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THE RELATIONSHIP BETWEEN NANOMECHANICAL AND CHEMICAL PROPERTIES IN POLYMER COMPOSITES

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ABSTRACT

Polymer matrix composites have seen increasing use in evermore demanding situations in aerospace (B-2 stealth bomber), automotive (leaf springs) and recreational (bicycle frames) applications. The unique advantages of polymer matrix composites, such as high specific stiffness and strength, long fatigue life, corrosion resistance and ease of fabrication into complex geometries, make them ideal candidates for such applications. It is recognized today that a key region within a polymer matrix composite is the *interphase* region, lying between the reinforcement and bulk polymer.

The interfacial force microscope (IFM), a scanning probe microscope utilizing a self-balancing differential capacitance force sensor, was used to measure directly the interphase elastic and visco-elastic properties in model siloxane-glass and silica systems. The elastic modulus was determined directly from the IFM force profiles using a contact mechanics analysis. The elastic modulus of the model interphases varied by a factor of three depending on the substrate. The interphase chemistry was interrogated with infrared spectroscopy and x-ray photoelectron spectroscopy. A model is proposed to explain the observed results.

Model composites were fabricated from an epoxy, amine curing agent, organosilane and optical silica fibers that were used as the reinforcement and chemical sensor. It was found that the elastic modulus varied significantly in the model composite within a 1-5 micron region surrounding the 20-micron optical glass fibers. Subsequently, the IFM was used to map the elastic modulus of the polymeric region surrounding the embedded fiber. Initial results of this elastic modulus mapping technique are discussed.

INTRODUCTION

This work focuses on revealing the relationship between nanomechanical properties and the chemistry within the interphase region. To accomplish this task model interphases and composites were systematically fabricated. To expose the chemical and nanomechanical relationship transmission and evanescent wave Fourier transform infrared (FT-IR) spectroscopy and angle resolved x-ray photoelectron (XPS) spectroscopy are used to obtain information on the former and interfacial force microscopy (IFM) is utilized for the latter. Atomic force microscopy is used to provide surface morphological information.

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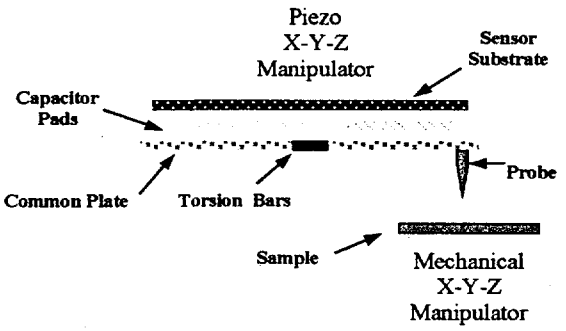
1.1 Experimental Analysis

Interfacial force microscopy (IFM), a scanning probe technique, is utilized to quantitatively measure the elastic modulus of the systems of interest. The heart of the IFM (Figure 1) is its self-balancing differential capacitance force sensor [1]. Using the IFM, force

Figure 1. Schematic of Interfacial Force Microscope sensor.



profiles are measured as the electrochemically sharpened tungsten sensing tip is brought into contact with the surface under study, resulting in force versus distance curves (Figure 2). Contact mechanics [2]

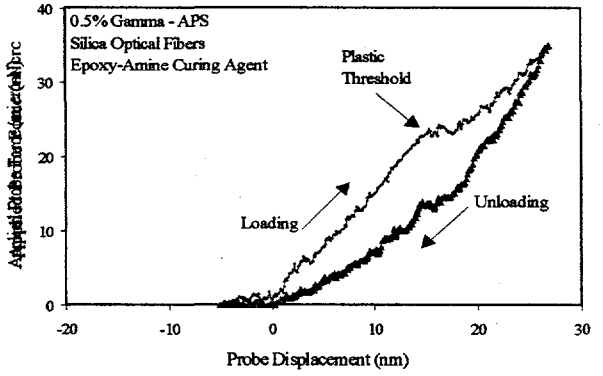


Figure 2. Typical force profile within polymeric phase near a fiber.

analyses can be used to analyze the force profiles as shown in previous IFM studies [3,4,5]. In particular a Hertzian analysis [2] is used to analyze the initial region of the loading curve to obtain a value for the elastic modulus through the application of Equation 1,

$$F = 4/3 * R^{0.5} * E'' * D^{1.5} \qquad (1)$$

Where F is the applied probe force, R is the radius of the tungsten tip, E" is the effective elastic modulus and D is the deformation of the surface. The elastic modulus, E_s, of the probed region can be obtained from the effective modulus (where s - sample, t – tip, ν - Poisson's ratio),

$$1/E'' = (1-\nu_s^2)/E_s + (1-\nu_t^2)/E_t . \qquad (2)$$

Chemical analysis of the interphase in the model composites is achieved using Fourier transform infrared evanescent wave spectroscopy (FT-IR EWS). In this technique the substrate (e.g. a flint glass optical fiber) is used as an IR sensor and reinforcement. For the model interphase systems, angle resolved x-ray photoelectron spectroscopy and transmission Fourier transform infrared spectroscopy are used.

1.2 Model Interphases

The interphase in polymer matrix composites can be thought of as consisting of distinct layers. These layers are comprised of the silane coupling agent which is adsorbed directly onto the substrate surface, the bulk polymer "far" away from the substrate, and a region formed from the diffusion of the polymer and coupling agent into the others bulk. It is the coupling agent and mixed layer that are thought of as the "interphase".

To obtain a reproducible coupling-agent model interphase, a 5 wt% aqueous γ-aminopropyltriethoxy silane (γ-APS) solution was spin-coated (2000 rpm, 40 seconds) on glass microscope slides (Fisher) and silicon wafers (Si(100)). Prior to spincoating the glass was cleaned by immersion in NH_4OH for 1 hour, followed by ultrasonication and rinsing with 18 M-Ohm water and heating to 140 °C for 30 to 60 minutes. The Si(100) was ultrasonicated in piranha solution and 18 M-Ohm water and rinsed in 18 M-Ohm water.

Optical fibers on which γ-APS was adsorbed were embedded in epoxy resin to create model composites. γ-APS at various concentrations was adsorbed onto cleaned silica optical fibers. The coated fibers where then treated at 100 °C and cooled. The fibers where then embedded into an epoxy resin/curing agent mixture and cured per the manufacturer's instructions. The samples were cut and meticulously polished to expose the end of the fibers for interrogation by IFM.

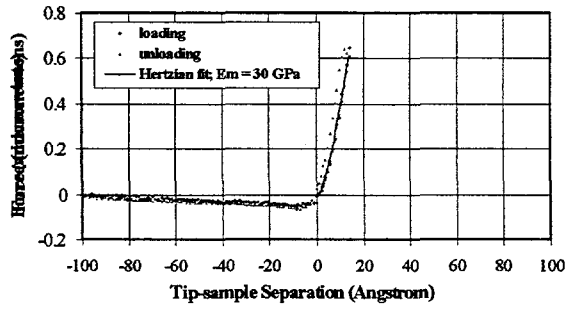
2 INVESTIGATION

2.1 Model Siloxane Interphase

When γ-APS is introduced into water it hydrolyzes forming the silanol. If the pH is basic the individual silanol molecules undergo condensation creating oligomers. The idealized γ-APS polymer would have a stoichiometry of $C_3NSiO_{1.5}$ (excluding H). XPS analysis of a freshly prepared film reveals a bulk chemical formula of $C_{3.3}N_{0.8}SiO_{1.7}$, showing a loss in

nitrogen and enrichment in carbon and oxygen with respect to silicon. Transmission FT-IR analysis of the film showed evidence of $-CO_2^-$ stretching and $-NH_3^+$ stretching bands which are attributed to a carbamate salt. These observation were the same for both the freshly made films as well as those cured at 100 C and left to equilibrate for several days. Films measured immediately after curing showed an increase in the –Si-O band indicating crosslinking and the decrease of the $-CO2^-$ and $-NH3^+$ bands representing the dissociation of the carbamate salt. Angle resolved XPS showed that the carbamate salt is located near the free surface of the film and its concentration decreases with depth into the film toward the substrate.

Figure 3 shows two IFM force profiles for 50 nm thick γ-APS films, prepared as previously described, on Si(100) (upper graph) and soda-lime glass (lower figure). A 250 percent difference in the slope of the force profiles is seen. Hertzian contact mechanics (Equation 1) was used to analyze the force profiles from which the elastic modulus of the film was determined (Equation 2). The film on SiO_2 with a modulus of 30 GPa was significantly stiffer than the film on soda-lime glass with an modulus of 8 GPa.



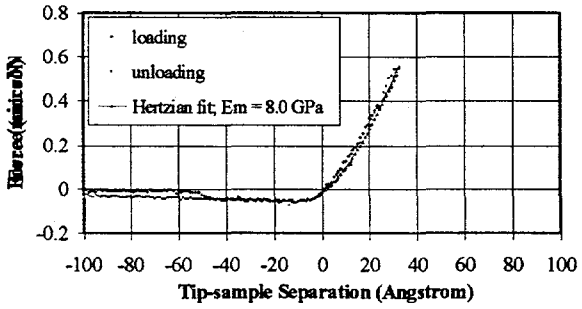


Figure 3 Force curves of ~50 nm APS films (airdried) adsorbed on SiO_2 (top graph) and glass (bottom graph). These measurements were taken using a W probe (~1000 A and 850 A) at a speed of 37 A/sec.

To explain these results we propose the model represented in Figure 4. In the case of the soda-lime glass, Na^+ ions diffuse into the silane film catalyzing the depolymerization of the silane film. This results in stable sodium and ammonium carbamate salts. The net effect of the depolymerization is a reduction in the stiffness of the film as observed by the lower elastic modulus in soda-lime glass substrates (8 GPa) as opposed to native SiO_2 substrates (30 GPa). Interestingly, nano-filaments are observed on glass and their growth has been monitored over several days using atomic force microscopy. The nano-filaments were not observed on the native silicon dioxide substrates.

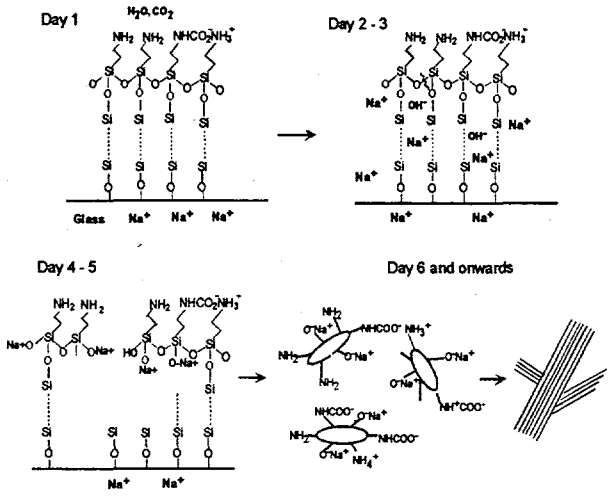


Figure 4. Model representation of depolymerization of silane film on soda-lime glass.

2.2 Model Composite Interphase

The IFM was used to obtain quantitatively the variation in the elastic modulus as one probes from the fiber surface radially into the interphase and bulk polymer. Figure 5 provides the results of such an analysis.

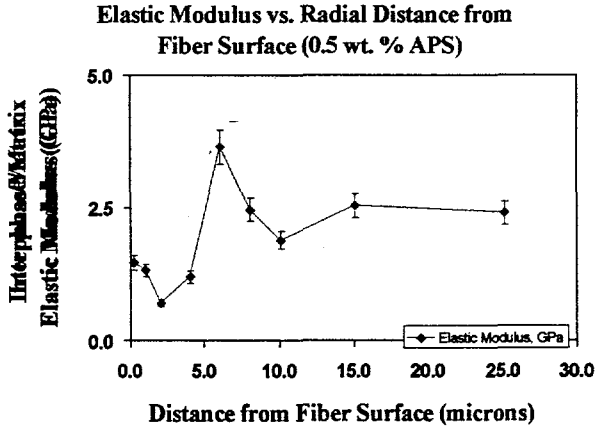


Figure 5. Elastic modulus as a function of distance from fiber surface. Fiber treated with γ-APS.

There are three noteworthy observations. First the modulus of the interphase region decreases near the surface. The initial higher value very near the fiber surface is supported by Figure 3, which provides evidence that the thin siloxane film's modulus is 2-3 times that of the bulk epoxy. In addition, recent evanescent wave FT-IR spectroscopic studies [6] show that this region is epoxy rich which leads to diminished crosslinking and a lower modulus. A peak in the elastic modulus is observed beyond this region. Wingard and Beatty [7] report a strong influence on the mechanical properties of neat epoxy/amine curing agent resins for changes of ~5% in the stoichiometry ratio of epoxy/amine end groups. Finally, "far" from the fiber the elastic modulus is that of the bulk polymer.

We have recently extended the capabilities of the IFM to "mapping" the modulus of a surface. This is accomplished by modulating the sensor a few nanometers along the tip axis and detecting the sensor's response with a lock-in amplifier. Preliminary results shown in Figure 6 reveal that a response is observed as a function of material modulus. The image on the left is a topographical image obtained at a constant imaging force and the right image is that of the ac modulation response, obtained simultaneously. The higher modulus fiber (~70 GPa) is easily identified from the lower modulus epoxy (~2.5 GPa). The IFM modulation technique holds promise to provide quantitative surface modulus imaging with nanometer resolution. Also, in the right- hand image the ridge

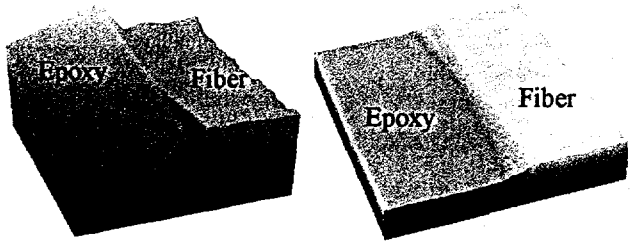


Figure 6. Topographical and ac modulation images of an embedded fiber.

between the epoxy and fiber could be mistaken for a thin interphase region but is a result of the discontinuity in height at the epoxy-fiber interface as a result of surface preparation. This observation encourages caution when interpreting phase images without the use of height images.

3 CONCLUSIONS

The interphase region found between the reinforcement and bulk polymer in polymeric composites is a complicated chemical and mechanical system. The work reported in this paper attempts to shed light on the critical interphase region. Thin films of silane coupling agents show 300 percent differences in mechanical properties when deposited on glass and silicon dioxide surfaces. A model is proposed to explain the observed variation in terms of oligomerization and depolymerization. The elastic modulus of the interphase surrounding embedded optical fibers varies significantly and chemical analyses support this observation. Finally, preliminary results are presented showing the potential of the IFM in quantitative mapping of the elastic modulus. These results represent major progress in understanding the relationship between the chemistry and the nano-mechanical properties in the interphase region of polymeric composites.

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