THE ORIGIN OF CRITICAL RELATIVE HUMIDITY IN ADHESION

Christopher C. White, Dr., National Institute of Standards and Technology, Gaithersburg, MD
Kar Tean Tan, Dr., National Institute of Standards and Technology, Gaithersburg, MD
Bryan D. Vogt, Dr., Arizona State University, Tempe, AZ
Donald L. Hunston, Dr., National Institute of Standards and Technology, Gaithersburg, MD

Introduction

Adhesive bonds are susceptible to environmental attack by water, leading to significant depreciation in joint strength and subsequently to premature failures [1-6]. This susceptibility to moisture attack has been a subject of concern for many years, and there are many unanswered questions concerning the durability of adhesive joints in hostile environments, particularly the presence of sudden adhesion loss at a critical relative humidity. This has been a stumbling block for wider application of adhesives in load-bearing structures. Understanding the mechanics and mechanisms of adhesive joint degradation is a key factor for more extensive use in future engineering applications. The aim of the present study is to obtain a more complete understanding of mechanisms of moisture attack. Model adhesive joints consisting of homologous series of poly(n-alkyl methacrylate)s (PAMA) supported on SiO$_2$ substrates were studied. This polymer series enables subtle chemistry effects on moisture-induced adhesion loss to be examined. A fracture mechanics approach based on a shaft-loaded blister test was adapted to measure adhesive fracture energy of the joints over humidity extremes. Infrared spectroscopy and contact angle measurement were used to elucidate mechanisms of adhesion loss.

Experimental§

Materials

The substrate used was a 0.32 mm thick borosilicate glass with an 8 mm diameter hole bored through its center. Four different model adhesives were examined: poly(methyl methacrylate) (PMMA, $M_w = 120$ kg/mol, $T_g = 105$ ºC), poly(ethyl methacrylate) (PEMA, $M_w = 250$ kg/mol, $T_g = 63$ºC), poly(propyl methacrylate) (PPMA, $M_w = 150$ kg/mol, $T_g = 35$ ºC) and poly(n-butyl methacrylate) (PBMA, $M_w = 180$ kg/mol, $T_g = 15$ ºC). The chemical structures of these polymers are shown in Figure 1. The specimen was multi-layered and prepared as follows. First, a circular piece of pre-crack Kapton pressure sensitive adhesive tape (PSAT) having a 0.95 mm diameter and thickness of 25 μm was adhesively bonded to the substrate hole using a 3.75 μm thick acrylic pressure sensitive adhesive. A nominally 15 μm thick PAMA film consisting of 15 % mass fraction of PAMA in toluene was then spin-coated at a speed of 104.7 rad/s for 20 s over the glass substrate and the Kapton PSAT. On top of the poly(methacrylate), a 1.1 mL of Bisphenol-A (diglycidyl ether of bisphenol A, DGEBA) resin cured with 43 phr Jeffamine T-403 curing agent was spincast at 104.7 rad/s for 20 s. A 50 μm thick piece of Kapton E film was then placed on top of the uncured epoxy resin to act as a mechanical reinforcing layer for the poly(methacrylate) coating. The resulting adhesive layer was therefore a multi-layered composite consisting of the precrack Kapton PSAT, poly(methacrylate), epoxy resin and Kapton film. A schematic diagram of the multi-layered composite is shown in Figure 1.

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§Certain commercial products or equipment are described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.
illustration of the joint is shown in Figure 2. The layered composite was cured at room temperature for 48 h followed by curing at 60 °C for 1 h.

![Molecular structures of poly(n-alkyl methacrylate)s. For PMMA, n = 0; PEMA, n = 1; PPMA, n = 2; PBMA, n = 3.](image)

**Figure 1.** Molecular structures of poly(n-alkyl methacrylate)s. For PMMA, n = 0; PEMA, n = 1; PPMA, n = 2; PBMA, n = 3.

![Schematic of the shaft-loaded blister test joint (not to scale). The arrow indicates the direction of loading.](image)

**Figure 2.** Schematic of the shaft-loaded blister test joint (not to scale). The arrow indicates the direction of loading.

**Fracture-Mechanics Tests**
The joints were tested using a shaft-loaded blister test geometry on a tensile testing machine with a crosshead displacement rate of 5 μm/s. The adhesive fracture energy, $G_c$, was ascertained from the load-based equation [7]:

$$
G_c = \left(\frac{1}{16\pi^4 E h}\right)^{\frac{1}{3}} \left(\frac{P}{a}\right)^{\frac{4}{5}}
$$

(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 from the rule of mixtures:


\[ E = \sum_{i=0}^{n} v_i E_i \]  

(2)

where \( E_i \) and \( v_i \) are the modulus and volume fraction of the \( i \)th component, respectively. Prior to fracture testing, the joints were preconditioned at room temperature over a wide range of RH for 72 h. Three joints were tested at each RH and the error bars represent \( \pm 1\sigma \) from the mean value.

**Examination of Fracture Surfaces**

Fourier transform infrared spectroscopy (FTIR) was utilized to characterize the fracture surfaces. Reference spectra for the pure materials (glass substrate, PAMAs and epoxy) were used for comparison to the failure surfaces. Infrared analysis was carried out using a Nicolet Nexus FTIR Spectrometer equipped with a mercury-cadmium-telluride detector and a SensIR Durascopy attenuated total reflectance (ATR) accessory. Dry air was used as the purge gas. Consistent pressure on the specimens was applied using the force monitor on the Durascopy, and the sampling area was approximately 1 mm in diameter. All spectra were collected in the range from 650 cm\(^{-1}\) to 4000 cm\(^{-1}\) at a nominal resolution of 4 cm\(^{-1}\), and averaged over 132 scans. Five different locations on each specimen were analyzed.

**Contact Angle Measurement**

Contact angles of distilled water and diiodomethane were measured on glass substrates and PAMA surfaces using the sessile drop method, employing a Ramè-Hart A-100 goniometer. The thermodynamic work of adhesion in a dry environment, \( W_A \), and in the presence of moisture, \( W_{AL} \), for the PAMA/glass interface was calculated from these contact angle values [8].

**Neutron Reflectivity**

Specimens for neutron reflectivity (NR) were prepared on silicon wafers with a thermal oxide layer. This oxide layer mimics the glass utilized in the adhesion measurements. Thin films of PMMA and PBMA were spin coated on the silicon wafer. Contrast in neutron experiments is based upon the differences in neutron scattering length density, a quantity that is dependent upon nuclei details. Deuterium oxide (Aldrich, 99.9 % pure) was utilized to enable direct quantification of the water distribution within the film as a function of the partial pressure (humidity) of D\(_2\)O. NR measurements were performed at the Center for Neutron Research on the NG-7 reflectometer at the National Institute of Standards and Technology (Gaithersburg, MD) in the following configuration: wavelength (\( \lambda \)) = 4.768 Å and wavelength spread (\( \lambda/\Delta \lambda \)) = 0.025. NR is capable of probing the neutron scattering density at depths of up to several thousand Å, with an effective depth resolution of several Å. The reflectivity profiles were fit with a recursive algorithm to quantify the distribution of water within the polymer film.

**Results and Discussion**

The values of \( G_C \) over a wide range of RH for PMMA and PBMA are shown in Figure 3a. It is evident that there is a critical RH range between ca. 60 % RH and 68 % RH where the values of \( G_C \) decreased abruptly for the PMMA/glass joints; while such a critical range is absent for the PBMA/glass joints. The mechanism of moisture attack at these interfaces has been proposed to be a combination of bulk swelling induced stress and weakening of the interfacial bond by moisture accumulation at the polymer/substrate.
interface [3]. In this paper, it is of interest to examine the adhesion performance for dry (ca. 2 % RH) and wet (ca. 100 % RH) specimens, which are shown in Figure 3b. In the dry environment, the $G_C$ values for the PMMA/glass joint and the PEMA/glass joint were relatively high and statistically the same for both joints. Crack propagation was found to occur in a stick-slip manner. While the analogous stick-slip fracture mode was observed for the PPMA/glass joints, the $G_C$ value is lower than those for PMMA and PEMA/glass joints. The PBMA/glass joints exhibited significantly lower adhesion in comparison with the PMMA, PEMA, and PPMA/glass joints, which have comparable behavior.

In the wet environment, the values of $G_C$ for the PMMA/glass and PEMA/glass joints decreased substantially and a change from stick-slip fracture to stable fracture mode was observed. This clearly indicates the deleterious effect of high humidity. Further, the presence of a critical RH range for PEMA/glass joints is evidently shown in Figure 3b. Although a decrease in the value of $G_C$ for the PPMA/glass joint was observed, the extent of adhesion loss was not as significant as those seen in the PMMA and PEMA/glass joints. Also, it is noteworthy that the values of $G_C$ for the PBMA/glass in both the dry and wet conditions were statistically identical, indicating that the moisture did not impact the adhesion of this system. A stick-slip fracture mode was seen for both PPMA and PBMA/glass joints in the wet environment. Therefore, a critical adhesion loss is absent for the PPMA and PBMA/glass joints.

3 (a)
The failure location of the joint provides insight into the moisture degradation mechanism. Fracture surfaces were examined using ATR-FTIR spectroscopy to determine the locus of failure in the joints. In any assessment of the locus of joint failure, it is essential to establish the condition of the surfaces prior to the bonding process. Figures 4a through 4e show the spectra of fresh PMMA, PEMA, PPMA, PBMA and glass substrate, respectively. A comparison of these control spectra with Figure 5a and 5b (the glass failure surfaces for PMMA and PEMA/glass joints) shows that the spectra for the glass substrate of the fractured joints preconditioned under the dry condition appear to be similar to that of the polymer controls. This is an indication of cohesive failure within the adhesive layer. However, when exposed to the wet environment, interfacial failure was observed for these joints (cf. Figures 6a, 6b and 4e), which was accompanied by a substantial decrease in the values of $G_c$ as mentioned earlier. In the case of PPMA and PBMA/glass joints, cohesive failure was seen irrespective of RH (see Figure 4c, 4d, 6c and 6d). Work is currently on-going to examine the fracture surfaces using X-ray photoelectron spectroscopy.
Figure 4. ATR-FTIR control spectra for (a) PMMA, (b) PEMA, (c) PPMA, (d) PBMA and (e) glass substrate.

Figure 5. ATR-FTIR spectra for the glass failure surfaces for (a) PMMA/glass joint, (b) PEMA/glass joint, (c) PPMA/glass joint, and (d) PBMA/glass joint, preconditioned at 2 % RH.
There are two key questions to be answered from the above observations. First, why did the glass polymers which exhibited good adhesion strength in the dry environment perform poorly in the wet environment; second, why did rubbery polymers show no or little depreciation in the value of $G_C$ upon exposure to high humidity? It is known that increasing the length of the alkyl side chains tends to render the PAMA more hydrophobic. This is indeed observed in our prior measurements of bulk water uptake in several PAMAs with side chains varying from methyl to octyl groups using a quartz crystal microbalance [9]. The equilibrium moisture sorption in PMMA film is approximately 100% greater than that in PBMA film in nearly saturated humidity. In contrast to the increasing hydrophobicity with the alkyl chain length, the glass transition temperatures, $T_g$, of the PAMAs monotonically decrease from 105 ºC for PMMA to 15 ºC for PBMA. The $T_g$ is an indicator of the molecular mobility of the polymer, thus, a decrease in $T_g$ with increasing alkyl side chain length is attributed to increased molecular mobility and the ability to vary molecular conformations at the interface. The role of the surface functional groups and interfacial conformation in the wet adhesion loss may not be precluded. Therefore, there are two potential mechanisms in affecting the joint performance.

When the side chain becomes shorter, the surface energy of the PAMA increases. Thus, the more hydrophilic ester group may play a role in polymer/substrate adhesion. Strong adhesion at the PAMA/glass interfaces is a result of strong acid-base interaction between basic ester carbonyl groups of PAMA and acidic surface silanol groups on the glass via formation of hydrogen bonds. To examine the hydrolytic stability of the interfaces, the values of the thermodynamic work of adhesion in a dry environment, $W_A$, and in the presence of moisture, $W_{AL}$, for the different PAMAs were calculated and are shown in Table 1. The lower values of $W_{AL}$ in high humidity environment indicate that the interface is significantly weakened in the presence of moisture but is relatively stable, i.e., water can weaken the
adhesion but is not capable of displacing the adhesive layer from the substrate. The similarities in the $W_A$ and $W_{AL}$ values for the three PAMAs suggest that the alkyl side chain may not be a significant factor in adhesion to the glass substrate. This hypothesis is consistent with infrared-visible sum frequency generation (SFG) vibrational spectroscopic study revealing that the ester methyl group is slightly less hydrophobic than the ester butyl group [10].

<table>
<thead>
<tr>
<th>Types of interface</th>
<th>$W_A$ (mJm$^{-2}$)</th>
<th>$W_{AL}$ (mJm$^{-2}$)</th>
</tr>
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<tbody>
<tr>
<td>PMMA/glass interface</td>
<td>91 ± 2</td>
<td>7.0 ± 0.3</td>
</tr>
<tr>
<td>PEMA/glass interface</td>
<td>79 ± 1</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>PPMA/glass interface</td>
<td>83 ± 2</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>PBMA/glass interface</td>
<td>81 ± 2</td>
<td>5.0 ± 0.4</td>
</tr>
</tbody>
</table>

The water concentration profiles within the PAMA films in the dry and wet environments are measured using neutron reflectivity. This work is currently ongoing but some preliminary results obtained for PMMA and PBMA will be presented here. Figure 7 illustrates a typical moisture distribution for PMMA film conditioned at low RH. The volume fraction of D$_2$O ($\phi_{D2O}$) is enhanced near the glass interface. This excess concentration is quantified by the maximum in concentration above the bulk moisture content. Figure 8 illustrates the influence of polymer structure on the excess and bulk concentrations of D$_2$O. In the dry environment, the moisture distribution profiles are similar for PMMA and PBMA as would be expected. Additionally the bulk concentration of D$_2$O within the films decreases from PMMA to PBMA due to the increase in the hydrophobicity of the adhesive. However at high RH, there is a significant increase in the interfacial concentration of D$_2$O for PMMA relative to PBMA. This difference in interfacial concentration is unexpected based on previous studies involving glassy polymers that have demonstrated that the moisture distribution at a buried glassy polymer/glass interface is statistically independent of the polymer chemistry [11]. As the role of polymer chemistry on the interfacial adhesion is minimal based on the $W_A$ data, these results suggest that the different $T_g$ values could impact both the relationship between $G_C$ and RH, and the interfacial water content at interfaces. A SFG study showed that surfaces of PAMA with varying alkyl side chain lengths behave differently in water [10]. In air, the methyl group in ester chain of PBMA tends to tilt more towards the surface normal, but in water it lies closer to the surface. However, such surface restructuring is absent at the PMMA surface. Note that there is a potential constraint effect at the polymer/substrate interfaces but the relatively unrestricted molecular movement in the low-$T_g$ PBMA promotes molecular arrangement towards a thermodynamically stable molecular conformation such that the hydrophobic alkyl chains are closer to the interface. Therefore, the moisture-induced adhesion loss for these systems is governed predominantly by the relaxation behavior of the polymers, which in turn brings forth their hydrophobic effect on the interfacial adhesion. These may explain why rubbery polymers are able to suppress the accumulation of moisture at interface and thus, are more resilient to moisture attack.
Figure 7. Distribution of D$_2$O within PMMA film supported on a silicon wafer with a thermal oxide layer at a RH of approximately 50 %.

Figure 8. D$_2$O concentration profiles obtained for PMMA and PBMA at (top) low RH and (bottom) high RH.
Conclusions

The fracture behaviors of poly(n-alkyl methacrylate)s (PAMA)/glass joints were investigated using shaft-loaded blister tests over a range of relative humidity (RH). The presence of a critical RH where sudden adhesion loss took place was clearly evident for PMMA and PEMA/glass joints; while such a critical range was absent for the PPMA and PBMA/glass joints. Particular emphasis has been placed on elucidating mechanisms of moisture attack under dry (ca. 2 % RH) and wet (ca. 100 % RH) conditions. The adhesive fracture energy, $G_C$, was relatively high in the dry environment for the glassy PMMA and PEMA, and the predominant failure mode was cohesive, as indicated by attenuated total-reflection Fourier transform infrared spectroscopy. For the PPMA and PBMA/glass joints, the analogous cohesive failure was found to occur at relatively low $G_C$ values. In the wet environment, the $G_C$ decreased significantly for PMMA and PEMA and the predominant failure mode changed from cohesive to interfacial failure. Conversely, there was no or little depreciation in the values of $G_C$ for the PPMA and PBMA/glass joints in the wet environment. The fundamental mechanism governing the relationship of $G_C$ and RH for the different PAMAs appears to be related predominately to their rheological properties.

References

The Origin of Critical Relative Humidity in Adhesion

Christopher C. White, Ph.D., National Institute of Standards and Technology

Christopher C. White, Ph.D., M.B.A., joined NIST in 1997 as a National Research Council Postdoctoral Research Associate. In his present position as a research chemist, Dr. White is involved in a number of projects related to developing metrology for service life prediction of organic materials. He is leading a team of dedicated researchers who are investigating the role of acceleration on the degradation of elastomeric materials, such as building sealants.

Prior to joining NIST, Dr. White was honored by receiving a University of Connecticut/Institute of Materials Science Post-doctoral fellowship. He worked on the specific interactions between extender and matrix and the affects on the rheology of recycled plastic materials. Dr. White was awarded a Ph.D. from the University of Wisconsin in 1994. He also earned a Masters of Business Administration from the University of Maryland in 2007.

He can be reached at christopher.white@nist.gov.