be assigned to the out-of-plane CH stretch in the vinyl group.²⁸ The small peak at 1406 cm^{-1} has been assigned to the scissoring mode of the vinyl species,²⁸ and a band

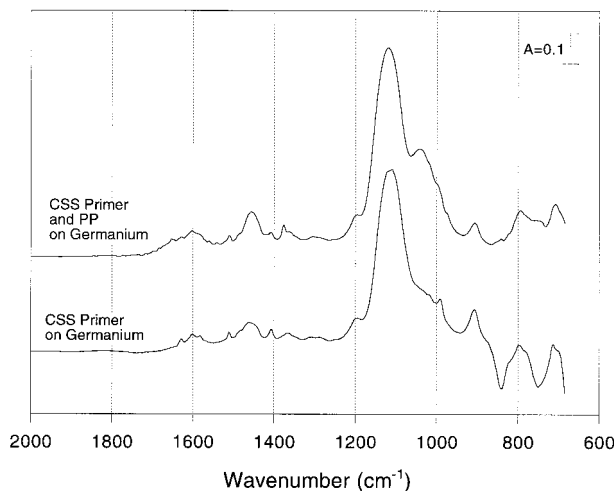


Figure 5 FTIR-ATR spectra of CSS film and the CSS-PP bilayer on a germanium IRE. Note the increase in the siloxane peak and the decrease of the silanol peak. Also, the intensity of the vinyl bands has greatly diminished.

appears at 1628 cm^{-1} arising from the asymmetric stretch of the bond.²⁸ In general, the appearance of this spectrum is very similar to spectra of CSS coupling agents adsorbed on aluminum substrates obtained previously using RAIR,⁶⁻⁷ as would be expected.

The upper spectra in Figure 3 were obtained after PP was bonded to the silane-treated germanium surface at 200°C . Two important chemical changes are evident. First, the intensity of the band assigned to the silanol groups (905 cm^{-1}) has substantially decreased, and the intensity of the siloxane peak (1058 cm^{-1}) has increased, indicating further cross-linking in the siloxane network. These results are consistent with previous RAIR studies of silane coupling agents on metallic substrates that indicated increased siloxane formation after heating.^{2-3,6-7} At this point, it should be noted that aromatics often show out-of-plane bending in the $900\text{--}700\text{ cm}^{-1}$ range. The large change of intensity of the band at 905 cm^{-1} upon heating, and the corresponding increase of the Si—O—Si peak, would seem to indicate that the band at 905 cm^{-1} does not arise from the aromatic vibrational mode. More likely, the aromatic species are indicated by the band located near 790 cm^{-1} , which does not change intensity appreciably after heating. This assignment is in agreement with previous IR studies of silane coupling agents containing aromatic species³ and is consistent with the $900\text{--}700\text{ cm}^{-1}$ range for this vibration.²⁸ Therefore, it is reasonable to assume that relative changes in the bands at 1038 and 905 cm^{-1} can be attributed to changes in the siloxane network formed in the silane primer layer.

Interestingly, the absorbance of the peaks associated with the vinyl groups has decreased. These changes appear to indicate that some of the vinyl groups in the silane have reacted to form a network structure in the presence of the PP. Characteristic bands from the bonded PP film can be clearly seen as well. The CH deformation vibrations for the main-chain and methyl side groups²⁸ are observed at 1458 cm^{-1} , and the symmetric CH_3 deformation band is evident at 1364 cm^{-1} . No new bands appeared in the ATR spectrum of the silane-PP bilayer that were not identified in the individual spectra of the CSS or PP. Therefore, no obvious grafting reaction between the silane and the PP could be detected at the level of sensitivity of the ATR method.

These results are interesting, as they provide evidence that tends to support the previously proposed diffusion based mechanism responsible for

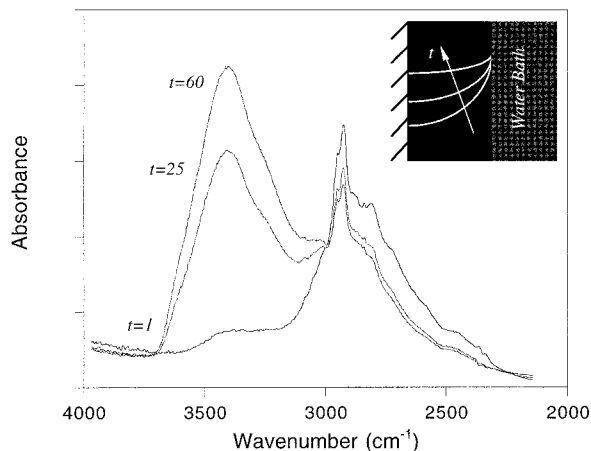


Figure 6 Evolution of the OH stretching band at 3400 cm^{-1} during a diffusion experiment. A corresponding decrease in the organic peaks is also observed, indicating a change in composition in the polymer film. A schematic of the water concentration profile in the film with increasing time is inset.

adhesion enhancement between silane and non-reactive polymer systems.^{1,6-7} Furthermore, while several earlier RAIR studies have observed the condensation of the silanols to form a siloxane network on silane-coated metal surfaces,^{2-3,6-7} little direct evidence has been presented that shows network formation in the silane while buried under a polymer coating. These findings help to develop a clearer understanding of the polymer-silane interphase, as they demonstrate that the siloxane network will form and the vinyl groups appear to react while buried beneath a polymer coating.

Diffusion of Water to the PP-Silane Interface

After the initial spectra were obtained, the boat cell was filled with water, spectra were taken at regular intervals, and the changes in the spectra were examined. Diffusion of moisture could be clearly observed, as evidenced by significant changes in the IR spectra. Figure 6 shows the increase of the OH stretching band (3400 cm^{-1}) that occurs during the experiments. The increase in the water peak with time demonstrates the transport of water through the polymer film and the increase of water concentration. In all of the experiments, an initially rapid increase in absorbance of the OH band was seen, followed by a gradual increase to an asymptotic value corresponding to the equilibrium state. Simultaneously, there was a complementary decrease in the

organic peaks. The reduction in absorbance from the organic species can be attributed to a decrease in relative concentration of the organic groups. Analysis of the absorbance data using eq. (7) will yield a calculation of the apparent diffusion constant for water through the PP-silane bilayer for each experiment.

A set of typical normalized experimental data for water diffusing through the PP-silane bilayer at 65°C and room temperature is shown in Figure 7(a) and (b), along with the fits obtained using eq. (7). Reasonable agreement between the experimental data and the Fickian fit is observed. The calculated diffusion coefficients were the same order of magnitude as the PP film ($\approx 3.8 \times 10^{-8}$ cm²/s) for all of the 65°C studies. The small discrepancies in absolute value of the diffusion coefficient are to be expected due to effects such as uncertainty in film thickness measurements, thickness variations, and film defects. At room temperature, the diffusion coefficients were calculated to be about an order of magnitude lower. This is consistent with previous studies on the temperature dependence of diffusion of water in polymers. A summary of the experimental results is listed in Table III. In addition to the reasonable apparent diffusion values, the R²-value was above 0.92 in all cases, indicating good agreement between the model and the data. However, there were some anomalies observed in all of the data, despite the high correlation coefficients. Most commonly, the fits occasionally overestimated the amount of water in the interphase at long times.

This behavior may be attributed to a number of mechanisms. These could include nonFickian behavior at higher concentrations, a concentration dependence on the diffusivity, and the fact that the film is not homogenous. Some researchers have shown that water at the IRE-polymer interface can cause debonding of the film from the IRE.¹⁷ Since the material closest to the IRE surface contributes most significantly to the absorbance, a layer of pure water adjacent to the IRE surface would certainly result in a higher measurement of final absorbance. This effect would tend to artificially shift the calculated values of normalized absorbance at shorter times to comparatively lower values. However, in the cases in which water was observed at the IRE-sample interface, the films were easily removed from the IRE after the experiment was finished, and a fine layer of water was observed on the IRE beneath the film.¹⁷ No such physical observations of water

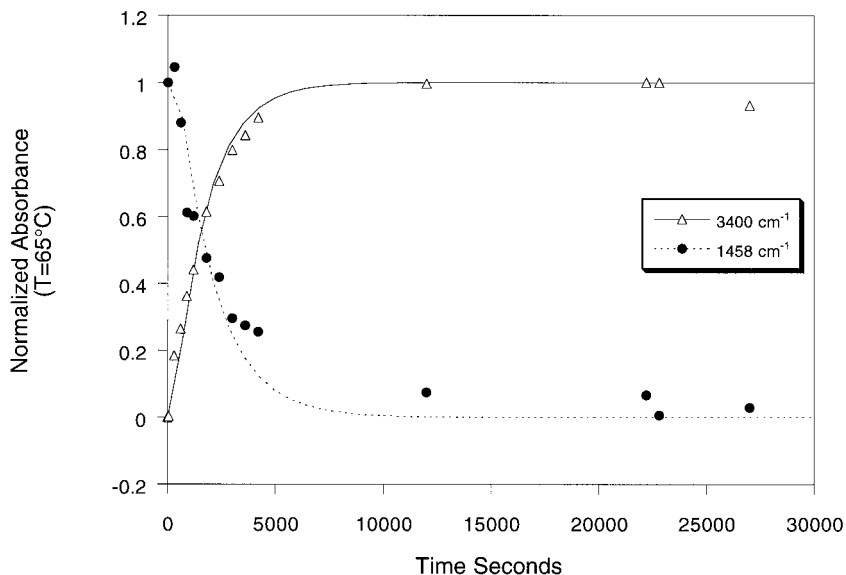
on the IRE surface were made in the present study. In fact, the films could not be removed from the IREs after the experiments, thereby discounting the debonding mechanism for increased water content at the interphase.

Another very important issue to consider is any potential reaction of the diffusing species. The Fickian diffusion analysis assumes that no chemical reactions take place in the films. Previous studies in our laboratories have indicated that siloxane hydrolysis in bare CSS films on aluminum will readily occur.^{6,7} Any hydrolysis reaction of the siloxane with the incoming water will obviously change the concentration of the water as a function of time. Water will be consumed by the hydrolysis reaction; hence, the concentration of free water as measured by ATR will appear to be less. This argument is consistent with the observations seen in the ATR experiments. The findings of the diffusion study motivate a close examination of the changes in the chemical nature of the PP-silane interphase to understand some of the anomalies in the long time results. However, it is very clear that migration of water through the PP-silane bilayer does occur at a rate that is comparable to the rate of moisture uptake in the bulk PP. The effects of the moisture on the silane layer will be discussed in the following section.

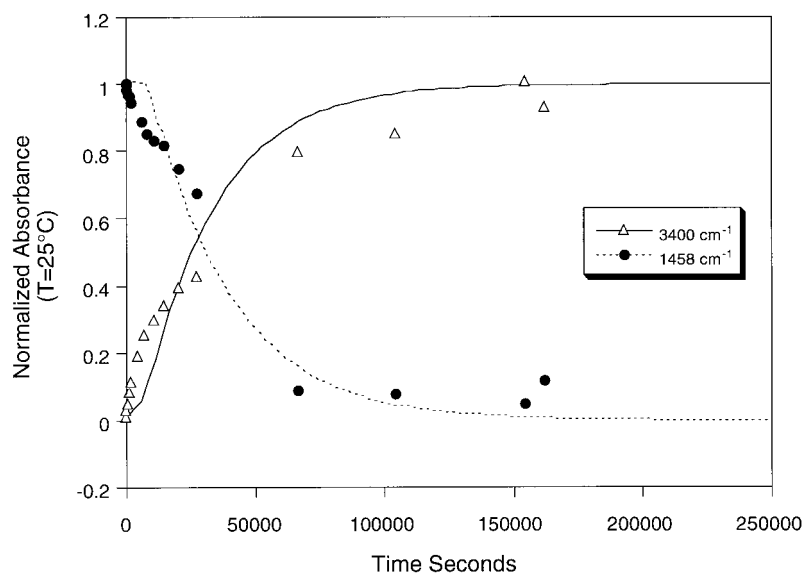
Changes in the Silane Layer Due to the Presence of Water

The results of the diffusion study indicated that water will migrate through the PP to the silane layer. It is now important to consider whether moisture may affect the chemical structure of the silane. Changes due to chemical reactions between the water and the siloxane are more relevant to the decrease in hot-wet performance observed in silane-modified adhesive bonds. As previously noted, some researchers have suggested that the reduction in hot-wet mechanical properties of certain glass-fiber (silane-treated) composites is due to the hydrolysis of the siloxane network found in sizings.¹ Previous work in our laboratories proposed that hydrolysis of the siloxane layer preceded joint separation, and the hydrolysis was actually one cause of the mechanical degradation.⁶ Thus, direct spectroscopic evidence of the hydrolysis reaction would support this hypothesis.

Figure 8 shows a portion of the ATR spectra obtained as a function of time (temperature = 65°C; germanium IRE; 60-degree angle of inci-



(a)



(b)

Figure 7 Typical plots of the normalized absorbance data and the associated Fickian fits obtained from eq. (7): (a) data for 65°C; (b) data for 25°C (note differences in time scales for each plot).

dence). Some interesting features should be noted. Much attention can be focused on the Si—O regions of the spectra obtained during the moisture diffusion experiments. Two bands that can be examined to study the hydrolysis behavior of CSS are the Si—OH and Si—O—Si peaks assigned at 905 and 1058 cm^{-1} , respectively. Increases in the Si—OH peak would be a direct measure of the degree of hydrolysis as the siloxane undergoes the reaction. Likewise, the de-

crease in the siloxane band would represent decreases in that chemical group. Here, it is clear that the peak corresponding to Si—O—Si at 1058 cm^{-1} changes as moisture is incorporated into the interface. After an induction period of about 20 minutes, the peak begins to disappear and is eventually only represented by a weak shoulder. The decrease in the intensity of this peak is completely reversed from the changes that were observed upon heating and point to hydrolysis of the

Table III Summary of the Results from FTIR-ATR Diffusion Experiments

Number of Experiment, Type of IRE, and Peak	T ($^{\circ}\text{C}$)	PP Thickness (μm)	D (apparent) ($\times 10^{-8}$ cm^2/s)	Standard Error ($\times 10^{-8}$ cm^2/s)	R^2
1) Germanium (3400 cm^{-1})	65	100 ± 10	2.68	0.124	0.992
1) Germanium (1458 cm^{-1})	65	100 ± 10	2.29	0.153	0.978
2) Germanium (3400 cm^{-1})	25	101 ± 12	0.150	0.0151	0.972
2) Germanium (1458 cm^{-1})	25	101 ± 12	0.13	0.014	0.973
3) Silicon (3400 cm^{-1})	65	100 ± 14	5.27	0.583	0.958
4) Silicon (3400 cm^{-1})	65	110 ± 14	2.042	0.287	0.922
5) Silicon (3400 cm^{-1})	25	95 ± 13	0.459	0.0599	0.951

siloxane. Furthermore, the intensity of the silanol band remains approximately constant as the exposure to moisture continues. As previously dis-

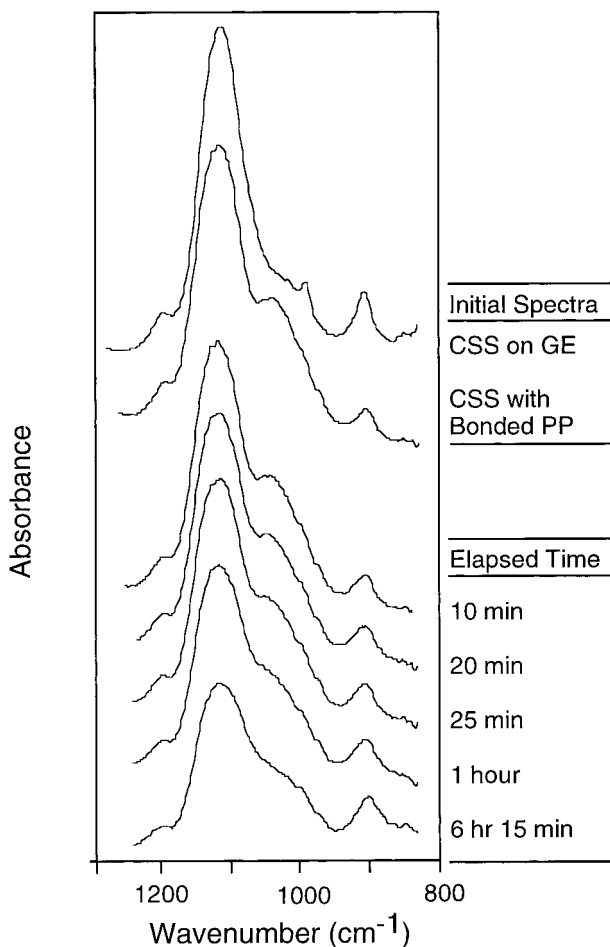
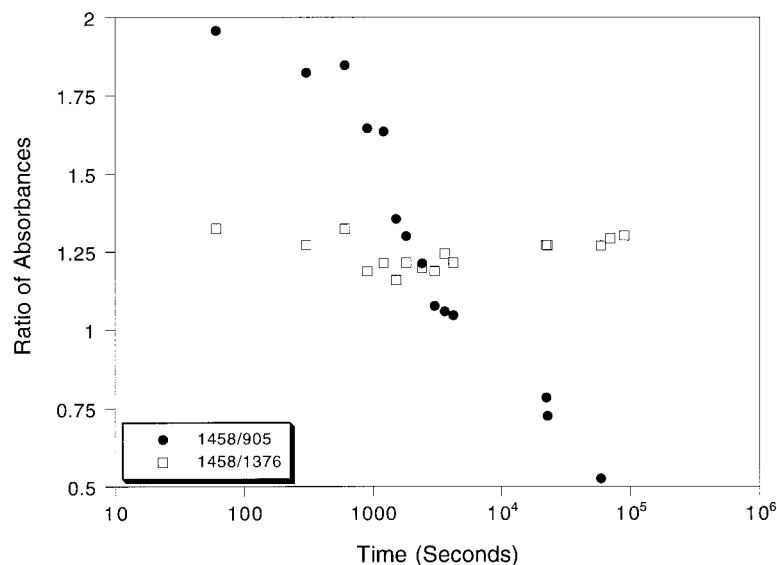


Figure 8 Region of an FTIR-ATR spectra taken during a diffusion experiment. Hydrolysis appears to be occurring, as shown by the disappearing Si—O—Si band at 1038 cm^{-1} and the relative increase of the silanol band appearing at 905 cm^{-1} .

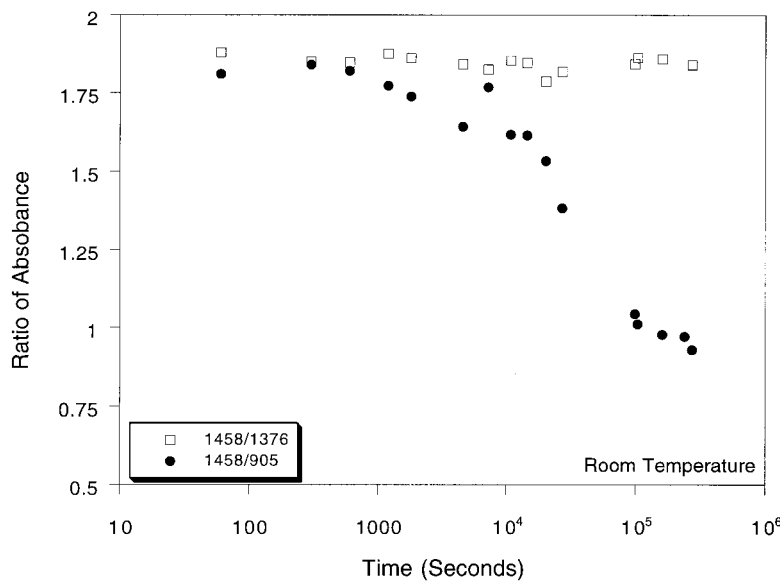
cussed, the decreasing concentration of polymer due to the diffusion of water into the film results in an overall decrease in the polymer signal. Thus, the unchanging signal from the silanol peak indicates that the silanol concentration is actually increasing in the system. These changes in the spectra demonstrate that hydrolysis of the siloxane network occurs under the PP surface layer.

Detailed measurement of the rate of change of the siloxane and silanol peaks has been used to determine the kinetics of hydrolysis and condensation reactions in silane solutions.⁴ There are problems with using such a simple analysis on the case presented here. First, the kinetic models assume that there is a constant concentration of solution adjacent to the crystal surface; therefore, changes in the spectra would be due to chemical and not compositional changes. That is clearly not the case in our study. Since water is diffusing to the interface, the appearance of the spectra will change due to relative concentration changes. The overall intensity of the spectra in Figure 8 is decreasing as the relative concentration of the organic species decreases compared to the water. Therefore, a modified methodology must be used to study hydrolysis occurring simultaneously with diffusion.

An approach that enables an investigation of the hydrolysis process is to ratio the absorbance of the band from a reacting group to that from a non-reaction species. There are chemical groups in the PP-silane layer whose intensities should not change due to the hydrolysis of the siloxane network. These bands should only change with changes in relative concentration caused by diffusion of water into the PP-silane bilayer. If it is assumed that the relative changes due to diffusion are similar for the groups that react and do not react, the non-reacting group can be used to scale the changes in the reacting species.



(a)



(b)

Figure 9 Plot of the normalized absorbance for two nonreacting bands, as well as the silanol group normalized to a nonreacting band. The change in the ratio indicates that hydrolysis of the siloxane is occurring: (a) data for 65°C; (b) data for 25°C (note log time scale for each plot).

Figure 9 shows a representative plot of the normalized change in intensity for a non-reacting band (side group methyl CH) and reacting band (Si—OH). Both bands have been normalized with respect to a second non-reacting band (CH stretching on PP main chain). The relatively flat response for the two non-reacting bands is easily contrasted by the rapidly changing relative intensity of the silanol group. A similar plot is shown

in Figure 9(b) for the room temperature study. Hydrolysis occurs at room temperature as well. However, the final extent, as well as the rate, is significantly less for the room temperature case.

These results are easily interpreted in terms of the hydrolysis reaction. As the silanols are produced from hydrolysis of the siloxane, their concentration increases with respect to the non-reacting groups (e.g., the CH groups in the PP).

The initiation of this reaction occurs after only 10 minutes. Thus, the PP does not have to be saturated for the reaction to take place. This finding provides direct spectroscopic evidence for hydrolysis of silane layers beneath a polymer coating. Furthermore, the fact that hydrolysis occurs beneath the PP lends support to the degradation mechanism for PP-CSS/aluminum joints exposed to hot-wet conditions.⁶⁻⁷ It is now reasonable to conclude that hydrolysis of the silane layer can occur prior to joint separation.

It is also important to note that no changes were found in the regions corresponding to the vinyl groups. Not surprisingly, the stability of cross-links formed by reaction of the vinyl species are much more stable in the presence of water. The cross-linking that forms the silane network structure results from both silanol condensation and reaction of the vinyl groups. If hydrolysis only affects the siloxane backbone, some network integrity should remain due to the cross-links between the functional groups. Therefore, some degree of mechanical toughness in joints exposed to hot-wet conditions should be retained. This is consistent with previously reported durability studies.

CONCLUSIONS

An *in-situ* spectroscopic technique was employed to study a polymer-silane interphase and to monitor both the rate and effects of moisture ingress to the silane interphase. FTIR-ATR experiments were conducted using germanium and silicon internal reflection elements, and PP was fused to the silane-treated IRE surface. Inspection of the spectra after processing showed that the silane layer had condensed into a siloxane network. Also, the vinyl groups were observed to disappear, which indicates reaction of these species. These are important findings, as they provide direct evidence of network formation under a polymer coating and lend support to the diffusion theory of silane adhesion promotion for non-reacting polymer systems.

In order to analyze the diffusion data obtained from the FTIR-ATR experiments, appropriate diffusion models were presented. It was shown that the one-film solution should accurately yield an apparent diffusion constant that is on the same order as the PP film. The results of the diffusion experiments showed that moisture does readily migrate to the silane interphase at a rate that is

comparable to the diffusivity of moisture in neat PP. Anomalies found in the diffusion data pointed to chemical reactions between the water and the polymer and provided further motivation for a more thorough analysis of the chemical changes in the spectra as a function of exposure time.

Examination of the spectra in the siloxane region showed that the siloxane peaks decreased in intensity and shape. This reduction could be attributed to two factors: 1) a change in the relative concentration of the polymer with respect to the water; and 2) hydrolysis of the siloxane network. To separate the two effects, a normalization scheme was used to track the relative changes of the peaks as a function of time. When two non-reacting peaks were ratioed at each time, a relatively flat response was seen. In contrast, dramatic changes were seen when the silanol band was normalized to a nonreacting peak. This indicates that hydrolysis was readily occurring at the silane interphase.

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