



Characterization of Pressure Sensitive Adhesives by Rheology

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ABSTRACT

Three properties, shear resistance, tack and peel strength, generally characterized pressure sensitive adhesives (PSA). These properties are directly related to the PSA's response to the application of stress and may be measured using rheology. For example, tack describes the ability to spontaneously form a bond to another material under light pressures within a short application time. As the contact time increases, higher shear resistance and peel strength properties (related to a materials long time flow behavior) are found. A single rheological test is described to directly determine the response of a PSA to varying deformation times, related directly to its shear resistance, tack and peel strength behavior.

INTRODUCTION

An adhesive is usually a polymeric material applied between two solid layers that form a bond with cohesive strength (I). Most adhesives exhibit viscoelastic behavior. Rheology, using small amplitude oscillations, may be used to test adhesives throughout the whole viscoelastic profile. Applying small amplitudes causes the shear stress to be proportional to the shear strain, a necessary condition for linear viscoelasticity. In linear viscoelasticity, the dynamic modulus ($G[\omega]$) is the ratio of shear stress to shear strain and is independent of the shear amplitude. Dynamic modulus may be separated into elastic (storage) modulus (G') and the viscous (loss) modulus (G''). The ratio of the G'' to G' is equal to the tangent of the phase angle between them: $\tan \delta = G''/G'$.

The ability to form a bond and resist debonding from a substrate determines how appropriate a particular PSA is for a certain application. Oscillatory frequency sweeps are well suited for characterizing the bonding and debonding behavior of a PSA. In an oscillatory frequency sweep, a constant sinusoidal amplitude is applied to a material, within the linear viscoelastic region, while varying the frequency of the oscillation. Low rates of deformation (*i.e.*, low frequency) characterize the bond formation, while high frequency (*i.e.*, high rates of deformation) is used to characterize debonding behavior. The latter describes a materials shear resistance and the former relates to PSA's tack and peel strength. Chiu describes how the modulus values at high frequency are related to peel or quick stick tests, and at low frequencies, to shear resistance of adhesives (2).

Further information can be obtained by using the Cox-Merz rule (3) to predict shear viscosity ($\eta(\dot{\gamma})$) from oscillatory frequency sweep measurements. The Cox-Merz rule is an empirical relationship that describes the relationship between the steady state

shear viscosity (plotted against shear rate) and the magnitude of the complex viscosity (plotted against angular frequency). The complex viscosity, $|\eta^*|$, is defined by $|\eta^*| = |G^*| / \omega$ where G^* is the complex modulus and ω is the angular frequency.

Table 1 shows a summary of the rheological properties that indicate specific adhesive behavior using dynamic mechanical properties. Pressure sensitive adhesives and other polymeric materials (because of their viscoelastic nature) exhibit temperature and time (frequency) dependent behavior during deformation and flow. Such data can be treated using time-temperature superposition (TTS) theory, overcoming the difficulty of extrapolating limited laboratory tests at shorter times to longer term, real world, conditions. TTS treatment is well grounded in theory (4, 5, 6) and may be applied to the rheology data obtained from oscillation experiments. The underlying bases for time/temperature super-positioning are (a) that the processes involved in molecular relaxation or rearrangements in viscoelastic materials occur at accelerated rates at higher temperatures and (b) that there is a direct equivalency between time the stress is applied (the frequency of measurement) and temperature. Thus, oscillatory frequency sweeps are commonly used. The time over which these processes occur can be reduced by conducting the measurement at elevated temperatures and shifting the resultant data to lower temperatures. The result of this shifting is a "master curve" where the material property of interest at a specific end-use temperature can be predicted over a broad time/frequency scale.

Table 1 – Viscoelastic Properties Related to PSA Characteristics

Tack	-Low $\tan \delta$ peak and Low G' -Low cross-links ($G'' > G'$) @ ~ 1 Hz ⇒ High tack
Shear resistance	-High G' modulus @ low frequencies <0.1 Hz -High Viscosity at low shear rates ⇒ High shear resistance
Peel Strength	-High G'' @ higher frequencies (~>100 Hz) ⇒ High peel strength
Cohesive Strength	-High G' and low $\tan \delta$ ⇒ High cohesive strength (Bulk property)
Adhesive Strength	-High G'' and high $\tan \delta$ ⇒ High adhesion strength with surface

EXPERIMENTAL

For illustrative purposes, three examples of hot melt, pressure sensitive adhesives are characterized using an AR2000 Advanced Rheometer.

Sample A: high cohesive strength, low tack properties, moderate peel strength, possible low temperature adhesive

Sample B: lower cohesive strength, higher tack, lower viscosity, low shear resistance compared to A

Sample C: lower tack, higher cohesive strength, lower peel strength, lower shear resistance compared to A

The Smart Swap® Parallel Plate temperature stage with 8 mm plates is used in conjunction with the Environmental Test Chamber to control the temperature from the glassy to the terminal region of each sample. Oscillatory frequency sweeps are conducted at different isothermal temperatures, ranging from -100 to 130 °C, stepping every 10 °C for each frequency sweep. The range of frequencies is 0.1 to 100 Hz at an oscillation amplitude of 0.025 % strain. The normal force is controlled to account for the thermal expansion of the sample throughout the test.

RESULTS AND DISCUSSION

The modulus values in the frequency range of 0.1 to 100 Hz describe the wetting and creep behavior of PSA's. When the modulus becomes too large, the ability to wet the substrate reduces (2). The unshifted TTS profile for sample A is shown in Figure 1 and the TTS master curve for A and B at 20 °C is shown in Figure 2. In the frequency range of 0.1 to 100 Hz of Figure 2, sample A possesses a higher G' and a lower $\tan \delta$ value than B, indicating that the PSA has a higher cohesive strength or low creep compliance. Sample B exhibits a lower G' and a higher $\tan \delta$ value than A. The lower modulus value indicates that the adhesive will deform more easily when in contact with the substrate.

For tack enhancement, $\tan \delta$ should be greater than unity. That is, G'' is greater than G' indicating that the polymer dissipates energy through its own deformation. This allows the material to adhere and easily form good contact to the substrate. In Figure 2, $\tan \delta$ is shown to be greater than unity for B and is greater than A, correlating well with the supplier's observations.

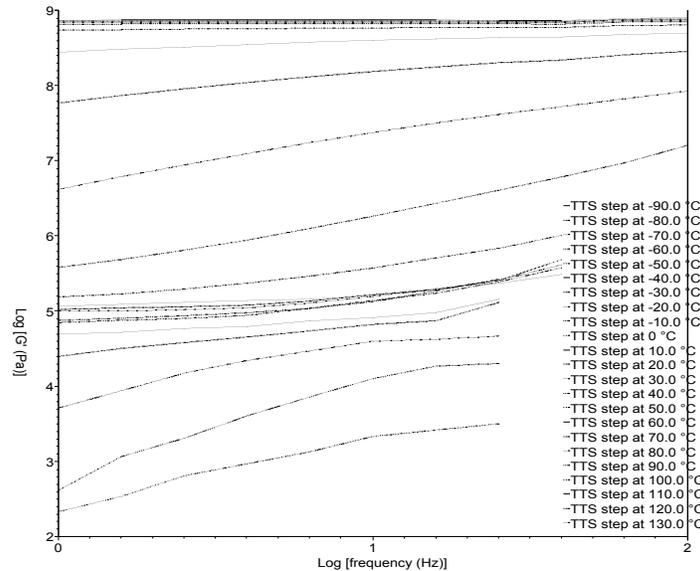


Figure 1 – Raw Data

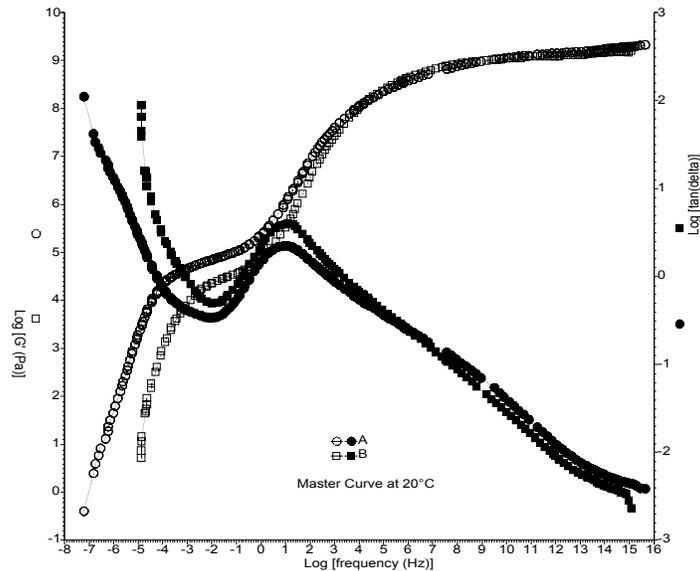


Figure 2 – TTS Master Curves (Samples A and B)

Rheological information at high frequency is related to the peel strength of the materials. These rheological behaviors for samples A and B indicate that similar peel strength properties should exist. The low frequency information (<0.1 Hz) shows that sample B drops off in properties faster than sample A, directly related to its observed low shear resistance behavior.

Figure 3 shows the master curves at 20 °C of samples A and B after being transformed to steady shear via the Cox-Merz rule. At lower shear rates, sample B has lower viscosities than sample A, correlating to their observed behavior. As the shear rate increases, both samples converge to have the same profile, as is expected.

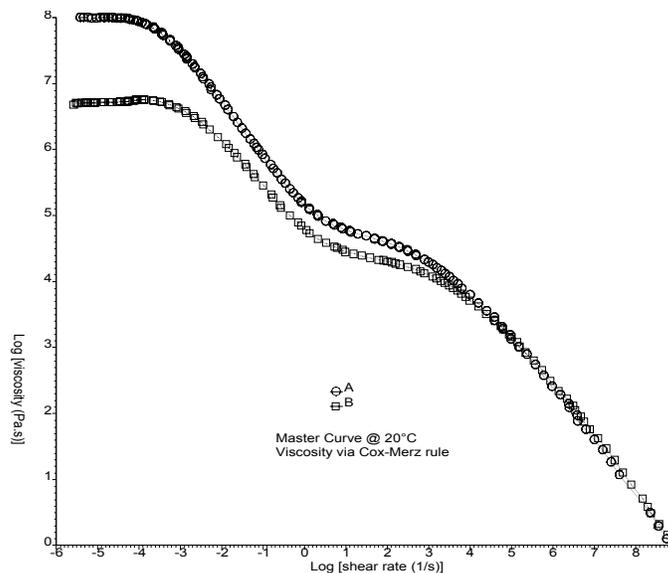


Figure 3 – TTS Master Curves with Steady Shear Treatment (Samples A and B)

Another way to treat the information from Figure 1 is to convert the rheological information versus frequency to that versus temperature. This is shown in Figure 4 and 5. The spread in the curves shows the dependence of the rheological properties with

frequency. Each set of connected data points represents G' as it changes with temperature at a fixed frequency of 0.1 to 100 Hz.

Low temperature limit for an adhesive is indicated by the glass transition. Figure 4 shows that, as expected, the elastic modulus within the glassy region (*i.e.*, the transition near 0 °C) is independent of frequency. As the temperature is increased, a large dependence on frequency is seen during the glass transition region and into the terminal region. Taking the peak of $\tan \delta$ to represent the glass transition temperature (Figure 5), a value of T_g at 15 °C is observed indicating that sample A is not suitable for low temperature applications.

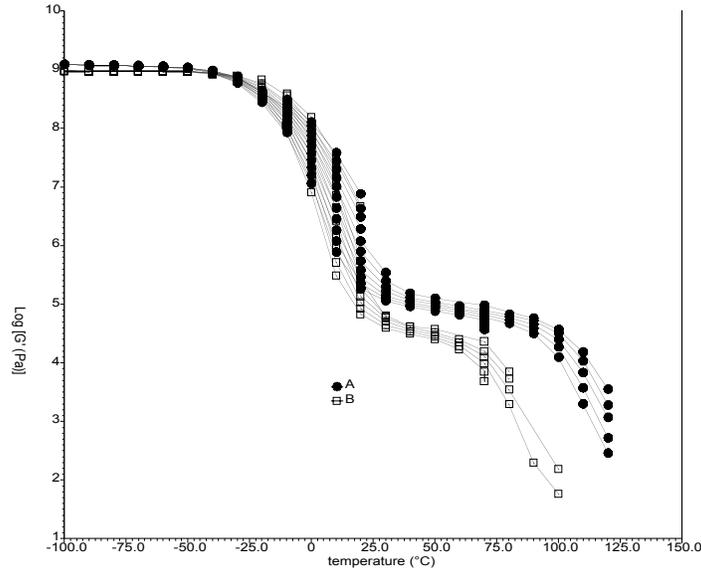


Figure 4 – Temperature Dependence of Modulus (Sample A and B)

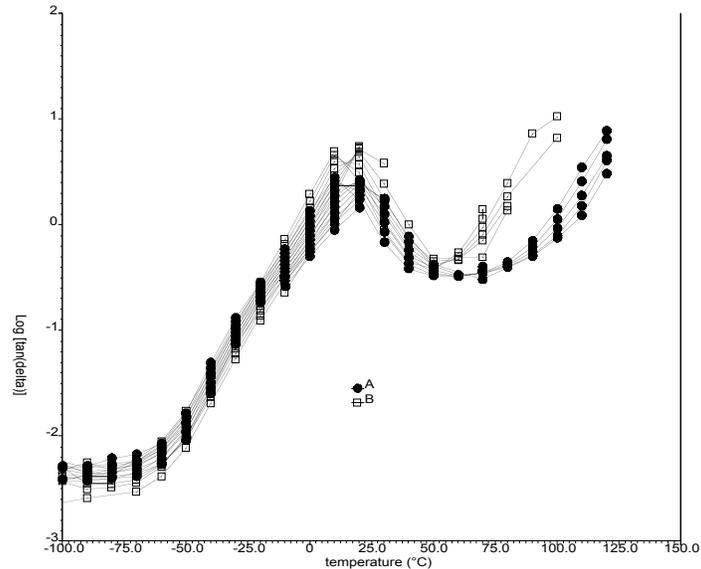


Figure 5 – Temperature Dependence of Phase Angle (Sample A and B)

Sample C exhibits high cohesive strength, low shear resistance and low viscosity. In Figure 6 sample C is compared to sample A showing similar values for modulus and a

lower $\tan \delta$ value over a broad range of frequency. This indicates that the cohesive strength of sample C out performs that of sample A. The low shear resistance and the low viscosity behaviors are observed in Figures 6 and 7. Figure 6 shows that the terminal region for sample C begins at higher frequencies compared to sample A at reference temperature of 20 °C, indicating a lower shear resistance. After converting the oscillatory information to steady flow by the Cox-Merz rule, shown in Figure 7, the viscosity profile of C is found to have a lower overall behavior, as described by the supplier. Temperature sweeps, in Figure 8, indicate that the T_g occurs at about -10 °C, making this material more suitable for low temperature applications, compared to samples A and B.

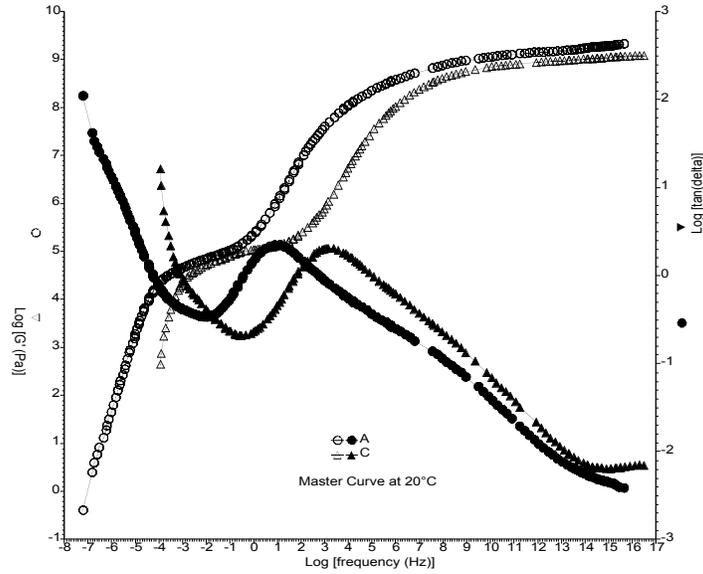


Figure 6 – TTS Master Curve (Sample A and C)

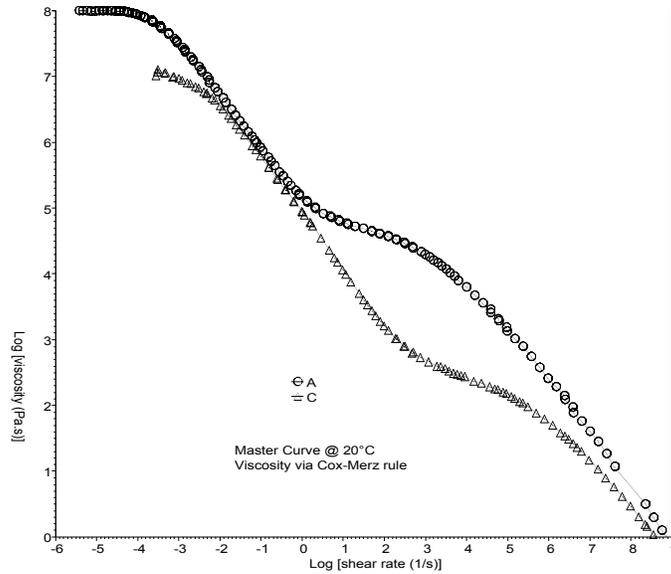


Figure 7 – TTS Master Curves with Steady Shear Treatment (Sample A and C)

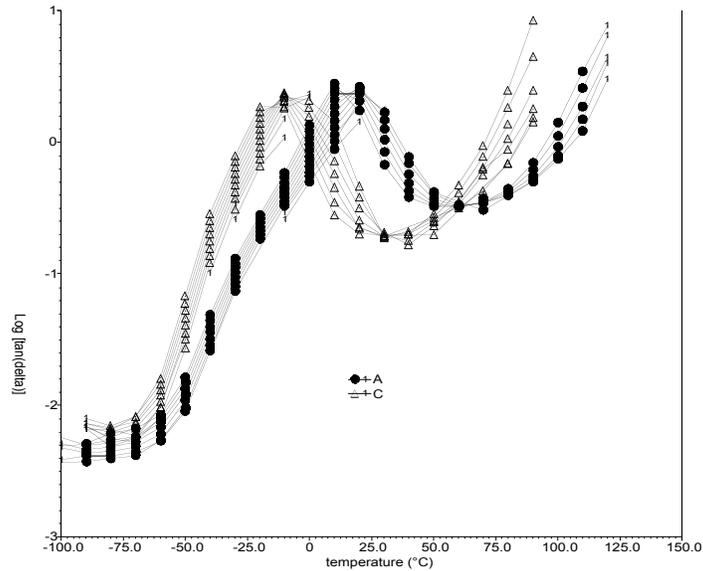


Figure 8 – Temperature Dependence of Phase Angle (Sample A and C)

Another powerful TTS technique is to determine the overall behavior of a material at a different reference temperature; by shifting the multiple frequency sweeps, shown in Figure 1, to another reference temperature and overlaying the profiles. This is valuable in determining the best working temperature of a material to yield specific rheological behavior. By changing the reference from 20 to 50 °C for sample A, in Figure 9, the properties of peel strength for sample A is similar to sample C, while the properties of shear resistance and tack are drastically reduced.

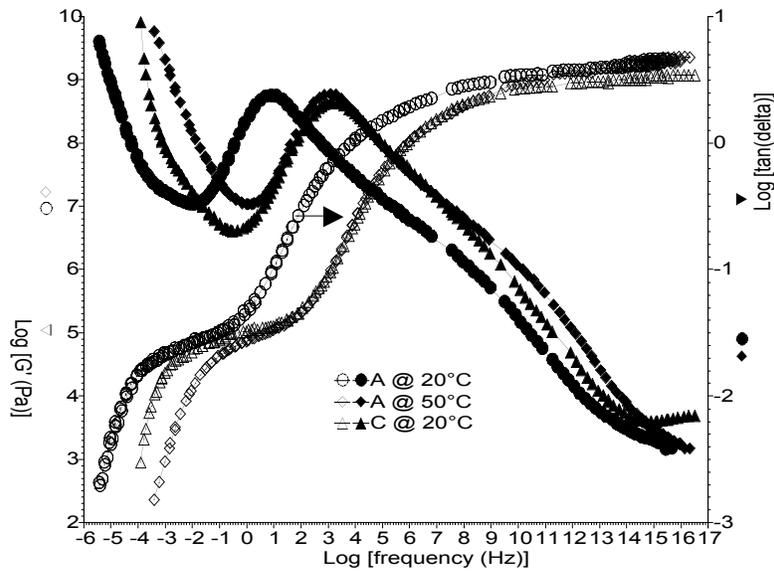


Figure 9 – TTS Master Curves Referenced to 50 °C

SUMMARY

The rheological behavior of three different pressure sensitive adhesives is well characterized using rheometry and successful correlations to describe PSA behavior are shown. All of the results for each PSA were determined by using one Time-Temperature-Superposition (TTS) procedure. Since all the information is collected from a single test, time and cost savings for the end user is tremendous. From this test, the information was easily transformed using TTS theory and Cox-Merz rule.

REFERENCES

1. I. Krieger, and L-H. Lee, Lieng-Huang (Eds.), "Flow Properties of Adhesives", *Adhesive Bonding*, Plenum Publishing, **1991**, pp. 31-45
2. S. G. Chu, L-H. Lee, (Eds.), "Dynamic Mechanical Properties of Pressure Sensitive Adhesives", *Adhesive Bonding*, Plenum Publishing, **1991**, pp. 97-115
3. W. P. Cox and E. H. Merz, *Journal of Polymer Science*, **1958**, 28, p. 619
4. A. V. Tobolsky, *Properties and Structures of Polymers*, Wiley, New York, **1960**
5. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, **1980**
6. M. L. Williams, R. F. Landel, and J. D. Ferry, *Journal of the American Chemical Society*, **1955**, 77, p. 3701

KEYWORDS

adhesives, flow properties, glass transition, thermoplastic polymers, rheology, viscosity