

INTERFACIAL CHEMISTRY AND ADHESION: RECENT DEVELOPMENTS AND PROSPECTS

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Abstract - Recently, considerable attention has been devoted to understand the mechanism(s) by which materials adhere together. Strictly speaking, adhesion is an interfacial phenomenon, and if the events in the narrow arena of the interface can be understood and tailored, much progress can be made. The subject of adhesion, however, is both inter- and multidisciplinary in scope; and for a holistic approach to adhesion, a synergistic interaction is required among the various disciplines involved, viz., surface chemistry, rheology, and fracture mechanics. The availability of sophisticated surface analytical tools has been a boon in the realm of adhesion.

In this paper, some recent advances in the following areas have been discussed: use of surface analytical tools in ascertaining the locus of failure; use of ESCA in surface analysis of polymers and in investigating the interfacial interactions; acidity and basicity of polymers; polymer surface modification and adhesion; use of IETS in adhesion; and understanding of the chemistry of coupling agents or adhesion promoters. All available signals indicate that the prospects for adhesion science are very bright.

INTRODUCTION

Adhesion is a very pervasive phenomenon, e.g., adhesion of thin films, thick films and bulk coatings, biological and cell adhesion, soil adhesion, ice adhesion, particle adhesion, and the adhesion of adhesives in adhesive joints are very familiar in everyday life. Strictly speaking, adhesion is an interfacial phenomenon, but for a holistic approach to adhesion one must also consider the fracture mechanics, and in the case of polymeric coatings, the rheological aspects are also important. So in order to understand the phenomenon of adhesion in toto, an inter- and multidisciplinary approach involving various scientific disciplines is needed. Even a casual glance at the published literature on adhesion reveals that researchers with varied and diverse backgrounds are indeed involved in adhesion studies. As the interfacial chemistry constitutes the marrow of adhesion science, so in this paper only the interfacial aspects will be considered. Recently, there has been a brisk activity in understanding and modifying interfacial events with the eventual objective of controlling adhesion in a variety of situations, e.g., composites, adhesive joints, multilayers. This paper is not at all intended to be an exhaustive review, but here are selected certain areas pertaining to interfacial chemistry and adhesion where there have been some interesting and enlightening recent developments and a few representative examples are cited in each category. Selected key references are provided for future study. It should be pointed out at the outset that the availability of sophisticated surface analytical tools has been a boon in adhesion science, and these techniques have provided information which had been inaccessible before.

Making and Breaking of a Bond

It should be emphasized that different factors are important in the

making and breaking of a bond, and the interfacial chemistry is important during the making stage of the bond. However, in real life it is the practical adhesion (i.e., the force or the work required to disrupt an adhering system) which is important, and it may or may not be directly related to or influenced by the fundamental or interfacial adhesion (summation of all intermolecular interfacial interactions, i.e., interfacial chemistry). This is due to the fact that the practical adhesion (of, e.g., films, coatings) depends upon the fundamental adhesion (interfacial interactions) and "other factors", e.g., stresses in the film or coating. It should be added that the rationale behind modifying or tailoring interfacial chemistry is the hope that the improved fundamental adhesion should culminate in improved practical adhesion. In other words, in order to improve practical adhesion, the improvement or proper modification of interfacial chemistry is necessary but not sufficient. For a detailed discussion of the relationship between the practical adhesion and fundamental or interfacial adhesion see References 1-4. The various techniques for measuring practical adhesion of thin films, thick films, and coatings have recently been reviewed in References 2, 5, and 6. Also, in an adhesion study, it is not sufficient to only measure the practical adhesion, but the locus of failure or separation is equally important. Incidentally, the issue of cohesive vs. adhesive failure is quite polemical, and for the latest discussion and controversy, see References 7 and 8.

RECENT DEVELOPMENTS

Use of Surface Analytical Tools in Ascertaining the Locus of Failure

As pointed out earlier that the availability of sophisticated surface analytical tools has been a boon in the realm of adhesion science. These tools have been used a great deal in the recent past for surface characterization and for studying interfacial interactions (vide infra). There is available a voluminous literature dealing with surface analysis or characterization techniques, see e.g., References 9-12.

As far as the locus of failure is concerned, quite often visual or microscopic inspection is employed to look at the substrate side (after disrupting an adhering system), but such inspection is not sensitive enough to detect a thin layer (say, e.g., 5 nm) of the coating left on the substrate, with the result that even with the presence of the coating on the substrate, one would construe that there has been an adhesive or clear-cut interfacial failure. This is where the power of these sophisticated surface analytical tools has been of immense value, and the following examples illustrate that these instruments now make it possible to discern cohesive from adhesive failure. Wyatt et al. (13) used Electron Spectroscopy for Chemical Analysis (ESCA) to identify very thin layers of polymeric species remaining on aluminum plates after the polymer was cured and stripped from the aluminum. The results of their study showed that when the polymers studied were mechanically pulled from the aluminum substrate, the failure was a cohesive separation within the polymer, rather than failure at the polymer-aluminum interface. Gettings et al. (14) used Auger Electron Spectroscopy (AES) and ESCA to study the locus of failure of epoxy resin joints. The effects of a long term water immersion and the application of a silane-based primer were also studied. Interestingly, they found that for dry joints failure occurred near an epoxy resin/metal interface while with water-soaked unprimed joints, the failure occurred interfacially between the adhesive and the iron oxide. Baun (15) has used successfully the Ion Scattering Spectrometry (ISS) and Secondary Ion Mass Spectrometry (SIMS) to determine the true locus of failure in adhesive joints and coating-substrate combinations. For example, he found (15b) that in the case of anodized aluminum adherend bonded with TiO₂ filled epoxy, the failure did not occur cleanly at the Al₂O₃ surface, but rather in a complex region containing both adhesive and adherend.

The above examples underscore the importance of these analytical tools in obtaining an unequivocal answer to the site of failure.

Use of ESCA in Surface Analysis of Polymers and in Investigating Interfacial Interactions

Among all the available surface analytical tools, ESCA has been of

singular importance and usefulness in adhesion as this technique can be used to analyze organic polymer surfaces. There is a great deal of literature available relative to the use of ESCA in characterizing surfaces in general (16-18), and a number of recent excellent review articles have been written dealing with application of ESCA to polymer structure and bonding (16).

The adhesion of various materials to polymeric substrates is very important in many technologies, and polymer surfaces are generally modified (e.g., by chemical means or by plasma) to render them adhesionable. In order to provide the proper modifying treatment, it is imperative to have some reliable means of characterizing the chemical moieties on polymer surfaces, and this is where ESCA has proved to be of invaluable help. Below are cited a few examples to show the usefulness of ESCA.

Clark and associates (16) have carried out an extensive investigation of a number of polymeric surfaces using ESCA. Dwight (19) used ESCA to chemically characterize fluoropolymer surfaces and to follow changes in their surface chemical make-up as a function of various treatments. Using the data of Dwight and Riggs (20) he showed (19b) a trend between fluoropolymer/acrylic adhesive/aluminum peel strength and the percent hydrocarbon surface of the fluoropolymer as determined by ESCA. Later, Dwight et al., (21) studied a number of engineering polymers and followed changes which took place during processing using ESCA. Blythe et al. (22) used ESCA to follow chemical changes taking place at the polyethylene surface as a result of corona discharge treatment, and showed that surface oxidation resulted from treatment in "inert" gases. Using ESCA, Briggs et al., (23) showed that a normal flame treatment caused a high level of oxidation in low-density polyethylene. Burkstrand (24) has examined the surfaces of commercial ABS and polypropylene with ESCA both before and after oxygen plasma treatment and showed that the plasma treatment changed the basic chemical nature of these polymeric surfaces by increasing the number of single and double bonds between carbon and oxygen atoms. Anderson et al., (25) used ESCA to reveal surface compositional differences between the plasma-polymerized tetrafluoroethylene and Teflon PTFE, and found that the former contained -CF and -CF₃ species also in addition to -CF₂ moieties.

Investigation of Interfacial Interactions

The examples cited above manifest the usefulness of ESCA in analyzing polymeric surfaces, but the ESCA can also be used to study interfacial interactions provided the coating on the substrate is thin (<5nm). And if these interfacial interactions can be fully understood, then one can devise the proper interfacial chemistry in order to improve adhesion. Again there is a plethora of literature published pertaining to the use of ESCA in unravelling interfacial interactions, and here only a few examples will be cited in this regard. Roberts and Schonhorn (26) studied the interactions of very thin (1-6nm) films of metals (gold, aluminum, and titanium) with polytetrafluoroethylene. Their results are shown in Table 1.

TABLE 1. ESCA data of Teflon FEP, metallized Teflon FEP and metal fluorides (from Ref. 26)

Sample	Electron Binding Energy (eV) ^a		
	Fluorine 1s		Metal
Teflon FEP	689.3	----	-----
Gold/Teflon FEP	689.3	----	84.0 ^b
Aluminum/Teflon FEP	689.3	685.4	75.0 ^c
AlF ₃	686.8		76.3 ^c
AlF ₃ xH ₂ O	686.9		76.2 ^c
Titanium/Teflon FEP	689.3	684.6	458.9 ^d
TiF ₃	685.4		460.4 ^d
TiF ₄	685.5		462.0 ^d

^aEstimated uncertainty, ± 0.3 eV, ^bAu4F_{7/2}, ^cAl 2p, ^dTi 2p

It is clear from the data that gold does not interact with PTFE, whereas Al

and Ti do form some kind of bonds with PTFE as new F(1s) peaks appear in the ESCA spectra. Such findings were used to explain the different adhesion behavior of these metals on PTFE. More recently, Burkstrand (27-28) has studied the interactions between copper, chromium and nickel on clean and oxygen-treated polystyrene surfaces using ESCA, and his results indicate the formation of metal-oxygen-polymer complexes; and the presence of these complexes is correlated with the increase in adhesion of these metal films to the oxygen-treated substrate compared to the clean polystyrene substrate.

Van Ooij (29) has used ESCA to study the mechanism of the adhesion of rubber to well-characterized metal surfaces. Reaction of brass with rubber results in the formation of both Cu_xS and ZnS , and the amount of Cu_xS must be carefully controlled to obtain good adhesion. On the one side, it improves the adhesion as a result of a catalytic effect on the rubber vulcanization. On the other hand, excessive Cu_xS formation leads to embrittlement of the interfacial Cu_xS/ZnS film and a loss of adhesion. Table 2 summarizes some adhesion and XPS (ESCA) data from his study.

Table 2. Adhesion of some selected materials to rubber^a
(from Ref. 29)

Material	Adhesion level ^b	XPS of interface	Remarks
1. iron, steel	0	-	no adhesion
2. copper sheet	0	excess Cu_2S	some adhesion if undercured
3. copper-plated steel ^c	700-900	-	good adhesion if plating thickness <50nm
4. steel+ Cu_2S coating ^d	700-800	-	good adhesion for fresh Cu_2S layer (<50nm)
5. zinc sheet	100-200	ZnS formation	poor adhesion
6. copper-plated zinc ^c	700-800	Cu_2S formation	good adhesion if plating thickness <50nm
7. 70/30 brass sheet	700-1000	formation of Cu_2S and ZnS	good adhesion; level depends on surface preparation

^aVulcanized at 150°C for 25 min.

^bIn $N/64mm^2$.

^cBy electroless immersion plating.

^dPrepared from sample 3 by reaction with sulfur liquid paraffin at 180°C.

Anderson and Swalen (30) have used ESCA to show the acid-base interactions between monolayers of cadmium arachidate and oxidized samples of indium, rhodium, silicon, and tin. The summary of their interesting results is shown in Figure 1.

It is clear from the data in this figure that by monitoring chemical shifts of appropriate elements, one can determine the direction of electron flow which signifies the acidic or basic characteristics of the materials involved. It should be added here that quite often the researchers may simply talk about the interfacial interactions (without expressly stating acid-base interactions) but, generally speaking, one simply measures in the ESCA the electronic environment of a particular element, and changes in this environment (due to electron donating or accepting tendencies) reflect in chemical shifts.

Bailey and Castle (31) used ESCA to study the adsorption of ethoxysilanes on iron surfaces. They found, among other things, that aminopropyltriethoxy silane was less strongly adsorbed than vinyltriethoxysilane, and the presence of unsuspected impurities in the solvent used in the preparation of test media had an important effect on the adsorption of these silanes.

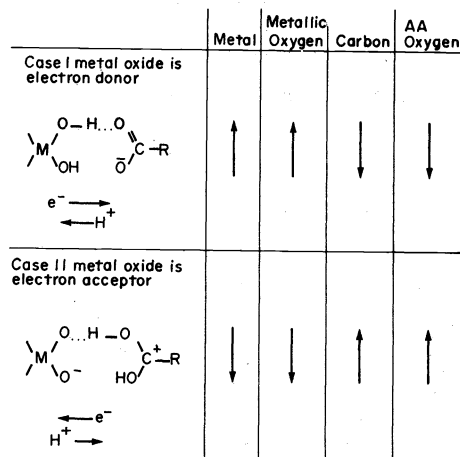


Fig. 1. Schematic diagram showing the direction of binding energy shifts predicted on the basis of electron and proton transfer. If a partial valence electron is transferred, it is inferred that the core electrons associated with the donating species will be bound more tightly, and conversely. (from Ref. 30)

The examples above illustrate very clearly that ESCA really provides a very powerful means of understanding interfacial interactions (in a broad range of situations) which are important not only to explicate different adhesion behaviors but also to control adhesion by modifying these interactions.

Use of IETS in Adhesion

A relatively new technique known as IETS (inelastic electron tunneling spectroscopy) has been developed and used to study the adsorption of organic compounds including coupling agents (32, 33) and adhesive components (34,35). Fig. 2 shows the IETS spectra for amino and vinyl silanes adsorbed on aluminum oxide. Of particular interest in Fig. 2A is the presence of bands at 1070, 2853 and 2944 cm^{-1} which indicate the presence of $-OCH_2CH_3$ groups on the surface, which signifies that some ethoxy groups survive the silylation reaction and remain intact as $Si-O-CH_2CH_3$. For further interpretation of these spectra, see original reference.

The application of IETS in adhesion is a relatively recent development, as it had been primarily used in the past to study $Al/Al_2O_3/Pb$ junctions. The principle of the technique is as follows: A metal/insulator/metal junction is formed, a voltage is applied across the junction, and the current is measured. Subsequently, one plots $\frac{d^2I}{dV^2}$ vs. applied voltage to obtain the IETS spectrum. For a detailed description of the principle, interpretation, and applications of this technique, see References 36-38.

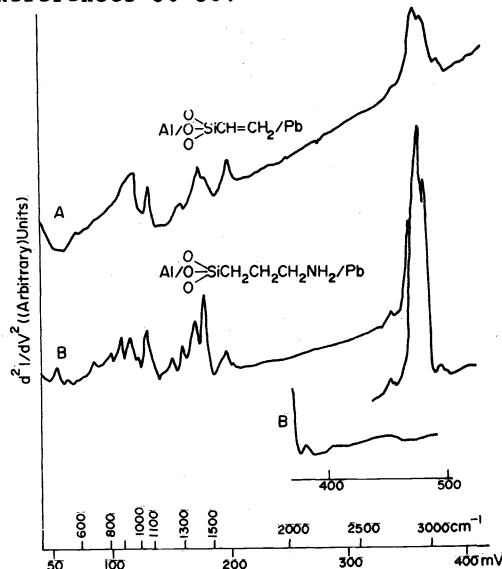


Fig. 2. Tunneling Spectra at 4.2°K of covalently bonded vinyl silyl (A) and 3-amino propylsilyl (B) derivatives. (from Ref.33)

It should be pointed out that the insulator film should be very thin (2-3nm) and it could be pure Al_2O_3 , Al_2O_3 doped with material of interest, or only the material (e.g., silane, adhesive, thin polymeric film) whose interaction with the substrate is under study. Although in most IETS studies, aluminum has been used as the substrate, but other metals can also be used. The IETS measurements are normally done at 4.2°K, and Pb is the material of preferred choice as the counter electrode as it becomes superconductor at this temperature; also, the lower the temperature at which measurement are made, the better the resolution of IETS spectrum.

Although ESCA (as shown above) provides a powerful means to study interfacial interactions, but the information derived using IETS should supplement and complement that obtained using ESCA. An interesting feature of this technique is that a fraction of a monolayer of adsorbed substance is sufficient for analysis by this technique. The technique offers a considerable promise for the study of orientation and interfacial interactions of an adsorbed species. Also the effect and mechanism of adsorbed water at the interface in disrupting otherwise "healthy" bonds is extremely important to understand, and the IETS provides a means to follow changes which take place as a result of water adsorption at the interface. Such studies are not amenable to ESCA technique, as ESCA measurements are done in vacuum. The IETS spectrum contains both Raman and IR active modes of the adsorbed substance.

Acidity and Basicity of Polymers

Various types of interfacial interactions are important in the adhesion of different materials including polymers, but recently it has been emphasized that the most important of these interactions are van der Waals type and acid-base in character (39, 40). Michaels and Bolger (41) discussed the importance of acid-base reactions in adhesion, but their analysis was based on the Bronsted concept of acids and bases. A more general treatment should be based on the electron donor-acceptor (Lewis concept) characteristics of the materials involved. The acidity or basicity of simple organic and inorganic molecules, metals and oxides have been documented in the literature, but it is not straight forward to ascertain the acidic or basic nature of polymers. Recently two approaches have been published in the literature to determine the acid-base characteristics of polymers. Anderson et al., (25) using the MIS (metal-insulator-semiconductor) technique have shown that the plasma-polymerized polytetrafluoroethylene accumulates only negative charge (electron acceptor) near the silicon surface; in other words, it behaves as a Lewis acid. Earlier it had been shown (42) that polymers could either (i) accumulate positive charge (Type I), or (ii) accumulate both positive and negative charge (Type II), so the plasma deposited PTFE is considered as Type III. Figure 3 shows the voltage shifts as a function of applied voltage for several polymer film structures, and such curves are used to ascertain the electron donating/accepting tendencies of polymers.

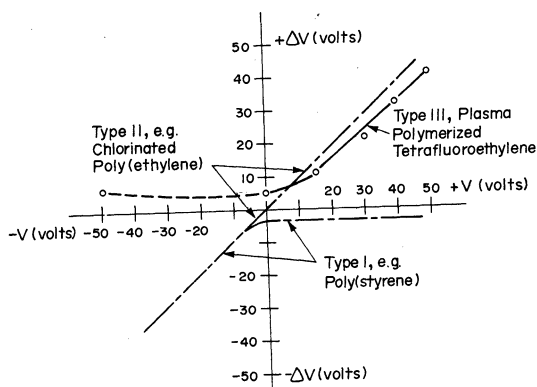


Figure 3. Types of voltage shifts (ΔV) for various polymers as a function of applied voltage. (from Ref. 25).

For details of the MIS technique and the interpretation of voltage shifts, the reader should consult the original references.

Another approach to determine the acidity or basicity of polymer surfaces via contact angle measurements using selected liquid(s) has been described

by Fowkes and Maruchi (40). This approach is based on the assumption that the thermodynamic work of adhesion, W_A , is composed of only W_{A_d} and $W_{A_{ab}}$ where d and ab stand for dispersion and acid-base. So by determining W_{A_d} and $W_{A_{ab}}$ using contact angle data of certain selected liquids, one can determine the W_A . Using this technique they found that (i) copolymers of ethylene with vinyl acetate have basic properties; (ii) polyvinylchloride and other chlorinated polymers have appreciable surface acidity. The most acidic polymer investigated was polyvinylidene fluoride; and (iii) strongest acid-base interaction is between polyimide and water, especially acidic water.

These acid-base studies of polymer surfaces have important implications in adhesion, and by a judicious choice of acid-base interactions, one should be able to control adhesion, and to, hopefully, provide a moisture resistant bond.

Polymer Surface Modification and Adhesion

As pointed out earlier, polymer surfaces have been modified by various treatments to render them more adhesionable. For recent reviews of this topic, see, e.g., References 43 and 44. Quite recently, a new technique known as SABRA (Surface Activation Beneath Reactive Adhesives) has been successfully used to improve the strength of bonded joints between various polymeric materials and different adhesives due to the creation of free radicals through mechanochemical activation (45-47). Table 3 summarizes some of the findings from this study.

TABLE 3. Tensile shear tests of polypropylene bonded to itself with epoxy adhesives (from Ref. 47)

Sample No.	Activated in adhesive Kg/cm ²	Sample No.	Activated in air (control) Kg/cm ²
1	63	6	41
2	58	7	36
3	59	8	32
4	66	9	40
5	60	10	42

The surfaces were treated with emery paper in the presence of adhesive (epoxy) itself or some suitable primer. The authors have cited a number of experimental observations to prove the existence of free radicals.

Understanding of Coupling Agents or Adhesion Promoters

Coupling agents (e.g., silanes) are commonly used to improve adhesion between polymeric resins and a variety of substrates (e.g., glass, metal oxides). Most of the literature published deals with the application of silanes on glass, and a great deal of information has been published on the wettability characteristics of the deposited silane layers. For a discussion of the various silanes and the proposed mechanisms by which these functions as adhesion promoters, see References 48-50. However, recently a number of sophisticated surface analytical tools have been used to characterize the outer surface chemistry of deposited silane layers and also to investigate the interfacial interactions between silanes and non-glass substrates. Some examples of the use of ESCA and IETS in the study of silanes have been described earlier (vide supra). Other examples include the study of trialkoxyalkyl-amine silanes bound to metal oxide electrodes using ESCA (51), and the investigation of the behavior of a series of silanes as adhesion promoters to promote the adhesion of a simple acrylic formulation on a steel substrate using ESCA and FT-IR (52).

Boerio et al. (53) have studied the adsorption of γ -aminopropyltriethoxysilane onto bulk iron from aqueous solutions using reflection-adsorption infrared spectroscopy and observed a band near 1510 cm^{-1} that was assigned to NH_3^+ groups. Formation of NH_3^+ groups indicates that the aminosilane may have been adsorbed initially as cyclic, internal zwitterions. More recently, Boerio and Cheng (54) have investigated the behavior of γ -methacryloxypropyltrimethoxysilane adsorbed onto copper using the same technique as used earlier. The spectra were interpreted to indicate that γ -MPS is adsorbed onto copper with most of the Si-O bonds and methacryloxypropyl functional groups parallel to the surface and with the C=O bands perpendicular to and directed toward the surface.

Ishida and Koenig (55) have used the Fourier transform infrared spectroscopy to study the structure of silane coupling agents on E-glass fiber. More recently (56), they have used FT-IR to study the molecular structural changes of silane coupling agents (on E-glass) in the presence of water. The formation of silanol groups as a result of hydrolysis of the polymeric siloxanes has been observed often prolonged immersion in water at 80°C. The newly formed silanols can reform siloxanes with drying. Short term water treatment of amino and methacryl functional coupling agents cause significant structural changes.

Schrader and Cardamone (57) have investigated the use of γ -aminopropyltriethoxysilane as adhesion promoter for bonding titanium surfaces with epoxy and found that the aminosilane provided better dry and wet lap shear strength than joints prepared utilizing standard surface treatments. Also, one may infer from these studies that similar improvements can be expected utilizing suitable organosilane compounds as adhesion promoters for bonding titanium with polyester, phenolic, and other thermosetting resins.

Recently, some work has also been published relative to the composition of silane layers as a function of thickness. Cain and Sacher (58) have used Auger electron spectroscopy to determine the depth profile of γ -glycidoxypropyltrimethoxy and γ -aminopropyltriethoxysilanes as deposited from the solution phase. Paik Sung and Lee (59) have employed IR spectroscopy to determine the structure of the polymer network formed by γ -aminopropyltriethoxysilane when adsorbed on aluminum using Al_2O_3 single crystal as model surface. According to the authors their results indicate that the polysilane network is more tightly crosslinked near the Al_2O_3 surface than in the region far from the surface.

In addition to these developments, the following should also be mentioned. Mittal and O'Kane (60) have described the vapor phase deposition of silanes which offers certain advantages (uniformity of thickness, thickness control, etc.) over the commonly used solution deposition method of applying silanes. Also, metals which are susceptible to corrosion in liquid media can be coated with silanes from the vapor phase without incurring any danger of corrosion. Haller (61) has also discussed the application of silanes from the vapor phase and found that treatment of silicon or gallium arsenide with the refluxing vapors of γ -aminopropyltriethoxysilane in toluene or xylene solution results in a strictly monolayer coverage of the surface with aminopropylsilyl groups. His technique of vapor phase deposition differs from the one described by Mittal and O'Kane.

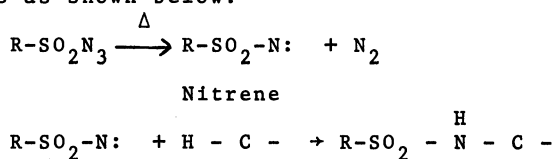
McFarren et al. (62) have discussed the use of azidosilane as a polymer-filler coupling agent for hydrocarbon-type polymers, and their results (summarized in Table 4) show that the azidosilane is very effective in improving the adhesion of hydrocarbon type polymers.

TABLE 4. Comparative flexural strengths of silane treated glass fabric-pp laminates (from Ref. 62)

Silane coupling agent	Flexural strength, PSI	
	Dry	After 2 hr boil
None	12500	11900
Azidosilane S3046*	41000	31400
Azidosilane S3046*	39000	32000
γ -Aminoethylaminopropyltrimethoxysilane	16200	Not determined

* Product of Hercules Inc.

The chemistry of azidosilane [silane sulfonylazide, general formula $(\text{CH}_2\text{O})_3\text{Si-R-SO}_2\text{N}_3$] is such that nitrene is formed during heating and the nitrene thus formed reacts chemically with the aliphatic or aromatic hydrocarbon polymers as shown below:



Very recently an interesting paper covering a series of organic titanates as adhesion promoters to steel substrate has appeared (63), and the authors have used ESCA also (in addition to adhesion testing) to study the polymeric film-steel interface. Their results indicate that titanates with certain organic moieties are superior in promoting adhesion, whereas with other titanates the adhesion was extremely poor.

Other Developments

In addition to what has been said above, the following interesting developments should also be noted. By using certain complexing agents Brockmann (64) has discussed the possibility of creating water resistant bonds at the aluminum surfaces. Kaelble (65) has developed a surface energetic criterion for adhesive bonding and fracture and its applications in such diverse areas as structural adhesive bonding, fiber reinforced composites, biomaterial development, and lithographic printing.

PROSPECTS

This brief survey of the recent developments reveals that the prospects for adhesion science are very bright, and all signals indicate that the present tempo of fundamental understanding of adhesion will continue. Great strides have been made in understanding the basic mechanism(s) of adhesion and this is directly attributable to the availability and capability of the sophisticated surface analytical tools, particularly ESCA, which provide a means to unravel the interfacial interactions or the chemistry at the interface. The understanding of the interfacial chemistry should provide the basis for tailoring the interface, and a proper choice of acid-base interactions should, hopefully, culminate in a water resistant bond which is a sine qua non for bond stability or durability.

In the end Table 5 points out certain areas for further investigation.

TABLE 5. Some areas for further or future investigations

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- Development of high temperature coupling agents.
 - Chemistry of coupling agents on metal surfaces, keeping in mind the acid-base characteristics of the materials involved.
 - Rendering of certain difficult to bond polymers bondable.
 - Rendering of interfacial bonds to be resistant to the deleterious effect of moisture. Durability or longevity of bonds.
 - Use of inelastic electron tunneling spectroscopy in gaining further insight into the interfacial interactions and in understanding the state of adsorbed water and the mechanism by which bonds get disrupted.
 - Acid-base characteristics of polymers.
 - Mechanochemical approach to improvement of adhesion
 - Composites
 - Marine and biological adhesion.
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