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INTERPHASE MECHANICAL PROPERTIES IN EPOXY-GLASS FIBER COMPOSITES AS MEASURED BY INTERFACIAL FORCE MICROSCOPY

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R.M. Winter* and J.E. Houston**
*Department of Chemistry and Chemical Engineering
South Dakota School of Mines and Technology, Rapid City, SD 57701-3995
**Surface and Interface Science Department
Sandia National Laboratories, Albuquerque, NM 87185-1413

There is growing body of experimental evidence substantiating the existence of an interphase region and the important role that it plays in the overall mechanical properties of polymer matrix fiber composites. The *interphase* is the region between the surface of the reinforcement and the polymer matrix where the chemistry differs from that of the bulk matrix and the mechanical properties are also expected to differ. In addition, the level of adhesion at the reinforcement surface will influence the mechanical properties near the interface. It is recognized that the stress transfer between the polymer matrix and the reinforcement takes place across the interphase and hence the properties of the interphase are critical to composite performance. Vibrational spectroscopy, namely Fourier transform infrared (FT-IR) spectroscopy, has substantiated the existence of an interphase region where the chemical composition varies from that of the bulk polymer matrix [1,2]. Micro-mechanical techniques have provided additional evidence of an interphase and have begun to elucidate the impact the interphase and interface adhesion has on the composites' overall mechanical properties [3,4]. Continuum mechanics analyses have clearly shown that the interphase plays and important role in the transverse properties of polymer composites, to lesser degree in their unidirectional priorities, and in their macroscopic elastic constants [5,6].

Prior to the invention of scanning probe microscopes the measurement of the mechanical properties of the interphase in polymer matrix composites on the nanometer level had been unattainable. A recent development in scanning probe microscopy, the interfacial force microscope (IFM), now makes it possible to map nanomechanical properties at the nanometer level. The IFM, employing a self-balancing differential-capacitance force sensor [7], is key to making these measurements (Figure 1). The IFM is capable of direct measurement of the forces between two materials in near contact and into contact [8-10].

The research focuses on the measurement of the nanomechanical properties associated with the interphase region of a polymer matrix fiber composite with a nanometer resolution in chemically characterized model composites. The IFM is employed to measure, with nanometer resolution, the mechanical properties of the interphase region of epoxy/glass fiber composites. The chemistry of the interphase is altered by the adsorption on to the fiber surface a coupling agent, 3-aminopropyltrimethoxy silane (γ-APS) which is know to covalently bond to the glass-fiber surface and the epoxy resin. Recent work [11,12] utilizing FT-IR fiber optic evanescent wave spectroscopy provides a method for the characterization of the interphase chemistry. This technique has been used to investigate the interphase chemistry of epoxy/amine curing agent/amine-terminated organosilane coupling agent/silica optical fiber model composites. This body of work has shown that a substantial fraction of the amine of the organosilane-coupling agent does not participate in a reaction with the epoxy resin. This evidence suggests an interphase that will have mechanical properties significantly different than the bulk epoxy/amine matrix. Previous research [2,13] has shown that drastic changes occur in the coupling agent chemistry, interphase chemistry, and composite mechanical properties as the amount of adsorb coupling agent is varied over the industrially relevant range used in this work. A commercially available epoxy resin, EPON 828, and aliphatic amine-curing agent, EPI-CURE 3283, make up the polymer matrix in this study. The reinforcement is silica optical or E-glass fibers.

Force profiles are measure as the electrochemically sharpened tungsten sensing tip is brought into contact at various locations within the interphase region and bulk matrix, resulting in force versus distance curves (Figure 2). Contact mechanics analyses can be used to analyze the force profiles as shown in previous IFM studies [8-10,14]. A Hertzian [15] analysis (Equation 1) is used to analyze the initial region of the loading curve to obtain a value for the elastic modulus.

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

Where F is the applied probe force, R is the radius of the tip, E" is the effective elastic modulus and D is the

deformation. The elastic modulus of the probed region can be obtained from [15],

$$1/E" = (1-\nu_s^2)/E_s + (1-\nu_i^2)/E_i \qquad (2)$$

where ν is Poisson's ratio and subscripts s and i refer to sample and probe, respectively. The onset of plasticity can be interpreted as where the loading curve deviates from the Hertzian response. Figure 3 shows the results of the Hertzian analysis applied to the force profiles obtained from a model composite utilizing a 0.5 wt. % γ-APS surface treatment. Force profiles were acquired on the fiber end surface and radially from the fiber surface across the interphase and bulk matrix. A significant variation (~3x) in the elastic modulus is indicated within an 8 μm region next to the fiber surface which would constitute the interphase. Beyond 8 μm the elastic modulus does not vary significantly indicating the bulk matrix. The initial decrease in the modulus could be due to the influence of the partitioning of the curing agent near the fiber surface [1] as well as incomplete reaction of the coupling agent [16] resulting in a stoichiometrically unbalanced region. Wingard and Beatty [xx] 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 endgroups.

Time response measurements such as creep are conducted to obtain additional information for the characterization of the interphase. In addition to obtaining force profiles of the fiber, interphase, and bulk matrix materials, the IFM is used to obtain scanning probe images of the investigate surfaces before and after interrogation (Figure 4).

Relative comparisons in elastic and inelastic behavior are made between the coupling agent modified systems and the non-coupling agent system as a function of distance from the fiber surface. These data provide insight into the influence of adhesion and interphase chemistry on the nanomechanical properties of polymer matrix composites. The utility of the IFM to measure interphase mechanical properties of polymer composites is demonstrated and shows promise, providing unique information concerning the role of adhesion and interphase chemistry on the nanomechanical properties of polymer matrix composites.

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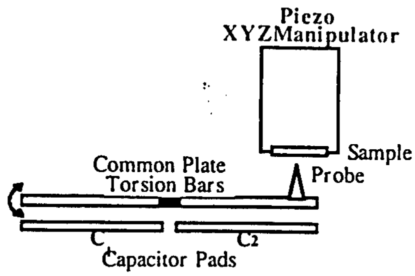


Figure 1. Schematic of IFM Sensor.

Sensor: State of the Art

- Normal Force Sensitivity
  1 nN to 400 μN
- Feedback Response Time
  500 μ sec
- Image Resolution
  ~ 100 Å
- Lateral Force Sensitivity
  2 nN to 50 μN

Fig. 2. Force Profile, 0.5 % Gamma-APS

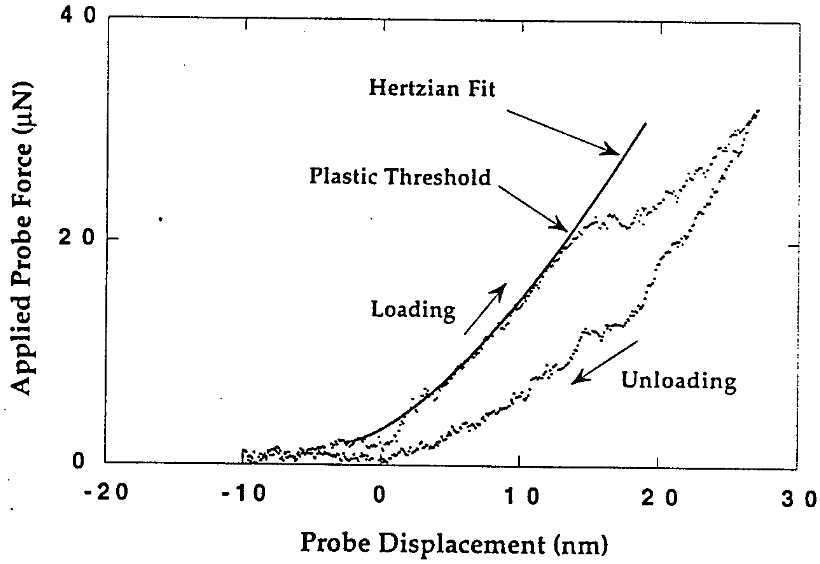
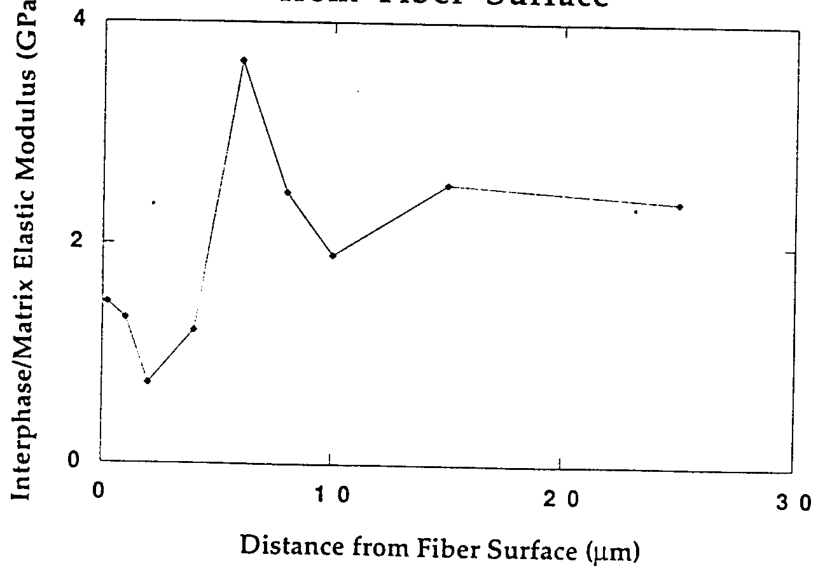


Fig. 3. Elastic Modulus vs. Radial Distance from Fiber Surface



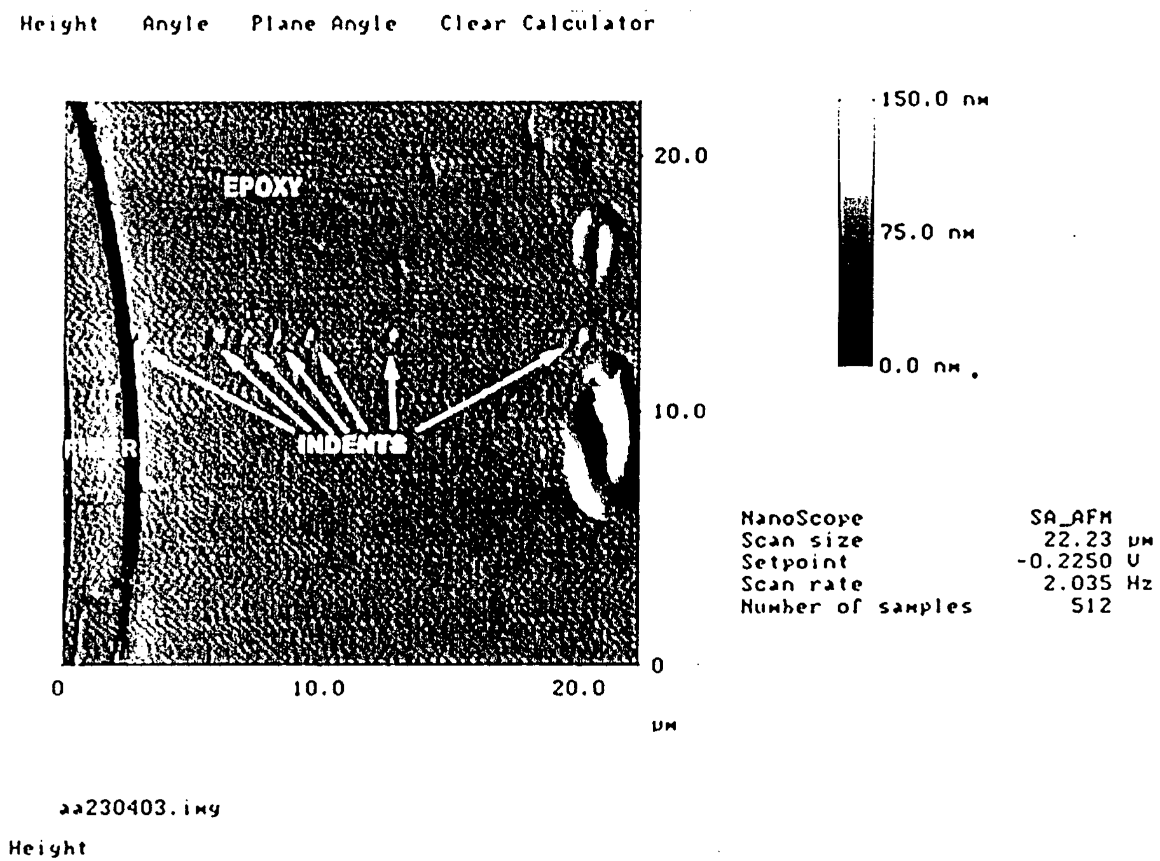


Figure 4 .IFM Micrograph of Region Investigated, 0.5 wt.% gamma-APS

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