

ADHESION AND DEBONDING OF A PRESSURE SENSITIVE ADHESIVE MEASURED WITH HYDROPHILIC AND HYDROPHOBIC PROBES UNDER AQUEOUS SOLUTION

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Abstract

We investigate the effect of an aqueous environment on the adhesion of a model acrylic pressure sensitive adhesive (PSA) composed of 2-ethylhexylacrylate-co-acrylic acid. We use probe-tack adhesion measurements accompanied by *in situ* imaging of the contact region during bonding and debonding. Within the probe-tack tests we use both hydrophilic (piranha and plasma treatment) and hydrophobic (C₁₈-silanization) surface treatments to investigate the contribution of probe's surface energy on the underwater adhesion. In examining contact formation in air and underwater we find that the presence of water when contact is made leads to different modes of PSA relaxation and contact formation. For all probes investigated the adhesive strength between the PSA and the probe decreases when measured underwater.

Introduction

We examine the adhesion of a model acrylic pressure sensitive adhesive with substrates of different surface energy under aqueous environment[1]. Our model PSA is composed of 2-ethylhexylacrylate-co-acrylic acid[2].

	M_n	M_w	M_p	\mathcal{D}
	g/mol	g/mol	g/mol	
PSA	286667	1199002	1175371	4

Table 1. Molecular weight result of selected PSA. Molecular weight result of selected PSA. Results are averages from duplicate injections. M_n = Number-average molecular weight, M_w = Weight-average molecular weight, M_p = Molecular weight at signal peak, \mathcal{D} = Dispersity = M_w/M_n (Previously known as polydispersity index). From[1].

Previous study has shown that the debonding mechanism of acrylic PSA changed on exposure to higher levels of humidity even though the maximum debonding force did not significantly vary [3, 4]. In particular, for a poly(butyl acrylate) pressure sensitive adhesive, total internal reflection infrared (IR) absorption and visible-IR sum-frequency spectroscopies revealed that acrylic acid causes changes in the orientation of butyl acrylate at surface due to favorable hydrogen bonding interactions with water[5]. As these studies suggest, aqueous environments have an effect on the pressure sensitive adhesive. A better understanding of mechanisms of bonding and debonding are required to further elaborate this effect to be able to design better adhesives[6].

Experimental

Probe-tack measurements[7] are performed using a custom-built MMFM instrument[8], on 2-EHA-co-AA acrylic PSA using glass probes that were either functionalized to be hydrophilic by piranha or

plasma treatment or hydrophobic by OTS silanization. The probe is brought into contact with the stationary PSA sample at 50 $\mu\text{m/s}$ until the cantilever applies a force of 10 mN. This force is maintained by the force-feedback loop for 100s after which the probe is detached at a velocity of 50 $\mu\text{m/s}$. Images are taken with a 5x microscope objective at a frame rate of 10 fps. Bonding[9-11] and debonding images[12, 13] are analyzed with the help of ImageJ and MATLAB softwares. Probe-tack tests in air and in water follow the same protocol, except for PSA being immersed in DI water (conductivity 18.2 M Ω) for tests in water. The pH of the DI water was not controlled and could vary from pH 8 to pH 6. All adhesion measurements are repeated three times for each lens treatment (plasma, piranha, and OTS) and for each environmental condition (in air, 5 min water immersion, and 60 min water immersion). Measurements are performed at room temperature and at less than 50% relative humidity. Fingering instability[14-17] images during debonding are analyzed to evaluate the in-situ surface energy of the PSA in air and in water. Supplementary experiments are performed to understand the wetting[18] and rheological properties[19, 20] of PSA. FTIR measurements[21-23] are also performed to investigate diffusion of water into the 25 μm thick PSA film.

Results and Discussion

The maximum stress and work of debonding are reduced in water for all probes, however immersion time has different effects if the probe is hydrophilic or hydrophobic. This decrease is more pronounced for hydrophilic probes at 5 min water immersion.

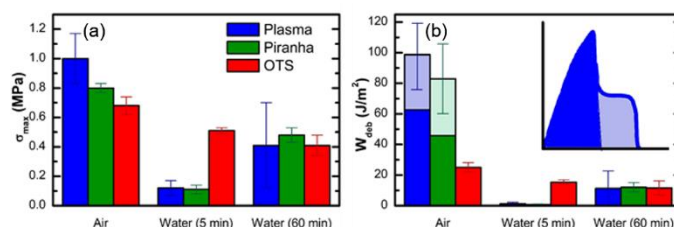


Figure 1. (a) Maximum debonding stress and (b) work of debonding of acrylic PSA in air and in water (5 min and 60 min immersion time). The glass probe is functionalized by Plasma, Piranha or OTS. For measurements in air with hydrophilic probe, lighter regions represent work associated with plateau formation as shown in the inset. From[1].

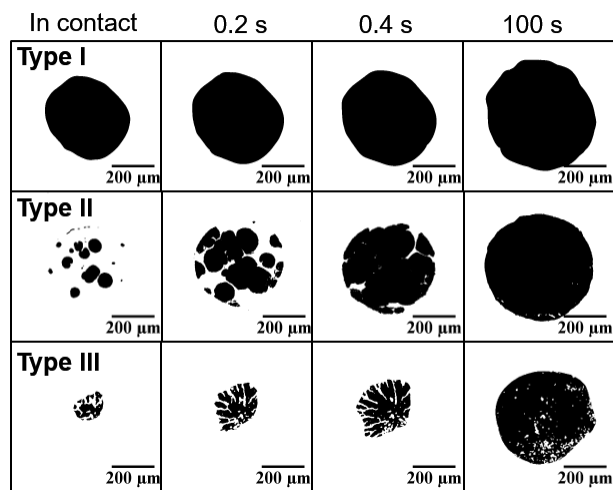


Figure 2. Bonding images of PSA showing three types of contact mechanisms. Type I is homogeneous contact formation. Type II has circular contact spots that merge with time. Type III shows dispersed contact that grows over time. From[1].

Contact images reveal three different types of contact mechanisms as shown in Figure 2. Bonding in air with any probe always results in Type I contact formation. Bonding in water with hydrophobic probe results in Type II contact formation. Bonding in water with hydrophilic probe can result in Type II or Type III contact formation. We also observe trapped water spots on bonding in water.

Looking at debonding images, we find that debonding in air occurs via fingering and cavitation. Debonding from a hydrophobic probe in water follows the same mechanism, however the debonding from hydrophilic probe in water can happen by external crack propagation.

Conclusions

Probe-tack measurements are performed using both hydrophilic (piranha or plasma treated probe) or hydrophobic (C-18 silanization) and are accompanied by in situ imaging of the contact region during bonding and debonding. We observe the presence of water on contact formation under aqueous environment. The adhesive strength between the probe and PSA decreased underwater for each surface. This is consistent with a decrease in van der Waals interactions[24] in water compared to in air. Bonding images reveals three types of contact formation. We suspect that trapped or adsorbed water is largely responsible for differences in contact in air and water. In-situ fingering image analysis suggest a large increase in the PSA-water surface energy, likely due to reorganization of the functional group at the PSA-water interface. The pH[25] of water was not controlled and could vary from 8 to 6 between 5 min and 60 min water immersion time. The change in adhesive strength over time in water could also be possibly due to a variation in pH.

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References

1. Karnal, P.; Roberts, P.; Gryska, S.; King, C.; Barrios, C.; Frechette, J., *Importance of substrate functionality on the adhesion and debonding of a pressure sensitive adhesive under water*. ACS Appl Mater Interfaces, 2017.
2. Czech, Z.; Kowalczyk, A.; Kabatc, J.; Świdorska, J., *Photoreactive UV-crosslinkable solvent-free acrylic pressure-sensitive adhesives containing copolymerizable photoinitiators based on benzophenones*. Eur Polym J, 2012. 48(8): p. 1446-1454.
3. Schindler, M.; Koller, M.; Muller-Buschbaum, P. *Pressure-Sensitive Adhesives under the Influence of Relative Humidity: Inner Structure and Failure Mechanisms*. ACS Appl Mater Interfaces 2015, 7, 12319-27
4. Moon, S.H.; M.D. Foster, *Influence of Humidity on Surface Behavior of Pressure Sensitive Adhesives Studied Using Scanning Probe Microscopy*. Langmuir, 2002. 18(21): p. 8108-8115.
5. Roy, S.; Freiberg, S.; Leblanc, C.; Hore, D. K. *Surface Structure of Acrylate Polymer Adhesives*. Langmuir 2017, 33, 1763-1768.
6. Tan, H. S.; Pfister, W. R. *Pressure-sensitive adhesives for transdermal drug delivery systems*. Pharm Sci Technolo Today 1999, 2, 60-69.

7. Creton, C.; Ciccotti M., *Fracture and adhesion of soft materials: a review*. Rep Prog Phys, 2016. 79(4): p. 046601.
8. Roberts, P., Pilkington G.A.; Frechette J., *A multi-mode force microscope for soft matter*. to be submitted.
9. Defante, A. P.; Burai, T. N.; Becker, M. L.; Dhinojwala, A. *Consequences of water between two hydrophobic surfaces on adhesion and wetting*. Langmuir 2015, 31, 2398-2406.
10. Nanjundiah, K.; Hsu, P. Y.; Dhinojwala, A. *Understanding rubber friction in the presence of water using sum-frequency generation spectroscopy*. J Chem Phys 2009, 130, 024702.
11. Wang, Y.; Tan M.R.; Frechette J., *Elastic deformation of soft coatings due to lubrication forces*. Soft Matter, 2017: p. DOI:10.1039/C7SM01061C.
12. Davis, C. S.; Lemoine, F.; Darnige, T.; Martina, D.; Creton, C.; Lindner, A. *Debonding Mechanisms of Soft Materials at Short Contact Times*. Langmuir 2014, 30, 10626-10636.
13. Lakrout, H.; Sergot P.; Creton C., *Direct observation of cavitation and fibrillation in a probe tack experiment on model acrylic pressure-sensitive-adhesives*. J Adhes, 1999. 69(3-4): p. 307-359.
14. Ghatak, A.; Chaudhury M.K., *Adhesion-induced instability patterns in thin confined elastic film*. Langmuir, 2003. 19(7): p. 2621-2631.
15. Nase, J.; Lindner A.; Creton C., *Pattern formation during deformation of a confined viscoelastic layer: From a viscous liquid to a soft elastic solid*. PRL, 2008. 101(7): p. 074503.
16. Saffman, P.G.; Taylor G., *The penetration of a fluid into a porous medium or Hele-Shaw cell containing a more viscous liquid*. Proc R Soc London A, 1958. 245: p. 312-329.
17. Paterson, L., *Radial fingering in a Hele Shaw cell*. J Fluid Mech, 1981. 113: p. 513-529.
18. Good, R.J., *Contact angle, wetting, and adhesion: a critical review*. J Adhes Sci Technol, 1992. 6(12): p. 1269-1302.
19. Deplace, F.; Carelli, C.; Mariot, S.; Retsos, H.; Chateauminois, A.; Ouzineb, K.; Creton, C. *Fine tuning the adhesive properties of a soft nanostructured adhesive with rheological measurements*. J Adhes 2009, 85, 18-54.
20. Creton, C.; Hooker J.; Shull K.R., *Bulk and interfacial contributions to the debonding mechanisms of soft adhesives: extension to large strains*. Langmuir, 2001. 17(16): p. 4948-4954.
21. Fieldson, G.; Barbari T., *The use of FTi. r.-atr spectroscopy to characterize penetrant diffusion in polymers*. Polymer, 1993. 34(6): p. 1146-1153.
22. Nguyen, T.; Bentz D.; Byrd E., *Method for measuring water diffusion in a coating applied to a substrate*. JCT, J Coat Technol, 1995. 67(844): p. 37-46.
23. Linossier, I.; Gaillard, F.; Romand, M.; Feller, J. *Measuring water diffusion in polymer films on the substrate by internal reflection Fourier transform infrared spectroscopy*. J Appl Polym Sci 1997, 66, 2465-2473.
24. Israelachvili, J.N., *Intermolecular and surface forces*. 2015: Academic press.
25. Wang, T.; Canetta, E.; Weerakkody, T. G.; Keddie, J. L., *pH dependence of the properties of waterborne pressure-sensitive adhesives containing acrylic acid*. ACS Appl Mater Interfaces, 2009. 1(3): p. 631-639.