RHEOLOGY AS A QUALITY CONTROL TEST FOR ACRYLIC PSAs

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Pressure sensitive tapes are a versatile product technology for many reasons. One of their significant advantages is that this technology can provide a wide range of peel (adhesion) and shear (cohesive strength) values via the choice of adhesive technology, and that the adhesive technology can readily be customized to meet specific performance targets. This customization is commonly executed by several product design approaches including adjusting the polymer composition, modifying the polymer molecular weight distribution and addition of formulation components.

Looking at this in more detail, solvent acrylics pressure sensitive adhesives (PSAs) are used in applications requiring targeted adhesive and cohesive strengths. Acrylic PSAs in general have broad temperature ranges and good to excellent environmental resistance, and solvent acrylic PSAs in specific are often preferred for more demanding conditions such as the need for high temperature performance, excellent chemical resistance, and high cohesive strength. To obtain these desired characteristics, crosslinking via single component crosslinkers are widely used. Diving in further, a significant majority of solvent acrylic PSA products use metal chelate self-crosslinking (1K/single component) technology. Based on this common PSA product design, the ability to accurately measure the impact of crosslinkers in solvent acrylic PSAs is important to ensuring acceptable and consistent product quality.

The traditional approach for measuring cohesive strength has been the static shear test. The standard method is PSTC-107, "Shear Adhesion of Pressure Sensitive Tape", and has related ASTM, AFERA and CEN standards referenced within. It is a versatile test but known to have large testing variations arising from multiple potential sources. In this paper, we will present our work on implementing a temperature sweep rheology test as a significantly more robust quality control methodology for evaluating cohesive strength performance of acrylic PSAs. We will demonstrate the applicability of this novel methodology to two adhesives: a high peel/high tack adhesive, and a high cohesive strength acrylic adhesive. The advantages and method implementation approach of temperature sweep rheology for QC testing will be discussed in detail.

Temperature Sweep Rheology Basics

Temperature sweep rheology is a readily available rheology technique and approach used on adhesives to measure physical characteristics as a function of temperature. A typical example of the output of a temperature sweep rheology run is shown in Figure 1. G' is the elastic modulus and is a measure of the cohesive strength of the adhesive. G" is the loss modulus and indicates the ability of the adhesive to dissipate energy. Tan δ, with is G"/G' is used to identify changes in the physical state of the material such as the glass transition temperature (Tg). As a side note, care must be taken when using the Tg value from temperature sweep rheology as compared to the Tg from differential scanning calorimetry (DSC). There is a significant offset between temperature sweep rheology and DSC Tg values due to the impact of how the values are measured. As such, DSC Tg values are always significantly lower than temperature sweep rheology measured values.

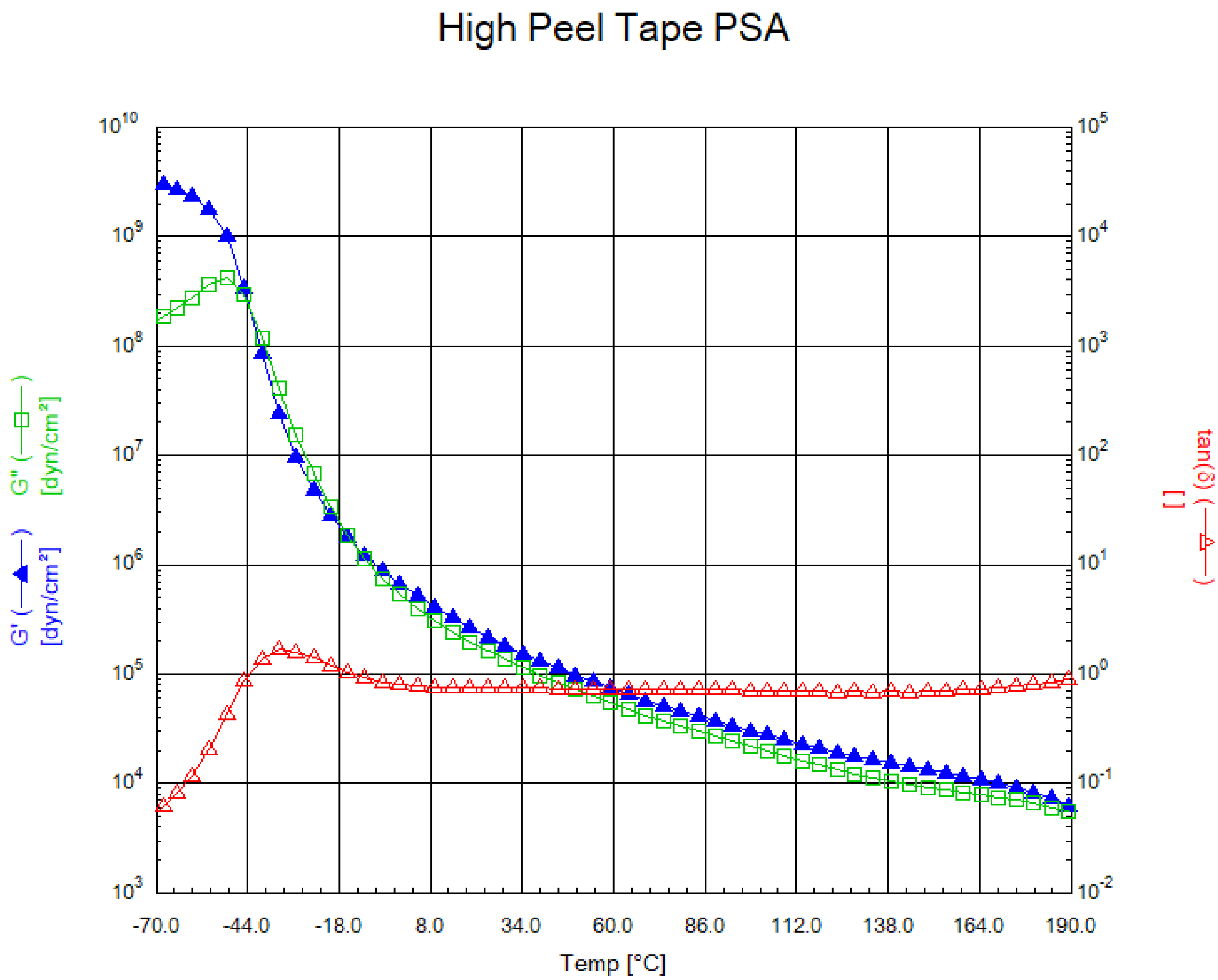

Figure 1: Example of a temperature sweep rheology curve for an acrylic PSA.

Temperature Sweep Rheology Measurements

The temperature sweep rheology measurements were performed on two different instruments. The method development work was conducted using a TA Instruments RDA III rheometer located in Bridgewater, New Jersey. The geometry type was parallel plates (7.9 mm diameter), and the temperature sweep was conducted at 5 °C/minute at 10.0 rad/seconds. The minimum and maximum temperature were different for each adhesive. The minimum temperature is chosen based on the temperature range of the rigid plateau, while the maximum temperature is based on where the modulus (G') has dropped significantly. Sample preparation involved 1 mil free film/transfer tape coatings and then stacking multiple layers of adhesive while ensuring no air pockets were present.

Temperature sweep rheology measurements for Quality Control purposes were conducted in a QC laboratory located in Salisbury, North Carolina. The equipment used was a TA Instruments Hybrid II rheometer; all other experimental conditions and sample preparation were identical to the method development work conducted in Bridgewater, New Jersey.

For QC purposes, tan δ at specific temperatures was chosen for specification setting. While G’ is the value directly correlated to the impact of crosslinker in a solvent acrylic, the G’ data shows variation that is not present in the tan δ data. This difference is postulated to arise from the exact amount of material between the parallel plates. A closer look at the data below in Figure 2 for the High Peel PSA illustrates clearly that the G’ traces are equivalent in shape but slightly offset from each other in their starting modulus (G’ maximum value). When you enlarge the data to evaluate it more closely in Figure 3, the G’ curves are slightly offset from each other, but that the tan δ curves overlay perfectly. Based on this finding, the use of tan δ values is the preferred approach.

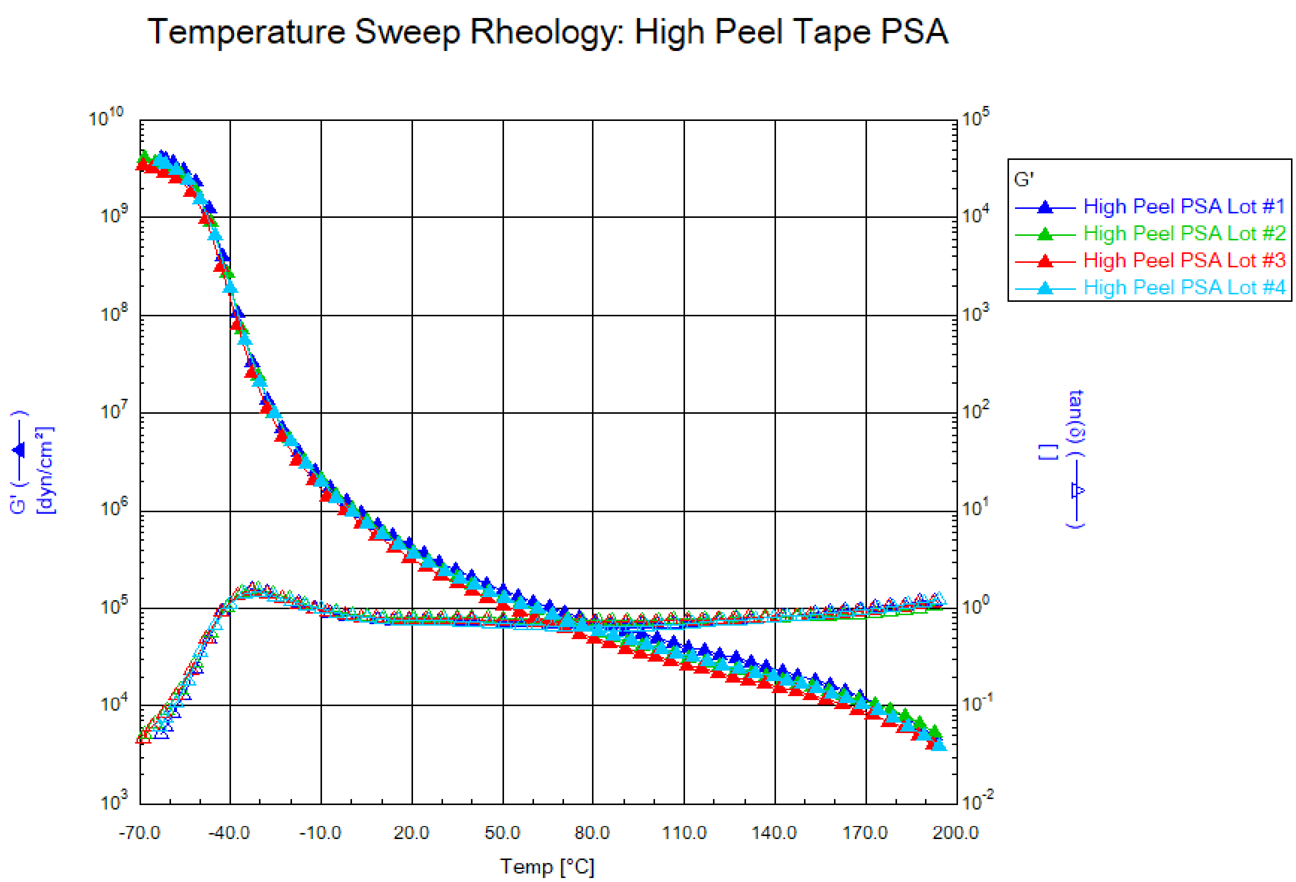

Figure 2: Temperature sweep rheology results for multiple commercial lots of a High Peel PSA

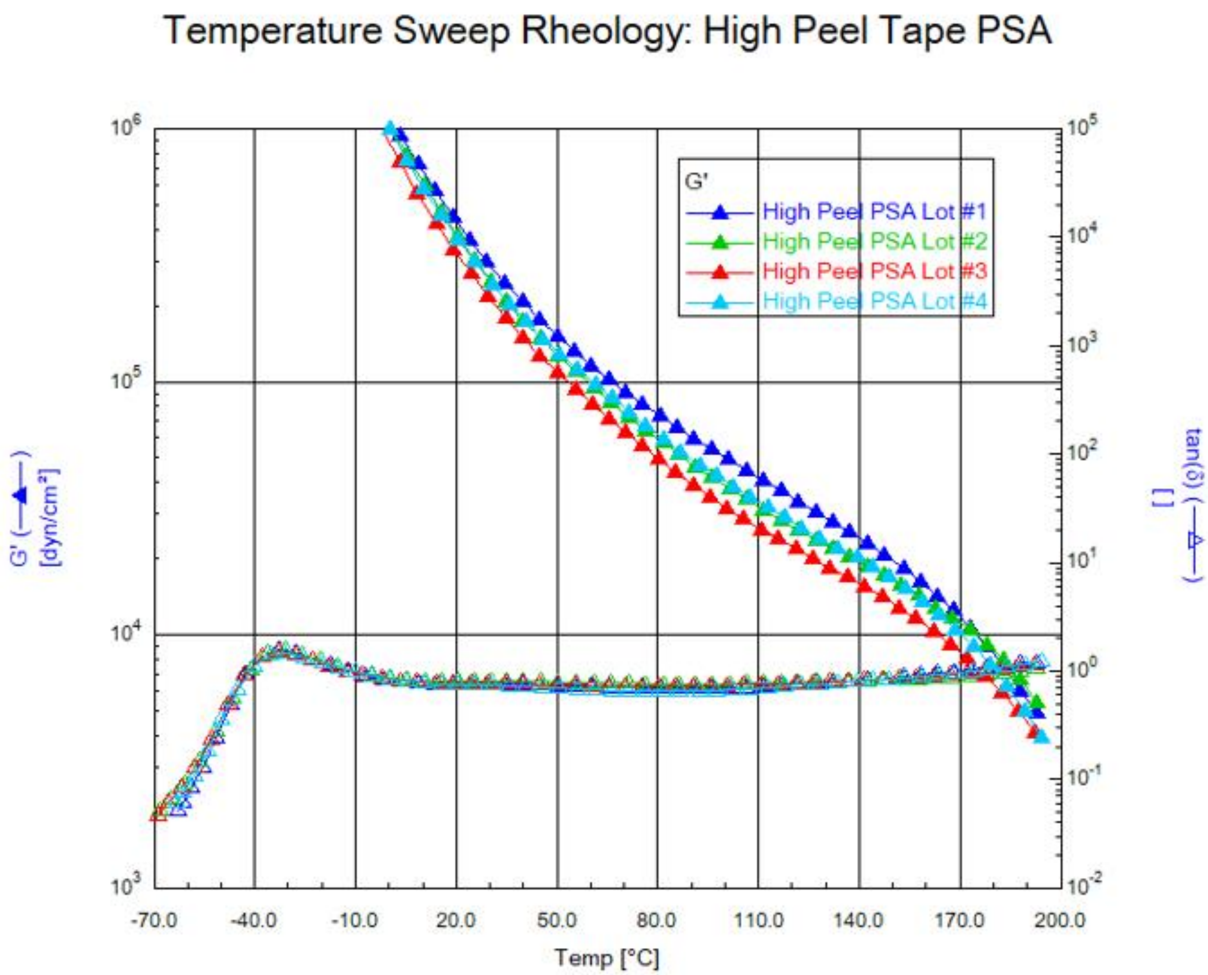

Figure 3: Enlargement of the temperature sweep rheology data from Figure 1

Formulations

Formulations of two different adhesives were prepared: a High Peel Tape PSA and a High Temperature Foam Tape PSA. For both adhesives, formulations with varying amounts of crosslinker were prepared, with 100% crosslinker defined as the standard crosslinker level for that adhesive. Formulations were prepared with crosslinker levels both above and below 100% crosslinker.

Analytical Methodology

The analytical methodology and approach:

1. Samples were prepared at a range of crosslinker levels both above and below the target level
2. All samples were coated and dried and then analyzed by temperature sweep rheology. Based on these results, appropriate temperatures for quantifying tan δ were identified.
3. Statistical analysis was performed with multiple QC analysts to confirm that the method is capable when performed in a multi-analyst QC environment.
4. Rheology data was collected on multiple commercial production lots of material that was validated as in-specification via the static shear test.
5. Specification limits were then identified using the data in the previous steps.

Using this analytical methodology, two different tape adhesives were analyzed:

1. The initial evaluation and method development was performed on a High Peel Tape PSA. This product has a relatively low static shear value of less than 10 hours at 4.4 psi. Historical internal experience has shown that 4.4 psi static shear tests are the most robust; 2.2 psi and 8.8 psi testing are more likely to show testing issues.
2. The method was then applied to a High Temperature Foam Tape PSA with a static shear value of excess of 60 hours at 8.8 psi. This product has historically illustrated many issues with static shear testing.

High Peel Tape PSA

The rheology results for the crosslinker ladder study for the High Peel Tapes PSA are shown below in Figure 4. Based on these results, tan δ values at 75, 100 and 125 °C were identified as the appropriate values for QC specification setting. These temperatures were chosen due to sufficient differentiation of the tan δ between the various curves. Lower temperatures did not show sufficient differentiation between the curves.

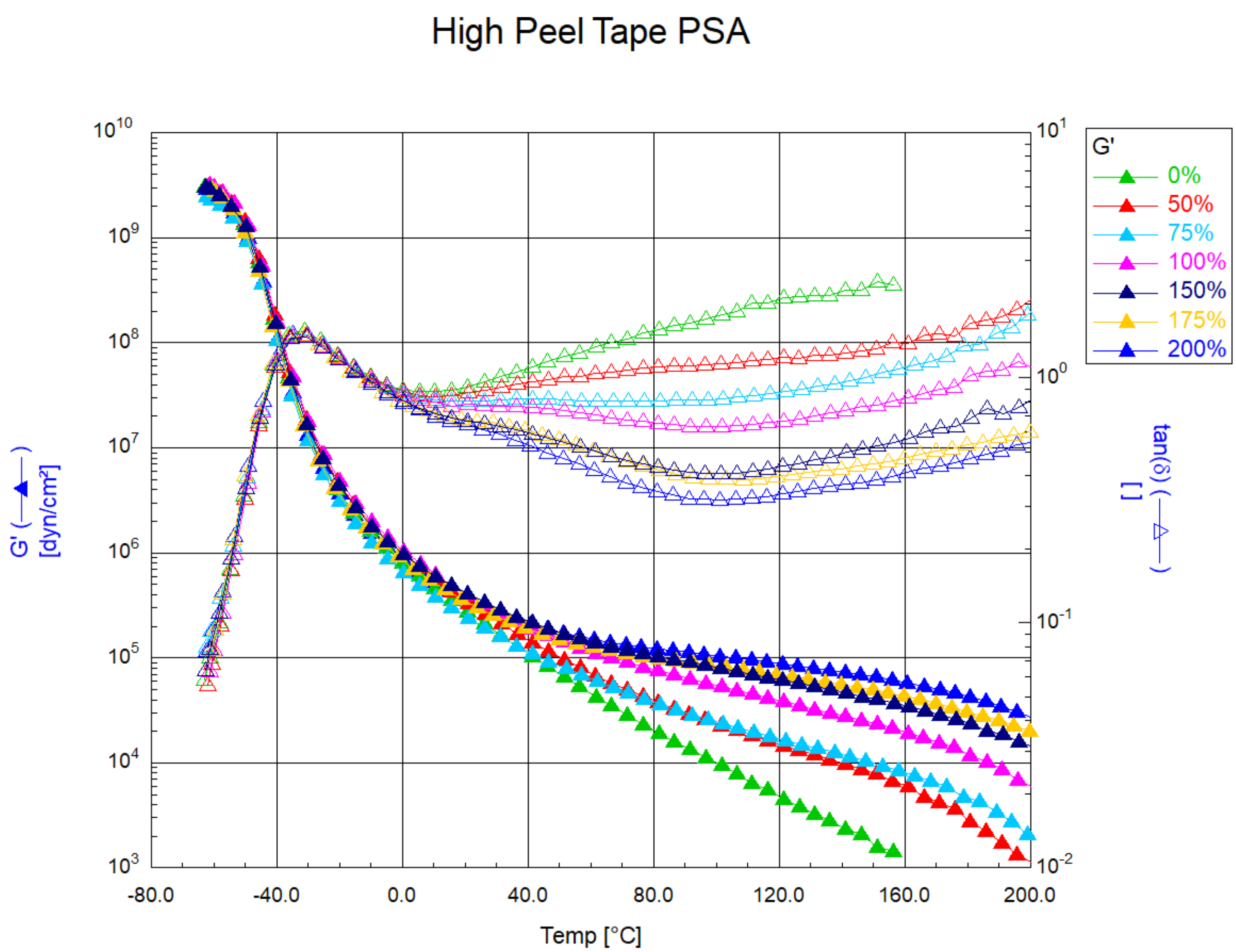

Figure 4: Temperature sweep rheology results for different crosslinker levels of the High Peel Tapes PSA adhesive.

For these formulations, five (5) different analysts then performed rheology measurements on three of the samples: the 75%, 100% and 150% crosslinker samples. Those results are shown below in Table 1. Based on these results, the differentiation is not uniform over the full crosslinker range; the method is able to differentiate smaller crosslinker content differences at lower crosslinker levels than at higher crosslinker levels. Put another way, the impact of crosslinker level change on G' (and hence on tan δ) decreases as the crosslink density is increased.

Table 1: Multiple analyst temperature sweep rheology testing on three different crosslinker levels of the High Peel Tape PSA.

	75% X-linker				**100% X-linker**				**150% X-linker**		
	75°C	100°C	125°C		75°C	100°C	125°C		75°C	100°C	125°C
QC1	0.87	0.87	0.89		0.64	0.63	0.63		0.48	0.42	0.41
QC2	0.76	0.73	0.73		0.55	0.51	0.50		-	-	-
QC3	0.80	0.77	0.79		0.57	0.50	0.51		0.48	0.40	0.38
QC4	0.82	0.78	0.78		0.69	0.60	0.58		0.47	0.38	0.36
QC5	0.91	0.92	0.98		0.69	0.60	0.58		0.46	0.37	0.36
Avg.	0.83	0.81	0.83		0.63	0.57	0.56		0.47	0.39	0.38
Std. Dev.	0.06	0.08	0.10		0.07	0.06	0.05		0.01	0.02	0.02

In addition to the multiple analyst testing, data was collected over twenty (20) different production lots. That data is shown below along in Table 2 with the proposed specification limits.

Table 2: Temperature sweep rheology results for in specification (per static shear) production lots of the High Peel Tape PSA.

	tan δ 75 °C	**tan δ 100 °C**	**tan δ 125 °C**
Avg.	0.70	0.65	0.64
Std. Dev.	0.04	0.05	0.05
Mean+/-3SD			
-3SD	0.58	0.50	0.48
+3SD	0.82	0.79	0.80
Spec Limits			
Lower	0.55	0.50	0.50
Upper	0.80	0.80	0.80

High Temperature Foam Tape PSA

The next product for which this approach was applied is a High Temperature Foam Tape PSA. Unlike the High Peel Tape PSA, for which reproducible and consistent static shear data was available, the High Temperature PSA is poorly suited to static shear testing. This adhesive had a long history of extra requirements for static shear testing (including dedicated test panels) that did not solve issues with inconsistent shear values and failure modes. Many different approaches were evaluated unsuccessfully to improve the status shear testing including different thickness facestocks, different coat weights and moving to a dynamic shear test instead of the existing static shear.

Static shear data at 8.8 psi is shown below under several different conditions for three production lots to demonstrate the significant variation seen for the High Temperature Foam Tape PSA adhesive. These conditions included preparing additional test strips from the same coating, preparing a new coating, using a longer dwell time on panel, and reconditioning the panels: in essence, a "deep clean" to make the panel surface as close as possible to original. There is significant variation not just between the various approaches but even within a given condition: values of 18.57, 29.23 and 51.25 hours (Lot #1, recoat) is simply too large a variation.

Table 3: Shear testing results, High Temperature Foam Tape PSA, multiple values

	High Temp Foam Tape PSA Lot #1		**High Temp Foam Tape PSA Lot #2**		**High Temp Foam Tape PSA Lot #3**	
Original	15.67		16.46		17.35	
	13.12		17.72		22.04	
	19.35	16.04	7.43	13.87	21.51	20.30
Rehang	20.95		30.95		10.75	
	19.92		11.97		12.51	
	18.86	19.91	18.24	20.39	11.30	11.52
Recoat	29.23		31.00		19.06	
	51.25		18.68		34.71	
	18.57	33.02	14.94	21.54	51.14	34.97
Longer dwell on panel	5.88		47.34		45.47	
	9.85		27.91		46.25	
	9.05	8.26	68.70	47.98	22.34	38.02
Panels reconditioned	14.66		8.98		-	
	6.99		11.32		-	
	12.16	11.27	14.66	11.65	-	-
Panel reconditioned, add'l cleaning	10.36		5.59		8.60	
	10.87		12.74		12.89	
	9.19	10.14	2.37	6.90	8.20	9.90

For the next step, molecular weight and temperature sweep rheology testing was conducted on a set of samples with significantly different 8.8 psi static shear values. The two main drivers of batch-to-batch variation in static shear are crosslinker level and molecular weight. Metals analysis (not reported here) was also conducted and confirmed that all production lots were at the targeted crosslinker charge.

The molecular weight distribution results (as measured by GPC [gel permeation chromatograph]) for a set of production lots with measured static shear values ranging from 9 to 110 hours are shown below in Figure 5. The minor lot-to-lot variation in molecular weight are far too small to account for the large differences in static shear values.

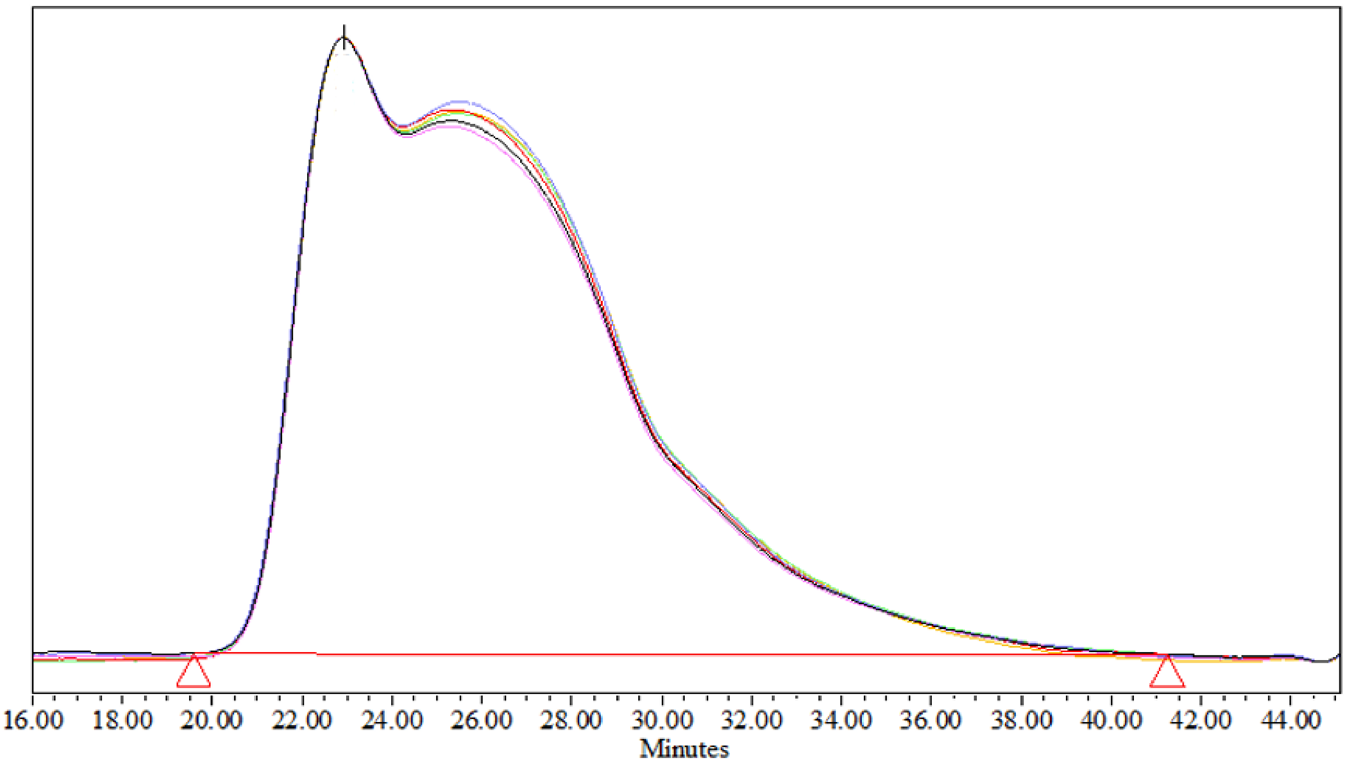

Figure 5: Molecular weight distribution results for multiple in specification production lots of the High Temperature Foam Tape PSA.

Figure 6 illustrates the temperature sweep rheology results for this adhesive over a wide range of measured static shear values. Based on these combined results from molecular weight, metals analysis and temperature sweep rheology, we have demonstrated that the variation of the static shear results are due to a testing issue and not arising from lot-to-lot variation in the adhesive itself. Thus, temperature sweep rheology is a technique well suited to applicability for this adhesive.

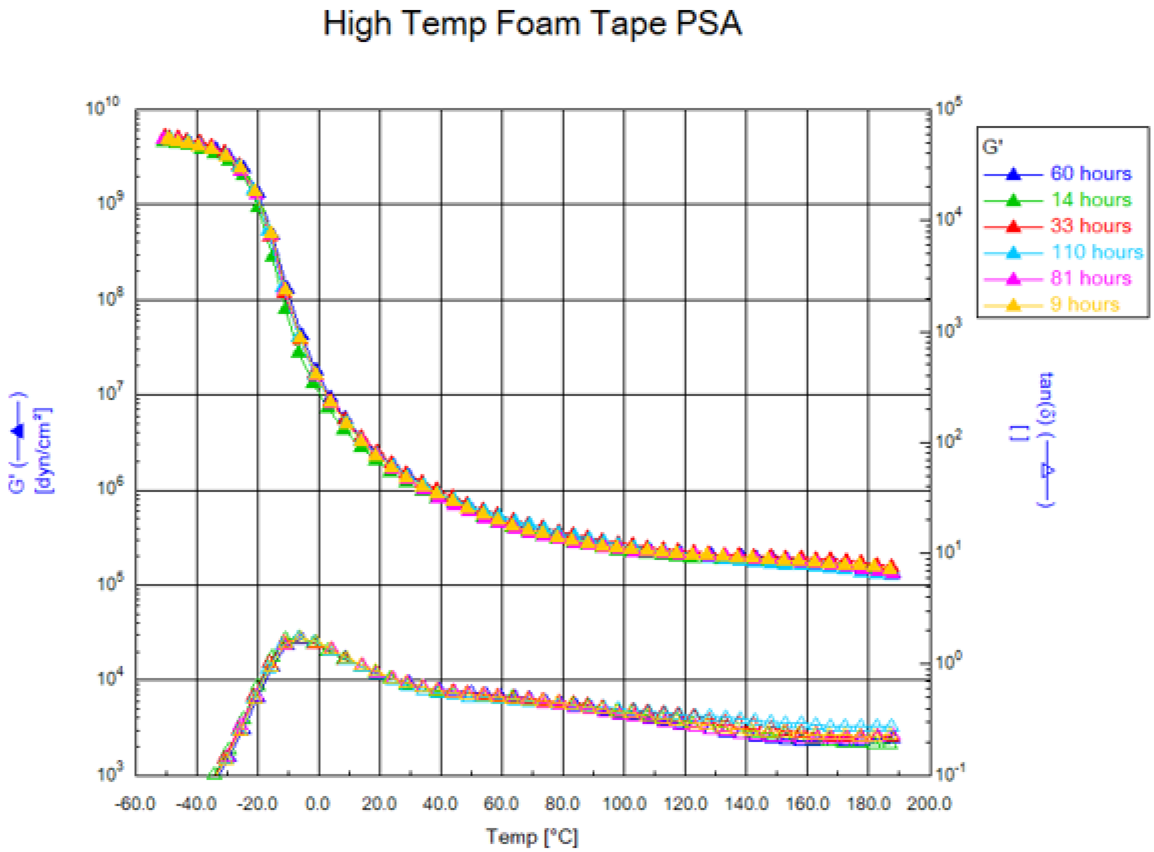

Figure 6: Temperature sweep rheology results for multiple lots of the High Temperature Foam Tape PSA.

Figure 7 below illustrates the temperature sweep rheology results over a wide range of crosslinker levels for this adhesive. The results show that for this adhesive, appropriate temperatures for measurement of tan δ are 125, 150 and 175 °C. This illustrates a key point on this QC method: the specific measurement temperatures for tan δ will vary between product types/product families.

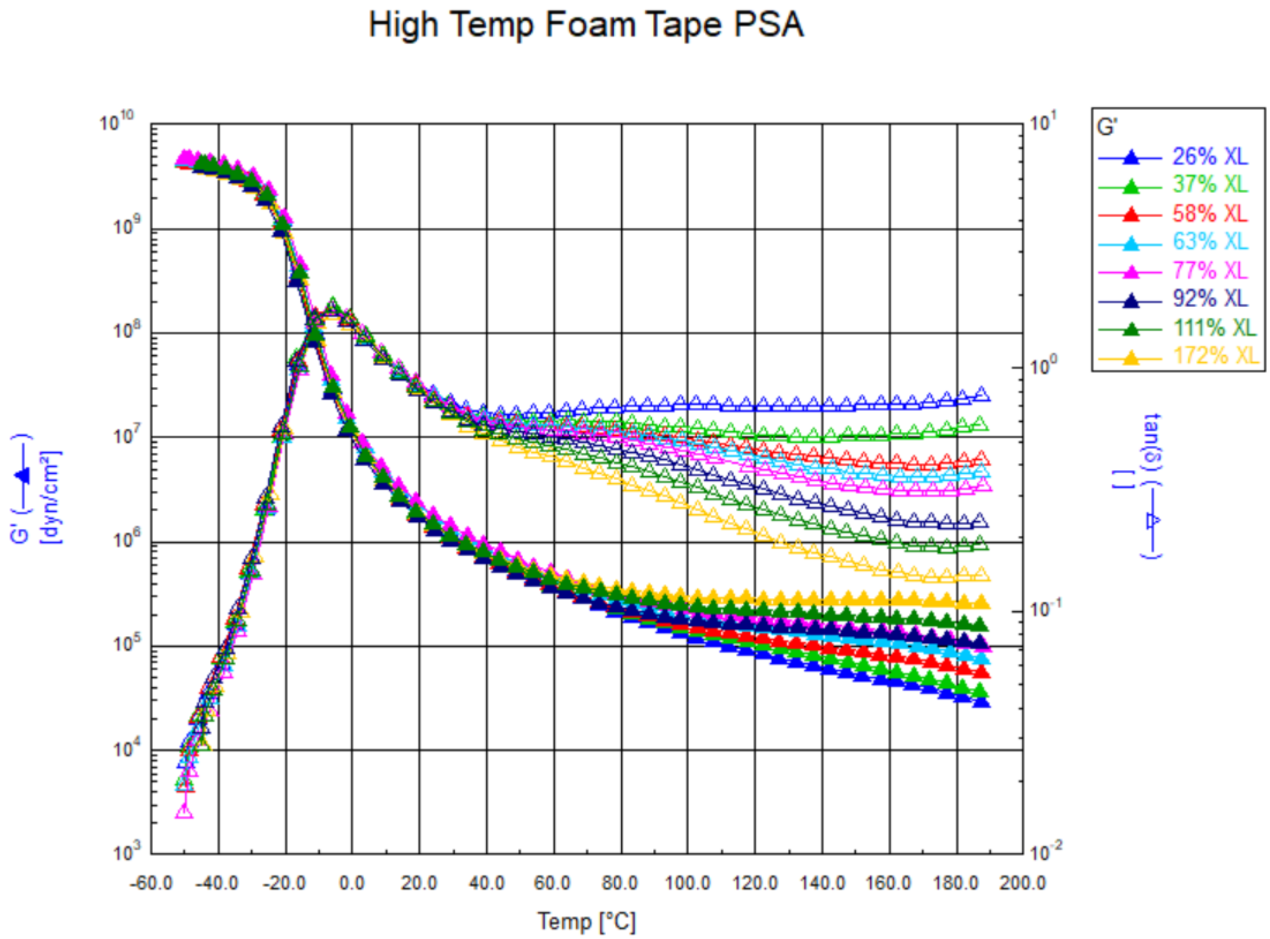

Figure 7: Temperature sweep rheology results for the High Temperature Foam Tape PSA as a function of crosslinker level.

Conclusions

This paper has illustrated the suitability of temperature sweep rheology as a potential replacement for static shear testing in a QC environment for solvent acrylic PSA products. Its applicability to a range of solvent acrylic products has been demonstrated, and the detection limits and reproducibility of the test has been shown.

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