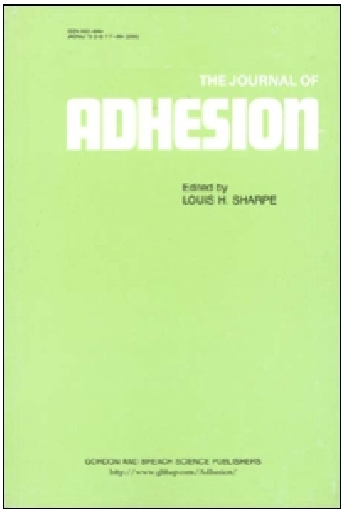


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion Promoters for the Titanium-Resin Interface

Malcolm E. Schrader[a]; Joseph A. Cardamone[a]
[a] David W. Taylor Naval Ship Research and Development Center, Annapolis, Maryland, U.S.A.

To cite this Article Schrader, Malcolm E. and Cardamone, Joseph A.(1978) 'Adhesion Promoters for the Titanium-Resin Interface', The Journal of Adhesion, 9: 4, 305 — 310

To link to this Article: DOI: 10.1080/00218467808075122

URL: http://dx.doi.org/10.1080/00218467808075122

J. Adhesion, 1978, Vol. 9, pp. 305–310

Printed in Scotland

Adhesion Promoters for the Titanium–Resin Interface[†]

MALCOLM E. SCHRADER and JOSEPH A. CARDAMONE

David W. Taylor Naval Ship Research and Development Center,
Annapolis, Maryland 21402, U.S.A.

(*Received November 15, 1977; in final form April 14, 1978*)

An investigation was undertaken to determine the feasibility of using adhesion promoters to improve the interfacial bond between structural adhesives and titanium. A compound was sought whose molecules contain one functional group that can chemically bond to the titanium surface and another functional group that can chemically bond to the desired adhesive resin. Inasmuch as certain titanium compounds chemically bond to a silica surface *via* a Si_s—O—Ti linkage (the subscript represents a surface atom), it was deemed possible that compounds of silicon can chemically bond to a titanium surface *via* a Ti_s—O—Si linkage, where the oxygen originates from the surface oxide layer present on titanium. To verify this postulate, the dry and wet strengths of titanium/epoxy/titanium lap-shear joints were determined, utilizing gamma-aminopropyltriethoxysilane as the adhesion promoter. The lap-shear joints using gamma-aminopropyltriethoxysilane were found to be approximately 25% stronger dry and more than 50% stronger after water exposure, than joints prepared utilizing standard surface treatments. It may be inferred that similar improvements can be expected utilizing suitable organosilane compounds as adhesion promoters for bonding titanium with polyester, phenolic and other thermosetting resins.

INTRODUCTION

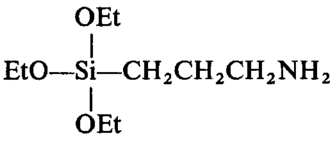
A method of alleviating problems arising in the fabrication of titanium has been the use of thermosetting resins as high strength organic adhesives in place of conventional welding or riveting. Since adhesion at the interface of metal and resin is often the weak link in this type of bonding, treatment of the metal surface is of vital importance in improving the strength, reliability,

---

[†] Presented at the Borden Award Symposium honoring William A. Zisman during the National Meeting of the American Chemical Society in New Orleans, LA, March 21–25, 1977.

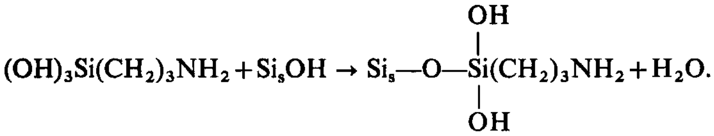
and environmental resistance of the structural adhesive bond. Of particular importance is the possibility of water penetration at the interface of adhesive and titanium, due to the strongly hydrophilic nature of the titanium surface.

A similar problem has been encountered in glass-fiber reinforced plastics, where the hydrophilic nature of glass resulted in the entry of liquid water along the fiber-resin interface when subjected to long term immersion in water at ambient temperature or short periods of immersion in water at elevated temperatures. It was found that this problem could be solved through the use of adhesion promoters called coupling agents which would form a bridge of chemical bonds between the glass surface and the resin matrix, thus preventing the entry of liquid water into the interface with concomitant debonding of resin from fiber.[1] In addition to the prevention of degradation from moisture exposure, it has been found that these adhesion promotors also improve dry-state adhesion at the interface in these composites. Coupling agents for glass-resin systems are usually silane derivatives. An example of a coupling agent for glass reinforced epoxy resin systems is gamma-aminopropyltriethoxysilane (APS).



$$\mathrm{EtO{-}\underset{\displaystyle OEt}{\overset{\displaystyle OEt}{Si}}{-}CH_2CH_2CH_2NH_2}$$

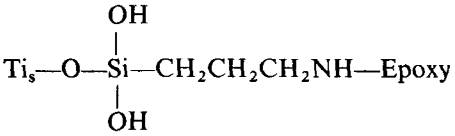
where the ethoxy (OEt) groups hydrolyze to form hydroxyls, which in turn condense with silanols on the fiber surface to form siloxane linkages, as follows:



$$\mathrm{(OH)_3Si(CH_2)_3NH_2 + Si_sOH \rightarrow Si_s{-}O{-}\underset{\displaystyle OH}{\overset{\displaystyle OH}{Si}}(CH_2)_3NH_2 + H_2O.}$$

The NH_2 in turn reacts with the epoxy resin to complete the bridge of chemical bonds. The stability of the surface siloxane linkage is of course not surprising since glass itself is composed of siloxane linkages. When silane based coupling agents have been randomly tried on other types of reinforcement, such as carbon fibers, however, the treatment was not effective since no bond of comparable stability to the siloxane bond could be formed.

In a recent study on the kinetics of reaction of various vapors with the surface of silica gel,[2] it was found that $TiCl_4$ is very reactive to Si_sOH (where Si_s is surface silicon) groups, apparently yielding the $Si_s{-}O{-}Ti$ group. Inasmuch as the $Si_s{-}O{-}Ti$ linkage, based on a surface silicon and attached titanium, is so stable, it is quite likely that the $Ti_s{-}O{-}Si$ linkage, consisting of a surface titanium and attached silicon, is also stable. Since there is always a layer of chemisorbed oxygen or oxide on an air-exposed Ti surface, the same compounds and methods used to form the Si_s—O—Si linkage on glass might be used to form the Ti_s—O—Si bond on titanium. This means that the coupling agents presently used to chemically link glass to various resins can be used to link titanium to these same resins. For example, APS could couple titanium to epoxy as follows:



$$Ti_s\text{—O—}\underset{\displaystyle OH}{\overset{\displaystyle OH}{Si}}\text{—}CH_2CH_2CH_2NH\text{—Epoxy}$$

Since the efficacy of the —NH— epoxy bond is well established, the performance of this compound should depend solely on whether or not hydrolytically stable Ti_s—O—Si linkages are indeed formed on application of the coupling agent to the titanium surface under suitable conditions. If they are formed, then members of the family of silane derivatives that have been developed for selectively coupling glass fibers to different types of resin (each derivative is specific to a certain type of resin) could now be useful for selectively improving the adhesion of titanium to these resins when used as structural adhesives. To test the validity of the concept (formation of the Ti_s—O—Si linkage), epoxy titanium adhesive joints were prepared with and without APS coupling agent and their strengths compared both in the dry state and after prolonged exposure to water at elevated temperature.

EXPERIMENTAL

Materials

A 6Al–4V alloy of titanium was used in fabricating the adhesive joints. A liquid adhesive was formulated from a commercial diglycidyl ether of bisphenol epoxy resin catalyzed with 90 parts per hundred nadic methyl anhydride and 1 part per hundred benzyldimethylamine and cured at elevated temperatures. The two solid adhesives utilized were commercial structural films consisting, respectively, of a nitrile modified epoxy and a nylon modified epoxy. The pickling bath was an aqueous solution of 15% by volume 70% HNO_3 and 3% by volume 50% HF. One percent aqueous solutions of APS were prepared from the pure concentrate.

Adhesive—joint preparation

Adhesive lap joints 6.5 cm^2 in area were prepared from $11.4 \times 2.5 \times 0.16$ cm titanium bars. The titanium surfaces were prepared for adhesive bonding by degreasing with acetone, sandblasting with alumina and then rinsing in methanol. The methanol rinse is a cleaning procedure for testing purposes only, and should not be applied to a titanium surface that is to be incorporated into a structure.

In one method, Procedure I, a set of five joints, designated as "untreated", were prepared by drying at 110°C for 20 minutes immediately after the methanol rinse and then bonding with epoxy adhesive. A second set of five joints, designated as "treated", were immersed for two minutes in freshly prepared 1% aqueous APS solution immediately after the methanol rinse, dried at 110°C for 20 minutes and then bonded with epoxy adhesive.

In Procedure II, the same method as in Procedure I was followed except that both "treated" and "untreated" titanium bars were rinsed in distilled water immediately prior to heating at 110°C for 20 minutes, and then bonded with epoxy adhesive. In Procedure III, five samples were degreased with acetone, sandblasted with alumina, rinsed in methanol, then immersed in pickling solution for 30 seconds.[3] This was followed by rinsing in distilled water and drying at 110°C for 20 minutes, and then bonding with epoxy adhesive. The other five samples were treated with APS as in Procedure II. In all three procedures, after applying the epoxy adhesive, the bars were aligned in a jig with provision for controlling the adhesive thickness to approximately 0.01 cm. A pressure of 8.42 kg/cm^2 was maintained during cure.

Adhesive joint testing

Tensile single–lap-shear tests were performed in both the dry and wet condition on a Universal Testing Machine at a test speed of 2.1×10^{-3} cm/sec. Tests in the dry condition were performed at room temperature in air. Specimens to be evaluated in the wet condition were immersed in boiling water for 24 hours and then tested at room temperature in air immediately after removal from the water bath.

RESULTS

Table I presents the results of lap-shear tests on titanium adhesive joints formed with the liquid epoxy adhesive system, utilizing three different surface treatments (Procedures I–III). The test results using the Procedure I surface treatment, indicate an improvement of 21% in dry strength for the APS treated titanium epoxy adhesive joints as compared to the adhesive joints formed from untreated titanium surfaces. Wet strength tests yield an improvement of 64% for the APS treated titanium joints as compared to the untreated set.

In the case of Procedure II, where APS treatment was followed by a distilled water rinse, the dry strength of the APS treated joints increased by 28% while their wet strength increased 48%.

In Procedure III, where APS treatment was compared to a surface pickling treatment often used commercially, the APS treated joints yielded an improvement of 26% in dry strength and 53% in wet strength.

While the APS treatment used in this investigation is intended for bonding of titanium by means of liquid epoxy resin-forming systems, lap-shear

TABLE I

Strength of titanium/liquid—epoxy adhesive joints with and without APS adhesion promoter

Procedure	Test mode	Lap shear strength (psi)[a] Treated with APS	 Untreated	 Treated with pickling solution	Increase in strength of treated over untreated specimens (%)
I	Dry	3080±227	2550±330	—	20.8
	Wet	2280±172	1390±153	—	64.0
II	Dry	2630±241	2050±335	—	28.3
	Wet	2120±120	1430±230	—	48.2
III	Dry	2720±261	—	2160±174	25.9
	Wet	2300±222	—	1500±56	53.3

[a] Average of five tests, ± standard deviation.

TABLE II

Strength of titanium/modified solid-epoxy adhesive joints with and without APS adhesion promoter

Test mode	Adhesive system	Lap shear strength (psi)[a] Untreated	 Treated with APS	Increase in strength of treated over untreated specimens (%)
Dry	Nylon modified epoxy	5670±940	6430±217	13.4
Wet	Nylon modified epoxy	3070±608	4100±693	33.5
Dry	Nitrile modified epoxy	4770±60	4840±250	1.5
Wet	Nitrile modified epoxy	3270±153	3910±246	19.6

[a] Average of five tests, ± standard deviation

joints were also prepared using two solid-state film adhesive systems, namely a nylon modified epoxy and a nitrile modified epoxy. The results in Table II indicate that the APS treatment was of benefit even in these cases.

DISCUSSION

The salient features of the action of APS as an adhesion promoter for the titanium-epoxy interface are a rather dramatic increase in wet strength retention (even under the severe conditions of 24 hours exposure to boiling water) combined with a more moderate increase in the dry strength. This behavior is typical of the well established action of organosilane compounds in promoting adhesion at glass–resin interfaces. It may therefore be assumed that hydrolytically stable Ti_s—O—Si linkages (analogous to the Si_s—O—Si linkage formed on glass) have been formed by APS on the titanium surface.

The performance of APS at the interface of titanium–epoxy adhesive joints warrants the inference that other silane based coupling agents will generally perform for specific titanium-resin systems in the same manner as for glass-fiber resin systems. That is, a given organosilane which has been useful for a certain glass-fiber reinforced polyester resin system should also improve the properties of a titanium joint bonded with the same polyester resin, etc.

CONCLUSIONS

The chemical linking of titanium compounds to a silica surface *via* the Si_s—O—Ti linkage can be reversed by linking silicon compounds to a titanium surface *via* the Ti_s—O—Si linkage. Any organosilane which is used to couple glass fibers with a specific resin will consequently couple titanium with the same resin. The use of APS to promote adhesive bonding of titanium with an epoxy adhesive, for example, results in lap-shear joints 25% stronger dry and more than 50% stronger after water exposure than joints prepared utilizing a standard surface treatment without APS.

References

1. M. E. Schrader, in *Interface Phenomena in Polymer Matrix Composites* (Academic Press, New York, 1974), and references therein.
2. M. L. Hair and W. Hertl, *J. Phys. Chem.* 77, 2070 (1973).
3. General methods of cleaning titanium, in *Handbook of Adhesive Bonding*, R. Chevalier, Ed. (April 1974).