

The Adhesion Promotion Mechanism of Organofunctional Silanes

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ABSTRACT: The adhesion promotion mechanism of organofunctional silanes has historically been attributed to the formation of an “interpenetrating polymer network” between a polymerized silane film and the polymer. This notion was investigated by formulating and testing two hypotheses. First, if the adhesion promotion is due to the formation of an interpenetrating polymer network, variation in the time-temperature profile of the bonding conditions should alter the extent of interdiffusion and thus interfacial strength. Second, if the adhesion promotion is due to compatibility and penetration of the silane organofunctional group, not the bulk silane film, variation in the structure of that group should change interfacial strength. Direct interfacial strength measurements using single-particle composites show that variation in the time-temperature profile of bond formation does not significantly affect interfacial strength. However, use of a series of aminofunctional silanes (with constant C : N ratio and identical surface energetics) revealed a relationship between length of the aminofunctional group and interfacial strength. These results suggest that the adhesion promotion for the system studied is controlled by compatibility and penetration of the silane organofunctional group. Whereas all of the interfaces studied here featured poly(vinyl butyral), the conclusions should apply to all amorphous polymeric materials. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1025–1033, 1998

Key words: organofunctional silane; interfacial strength; single-particle composite; adhesion

INTRODUCTION

Silane coupling agents are a broad class of surface-modifying chemicals used primarily as adhesion promoters in composite materials,¹ particularly for treating the surfaces of metals, glass, and minerals to achieve enhanced bond strength with polymeric materials. These compounds—which typically have the structure $(R'O)3-Si-R$, where R' is an alkyl group and R is an organofunctional group—are prepared as aqueous solutions, which are then applied to the surface. The alkoxy groups

hydrolyze in the aqueous environment, enabling condensation reactions with hydroxyl groups on the surface and other hydrolyzed silane molecules. Subsequent drying leads to formation of both covalent linkages with the treated surface and development of a polymeric thin film of silane. The organofunctional group, R , is available commercially in a wide array of chemistries, and a properly chosen group for a specific application will provide significant increase in interfacial strength. Although in some cases this strength enhancement is due to the formation of covalent linkages with the polymer, this article deals only with those that form bonds *via* physical interactions.

The widespread use of organofunctional silanes warrants detailed study of the mechanism by

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which they promote adhesion. Previous workers have reported that the adhesion promotion is due to interdiffusion of the polymerized silane film and polymer, and the resulting formation of a so-called "interpenetrating polymer network" (IPN).¹⁻⁵ They conclude that the silane must be applied in amounts sufficient to produce a silane film of finite thickness (multiple monolayers) that can interdiffuse with the polymer and increase bond strength. Excessive application of silane, however, can lead to a weak boundary layer, and optimal application levels have been observed.²⁻⁴ Drying of the silane film drives off water and initiates condensation reactions to produce a more highly crosslinked matrix and corresponding reduction in film thickness with increasing drying temperature.^{3,5-7} The increased crosslinking with higher drying temperature may restrict interdiffusion with the polymer and limit formation of an IPN, resulting in a corresponding drop in bond strength with increased drying temperature.^{3,4,6} Compatibility between the silane organofunctional group and polymer is an important consideration, as recognized by Plueddemann¹ and studied by Gentle and colleagues,⁸ who investigated the relationship between the penetration distance and similarity in solubility parameter between the silane organofunctional group and the polymer. Results from sputtered neutral mass spectroscopy experiments indicated that the closest match in solubility parameter yielded the highest IPN thickness.

Despite the body of work attributing the adhesion promotion of organofunctional silanes to the formation of an interpenetrating polymer network, evidence exists supporting an alternate explanation. In some of the aforementioned studies, a strong dependence of bond strength on silane surface treatment concentration was observed at low concentrations,³⁻⁵ below that expected to yield multilayer coverage. Other studies have been restricted to submonolayer silane coverage and have illustrated significant bond strength enhancement.⁹⁻¹¹ These results require an explanation focusing on the role of the organofunctional group, and some recent studies provide valuable insight. Chou and Penn¹² attached chemical groups of varying chemistry and size to polyaramid fibers that were then embedded in a polar epoxy matrix. They found that, in attaching chains of varying length, improvements in bond strength were observed for the polar groups and the improvement increased with increasing group length. The nonpolar moieties degraded the bond strength, with no dependence on length. Mieck

and colleagues¹³ attempted to enhance the yield strength of a flax fiber/polypropylene layered composite by treating the fibers with silanes featuring nonpolar organofunctional groups of varying length to match the nonpolar polymer matrix. Despite the nonpolar nature of both silane and polymer, the composite yield strength was not improved, and there was no dependence on organofunctional group length. This may be explained by the crystalline nature of this polymer and its tendency to exclude all other materials unless the chain is of sufficient length to be incorporated into the crystalline structure.¹⁴ Lin and colleagues^{15,16} attached polymeric chains to glass fibers, dispersed the fibers in a polystyrene matrix, and studied the effects of tethered chain length and areal attachment density. They found interfacial toughness to increase with chain length and decrease with areal attachment density, attributing the former to increased molecular penetration and the latter to exclusion of the polymer chains with high areal density.

These studies support an argument that the adhesion promotion comes about from chemical compatibility between the silane organofunctional group and the corresponding penetration into the polymer. Recent results from this laboratory¹¹ included a study on adhesion in filled poly(vinyl butyral) composites (as summarized in Fig. 1). Organofunctional silanes were used to treat a filler material to varying degrees of monolayer surface coverage. Two silanes were used: an octylsilane with a deleterious effect on composite yield stress and a diaminosilane that enhanced composite yield stress. For each silane, the data point for a surface coverage of unity corresponds to multilayer coverage and the opportunity for interfacial strength enhancement *via* an IPN. Pertinent to the present study, there was no improvement in the composite yield stress with multilayer coverage of diaminosilane.

The present work seeks to investigate further the mechanism of silane adhesion promotion for the silane-poly(vinyl butyral) interface by systematically varying both bond formation conditions, and the size and structure of the organofunctional group of the silane. This is expected to isolate the effects of two mechanism candidates: (1) an interpenetrating polymer network and (2) penetration of the silane organofunctional groups. The time-temperature profile during bond formation is controlled to provide different levels of interdiffusion between the polymerized silane film and matrix polymer. A series of aminofunctional

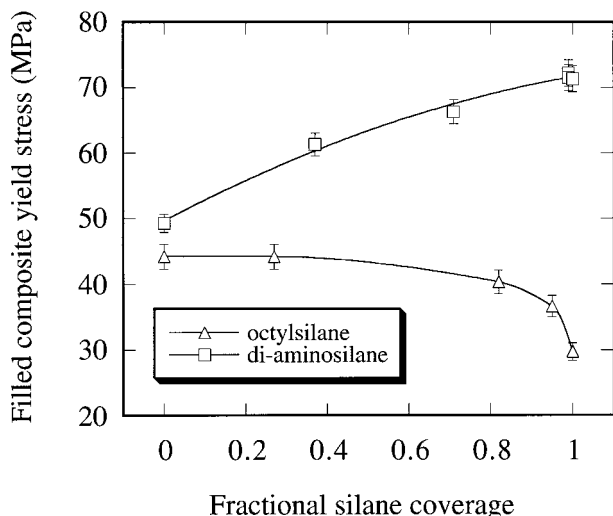


Figure 1 Yield properties of filled polymer composites as a function of fractional silane coverage and silane organofunctionality.¹¹ The points corresponding to full coverage represent multi-monolayer coverage for both silanes. In the case of adhesion-promoting diaminosilane, the presence of multi-monolayers of silane does not increase composite yield stress above that for monolayer coverage. Error bars correspond to the 95% mean confidence interval.

silanes with identical chemistry is used to investigate the role of organofunctional group length. Direct interfacial strength measurements are made using single-particle composites. The results of this study should be applicable to all systems featuring amorphous polymers and adhesion-promoting organofunctional silanes.

EXPERIMENTAL

Surface Modification

Smooth spherical glass particles of 650 μm diameter (Cataphote, Inc., Jackson, MS) and smooth glass rods of 3 mm diameter were surface-modified with the four organofunctional silanes listed in Table I. Silane agents were selected that both reduce interfacial strength (octylsilane) and enhance interfacial strength (aminofunctional silane series) relative to an unmodified glass surface. The aminofunctional series is selected to investigate the role of organofunctional group length while maintaining constant chemistry (in this case, the C : N ratio), as shown by the structures in Table I. Solution concentrations of 2% for the octylsilane and 0.5% for the aminofunctional

silanes were used with isopropanol and aqueous solutions, respectively. These treatments provide multilayer coverage of these silanes.^{1-3,5,11} The treated surfaces were dried at 125°C.

Single Particle Composites

Poly(vinyl butyral) was obtained from Scientific Polymer Products, Inc. (Ontario, NY), and disks of 15 cm diameter and 2 mm thickness were made by compression molding 40 g of the as-received poly(vinyl butyral) powder at 90°C. Cast films were prepared by dissolving poly(vinyl butyral) in ethanol to 10 mass %, depositing the solution onto a flat polytetrafluoroethylene surface and drying under ambient conditions. Surface-modified spheres were then carefully placed into a folded section of the cast poly(vinyl butyral) film, and the film placed between two poly(vinyl butyral) disks to form a sandwich. This arrangement was compression-molded in a Tetrahedron MTS-14 automated hot press (Tetrahedron Associates, Inc., San Diego, CA) with carefully controlled time-temperature-pressure profiles, each with a 10 min annealing step at 10°C above the glass transition temperature, T_g . Temperature was monitored with a thermocouple placed 1 mm from the molding surface. Three molding time-temperature profiles were developed and are shown in Fig. 2. The "base" profile corresponds to a base case used in previous work with filled polymer composites¹¹ and single-particle composites.¹⁷ The "quench" and "hold" profiles were designed to minimize and maximize the opportunity for interdiffusion between the silane film and polymer, respectively, without allowing macroscopic defects such as voids.

Rectangular single-particle composites of 9 mm width and 65 mm length, each with a centered spherical particle, were cut using a surface grinder with diamond blade. A 15 mm length of each composite was subjected to tensile strain with the remainder of the length taken up in the grips of a Satec T-1000 mechanical tester (Satec Systems, Inc., Grove City, PA). Before testing, a Wild Makroskop M420 microscope (Wild Heerbrugg Ltd., Heerbrugg, Switzerland) with a MTI 65 videocamera (Dage-MTI, Inc., Michigan City, IN) was positioned to view the spherical particle in the direction normal to the tensile strain to allow the capture of video images during mechanical testing. The particle was illuminated from behind with a 100 W light bulb and the video image fed directly to a Macintosh computer using a

Table I Names and Structures of Organofunctional Silanes Used in This Study

Organofunctional Silane	Product Code ^a	Organofunctional Group (<i>R</i>)
Octylsilane ^b	A-137	—(CH ₂) ₇ CH ₃
Monoaminosilane ^c	A-1100	—(CH ₂) ₃ NH ₂
Diaminosilane ^c	A-1122	—(CH ₂) ₃ NH(CH ₂) ₂ NH ₂
Triaminosilane ^c	A-1130	—(CH ₂) ₃ NH(CH ₂) ₂ NH(CH ₂) ₂ NH ₂

^a Commercial organofunctional silanes obtained from OSI Specialties, Inc. (Tarrytown, NY).

^b Nonpolar organofunctional group incompatible with poly(vinyl butyral).^{11,17}

^c Aminofunctional silane series provides similar empirical chemistry with varying length.

frame grabber board and NIH Image software. Each experiment began with the mechanical straining of the single-particle composite at a strain rate of 0.039 min⁻¹. A stopwatch was simultaneously engaged and the live digital image monitored. Interfacial failure was readily observed and happened instantaneously for all but the strongest interfaces. Examples of the digital images obtained are provided in Fig. 3 for unstrained and failed interfaces. Interfacial failure was indicated by the sudden appearance of a dark, dewetted “cap” as shown in Fig. 3(b). The load at failure was obtained from the force-time data collected by the mechanical tester. Eleven samples were tested for each case, and the polar radial stress at failure was calculated as previously described.¹⁷

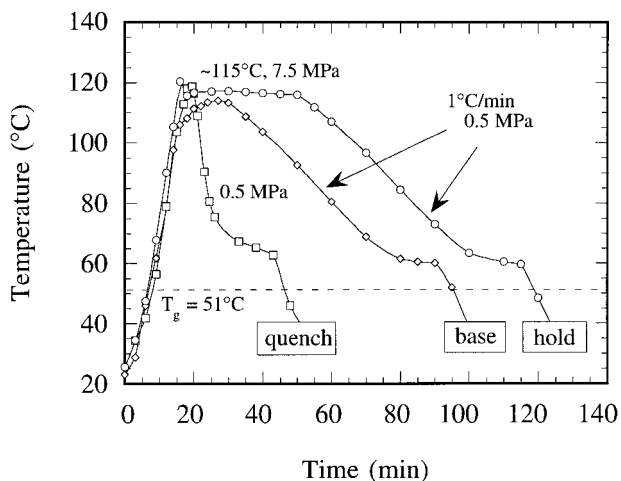


Figure 2 Time-temperature profiles used to investigate interdiffusion effects for an IPN of diaminosilane. The “base” profile corresponds to that used in previous work with filled composites¹¹ and single-particle composites.¹⁷ The “quench” profile features immediate and rapid cooling, whereas the “hold” profile includes sustained time at the maximum molding temperature.

Wetting Measurements

Dynamic contact angle analysis was used to characterize the surface energetics of the aminofunctional silane series. In this technique, a surface-modified rod of known perimeter is slowly advanced into or pulled from a liquid bath. The force exerted by surface tension on the perimeter measured during immersion and emersion correspond to the advancing and receding contact angles, respectively, after correction for buoyancy. If the contact angle, θ , is measured for a liquid capable of only Lifshitz–van der Waals (i.e., dispersive) interactions with the solid, that component of the solid surface energy, σ_s^{LW} , can be calculated from the contact angle.¹⁸ The LW-only probe α -bromonaphthalene is used in this study. The propensity of the surface to engage in Lewis acid–base interactions can then be investigated by using an appropriate liquid probe. Water is a bifunctional liquid probe, having the ability to serve as both an electron donor and an electron acceptor, and is used here to explore the Lewis acid–base properties of the aminofunctional silane surfaces. The acid–base component of the thermodynamic work of adhesion between water and the surface, W_a^{AB} , is obtained from the contact angle measurements.¹⁸

In preparation for DCA analysis, a small piece of aluminum foil was glued to the end of each silane-treated glass rod to allow suspension from a hangwire on a Cahn D-200 electrobalance (Cahn Instruments, Inc., Cerritos, CA). A Teflon[®] dish containing ~ 5 mL of the probe liquid was mounted atop a Burleigh IW-602 electronic translator (Burleigh Instruments, Inc., Fishers, NY) located below the suspended glass rod. Each treated glass rod was then advanced 3 mm into the liquid at a 10 $\mu\text{m s}^{-1}$ rate and withdrawn at the same rate. Force and position data were collected with a personal computer, corrected for

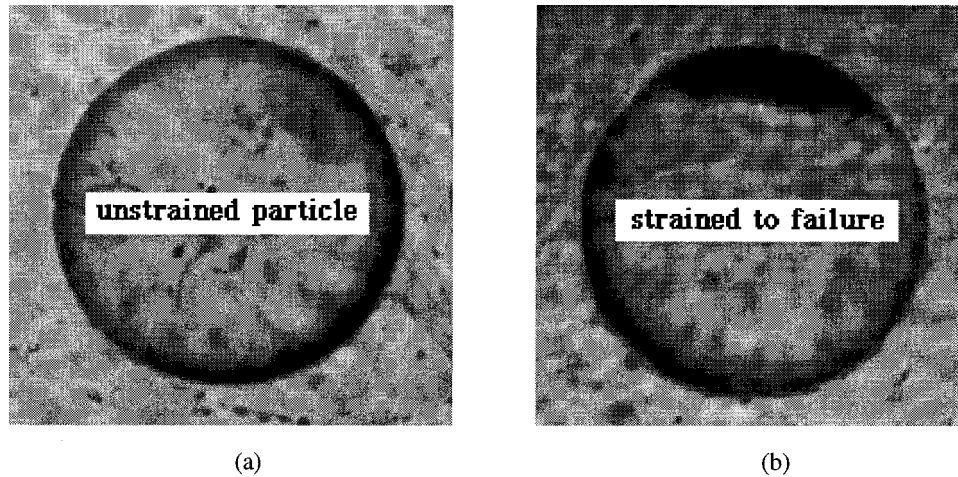


Figure 3 Digital video images of 650 μm glass spheres in poly(vinyl butyral) showing unstrained and failed interfaces: (a) particle before mechanical testing (b) diaminosilane-modified sphere after failure. The shadows in (a) are due to poor lighting.

buoyancy, and the average force due to surface tension calculated for the advancing and receding modes. Decane was assumed to wet each surface completely ($\theta = 0^\circ$) in the receding mode, and its force trace used to determine the perimeter of each glass rod accurately. The force traces for α -bromonaphthalene and water were then used to calculate values for the dynamic advancing and receding contact angles and the corresponding values for σ_s^{LW} and W_a^{AB} . Three measurements were made for each surface.

RESULTS AND DISCUSSION

Bond formation effects were studied by using the time-temperature profiles shown in Fig. 2 to manufacture single-particle composites featuring octylsilane and *di*-aminosilane surfaces. Differences in bond formation should alter interdiffusion between the polymerized silane film and polymer and provide insight into the importance of an IPN. The “quench,” “base,” and “hold” profiles should provide increasing opportunity for interdiffusion. Each time-temperature profile includes an annealing step 10°C above T_g to allow the composite to reach thermal equilibrium and relax thermal stresses. The annealing temperature is low relative to the maximum molding temperature, and interdiffusion is negligible. The maximum molding temperature for the different profiles was kept approximately constant to avoid differences in thermal oxidation or rheological effects. Octylsilane is known to be incompatible

with poly(vinyl butyral),^{11,17} and interdiffusion should thus be negligible. This silane was used to monitor the bond quality (e.g., the presence of interfacial voids) for the different profiles.

The results of the time-temperature profile experiments are shown in Fig. 4. The error bars correspond to the 95% mean confidence interval, and thus any overlap indicates lack of significant difference. The octylsilane case showed no change with variation in time-temperature profile, thus eliminating variation in bond quality as a concern. Octylsilane features a nonpolar organofunctional group that is incompatible with the polar

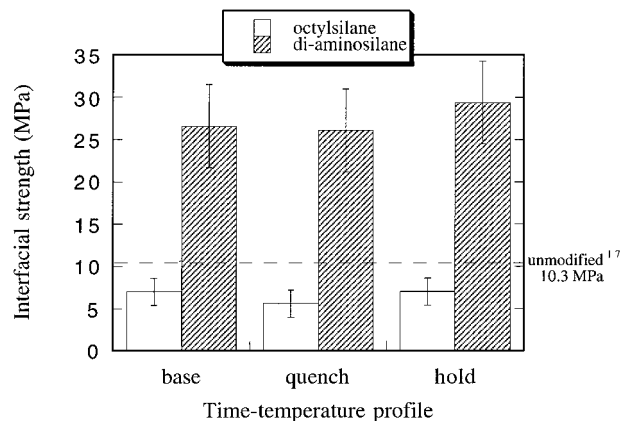


Figure 4 Interfacial strength measurements for single-particle composites molded with different time-temperature profiles. The molding time-temperature profile has no observable effect on the interfacial strength. Error bars correspond to the 95% mean confidence interval.

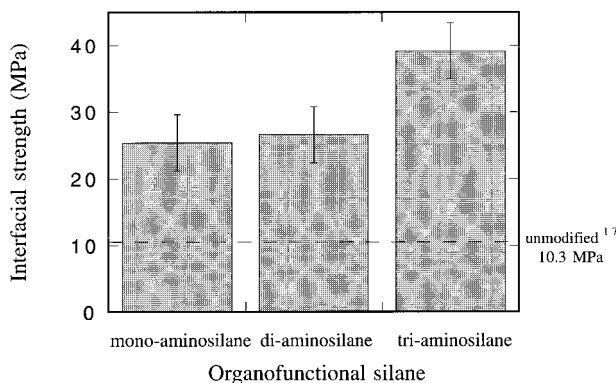


Figure 5 Interfacial strength measurement results for aminosilanes of various length. The monoaminosilane and diaminosilane results are not significantly different, but a large increase in interfacial strength is observed with triaminosilane. The additional aminoethyl group may provide the triaminosilane with length and flexibility to form another acid-base adduct. Error bars correspond to the 95% mean confidence interval.

polymer, and no interdiffusion would be expected at the interface. The interface is correspondingly weak. The adhesion promotion provided by diaminosilane with poly(vinyl butyral), which has been demonstrated previously,^{11,17} was not significantly affected by variation in bond formation conditions. This indicates that, within the range tested, there is no apparent incremental benefit from interdiffusion and the formation of an IPN.

The role of the organofunctional group length was then explored by using the aminofunctional silane series having interfaces formed with the “base” time-temperature profile. Results are shown in Fig. 5. All of these silanes serve as adhesion promoters, markedly increasing interfacial strength over that for an unmodified glass surface.¹⁷ The triaminosilane shows a large increase in interfacial strength over the others—in fact, the highest value measured thus far with the single-particle composite technique. Contact angle measurements were conducted to identify any differences in surface chemistry and energetics between the three aminofunctional silane surfaces. Differences of this sort would alter the Lifshitz–van der Waals and Lewis acid–base interactions across an interface and convolute the issues being investigated in this study. The results of these measurements are shown in Table II and indicate no significant differences between the surfaces. The interfacial strength differences in Fig. 5 are thus attributed solely to structural effects.

Attribution of the incremental strength en-

hancement observed with triaminosilane to increased penetration of the longer organofunctional group does not explain the identical values for the monoaminosilane and diaminosilane. Similar results were obtained by Cayless and Perry,⁹ who deposited the same two aminofunctional silanes from an organic solvent to obtain monolayer coverage on steel adherends and then formed bonds against polystyrene. Their results share two important similarities with the present study: (1) an approximate threefold increase in interfacial strength was observed relative to the unmodified surface, and (2) the mono- and diaminofunctional silanes provided identical strength enhancement. They recognized that the presence of only a silane monolayer precluded an IPN as a mechanism candidate and attributed the adhesion promotion of the two aminosilanes to “molecular overlap with the polymer chains” and the corresponding improvement in physical interactions at the interface. They did not, however, explain the identical interfacial strength for the two silanes of different organofunctional group length. A monotonic change in interfacial strength is expected with increasing organofunctional group length.

The identical interfacial strength values observed for mono- and diaminofunctional silanes by Cayless and Perry⁹ and in the present study are possibly explained by considering the physical interactions between a penetrating organofunctional group and the polymer. The polymer used in this study features 88% poly(vinyl butyral), 11% poly(vinyl alcohol), and ~1% poly(vinyl acetate). The alcohol groups likely provide the Lewis acidity reported by Fowkes¹⁹ and hence the opportunity to form acid-base adducts with amino groups in the silanes. An aminofunctional silane tethered to the surface of the silane film has access to the functional groups in the polymer, but this is limited by its length and flexibility. The volume of polymer, and therefore the number of alcohol groups, sampled by the tethered group is roughly proportional to the cube of the organofunctional group length. The length and flexibility of the triaminosilane may allow it to form two acid-base adducts. The diaminosilane is limited to one by the proximity of its two amino groups, and the adhesion promotion is therefore almost identical to that of monoaminosilane. The incremental interfacial strength increases shown in Fig. 5 support this hypothesis. The areal density of acid-base adducts may ultimately determine the interfacial strength.

Table II Characterization of Surface Energetics Using Contact Angle Measurements

Organofunctional Silane	Contact Angle Measurements ^a				Surface Energetics ^b	
	α -Bromoaphthalene ^c		Water ^d		σ_s^{LW}	W_a^{AB}
	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}		
Monoaminosilane	45.7	30.7	88.4	52.5	35.3	40.7
Diaminosilane	42.8	32.4	84.9	55.3	35.6	41.0
Triaminosilane	41.8	29.8	88.3	49.7	36.4	41.3

^a Reported values are the average of three measurements; error is $\pm 4^\circ$.

^b Average of values calculated from advancing and receding contact angles.

^c Lifshitz–van der Waals liquid probe.

^d Bifunctional Lewis acid–base liquid probe.

The results presented in this study support the conclusion that the adhesion promotion mechanism of organofunctional silanes comes from compatibility of organofunctional groups with the polymer and the corresponding degree of penetration of those groups, not an IPN formed between the polymerized silane film and the polymer. This is shown schematically in Fig. 6. An organofunctional group that is incompatible with a polymer, such as the octylsilane portrayed in Fig. 6(a), is unable to penetrate into the polymer. The interfacial strength for this case comes only from Lifshitz–van der Waals interactions at the *interface*. Compatible organofunctional groups [e.g. the aminofunctional silane series shown in Fig. 6(b–d)] penetrate and almost instantaneously reach conformational equilibrium with the molten

polymer. The interfacial strength they provide comes not only from Lifshitz–van der Waals interactions, but also Lewis acid–base adduct formation and molecular overlap active in a thin *interphase*. There may thus be a critical organofunctional group length where interfacial failure corresponds to the scission of covalent bonds.

This proposed mechanism of adhesion promotion seems in agreement with the bulk of the pertinent experimental data, the exception being the reported dependence of interfacial strength on the silane film drying temperature.^{3,4,6} This evidence belies the lack of importance of interdiffusion as previously suggested, but may be reconciled by considering the effects of silane film consolidation on silane film surface properties. The condensation reactions that form siloxane bridges between

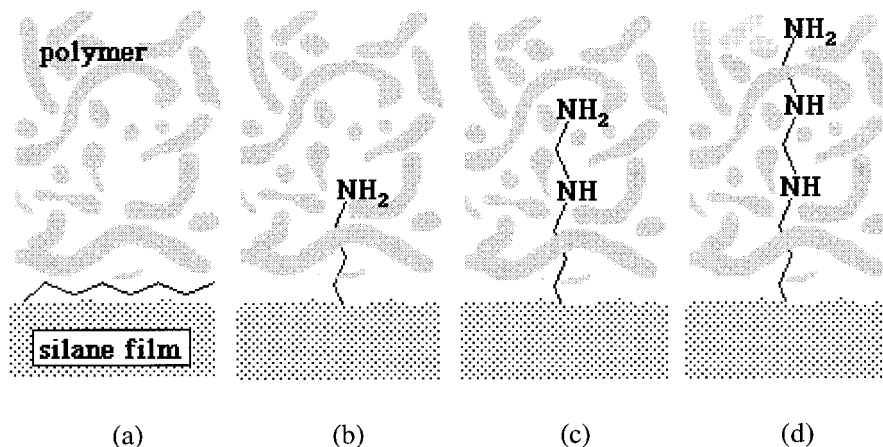


Figure 6 Proposed conformations for the organofunctional silanes used in this study: (a) octylsilane, (b) monoaminosilane, (c) diaminosilane, and (d) triaminosilane. The octylsilane is nonpolar and therefore excluded from the polar matrix. The aminofunctional silanes engage in acid–base interactions with the matrix and readily penetrate, thus providing a dramatic increase in interfacial strength.

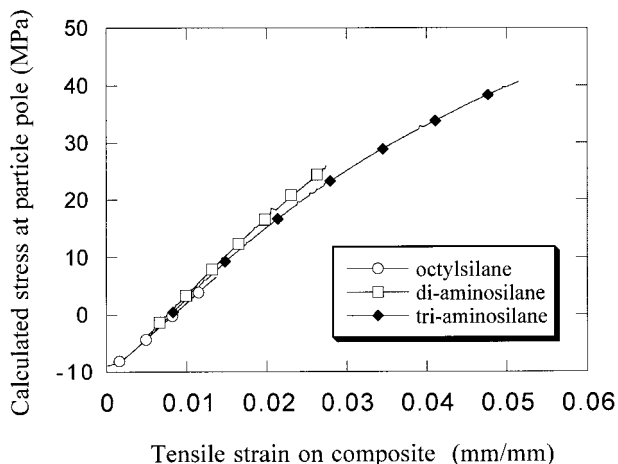


Figure 7 Examples of the relationship between calculated polar stress and tensile strain of the single-particle composite. These curves demonstrate that the case of highest interfacial strength (triaminosilane) departs the elastic region of polymer deformation. (Note: The particle is under initial compressive stress due to differences in the coefficients of thermal expansion between the polymer and glass particle.)

silane molecules during drying may increase the areal density of organofunctional groups and begin to exclude polymer from the thin interphase, as described by Lin and colleagues.¹⁶ The result would be reduced physical interactions between the surface of the silane film and the polymer and a correspondingly weaker interface. This may be a topic for future study in this laboratory.

Finally, it was previously described that the interfacial strength observed for the triaminosilane case was the highest thus far measured using the single-particle composite technique.¹⁷ The closed-form analytical expressions used with this technique require elastic behavior of both the polymer and inclusion to calculate accurately the thermal stresses and relate the applied macroscopic stress to the stress at the particle pole at failure. This condition was violated for the triaminosilane because the high tensile strain necessary to induce interfacial failure resulted in plastic behavior of the polymer. This is shown by the sample stress-strain curves in Fig. 7. The plastic behavior of the triaminosilane case at high strain levels deviates from the linearity required for the analytical solution of the stress distribution about the inclusion. This observation does not alter any of the conclusions previously made, but the slight deviation in linearity indicates that numerical analysis would be necessary to investigate cases of high interfacial strength.

CONCLUSIONS

The adhesion promotion mechanism of organofunctional silanes was studied to determine the importance of the formation of an IPN, as opposed to the penetration of a monolayer of the silane organofunctional groups into the polymer overlayer. This was accomplished by systematically varying both interfacial bond formation conditions and the size and functionality of the silane organofunctional group. Varied time-temperature profiles during bond formation were found to have no effect on the level of adhesion promotion, indicating that interdiffusion between the polymer and polymerized silane film and formation of an IPN is not a significant contributor to bond strength. Profound effects were observed, however, with differences in compatibility and length of the silane organofunctional group. Compatibility between the polymer and organofunctional group resulted in high interfacial strength *via* the formation of Lewis acid-base adducts and molecular overlap. The results indicate that optimal adhesion promotion for the case of noncovalently bonding silane against an amorphous polymer is obtained with monolayer coverage of organofunctional silane.

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