Cold Gas Plasma and Silanes

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Abstract:
For many decades use of silane coupling agents has dominated as the approach of choice to significantly enhance adhesion between inorganic materials and a wide variety of resins, thermoplastics and elastomers. In the past two to three decades cold gas plasma has become a preferred means of treating materials, especially polymers, to enhance adhesion. What happens if these two potent methods work in concert? This paper presents data on the use of plasma processes employing silanes to promote adhesion.

Keywords: silanes, PTFE, HDPE, adhesion, plasma surface treatment

Introduction:
Silane coupling agents have been in common use for decades providing enhanced adhesion between a variety of inorganic substrates and organic resins.[1,2] The general formula of these organosilane coupling agents is $R_nSiX_{(4-n)}$ having dual functionality. The majority of silane coupling agents contain a hydrolyzable group (X) , typically, methoxy or ethoxy, which readily reacts with a proton to give methanol or ethanol as byproducts of the coupling. Many mineral fillers and reinforcing fibers contain hydroxyl groups providing the necessary proton for the coupling reaction. The "R" group is a non-hydrolysable organic group designed to provide reactivity to the specific polymer or resin for that application.

The use of silane coupling agents, while not difficult, is energy intensive. The manufacturers recommended procedures for the use of silane coupling agents follow:

Deposition from aqueous alcohol solution**:**
Deposition from aqueous alcohol solution is the most facile method for preparing silylated surfaces. A 95 ethanol-5 water (vol. %) solution is adjusted to pH 4.5-5.5 with acetic acid. Silane is added with stirring to yield a 2% final concentration. Five minutes should be allowed for hydrolysis and silanol formation. Large objects, e.g. glass plates, are dipped into the solution, agitated gently and removed after 1-2 minutes. The treated materials are rinsed free of excess materials by dipping briefly in ethanol. Particles, e.g. fillers and supports, are silylated by stirring them in solution for 2-3minutes and then decanting the solution. The particles are usually rinsed twice briefly with ethanol. The cure of the silane layer is for 5-10 minutes at 110°C or 24 hours at room temperature.

Deposition from aqueous solutions**:**
This deposition procedure is employed for most commercial fiberglass systems. The alkoxysilane is dissolved at 0.5-2.0 weight % concentration in water. For less soluble silanes,0.1% of a non-ionic surfactant is added prior to the silane and an emulsion, rather than a solution, is prepared. If the silane does not contain an amine group the solution is adjusted to pH 5.5 with acetic acid. The solution is either sprayed onto the substrate or employed as a dip bath. Washing off excess solution after 5-10 minutes is recommended to minimize particle oligomerization. The cure is carried out at 110-120°C for 20-30 minutes. Stability of aqueous silane solutions varies from hours for the simple alkyl silanes to weeks for the aminosilanes. Poor solubility parameters limit the use of long chain alkyl and aromatic silanes by this method. Distilled water is not necessary, but water containing fluoride ions must be avoided.

While many plastics, resins and elastomers contain functional groups, namely carboxyl, hydroxyl and amine, these groups generally are insufficiently reactive to participate in the silanol hydrolyzation. Thus, silane coupling agents are found not to be particularly useful for enhancing adhesion strength of between similar or different polymers.

Plasma Processes:
Cold gas plasma, aka glow discharge plasma, has been proven[3,4,5] to modify or activate the surface of organic materials providing reactivity with a wide variety of materials. As generally practiced in the non-semiconductor industries, cold gas plasma is recognized as both a worker and workplace clean air technology. Plasma treatment imparts reactive groups depending on the process gas employed. This reactivity permits the formation of covalent bonds between the adhesive or

[1] K.L. Mittal (Ed.), Silanes and Other Coupling Agents, VSP, Utrecht (1992)
[2] K.L. Mittal (Ed.), Silanes and Other Coupling Agents, Vol. 2, VSP, Utrecht (2000)
[3] K.L. Mittal (Ed.), Polymer Surface Modification: Relevance to Adhesion, VSP, Utrecht (1996)
[4] K.L. Mittal (Ed.), Polymer Surface Modification: Relevance to Adhesion, Vol. 2, VSP, Utrecht (2000)

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other materials and the substrate to be bonded, thus providing enhanced adhesion performance and environmental stability.

The use of gas plasma processes to enhance the strength of adhesive bonds is a well proven and documented industrial tool. This is achieved through a vacuum process. The components to be treated are placed in a chamber and the air removed via a vacuum pump to pressures typically less than 100 mTorr (atmosphere = 760 torr). The process gas is then flowed into the chamber and allowed to reach equilibrium, typically 100 – 500 mTorr. Radio-frequency energy supplied to electrodes within the chamber excite the gas(es) into a plasma. Plasma, the 4th state of matter, is a gas comprised of modest concentrations of electrons, ions, as well as other excited meta-stables. These excited species have sufficient energy to rupture chemical bonds of the component (substrate). These ruptured bonds are thermodynamically unstable and reach out into the plasma to combine with gas fragments to normalize its energy, thereby molecularly re-engineering the surface of the material placed into the plasma. Cold gas plasma processes are low energy processes and the species created have little penetrating energy, thus the modification is limited to the surface typically no deeper than a few molecular layers. Ultra-thin temperature sensitive materials can be easily modified in a cold gas plasma without deteriorating the bulk properties of the material being treated. Table 1 shows the dramatic improvement possible with a variety of engineering plastics with oxygen plasma treatment. In each case the mode of failure changed from interfacial to cohesive either within the substrate or the adhesive.[5]

Table 1. Lap Shear Strength of Specimens Bonded with Epoxy Adhesive

Material	Control MPa	Plasma MPa	Improvement	Failure Mode
Valox 310	36.70	115.59	3.1X	from interfacial to tensile*
Noryl 731	43.38	126.48	2.9X	ibid
Durel	17.58	151.93	8.6X	cohesive†
Vectra A-625	66.02	87.18	1.3X	from interfacial to tensile*
Delrin 503	11.60	45.49	3.9X	ibid
Ultem 1000	12.94	146.59	11.3X	ibid
Lexan 121	119.87	157.63	1.3X	ibid

*tensile failure is cohesive failure through the substrate outside of the lap shear joint.
† failure was cohesive within the adhesive

A simple oxygen plasma creates a variety of different oxygen moieties. Carbonyl, carboxylic, and hydroxyl are readily found by chemical analysis on the substrate being treated. Adding other gases or liquids to the plasma allows the favoring of specific functional groups. For instance, hydroxyl groups can be favored by introducing water vapor as the prime process gas or as a co-process gas. Cold gas plasma with any one gas is not the panacea for all adhesion problems. Oxygen functional moieties may not be the best solution. If amine functionality is desired an ammonia plasma may do the modification quite well. As seen in Table 2, while both oxygen and ammonia plasmas provide significant improvement, the choice will be governed by both the substrate being treated as well as the chemical class of the preferred adhesive.

Table 2. Effect of Plasma Treatment on the Lap Shear Strength of Delrin™ bonded with epoxy and urethane adhesives

Plasma	Epoxy Adhesive	Urethane Adhesive
	MPa	MPa
None	1.14	0.22
Oxygen plasma	4.46	9.30
Ammonia plasma	3.97	2.70

Plasma re-engineers the surface of a polymer to provide not only specific surface energy, but also specific chemical reactivity. In the majority of cases this approach works amazingly well, solving many difficult challenges.

One problem with the above approach is that the molecular modification is only a few atoms above the substrate surface. It takes only a small concentration of contaminants to contaminate the surface submerging the created functional groups below the contaminant laden surface. Silanes possess the marvelous dual capacity of acting both as a surfactant as well as a coupling agent. In addition, the organic functionality of the silane is typically a multi-carbon chain providing more height above the substrate, thus more tolerant to contamination.

Employing reactive silanes as the process gas in a plasma process provides the best combination of two worlds. The dual functional silanes can be covalently coupled to even the most unreactive surfaces in a dry process employing the silanes as they are received, i.e. no dilution, hydrolyzation, or pH adjustment, and in low concentrations.

[5] S. Kaplan and P. Rose, Plasma treatment upgrades adhesion in plastic parts, Plastics Eng., 44, No. 5, 77-79, 1988

Experimental:
High density polyethylene(HDPE) and poly(tetrafluoroethylene) Teflon® (PTFE) were selected as the test substrates. Both polymers are used in industry for their nonstick and unreactive surfaces making them particularly challenging for adhesive bonding. They were chosen for this study because, in addition to their non-reactivity the two materials are basically different in their forming processes. PTFE is sintered whereas the HDPE is a melt formed material.

15.5 by 15.5 cm plaques of the PTFE and HDPE were treated in a Plasma Science PS0500 plasma system employing 3-aminopropylethoxy silane (99% purity) as one of the process gases. The silane was purchased from Aldrich Chemical and used as received.

Aluminum pull studs (also referred to as dollies) were purchased from DeFelsko Industries, Ogdensburg, NY and used as received. The pull studs were bonded to the plaques using "Super Glue Epoxy" (product number SY-SS), manufactured by Pacer Technology, Rancho Cucamonga, CA. Super Glue is a two part epoxy supplied in mated syringes with a common plunger. Super Glue is conveniently obtained in most hardware stores. It was cured at room temperature for a minimum of 72 hours before testing.

Adhesive bond strength was determined employing a PosiTest® Adhesion Tester, DeFelsko Industries, Ogdensburg, NY (Figure 1) that measures the force required to pull a specified test diameter of adhesive bonded aluminum, DeFelsko dollies (Figure 2), from a substrate using hydraulic pressure. The required force is displayed in MPa on a precision dial indicator.

Results:
Two aminosilane plasma deposition processes were evaluated. Process 1 and 2 both employ the same aminosilane, but differ in the process parameters of power and pressure. Bonding and testing for the two materials, HDPE and PTFE, were performed in identical manner. A PosiTest® Pull-Off Adhesion tester was used to measure the strength of the adhesive bond. The results are reported in Table 3.

Table 3. PosiTest® Pull Strength Results

Material	Process	Pull Strength MPa	Comments
PTFE	Control	--	failed loading test fixture
PTFE	Tetra-etch®	2.39	cohesive – divot pulled
PTFE	Process #1	1.85	cohesive in PTFE
PTFE	Process #2	2.24	cohesive in PTFE
HDPE	Control	--	Too weak to test
HDPE	Process #1	2.14	mixed failure*
HDPE	Process #2	2.88	mixed mode **

*mixed mode of failures with divots pulled out from HDPE
** mixed mode of failure with divots pulled from HDPE as well as significant adhesive failure to the aluminum pull test stud. Locus of failure determined by visual inspection. Shiny aluminum indicated interfacial failure at the Aluminum surface and corresponded to adhesive left on the polymer. Whereas white polymer surface indicative of interfacial failure at the polymer surface.

Discussion:
The objective of adhesive bonding is to achieve cohesive failure either in the adhesive layer or in the substrates being bonded. The Tetra-etched plaque provided both the highest bond strength and most obvious cohesive failure of the PTFE samples. PTFE is not melt formed but sintered and under high magnification the bulk structure appears to be the agglomeration of small spheres. This microstructure limits the cohesive strength of PTFE. The failure loci of the silane plasma treated plaques were much closer to the interface than of the Tetra-etched plaque. Tetra-etch, a metallic sodium etchant, dehalogenates the fluoropolymer causing considerable change to the polymer structure. Sodium etchants turn PTFE surfaces blotchy brown-black. This discoloration is like a scab on a wound reinforcing the surface structure in effect toughening the PTFE surface. Both processes, sodium etch and silane plasma, provide covalent bonds between the adhesive and PTFE, but the sodium etch provides a benefit of "hardening" the surface, thereby providing somewhat higher bond strengths. This explanation has been confirmed with XPS data that showed the aluminum pull stud of the plasma treated PTFE to be completely coated with PTFE.[6]

[6] S.L. Kaplan, E. S. Lopata, and J. Smith,. Plasma Processes and Adhesive Bonding of Polytetrafluoroethylene, Surface And Interface Analysis, **20**: 331-336 (1993)

High density polyethylene (HDPE), like the vast majority of polymers, is melt processed providing uniform bulk properties throughout its cross-section. All silane plasma treated plaques exhibited a mixed failure mode accompanied in some cases with significant pull out of divots from the HDPE (Figure 3). In most samples there was evidence of interfacial failure to the aluminum (Figure 4), as well as cohesive failure in the adhesive. In addition, the two plasma processes employed were not optimized. Therefore, considerable improvement is anticipated when the plasma parameters are optimized for the specific HDPE and adhesive combination. XPS analysis shows 17.7 and 15.4% nitrogen incorporation respectively for Process #1 and Process #2 consistent with a grafting of the aminosilane to the HDPE surface.

Conclusions:
Cold gas plasma is an environmental and workplace friendly technology that can be used to modify any polymer or elastomer, as well as ceramics and metals to enhance strength of adhesion characteristics. Silane coupling agents have for many decades proven very effective in bonding of dissimilar materials, especially where one of the materials is a mineral or ceramic. Combining these two technologies into one user friendly system offers a unique and effective tool. The plasma process described here provides the efficiency and ease of use of plasma technology with the unique characteristics of organo-functional silanes to provide effective reactive coupling.

Figure 1: PosiTest Testing System

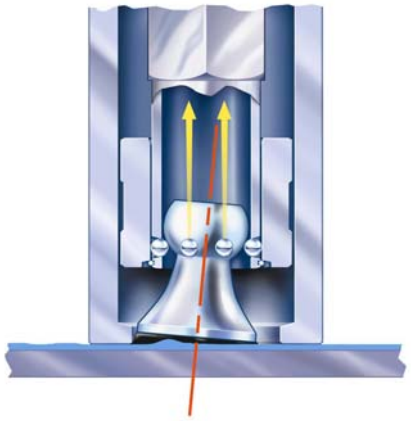

Figure 2: Test Specimen

Figure 3: HDPE Pull Out

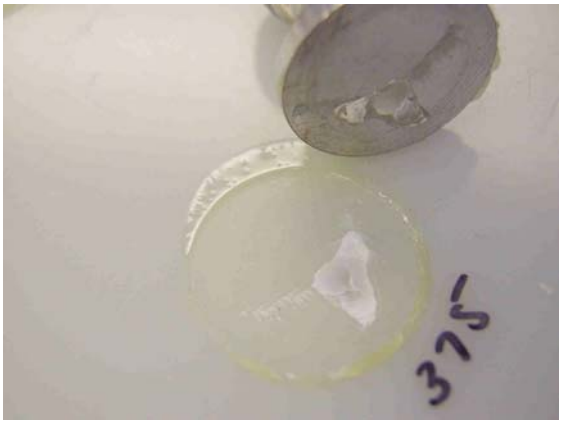

Figure 4: Interfacial failure to Aluminum