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WORK OF ADHESION MEASUREMENTS OF SILICONE NETWORKS USING CONTACT MECHANICS

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INTRODUCTION

Work of adhesion, Wa, measurements are being studied for several types of polymer/metal combinations in order to obtain a better understanding of the adhesive failure mechanisms for systems containing encapsulated and bonded components. A primary concern is whether studies of model systems can be extended to systems of technological interest.

One study performed in our laboratory involved the determination of Wa between silicone (PDMS) and Al surfaces in order to establish potential adhesive failure mechanisms. Our initial work with PDMS was based on Dow Corning 170 Sylgard [1]. PDMS hemispheres were synthesized following the procedure outlined by Chaudhury and Whitesides [2] where the filler was stripped from the commercial silicone by centrifuging. Wa between PDMS surfaces was determined using the JKR method. Our results for the Wa of PDMS were in agreement with those reported by Chaudhury and Whitesides. However, further JKR studies using these PDMS hemispheres on flat Al surfaces were fraught with difficulty. We could not discriminate hydrogen-bonding effects between Al_2O_3 and hydroxyl groups in the PDMS and other possible bonding mechanisms. It was suggested that commercial systems contain inhibitors and additives that interfere with understanding the PMDS/Al interface.

Therefore, the current study uses pure PDMS networks synthesized in our lab. Also, two contact mechanics methods were deployed to measure the Wa – JKR method using two hemispheres and a LEFM method using a cylinder containing a circumferential crack. This paper contains a description of the synthesis of the PDMS used for these studies and the determination of Wa between PDMS surfaces using the JKR method, contact angle measurements, and a LEFM method that consists of a cylinder containing a circumferential crack.

EXPERIMENTAL

PDMS Synthesis

Model networks of poly(dimethylsiloxane) were synthesized by reacting vinyl-capped poly(dimethylsiloxane) with tetrakis(dimethylsiloxy)silane in the presence of a platinum catalyst. The use of the platinum – divinyltetramethyldisiloxane complex allowed the polymerization to proceed at room temperature without the formation of by-products. All reactants were used as received from Gelest Inc.

The procedure used to synthesize the PDMS networks is as follows. First, tetrakis (dimethylsiloxy)silane was added using an Eppendorf volumetric dispenser. With the amount of cross-linker fixed, a 0.75 stoichiometric amount of vinyl-capped PDMS (6000 g/mol) was added with a 3 ml syringe. The contents were then mixed thoroughly in an ice bath. Once the temperature was low enough to inhibit the reaction, approximately 150 ppm of platinum – divinyltetramethyldisiloxane complex was worked into the system. Solid PDMS cylinders were prepared by pouring the mixture into hollow polypropylene cylinders that were bound on the bottom by smooth Mylar® sheets. A second Mylar sheet covered the top of the cylinder once the contents were poured into the vessel. Hemispheres, which are used as the JLR lens, were prepared using a pipette. Drops of the mixture were placed on tridecaflro-1,1,2,2-tetrahydroctyl trichlorosilane treated glass surface. Although the mixture would fully solidify after 15 min at room temperature, an additional hour at 150°C was needed to complete the reaction.

Contact Angle Measurements

Water and hexadecane were used for contact angle measurements. Advancing and receding contact angles were measured using a sessile drop technique in a saturated vapor environment. The sessile drop technique involves dispensing a small drop on the PDMS surface using a microsyringe. The drop is advanced or receded

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by adding or removing liquid from the drop. ontact angles were measured using a contact angle goniometer. Reported contact angles are the average of at least ten measurements. Contact angles were converted to surface energies using the Good-Girifalco-Fowkes equation. In the absence of polar for forces the thermodynamic work of adhesion is: $Wa = 2 (\gamma_d \gamma_d)^{1/2}$.

JKR studies

Two hemispherical lenses were mounted into a custom built JRK apparatus. Measurements were made at 40 - 60 %RH. Loading and unloading measurements under done with an incremental change in displacement of 5 μm per step. The work of adhesion was determined by recording the contact radius as a function of contact load and using the JKR equation to fit the data:

$$a^3 = (R/K) \{P + 3\pi WR + [6\pi WRP + (3\pi WR)^2]^{1/2}\}$$

Where a is the contact radius, R is the effective radius of the lenses, P is the contact load, and W is the work of adhesion.

Cracked Cylinder Test

The samples consisted of two cylindrical sections of PDMS with their round bases placed in contact. Each half measured 16.44 mm in diameter by 8.64 mm in length. In between the two surfaces was placed a Teflon® ring with an inner diameter of 11.79 mm. Measuring only 0.01 mm in thickness, the Teflon® did not interfere with the mating of the two PDMS surfaces nor did it adhere to them to a significant degree. Because of the low modulus of PDMS, the crack opening displacements were typically larger than 0.01 mm. The presence of the ring was therefore a nonfactor in the loaded sample. The sample could then be loaded in tension, using a Rheometric Solids Analyzer, at a variety of strain rates. The strain rates chosen for these experiments were as follows: 10^{-5} s^{-1}, 10^{-4} s^{-1}, 10^{-3} s^{-1}, 10^{-2} s^{-1}, and 10^{-1} s^{-1}. All tests were performed after applying a pre-load of 20 N for one second to bring the samples together. Five measurements were performed for each strain rate, with a 5-minute rest period being taken in between each test to allow for the relaxation of any surface or bulk rearrangements that may have occurred during the previous test. Afterwards, the elastic modulus was determined for each strain rate in uniaxial compression to assist in the calculation of G_{IC} from K_{IC}. In the absence of plastic and viscoelastic loses $Wa = G_{IC}$.

RESULTS AND DISCUSSION

From the advancing contact angle measurements, the work of adhesion, W_a, was determined to be 47 mJ m^{-2}.

This value is slightly higher and may represent some swelling of the PDMS network. Our contact angle measurements took longer than the few seconds used by Chaudhury and Whitesides to avoid swelling. Literature values appear to cluster around 44 mJ m^{-2}.

The two hemispheres, approximately 2.2 mm diameter, were compressed (loaded) at 5 μm steps, held for 5 min before recording the force and area. The unloading (tension) data was collected in the same way, Figure 1 shows the hysteretic curve for a PDMS sample. The results are consistent with good PDMS samples: little hysteresis is observed, the value of Wa is near 44 and curve did not cross zero showing nearly idea behavior. A set of hemispheres was extracted with toluene for 24 hour at room temperature. The excess toluene was removed by heating at 100° for 1 hour. The experimental data are plotted in Figure 2. Hysteresis was observed at lower forces for the extracted PDMS sample. However, none was observed for nonextracted PDMS samples. Ulman's group [3] reports the same behavior. Their explanation for differences in hysteresis between extracted and nonextracted is -- entanglement of tethered chains and their interdigitiation with the extracted cross-linked PDMS networks at the interface are probably the dominating mechanisms.

As can be seen in Table 1, G_{IC}, critical strain energy release rate, measurements came surprisingly close to the literature value [2] for the work of adhesion of PDMS (44 mJ/m^2) at lower strain rates of 10^{-5} s^{-1} and 10^{-4} s^{-1}. Such close agreement to the literature value was not expected because of the many confounding variables involved in this experiment such as: surface aspirates, Teflon® adhesion, sample misalignment, elastic constraint, static charge, and interdiffusion. These were offset only by the low elastic modulus of the PDMS and the small strains experienced by the samples. At higher strain rates, G_{IC} approximately fits the common power law function of the strain rate, $K_{IC} \propto \dot{a}^n$, where a is crack growth rate.

More applicable to the current data is the equation proposed by Gent [4]:

$$G = G_0 (1 + \phi(a_T v))$$

where: G = strain energy release rate
G_0 = equilibrium work of adhesion
    a_T = WLF shift factor
    v = crack growth velocity
    ϕ = bulk viscoelastic loss function = $(v/v^*)^n$

n = experimentally determined exponent

Notice that the equation predicts a lower value for G, then rises as a power function. The same was found for the current data. The data fits the following form:

$$G_{IC} = 0.04196\left[1 + \left(\frac{\dot{\varepsilon}}{0.00476}\right)^{0.38}\right]$$

Thus for zero strain, G_{IC} is 42 mJ m^{-2} again close to the work of adhesion of PDMS (44 mJ/m^2). Although the data bears a superficial resemblance to the above relation, no direct comparisons can be made because the crack velocity was not being measured. Rather, the current study is focused on strains that occur orthogonal to the crack growth. Such strains are easier to compare with data that can be obtained from more common mechanical tests, such as dynamic mechanical spectra.

ACKNOWLEDGEMENT

REFERENCES

1. J. A. Emerson, E. O'Toole, D. Zamora, and B. Poon, 21st Annual Meeting of Society of Adhesion, 1998.
2. M. J. Chaudhury and G. M. Whitesides, Langmuir, 7, 1013 (1991).
3. G. Choi, S. Kim, and A. Ulman, Langmuir 13, 6333 (1997).
4. Gent, Langmuir 12, 4492 (1996).

Strain Rate s^{-1}	Modulus MPa	σ_f kPa	K_{IC} Pa m$^{1/2}$	G_{IC} mJ m^{-2}	Std. Dev.
1.00E-5	1.15	4.95	254	42.0	5.6%
1.00E-4	1.15	4.95	254	42.0	8.1%
1.00E-3	1.17	6.04	310	61.8	16.9%
1.00E-2	1.20	7.83	401	101.0	8.5%
1.00E-1	1.28	10.64	546	175.0	10.8%

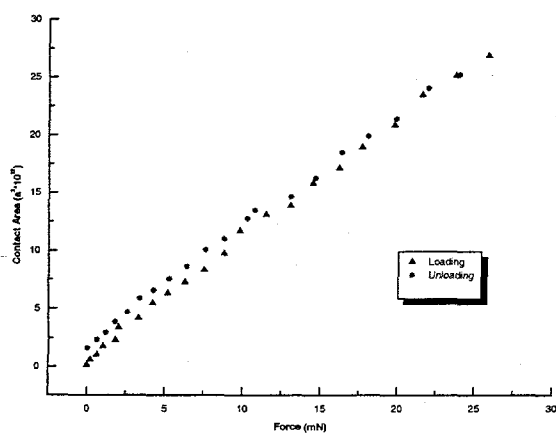**Table 1** PDMS Adhesion Data from LEFM Measurements

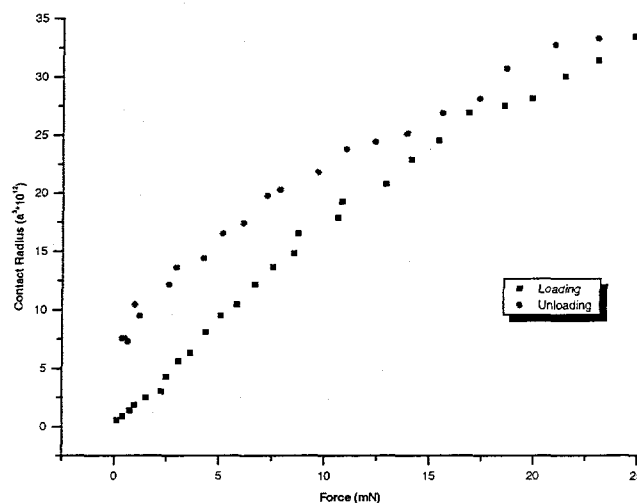**Figure 1** JKR Results of Two PDMS Hemispheres – Wa = 44.03, K= 6.48x10^5

Figure 2 JKR Results of Two Extracted PDMS Hemispheres – Wa = 44.01, K= 4.91x10^5

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