

# Enhanced Interfacial Toughness of Thermoplastic–Epoxy Interfaces Using ALD Surface Treatments

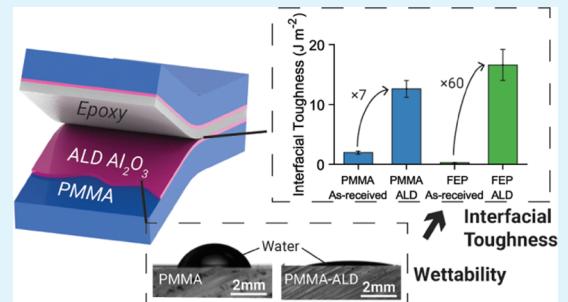
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## Supporting Information

**ABSTRACT:** Interfacial fracture and delamination of polymer interfaces can play a critical role in a wide range of applications, including fiber-reinforced composites, flexible electronics, and encapsulation layers for photovoltaics. However, owing to the low surface energy of many thermoplastics, adhesion to dissimilar material surfaces remains a critical challenge. In this work, we demonstrate that surface treatments using atomic layer deposition (ALD) on poly(methyl methacrylate) (PMMA) and fluorinated ethylene propylene (FEP) lead to significant increases in surface energy, without affecting the bulk mechanical response of the thermoplastic. After ALD film growth, the interfacial toughness of the PMMA–epoxy and FEP–epoxy interfaces increased by factors of up to 7 and 60, respectively. These results demonstrate the ability of ALD to engineer the adhesive properties of chemically inert surfaces. However, in the present case, the interfacial toughness was observed to decrease significantly with an increase in humidity. This was attributed to the phenomenon of stress-corrosion cracking associated with the reaction between  $\text{Al}_2\text{O}_3$  and water and might have a significant implication for the design of these tailored interfaces.

**KEYWORDS:** adhesion, interfacial toughness, atomic layer deposition, vapor-phase infiltration, polymers



## INTRODUCTION

Thermoplastics, such as poly(methyl methacrylate) (PMMA) and fluorinated ethylene propylene (FEP), have widespread applications in consumer products, structural components, biomedical devices,<sup>1</sup> and electronics.<sup>2</sup> In many of these applications, formation of an adhesive bond between the thermoplastic and a dissimilar material surface is crucial. For example, in aerospace and space applications, thermoplastic–epoxy interfaces play a critical role in toughening the bulk composite.<sup>3</sup> However, for an adhesive to wet and bond effectively to a surface, the surface energy of the substrate must be equal to or higher than the surface energy of the adhesive.<sup>4</sup> Common thermoplastics have surface energies of  $\sim 20\text{--}45\text{ mJ m}^{-2}$ ,<sup>5</sup> which are lower than the surface energies of polymeric adhesives, such as epoxies ( $\sim 45\text{--}50\text{ mJ m}^{-2}$ ).<sup>6</sup> Therefore, to improve adhesion, there is a need for new methods to increase the surface energy of thermoplastics without changing their bulk properties.

Several pretreatment methods have been developed to increase the surface energy of polymers. For example, nanofabrication techniques have been used to introduce surface structuring.<sup>7</sup> Chemical treatments have also been explored, including soaking the polymer in a solution of reactive molecules,<sup>8</sup> exposing the surface to solvents,<sup>9</sup> and grafting the surface with a monomer.<sup>10</sup> Plasma treatments have also been applied to a variety of polymers, including polydimethylsiloxane (PDMS), Kapton, and polypropy-

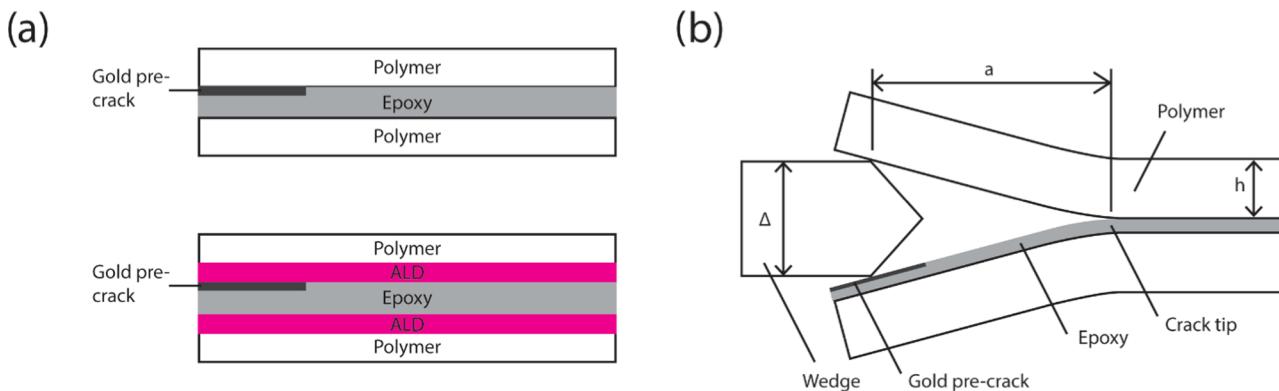
lene.<sup>11–13</sup> Plasma treatment of PMMA has been shown to introduce cross-linking on a subsurface layer of 150 nm or thicker, thus increasing its surface energy.<sup>14,15</sup> Flame treatment can also enhance adhesion by reorienting oxygen containing functional groups near the surface.<sup>16</sup> Additionally, mechanical treatments, including grit blasting,<sup>9</sup> can be used to improve wettability of polymer surfaces.<sup>9</sup> However, many of these approaches lead to undesirable changes in either the bulk properties or surface roughness of the polymer, motivating the search for new methods to decouple surface chemistry from the morphology and bulk response of the underlying material.

An alternative method to increase the surface energy of polymers is atomic layer deposition (ALD) of metal–oxide thin films.<sup>17–19</sup> ALD is a modified chemical vapor deposition technique based on sequential exposure of gas-phase reactants that exhibit self-limiting surface reactions. Ideal ALD processes deposit films in a layer-by-layer fashion, providing sub-nanometer control of film thickness.<sup>20</sup> ALD is also known for creating conformal, pin-hole free films over large areas or high-aspect-ratio substrates.<sup>21</sup> Moreover, several ALD processes are feasible at low temperatures, allowing for ALD on low-melting-point materials such as polymers. For instance, deposition temperatures as low as 33 °C have been reported

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**Figure 1.** (a) Schematic illustration of DCB samples before testing, with and without ALD interlayers. (b) Geometric parameters used in the wedge test, including crack length,  $a$ , wedge thickness,  $\Delta$ , and beam thickness,  $h$ .

for ALD  $\text{Al}_2\text{O}_3$ , which is below the glass transition temperature for many polymers.<sup>22</sup>

Unlike the ideal ALD model described above, when ALD is performed on certain polymers, gas-phase reactants can diffuse into the polymer, causing subsurface reactions and entrapment within the polymer chains.<sup>23,24</sup> This has led to the development of a range of vapor-phase polymer treatments that fall within the category of vapor-phase infiltration (VPI).<sup>23,25,26</sup> In VPI processes, the subsurface region forms an interphase that is often composed of a hybrid between the organic substrate and the inorganic ALD film. Since VPI processes depend on several concurrent processes, including diffusion, adsorption, and chemical reactions, they are highly dependent on the selection of both the polymer and ALD precursor and can be influenced by temperature and exposure time.<sup>23,27–29</sup>

In this work, we demonstrate that ALD surface treatments can be applied on PMMA and FEP to increase interfacial toughness when bonded to an epoxy, which corresponds with an increase in surface energy. Cross-sectional transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to characterize the film morphology, and sessile drop tests were used to measure the surface energies before and after ALD. The interfacial toughness of the polymer-epoxy interfaces was measured in the double-cantilever-beam (DCB) geometry. After ALD surface treatment, the interfacial toughness of the PMMA–epoxy interface increased by 7 times and the interfacial toughness of the FEP–epoxy interface increased by 60 times in a dry environment. Furthermore, as the ambient humidity increased, the interfacial toughness decreased, which is a common characteristic of adhesive interfaces on metal oxides.

## EXPERIMENTAL SECTION

**Atomic Layer Deposition (ALD).** Polymer substrates were cut from extruded sheets of PMMA (Acrylite FF) and FEP (Teflon FEP 100). Before any treatment, the PMMA and FEP samples were thoroughly cleaned by sonication in water and rinsing in solvents (further details in the *Supporting Information, SI*). ALD was performed in a Savannah S200 (Veeco/Cambridge Nanotech Inc.). Trimethylaluminum (TMA) and water were evaporated at room temperature as the precursors. The carrier gas was ultrahigh purity argon flowing at 10 sccm. During film growth, each precursor was pulsed into the chamber for  $t_1$ , then the chamber was closed for  $t_2$  to allow the precursor to diffuse onto and partially into the substrate, and finally the chamber was purged with argon for  $t_3$  to remove the excess precursor. For the TMA half cycles,  $t_1$ ,  $t_2$ , and  $t_3$  were 0.1, 10, and 45 s, respectively. For the water half cycles,  $t_1$ ,  $t_2$ , and  $t_3$  were 0.02, 10, and

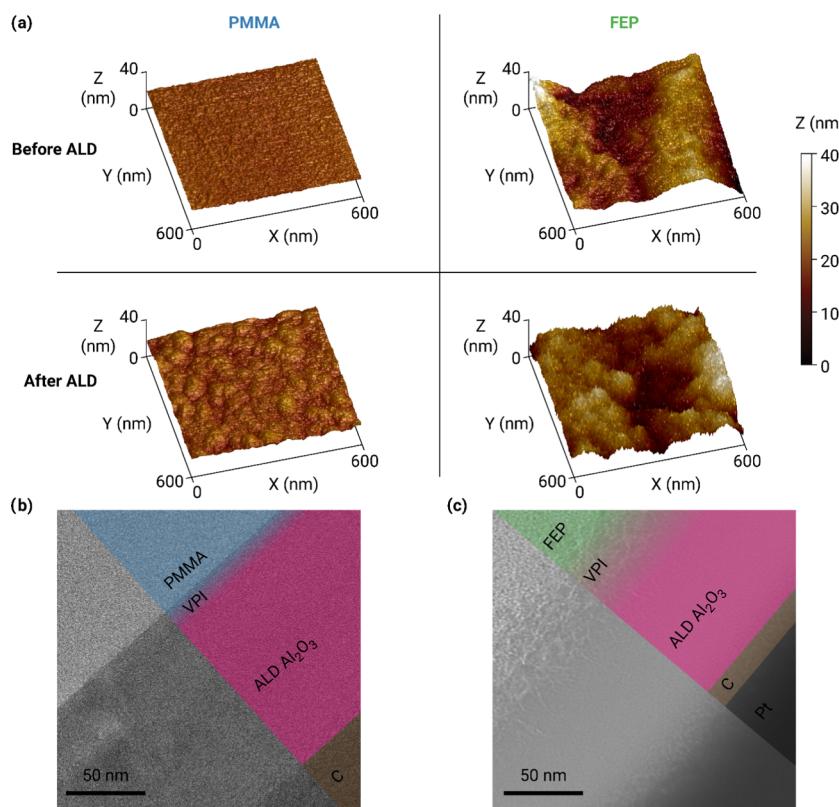
45 s, respectively. During the holds, carrier gas was constantly flowing at 5 sccm, as we do not have a valve to isolate the mass flow controller from the chamber. Therefore, the total pressure constantly rose in the range of 1–5 torr during the exposure. The substrate temperature was maintained at 65 °C for PMMA samples and 74 °C for FEP samples. A total of 750 cycles were performed for both polymers.

**Material Characterization.** AFM measurements were performed using a Veeco Dimension Icon atomic force microscope. Cross-sectional transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 probe-corrected analytical electron microscope after a lift-out procedure with a focused ion beam (FIB). Spectroscopic ellipsometry was conducted with a Woollam M-2000. A Kratos Axis Ultra with a monochromated Al source was used for X-ray photoelectron spectroscopy (XPS) analysis. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) was performed inside a TESCAN MIRA3 FEG-SEM.

**Sessile Drop Test.** Sessile drop tests on as-received, cleaned, vacuum-annealed, and ALD-treated samples were conducted to measure the surface energies. Contact angles were measured between the polymers and water, glycerol, hexadecane, ethylene glycol, and octane. All contact angle measurements are provided in *Tables S1* and *S2*. Surface energies were calculated using relationships derived by Van Oss et al.,<sup>30</sup> and liquid surface energies were used from Preston et al.<sup>31</sup> (further details in the *SI*).

**Fabrication of Double-Cantilever-Beam Samples.** The double-cantilever beam (DCB) samples consisted of two identical polymer beams bonded by an epoxy layer (Figure 1a). Each beam was 25.4 mm wide, 76.2 mm long, and 2.38 mm thick. Before applying the epoxy, a 30 nm-thick gold film was deposited onto one of the beams using e-beam evaporation through a shadow mask. The purpose of this film was to form a pre-crack at a known interface with a defined length of 25 mm. For ALD-coated samples, the pre-crack was deposited after ALD. The adhesive was a two-component epoxy (EPO-TEK 353-ND). To control the thickness of the epoxy layer, 23–26  $\mu\text{m}$  soda-lime glass beads (Cospheric) were mixed into the epoxy (further details in the *SI*). The DCB sample was clamped and cured at 60 °C for 2 h and then at 80 °C for 35 min. The four sides of the cured samples were polished with 320, 600, and 1200 grit silica papers to remove any epoxy overflow.

**Measurement of the Interfacial Toughness.** The interfacial toughness of the DCB samples was measured in the wedge test configuration (Figure 1b). The wedge was a razor blade that was 230  $\mu\text{m}$  thick ( $\Delta$ ). To initiate the test, the wedge was inserted along the pre-crack. The poor adhesion of the gold to the polymer allows it to delaminate from the polymer once the wedge was inserted. The wedge was controlled by a stepper motor that pushed it into the DCB at 2  $\text{mm s}^{-1}$ , for a total travel length of 4 mm. Top-down digital photographs were captured periodically, beginning within 2 s after the wedge insertion. From each image, the area of the crack was measured and the crack length was defined as the crack area divided by the width of the sample (Figure S1). The time stamp for each image was



**Figure 2.** (a) AFM scans of PMMA and FEP substrates before and after ALD surface treatment. Cross-sectional TEM analysis of (b) PMMA-ALD and (c) FEP-ALD samples, indicating the location of the VPI interphases. The colored regions on (b) and (c) are added to label each layer. These samples were treated with the same ALD procedure as the samples used for DCB fabrication.

used to calculate the crack speed. The test was conducted with a constant crack mouth opening displacement ( $\Delta$ ), so the energy-release rate,  $\mathcal{G}$ , decreased as the crack propagated.

As shown in Figure 1b,  $h$  is defined as the thickness of the polymer beam,  $a$  is the length of the crack from the contact point of the DCB with the wedge to the crack tip between the polymer and epoxy, and  $\Delta$  is the thickness of the wedge. The energy-release rate,  $\mathcal{G}$ , was calculated as

$$\mathcal{G} = \frac{\Delta \bar{E}}{h \left[ 8 \frac{a^3}{h^3} + 16.2 \frac{a^2}{h^2} + 10.9 \frac{a}{h} + 3.66 \right]} \left[ 12 \frac{a^2}{h^2} + 16.2 \frac{a}{h} + 5.45 \right] \quad (1)$$

where  $\bar{E} = E/(1 - \nu^2)$  for plane strain,<sup>32</sup>  $E$  is the Young's modulus of the polymer beam, and  $\nu$  is Poisson's ratio, which were measured separately (further details in the SI). To determine the interfacial toughness,  $\Gamma$ ,  $\mathcal{G}$  was plotted as a function of crack velocity (Figure 4).  $\Gamma$  is reported as the energy-release rate where the crack reached equilibrium.

## RESULTS

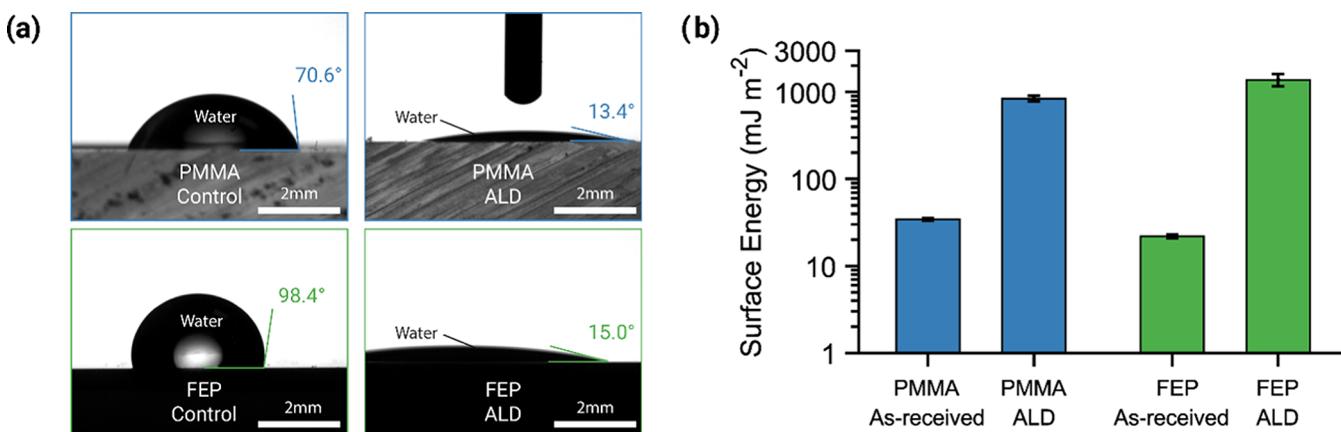
As shown by the AFM images in Figure 2a, the ALD treatments did not significantly increase the surface roughness of the polymers. The RMS roughnesses of PMMA before and after ALD treatment were  $1.5 \pm 0.8$  and  $1.9 \pm 1.8$  nm, respectively. The RMS roughnesses of FEP before and after ALD treatment were  $18 \pm 10$  and  $19 \pm 7$  nm, respectively. The surface composition of both polymers after ALD treatment was confirmed by XPS to be Al<sub>2</sub>O<sub>3</sub> with an O/Al ratio of 1.5 (Figure S2). We note that it has been previously reported that the hydrogen content in Al<sub>2</sub>O<sub>3</sub> films also increases at low temperatures.<sup>22</sup> This demonstrates the potential of ALD to

modify surface chemistry without significantly affecting the morphology.

ALD treatment resulted in an Al<sub>2</sub>O<sub>3</sub> film on the polymer surfaces and VPI interphases between the film and bulk polymer, as shown by cross-sectional TEM analysis (Figure 2b,c). Prior works for ALD on polymers have shown that during the initial cycles, subsurface modification can occur until a dense surface layer forms.<sup>19,20,23,28,33,34</sup> The extent of subsurface modification can depend on a number of variables including temperature, exposure time, precursor selection, and polymer chemistry.

For the PMMA sample, the interface between the ALD and polymer appeared abrupt. Cross-sectional TEM indicated that the surface layer on PMMA was 130 nm thick (Figure 2b), while the film thickness on a silicon substrate in the same ALD run was only 110 nm. Therefore, despite the abrupt appearance of the interface between the PMMA and ALD, this discrepancy suggests that subsurface modification may have occurred in the PMMA sample. This is consistent with previous observations of ALD growth of Al<sub>2</sub>O<sub>3</sub> using TMA and water as precursors on PMMA, where the initial cycles experienced a larger mass uptake before steady-state ALD growth was observed.<sup>27,33</sup> STEM-EDS analysis further demonstrates that Al is not present deeper within the polymer and is confined to the region shown (Figure S3). We note that a range in the degree of VPI into PMMA using TMA as a precursor has been reported in the literature, which depends on process variables including temperature, time, and pressure.<sup>23,27–29</sup>

In contrast, the FEP sample indicates a very clear VPI interphase (Figure 2c) between the ALD and polymer. This



**Figure 3.** (a) Sessile water drop tests before and after ALD treatments. (b) Surface energies are calculated from contact angles with multiple liquids (further details in the *SI*).

interphase region resembles an organic–inorganic hybrid composite. A previous work on ALD  $\text{Al}_2\text{O}_3$  growth on polytetrafluoroethylene (PTFE) observed a similar growth mechanism where subsurface  $\text{Al}_2\text{O}_3$  particles formed during the initial cycles before a continuous film was developed on the surface.<sup>35</sup>

The difference in VPI morphology on PMMA and FEP could be attributed to the distinct functional groups of the two polymers. For PMMA, the carbonyl groups on the polymer chains form covalent bonds with TMA upon exposure to the precursor.<sup>36–38</sup> These carbonyl reaction sites are abundant in PMMA, which could explain the more homogeneous nature of the interphase compared to FEP. In contrast, FEP has no functional groups that react with TMA. Therefore, subsurface growth relies on physical entrapment of the TMA precursor, which reacts with water in the subsequent pulse to nucleate  $\text{Al}_2\text{O}_3$  regions within FEP.<sup>20,23</sup>

Although ALD treatment did not significantly change the surface roughness of PMMA and FEP, it dramatically increased the surface energy of the polymers.<sup>17–19,39</sup> As shown in Figure 3a, ALD decreased the water contact angles for both polymers, from  $70.6 \pm 1.8$  to  $13.4 \pm 1.0^\circ$  for PMMA and from  $98.4 \pm 1.0$  to  $15.0 \pm 0.5^\circ$  for FEP. As shown in Figure 3b, the decrease in contact angles corresponds to an increase in the surface energy of PMMA from  $34.5 \pm 1.0$  to  $844 \pm 63 \text{ mJ m}^{-2}$  after ALD and an increase in the surface energy of FEP from  $21.9 \pm 1.1$  to  $955 \pm 224 \text{ mJ m}^{-2}$  (calculation details in the *SI*). These results agree with published surface energies of PMMA, FEP, and  $\text{Al}_2\text{O}_3$ , which were reported to be from  $30$  to  $45 \text{ mJ m}^{-2}$ ,<sup>40</sup> from  $16.9$  to  $22.7 \text{ mJ m}^{-2}$ ,<sup>41</sup> and  $880 \text{ mJ m}^{-2}$ ,<sup>42</sup> respectively. The surface energy of the polymers did not change after cleaning the samples or after annealing the samples in vacuum under the temperature at which ALD was performed (Tables S1 and S2), confirming that the change in surface energy was a result of the ALD treatment.

For a system of two materials bonded at an interface, the energy required for a crack to propagate along the interface is controlled by the interfacial toughness ( $\Gamma$ ). Previous works have explored the ability of ALD  $\text{Al}_2\text{O}_3$  to improve the interfacial adhesion of polymers using peel and pull-off tests.<sup>17,18</sup>

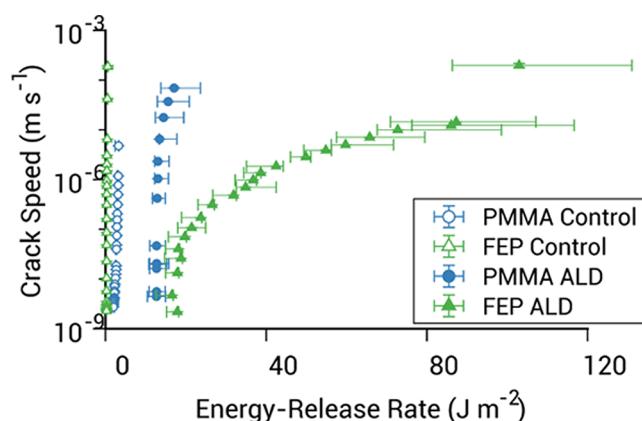
Here, we utilize the DCB measurement technique to quantitatively probe the effect of ALD  $\text{Al}_2\text{O}_3$  on interfacial toughness.

One of the many parameters that can influence the toughness of an interface between two materials is the work of adhesion ( $w_a$ ),<sup>43</sup> which can be described as

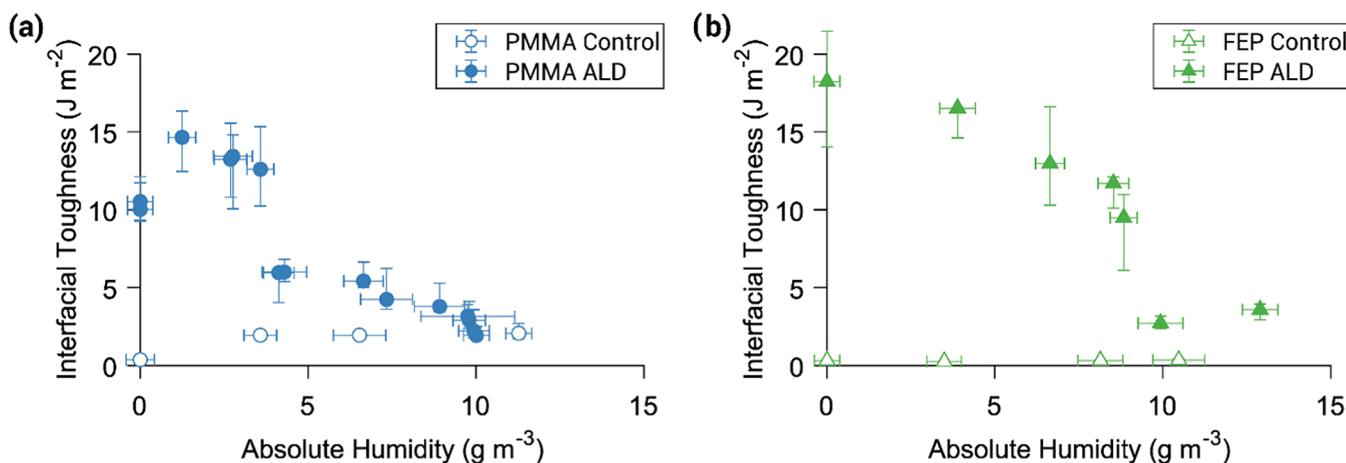
$$w_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (2)$$

where  $\gamma_1$  and  $\gamma_2$  are the surface energies of phase 1 (polymer or ALD-treated polymer) and phase 2 (epoxy), respectively,  $\gamma_{12}$  is the interfacial energy between phases 1 and 2.<sup>43</sup> Although the relationship between  $\Gamma$  and  $w_a$  is generally too complex to state in a simple form, often an increase in  $\Gamma$  may correlate with an increase in  $w_a$ . Of particular interest for the present paper is to note that an increase in  $\gamma_1$  results in an increase in  $w_a$  and is thus expected to also be associated with an increase in interfacial toughness.

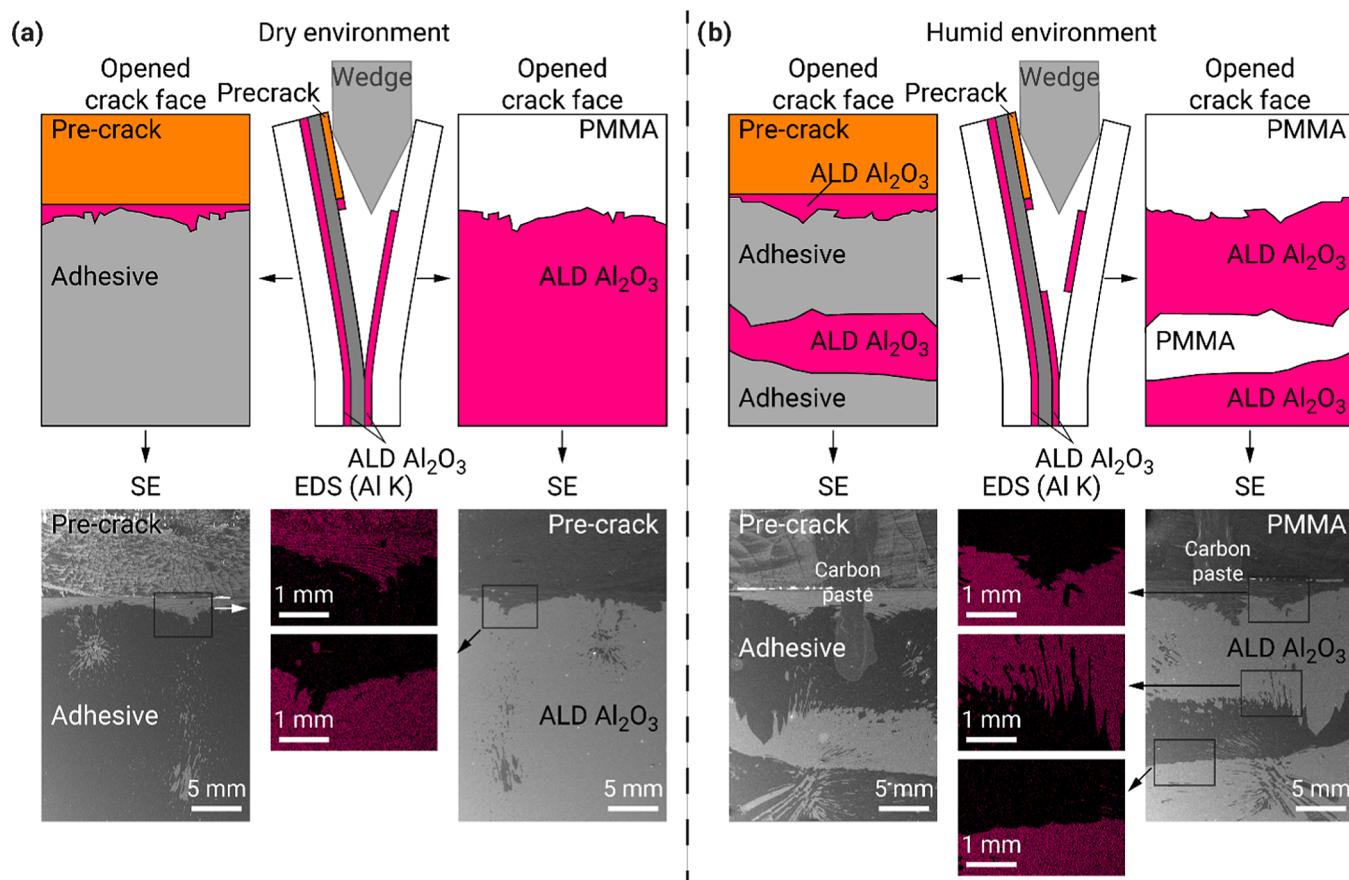
DCB measurements were performed on PMMA and FEP samples, with and without ALD treatment. After the insertion of the wedge, the crack length was observed to grow with time (Figure S4a). From the crack length at each moment in time, the energy-release rate was calculated according to eq 1 (Figure S4b). As the energy-release rate decreased, the crack speed also decreased, resulting in an apparent threshold for the energy-release rate below which the crack did not grow (Figure 4). This was taken to be the interfacial toughness ( $\Gamma$ ).



**Figure 4.** Crack speed vs energy-release rate. All samples were tested at  $3.5 \pm 0.5 \text{ g m}^{-3}$  absolute humidity. Error bars in all images correspond to the variations in crack length measurement within a single image, with average values reported according to the analysis shown in Figure S1.



**Figure 5.** Humidity dependence of interfacial toughness with and without ALD treatment for (a) PMMA and (b) FEP. Horizontal error bars indicate the standard deviation and precision error of absolute humidity during the steady-state phase of crack growth. All experiments were performed at  $22.7 \pm 0.6^\circ\text{C}$ .



**Figure 6.** Postmortem failure analysis of DCB inner-surfaces using SEM-EDS on ALD-treated PMMA that were tested at humidities of (a)  $1.3 \pm 0.4 \text{ g m}^{-3}$  and (b)  $9.9 \pm 0.5 \text{ g m}^{-3}$ . Schematic representations of the failure modes are presented above the SEM images for clarity. Carbon paste was applied to the sample to reduce charging.

After ALD treatment, the interfacial toughness of the PMMA–epoxy interface increased from  $1.95 \pm 0.26$  to  $12.6 \pm 1.4 \text{ J m}^{-2}$  and the interfacial toughness of the FEP–epoxy interface increased from  $0.25 \pm 0.03$  to  $16.6 \pm 2.6 \text{ J m}^{-2}$ . This represents an increase in interfacial toughness by a factor of 7 for PMMA and 60 for FEP relative to uncoated samples. Before ALD, the interfacial toughness of FEP was an order of magnitude lower than that for PMMA, which was consistent

with the lower surface energy of FEP (Figure 3b). In contrast, the difference in interfacial toughness between PMMA and FEP after ALD treatment was within a factor of 2, demonstrating the power of ALD to decouple surface chemistry from bulk properties. Moreover, to contextualize the observed results, the effect of an oxygen plasma pretreatment and a thinner ALD treatment with 250 ALD cycles was tested as a comparison (see the Supporting

Information). To confirm that the bulk polymer response after ALD treatment did not change, tensile tests were conducted on PMMA and FEP samples with and without ALD (Figure S5).

Interestingly, an increase in humidity generally degraded the toughness of the ALD-treated interfaces for both thermoplastics tested at  $22.7 \pm 0.6$  °C (Figure 5). The fact that the toughness decreased demonstrates that the effect of humidity was to decrease the toughness of the  $\text{Al}_2\text{O}_3/\text{PMMA}$  interface, rather than simply increasing the toughness of the  $\text{Al}_2\text{O}_3/\text{epoxy}$  interface. For FEP-ALD samples, interfacial toughness decreased monotonically with humidity (Figure 5b). In contrast, for FEP-control samples, interfacial toughness remained constant at  $0.32 \pm 0.06$  J m<sup>-2</sup> across all levels of humidity (Figure 5b). This demonstrates that the humidity dependence observed was directly caused by the ALD treatment.

For PMMA-ALD samples, the same trend of decreasing interfacial toughness with increasing humidity was observed at absolute humidity levels above  $1.2 \pm 0.4$  g m<sup>-3</sup>. At an absolute humidity level of  $10.0 \pm 0.4$  g m<sup>-3</sup> ( $50 \pm 3\%$  relative humidity at  $22.7 \pm 0.6$  °C), the interfacial toughness of PMMA-ALD sample decreased to a level that is close to the PMMA control sample. For PMMA control samples in this humidity range, interfacial toughness remained constant at  $1.9 \pm 0.2$  J m<sup>-2</sup> (Figure 5a). The exception to this trend occurred at an absolute humidity of  $0.0 \pm 0.4$  g m<sup>-3</sup>, where the interfacial toughness of both the PMMA-ALD and PMMA control samples decreased compared to nonzero humidity conditions (Figure 5a).

The decrease in interfacial toughness observed at zero humidity can be attributed to the plasticization effect of water on PMMA that can absorb 2.25% water at room temperature.<sup>44</sup> When the DCB samples were tested with the presence of water, water enhanced the plastic zone in front of the crack tip, which absorbs energy as the crack propagates. This energy dissipation reduces the amount of energy available for forming new surfaces and thus reduces the crack length at equilibrium, resulting in a higher interfacial toughness compared to PMMA in a zero humidity environment. Similar results have been observed for crack growth in PMMA.<sup>45</sup> Contrarily, FEP only absorbs 0.04% water even at 55 °C<sup>46</sup> and thus water cannot have significant plasticization effect on it. This is consistent with the result that for FEP-control samples, no change in interfacial toughness was observed at zero humidity.

To determine the crack path, postmortem analysis was performed using optical microscopy and SEM-EDS. An example of the edge view of a sample after wedge testing can be found in Figure S6. The crack path was further examined via SEM-EDS (Figure 6). In a dry environment (absolute humidity of  $1.3 \pm 0.4$  g m<sup>-3</sup>), crack propagation was observed to occur along the ALD/adhesive interface (Figure 6a), demonstrating that adhesive failure occurred between the ALD and epoxy. In contrast, for the ALD-treated PMMA in a humid environment (absolute humidity of  $9.9 \pm 0.5$  g m<sup>-3</sup>), the crack deflected along the  $\text{Al}_2\text{O}_3/\text{adhesive}$  interfaces on either side of the adhesive (Figure 6b), suggesting that the failure mechanism was affected by humidity. To demonstrate that this is reproducible, two samples were tested in a humid environment and two samples were tested in a dry environment and the observed phenomena were consistent within each set.

The fact that a strong humidity dependence on interfacial toughness was only observed in the ALD-treated samples demonstrates that the observed results were not due to changes in the bulk thermoplastic or thermoplastic–epoxy interface. The humidity-dependent crack growth is consistent with the fact that  $\text{Al}_2\text{O}_3$  is known to react with water in a stress-dependent manner by forming hydroxide species.<sup>47</sup> This effect is analogous to stress-corrosion cracking in bulk ceramics, where environmental species, such as water molecules, react with the ceramic bonds in the crack front tip, resulting in a decrease in fracture toughness in a humid ambience.<sup>47,48</sup> We also note that while the interfacial toughness of ALD-treated PMMA approaches that of the control samples at a high humidity, the ALD-treated FEP interfacial toughness remains 1 order of magnitude larger than the uncoated control. This points toward the need to consider humidity in design applications involving ALD-modified interfaces. For example, for the encapsulation of electronic devices, including solar cells, adhesive bounding to a thermoplastic is required. In particular, formation of adhesive bonds to encapsulation layers is required to protect the active layers from environmental species, such as water.<sup>49</sup>

## CONCLUSIONS

To overcome challenges with bonding to polymers, this work presents ALD as a strategy for increasing the surface energy of polymers. For ALD  $\text{Al}_2\text{O}_3$  on PMMA and FEP, VPI interphases were observed underneath the dense ALD  $\text{Al}_2\text{O}_3$  surface films by cross-sectional TEM. The ALD  $\text{Al}_2\text{O}_3$  film increased the surface energy of PMMA from  $34.5 \pm 1.0$  to  $844 \pm 63$  mJ m<sup>-2</sup> and the surface energy of FEP from  $21.9 \pm 1.1$  to  $955 \pm 224$  mJ m<sup>-2</sup>. After ALD film growth, the interfacial toughnesses of the PMMA–epoxy and FEP–epoxy interfaces in dry environments increased by factors of 7 and 60, respectively. These results demonstrate that ALD can modify the surface chemistry of relatively inert substrates such as polymers to improve wettability, adhesion, and interfacial toughness, without affecting their bulk mechanical response or surface roughness. However, the interfacial toughness of the ALD-treated interfaces in the present system showed a strong dependence on humidity. It is clear that the use of a metal oxides for these applications may cause significant sensitivity to ambient humidity, and this phenomenon of stress-corrosion cracking must be considered when designing such tailored interfaces.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b15193.

Experimental details; contact angle measurements; optical microscopy analysis; and bulk mechanical testing of polymers (PDF)

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

ALD, atomic layer deposition  
PMMA, poly(methyl methacrylate)  
FEP, fluorinated ethylene propylene  
PDMS, polydimethylsiloxane  
VPI, vapor-phase infiltration  
TMA, trimethylaluminum  
RH, relative humidity

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