

Multilayer Adhesives - Tuning Properties Using Bulk and Interfacial Contributions

Melinda Einsla¹, Bill Griffith¹, Dave Keely¹, Sipei Zhang¹, Qifeng Wang², and Ken Shull²

¹The Dow Chemical Company, 400 Arcola Road, Collegeville, PA 19426

²Northwestern University, Materials Science and Engineering Department, 2220 Campus Drive, Evanston, IL 60208

Introduction

Surface and Rheological Effects

The adhesive forces that we measure for pressure sensitive adhesives (PSAs) are the result of both interfacial energies as well as polymer rheology (or viscoelasticity). In the simplest case, let us consider the separation of two rigid materials (Figure 1). These materials, 1 and 2, start out by being in contact with one another, with an interfacial tension γ_{12} . After separation, that interface is destroyed and two new air interfaces are created with interfacial tensions (surface energies) represented by γ_1 and γ_2 .

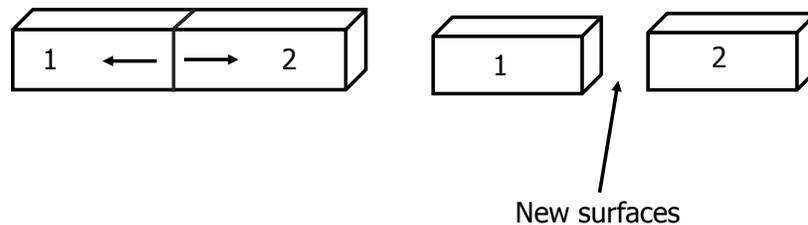


Figure 1: Separation of Two Rigid Materials, where the Interface is Destroyed and Two Air Interfaces are Created

Neglecting the viscoelastic component of a PSA, the work of adhesion can be described in terms of the Young-Dupre equation (Eq. 1).¹

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad \text{Equation 1}$$

Where W_A represents the work of adhesion, γ_1 and γ_2 are the surface energies of two new surfaces being formed during the breaking of an adhesive bond, and γ_{12} is the interfacial tension of the interface being destroyed. In an ideal case, γ_{12} can be neglected and Equation 1 reduces to:

$$W_A = 2\gamma \quad \text{Equation 2}$$

A typical surface energy for polymers would be around 35 dynes/cm (same as ergs/cm²). If the interfacial tension is assumed to be small, then the peel force for peeling an adhesive from a polymeric substrate should be on the order of 2.54 in/cm x 2 (sides) x 35 dynes/cm = 0.0018 Newton/in of peel force. The discrepancy between this value and the actual measured peel forces, which are typically several Newtons for PSAs, is mainly attributed to rheological effects. Taking this analysis at face value, it may seem like surface energetics do not contribute to the peel force. However, if there were no

interactions whatsoever, then the adhesive would release from the substrate before rheological effects could come into play. Stronger surface interaction permits greater rheological forces to be withstood before the adhesive releases from the substrate. In other words, a relatively weak force at an interface can be markedly amplified through rheological deformation processes. A more accurate way of describing work of adhesion where at least one of the materials is a viscoelastic polymer would therefore be:

$$W_A = 2\gamma + G_p$$

Equation 3

Where G_p is a term accounting for the energy dissipated in deforming the polymer, which is likely to be significant, especially at high deformation rates.^{2,3} From this it becomes clear that work of adhesion, and therefore measured peel forces, are the result of both interfacial and rheological effects.

Probe Tack Measurements

Probe tack (also known as indentation debonding test) is a standard measurement technique in PSA characterization, which allows for a quick and relatively simple method of measuring adhesion.⁴ In a probe tack measurement, a probe consisting of stainless steel, glass, or another material is brought into contact with an adhesive film, left there for a specified period of time, then pulled away. As the probe is brought into contact with the adhesive, the adhesive deforms and is pushed to the outer edge of the probe. Next, the probe is pulled away from the adhesive film and the adhesive is forced to deform as displacement increases. Finally, the adhesive detaches from the probe and the measurement is concluded. Traditional probe tack instruments record only the peak force as the probe is pulled away from the adhesive film. Alternatively, texture analyzers can be used in place of the traditional instrumentation, which allows the force to be recorded over the entire cycle rather than just the peak number. The forces measured during this test, particularly peak stress, are thought to be dependent on how the adhesive itself cavitates (forms voids) during the deformation.⁵ Cavitation occurs in order to relieve the hydrostatic pressure that builds as the adhesive is stretched resulting in the growth of existing defects or the formation of new ones.⁶ The probe tack measurement lends itself nicely to the use of a camera to observe the cavitation profile throughout the deformation (Figure 2).

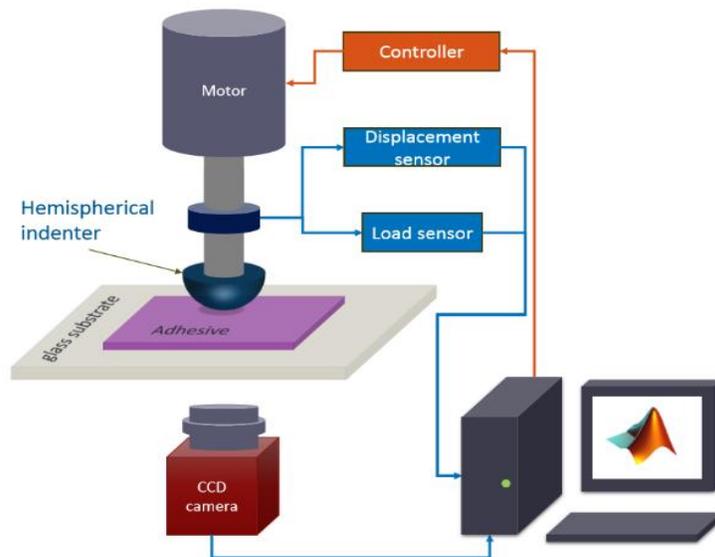


Figure 2: Probe Tack Microindenter Instrument with Camera

Experimental

Water-borne PSAs were prepared by standard emulsion polymerization techniques. For probe tack testing, samples were prepared with 50 μm total thickness. For multilayered samples, 3 μm of a second polymer was spin-coated onto each ~ 47 μm thick core sample. A hemispherical probe was lowered onto the test sample and force as function of displacement was recorded as the probe was lifted from the sample. In all testing, glass was used as the substrate. Testing was performed with either a glass or HDPE probe. In most cases, the failure occurred between the probe and the adhesive. Although the separation rate can be varied, $d\varepsilon/dt$ was set at 0.5 sec^{-1} for the studies where multilayer constructions were tested.

Results and Discussion

Standard PSAs

As a model system, a series of butyl acrylate/acrylic acid copolymers were synthesized and studied, each containing between 0 and 3% acrylic acid residues by weight. A representative stress-vs. strain curve is shown in Figure 3, and the stress vs. strain curve for the sample with 2% acrylic acid is shown in Figure 4. Starting at the top right-hand corner of the stress vs. strain curve and moving to the left, the stress increases sharply as the probe is pulled away from the substrate. The peak stress corresponds to the point where cavitation begins to occur within the adhesive. As the cavities grow and the fibrils (or fingers) elongate, the stress goes through a plateau region before the adhesive debonds from the probe (Figure 4, left).

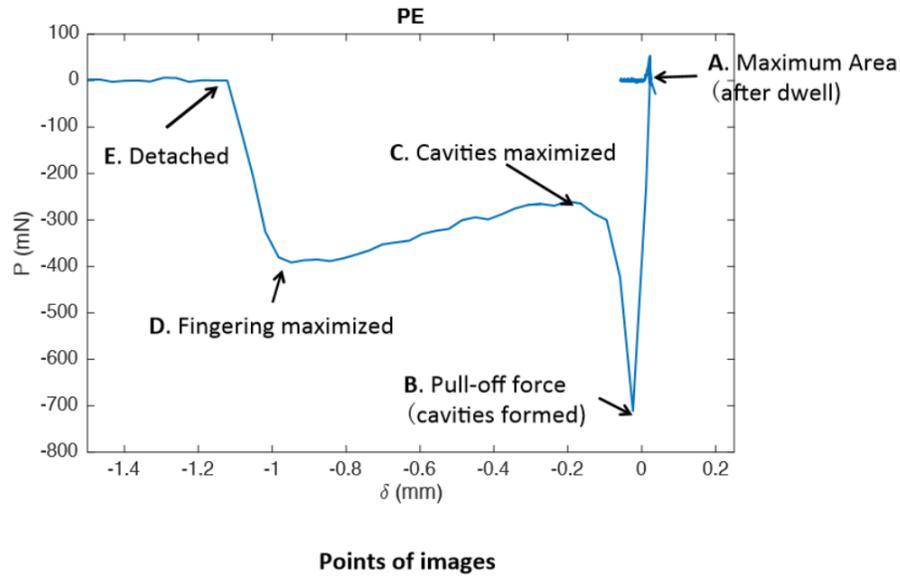


Figure 3: Representative Force Curve Describing Important Points During Deformation

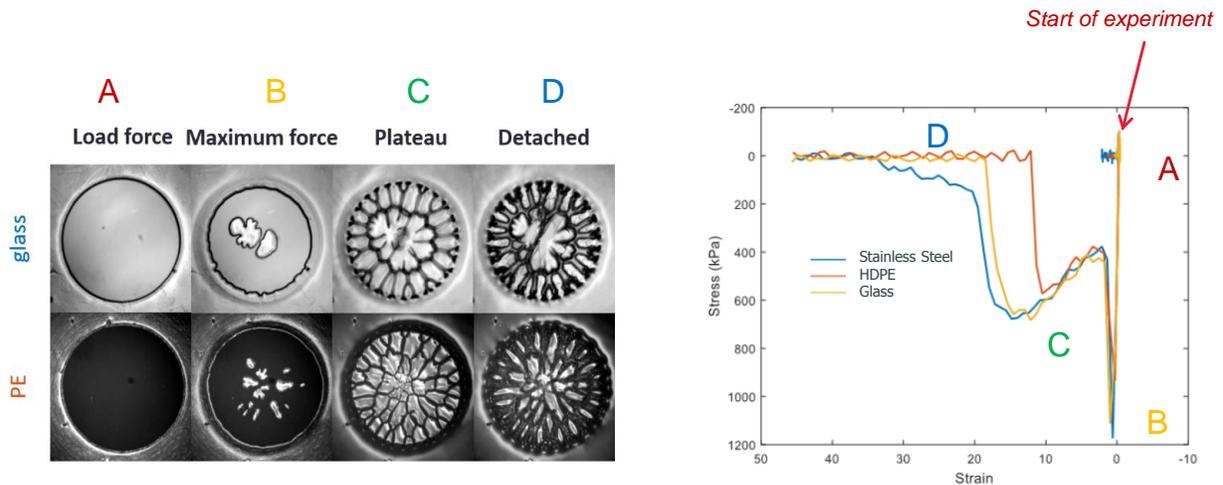


Figure 4: Probe Tack of Butyl Acrylate/Acrylic Acid Copolymer (Right) with Cavitation Profile (Left)

The effect of acid level on the behavior of the butyl acrylate/acrylic acid copolymers was studied both with a glass probe and with a polyethylene probe (Figure 5). All of the adhesives in this series showed a higher force (better adhesion) to glass than to polyethylene. Not surprisingly, the probe tack peak strain increased with increasing acid in the polymer, and the debonding occurred at lower strains as the acid content was increased. This is most likely attributable to a higher bulk modulus as the acid level increased.

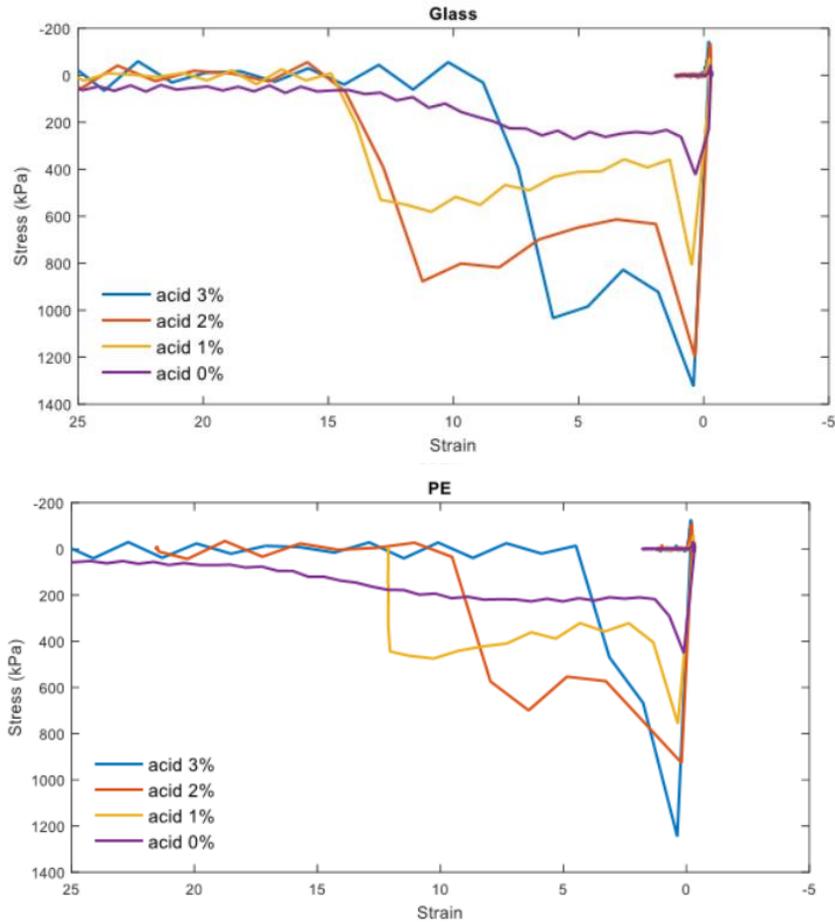


Figure 5: Stress vs. Strain Curves for Butyl Acrylate/Acrylic Acid Copolymers from Glass (Top) and Polyethylene (Bottom)

To illustrate the deficiency of linear rheological measurements in predicting differences in adhesive behavior, two adhesives with very different PSA performance but similar DMA (dynamic mechanical analysis) profiles were tested. Adhesive A is an all-acrylic water-borne PSA with T_g of $-45\text{ }^\circ\text{C}$. Adhesive B is also an all-acrylic water-borne PSA, but with higher T_g of around $-34\text{ }^\circ\text{C}$. Adhesive A exhibits high HDPE peel and tack, as well as high shear, while Adhesive B lower HDPE peel and tack, and much lower shear (Table 1). However, these two polymers show very similar response in DMA testing (Figure 6).

Table 1: PSA Properties of Robond™ PS-68 and Rhoplex™ N-619

	SS Peel (N/in)	HDPE Peel (N/in)	HDPE Tack (N/in)	SS Shear (Hrs)
Adhesive A	21 (C)	4.9 (A)	5 (A)	100 (C)
Adhesive B	17 (AFB)	3.8 (A)	4 (A)	4 (C)

“C” denotes Cohesive failure; “A” denotes Adhesive failure; “AFB” denotes Adhesives failure from facestock.

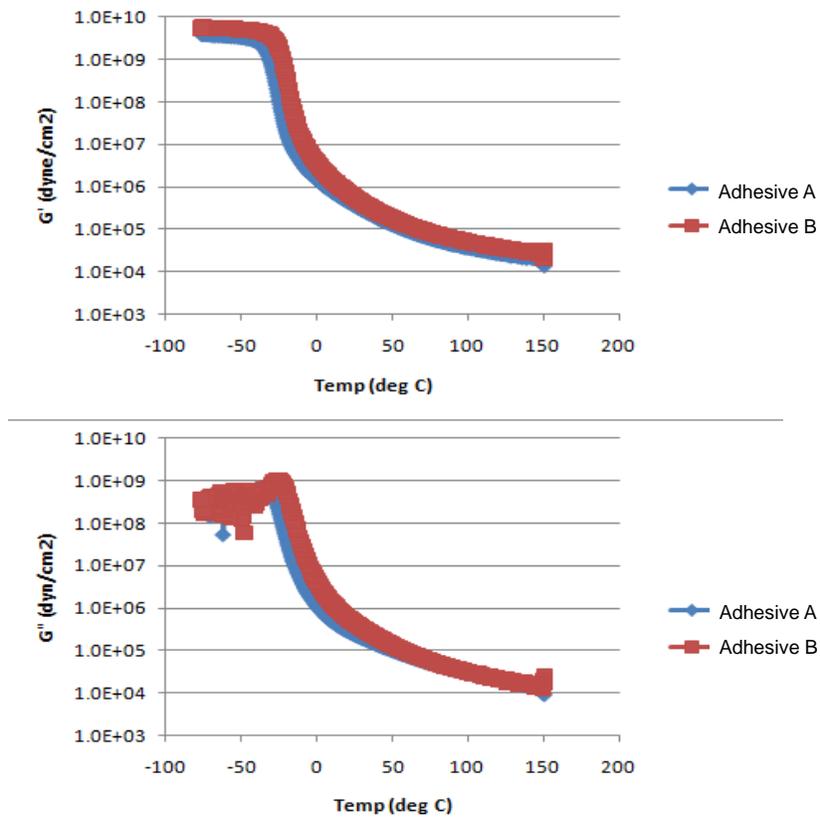


Figure 6: Dynamic Mechanical Analysis of Adhesive A and Adhesive B

From the stress vs. strain probe tack curves (Figure 7, left), we can see that these two adhesives exhibit a very similar peak stress, while Adhesive A has a much lower plateau and does not detach from the probe until later than Adhesive B (a tape adhesive, Adhesive C with tackifier, is shown for comparison). Perhaps the most interesting aspect of this particular measurement was that the cavitation profiles of these two adhesives were strikingly different (Figure 7, right).

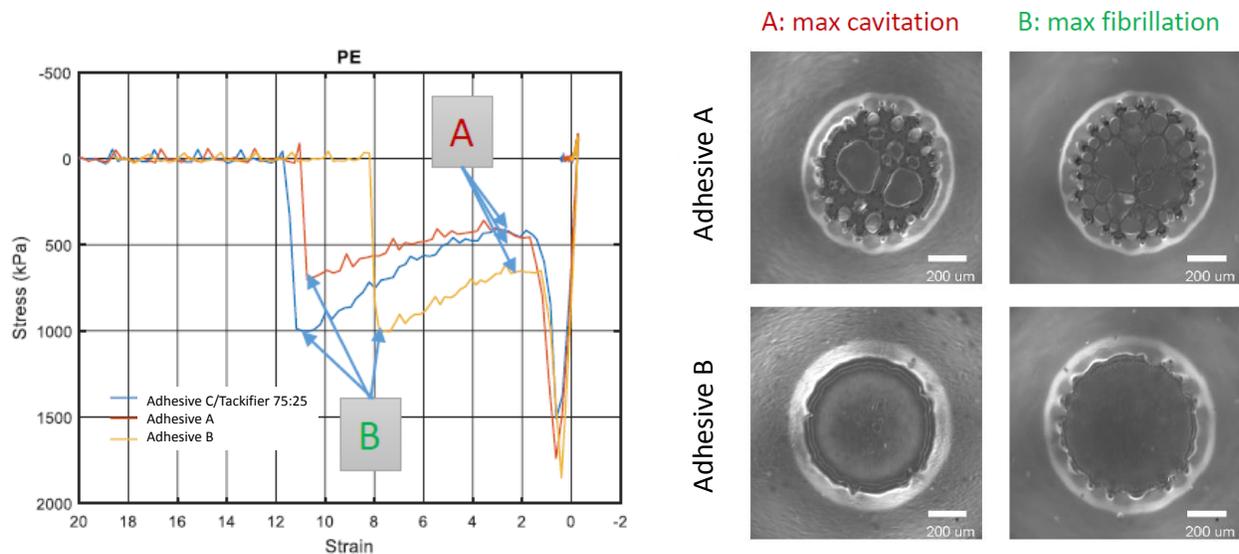


Figure 7: Stress vs. Strain Curves (Left) and Cavitation Profiles (Right) for Adhesive A and Adhesive B

Multilayer PSAs

The probe tack technique described here may also allow for a more in-depth study of elaborate PSA constructions, such as multilayer adhesives. These systems can be coated in one pass via slot-die, curtain, or slide coaters. A schematic of a multilayer slide coater is shown in Figure 8. Multilayer PSA constructions are gaining interest as a means of maximizing tackifier benefit while minimizing complexity.⁷ However, there may also be performance advantages to non-tackified, all-acrylic multilayer constructions.

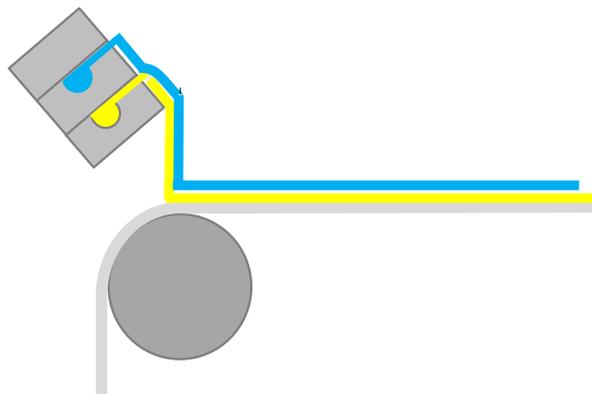


Figure 8: Schematic Representation of a Dual-Layer Slide Coater

The effect of a multilayer all-acrylic PSA coating was studied using a BA-based acrylic polymer (Adhesive C) as the bulk polymer and Adhesive B as the minor component at the surface. In most cases throughout this work, the failure occurred between the probe and the adhesive. The one exception was that if Adhesive B was coated on just the top layer, failure would occur at the adhesive /substrate interface. By coating a thin (3 μm) layer of Adhesive B on both sides, failure was maintained at the

probe/adhesive interface. The stress vs. strain curves in Figure 9 show that the multilayer construction had higher stress and strain at detachment than either of the parent polymers alone. This translated into an appreciable increase in work of adhesion (W_A) for the multilayer construction versus either of the parent polymers (Table 2). This is interesting because Adhesive B is a relatively high- T_g polymer for a PSA, and even when this material is present at the surface, high work of adhesion is possible. This further illustrates the important roles that both surface energetics and bulk rheology have to play in determining PSA performance. Further, this result shows that the surface energy and bulk rheological contributions of an adhesive can be controlled *independently* through multilayer constructions, offering maximum versatility and enhanced performance.

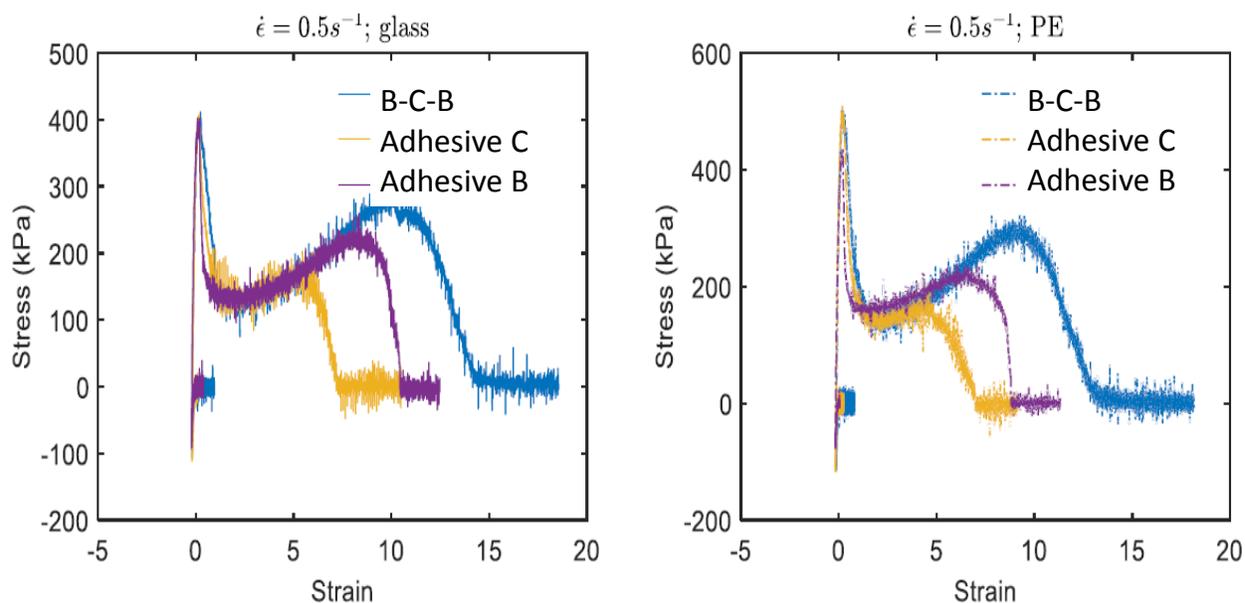


Figure 9: Stress vs. Strain Curves for Multilayer Constructions

Table 2: Characteristics of Probe Tack Measurements for Multilayer PSA Construction

	h (μm)	Glass			Polyethylene		
		W_A (J/m^2)*	Max Stress (MPa)	Failure Strain	W_A (J/m^2)*	Max Stress (MPa)	Failure Strain
Adhesive C	52	56	0.41	7.2	56	0.51	7.0
Adhesive B	65	120	0.40	10.4	112	0.44	8.8
B-C-B	51	143	0.41	14.2	143	0.50	13.6

* W_A was calculated from the area under the stress-strain curves

Conclusions

Microindentation probe tack was used to measure the adhesion and cavitation performance of acrylic pressure sensitive adhesives (PSAs). The use of a digital camera helped to relate the force at various

points along the displacement curve with cavitation and fibrillation within the adhesives layer. The most interesting results were obtained with dual-layer films where two PSAs of different composition were coated sequentially. These films resulted in very different properties than the two parent polymers separately, and the work of adhesion was found to be strongly dependent on the order of the two adhesives.

Acknowledgements

The authors would like to thank the Dow Adhesives and Analytical Sciences teams, as well as our collaborators in the Northwestern University Materials Science and Engineering Department. We would also like to thank PSTC for the opportunity to present this work.

¹ Pocius, A. (2002). *Adhesion and Adhesives Technology*. Munich: Hanser.

² Ahagon, A.; Gent, A. "Effect of Interfacial Bonding on the Strength of Adhesion," *J. Polym. Sci., Polym. Phys. Ed.*, 13, 1285-1300, 1975.

³ Gent, A.; Schultz, J. "Effect of Wetting Liquids on the Strength of Adhesion of Viscoelastic Material," *J. Adhesion*, 4, 281-294, 1972.

⁴ Lacombe, R. (2006). *Adhesion Measurement Methods*. Boca Raton: CRC Press.

⁵ Creton, C. and Shull, K. (2008). Probe Tack. I. Benedek and M. Feldstein (Eds.), *Fundamentals of Pressure Sensitivity* (6-1 – 6-17), Boca Raton: CRC Press.

⁶ Lestriez, B.; Lakrout, H.; Chiche, A.; Roos, A.; Creton, C. "Probe Tack Tests as a Characterization Tool in Pressure Sensitive Adhesives," PSTC, 2001.

⁷ Donkus, L.; Griffith, W.; Lane, M.; Keely, D. "Novel Approaches to the Tackification of Pressure Sensitive Adhesives," PSTC, 2013.