

Adhesion mechanism of polyvinyl chloride to silane primed metal surfaces

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Abstract—The interface of partially hydrolyzed organosilane primer Dow Corning® Z-6020 [*N*-(2-aminoethyl-3-aminopropyl trimethoxy silane)], which will be referred to in this paper as simply AEAPS, and polyvinyl chloride (plastisol) was examined by XPS (X-ray photoelectron spectroscopy) depth profile analysis. These studies and the adhesion strength measurements under dry and wet conditions showed that the net bond strength and its resistance to moisture are determined by two factors: the extent of crosslinking of the primer and the interdiffusion of the two phases. Best adhesion is achieved as a result of the optimal balance between the above two conflicting tendencies, i.e. when the primer crosslinks after it has diffused into the polymer.

Keywords: XPS; depth profile; interdiffusion; adhesion; silane; PVC.

1. INTRODUCTION

The adhesion performance of a polymer to a glass or metal substrate can be improved with the application of a suitable organosilane primer or coupling agent. A coupling agent is a material that provides a water-resistant bond across the interface between an inorganic substrate and an organic matrix resin [1]. The same materials may at times promote adhesion between organic polymers [2, 3]. The silane coupling agents are of the general structure $X_3\text{Si}-R-Y$, where Y is an organofunctional group selected for bonding to organic polymers while X is a hydrolyzable group on silicon that forms $\text{Si}-\text{OH}$ group in water or may react directly with surface hydroxyl groups $\text{M}-\text{OH}$ to form oxane bonds $\text{M}-\text{O}-\text{Si}$. Y groups are attached to silicon through stable $\text{C}-\text{Si}$ bonds. Other proposed commercial coupling agents [1] have organofunctional groups bonded to a central atom (Z) through oxygen. The resulting $Z-\text{O}-R-Y$ compounds have much poorer hydrolytic stability than comparable $\text{Si}-R-Y$ structures, and therefore do not provide the degree of water-resistant 'coupling' that is possible with silanes. Silane coupling agents are generally applied to an inorganic surface from dilute aqueous solutions and dried. Silanol groups may first form hydrogen bonds with the surface, but during drying they condense to siloxane structures chemically bonded to the surface (Fig. 1). The extent of adhesion of the silane primer film with the polymer matrix then determines the ultimate bond strength. The mechanism involved in the adhesion of the primer to the polymer can be categorized in three different ways [1]. In the first type of adhesion the silane primer is sufficiently crosslinked so that the adhering polymer tends to form a geometrically sharp interface with respect to the primer film with little or no interdiffusion of the two phases. In such types of adhesion, the bond strength is

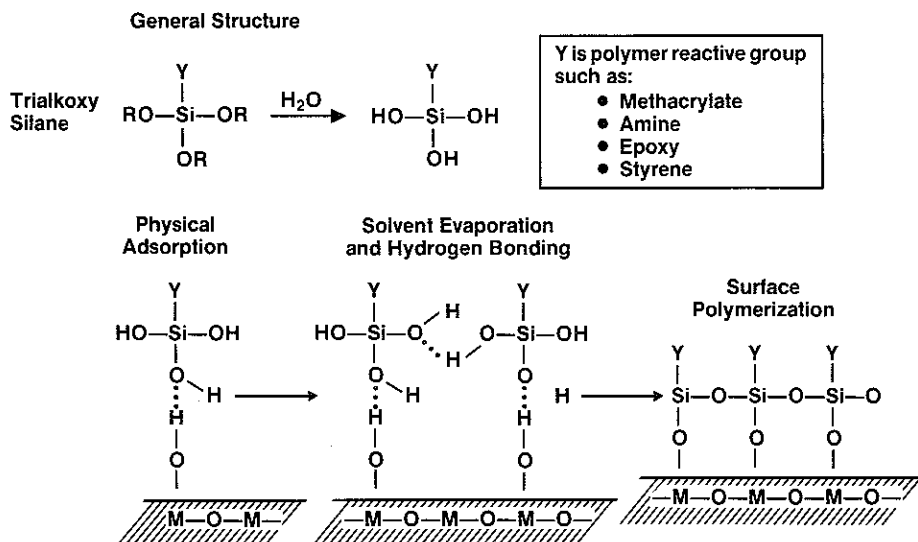


Figure 1. Bonding of silane coupling agents to mineral surface (adapted from ref. [4]).

generally poor and is solely dependent on the surface free energy of the primer film. The adhesion strength in this case varies linearly as a function of the solubility parameter without exhibiting any maxima or minima. In the second type of adhesion, the primer and polymer undergo interdiffusion (Fig. 2) into each other resulting in a large increase in the effective contact area of the two phases and thus greatly improving the adhesion strength. In this type of adhesion system, the bond strength depends significantly on the solubility parameters of the two phases and exhibits a maximum where the solubility parameters of the two phases are equal to each other. Interdiffusion of a siloxane primer layer with a crosslinkable polymer was proposed as the probable bonding mechanism for an ethylene-vinyl acetate copolymer (EVA) to glass through silane coupling agents [4]. If the two phases undergo interdiffusion and crosslinking, the bond strength improves dramatically to a level which is comparable to or exceeds the cohesive strength of the polymer. The bonding of the above type through the formation of

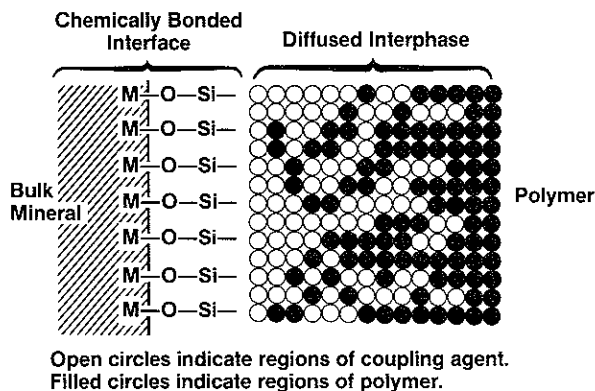


Figure 2. Interdiffusion model for a silane-primed mineral/polymer bonding system (adapted from ref. [4]).

Three Adhesion Mechanisms

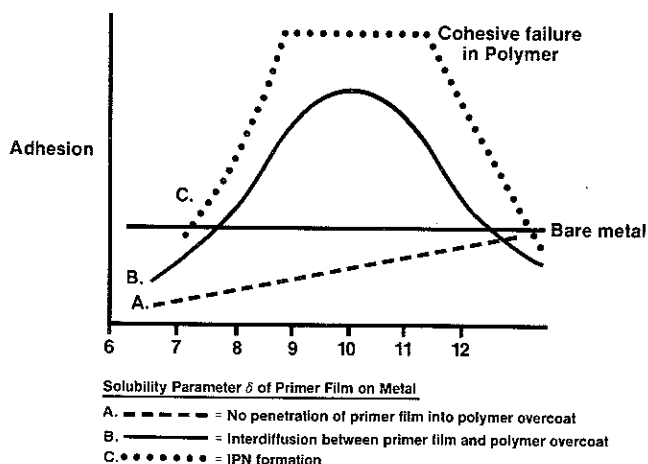


Figure 3. Diagrammatic representation of the three adhesion mechanisms.

interpenetrating polymer network constitutes the third type of adhesion mechanism. The three adhesion mechanisms discussed above are shown schematically in Fig. 3.

During the past few decades several theoretical and experimental studies have addressed the question of interdiffusion of polymer phases at the molecular level. Several mean field and lattice theories [5–10] have been developed to correlate the interfacial thickness to the fundamental physicochemical properties of the two polymer phases. The physical properties of importance are the solubility parameter, molecular weight, radius of gyration and diffusion coefficient. The theoretical calculations have predicted values of the equilibrium interfacial thickness ranging from 10 Å to 1000 Å. Simultaneous experimental observations have further provided proof for diffused interfacial structure. Electron microscopy [11–14], radiothermoluminescence [15] and other techniques [16–18] have shown indications of interfacial thickness comparable to the theoretical estimates. A number of surface characterization techniques [19–24] have been used to probe the surface conditions of the adherend before bonding and to determine the locus of adhesion failure when the visual inspection fails to distinguish the interfacial weak boundary layer. Occasionally the fractured surfaces were investigated by XPS (X-ray Photoelectron Spectroscopy) or AES (Auger Electron Spectroscopy) depth profiling technique, yielding information about the chemical composition and the locus of bond failure. In recent years, Kaul and his collaborators [25–28] have studied the roles of silane structure and the interdiffusion between a siloxane primer (Gamma-aminopropyl triethoxy silane) and polymer in determining the adhesion strength of alumina/polyethylene bonding system. The evidence for interdiffusion between the siloxane film and polyethylene was obtained by measuring the Si concentration profile across interface of the laminate of polyethylene/primer/polyethylene by scanning electron microscopy coupled with energy dispersive X-ray analysis. The authors proposed that the interdiffusion between the siloxane primer and

polyethylene is an important mechanism for initial adhesion and the retention of the bond strength under wet conditions. In the present paper we report a study that adds further evidence for the joint roles of interdiffusion and crosslinking in the adhesion of polymer to a silane primed metal substrate. It was reported earlier [1] that partially hydrolyzed AEAPS primed metal surface improves adhesion to polyvinyl chloride (PVC). The final adhesion strength and the moisture resistance was found to depend critically on the predrying temperature of the primer. It was hypothesized that both the degree of crosslinking and interdiffusion play significant roles in determining both the dry and wet strength of the bonding system. We have currently extended this study to critically examine the validity of the above hypothesis by taking advantage of a novel depth profiling technique developed by Solomon and his collaborators [29].

Solomon *et al.* have introduced an Auger depth profile technique for examining the interface of two materials which does not require the fracturing of the bonding system before surface analysis. These authors have used a vacuum deposited metal film as an adherend and conducted a depth profile analysis by Auger electron spectroscopy starting from the metal side. A number of bonding parameters have been investigated using this technique including the effects of an adherend surface treatments and cure conditions. The depth profile technique of Solomon *et al.* has certain advantages over the conventional techniques where the fractured surfaces are employed. Dwight has suggested [19] that polymer surfaces may undergo reorganization after fracturing of the bonding system hence limiting the application of conventional surface analysis. The particular advantage of the technique described by Solomon *et al.* is that this technique, in addition to minimizing the above difficulty, offers an opportunity for a direct investigation of the extent of interdiffusion of the two polymer phases, which constitute the bonding system.

2. EXPERIMENTAL

In the previous experimental report [30], partially hydrolyzed AEAPS was applied from an isopropanol solution. We have found that the primer films so cast were hazy and the surface when examined under optical microscope appeared somewhat irregular. The quality of the film was improved by applying the primer from a methanol solution, which produced smooth and homogeneous films in addition to improving the bond strength. 2024 aluminum was used as the bonding substrate. The aluminum coupons (1" × 4") were cleaned by commercial Oakite® solution. The formation of clean surface was indicated by the complete spreading of high surface tension liquids such as diiodomethane and water. Partially hydrolyzed oligomeric AEAPS was applied onto the aluminum surface to an estimated thickness of about 1500 Å. The preparation of partially hydrolyzed AEAPS is discussed in ref. [30]. In general, 50 parts of silane in 45 parts of methanol and 5 parts of water (distilled, deionized) was allowed to age for a few hours to allow hydrolysis and equilibration to oligomeric methoxy siloxanes. The concentrated oligomer solution was diluted with additional solvent to make the final concentration of oligomer in methanol to 0.15% by weight. About 330 µl of this solution was applied onto the metal surface. The solution immediately spread on the surface and covered it uniformly. The

methanol is readily evaporated leaving a uniform film of hydrolyzed AEAPS on the metal surface. The film thickness was estimated from the density and the amount of the oligomeric AEAPS deposited. The oligomeric primer deposits soluble, flexible films that crosslink rather slowly at temperatures below 150°C. Some initial precuring of the primer was beneficial in promoting a water resistant bond. When the primers were over-cured, they had very good water resistance but the compatibility with the polymer overcoat was too poor to provide good dry adhesion. The methoxy cyclic siloxane had a broader 'window' of drying conditions than monomeric silane for providing good wet adhesion of PVC. In all cases, adhesion could be further improved by fusing the plastisol at higher temperatures.

The primed metal surfaces were predried in air at various temperatures ranging from 25°C to 175°C for 15 min each. The PVC plastisol needed in this study was prepared by mixing in a waring blender® 52 parts of polyvinyl chloride 0565 (Tennoco, Piscataway, NJ), 47 parts of di-isodecyl phthalate (Exxon Chem Co., Cartaret, NJ) and 1 part of Halbase-10® stabilizer (Hammond Lead products, Hammond, Ind). PVC plastisol, thus prepared, was applied onto the primed surface at an estimated thickness of 2 mm, and was fused at 175°C for 4 min. Some samples were used for wet strength measurements after immersing in water (distilled and deionized) at room temperature for three days. The bond strengths were determined with an Instron tester using a nearly 180° peel configuration at a speed of 0.1 in./min. The fractured metal surfaces were examined by external reflection infrared spectroscopy using a polarized beam at 3° off-glancing incidence in a Nicolet FTIR (Fourier Transformed Infrared Spectrometer).

In order to investigate the question of diffusion of AEAPS into the polymer overcoat we have used the following technique. Smooth glass slides (1" × 3") were cleaned by acetone and then by oxygen/nitrogen plasma for 10 min. A thin layer of fluorocarbon was then deposited onto the glass slide by thermal degradation of Teflon FEP. The thickness of the fluorocarbon layer was about 80–100 Å as determined by ellipsometric measurements. On the top of the fluorocarbon layer, a thin film of germanium was deposited corresponding to a thickness of about 1500 Å estimated by the quartz crystal oscillator installed in the vacuum evaporator. The measurements were made at a base pressure of less than 10⁻⁶ torr. Germanium was chosen in this experiment because the Si(2P) photoemission peak was well separated from all the photoemission and Auger transitions of germanium, thus exhibited no serious interfering transitions in the XPS experiments. The germanium-coated glass slide was exposed to air and the prehydrolyzed AEAPS primer was applied from methanol solution to an estimated thickness of 1500 Å (calculated from the density and the weight of the deposited primer). Two extreme temperatures, i.e. 25°C and 175°C, were used in predrying the primer. Care was taken to deposit primer layers of the same thicknesses on both the germanium coated glass mirrors. The PVC plastisol was applied on the two primed surfaces at an estimated thickness of 2 mm. The germanium/primer/PVC bonded system is shown schematically in Fig. 4. When the primary bonding system (germanium/primer/PVC) was delaminated it was found that fracture propagated at the glass/fluorocarbon interface as evidenced from the spreading behavior of water droplets. The germanium film appeared

Investigation of Interdiffusion

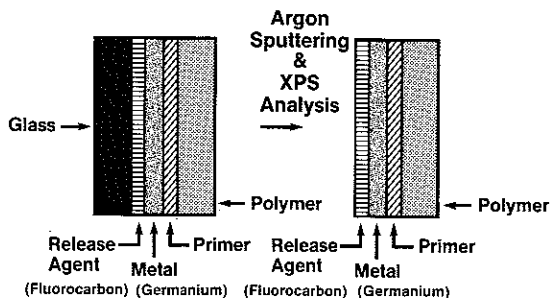


Figure 4. Schematic representation of the germanium/primer/PVC bonding system which was employed for XPS depth profile analysis.

shiny, exhibiting the intactness of the film although a few cracks were visible on portions of the surface. An area of approximately $\frac{1}{2}'' \times \frac{1}{2}''$ was cut out of the film where no cracks were visible.

Surface analysis was performed in a Perkin-Elmer Model 550 ultra-high-vacuum system. The chamber is equipped with a dual anode X-ray source (Mg and Al). All XPS experiments were performed using the aluminium anode. Electron energy analysis was carried out with a double pass cylindrical mirror analyzer which was interfaced to a digital PDP 11/34 computer for data collection and analysis. A pass energy of 100 eV was employed. A differentially pumped ion gun was used for argon ion bombardment. The sputtering rate was calibrated using a tantalum oxide standard obtained from the Perkin-Elmer Corporation. The depth profiling experiments were performed using alternate XPS analysis and ion bombardment (beam voltage 5 kV). Oxygen (1S), Carbon (1S), Silicon (2P) and germanium ($2P_{3/2}$) photoemission peaks were used for the atomic counts. Nitrogen (1S) peak, however, was unfortunately interfered with germanium Auger transition (LMM) and hence was not taken into consideration for atomic counts. This practice will lead the theoretical concentration of silicon in the primer phase to about 15% instead of about 11%.

3. RESULTS AND DISCUSSION

Figure 5 depicts the dry and wet adhesion strengths as a function of the pre-drying temperature of the primer. The adhesion results exhibited a bell shaped curve with a maximum of 7.5 pounds per linear inch (PLI) (1 PLI = 1.75 N/cm) at a pre-drying temperature of 50°C. The adhesion strengths corresponding to drying temperatures other than 50°C were lower than 7.5 PLI. At drying temperatures corresponding to 150°C and above, no significant adhesion was observed. These results may be explained if one considers the simultaneous effects of diffusion and crosslinking. At lower drying temperatures, the primer is not sufficiently crosslinked, although the diffusion of the primer into PVC plastisol will be greater than that at higher temperatures.

The net adhesion strength is the result of the two conflicting tendencies which produce the observed bell shaped curve shown in Fig. 5. The fractured metal surfaces were examined by reflection absorption infrared spectroscopy at three

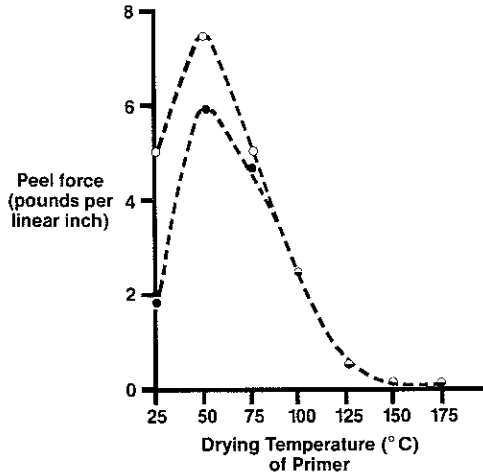


Figure 5. Peel force of polyvinyl chloride on AEAPS primed 2024-aluminum. Open circles represent dry strength and closed circles represent wet strength.

pre-drying temperatures of the primer (25°C, 50°C and 150°C). The results are summarized in Table 1. The surface corresponding to the pre-drying temperature of the primer at 150°C showed only the siloxane band covering the region 1000–1200 cm^{-1} . For this particular case, the IR spectra of the fractured metal surface after the removal of the PVC coating was compared with the IR spectra of the silane primed metal surface prior to adhesive bonding. The two spectra appeared to be identical to each other. These observations suggest that the fracture in this bonding system is probably totally interfacial. The surfaces corresponding to the pre-drying temperatures of 25°C and 50°C exhibited the presence of PVC in the 1279 cm^{-1} region indicating a non-ideal failure near the interface. None of the surfaces showed any fracture in the primer region. These results indicate that the strength of the primer/PVC interface is solely responsible for the ultimate bond strength. The fact that the primer cured at lower temperature diffused more into the polymer film than that cured at higher temperature is clearly indicated by the XPS depth profile experiments. Figure 6 summarizes the results of these studies.

In Fig. 6, the atomic concentration of silicon is plotted as a function of sputtering depth. Since the primer is the only phase which contains silicon the estimate of the diffusion of the primer into the polymer can be made. Initially the silicon concentration is zero and then it rises to a high value with increasing

Table 1.
Nature of fractured metal surface after removal of PVC coating

Temperature (°C)	Metal surface after dry strength measurements	Metal surface after wet strength measurements
25	+	+
50	+	+
150	–	–

+ Indicates Presence of PVC
– Indicates Absence of PVC

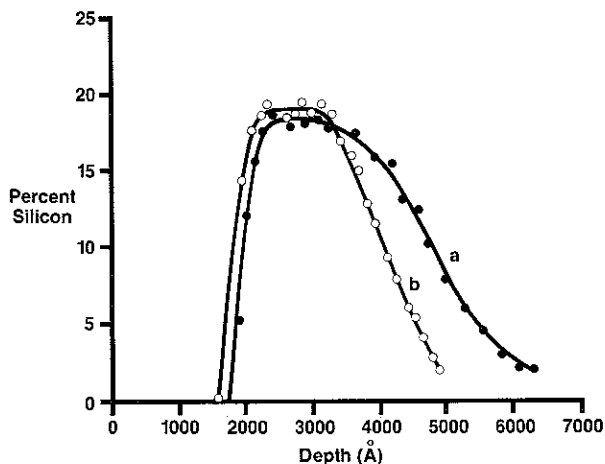


Figure 6. Atomic percent of silicon as a function of sputter depth. Open circles correspond to the predrying temperature of primer as 175°C (curve b) and the closed circles correspond to the predrying temperature of primer as 25°C (curve a).

sputtering time. This indicates that the germanium layer is uniform and rather free of defect. The concentration profiles of silicon corresponding to drying temperatures of 25°C and 175°C are significantly different from each other. The silicon concentration drops more slowly indicating the primer is more penetrated into the polymer when the drying temperature is 25°C compared to 175°C (Fig. 6). The fact that the curve (b) still indicates a certain amount of penetration of primer into the polymer phase is not strictly in accordance with the adhesion results. This apparent diffusion may be due to sputtering artifacts and, therefore, one has to be careful in making quantitative comparisons of the two cases. We can however, emphasize the large qualitative difference in the two situations and can conclude that the primer cured at the lower drying temperature is more diffused into the polymer film by about 1000 Å than that pre-dried at higher temperature. At this juncture, we would like to note that the concentration of silicon (18%) in the plateau region is somewhat larger than the expected value (15%). This difference seems to be due to partial degradation of the primer during sputtering, which leads to a slightly altered stoichiometry. We again emphasize the qualitative differences of the two situations rather than the quantitative differences.

The second effect, i.e. the degree of crosslinking has a dominant effect on net adhesion strength, is further reinforced by the experiments under wet conditions. It is clear from Table 2 that the net adhesion loss varies inversely with the increase of pre-drying of the primer. The maximum adhesion loss is at 25°C whereas it is negligible at 100°C or higher temperatures. These results indicate that the primer cured at lower temperature, owing to its lower degree of crosslinking, is more hydrophilic and hence is less water resistant than those dried at higher temperatures. The fractured metal surfaces when examined by IR spectroscopy still indicated the locus of bond failure close to the interface of the primer and polymer.

Table 2.

Loss of wet strength as a function of the pre-drying temperature of primer

Temperature (°C)	Percentage loss in adhesion after water immersion
25	64
50	20
75	4
100	0
125	0
150	0
175	0

4. CONCLUSIONS

The present studies indicate that the adhesion strength of PVC on partially hydrolyzed AEAPS primed metal surface is primarily determined by the strength of the diffused interface of the primer and polymer. It has been demonstrated that the primer dried at lower temperature diffuses more into the polymer film than when the primer is dried at higher temperature. The net adhesion strength is, however, determined by simultaneous action of crosslinking and diffusion as was exemplified by the dry and wet strength measurements.

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NOTE

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