

COMPARISON OF THREE WORK OF ADHESION MEASUREMENTS

John A. Emerson, Edward O'Toole,
and David Zamora

Sandia National Laboratories
Department of Organic Materials
Albuquerque, NM 87185-0958

and

Benjamin Poon
Case Western Reserve University
Department of Macromolecular Science
Kent Hale Smith Building
Cleveland, OH 44106-7202

INTRODUCTION

Practical work of adhesion measurements are being studied of interest 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. The primary question is whether studies of model systems can be extended to systems of technological interest. We report on our first attempts to obtain the work of adhesion between a PDMS polymer and stainless steel. The work of adhesion measurements were made using three techniques - contact angle, adhesive fracture energy at low deformation rates [1,2], and JKR [3]. Previous work by Whitesides' group [4] show a good correlation between JKR and contact angle measurements for PDMS.

Our initial work focused on duplicating the PDMS measurements of Chaudury [4]. In addition, in this paper we extend the work of adhesion measurement to third technique - interfacial failure energy. The ability to determine the reversible work of adhesion for practical adhesive joints allows understanding of several issues that control adhesion: surface preparation, nature of the interphase region, and bond durability.

EXPERIMENTAL

The PDMS lens and films used in the contact angle and JKR measurements were made using Sylgard 170. The colorants and silica fillers were removed by centrifuging. The clear two part resins were mixed 1:3 (w:w) of part A and part B in a Teflon® crucible for 15 min at room temperature. The higher ratio of part B, the crosslinker, prevents blooming. Drops, used as the JLR lens, of the mixture were placed on tridecafluoro-1,1,2,2-tetrahydroctyl

trichlorosilane treated glass surface. The two semihemispherical lens were then mounted in a JKR apparatus that was constructed from a hybrid design of two different published apparatus [5,6]. The peel samples were made by bonding a 3M 5413 silicone backed Kapton® tape onto a 38 μm thick 304 stainless steel foil with dimensions 20 x 75 mm. This structure was secondarily bonded with an acrylic adhesive to a 200 μm thick Al plate. The 90° peel values were measured on a custom built apparatus allowing temperature ranges from 20° to 250° C and peel rates of 1 to 20 $\mu\text{m s}^{-1}$. Advancing contact angles were taken using a standard Ziman type goniometer using water and hexadecane as the probing fluids.

RESULTS AND DISCUSSION

From the contact angle measurements, the work of adhesion, W_a , was determined to be 42 mJ m^{-2} . As shown in Figure 1 from the JKR measurements, W_a is 44 mJ m^{-2} and $K=483\text{kPa}$ was determined from plotting the relationship $a^3 = 6\pi W_a R^2 K^{-1}$. There is no observable hysteresis from the loading and unloading operations, indicating nearly ideal behavior. Some overshoot occurs on the force axis and the curve does not cross the zero. These factors do not effect the calculated results because the values are calculated from the slope. The contact angles were measured in the saturated vapor of the probing fluid. The JKR measurements were made at 40 - 60 %RH. Because these two measurements were conducted at the same temperature but in different environments, the difference in the calculated values is likely to be due to the different equilibrium conditions.

The adhesive fracture energy, G , was obtained by peeling the silicone adhesive from 302 stainless steel. The peel angle was fixed at 90°. Thus G equals the experimental peel force (P), $G = P(1 - \cos \theta)$. Figure 2 shows G versus the peel rate at 23.4°C. Peel forces were determined for a series of rates, c , and temperatures. The data was reduced to an equivalent rate, $c \times a_T$, by the WLF equation: $\log a_T = -C_1(T - T_g)/(C_2 + T - T_g)$, where T_g is -45° for this material. The adhesive fracture energy, G , versus $c \times a_T$ is plotted in Figure 3. The adhesive energy can be separated into two multipliers, thermodynamic and viscoelastic. At lower value of $c \times a_T$, this viscoelastic term should be nearly one and G should be equivalent to W_a [1,2]. From our measurements, value of $G = 3.4 \text{ J m}^{-2}$ was determined at low viscoelastic conditions. This is a factor 100 higher than value determined from contact angle and JKR measurements. Several possibilities could explain the large differences: 1) A different silicone was

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

used for the the peel experiments because the thin bond lines of Sylgard 170 produced random results. It is common knowledge that thin structures of Pt catalysis, addition-cured silicones do not behave as a bulk structure. 2) Interfacial slippage and energy dissipation due to friction [7] could account for a 50% higher value of G at equilibrium conditions (low viscoelastic dissipation). From Figure 2, the value of G is 50 times larger than obtained by Newby and Chaudhury [7]. Part of this may be due to the differences in the adherent surfaces (stainless steel versus PDMS and fluorocarbon surfaces). 3) In experiments with modified SFA using silicones, equilibrium separation forces between two nearly perfectly contacted surfaces were 1000 times larger than predicted from W_a values [8].

Certainly, there are some interesting issues that need to be resolved in order to understand not only the results presented here, but other published work. This approach worked in correlating W_a values from contact angle and adhesive fracture energy measurements for rubbers and epoxies [1,2]. The unusual viscoelastic properties of PDMS-based silicones [8] may not allow true equilibrium measurements to be made with techniques involving the separation of surfaces .

ACKNOWLEDGEMENT

This work was performed at Sandia National Laboratories, which is supported by the United States Department of Energy under contract number DE-AC04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy. We thank Gary Jones for designing and constructing the JKR apparatus. Also, we thank Carol Jones Adkins for helpful discussions.

REFERENCES

1. E. H. Andrews, *J. Mater. Sci.*, **9**, 887 (1974).
2. A. N. Gent and A. J. Kinlock, *J. Poly. Sci.: Part A*, **9**, 659 (1971).
3. K. L. Johnson, K. Kendall, and A. D. Roberts, *Proc. R. Soc. Lond. A*, **324**, 301 (1971).
4. M. J. Chaudhury and G. M. Whitesides, *Langmuir*, **7**, 1013 (1991).
5. Deruelle, L. Leger, and M. Tirrell, *Macromolecules*, **28**, 7419 (1995).
6. P. Silberzan, S. Perutz, E. J. Kramer, and M. K. Chaudhury, *Langmuir*, **10**, 2466 (1994).
7. B. Z. Newby and M. K. Chaudhury, *Langmuir*, **13**, 1805 (1997).
8. M. Heuberger and J. Israelachvili, 1997 MRS Fall Meeting, Boston, MA, Symposium M2.3

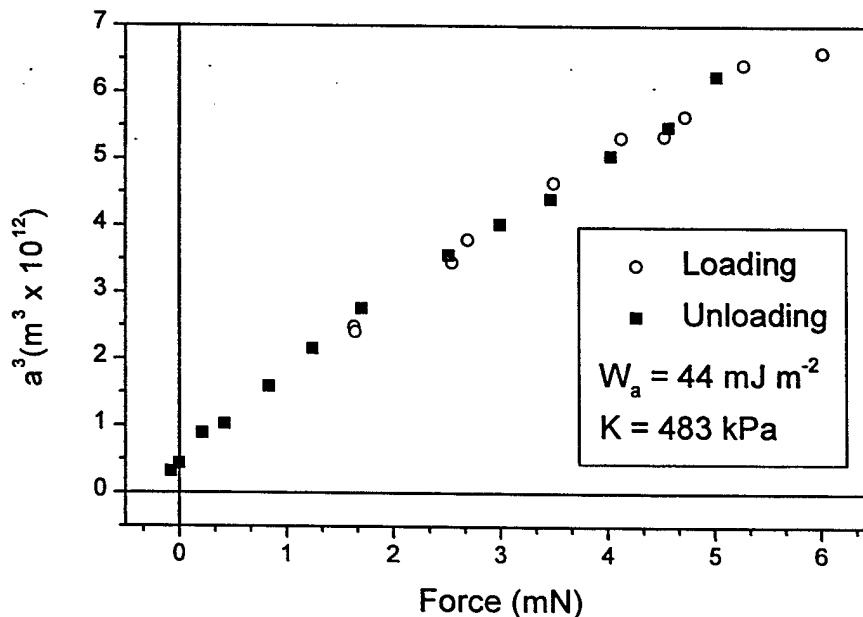


Figure 1 Plot of a^3 Versus the Contact Force for Two PDMS Hemispheres

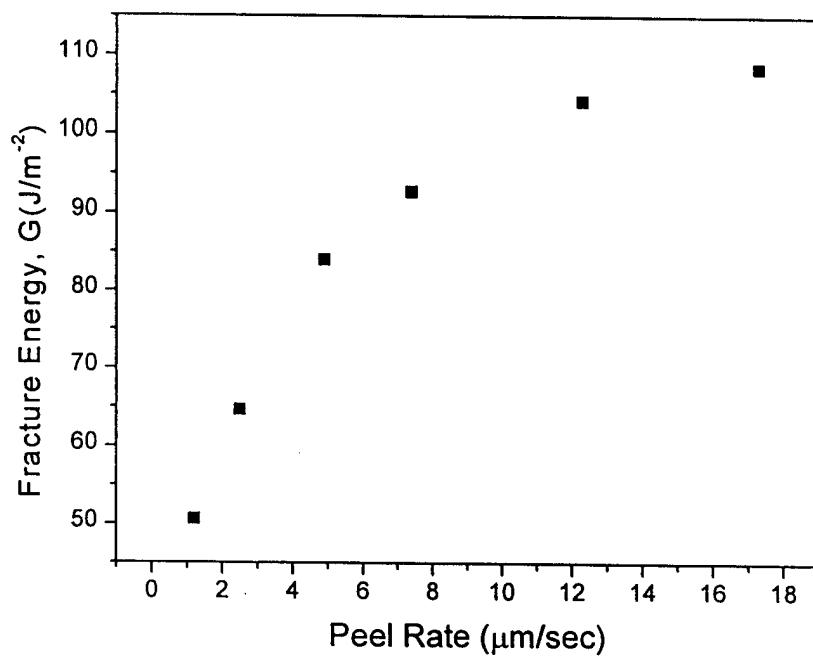


Figure 2 90°Peel of Silicone Adhesive on 302 Stainless Steel at 23.4°C for Various Peel Rates

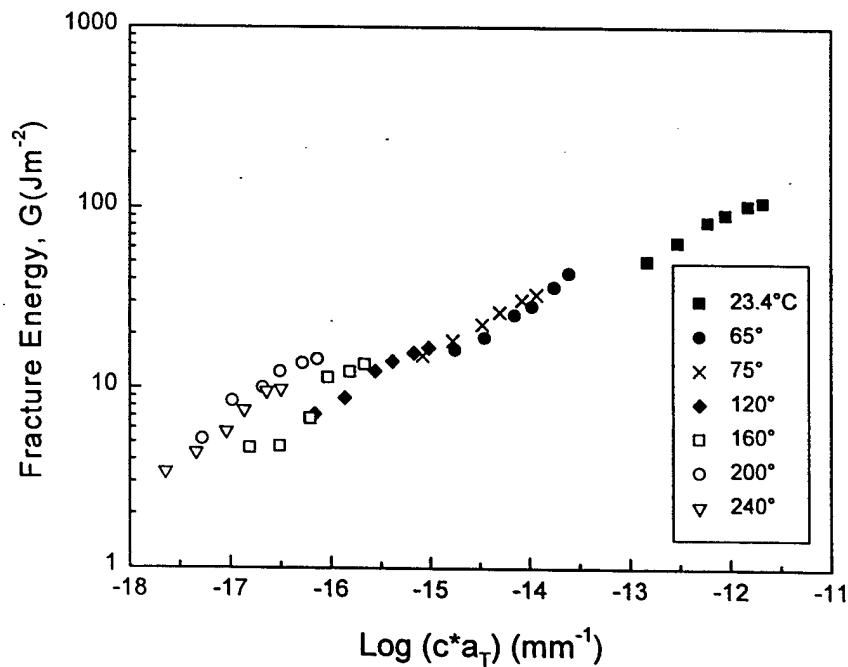


Figure 3 90°Peel of Silicone Adhesive on 302 Stainless Steel for Equivalent Rate of Peel

M98003341



Report Number (14) SAND--98-0617 C
CONF-980222--

Publ. Date (11)

1998 02

Sponsor Code (18)

DOE/CR, XF

UC Category (19)

UC-900, DOE/ER

DOE