HIGH THROUGHPUT MEASUREMENT OF PEEL OF A PRESSURE SENSITIVE ADHESIVE[1]

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Abstract

The peel force of a pressure sensitive adhesive (PSA) tape is measured on a surface that varied linearly in temperature. As the tape is peeled from the surface, the adhesive is peeled from a surface at a different temperature. The temperature can be correlated with peel distance, giving the temperature dependence of the peel force with one peel test. In addition, the temperature of the transition from cohesive to interfacial failure could be easily identified, not only by the relative peak in the peel force, but also by the clearly visible adhesive layer which remained on the stainless steel plate.

Introduction

The performance of a PSA can be characterized by adhesion, shear, and tack tests. Testing of the PSA is necessary since theoretical models have not been able to quantitatively predict the performance of the PSA based solely on rheological or surface properties.[1]

Adhesion tests include the T-peel test, the 180° peel test, and the 90° peel test. Standard peel tests are carried out at constant peel rate and temperature. However, to completely characterize the performance of the PSA, multiple peel tests are made at a variety of peel rates or temperatures and a peel force master curve is produced, as shown in Figure 1.
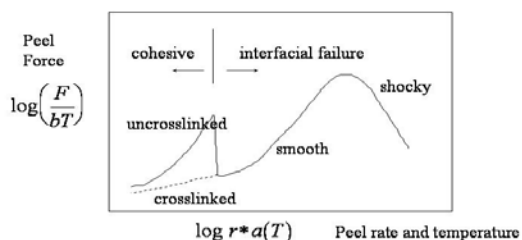
Figure 1 Typical shape of a peel force master curve for a PSA tape. The peel rate increases from left to right on the graph whereas the temperature increases from right to left. F is the peel force, b is the tape width, T is the temperature, r is the peel rate, and a(T) is the temperature dependent shift factor of the WLF equation.[2]

Because many peel tests are performed at various peel rates or temperatures, obtaining a peel force master curve can take a day or more. To shorten the time required to produce a peel force master curve, we applied high throughput methodology to the peel test. High throughput methodology allows rapid screening of materials and is particularly helpful when the fundamental properties of a material cannot be predicted from basic measurements. High throughput methodology often involves automated testing. It has been widely used in the pharmaceutical industry and is rapidly being applied to material science measurements.[3-5]

Multi-variant or combinatorial techniques are high throughput measurements whereby two or more parameters are varied in one experiment. For example, the chemical composition of a film can be varied across the film and the properties can be systematically measured as a function of temperature or film thickness to quickly obtain structure/property relationships.[6] The method allows a rapid approach to optimization of chemistry for material properties.

In our experiments, instead of measuring multiple peel tests at each desired temperature, we measured the peel force from a surface which varied linearly in temperature across the surface. As a PSA tape is peeled, the adhesive is peeled from a surface at a different temperature. Since we can correlate temperature with peel distance, we are able to determine the temperature dependence of the peel force with one peel test. In addition, we could measure the peel force from the gradient surface at various peel rates and use the WLF superposition principle to produce a peel force master curve.[2,7]

Experimental Design
The gradient temperature plate was made of type 304 stainless steel and was designed as shown in Figure 2. The 15 cm x 18 cm plate was 4.8 mm ± 0.1 mm thick and had a #8 polished finish.[2] The surface roughness, Ra, corresponded to 0.2 μm. One end of the plate was attached to a cylindrical heater (Omega Engineering, Inc., Stamford, CT); the other end of the plate had an open channel attached to it. Cold water was continuously run through the open channel to chill one end of the plate. Heat flows from the hot end of the plate to the cool end via thermal conduction. Similar designs of the gradient temperature plate can be found in the literature including a Kofler hot bench used to measure the melting point of organic compounds, an ASTM standard method for measuring the minimum film formation temperature of emulsion films, and a thermal gradient bar for the measurement of the surface tension of polymers.[8-12] The gradient hot plate has not been previously used to test PSA materials.

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[2] Unless otherwise noted, the ± refers to the standard uncertainty in the measurements and is taken as one standard deviation of the observed values.
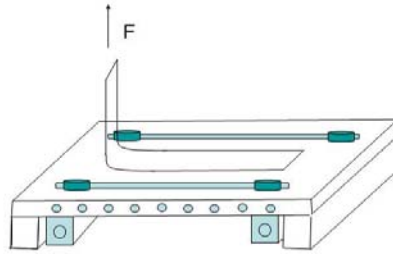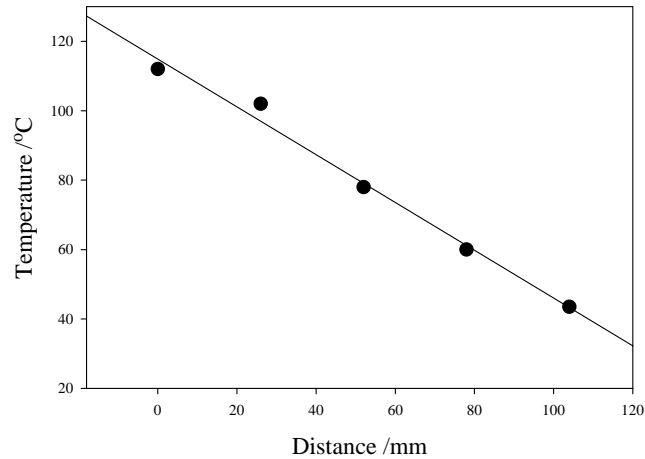
Figure 2 Diagram of the gradient temperature plate. The distance between the heating and cooling cylinders could be adjusted to change the length and steepness of the gradient temperature.   The plate was bolted onto the movable stage of a Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). The Texture Analyzer was configured to measure the tensile force at a 90° angle to the stage. The movable stage allows the 90° angle to be maintained as the tape is pulled from the surface.

The stainless steel gradient temperature plate was cleaned according to ASTM recommended cleaning procedures.[13] The plate was then allowed to reach equilibrium temperature by heating one end of the plate and cooling the other end for two hours prior to testing.

After equilibration, a 1.9 cm strip of PSA tape was applied to the gradient plate using a 2 kg rubber roller. The adhesive tape (Scotch Box Sealing Tape 353, 3M, St. Paul, MN) is a commercially available rubber resin adhesive tape. The nominal adhesive thickness is 25 μm. The adhesive is supported on a biaxially oriented polyester backing which has a thickness of 23 μm. The "hot" end of the tape is clamped by a metal grip on the Texture Analyzer. The tape was peeled less than 5 minutes after the PSA tape was applied to the surface.

Before each measurement, the temperature of the plate as a function of distance along the plate is measured via the thermocouple ports along the side of the plate using a thermocouple (Omega, Type J). A typical measurement is shown in figure 3 where the temperature gradient is shown to be linear across the region of measurement, as expected.

The steepness of the temperature gradient, i.e. the distance per unit temperature, could be changed by varying the temperature difference between the hot and cold inputs or by varying the distance between the hot and cold inputs. A steeper gradient would allow more data to be collected in an experiment. However, a steeper gradient will give an increasingly small distance at each temperature.

Figure 3 Calibration of the gradient temperature plate. The circles correspond to the measured temperatures whereas the straight line is a least squares fit to the data. The temperature gradient was linear along the distance of the plate. The temperature was measured to ± 2 °C.


Peel Force Measurements and Analysis
An example of a traditional steady peel measurement taken at constant temperature and peel rate is shown in Figure 4. The instantaneous peel force fluctuates around an average peel force. The time scale of the fluctuations is on the order of 1 s. Traditionally, peel forces are averaged over a peel length of approximately 5 cm once steady state peel is attained. This peel distance is shown by the small box in Fig. 4. We will define this average peel force measurement as the macroscopic average peel force. For these high throughput measurements, we wish to measure an average peel force at each 1 °C temperature increment. Because of space constraints, the peel length measured at each temperature increment must be much smaller than the traditional 5 cm length. We define a microscopic average peel force where the data is averaged over a smaller peel length than in traditional measurements. Our goal is to obtain a microscopic peel force measurement which is within ± 10 % of the macroscopic peel force measurement.
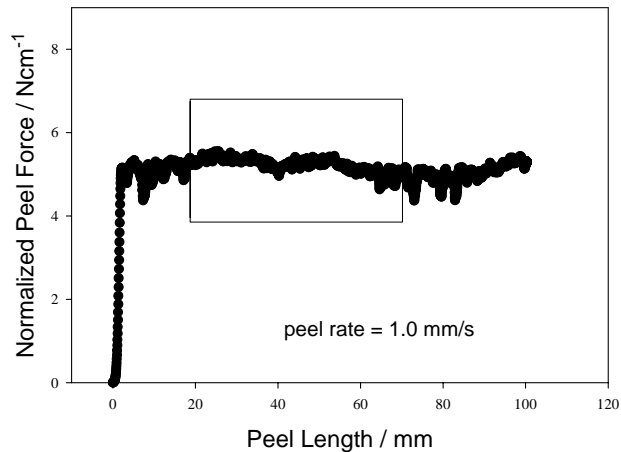
Figure 4 Measured 90° peel force, normalized by the tape width, as a function of peel length for a commercial PSA tape (Scotch Box Sealing Tape 353). The peel force was measured at a constant temperature of 22 °C on a stainless steel plate as described in the paper. The tape width was 1.9 cm and the peel rate was 1.0 mm/s. The peel force was measured to ± 5 %. The small box shows the area where peel forces are measured to give an average macroscopic peel force.

During steady adhesive failure, one might assume that the minimum peel length needed to obtain a microscopic average peel force within ± 10 % of the macroscopic peel force will be the distance where adhesive deformation occurs during the peel, defined as the peel zone, z. Cavitation, viscous fingering, and fibril elongation occur in pressure sensitive adhesives in the peel zone and contribute to the measured peel force. The stiffness of the adhesive backing also distributes the stress throughout the peel zone. As a consequence, most of the energy dissipation may extend well into the adhesive, far away from where the surfaces separate. To a first approximation, the peel zone is comparable to the adhesive thickness, which for this experiment was 25 μm.[1]
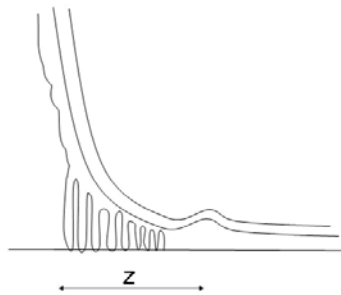
Figure 5 Schematic Diagram of the peel front of a PSA tape showing cavitation, viscous fingering, fibril elongation, and backing deformation in the peel zone, z.

Figure 6 shows traditional peel forces measured at T = 24 °C, T = 40 °C, and T = 60 °C (circles) compared with the peel force measured with the gradient temperature plate (solid curve). Clearly, the peel forces measured with the gradient temperature plate are similar to traditional peel force measurements, at least at this peel rate. The temperature gradient for this experiment was 2 mm/ °C, i.e., we are peeling 2 mm for each °C temperature increment.
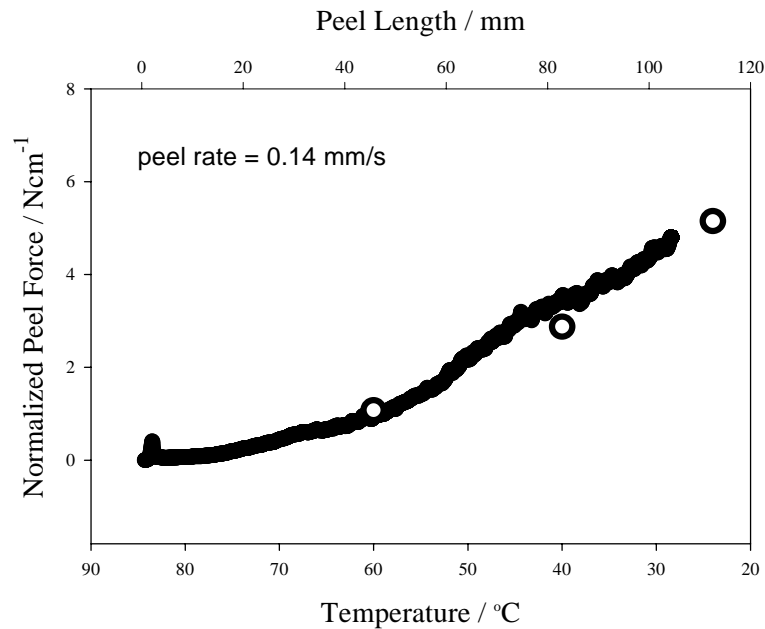

Figure 6 Comparison of the measurements of 90° peel of Scotch Box Sealing Tape 353 using the gradient temperature plate (solid curve) with traditional constant temperature measurements (circles). The peel force was measured to ± 5 % and the temperature was measured to ± 2 °C. The tape width was 1.9 cm and the peel rate was 0.14 mm/s. The peel force is normalized by the width of the PSA tape.

Figure 7 shows the peel force measured against the gradient temperature plate for peel rates 0.14 mm/s, 2.54 mm/s and 15 mm/s. The results show an increase in the peel force with increasing peel rate, as expected for interfacial failure. The relative peak measured for peel rates 2.54 mm/s and 15 mm/s corresponds to a transition from cohesive to interfacial adhesion. This transition was clearly visible on the reflective stainless steel plate. In the area where cohesive failure occurred, an adhesive layer remained on the plate after the tape was peeled from the surface. In the area where interfacial adhesion was measured, no residual layer could be seen by eye.

As previously mentioned, the adhesive was peeled from a gradient of 2 mm / °C. Clearly, in order for the average peel force obtained from a 2 mm peel length to be within ± 10 % of the average peel force obtained from a 5 cm peel length, the peel force must be reproducible and steady. Any fluctuations that might occur in the force signal must occur over a small distance or

time scale. During steady peel, figure 4 shows the fluctuations are on the order of 1 s. In shocky peel, this time scale can be orders of magnitude larger.
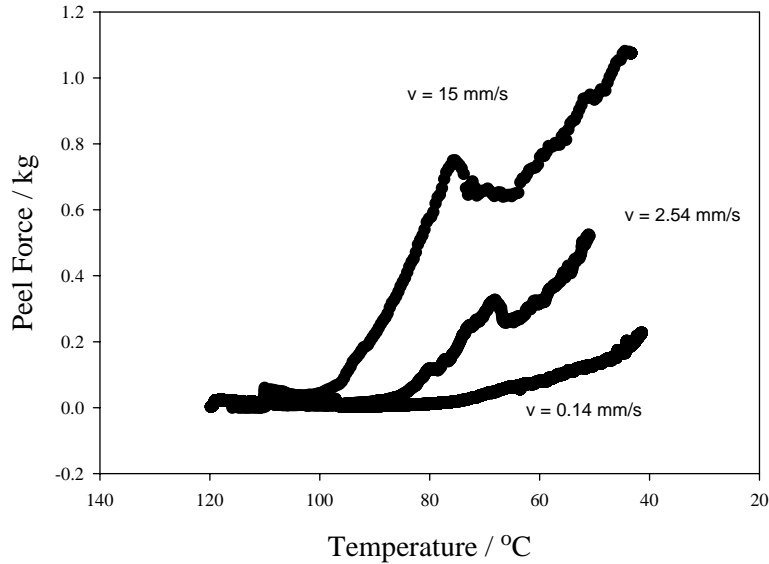

Figure 7 Measured 90° peel force of Scotch Box Sealing Tape 353 using the gradient temperature plate. The peel force was measured to ± 5 % and the temperature was measured to ± 2 °C. The tape width was 1.9 cm.

To further investigate the measured fluctuations in the peel force, we performed an autocorrelation analysis on the peel force. The autocorrelation function measures the degree to which pairs of data that are close to each other are more likely to be similar in magnitude, i.e. correlated, than data that are far apart from each other.

The results of the autocorrelation analysis depend on the variability of the measurements. In figure 4, the data shows short range fluctuations on the order of 1 s and longer range fluctuations at much longer times due to small variations in the surface and adhesive properties. For our analysis we are mainly interested in the short time fluctuations that are related to cavitation, viscous fingering, and fibril elongation occurring in the peel zone or beyond.

The autocorrelation function can be applied to original data and the residuals of the data. Analyzing the residuals of the data focuses on the short range fluctuations. The autocorrelation function was applied to the residuals of the data given in figure 4 and is shown in figure 8. The autocorrelation function shows an initial rapid drop to the background noise over a correlation length l_c. This correlation length corresponds to the smallest peel length over which statistically independent measurements can be made. According to Figure 8, $l_c = 0.8$ mm ± 0.1 mm. Since

we are peeling at 2 mm/°C, we are peeling more than twice the correlation length every °C. Thus, our design criterion of obtaining an independent measurement every °C is met.
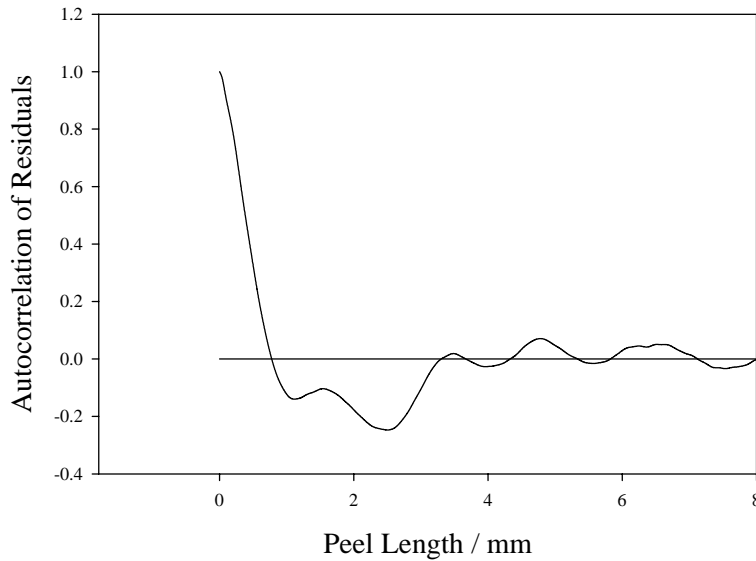
Figure 8. Autocorrelation Plot of the residuals of the data shown in Figure 4. The straight line at 0 is where the data is statistically independent and is shown as a reference line.

Further autocorrelation analysis of the peel force of a variety of PSA's shows that the correlation length varies with adhesive properties, backing properties, and peel rates. Previous studies of the peel force fluctuations for another adhesive have shown the time scale of the peel force fluctuations in interfacial, steady peel to be on the order of hundreds of ms.[14] Additional analysis of the correlation length will be published in a later publication.

Conclusion
The results presented demonstrate that accurate peel testing can be achieved using a gradient temperature plate. The gradient temperature plate allows the peel force as a function of temperature to be measured in one peel test. Additional information can be obtained by performing the test at multiple peel rates. The temperature dependence of the transition from cohesive to interfacial shear can be clearly measured, not only from measuring the peel force but also by observing the residual adhesive remaining on a part of the plate.

Acknowledgements

References

1. Yarusso DJ (1999) "Quantifying the relationship between peel and rheology for pressure sensitive adhesives", *Journal of Adhesion*, **70**: 299-320.
2. Williams ML, Landel RF, Ferry JD (1955) "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids", *Journal of the American Chemical Society*, **77**: 3701-3707.
3. Bunin BA, Plunkett MJ, Ellman JA (1994) "The Combinatorial Synthesis and Chemical and Biological Evaluation of A 1,4-Benzodiazepine Library", *Proceedings of the National Academy of Sciences of the United States of America*, **91**: 4708-4712.
4. Meredith JC, Karim A, Amis EJ (2000) "High-throughput measurement of polymer blend phase behavior", *Macromolecules*, **33**: 5760-5762.
5. Jandeleit B, Schaefer DJ, Powers TS, Turner HW, Weinberg WH (1999) "Combinatorial materials science and catalysis", *Angewandte Chemie-International Edition*, **38**: 2495-2532.
6. Chiang MYM, Wu WL, He JM, Amis EJ (2003) "Combinatorial approach to the edge delamination test for thin film reliability - concept and simulation", *Thin Solid Films*, **437**: 197-203.
7. Kaelble DH (1964) "Theory and Analysis of Peel Adhesion: Rate-Temperature Dependence of Viscoelastic Interlayers", *Journal of Colloid Science*, **19**: 413-424.
8. Kofler L, Kofler W (1949) "Uber eine Heizbank zur raschen Bestimmung des Schmelzpunktes", *Mikrochemie ver Mikrochim*, **34**: 374-381.
9. Vogel AI (1994) *Vogel's Textbook of Practical Organic Chemistry*, Longman Scientific & Technical, Essex, England
10. ASTM International, "Standard Test Method for Minimum Film Formation Temperature (MFFT) of Emulsion Vehicles", **D2354-98**, 1-3, 1998.
11. Severs ET, Austin JM (1957) "The Thermal Incline - A Means of Measuring Viscosities of Plastisols at Elevated Temperatures", *Transactions of the Society of Rheology*, **1**: 191-202.
12. Schreiber HP, Ewaneebele F (1978) "Surface-Tension and Its Temperature-Variation in Film-Forming Polymers", *Journal of Adhesion*, **9**: 175-184.
13. ASTM International, "Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape", **D 3330**, 1-5, 2004.
14. Scudiero L, Dickinson JT, Jensen LC, Langford SC (1995) "Electrical Transients Generated by the Peel of A Pressure-Sensitive Adhesive Tape from A Copper Substrate .2. Analysis of Fluctuations - Evidence for Chaos", *Journal of Adhesion Science and Technology*, **9**: 27-45.