

Impact of polymer chemistry on the durability of model adhesives supported on SiO_x substrates in humid environments using a homologous series of poly(n-alkyl methacrylate)s

K.T. Tan^{*1}, B.D. Vogt², C.C. White¹, D.L. Hunston¹, K. Hamilton¹, N. Wagman¹, J. Goldman¹, J.M. Torres², K. Steffens³, C. Clerici, S.K. Satija⁴ and J. W. Chin¹

¹Building and Fire Research Laboratory, ³Process Measurements Division, and ⁴Center for Neutron Research, NIST, Gaithersburg, MD; ²Department of Chemical Engineering, Arizona State University, Tempe, AZ.

**To whom correspondence should be addressed: kar.tan@nist.gov*

Introduction

Structural adhesives offer many advantages compared to traditional joining methods such as welding, bolting, mechanical fastening, etc. However, there are some issues that currently limit the wider application of adhesives. One of the most important issues is that there are still unanswered questions concerning the durability of adhesive joints in hostile environments [1]. Therefore, understanding the mechanics and mechanisms of degradation of adhesive joints is a key factor for more extensive use in future engineering applications. The aim of the present study is to develop a more complete understanding of mechanisms of moisture attack. Model adhesive joints consisting of a homologous series of poly(n-alkyl methacrylate)s (PAMA) supported on SiO_x 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 full details of the materials and preparation of joints are given elsewhere [2-4]. The substrate used was borosilicate glass. Specimens were fabricated from a commercially available homologous series of PAMAs with different molecular mass, M_w , and glass transition temperature, T_g , namely, PMMA ($M_w = 120$ kg/mol, $T_g = 105$ °C), PEMA ($M_w = 250$ kg/mol, $T_g = 63$ °C), PPMA ($M_w = 150$ kg/mol, $T_g = 35$ °C), and PBMA ($M_w = 180$ kg/mol, $T_g = 15$ °C). Preliminary results obtained from PMMA, PEMA and PBMA will be presented here. The chemical structures of these polymers are shown in Figure 1.

[§] 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. BDV and JMT acknowledge funding from NSF (CMMI-653989).

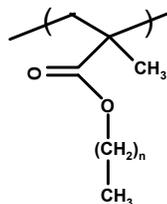


Figure 1. Molecular structures of PAMA. For PMMA, $n = 1$; PEMA, $n = 2$; PBMA, $n = 4$.

Testing and characterization techniques

The joints were tested using a shaft-loaded blister test geometry on a tensile testing machine with a crosshead displacement rate of 5 $\mu\text{m/s}$. Prior to fracture testing, the joints were preconditioned at room temperature either at 2 % relative humidity (RH) or at 100 % RH for 72 h. Three joints were tested at each RH and the error bars represent $\pm 1\sigma$ from the mean value. The loci of joint failure were determined using a Nexus 670 attenuated total-reflection Fourier transform infrared (ATR-FTIR) spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride detector. All spectra were collected between 650 cm^{-1} and 4000 cm^{-1} , and were averaged over 132 scans at a nominal resolution of 4 cm^{-1} . 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 were calculated from these contact angle values [2].

Results and Discussion

The values of G_C for dry (ca. 2 % RH) and wet (ca. 100 % RH) specimens are shown in Figure 2. 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. Fracture surfaces were examined using ATR-FTIR spectroscopy to determine the locus of failure in the joints. For control purposes, spectra of fresh PMMA, PEMA, PBMA and the glass substrate were also collected, as shown in Figures 3a through 3d, respectively. A comparison of Figures 4a and 4b with 3a and 3b 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. The values of G_C for these joints, however, decreased substantially at 100 % RH (see Figure 2) accompanied by apparent interfacial failure along the polymer/substrate interfaces (cf. Figures 5a, 5b and 3d). Work is currently on-going to examine the fracture surfaces using X-ray photoelectron spectroscopy.

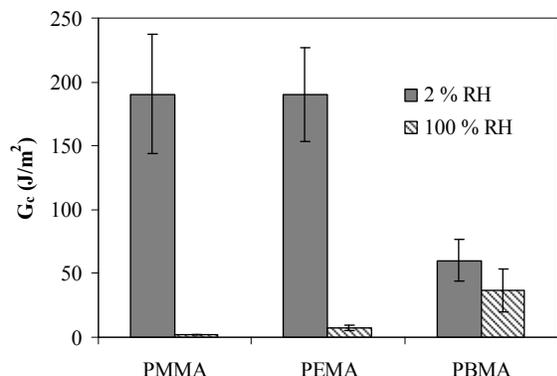


Figure 2. The fracture energy, G_C , for three different polymers on silica surfaces in dry and wet environments. Shaft-loaded blister tests were conducted at (23 ± 2) °C.

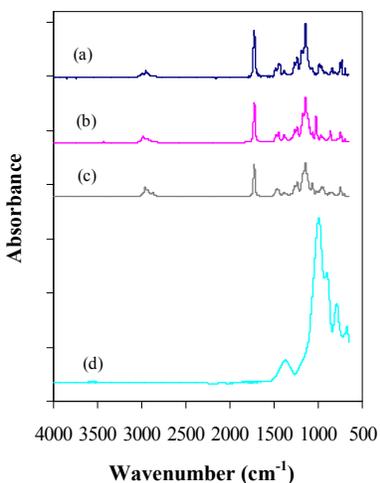


Figure 3. ATR-FTIR control spectra for (a) PMMA, (b) PEMA, (c) PBMA and (d) glass substrate. The spectrum and respective baseline are arbitrarily shifted for clarity.

In the dry environment, the PBMA/glass joints exhibit significantly lower adhesion in comparison with the PMMA/glass and PEMA/glass joints, which have comparable behaviour. However, the statistically identical values of G_C for the PBMA/glass in both the dry and wet conditions indicate that the moisture does not significantly impact the adhesion of this system. A stick-slip crack propagation mode was observed and cohesive fail-

ure was found for all PBMA/glass joints irrespective of humidity (see Figure 5c).

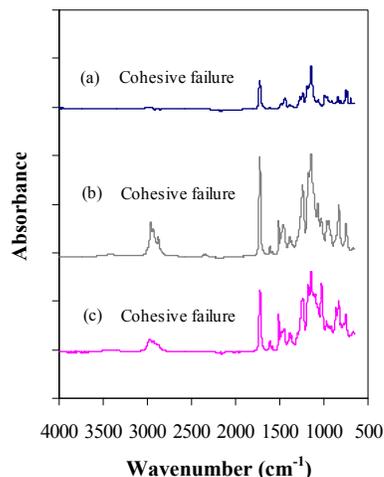


Figure 4. ATR-FTIR spectra for the glass failure surfaces for (a) PMMA/glass joint, (b) PEMA/glass joint and (c) PBMA/glass joint, preconditioned at 2 % RH.

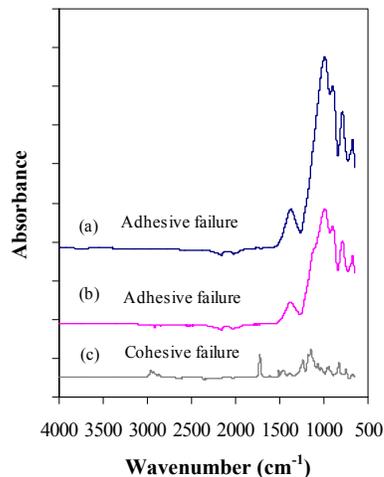


Figure 5. ATR-FTIR spectra of the glass failure surfaces for (a) PMMA/glass joint, (b) PEMA/glass joint and (c) PBMA/glass joint, preconditioned at ~ 100 % RH.

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 [2-4]. It is known that increasing the length of the alkyl side chains tends to render the polymer 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 [5]. 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 °C for PMMA to 15 °C 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. Thus, the role of the surface functional groups and interfacial conformation in the wet adhesion loss may not be precluded. This paper will focus on the relative importance of the effects of polymer chemistry and mechanical properties on the moisture-induced adhesion loss.

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 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 [6]. Additionally, based on neutron reflectivity measurements [7], the moisture distribution at a buried glassy polymer/glass interface is statistically independent of the polymer chemistry. However, a different result is observed for a series of PAMA/glass interfaces [4, 5], where it was observed that the total water accumulation at the interface is less for PBMA than PMMA. 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 previous SFG study showed that surfaces of PAMA with varying alkyl side chain lengths behave differently in water [6]. In air, the methyl group in ester chain of PBMA tend 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. These

results may explain why rubbery polymers are able to suppress the accumulation of moisture at interface and thus, are more resilient to moisture attack.

Table 1. W_A and W_{AL} for PAMA/glass interfaces.

	W_A (mJm ⁻²)	W_{AL} (mJm ⁻²)
PMMA/glass interface	91 ± 2	7 ± 0.3
PEMA/glass interface	79 ± 1	5 ± 0.3
PBMA/glass interface	81 ± 2	5 ± 0.4

Conclusions

The fracture behaviour of PAMA/glass joints under dry (ca. 2 % RH) and wet (ca. 100 % RH) conditions were investigated using shaft-loaded blister tests. 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 rubbery PBMA, the analogous cohesive failure was found to occur at an extremely low G_C . 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 difference between the wet and dry G_C values for the rubbery polymer (PBMA), and the locus of failure remained in the PBMA. The fundamental mechanism governing the relationship of G_C and RH for the different PAMAs appears to be related predominately to their mechanical properties.

References

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