Electronic Supplemental Information for:

Mechanisms of criticality in environmental adhesion loss

Christopher White,^{a,*} Kar Tean Tan,^{a,‡} Donald Hunston,^a Kristen Steffens,^a Deborah Stanley,^a Sushil K. Satija,^b Bulent Akgun,^{b,‡} and Bryan D. Vogt^{c,*}

1. Analysis of failure of joints

The failure surfaces from the shaft loaded blister test were analysed to determine the failure mechanism (adhesive vs. cohesive). Figure S1 illustrates the ATR-FTIR spectra for the four polymers examined. The control samples provide a baseline for understanding the differences between each polymer and the glass substrate. There is a clear peak in the spectra for all of the polymers near 1800 cm⁻¹, which does not appear in the spectrum for the glass substrate. Thus the presence of a peak at 1800 cm⁻¹ for the failure surface (this is the glass substrate side of the failure) indicates that significant polymer remains on the substrate after failure, which is consistent with a cohesive failure mechanism. For the glass substrate, there is an intense peak near 1050 cm⁻¹ that can be used to determine if glass is present near the failure surface. At low RH, the spectra for all the polymers are consistent with cohesive failure mechanism, but the surface from the PMMA and PEMA specimens appears glass-like with no evidence for polymer remaining in the spectra. In these cases, the failure mode is determined to be adhesive.



Figure S1. ATR-FTIR spectra for (left) control samples, (center) substrate surface after failure in a dry environment, and (right) substrate surface after failure in a wet (~100 %RH) environment.

As the sensitivity of FTIR for monolayers of residual polymer is limited, XPS is also used to assess the loci of failure in the PMMA, PEMA, and PBMA specimens as illustrated in Figure S2. The spectrum at the top of each panel is the glass control, while the bottom spectrum is the polymer control; note the presence of two peaks at binding energies less than 100 eV for the glass control that are not present in the polymer controls, while there is a sharp peak associated with carbon 1s binding at approximately 285 eV. These two features provide a route to distinguish between cohesive (carbon signal) and adhesive (silicon signal) failure. For PMMA below the critical RH, the failure is cohesive as the XPS spectrum is consistent with PMMA as shown in Figure S2A. However at 68.5 % RH and greater, the failure is adhesive as the XPS spectrum is consistent with glass. For PEMA (Figure 2B), a similar behaviour is observed, but the carbon signal at 85 % RH is slightly enhanced. We believe this to be due to adventurous carbon, but irrespective the failure at high RH appears to be predominately adhesive for both PMMA and PEMA. The XPS spectra illustrate a difference for the PBMA (Figure S2C), where all failure surfaces appear to be predominately PBMA, which is consistent with cohesive failure.



Figure S2. XPS survey scans of the substrate side failure after adhesion tests for (A) PMMA, (B) PEMA, and (C) PBMA. The reference spectra for the polymer and glass are shown in each pane.

A shaft-loaded blister test (SLBT) using a screw-driven Instron tensile-testing machine at a cross-head displacement rate of 5 μ m/s was used to determine the adhesive fracture energy, G_c , from the load based equation:

$$G_C = \left(\frac{1}{16\pi^4 Eh}\right)^{\frac{1}{3}} \cdot \left(\frac{P}{a}\right)^{\frac{4}{3}} \tag{1}$$

where P is the load, a is the crack length, E is the Young's modulus and h is the total thickness of the composite layer. The modulus of individual composite layers was estimated using the rule of mixture:

$$E = \sum_{i=0}^{i} \upsilon_i E_i \tag{2}$$

where E_i and v_i are the modulus and volume fraction of the *i*th component, respectively. Joints were tested in triplicate at each relative humidity. The ability of the SLBT to determine the adhesive fracture energy requires accurate measures of the load, and the crack length. At high adhesive fracture energy, there can be issues with the SLBT when the adhesive fracture energy is greater than the tear strength of the polymer film. To overcome this limitation, a Kapton film cap was used to prevent rupture of the polymer film from the probe. In this case, the crack advances in a stick slip non-uniform manner due to the failure at the crack tip as illustrated by the characteristics sawtooth profile in Figure S3a and S3b. This non-uniform crack front leads to greater uncertainty in the actual crack length. At low relative humidity (<50 % RH), the determination of the adhesive fracture energy is more uncertain. The peak values of the load provide the force required for the onset of crack growth and the average of these values was used to determine the value of G_c . In these cases, locus of joint failure was always cohesive through the polymer layer. In this RH range, moisture does not significantly impact G_c . As the system approaches and exceeds the critical relative humidity, the force required to separate the film from the surface drops significantly (Figure S3c and S3d) and the crack front becomes uniform and circular. The constant crack front progression is also evident, which decreases the uncertainty in G_c .



Figure S3. Raw data from the shaft loaded blister test of applied load, *P*, versus crack length, *a*, for PMMA at (a) 0 % RH, (b) 50 % RH, (c) 68.5 % RH, and 70 % RH. Note the change from slip stick (a-b) to stable fracture as the critical humidity is passed.

2. Neutron reflectivity

The neutron reflectivity data are fit with a recursive model that describes the structure of the joints in terms of 3 distinct layers: polymer, silicon oxide, and silicon. The silicon is modelled as a semi-infinite slab with a NSLD of 2.1×10^{-6} Å² with a roughness of < 5 Å and absorption coefficient of 1.02×10^{-10} Å⁻¹. The model fit parameters for the polymer and silicon oxide are shown below in Table S1 for PMMA and Table S2 for PBMA. There are small differences in the NSLD of the silicon oxide due to the process associated with growing the thin thermal oxide.

D ₂ O	Polymer				Silicon oxide			
activity	NSLD	Thickness	Roughness	Abs.	NSLD	Thickness	Roughness	Abs.
	(10^{-6} Å^2)	(Å)	(Å)	(10 ⁻⁹ Å ⁻¹)	(10^{-6} Å^2)	(Å)	(Å)	(10 ⁻⁹ Å ⁻¹)
0	1.0637	683.8	17.0	30	3.749	88.6	9.6	0.062
0.308	1.0904	680.6	18.7	30	3.749	89.6	11.0	0.062
0.380	1.1078	678.2	18.2	30	3.749	90.2	10.3	0.062
0.478	1.1162	679.3	17.6	30	3.749	90.2	11.2	0.062
0.536	1.1246	680.8	17.7	30	3.749	90.2	10.5	0.062
0.612	1.1291	678.6	19.3	30	3.749	90.5	10.7	0.062
0.623	1.1492	678.8	17.8	30	3.749	90.9	10.8	0.062
0.654	1.1495	679.9	18.7	30	3.749	91.0	10.1	0.062
0.698	1.1447	677.8	18.8	30	3.749	91.3	10.6	0.062
0.755	1.2628	698.1	25.5	30	3.749	90.8	10.5	0.062
0.794	1.2649	695.0	17.8	30	3.749	90.9	13.8	0.062
0.847	1.2622	691.5	14.1	30	3.749	91.5	14.0	0.062

Table S1. Fit parameters for the PMMA film as a function of D₂O activity.

Table S2. Fit parameters for the PBMA film as a function of D₂O activity.

D_2O	Polymer				Silicon oxide			
activity	NSLD	Thickness	Roughness	Abs.	NSLD	Thickness	Roughness	Abs.
	(10 ⁻⁶ Å ²)	(Å)	(Å)	(10 ⁻⁹ Å ⁻¹)	(10 ⁻⁶ Å ²)	(Å)	(Å)	(10 ⁻⁹ Å ⁻¹)
0	0.45937	746.7	31.2	82.6	3.6762	90.0	7.8	0.062
0.308	0.48195	750.4	31.6	82.6	3.6762	91.0	8.1	0.062
0.478	0.48714	751.3	31.8	81.7	3.6762	91.4	8.5	0.062
0.624	0.49017	753.3	31.8	81.7	3.6762	91.6	8.5	0.062
0.755	0.4915	753.2	32.6	49.7	3.6762	91.7	9.0	0.062
0.930	0.5210	756.8	38.3	19.4	3.6762	92.3	9.6	0.062

Figure S4 illustrates the NSLD profiles for the NR data shown in Figure 4. In this case, the polymer-air interface is defined as the zero distance. At negative distance, the NSLD is essential zero as the density of atoms in the vapour is very small. The first layer with a positive NSLD is the polymer. Due to the negative NSLD associated with ¹H, the NSLD for the PMMA is greater than that for the PBMA. Exposure to D₂O vapour increases the NSLD for the polymer due to the large NSLD of D₂O ($3.3 \times 10^{-6} \text{ Å}^2$). Then the silicon oxide is encountered at larger distances. The NSLD of the silicon oxide is intermediate to the polymer and D₂O, so accumulation of D₂O at the interface can lead to an apparent increase in the thickness of the silicon oxide layer. Finally, the NSLD decreases to the silicon.



Figure S4. NSLD profiles obtained from recursive fits of the NR data for (a) PMMA and (b) PBMA films in the dry (red) and hydrated (blue) states. The inset illustrates the change in the NSLD near the polymer-silicon oxide interface.

As the concentration of elements is directly related to the NSLD, the volume fraction of components at interfaces can be calculated. The thermal oxide layer is not atomically smooth with the SiO2-polymer interface approximately 1 nm thick. As the two components at the interface are known, the volume fraction of silica (ϕ_{SiO2}) can be determined as:

$$\phi_{SiO_2} = \frac{NSLD_{polymer} - NSLD_{measured}}{NSLD_{polymer} - NSLD_{SiO_2}}$$

Figure S5 illustrates the profile obtained using this expression on the right axis. The distance is reset to the midpoint of the SiO₂polymer interface as zero with the polymer to the right in the graphic. This SiO₂ profile is then used to calculate the water profile by assuming that the volume fraction of SiO₂ at a given distance remains constant. This water profile is illustrated by the blue line in Figure S5. Note that the water concentration goes through a maximum near the SiO₂-polymer interface. This behaviour is due to the convolution with the SiO₂ concentration that is not swollen by D₂O. Far from the interface, a constant concentration of water is obtained, which is defined as the bulk concentration as determined by the NSLD. Near the SiO₂-polymer interface, the excess water content is defined.



Figure S5. Illustration of the extracted compositional profiles obtained from the fits of the reflectivity data. The excess concentration and bulk concentration of D_2O in the films can be obtained from the profiles.

Figure S6 illustrates the dependence of the water concentration near the SiO_2 -polymer interface on the activity of D_2O . The excess at the interface grows as the activity is increased. Note that the maximum concentration is greater for the PMMA (Figure S6a) at activity of 0.82 than that for the PBMA at a higher activity (0.93).



Figure S6. Influence of D_2O activity on the interfacial water concentration in (a) PMMA and (b) PBMA as determined from neutron reflectivity.

3. Adhesive tests for joints with poly(n-propyl methacrylate)

The adhesive performance of PMMA and PEMA as a function of RH appear to be quite similar, but the behaviour for PBMA is significantly different. To test the hypothesis that the elastic moduli of the polymer is important to assess the susceptibility to humidity, we examine poly(n-propyl methacrylate), PPMA. The T_g of this polymer is near room temperature and the elastic moduli is significantly less than that for PMMA or PEMA. Figure S7a illustrates a comparison between PPMA and PMMA for G_c as a function of RH. At low RH, G_c for PMMA is on average slightly greater than that for PPMA, but not outside of experimental uncertainty. Near RH = 60 %, G_c of PMMA drops precipitously by almost a full order of magnitude, which is representative of the critical RH behaviour. For PPMA, there is a more gradual decrease in G_c between 60 % and 80 % RH, but extent of the decrease is significantly less. Additionally, the failure for the PPMA is always primarily cohesive irrespective of RH. Figure S7b compares PPMA to PBMA. In this case, G_c of the PPMA is significantly more impacted by RH, but at high RH G_c appears to nearly identical for PPMA and PBMA. This behaviour is consistent with the proposed mechanism for critical RH.



Figure S7. Impact of humidity on the strength of an adhesive joint consisting of poly (n-propyl methacrylate) (PPMA) at a glass interface in comparison to both (a) PEMA and (b) PBMA. Note that G_c remains above 60 J/mm² at near 100 % RH for PPMA and there is no precipitous drop in strength generally observed at a critical relative humidity for either PPMA or PBMA.