

# USE OF RHEOLOGY AS A DEVELOPING AND TROUBLESHOOTING TOOL FOR PSA APPLICATIONS.

Michael DeFrancis, Applications Engineer, Henkel, Bridgewater, NJ  
Yayun Liu, Senior Development Scientist, Henkel, Bridgewater, NJ

In the PSA industry we are constantly looking for cutting edge ways to further improve our products in order to tackle more complex projects. The use of standard test methods such as peel, shear, and tack are very informative about the performance properties of adhesives, however can be very time consuming and do not paint the entire picture. To help us better understand more about properties of different adhesives, we can turn to rheology as a testing practice. Rheology is defined as the study of the deformation and the flow of matter, and reveals the structure-property relationship of the key components in PSA, and its viscoelastic behavior in response to time, temperature and stress. Utilizing this testing method can offer many benefits as a developmental, troubleshooting, and complaint resolution tool. This paper will discuss how we can relate rheological properties of adhesives to the performance in various applications.

## Rheology Background

Rheology is a science that studies the deformation and flow of materials. The deformation of the material is studied by examining the elasticity, which is a measurement of a material's ability to store deformational energy. The flow of material is studied by examining a material's viscosity, which is a measurement of the material's resistance to flow. Rheology is science that can be utilized in order to understand how these two variables work together in conjunction to define the viscoelastic properties of materials that are both solid-like and liquid-like, such as polymers. By subjecting the material to different types of stress, the response will combine both the elastic and viscous behaviors of the material. The elastic behavior of the material is measured using the storage modulus, or  $G'$ . Viscous flow and dampening is reflected in the loss modulus, or  $G''$ . Examples of typical oscillatory rheology measurements include temperature sweep, frequency sweep, and time sweep. Dynamic temperature sweep is a method that records data measurements at different temperatures while applying a sinusoidal strain at constant frequency. This test is used to analyze different features of a specific polymer, such as storage modulus  $G'$ , loss modulus  $G''$ , and  $\tan\delta$ . These features help us to understand physical properties of the polymer, such as the glass transition point ( $T_g$ ), melting point, effect of cross-linker, blend compatibility, etc. Frequency sweep rheology is another tool that can be used. This technique varies the frequency of the stress while holding temperature constant. The results of this test help us correlate the mechanical properties of the bulk adhesive materials to their actual adhesion performance [Hu and Puwar]. Understanding how different adhesives respond to different stresses and strains helps paint a picture of how the adhesive will perform in real world applications.

## Vinyl Shrinkage

The use of vinyl as a facestock is a major commonality across different markets to achieve their desired product. Monomeric and polymeric vinyl both serve as major contributors in their respective industries, however both face-stocks contain plasticizer, which over time has the ability to migrate through to the adhesive surface and effect adhesion. Understanding how specific plasticizers will effect adhesive performance is a very difficult task, since the plasticizer and polymer combination is unique to each construction. It is possible, however, to use performance characteristics, as well as rheology profiles to

predict how specific adhesives will perform against plasticizer migration. To do this, we need to understand that the more entangled the adhesive matrix is, the more difficult it will be for the plasticizer to migrate to the surface of the adhesive film. There are two main characteristics of the adhesive that can be adjusted in order to ensure higher entanglement. The first characteristic is the molecular weight of the polymer; the higher the molecular weight and longer the polymer chain is, the more physical entanglement there will be. The second characteristic is the cross-link density of the adhesive. Having a higher cross-link density in the adhesive can be achieved by either adding more of the component that is used as the cross-linking initiator, or adding more functional cross-linking sites to the polymer backbone. Both of these characteristics will increase the entanglement of the internal polymer matrix, and increase the cohesive strength of the adhesive. This increase in cohesive strength can be observed by running performance testing on the modified adhesives. A study was conducted by choosing one adhesive, using three samples that displayed variable vinyl shrinkage, and conducting room temperature shear as well as shear adhesion failure temperature (SAFT) to understand their differences. This test was conducted using the same batch of vinyl to eliminate variability.

**Table 1.** Room temperature shear of one adhesive, three different samples.

Room Temperature Shear (2 mil, 8.8 psi)			
Batch	Run	Hours	Average (hrs)
Lowest Vinyl Shrinkage	1	>479	>479
	2	>479	
	3	>479	
Highest Vinyl Shrinkage	1	69	65
	2	65	
	3	61	
Middle Vinyl Shrinkage	1	256	158
	2	145	
	3	73	

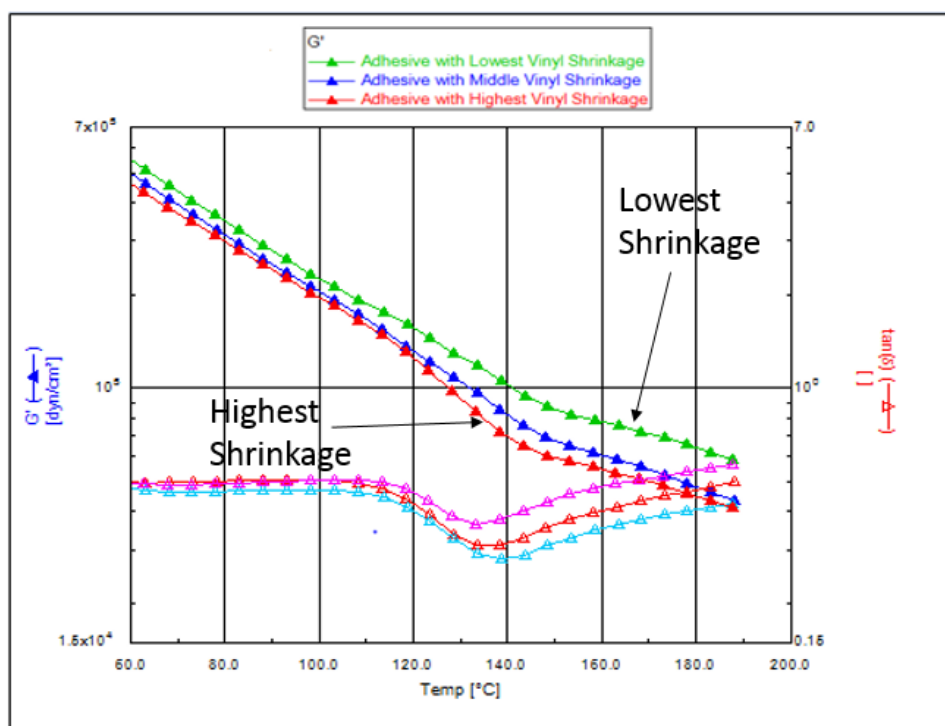
**Table 2.** Shear adhesion failure temperature (SAFT) of the same samples from Table 1.

SAFT (2 mil, 2.2 psi)			
Batch	Run	Failure Temp.	Average
Lowest Vinyl Shrinkage	1	>375	>375
	2	>375	
	3	>375	
Highest Vinyl Shrinkage	1	342	349
	2	355	
	3	350	
Middle Vinyl Shrinkage	1	>375	>375
	2	>375	
	3	>375	

As you can see from both Table 1 and Table 2 (above), the adhesive sample with the lowest degree of vinyl shrinkage showed to also have the highest performance values in both room temperature shear, as well as SAFT. Alternatively, the adhesive sample with the highest degree of vinyl shrinkage displayed

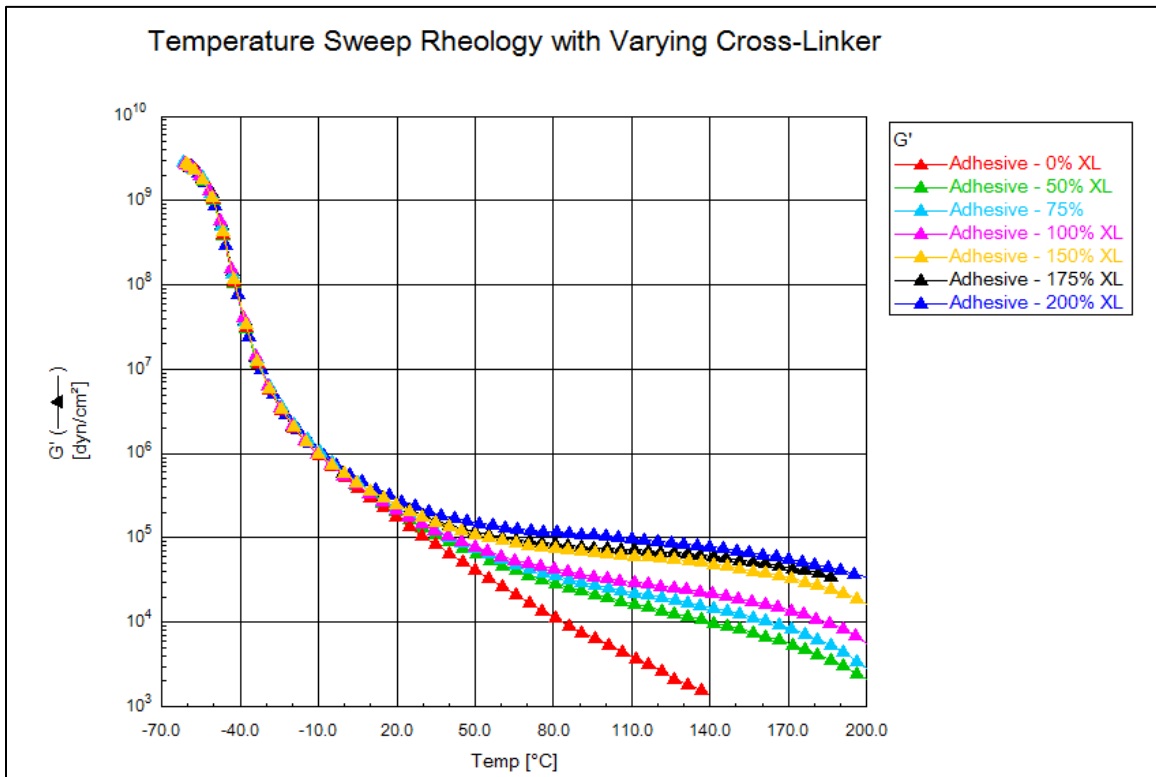
the lowest performance values in both tests. This data represents the fact that adhesives with higher entanglement will achieve better end use performance. While this performance data is very useful, it poses the problem of time sensitivity. What would happen if a study needed to be done to understand the difference in adhesives, but could not wait 400+ hours? For situations like this, rheology has many tools that would be able to show the differences in polymeric capabilities. In this experiment, we used a dynamic temperature ramp. This technique, temperature sweep rheology, measures both the  $G'$  and  $G''$  of the material. The storage modulus,  $G'$ , measures the elasticity of the material, or its ability to store energy. The loss modulus, or  $G''$ , measures the viscous behavior of the material, or its ability to dissipate energy in the form of heat. Both of these measurements are taken over a varying range of temperatures. As you can see in the Figure 1, below, the sample with the lowest vinyl shrinkage has the highest  $G'$  trend through the high temperature performance region (100°C – 200°C). The high elasticity (largest  $G'$  values) directly correlates to lower vinyl shrinkage. This rheological tool can help predict how an adhesive will perform in vinyl applications by testing the internal strength of the polymer.

**Figure 1.** Temperature sweep rheology on the three samples with varying vinyl shrinkage.



This testing method can be used for product development, as well. For instance, take a look at Figure 2, below. This temperature sweep rheology graph uses the same base adhesive, formulated seven different times using different concentrations of cross linker. As you can see, the step change in cross-linker concentration from 25%, 50%, 75%, etc. is reflected in the  $G'$  escalation. Understanding how cross-linker concentration changes will affect the rheology assists in developing an adhesive for various end use applications.

**Figure 2.** Temperature sweep rheology on the same adhesive, with 7 different cross linker formulations.

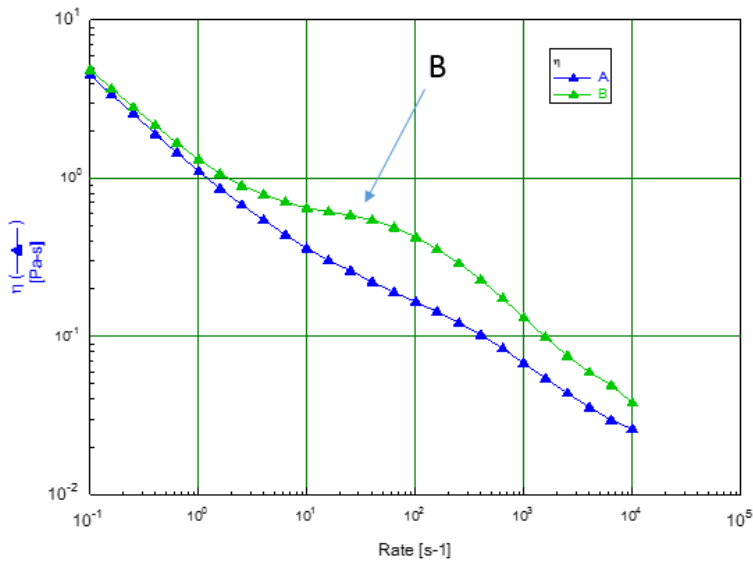


### Using rheology in optimizing coating of water based PSA:

Water based PSA's are typically an emulsion consisting of acrylic polymer, and surfactant, defoamer, thickener and leveling agent to optimize the processing property and performance. Normally, the adhesive films are generated by coating the dispersion on release liner or substrate and then remove water via drying. The most important rheological parameter of a water based PSA dispersion is its viscosity. The viscosity influences the coatability, the film forming characteristics and the properties of the adhesive layer thus formed [Benedek and Heymans, 1997]. The rheology of water based PSA is shear-sensitive. Under different coating speed and coater configuration, the viscosity of the water based PSA being coated could vary significantly depending on its shear behavior. To minimize coating issues and defects, understanding the shear behavior is very critical in formulation and coating operation.

A water based PSA could have very different shear thinning behavior with slight formulation changes. Figure 3 is a water based product with different thickener analyzed under steady shear rate sweep. Both materials A and B are shear thinning and have the same viscosity at low shear rate of  $10\text{s}^{-1}$ , typically measured by Brookfield viscometer. But the viscosity of A is much lower than that of B at higher shear rate ( $1000\text{s}^{-1}$ ) during coating. Shear thinning in the metering and transfer of the coating film can promote de-wetting (Figure 4). Changing the thickener type or amount to maintain higher viscosity under shear usually corrects this problem.

**Figure 3.** Steady rate sweep of water based PSA dispersion



**Figure 4.** Typical de-wetting seen in water based PSA coatings.

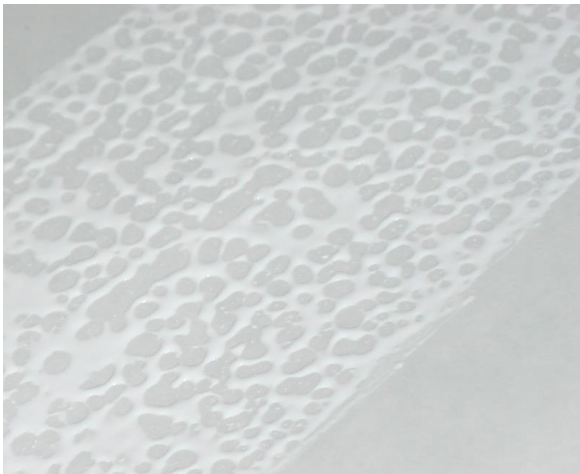


Figure 5 shows two types of coating problems often seen in water based PSA coated by reverse roll coater. Roll speed ratio, the gap between the applicator & metering rolls, and the pressure of the backup roll are the coater contributions to applied coating weight and smoothness. The coating material contributes based on its rheology and surface tension characteristics. These combine with the application roll speed to give the capillary number as:

$$Ca = \mu V_A / \sigma$$

Where:  $V_A$  = Application roll speed

$\mu$  = viscosity

$\sigma$  = surface tension

Ribbing (Figure 5a) is controlled by the capillary number and the metering roll to application roll gap setting and metering roll to application roll ratio (speed ratio,  $V_A/V_B$ ). Too low a gap setting and/or too high a capillary number will promote ribbing. Reducing the surface tension or increasing the viscosity have the effect of increasing the capillary number. In this case, sample A in Figure 5 would have less ribbing compared to sample B, due to the fact that the viscosity of A is much lower than that of B at high shear rate typically used during coating. Different thickener could be used in this case to target certain viscosity range to avoid ribbing. Cascade (Figure 5b) is controlled by the same operating parameters as ribbing: capillary number, roller speed ratio and gap setting. Since smaller capillary numbers move the wetting line further downstream and causes instabilities and cascading, increasing the viscosity or reducing the surface tension would move the wetting line in the right direction [Walter and Strong, 2003].

**Figure 5.** Typical coating flaws seen in water based PSA coated by reverse roll coater.



A) Ribbing



B) Cascading

### **Using rheology to improve pressure wash performance of PSA laminates:**

The protective and decorative film laminated with PSA on automobile, outdoor display are often required to pass multiple pressure wash test. The water pressure can reach very high level. This test cannot be easily done by product development scientist in a typical lab setting. In order to facilitate PSA development and product optimization, using material characterization tools such as rheology can provide insights on understanding of the key control factor and predicting performance in pressure wash test. For example, in a pressure wash test for a laminated film applied on the exterior of automobile, the pressurized water is typically applied at the edge of the film at 30-45 degree angle as shown in Figure 6. The water pressure is gradually increased from 1000psi up to 2000psi at 1000psi/5minutes interval. The pressure at which the film starts to have edge lift until complete delamination are recorded. The tested laminated film is required to survive 1800psi water pressure without having edge lift or delamination. Typically, the delamination initiates at the edge of the PSA/substrate interface. As the water pressure increases, the ability of the adhesive to resist increased peeling force is required. Good wet out, high adhesion and strong cohesion of the PSA material are the key factors for passing high pressure water wash.

Glass transition temperature ( $T_g$ ) is the temperature at which viscoelastic material change from a solid to a flowable melt. At the same application temperature, materials with lower  $T_g$  will have much better wet out and higher tack due to higher molecular mobility. In the rheological measurement,  $T_g$  can be determined by the peak temperature of the  $\tan \delta$  curve, as shown in Figure 8. In Figure 7, the pressure wash results of a set of PSA adhesives were plotted against their  $T_g$ s. It shows  $T_g$  play an important role in determining pressure wash performance. The materials with low  $T_g$  (A, B, C) started edge lift at higher water pressure relative to the materials with high  $T_g$  (D, E, F, G). At the same application temperature, materials with high glass transition temperature have difficulty completely wet out the substrate and cause defects at the interface that are vulnerable under pressure/stress. Once edge lift occurs, defect propagation is hard to avoid. To pass pressure wash test, it is critical to select PSA with low  $T_g$  to form stronger interfacial bonding in the first place.

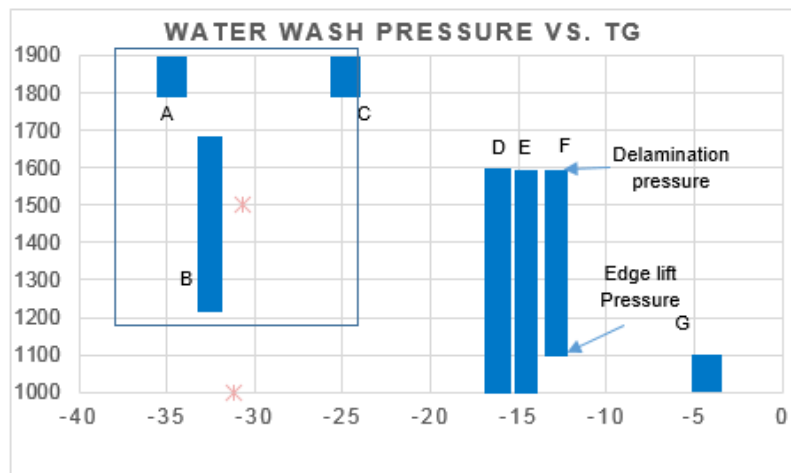
Cohesive strength is also important to pressure wash performance, which can be quantified by storage modulus ( $G'$ ) by dynamic temperature sweep. Figure 8 shows the temperature sweep of three low  $T_g$  PSA film A, B and C. Both A and B have the lowest  $T_g$ . However, B starts to edge lift at a much lower pressure and completely delaminated below required pressure level. The difference in performance can be explained by the much lower storage modulus ( $G'$ ) of B compared to A. Under high pressure, A has much higher cohesive strength to resist peel force exerted by water pressure to cause further delamination than B. Similarly, sample C has relatively higher  $T_g$  vs. A and B, but it has the highest storage modulus. It also passed required water pressure test. This result indicates that both low  $T_g$  and high cohesive strength are required for a PSA to form intimate initial contact with the substrate and to resist delamination. A PSA selection window can be determined based on  $T_g$  and  $G'$  determined by the rheology test (Figure 9).

The finding also provides directions for the formulator to further improve the performance of the current product. For sample B, adding cross-linker to increase the storage modulus will likely to help improve its pressure wash performance. Alternatively, increasing the higher molecular weight fraction of the sample B will also help to increase its  $G'$ .

**Figure 6.** Film laminate under pressure wash test.



**Figure 7.** Pressure wash results vs.  $T_g$  (peak of  $\tan \delta$ ) measured by dynamic temperature sweep

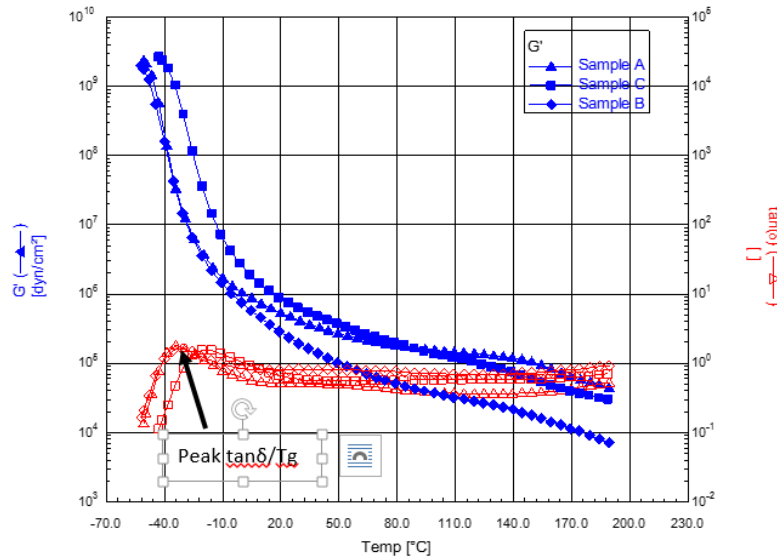


**Figure 8.**

Dynamic



temperature sweep of three PSA films tested by pressure wash.



**Figure 9.** PSA selection window for pressure wash performance

G'	High	Resist edge lift and delamination under high pressure: <b>Best PSA window</b>	Edge lift at low water pressure, will delaminate
	Low	Edge lift at higher pressure, <u>will delaminate</u>	Edge lift and delaminate at low water pressure
		Low	High

$T_g$

## Conclusion

The above information displays three case studies that show the benefit of using rheology to help solve technical problems as well as assist in development work. Rheology testing can provide exceptional information about the properties of adhesives that will assist in drawing conclusions about performance, physical characteristics, and even coating trends.

## Reference

1. Y. Hu and K. Puwar, Use of Rheology in Hot Melt PSA Formulations, National Starch & Chemical Company
2. I. Benedek and L. J Heymans, Pressure Sensitive Adhesives Technology, Marcel Dekker. Inc., New York, (1997)
3. P. Walter and B. Strong, Common Coating Flaws In Reverse Roll Coating, National Starch and Chemical White Paper (2003)