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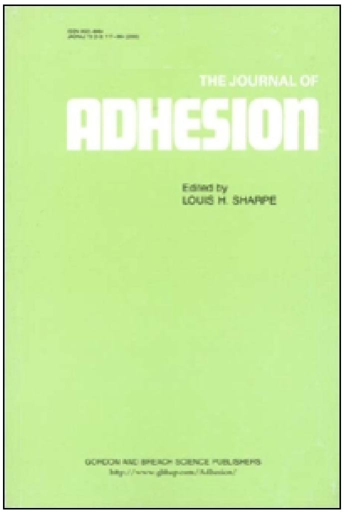

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Fracture Energy of Epoxy Interfaces with Layers of Different Silane Coupling Agents

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Fracture Energy of Epoxy Interfaces with Layers of Different Silane Coupling Agents

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We investigated the fracture energy, Gc, and the threshold fracture energy, Gth, in water at 80°C of interfaces between epoxy and layers of five silane coupling agents: (3-glycidoxypropyl)trimethoxysilane (GPS), (3-aminopropyl)trimethoxysilane (APS), [3-(phenylamino)propyl]trimethoxysilane (PAPS), (3-mercaptopropyl)trimethoxysilane (MPS), and [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPS) on the native silicon oxide surface. While 10-nm-thick layers of these all had similar high Gc, APS had the best overall values of Gth, but all adhesion promoters, except for AEAPS, performed roughly similarly. The results from the XPS analysis of the silicon side of the fracture surfaces suggest that for all silane layers, the fracture occurs somewhere within that layer. When the silane coupling agents were added to the epoxy, the samples with the higher threshold fracture energies exhibited a thicker layer of the epoxy remaining on the native silicon oxide surface. Silane coupling agents that perform well as deposited layers do not necessarily perform well as additives to epoxies.

Keywords: Epoxy; Fracture energy; Silane coupling agent; Silicon oxide; Threshold fracture energy; XPS

INTRODUCTION

Silane coupling agents used as adhesion promoters enable the bonding of inorganic surfaces to organic materials such as epoxy resins [1–3].

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Hence, they are responsible for durability and corrosion resistance of various structures and devices. One of the most successful strategies for improving the performance of these interfaces is to construct very thin layers of silane adhesion promoter between the polymer and the inorganic material to form covalent bonds that are resistant to hydrolysis [4–11]. Previous studies where (3-glycidoxypropyl)trimethoxysilane (GPS) was the coupling agent revealed network structures that were only loosely cross-linked in the center of the layers [9]. The penetration of epoxy into this swellable layer produced a relatively high fracture energy (*Gc*) of about 100 J/m^2 and a threshold fracture energy (*Gth*), immersed in water, of more than 55 J/m^2, a value that decreased only modestly between 20 and 80°C [8,10].

Silane coupling agents are molecules with the general structure $X_3Si(CH_2)_nY$, where X is a hydrolyzable group (*e.g.*, $-OCH_3$), n is a number between 0 and 3, and Y is an organofunctional group (*e.g.*, an epoxy group or an amine) chosen for reaction with the given polymer. Silane coupling agents are typically prepared in dilute solution with water or alcohol. The bonding structure of a silane film depends strongly upon the chemical structure of the silane coupling agent and the deposition conditions. For example, (3-aminopropyl)triethoxysilane is known to form three-dimensional polysiloxane films when deposited from its solutions [4,5,12,13]. In this work, we extended the *Gc* and *Gth* results on GPS to layers of four other silane coupling agents: (3-aminopropyl)trimethoxysilane (APS), [3-(phenylamino)-propyl]trimethoxysilane (PAPS), (3-mercaptopropyl)trimethoxysilane (MPS), and [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPS).

Adding silane to the polymer precursor, which is known as an integral blend method, avoids the cost penalty of layer-by-layer processing, provided enough silane will diffuse to, and react at, the interface. In this method, the silane is used as a simple additive, generally 0.2–1.0 wt% of silane in the total mixture [3]. We also investigated the *Gc* and *Gth* that resulted when GPS or APS was added directly to the epoxy.

EXPERIMENTAL

Film Preparation

The silane coupling agent layers were prepared by spin casting uniform layers about 10 nm thick onto the native oxide on 100 silicon wafers 7.5 cm in diameter and 0.38 mm thick. All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. All wafers were precleaned using Piranha solution (3 parts H_2SO_4, 1 part 30% H_2O_2) for 30 min, followed by a deionized water rinse. To allow for partial hydrolysis of the silane triols, the solution shown in Table 1 was stirred for 1 h at room temperature prior to spin casting (2500 rpm for 1 min). In the case of GPS, the pH of the solution was adjusted to about 4 by adding acetic acid to promote rapid hydrolysis, but this pH adjustment did not work for obtaining a 10-nm-thick film from MPS, probably because of the very slow hydrolysis of MPS under these pH conditions. All films were cured for 1 h at 90°C and rinsed with ethanol to remove any physisorbed material.

Surface Analysis

The thickness and surface roughness of each silane coupling agent layer were measured by X-ray reflection (MRD PRO X'pert thin film diffractometer, Philips, Eindhoven, The Netherlands). The Cu Kα X-rays were produced using a rotating anode X-ray generator with a 45-kV voltage and a 40-mA current. The incident beam slit was 0.125 cm wide, and the diffracted beam slit was 1.0 mm wide.

The chemical structures of the silane layers were analyzed by Fourier transform infrared spectroscopy (Nicolet Magna 850, Thermo Nicolet, Madison, WI, USA) with a grazing angle attenuated total reflection single bounce accessory (Harrick Scientific, Ossining, NY). The spectra were acquired using a germanium crystal at a 4-cm^{-1} resolution by averaging 256 scans. The resulting spectra were processed using the smoothing binomial function in Igor Pro 5.02 (WaveMetrics, Lake Oswego, OR, USA).

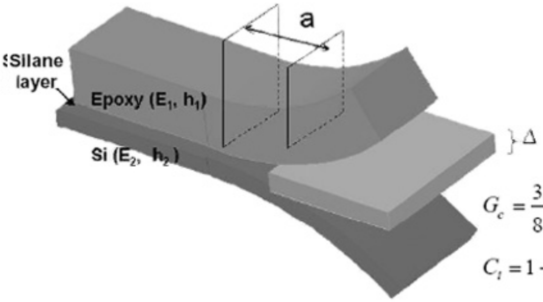
The silane layers and the fracture surfaces were examined by X-ray photoelectron spectroscopy (XPS). A Kratos Axis Ultra XPS system (Kratos Analytical, Manchester, UK) was used to perform the measurements over a binding energy range of 0–600 eV with a dwell time of 100 ms, an 80-eV pass energy with an energy resolution of 1 eV, and a current of 15 mA. Charge compensation was carried out by injection of low-energy electrons into the magnetic lens of the electron spectrometer. The inelastic electron mean free path of the photoelectrons generated by the monochromatic Al Kα X-ray beam (1486.7 eV) in the cured epoxy ranges from 1.9 nm (oxygen) to 2.5 nm (Si) [14]; 95% of all photoelectrons detected emerge from within three times this depth. XPS was used to determine the relative concentrations of C, O, N, S, and Si using Casa 220 software and relative sensitivity factors determined for the Kratos system using standard samples.

Each surface of the silane layers was imaged in tapping mode by scanning force microscopy (Digital Instruments 3100, Santa Barbara, CA, USA).

TABLE 1 Chemical Composition of the Spin-Casting Solution Used to Prepare Thin Silane Coupling Agent Layers, the Thickness of These Layers, and Their Surface Roughness

	Chemical composition of the spin casting solution (weight ratio)								Silane layers after 90°C × 1 h	
Entry	APS	PAPS	GPS	MPS	AEAPS	H_2O	C_2H_5OH	CH_3COOH	Thickness (nm)	Ra (nm)[a]
1			0.5			10	90	0.5	10.2	0.41
2	0.5					10	90		11.2	0.37
3		0.5				10	90		<2	
4		1				10	90		<2	
5	0.3	0.3				10	90		10.1	0.57
6		0.2	0.3			10	90		<2	
7				0.5		10	90		<2	
8				0.5		10	90	0.5	<2	
9	0.3			0.3		10	90		8.5	0.36
10					0.5	10	90		12.9	0.22

[a] Thickness and surface roughness (Ra) (nm) were measured by X-ray reflection.



$$G_c = \frac{3\Delta^2}{8a^4}\left(E_1E_2h_1^3h_2^3\right)\frac{\left(C_1^2E_2h_2^{\,3} + C_2^2E_1h_1^3\right)}{\left(C_1^3E_2h_2^{\,3} + C_2^3E_1h_1^3\right)^2}$$

$$C_i = 1 + 0.64h_i/a$$

SCHEME 1 Asymmetric double cantilever beam (ADCB) specimen and the calculation formula for fracture energy (*Gc*).

Fracture Energy

The fracture energies Gc of interfaces between these adhesion promoter layers and an amine-cured epoxy were measured using the asymmetric double cantilever beam (ADCB) method (Scheme 1). This technique allows one to measure the critical value of the strain-energy-release rate and thus *Gc* from the distance the crack propagates ahead of a thin wedge inserted into the interface [8,15]. By this equation, we calculate the mechanically applied strain-energy-release rate but do not consider the effects of a residual tensile stress in the epoxy arm due to the mismatch of coefficients of thermal expansion between the epoxy beam and the silicon wafer. Although the residual stress is important to determine the mode mixity, it is of less importance for the *Gth* measurements at 80°C [8].

The epoxy arms ($55 \times 8 \times 6.9$ mm) were made by mixing diglycidylether of bisphenol A [DER331, Dow Chemical (Freeport, TX, USA), epoxy equivalent wt. = 185 g/mol] and triethylenetetraamine (Sigma-Aldrich) (1:1 epoxy-to-amine-hydrogen ratio). The epoxy arms were precured in a mold at 80°C for 1 h and then coated with a thin layer (around 0.1 mm) of the same uncured epoxy composition to attach the silicon wafer, whose surface had been coated with one of the silane coupling agent layers. For comparison, similar epoxy beams were attached to silicon wafers with no silane layer. These wafers had only been etched with Piranha solution. Similar "bare" silicon wafers were used to test the efficacy of adding GPS or APS directly to the thin epoxy layer at concentrations of 1 or 5 wt% instead of spin casting and curing the silane layer on the wafer. Although the 5 wt% addition is more than would typically be added to form an integral blend of silane coupling agent and the bulk epoxy, because it would change the stoichiometry of the epoxy, we decided to investigate the *Gc* and *Gth* when the interface layer (not the main epoxy beam) had enough silane so that an interfacial layer of silane-rich composition could form at the Si that was comparable to the 10-nm-thick layers of the silane coupling agents.

All samples were given a final cure in air at 180°C for 3 h by applying some pressure between the precured epoxy beam and the uncured epoxy/silane-coated silicon wafer by means of spring-loading metal clips. The B-staged epoxy beams reacted with the uncured epoxy composition during this final cure to form a strong bond. Young's modulus of the epoxy beam was 1.96 GPa, calculated from the shear modulus (1.31 GPa) and Poisson's ratio (0.34), which were measured at 30-μm displacement, 0.2 Hz, and 25°C. The *Gc* was measured by inserting the wedge under ambient conditions. The samples were subsequently placed in deionized water at 80°C for a week to allow the measurement of the threshold fracture energy *Gth* for subcritical crack growth under these hydrothermal conditions following procedures developed in Ref. 9.

Viscosity Measurements

The viscosity changes of resin compositions were measured in air at 40–150°C at a heating rate of 5°C/min by dynamic mechanical spectroscopy (UBM, Kyoto, Japan) using 0.1 ml of sample and 18-mm-diameter parallel plates with 1.0-mm gap, a frequency of 1 Hz, and a normal load of 10 g.

Cross-Cut and Tape–Peel Adhesive Tests using the High *Tg* Epoxy Composition

Cross-cut and tape–peel adhesive tests were conducted as follows: the mixture of cresol novolac epoxy resin (N680, Dainippon Ink Corp., Tokyo, Japan, epoxy equivalent wt. = 210 g/mol) and triazine-containing phenol novolac resin (LA-7054, Dainippon Ink Corp., Tokyo, Japan, phenolic hydroxyl equivalent wt. = 120 g/mol) [1:0.8 epoxy-to-phenolic-hydroxyl ratio], dissolved in 2-butanone was hand-coated to produce a dried thickness of approximately 60 to 100 μm on the silicon wafer whose surface had been coated with one of the silane coupling agent layers by spin casting. For comparison, the same epoxy composition was coated on the silicon wafer with no silane layer. Then the samples were put into an oven in air at 80°C and heated up to 180°C at a heating rate of around 3°C/min and held at 180°C for 90 min. After cooling down, the resin layers were cross

TABLE 2 Percentages of O, C, N, Si, and S on the Silicon Surfaces

Element (at%)	No silane	Silane coupling agent layers					
	Bare Si	GPS	APS	PAPS/APS	MPS/APS	AEAPS	Before/after
O	35.7	32.1	20.4	18.1	23.8	15.6	before fracture
C	1.0	53.7	55.0	61.6	48.0	69.9	
N	0.0	0.0	9.9	7.4	7.6	8.5	
Si	63.3	14.2	14.7	13.0	18.4	5.9	
S	0.0	0.0	0.0	0.0	2.2	0.0	
O	31.3	31.2	25.9	21.2	27.3	23.4	after fracture Si side
C	13.4	26.6	38.8	52.6	35.2	34.9	
N	0.7	1.6	2.3	2.0	1.9	2.8	
Si	54.6	40.7	33.0	24.3	35.4	38.9	
S	0.0	0.0	0.0	0.0	0.1	0.0	

Top: silane coupling agent layers on Si wafers that were prepared by spin casting and curing at 90°C for 1 h. Bottom: the silicon side of the fracture surface after the threshold fracture energy (*Gth*) measurement at 80°C in water for 1 week.

cut as approximately 2 mm × 2 mm squares using knife blades, and their adhesion was evaluated by tape peeling using 3M Scotch^{TM} superstrength tape. The initial adhesion was evaluated under ambient conditions. The samples were subsequently placed in deionized water at 80°C for a week to allow the evaluation after these hydrothermal conditions.

The glass-transition temperature (*Tg*) of the epoxy composition after cure was measured as the maximum in tan δ by dynamic mechanical spectroscopy (TA Instruments, Inc., Santa Barbara, CA, USA) under air at a heating rate of 5°C/min and a frequency of 1 Hz using the film samples. *Tg* of this epoxy composition was 218°C, much higher than *Tg* of the diglycidylether of bisphenol A and triethylenetetramine (125°C).

RESULTS AND DISCUSSIONS

Film Preparation

The silane coupling agent layers were prepared by spin casting uniform layers about 10 nm thick onto the native oxide surface of silicon wafers. The compositions of the spin casting solutions are shown in Table 1. The silane coupling agents having a primary amine group, such as APS or AEAPS, could be obtained as 10-nm-thick films without adjusting pH. For layers of PAPS and MPS, mixtures with APS

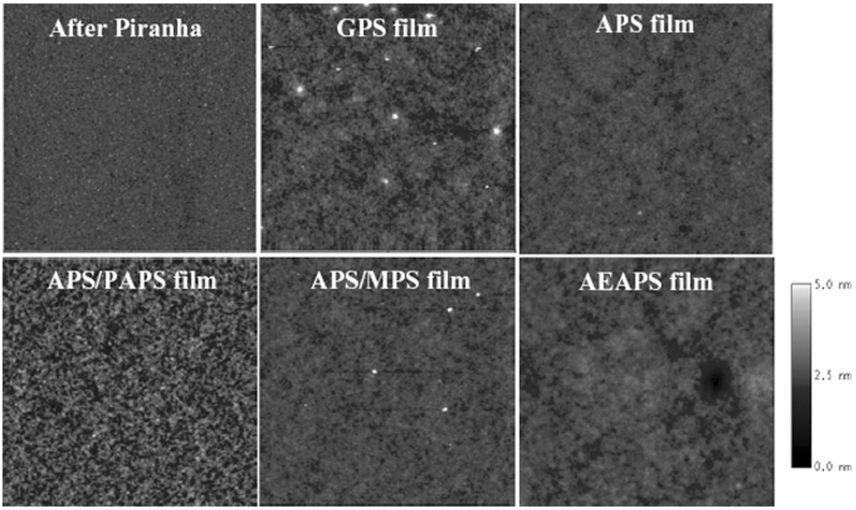


FIGURE 1 Scanning force microscopy height images (5 × 5 μm) of the silane coupling agent films produced by spin casting on silicon wafer surfaces and curing at 90°C for 1 h. A "bare" native oxide silicon surface after Piranha treatment is also shown.

were used to obtain films about 10 nm thick. The incorporation of PAPS into the silane layer was confirmed by Fourier transform infrared spectroscopy. The incorporation of MPS was confirmed by detecting sulfur using X-ray photoelectron spectroscopy. The top section of Table 2 shows the percentages of O, C, N, Si, and S from XPS for the silicon surfaces with silane coupling agent layers and no silane layer (after the piranha etch). Each surface was also imaged in tapping mode by scanning force microscopy, and representative SFM images are shown in Figure 1. The rms roughnesses derived from these images were consistent with the surface roughness derived from X-ray reflection.

Fracture Energy of Interfaces with Silane-Coupling-Agent Layers

Figure 2 summarizes the results of the *Gc* and *Gth* measurements for the silane coupling agent layers and no silane layer. Interfaces formed with 10-nm-thick layers of all five silane coupling agents had similarly high fracture energies *Gc* ($>80\,\mathrm{J/m^2}$) at room temperature that substantially exceeded that ($\sim 40\,\mathrm{J/m^2}$) of interfaces with the bare silicon. In water at 80°C, the APS layer interface had the best overall values

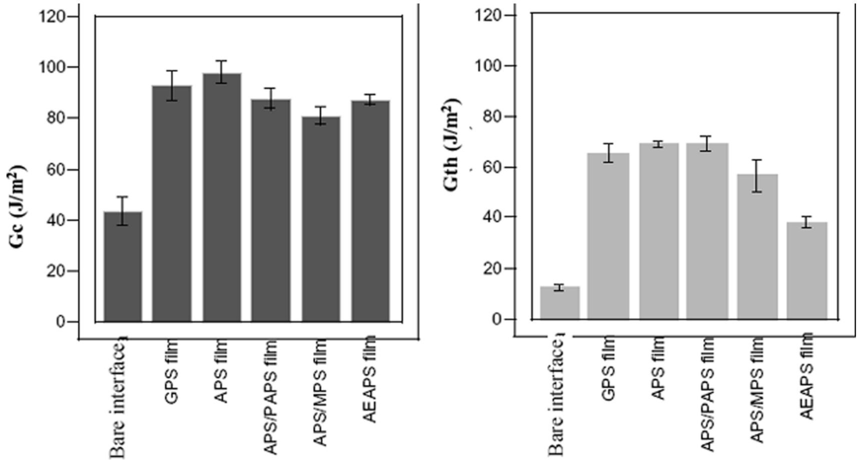
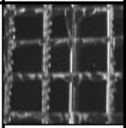
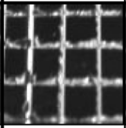
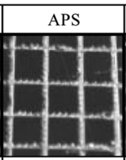
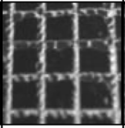
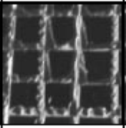
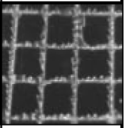
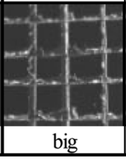
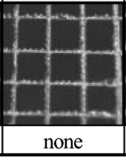
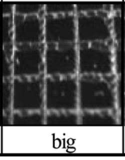
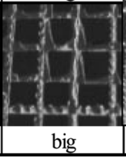
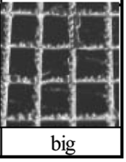


FIGURE 2 Fracture energies (*Gc*) measured at room temperature and ambient humidity and threshold fracture energies (*Gth*) measured on specimens that had been immersed in 80°C water for 1 week. Silane coupling agent layers were produced by spin casting before epoxy was applied. The error bars indicate the standard deviation of the measurements.

of *Gth* ($\sim 70\,\mathrm{J/m^2}$) but interfaces with all the 10-nm-thick adhesion promoter layers, except for AEAPS ($\sim 40\,\mathrm{J/m^2}$), performed roughly similarly and much better than the interfaces with bare silicon ($\sim 10\,\mathrm{J/m^2}$).

Table 3 shows the results of cross-cut and tape–peel adhesive tests for the silane coupling agent layers and no silane layer. A clear square remaining after tape peeling signifies good adhesion between this high *Tg* epoxy layer and silicon interface, but a large peeled resin chip, in contrast, signifies poor adhesion. From the results of tests both before and after immersion in hot water at 80°C for 1 week, the interfaces formed at the silane coupling agent layers in this empirical and qualitative test of adhesion rank in a similar order to their ranking based on their *Gc* and *Gth* values. The APS layer interface exhibited the best performance (almost no resin chips were removed), and the interface with bare silicon was the worst (the resin layer was completely removed after immersion in hot water). Although the differences between the others in the cross-cut and tape–peel adhesive tests were not clear, especially AEAPS and APS/MPS, which showed poor *Gth* results perhaps due to the differences in mechanical properties and water absorption at 80°C of the different cured epoxy compositions or different penetration of these mixtures into the silane layer, there

TABLE 3 Cross-Cut and Tape–Peel Adhesive Tests for the Silane Coupling Agent Layers and No Silane Layer Using the High *Tg* Epoxy Composition

Cross-cut tape –peel	No silane	Silane coupling agent layers				
	Bare Si	GPS	APS	PAPS/APS	MPS/APS	AEAPS
Initial						
Resin chip	big	little	none	little	big	little
at 80 °C in water for 1 week						
Resin chip	all resin	big	none	big	big	big

seems to be no significant difference of the qualitative adhesion ranking of the interfaces between a given silane coupling agent layer and the two different epoxy compositions (DGEBA/TETA and cresol novolac epoxy/triazine phenol novolac) having different *Tg*s (125 and 218°C, respectively, after cure).

Fracture Energy of Interfaces with an Integral Blend of Silane Coupling Agents

When we instead added the adhesion promoters to the epoxy, allowing these to form a layer by diffusing to the interface with silicon while the epoxy was being cured, the results were quite different, as seen in Figure 3. Whereas *Gc* and *Gth* for 1 wt% GPS are about the same as for the 10-nm-thick GPS film, adding 5 wt% GPS moderately decreases *Gc* and *Gth*. The APS, which achieved the best performance as a 10-nm film, showed the worst performance when added to the epoxy. Adding 5 wt% of APS produced *Gth* values ($\sim 15\,\mathrm{J/m^2}$) not much larger than the unmodified silicon interface with the epoxy.

Fracture Surface Analysis

After the measurement of *Gth*, both the epoxy and silicon sides of the fracture surface were examined using XPS to compare the composition of these with both an interface with bare silicon and with the silane coupling agent layer deposited on the initial silicon surface. The XPS results for the silicon sides are shown in Table 2 (top, the initial

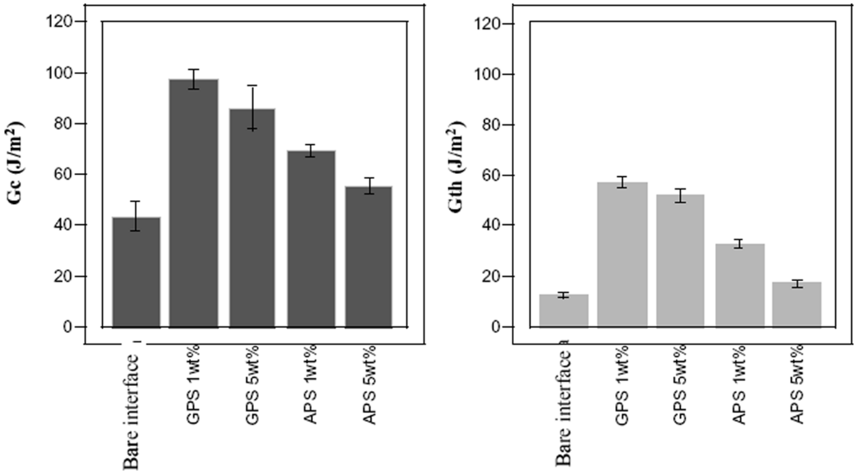


FIGURE 3 Fracture energies (*Gc*) measured at room temperature and ambient humidity and threshold fracture energies (*Gth*) measured on specimens that had been immersed in 80°C water for 1 week. GPS and APS were added to the epoxy in 1 wt% and 5 wt% amounts. The error bars indicate the standard deviation of the measurements.

surface; bottom, after the measurements of *Gth*). From each initial surface deposited with the silane layer, all fracture interfaces have smaller atomic percentages of C and larger atomic percentages of Si, as a result of less C-containing material adhering to the silicon surface after the water-assisted fracture. The fracture surfaces compared with a bare interface show that the signals from C and N increased and corresponded to a decrease in the Si signal. These changes result from more C- and N-containing material adhering to the silicon oxide surface. The analysis of the epoxy side of the fracture surfaces shows a decreased C signal and an increased Si signal compared with that after fracture of a bare interface (Table 4). Considering the high surface sensitivity of XPS, we conclude from these results that the fracture plane was always located inside the silane coupling agent layer close to the silicon surface. This result suggests that the hydrolysis of siloxane bonds is ultimately responsible for the mechanical failure of the interface. In addition, both the resistance to stress-assisted hydrolysis and the mechanical properties of the silane layer interpenetrated with the epoxy itself may influence the threshold fracture energies (*Gth*). The hydrophobic PAPS shows the smallest decrease from *Gc* to *Gth* ($Gc = 88\,\mathrm{J/m^2}$ and $Gth = 69\,\mathrm{J/m^2}$), and this result indicates the excellent resistance of the epoxy/silicon interface to water-assisted

TABLE 4 Percentages of O, C, N, Si, and S on the Epoxy Side of the Fracture Surface after the Threshold Fracture Energy (*Gth*) Measurement of Specimens Which Had Been Immersed in 80°C Water for 1 Week

Element (at%)	No silane Bare	Silane coupling agent layers GPS	APS	PAPS/APS	MPS/APS	AEAPS
O	20.2	23.8	22.1	20.8	20.2	19.8
C	72.7	65.7	63.3	68.7	65.6	71.5
N	3.5	3.6	3.8	3.1	3.2	3.8
Si	3.6	6.8	10.8	7.5	10.0	4.9
S	0.0	0.0	0.0	0.0	1.0	0.0

subcritical crack propagation. On the other hand, AEAPS has two amine groups that may give its deposited layer increased hydrophilicity, resulting in relatively high water absorption and increased susceptibility of the siloxane network to stress-assisted hydrolysis and also may give its interfacial layer cured with epoxies increased cross-linking density, resulting in more brittle mechanical properties than those of APS.

Figure 4 shows the percentages of O, C, N, and Si for the silicon side of the fracture surface after the measurement of *Gth* of an interface produced by adding 1 wt% and 5 wt% of GPS and APS to the epoxy. The C signal increased and the Si signal decreased in the following

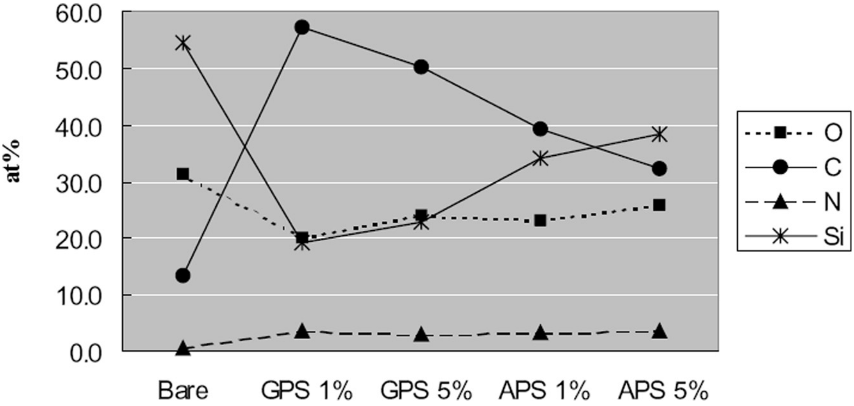


FIGURE 4 Percentages of O, C, N, and Si on the silicon side of the fracture surface after the threshold fracture energy (*Gth*) measurement of specimens that had been immersed in 80°C water for 1 week. GPS and APS were added to the epoxy in 1 wt% and 5 wt% amounts.

order: GPS 1% (highest percentage C, lowest percentage Si) > GPS 5% > APS 1% > APS 5% > bare interface (lowest percentage C, highest percentage Si), which is exactly the ranking of these interfaces based on their *Gc* and *Gth* values (Figure 3). Thus, when the silane coupling agents were added to the epoxy, the samples with the higher *Gth* exhibited a thicker layer of the epoxy remaining on the native silicon oxide surface.

Integral Blends of Silane Coupling Agents

We speculate that the differences between the performance of GPS and APS when added to the epoxy originates in part from differences in their ability to migrate to the native oxide interface during the cure. Figure 5 shows the viscosity changes of the epoxy resin compositions under air from 40 to 150°C at a heating rate of 5°C/min. [Epoxy + TETA]: diglycidylether of bisphenol A and triethylenetetramine (1:1 epoxy to amine hydrogen ratio), [Epoxy + TETA + GPS1%]: %]: GPS was added to the Epoxy + TETA in 1 wt%, and [Epoxy + TETA + APS1%]: APS was added to the Epoxy + TETA in 1 wt%. The viscosity of all these epoxy compositions drastically increased only at temperatures hotter than 100°C. Thus, GPS and APS might diffuse and react in the epoxy compositions for some time before the epoxy is fully cross-linked, thus preventing further long-range diffusion.

In the absence of reaction, one would suppose that the GPS and APS would diffuse to the interface at comparable rates because these molecules are of similar sizes. The diffusion of APS, however, may be slowed by its hydrogen-bonding interactions with components in the resin/molecules mixture. A more likely reason, however, is that even though the reaction rate of the primary amine of APS with the epoxy of the diglycidylether of bisphenol A (DGEBA) should be similar to the reaction rate between a primary amine on triethylenetetramine (TETA) and the epoxy group of GPS, the molecules that form after reaction should be quite different in mobility. The small, flexible GPS-TETA product should diffuse faster than the larger, less-flexible APS-DGEBA product, and more of it should accumulate at the silicon oxide interface before the network forms and diffusion is effectively stopped. This speculative hypothesis, however, cannot account for the fact that adding more APS (5 wt%) actually produced a poorer interface than the 1-wt% APS addition. A number of possibilities exist. The 5-wt% APS may lead to condensation of hydrolyzed alkoxysilanes to form small clusters of reacted silanes that are relatively immobile. The 5-wt% addition also significantly affects the stoichiometry, changing it to 0.89 epoxy groups per amine hydrogen. The

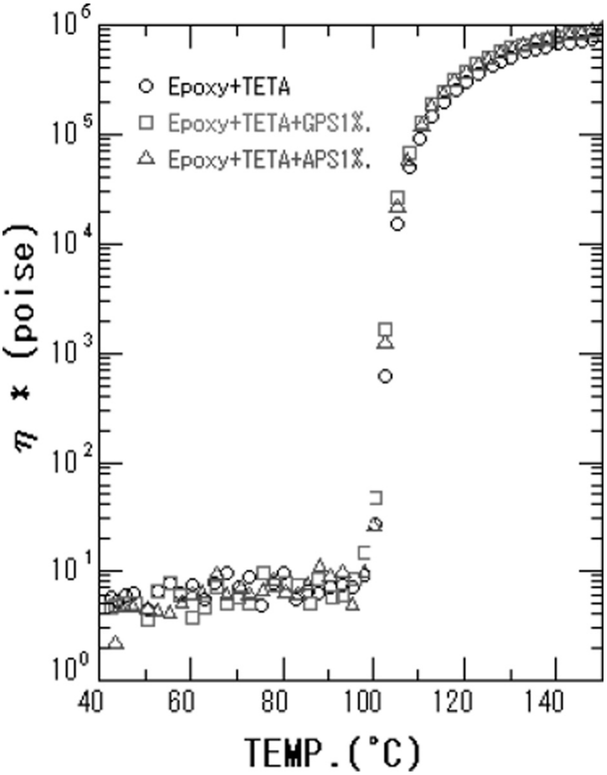


FIGURE 5 Viscosity changes of the epoxy resin compositions cured in air as the temperature was increased from 40 to 150°C at a heating rate of 5°C/min. [Epoxy + TETA]: diglycidylether of bisphenol A and triethylenetetramine (1:1 epoxy to amine hydrogen ratio), [Epoxy + TETA + GPS1%]: GPS was added to the Epoxy + TETA in 1 wt%, and [Epoxy + TETA + APS1%]: APS was added to the Epoxy + TETA in 1 wt%.

5-wt% addition of GPS, in contrast, produces a stoichiometry of 1.05 epoxy groups per amine hydrogen. In addition to weakening the epoxy network, the excess amine hydrogens that will remain after cure in the APS-epoxy network will render this network more hydrophilic than the 5-wt% GPS-epoxy network, possibly leading to a more rapid hydrolysis of Si−O−Si bonds near the interface.

CONCLUSIONS

We investigated the fracture energy, *Gc*, and the threshold fracture energy, *Gth*, in water at 80°C of interfaces between epoxy and layers of five silane coupling agents: GPS, APS, PAPS, MPS, and AEAPS on silicon. While 10-nm-thick layers of these all had similarly high *Gc*, APS had the best overall values of *Gth*, but all adhesion promoters, except for AEAPS, performed roughly similarly. Silane coupling agents that perform well as deposited layers do not necessarily perform well as additives to epoxies. For applications where silanes are added to epoxies or other functional resins, it seems to be important to have an idea of how the competition between diffusion and reaction is affected by the chemical architecture of the silane coupling agent itself as well as the curing temperature ramp profile. Addition of larger amounts of silane coupling agents actually led to decreases in both *Gc* and *Gth*.

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