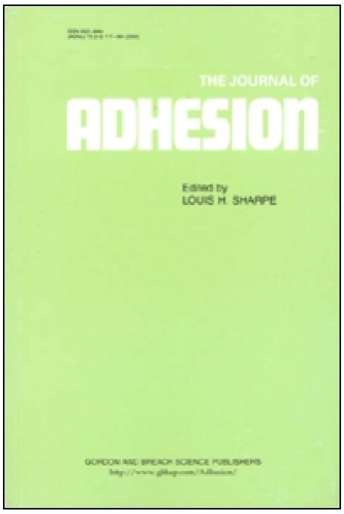

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Application of Acoustic Emission Measurements to Investigate Adhesion in Filled Polymeric Composites

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Note

Application of Acoustic Emission Measurements to Investigate Adhesion in Filled Polymeric Composites

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Adhesion in filled polymeric composites is characterized by an acoustic technique in which specimens of the composites are subjected to a ramped uni-axial tensile stress while particle-matrix debonding events are detected acoustically. The maximum in a fitted distribution of debonding events as a function of applied stress is related to the interfacial strength using elasticity theory. Results are reported for different silane-treated and untreated glass and aluminum spheres embedded in a poly(vinyl butyral) matrix. Silane treatment profoundly affects the adhesive strength, with the strongest bonds being formed when acid-base interactions between the particle surface and the matrix polymer are promoted. Significant differences are also found between the aluminum-particle and glass-particle cases, attributable in part to differences in mechanical interlocking.

Keywords: Acoustic emission; interfacial strength; organofunctional silanes; Lewis acid-base interactions; mechanical interlocking

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INTRODUCTION

Open questions remain concerning the mechanisms of adhesion in composite materials. For example, the importance of acid-base effects in adhesion promotion by organofunctional silanes is disputed [1, 2], and the influence of particle roughness on mechanical interlocking must be established. Key to the investigation of any such effects in composite materials is a test of mechanical adhesion appropriate to the system configuration. The present communication demonstrates that acoustic emission measurements [3] are especially convenient for testing adhesion in particle-filled polymeric composites. In particular, silane adhesion promotion was investigated in a poly(vinyl butyral) (PVB) polymer filled with untreated and silane-treated glass beads and with aluminum spheres. When subjected to uni-axial tensile stress, particle-matrix debonding is detected acoustically, and interfacial strength is determined in each case through the application of elasticity theory. Significant differences in adhesion were found between systems with untreated glass beads and those treated with silanes to promote acid-base interactions. Differences were also found between the glass beads and the aluminum spheres, possibly attributable to both mechanical interlock and acid-base effects.

MATERIALS AND METHODS

The fillers used in this study were smooth spherical glass beads of approximately 650 μm diameter (Cataphote Inc., Jackson, MS) and spherical aluminum particles of approximately 565 μm diameter (Starmet Corp., Concord, MA). The glass beads were modified with two different organofunctional silanes: 3-chloropropyltrimethoxysilane (United Chemical Technologies Inc. C-3300) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (United Chemical Technologies Inc. A-0700). These will henceforth be referred to as chlorosilane and di-aminosilane – names reflective of the chemistry of their organofunctional group. Solutions of 2.0 vol.% for the chlorosilane and 0.5 vol.% for the aminosilane were prepared with 95% ethanol – 5%

water and pure water solvents, respectively. The treatments were designed to provide complete, monolayer surface coverage. An "unmodified" glass surface was prepared by washing in a low-pH aqueous solution. An "unmodified" aluminum surface was prepared by degreasing, acid deoxidizing, rinsing and drying according to a Boeing Co. (Everett, WA) procedure for acid cleaning of aluminum substrates prior to conversion coating. AFM images $50 \times 50\,\mu m^2$ of unmodified glass beads and unmodified aluminum spheres were obtained using a Park Scientific Instruments AutoProbe CP in contact mode with a pyramidal tip.

Composite Preparation

The thermoplastic polymer poly(vinyl butyral) (PVB) was obtained from Scientific Polymer Products, Inc. (Ontario, NY) in powder form. For each filler, polymer and filler were mixed in a blender in weight proportions necessary to obtain a composite plate of $11 \times 11\,cm^2$, 4.0 mm thickness, and 1.0 percent volume fraction of filler. The mixture, made as homogeneous as possible, was poured into a $11 \times 11\,cm^2$ mold, to a depth of 14 mm (the thickness of the specimen), and the mold was then placed in a 130 kN Paul Weber hot press. The mold was heated and held at a constant temperature of 115°C for fifteen minutes and then a 10 mm thick section of the mold was removed. The mold was then left at 115°C for another 20 minutes before the pressure was raised incrementally to 30.5 kN (for the aluminum-filled composites, the pressure could only be raised to 15.0 kN before deformation of the particle occurred). The gradual increases in pressure were made to eliminate any entrapped air, *i.e.*, possible voids between the particles and matrix, while it was heated at the molding temperature. The pressure was then relieved and the mold cooled in a 130 kN Paul Weber cold press. Minimal mold leakage was observed. The composite plates were annealed in an oven for approximately ten minutes at 10°C above T_g(51°C) before the oven was turned off and the plates allowed to cool to room temperature. The slow cooling was intended to minimize residual stresses in the composite due to differences in thermal expansion coefficients between the matrix polymer and filler [4].

Composite Mechanical Testing

Three dog-bone-shaped specimens were cut from each composite plate using a diamond blade. Each specimen was then subjected to an uni-axial tensile test on a Zwick 1445 mechanical tester (Ulm, Germany) at a constant speed of 1.0 mm/min. Acoustic emission was monitored on an AET Model 5500 system (Hartford Steam Boiler Inspection Tech., Sacramento, CA). The AET 5500 was set up in single sensor mode, *i.e.*, single channel, with one transducer attached to the specimen by a spring clamp. The transducer was a standard µ80 (Physical Acoustics Corp., Princeton Junction, NJ) with a resonant frequency of 325 kHz and a sensitivity of – 65 dB. The detected signals were passed through an AET Model FL-25 band-pass filter with a flat frequency response between 250 and 500 kHz. They were then amplified in an AET Model 160 B preamplifier with a total gain of 60 dB and a flat frequency response between 1 kHz and 2 MHz. Final amplification was performed by the AET Signal Processing Unit with 30 dB. To eliminate noise effects, only acoustic emission events with three or more ring down counts (number of threshold crossings by the signal voltage) in 256 µs were accepted. For each acoustic emission event, strain, λ, stress, σ, and the number of ring down counts were recorded. The data were processed and analyzed off-line by custom-made software in order to avoid a reduction of system performance by real-time analysis. Five specimens were tested for each of the silane-treated and unmodified glass surfaces, while three specimens were tested for the aluminum surface.

RESULTS AND DISCUSSION

Figure 1 shows results from a typical acoustic experiment. Measured acoustic emission (AE) signals from uni-axially stressed specimens correspond to debonding of the matrix from the filler surface [3, 5]. This can be assured for the systems in this study since: (1) experiments with specimens of unfilled matrix showed no noticeable acoustic emission, (2) visual observation of filler particles removed from the composite specimens after loading suggest that they were not fractured, and (3) AFM topography scans of the post-failure surfaces showed

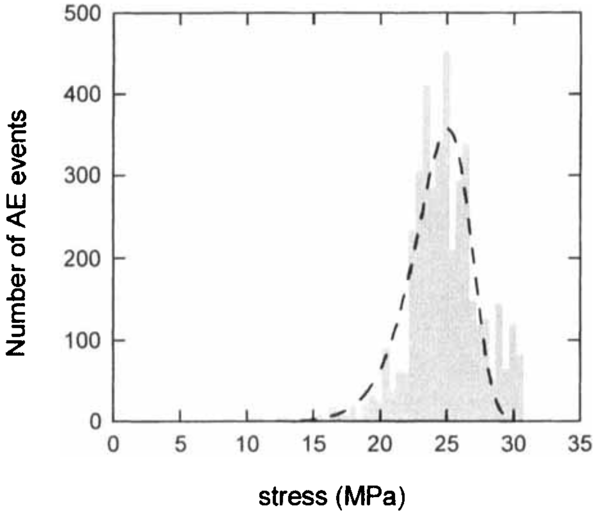


FIGURE 1 Number of acoustic emission events per stress interval for di-aminosilane treated glass spheres against PVB. $\sigma_{d,\text{fail}}$ is 25.0 MPa.

no evidence of residual polymer. The experimental distribution of the number of AE events per stress interval may be fitted with the Weibull distribution function [6]. The dotted line in Figure 1 shows a fit from this type of analysis. The discontinuous style of the curve is a result of statistical variation and graphical binning. The macroscopic debonding stress at failure is characterized by using the modal value, $\sigma_{d,\text{fail}}$, which can be determined from the maximum of the fitted distribution function [3]. The $\sigma_{d,\text{fail}}$ can then be used to calculate the interfacial strength by employing the theory of elasticity.

Goodier [7] provided an analytical solution to the radial, hoop, and shear stresses both within and outside a spherical inclusion submitted to an applied tensile field. Since composite specimens are typically subjected to uni-axial tensile stress only until adhesive failure occurs at the poles, Harding and Berg [8] recognized that only the simplified expression for the radial stress component is necessary, which is calculated as the interfacial radial stress at the pole, $\sigma_{rr,\text{pole}}$, experienced by the particle for a given macroscopic tensile stress, σ_d:

$$\left(\frac{\sigma_{rr,\text{pole}}}{\sigma_d}\right) = A - B + 1 \tag{1a}$$

where

$$B = \frac{1}{2}\frac{G_1 - G_2}{(7 - 5\nu_1)G_1 + (8 - 10\nu_1)G_2}, \tag{1b}$$

$$\begin{aligned} A = {} & \frac{[((1 - \nu_1)(1 + \nu_2)/(1 + \nu_1)) - \nu_2]G_2 - (1 - 2\nu_2)G_1}{2(1 - 2\nu_2)G_1 + (1 + \nu_2)G_2} \\ & - B\frac{2(1 - 2\nu_2)(6 - 5\nu_1)G_1 + (3 + 19\nu_2 - 20\nu_1\nu_2)G_2}{2(1 - 2\nu_2)G_1 + (1 + \nu_2)G_2} \end{aligned} \tag{1c}$$

ν and G are values of the Poisson's ratio and shear modulus, respectively, and the subscripts 1 and 2 correspond to the matrix and particle, respectively.

Harding and Berg also recognized that Goodier's derivation did not account for the thermal stresses that exist at the interface (prior to tensile testing) caused by differences in the thermal coefficient of expansivity. They used the solution of Beck *et al.* [9] to estimate the magnitude of the radial component, $\sigma_{rr,\text{thermal}}$, of the thermal stresses:

$$\sigma_{rr,\text{thermal}} = \frac{4(\alpha_2 - \alpha_1)(1 + \nu_2)G_1G_2\Delta T}{6(1 - 2\nu_2)G_1 + 3(1 + \nu_2)G_2}, \tag{2}$$

and then combined the solutions of Goodier [7] and Beck *et al.* [9] to determine the actual radial stress distribution experienced at the poles of a spherical particle submitted to a uni-axial tensile field. Since the interface of each composite filler particle is strained to failure, $\sigma_{d,\text{fail}}$ can be used with the theory of elasticity to calculate the interfacial strength of a *single* particle in the filled polymeric composite:

$$\text{Interfacial strength} = \left(\frac{\sigma_{rr,\text{pole}}}{\sigma_d}\right)\sigma_{d,\text{fail}} + \sigma_{rr,\text{thermal}} \tag{3}$$

One concern with using this expression, however, is that the stress fields around the particles are assumed independent. Interfacial strength measurements were thus conducted with filled polymeric composites containing only a *single* untreated or silane-treated glass bead (single-particle composite technique detailed in [8]) subjected to uni-axial stress until adhesive failure occurred at one of the poles of the sphere. The results from these measurements were within experimental error of the interfacial strengths obtained for the filled composites in this study. Thus, stress fields may be assumed independent for the systems studied in this work.

Acoustic emission curves were collected for each specimen tested and values for $\sigma_{d,\mathrm{fail}}$ and interfacial strength calculated from each. The results for interfacial strength are plotted in Figure 2. Lower values of interfacial strength were measured for the chlorosilane, while the di-aminosilane treatment provided much stronger interfaces. It is clear from this plot that the differences observed are statistically significant. There are two possible explanations for this result coming from the two ways that organofunctional silanes may affect adhesion. First, organofunctional groups can influence the short-range

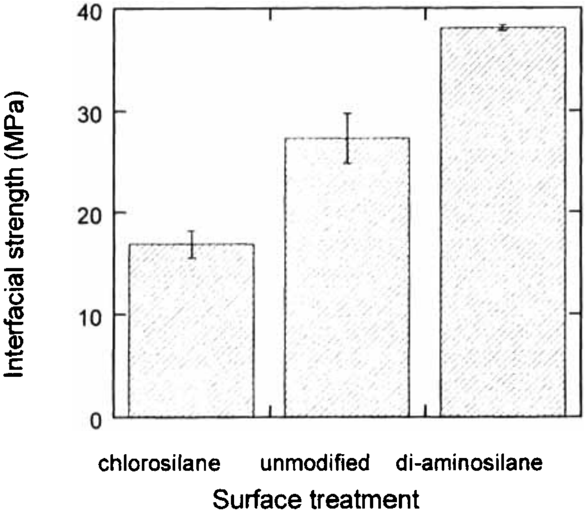


FIGURE 2 Interfacial strength measurement results for the filled polymer composites. The chlorosilane treatment has a deleterious effect on interfacial strength while the di-aminosilane treatment provided a much stronger interface. Error bars: 95 percent mean confidence interval.

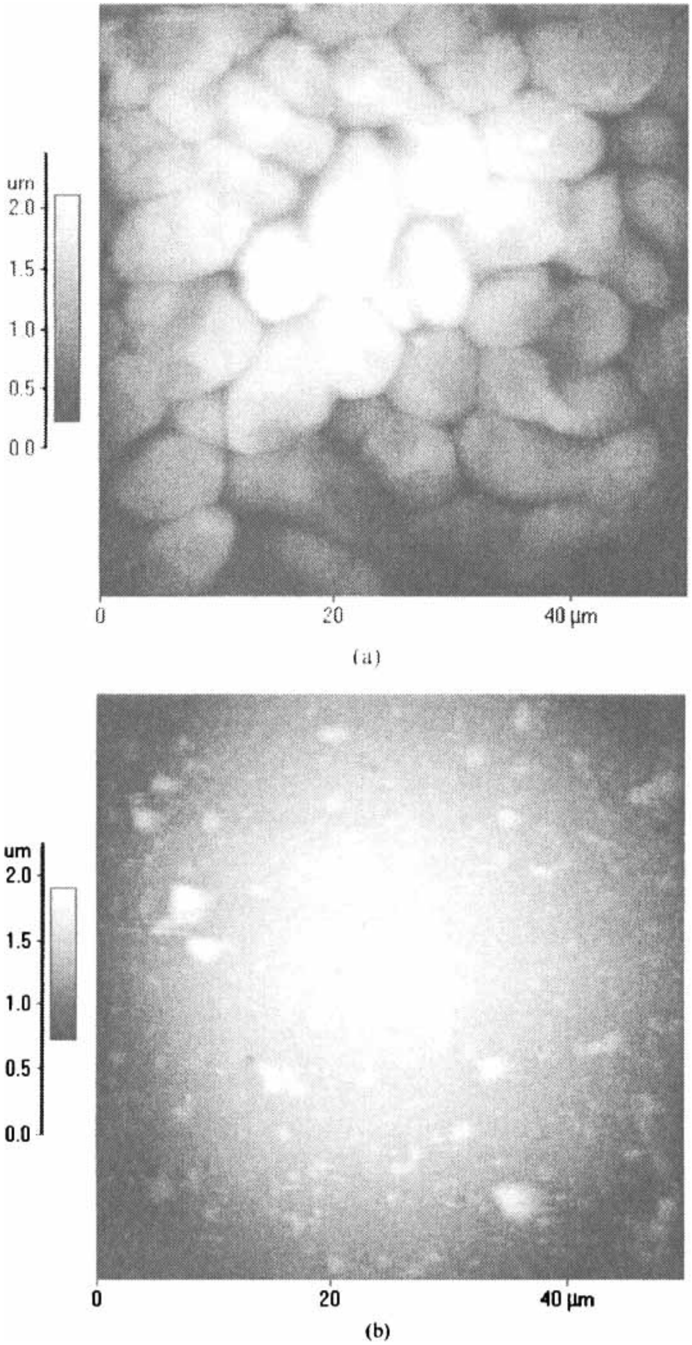
intermolecular forces active at an interface by modifying the dispersive and Lewis acid-base nature of the surfaces involved [10]. Second, the chain length of the organofunctional groups can be of a length that allows for penetration into the matrix polymer and enhanced adhesion *via* a diffusion mechanism [11]. Deconvolution of these two effects is required to understand and explain the observed behavior.

The chlorosilane features a Lewis acidic organofunctional group which is incompatible with the Lewis acidic PVB [2]. This silane will reside at the interface and not penetrate into the matrix during molding. Interfacial strength is due primarily to adsorption. The diaminosilane, on the other hand, features a Lewis basic organofunctional group of significant length that is capable of engaging in Lewis acid-base interactions with the PVB. This silane will penetrate into the matrix *via* the diffusion mechanism, dramatically increasing the interfacial strength.

It appeared that the mechanism of mechanical interlocking was an important factor when changing the filler particle from glass to aluminum. The results of the composite tests are shown in Table I. The aluminum shows a large increase in interfacial strength over the unmodified glass surface. This result may be explained by mechanical keying, or interlocking, of the PVB into the irregularities of the aluminum surface. AFM images of unmodified glass and unmodified aluminum particles are shown in Figure 3. It is clear from the images that the aluminum is significantly rougher than the glass allowing it to engage in mechanical interlocking with the PVB. Another possible contribution to the observed interfacial strength is that the aluminum surface, presumed to be of basic functionality [12], is engaging in Lewis acid-base interactions with the PVB.

TABLE I Comparison of results of filled polymeric composites featuring unmodified filler surfaces against PVB. The 95 percent mean confidence interval is ±2.5 MPa for the glass filler and ±1.1 MPa for the aluminum filler

Filler	*Interfacial strength (MPa)*
Glass	27.3
Aluminum	49.2



(a)

(b)

FIGURE 3 AFM image 50 × 50 µm^2 of unmodified sphere: (a) aluminum (565 µm dia.) and (b) glass (650 µm dia.).

CONCLUSIONS

The results indicate that acoustic emission measurement is a promising technique to investigate silane adhesion promotion between matrix polymers and fillers, and, in the present study, filler treatments were found to strongly affect the interfacial strength. Lewis acid-base interactions provide the possibility for enhanced adhesion between the di-aminosilane and PVB and a corresponding increase in interfacial strength. Changing the filler particle from glass to aluminum resulted in an enhancement in interfacial strength *via* mechanical interlocking as well as Lewis acid-base interactions.

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