MIXED-MODE FRACTURE AT THE MOLECULAR LEVEL

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Summary Self-assembled monolayers (SAMs) are used in MEMS devices to modulate adhesion and reduce friction and wear. They also offer unique opportunities to examine fracture at small scales and issues related to scale bridging. The paper describes the development of specimens with minimal defects and mode 1 and mixed-mode fracture experiments along with associated analyses for extracting traction-separation relations. The latter turned out to be mode-dependent, which has interesting implications for friction at these scales.

EXPERIMENTS & ANALYSIS

Specimens

Silicon strips (40×5 mm) were coated with carboxyl and amine terminated SAMs, brought together and then delaminated under mode 1 and mixed-mode fracture as a way of examining the adhesive interactions between carboxyl and amine groups. The two SAMs that were considered consisted of an alkyl chain with ten CH_2 groups that were terminated with either carboxyl or amine groups. The substrate was a 250 μm, N <111> 5-10 ohm-cm, double side polished silicon wafer that presents the Si(111) surface for deposition. Following cleaning with piranha solution and hydrogen termination with ammonia fluoride (NH_4F) treatments of the Si surface, the stage was set for the deposition of a 10-undecylenic trifluoroethyl ester SAM [$Si(CH_2)_{10}(CO)O(CH_2CF_3)$] using a 2,2,2-trifluoroethyl undec-10-enoate solution. The (CH_2CF_3) group was subsequently replaced by carboxyl or amine termini to form 10-undecylenic acid SAM [$Si(CH_2)_{10}(CO)OH$ and a 10-undecylenic N-(2-(dimethylamino)ethyl amide SAM [$Si(CH_2)_{10}(CO)(NH)(CH)_2$-$NMe_2$] SAM on the silicon strip.

Table 1: SAM thickness and roughness

Surface	RMS roughness (nm)	SAM thickness (nm)	Chain length (nm)
CF_3	0.306±0.104	2.20	2.21
COOH	0.299±0.096	1.87	1.94
NMe_2	0.360±0.110	2.59	2.46

The presence of the expected monolayers was checked using XPS (surface chemistry), AFM (surface roughness) and ellipsometry (layer thickness). The results of the latter are summarized in Table 1 where the carboxyl and diamine-terminated SAMs are designated COOH and NMe_2, respectively. The measured thickness via ellipsometry is also compared with the expected chain length. The agreement between the two, coupled with the roughness data indicates that monolayers were indeed being formed. Once SAMs had been successfully deposited on separate silicon strips they were brought together in the presence of a drop of de-ionized water. This presumably facilitated proton transfer between the SAMs before the most of the water evaporated. The clamp was removed after two minutes and the specimens were allowed to dry in ambient conditions or high vacuum.

Fracture

The specimens were separated under mode 1 and mixed-mode conditions using wedge and mixed-mode flexure test configurations. In the former, a 25 μm shim h_w was driven between the silicon strips using an instrumented linear stage, which allowed the displacement of the shim u_w to be controlled and measured. In the latter, the specimen was bonded to a carrier beam in four-point bending using a high vacuum rated piezo motor. Infra-red crack opening interferometry (IR-COI) was used to locate the crack front (and thus any crack growth, Δ) and measure the normal crack opening displacements (NCOD, δ_n). A schematic of the interactions near the crack front is shown in Figure 1. The normal tractions $\sigma(\delta_n)$ act over the cohesive zone c and, in the wedge test, the crack length $a = a_0 + \Delta - u_w$ is determined from the initial length prior to insertion a_0 and the measurements from the linear stage and IR-COI. In the mixed-mode test, the crack length was measured from the end of the specimen.

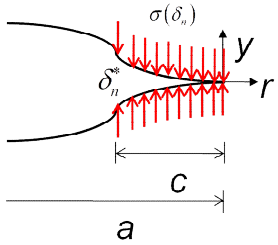

Fig. 1: Cohesive zone parameters

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The energy release rate or J-integral for the wedge test is $G = J = \frac{3Eh^3h_w^2}{16a^4}$. As the wedge is inserted, initially there is no growth and the crack length decreases, thereby increasing the energy release rate. When the crack does grow, the rate of increase in the energy release rate with wedge insertion generally drops to zero, thereby indicating the onset of a steady state growth condition. From the path independence of the J-integral, $J = \int_0^{\delta_n^*} \sigma(\delta_n) d\delta_n$ over a path taken round the cohesive zone. The quantity δ_n^* is the normal end opening, measured at the original crack front location using the IR-COI. Taking the derivative yields the traction-separation relation via $\frac{\partial J}{\partial \delta_n^*} = \sigma(\delta_n)$, which is interpreted as a measure of the molecular interactions. For the mixed-mode experiments $J = \frac{216E_{Fe}^2 I^2 \Delta_m^2}{L^2 E_{Si}(3N-4L)^2 b^2}\left[\frac{1}{h_1^3} - \frac{1}{(h_1+h_2)^3}\right]$ at a mode-mix $\psi = 50^\circ$. The normal component of the traction-separation relation was obtained from the derivative $\frac{\partial J_1}{\partial \delta_n^*} = \sigma(\delta_n)$, where $J_1 = G_1$ as determined from the mode-mix.

RESULTS

Wedge tests were conducted on two sets of specimens: one was cured in ambient conditions, the other in high vacuum (3×10^{-7} Torr). The change in J-integral with end-opening displacements is shown in Figure 2. Initially the increase in J-integral as the applied displacement was increased was within the resolution of the IR-COI. The "pop-in" J-values were higher for the vacuum cured sample. The rise in toughness thereafter was also steeper, but in the end, the "steady state" values were quite similar at approximately 140 mJ/m^2. Under mixed-mode conditions, there was no pop-in feature and the J-values increased gradually with end opening displacement. The J-values of the vacuum cured and tested specimens rose more quickly but reached the same steady state level of approximately 2 J/m^2 and 600 mJ/m^2 for J and J_1, respectively. These are considerably higher than the values from the wedge test and are surprising, given that plasticity effects should be minimal. The corresponding traction-separation relations follow in Figure 3, where the derivative was taken of the raw data in Figure 2. In all cases, the traction-separation law relation of the vacuum cured samples rose more steeply to a higher maximum value (strength) than the ones for the air dried samples. From the wedge test, the values of strength ranged from 2 to 2.5 MPa for ambient cured samples and 5-6 MPa for vacuum. Again the values from the mixed-mode experiments were higher, which appears to be an interesting and novel result. These interesting differences await the results of ongoing spectroscopic analyses aimed at determining the nature of the bonding in these Si/COOH/NMe$_2$/Si sandwiches.

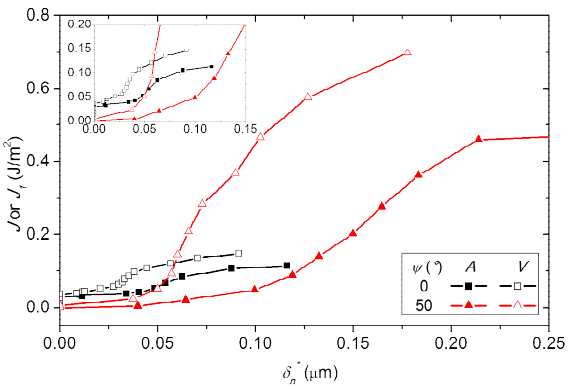

Fig. 2: Variation of J-integral with end opening displacement at phase angles of 0 and 50° for ambient and vacuum cured samples.

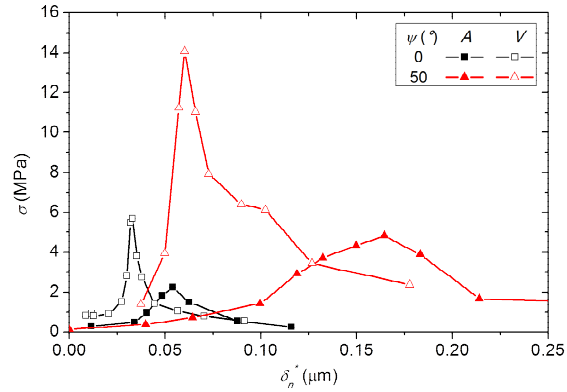

Fig. 3: Normal traction-separation relations at phase angles of 0 and 50° for ambient and vacuum cured samples.

CONCLUSIONS

We have been able to deposit high quality SAMs of a 10-undecylenic acid and 10-undecylenic N-(2-(dimethylamino)ethyl amide on smooth Si(111) surfaces of silicon strips. These were brought together and bonded, possibly via ion pairing between the carboxyl and amine end groups. The specimens were separated in instrumented wedge and mixed-mode tests under ambient and high vacuum conditions, where the NCOD were used to extract traction-separation relations associated with air and vacuum cured sandwiches. Interesting differences were noted and discussed.