ORAL/REFERENCE:ICF1003040R

INTERFACIAL FORCE MICROSCOPY STUDIES OF γ-APS ON GLASS AND SiO_2

K. M. Liechti[1], K. C.Vajapeyajula[1], M. Wang[1], H. Cabibil[1], H. Celio[1], J.M. White[1] and R.M. Winter[2]

[1]Research Center for the Mechanics of Solids, Structures and Materials, Texas Materials Institute, University of Texas, Austin TX 78712
[2]Department of Chemistry and Chemical Engineering, South Dakota School of Mines and Technology, Rapid City, SD 57701

ABSTRACT

Silane coupling agents are often used as adhesion promoters between polymers and ceramics or metals. They form a thin interphase region whose mechanical properties are thought to differ from those of the bulk polymer. This paper describes the use of an interfacial force microscope to conduct nanoindentation experiments on 50-nm thick layers of γ-APS on glass and SiO_2. The Young's modulus of the γ-APS on glass was one quarter of that on γ-APS on SiO_2. The reasons for this were explored via X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. It was found that the Na+ ions in the glass destroyed the cross-links in the γ-APS.

KEYWORDS

Coupling agents, mechanical properties, interfacial force microscope, spectroscopy, interfacial fracture.

INTRODUCTION

Swadener et. al. [1] have shown via X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) that mixed-mode fracture near a glass/epoxy interface left a 3 nm layer of epoxy on the glass surface. Such a cohesive crack path helped explain why the high intrinsic toughness of the interface was 20 times higher than the thermodynamic work of adhesion of the glass/epoxy interface. Other studies of glass/epoxy interfaces (Drzal [2]; Winter and Houston [3]) have indicated the presence of an interphase region where polymer properties are affected by the substrate so that there is a transition from the substrate to the bulk behavior of the polymer. Presumably, the subinterfacial fracture noted by Swadener et. al. [1] took place in such an interphase region. The traction-separation law of this region was extracted in an iterative manner via a combination of crack opening interferometry and finite element analysis. The objective of this work is to make more direct assessments of traction-separation laws of interphase regions.

EXPERIMENT

One promising instrument for these purposes is the interfacial force microscope (IFM). The IFM (Fig. 1) is unique in that it employs a self-balancing, force feedback sensor which allows force profiles (load vs. displacement data) to be obtained while the sensor remains rigidly fixed in position throughout the measurement (Joyce and Houston [4]; Houston and Michalske [5]).

In this study, the (IFM) was first used to probe the nanomechanical properties of hydrolyzed γ-aminopropyltriethoxysilane γ-APS films fabricated by spin coating on soda glass and SiO_2 surfaces. The γ-APS is widely used as a coupling agent for fiberglass-reinforced composites and as a primer for adhesive joints with thicknesses ranging from a few nanometers to hundreds of nanometers. The film was probed in the IFM apparatus with a Tungsten tip that had a 120-nm radius (Fig. 2).

The Young's modulus of the γ-APS was extracted from the measured load-displacement response from the IFM using Hertzian , JKR [6] and Maugis [7] analyses. The latter two approaches account for surface interactions inside and beyond, respectively, the contact region.

RESULTS

Typical load-displacement responses from the IFM indentation on γ-APS films on SiO_2 are shown in Figure 3. It was found (Table 1) that the modulus of 50 nm thick γ-APS films on glass was a quarter of the modulus values of the γ-APS films on SiO_2. XPS analysis revealed that leaching of Na^+ ions from the glass into the γ-APS destroyed cross-links, making it softer. The moduli listed in Table 1 were extracted on the basis of a Hertzian analysis. Accounting for surface interactions through JKR and Maugis analyses did not significantly alter modulus values.

The moduli of the two γ-APS films were considerably higher than polymers in their glassy state, which at first suggests that the substrates may have had an effect on the results. However, γ-APS the moduli were the same when 75 and 120-nm thick layers were employed and, in all cases, the indentations were less than 10% of the layer thickness. The modulus for glass was in line with typical values, which gave confidence to the operation of the IFM. The modulus for the SiO_2 was high, but was most likely influenced by the Si substrate beneath. As a result, there is a lot of confidence in the quoted modulus values of γ-APS and certainly that the glass substrate affected the chemistry of the γ-APS film. In current work, the modulus of remaining layers of polymer on the glass and SiO_2 fracture surfaces is being probed.

TABLE 1.
YOUNG'S MODULI FROM NANOINDENTATION WITH AN IFM

Film/ Substrate	Poissov Ratio*	Modulus** E_2 (GPa)	Roughness (A˚)
γ-APS/Glass	0.25	8±2	2.2±0.4
γ-APS/Glass	0.25	35±3	2.2±0.5
Glass	0.17	74±6	7.4±2.8
Native SiO_2	0.25	112±17	1.5±0.4

Tungsten tip $E_1 = 400\,\text{GPa},\ \nu_1 = 0.30$.
* Literature values
**Average of 7-10 loading cycles

REFERENCES

1. Swadener, J. G., Liechti, K. M. and de Lozanne, A. L. (1999). J. Mech. & Phys. Solids, 47, 223-258.
2. Drzal, L. T. (1986). Adv. in Polym. Sci., 75, 1-32.
3. Winter, R. M., and Houston, J. E., (1998), Proc. of the SEM Spring Conf. on Exp. and Applied Mechanics, Houston, TX, June 1-3, 1998.
4. Joyce, S. A., and Houston, J. E., (1991), Rev. Sci. Instr., 62 (3), 710 - 715.
5. Houston, J. E., and Michalske, T. A., (1992), Nature, 356, pp. 266 - 267.
6. Johnson, K. L., Kendall, K. and Roberts, A. D. (1971) Proc. R. Soc. London, **A 324**, 301-313.
7. Maugis, D. (1992) J. Colloid and Interface Sci., **150**, 243-269.

ORAL/REFERENCE:ICF1003040R

FIGURES

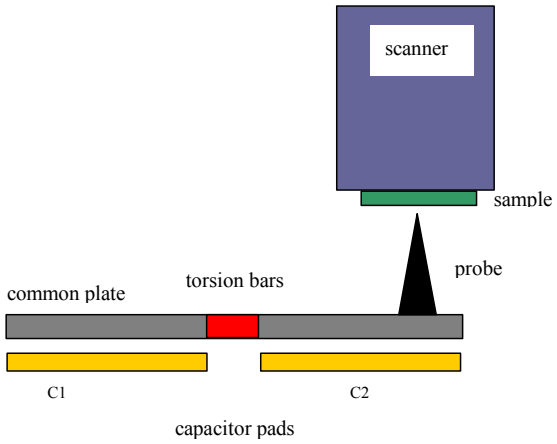

Figure 1. Interfacial force microscope.

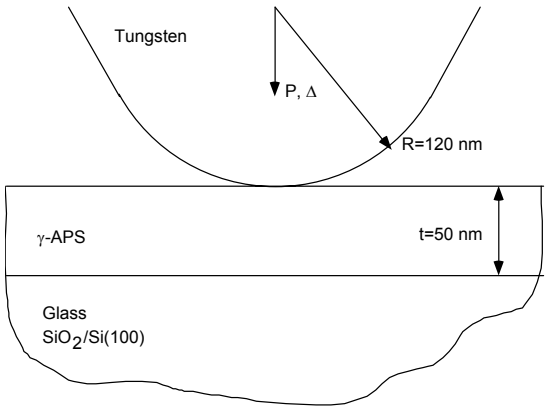

Figure 2. Specimen geometry for the nanoindentation experiment.

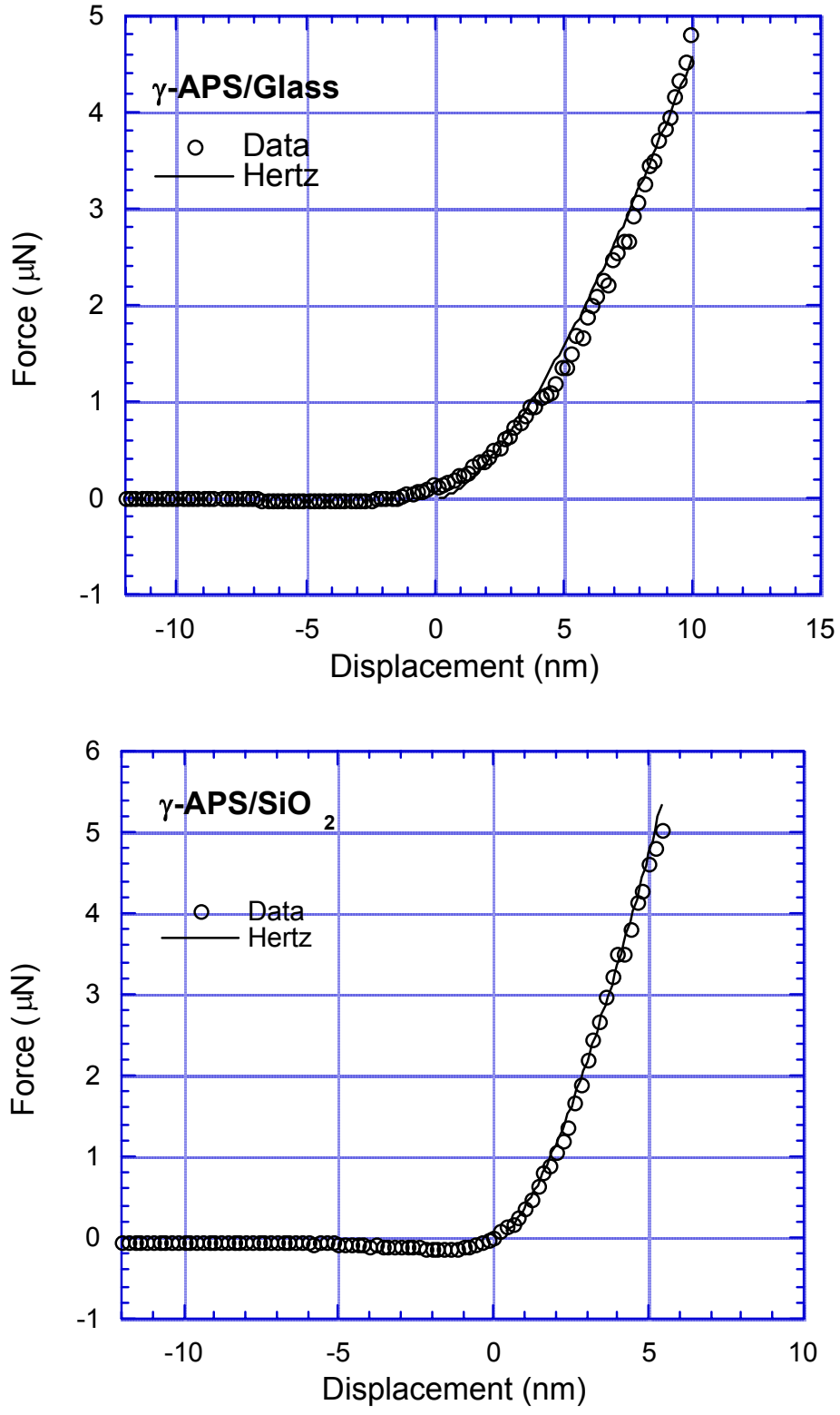

Figure 3. Contact force-displacement responses for γ-APS on glass and SiO_2