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Short communication

Use of silane coupling agents to enhance the performance of adhesively bonded alumina to resin hybrid composites

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Abstract

Silane coupling agents were employed to improve the adhesion of vinyl-ester to alumina (Al_2O_3). Shear test by compression loading (ASTM D905) was used to study dry and wet adhesion. Scanning electron microscopy (SEM) was used to study the uniformity of silane coatings and the fracture modes after shear testing. Results showed that the adhesion and durability of the sandwiched alumina/vinyl-ester systems were significantly improved by certain silane surface treatment for most of the systems. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: silane coupling agents; hybrid composites; adhesion; durability; interfacial strength

1. Introduction

Composite integral armor is being considered in army applications. Fig. 1 shows the representative integral armor design. Integral armor requires strong, tough, ballistic-resistant, and durable bonds among the constituent materials. It is well known that the adhesion between the constituent materials strongly affects the ultimate mechanical properties of bonded assemblies. Adhesion at the interface could be due to physical interactions, chemical bonding, or both. Silane coupling agents have been used extensively in the past few decades to improve the adhesion and durability between an organic adhesive (such as polymeric resin) and an inorganic surface (such as ceramic, glass) [1–5]. This study investigates the effects of silane coupling agents on the strength and durability of adhesion between vinyl-ester adhesive and alumina tiles for armor application.

2. Experimental

2.1. Materials

A number of silane coupling agents were purchased from Dow Corning Corporation (Midland, MI) and used without further purification. The chemical name, reactive functional group, and designation of the silanes used are given in Table 1. The resin used as adhesive was a vinyl-ester (Dow 411-C50, 97.8 wt %, from Dow Corning, Midland, MI) cured using a peroxide initiator (Trigonox 239A, 2 wt %, from Witco, Marshall, TX,) and cobalt naphtanate (0.2 wt %, from Akzo Nobel Chemicals Inc., Dobbs Ferry, NY) as an accelerator. The alumina 90 (90% of the theoretical density) ceramic used as the substrate was purchased from Coors Corporation (Golden, CO).

2.2. Silane treatment

The alumina 90 tiles were first sectioned into 25 mm-square specimens using a diamond saw blade and washed in water then acetone to remove organic contaminants.

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Table 1
Dow Corning silane coupling agents

Designation	Chemical name	Reactive functional group
Z-6030	3-Methacryloxypropyl trimethoxysilane	Methacrylate
Z-6032	N-[2-(vinylbenzylamino)-ethyl-3-aminopropyl-trimethoxysilane	Cationic styrylamine
Z-6124	Phenyltrimethoxysilane	Arylalkoxy

Fig. 1. Composite integral armor design.

Dow Corning silanes were applied to the alumina surfaces. Dilute aqueous or alcohol solutions of 0.35, 0.50 and 1.0% silane concentration were made using methacrylate, cationic styrylamine, and phenyl silanes, respectively[1]. The solutions were prepared by first adjusting the pH of the water or alcohol to ~4 with acetic acid and then adding the silanes. Following silane addition, the solutions were stirred in order to form homogeneous hydrolyzed solutions.

The alumina surfaces were treated with silanes by dipping in the solutions. A dwell time of 5 min was chosen to allow silane migration onto the surfaces. Then, the specimens were dried at 93°C for 30 min to promote the condensation of the silanols to siloxanes and the removal of water or alcohol.

Following treatment, the alumina surfaces were bonded together with vinyl-ester. The resin was brushed onto the alumina surfaces, and the sandwich structures were fabricated by stacking two alumina surfaces together and bonded by the resins. The sandwich specimens were cured at 95°C for 1 h.

2.3. Hot-wet exposure

The hydrothermal stability of the sandwich specimens was investigated by immersing the specimens in 65°C distilled water. The specimens were weighed before water exposure and then immersed in a constant-temperature water bath. The weight gain of the specimens due to water absorption was measured periodically. The values obtained were the results of averaging at least four specimens. Upon moisture saturation, the specimens were removed and set aside for testing.

2.4. Shear strength testing

Dry and wet sandwich specimens were tested for shear strength (ASTM D905) under compression loading. The shear test was performed to failure at a cross-head speed of 5.08 mm per minute. The average shear stress at failure was then calculated averaging at least three specimens.

2.5. Microstructure characterization

Scanning electron microscopy (SEM) was used to (1) characterize the fracture surfaces of dry and wet sandwich specimens after shear testing, and (2) study the uniformity and thickness of the various coupling agents on the alumina.

3. Results and discussion

In order to obtain a uniform silane coating on the alumina surface, the silanes were applied using dilute solutions. The uniformity of the coatings was examined with scanning electron microscopy (SEM). Figs. 2, 3 and 4 show the SEM micrographs taken from as-received, 0.50 wt % cationic styrylamine silane-treated, and 1.0 wt % phenyl silane-treated alumina surfaces, respectively. Qualitative observations showed that thin and uniform coatings were obtained, in general, when silane concentrations were 0.35–0.50 wt % in solution. On the other hand, higher silane concentrations resulted in nonuniform coatings.

The weight gain of the specimens at saturation is shown in Table 2. It was observed that the weight gain of the specimens due to water exposure was higher for the untreated control and phenyl silane-treated specimens, compared with the methacrylate and cationic styrylamine silane-treated sandwich specimens. The results show that the cross-linked network at the interface of samples treated with silanes (methacrylate and cationic styrylamine) capable of reacting with the vinyl ester lowered the water absorption. This cross-linked interface

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[1] Guide to Dow Corning Silane Coupling Agents, Dow Corning, Midland, MI, 1992.

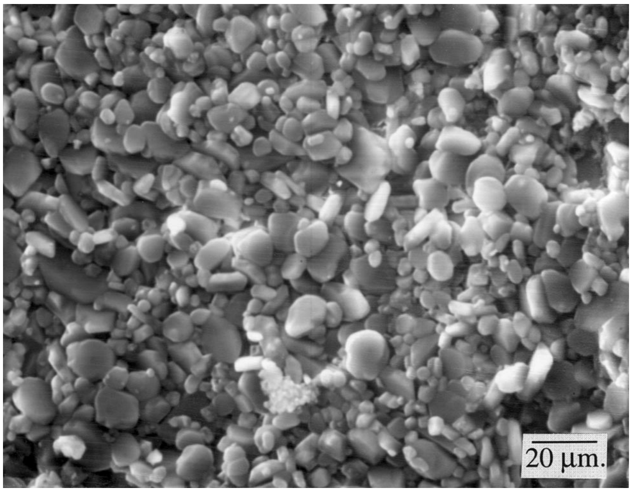

Fig. 2. Scanning electron micrograph of as-received alumina 90 surface.

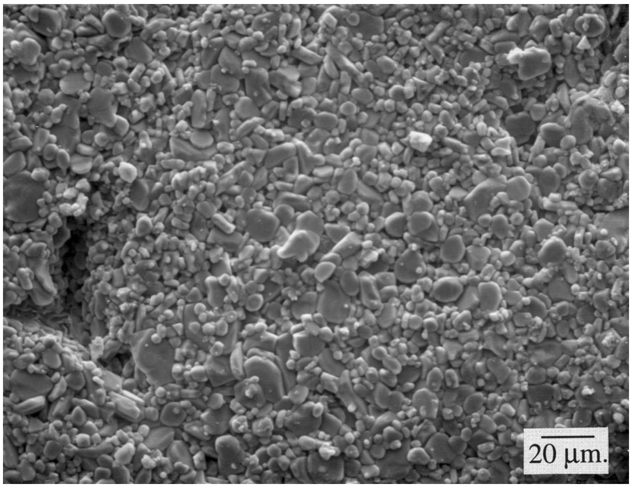

Fig. 3. Scanning electron micrograph of 0.50 wt % cationic styrylamine silane-treated alumina 90 surface.

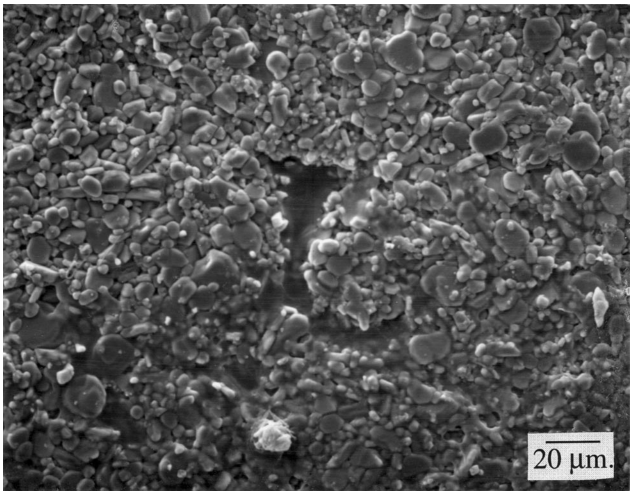

Fig. 4. Scanning electron micrograph of 1.0 wt % phenyl silane-treated alumina 90 surface.

was also responsible for higher bonding strength of the specimens as discussed below.

The shear strength of the silane-treated and untreated control sandwich specimens for dry as well as wet (water exposure at 65°C) conditions is presented in Fig. 5. As shown in Fig. 5, for the vinyl-ester resins, methacrylate (Z-6030) and cationic styrylamine (Z-6032) silanes provided a significant improvement in shear strength over the untreated control specimens. This improvement was due to the chemical bonding between the vinyl ester and the organic functional group of silanes. Moreover, the effect was more significant after water exposure at 65°C. Not surprisingly, the arylalkoxy (Z-6124)-type reactive functional group showed no improvement on the adhesion of alumina to vinyl-ester, since no chemical reactions were expected to occur.

SEM was also used to characterize the mode of fracture of sandwiched specimens after shear testing. Fig. 2 shows the SEM micrograph taken from the as-received alumina surface. Figs. 6 and 7 show fracture surface SEM micrographs of cationic styrylamine and phenyl silane treated specimens for dry conditions, representing good and bad adhesion, respectively. Cationic styrylamine silane-treated specimens showed a mixed-type cohesive failure of alumina and vinyl-ester surfaces for dry conditions. White particles in Fig. 6 are the alumina pieces left behind on the vinyl-ester layer after detachment of the sandwich specimen. In contrast, the phenyl silane-treated

Table 2
Weight gain of the specimens at saturation

Silane used	Weight gain (wt %)
Methacrylate	0.257 ± 0.03
Cationic styrylamine	0.206 ± 0.02
Phenyl	0.385 ± 0.07
None	0.490 ± 0.04

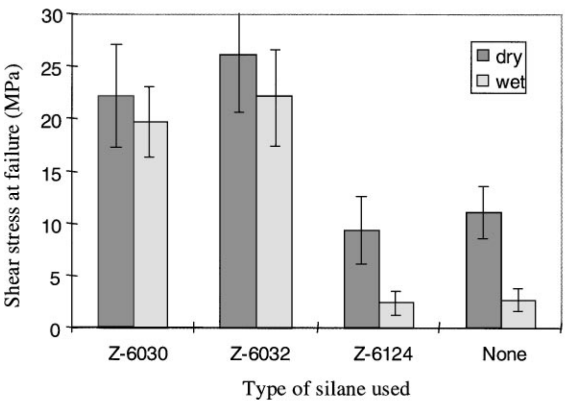

Fig. 5. Improvements in shear strength of the silane-treated specimens under dry and wet conditions.

Table 3
Modes of fracture after shear testing of various silane treated sandwich specimens

Silane used	Dry	Wet
Methacrylate	Cohesive at vinyl-ester	Cohesive at vinyl-ester
Cationic styrylamine	Cohesive at alumina and vinylester	Cohesive at alumina and vinylester
Phenyl	Interfacial debonding	Interfacial debonding
None	Interfacial debonding	Interfacial debonding

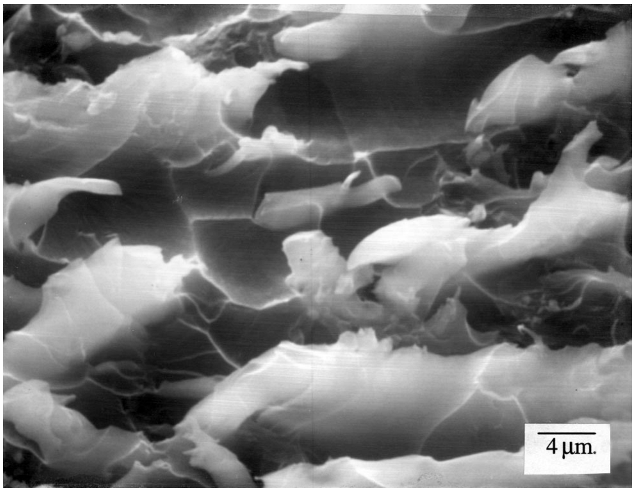

Fig. 6. Fracture surface of cationic styrylamine silane-treated alumina-to-vinyl-ester sandwich system for dry conditions.

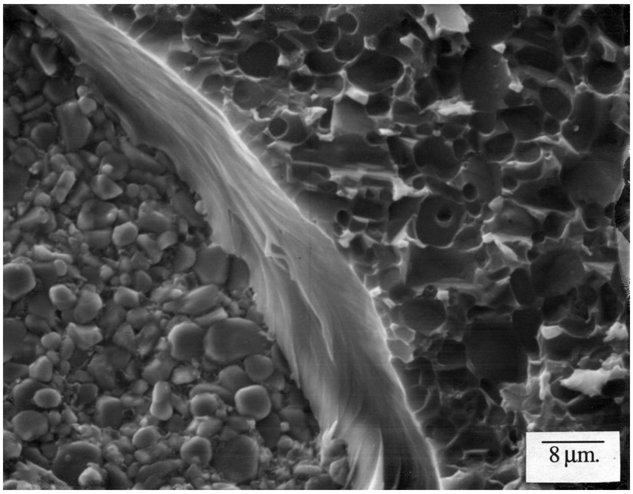

Fig. 7. Fracture surface of phenyl silane-treated alumina-to-vinyl-ester sandwich system for dry conditions.

specimen simply debonded at the alumina/vinyl-ester interface due to weak interfacial strength as shown in Fig. 7. Table 3 summarizes the mode of fracture after shear testing of various silane-treated sandwich specimens.

4. Conclusions

Modification of the alumina surfaces using methacrylate (Z-6030) and cationic styrylamine (Z-6032) silanes resulted in higher initial mechanical properties and also superior bond durability with vinyl-ester resin exposed to moisture. Qualitative observations showed that thin and uniform coatings were obtained, in general, when silane concentrations were 0.35–0.50 wt % in solution. On the other hand, higher silane concentrations resulted in non-uniform coatings.

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