Fracture Between Self-Assembled Monolayers

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1. Abstract

Molecular self-assembled monolayers (SAMs) can be used to functionalize surfaces and thereby control adhesion between stiff substrates and epoxy [1-3]. In this paper, fracture at the molecular level is examined via experiments and finite element analyses that examine the delamination between two silicon strips which are joined only by SAMs with no epoxy.

2. Background

While it is intuitive that molecular interaction should correlate to the mechanical properties of a material, it has only recently become possible to make the measurements necessary to trace the effects of molecular interaction across length scales to properties at the level of the material. The utility of "classical" polymeric adhesives is underscored by their widespread use in primary structural applications ranging from aerospace, automotive, and civil structures to biomedical implants and microelectronic devices. To date, the vast majority of the efforts directed toward improving the strength and durability of adhesives and fiber/matrix interfaces have been largely empirical. At the same time, the drive towards miniaturization in MEMS and NEMS devices and nano patterning means that an understanding of adhesion and fracture at smaller and smaller scales needs to be developed. This actually provides an opportunity to decrease the amount of empiricism as the number of variables is essentially decreased.

In examining the effect of SAMs on the toughness of sapphire/epoxy interfaces [3], it was found that the toughness increased as ionic interactions with the epoxy were increased. In addition, the nature of the epoxy fracture surfaces changed and this was reflected in the traction-separation laws that were extracted. In this work, we remove the epoxy layer and examine the interaction between shorter molecules.

The paper describes the development of an experiment with associated analysis to determine the toughness and traction-separation laws of laminated silicon beams that were bonded by molecular adhesives or interactions between SAMs that were deposited on the adherend surfaces prior to pressing them together.

3. Experiment

The Si(111) surfaces of the adherends were cleaned and coated with carboxy (COOH) and diamine (NMe_2). The presence of monolayers was ascertained by conducting X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) prior to and following deposition. AFM indicated that the RMS roughness of SAMs without clusters were less than 0.5 nm. The SAM thicknesses were measured by ellipsometery following deposition and agreed with calculations based on bond lengths and angles. The silicon beams were pressed together to form miniature laminated beams which were joined by the interactions between the SAMs. The specimens were loaded using a specially developed mixed-mode fracture tester (Fig. 1) that was designed to operate in high vacuum. Normal crack opening displacements (NCOD) were measured with infrared crack opening interferometry [4]. Fracture surfaces were examined using XPS and AFM.

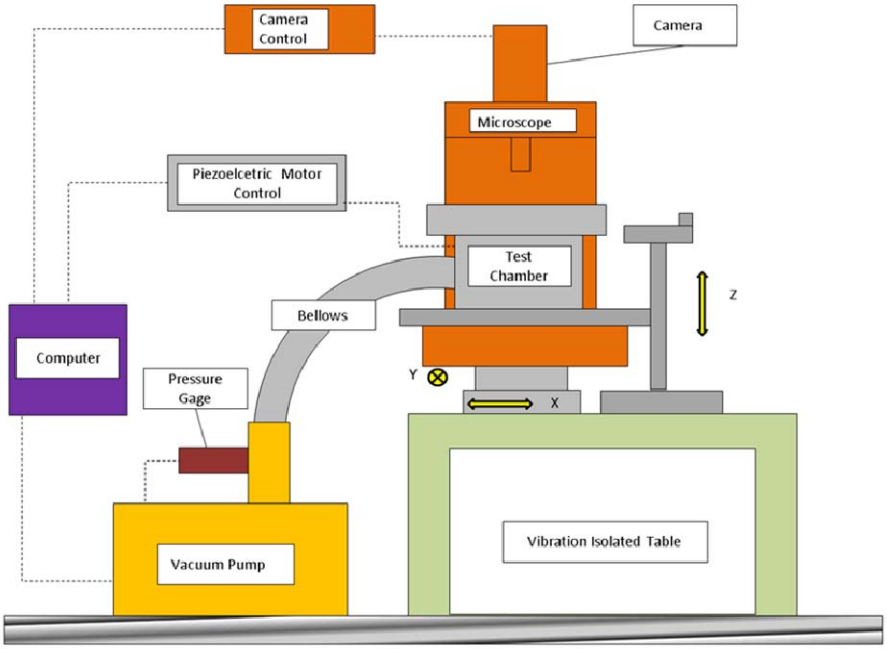

Figure 1. High vacuum fracture rig with infrared crack opening interferometry.

4. Analysis

Finite element analyses accounted for the mechanical and adhesive behavior of the SAMs via traction-separation laws that were based on those extracted from sapphire/SAM/epoxy fracture experiments [3] and interfacial force microscope (IFM) nanoindentation experiments [5] on octadecyltrichlorosilane (OTS) SAMs deposited on silicon. The triangular traction-separation laws gave rise to large scale and small scale bridging, respectively. The associated parameters are listed in Table 1.

Table 1 Traction-separation laws that were considered in the analysis. The maximum traction is σ_0, the associated crack opening is δ_0 and separation occurs at δ_c.

Case	Toughness [mJ/m^2]	σ_o [MPa]	δ_o [nm]	δ_c [nm]
SSB	90.5	26	5	7
SSB	90.5	9.84	9.25	18.5
LSB	90.5	0.91	100	200
SSB	188.4	25.33	7	15
SSB	188.4	15.83	12	24
LSB	188.4	1.9	100	200

5. Results

The measured NCOD from wedge tests on specimens laminated by COOH/NME_2 SAMs are shown in Figure 2. They are compared with solutions from classical linear elastic fracture mechanics (LEFM) analyses and the cohesive zone models mentioned above. Based on ten separate experiments on the same specimen, the toughness associated with COOH/NME_2 interactions was 90.5±14.2 mJ/m^2. The most striking aspect of the double logarithmic plot is that the measured asymptotic behavior of the NCOD was the classical square root signature of LEFM. The asymptotic behavior associated with small and large scale bridging was quite different. This suggests that the ionic interactions that are expected between carboxy and diamine occur over a much smaller scale than we can currently capture with IR-COI. Current experiments under mixed-mode loading are providing consistent results.

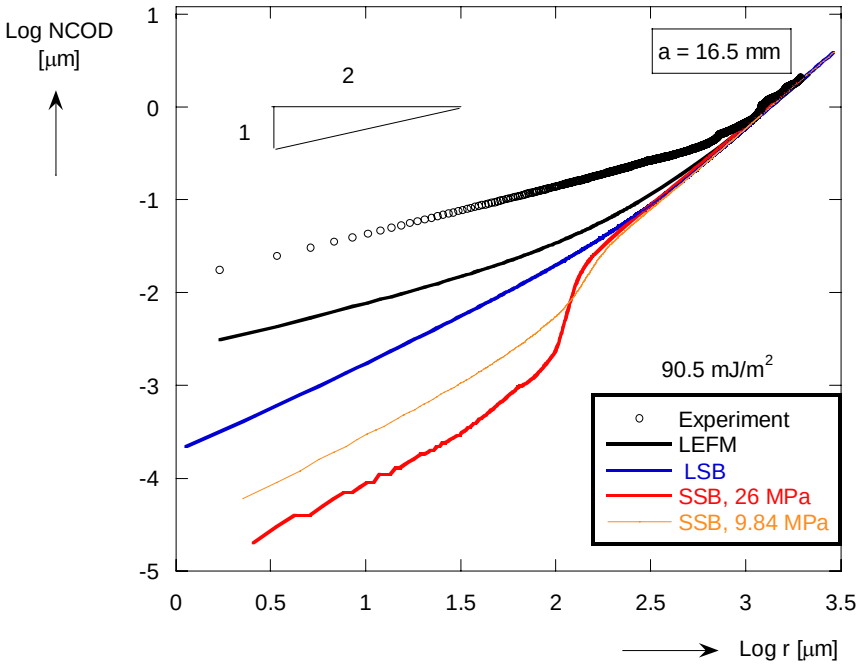

Figure 2. Comparison between measured NCOD and predictions based on linear elastic fracture mechanics and small scale and large scale bridging.

6. Conclusions

We have been able to successfully deposit carboxy and diamine SAMs with nanoscale uniformity and fracture laminated silicon beams that are joined by them. The results indicate that the interactions between carboxy and diamine are very short range in nature. This hypothesis is being checked via experiments with COOH/COOH interactions and molecular dynamics analyses.

Acknowledgements

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