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TRANSPOSABLE ADHESIVES: ACRYLIC PRESSURE SENSITIVE ADHESIVES WITH REACTIVE COMPONENTS

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Abstract

Pressure sensitive adhesives (PSAs) are used in many different applications where the performance properties of the adhesive are specific and constant as applied. However, recent increasing performance demands require performance windows beyond typical PSA properties after application. Those adhesives that can go from one PSA state to another, once applied, provide the opportunity to expand performance in situ. One example would be a removable adhesive that can transpose to a permanent adhesive after a triggered reaction. This presentation provides a fundamental characterization of PSAs via viscoelastic properties. In addition, routes to acrylic PSA systems that transpose from one set of properties once applied to another set of properties with supporting examples thereof will be discussed. The examples will focus on specific applications where high strength adhesives are needed to withstand harsh environments that standard PSAs cannot.

Introduction

Pressure sensitive adhesives (PSAs) have been an integral part of many industries that require the bonding of two or more materials. PSAs are commercially available in many forms: hot/warm melts, solvent borne, water based, and syrups. They are used from applications as simple as paper labels to high-performance tapes used to bond two pieces of an automobile. No matter the application, the PSA has a set of viscoelastic properties that exhibit permanent adhesion characteristics once applied to a substrate. These adhesion characteristics are constant outside the typical responses from degradation from external environmental conditions such as temperature and chemical exposure, for example.

With advancements in technology over the past decade, applications now exist that require PSAs to show different adhesion performances at different stages of the application process. An example would be a PSA that exhibits properties like a removable label at application, but transposes to a high-strength PSA similar to an HVAC tape in a second stage, when activated by an external stimuli. This concept extends beyond just transposition from one PSA state to another, but also includes transpositions from a PSA state to a structural bond. Additional uses include the need for transposition from high adhesion to low adhesion (debond on demand) that has been heavily researched and well documented.[2-6]

This paper will discuss PSAs that transpose from low adhesion properties to high adhesion properties via precise thermal- or UV-activated chemistries. Examples and data will be presented to support the transposition of adhesion properties of a base acrylic polymer using the activating chemistries. The examples are tested in tape form and are designed for tape applications. For structural adhesive applications, improved tape stability enables the adhesive to be supplied in tape form for easy and efficient application through controlled bond lines, which is an advantage over the less-favorable approach of using applicator guns.

Background

The adhesion properties of a PSA can be manipulated by multiple variables during the synthesis of the polymer. In Table 1 below, a few major contributing variables, along with their property effects, are displayed.

Table 1: Synthesis Variables and Their Resulting Property Effects

Variable	**Effect**
Monomer Choice	Glass Transition, Solubility Parameter
Functionality of Monomers	Adhesion Promotion, Crosslinking Sites
Molecular Weight	Peel/Shear Balance
Branching	Cohesive Strength

In addition to synthetic variables, there are additives that are introduced to the polymer post-synthesis that help enhance certain adhesion properties of the PSA. Some examples of these additives are shown in Table 2.

Table 2: Additives and Their Resulting Property Effects

Additive	**Effect**
Tackifier	Improve Tack/Peel
Crosslinker	Improve Cohesive Strength
Fillers	Resistance (*i.e.*, Flame, Chemical, etc.)
Antioxidants	Oxidative Degradation

With the combination of the synthetic variables and additives, a broad range of PSA performance can be achieved. Performance can be qualified by the viscoelastic properties of the PSA.[7] Dynamic Mechanical Analysis (DMA) enables the industry to measure the viscoelastic properties of PSAs. In this technique, the storage (G') and loss (G") moduli are measured at two frequencies which represent the bonding and debonding states. With the corresponding measurements, the PSA performance window can be predicted based on where it falls on the plot depicted in Figure 1. All PSAs will have a performance window somewhere in Figure 1.

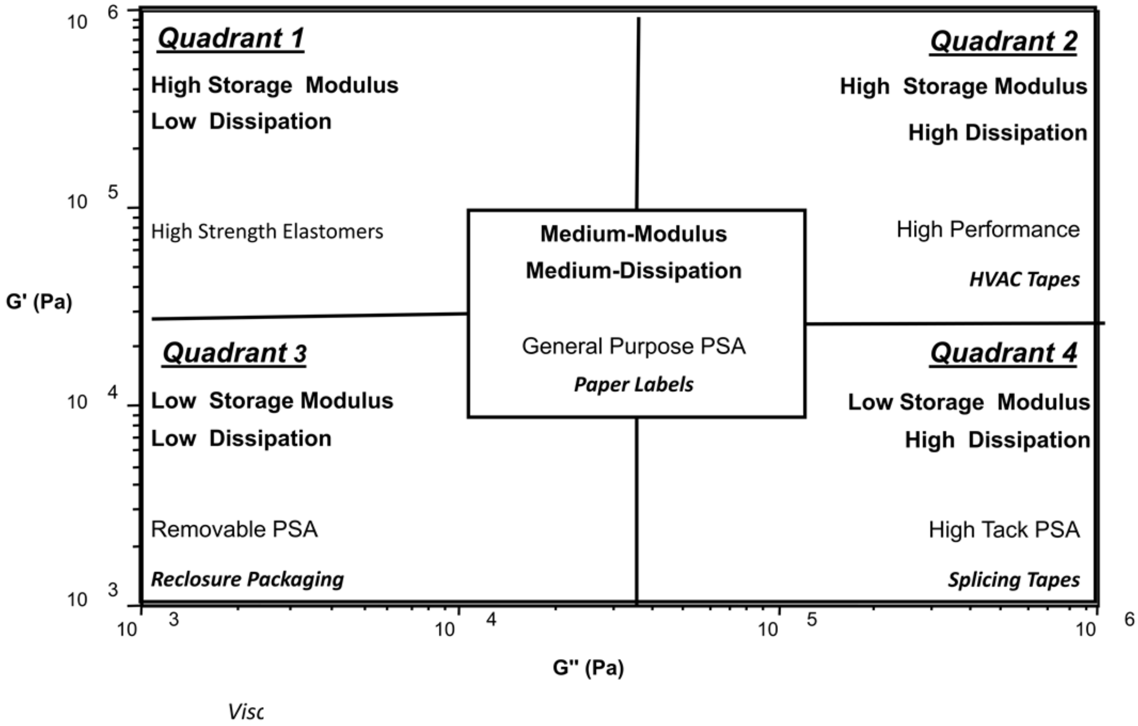

Figure 1: Overall Viscoelastic Window for All PSAs

Using this method of characterization, data will confirm the transposition of PSAs from one set of PSA performance to another (*i.e.*, from one quadrant to another). Data will also suggest a PSA transposing from one PSA quadrant to a structural state located well above the Dahlquist criteria ($G'=10^5$).[8]

The goal of the following transposable adhesive example was to use a thermal or UV activator that would trigger a chemical reaction to cause the adhesion properties to change after application. Whether the change in adhesion properties was to another PSA type or to structural was dependant on the application. For the examples in this paper, the transposition chemistry is epoxy polymerization via the activators. Figure 2 shows the transposition process as a function of cure/strength vs. time.

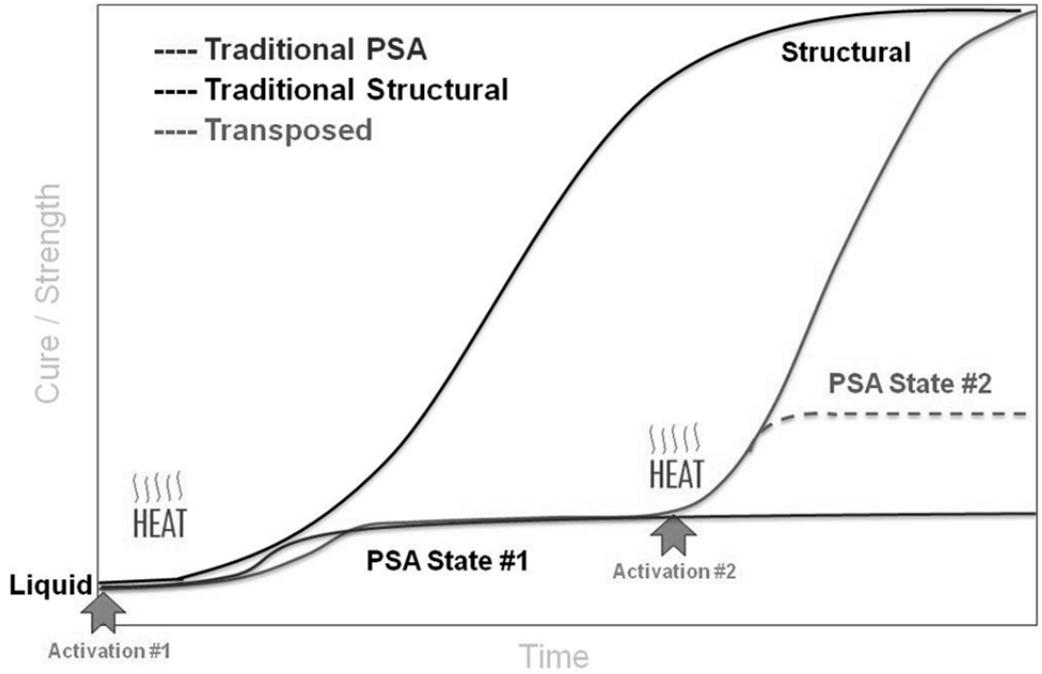

Figure 2: Illustration of the Curing of Traditional PSAs and Structural Adhesives Vs. Transposable Adhesives

Activation 1 designates the coating process or mixing of 100% solids two-part structural adhesive which yields a PSA of state #1 or structural state respectively. At this point, general crosslinking present in the base polymer system is contributing to the PSA performance, but not the epoxy chemistry. Activation 2 occurs sometime after application and designates the triggerable reaction to cause the transposition to PSA state #2 or structural. After activation #1, there is no change in performance state #1 after application until activation #2. In comparison, traditional PSA and structural adhesives have only one activation (coating/drying PSAs or mixing two-part structural adhesives) and directly reach their end state. Transposable adhesives allow the user to take advantage of PSA state #1 for extended periods of time and activate to state #2 on demand by either thermal or UV exposure.

Experimental

The same base solution polymer was used for all the examples in which the examples only differ by the amount of epoxy diluent added. Base acrylic esters such as 2-Ethylhexyl Acrylate (EHA), Butyl Acrylate (BA), and Acrylic Acid (AA) were obtained from various commercial suppliers and used as received to polymerize the base polymer. The acrylic polymerization was initiated with Azobis(isobutyronitrile) (AIBN) and made in organic solvents. The base polymer was formulated with aluminum acetoacetonate (AAA) at various levels by weight based on polymer solids. Epoxy S-21 was obtained from Synasia and used as delivered. The thermal super acid generator was obtained from King Industries and used as received. All samples were coated at approximately 2.0 mil adhesive thicknesses onto 100% solids platinum-cured silicone paper liner. The coatings were all air dried for 10 minutes and placed in a forced air oven for 10 minutes at 80°C and closed with 100% solids platinum cured silicone paper liner. Adhesion testing was done on transfer coatings to 2.0 mil Aluminum foil. The laminates were all aged in a controlled climate room (70°F @ 50% humidity) for 24 hours prior to testing. The transposition was done via thermal activation of epoxy polymerization at 140°C for 15 minutes after application by the designated dwell time. The UV example was transposed via an Uvitron Intella-ray unit fitted with 600 watt/in UV-B bulb. The adhesive was exposed to UV light and then immediately used to construct an Aluminum lap shear such that the transposition chemistry was initiated but completed after the lap shear construction was made.

Dynamic Mechanical Analysis (DMA) was performed on a TA Instrument AR-2000 rheometer using parallel plate clamps. 1.0 mm thick samples were placed in the clamp and equilibrated to 30 °C. Frequency sweeps were conducted from 0.01 rad/s to 100 rad/s at 30°C to construct the viscoelastic windows. Temperature sweeps were conducted from -80°C to 180°C to measure storage modulus at 10 rad/s.

Results and Discussion

The first example is shown in Table 3, where the adhesive system transposes from a low strength adhesive to a structural end state via UV activation. The tensile strength is reported for a 1"x1" overlapped Aluminum lap shear (ASTM D1002) for the base PSA, a high performance PSA modified with reactive silane oligomer to form a high strength interpenetrating network (IPN)[9], and the base PSA transposed to structural.

Table 3: Tensile Strength of Transposed Adhesive Vs. the Base Adhesive and a High Strength IPN PSA

	Base PSA	**IPN PSA**	**Transposed PSA**
1"x1" Aluminum Foil Lap Shear -Tensile (psi)	45	290	400+

The lap shear data shows that the transposable adhesive system improves the tensile strength of the base adhesive 10x and exceeds the tensile strength of a high performance IPN used in industrial tapes (Note: 400 psi was the max for the load cell used in the study). In comparison, high strength structural adhesives have a tensile strength of about ~1000 psi (7MPa); however some applications only require up to ~300 psi (2 MPa) to create a structural bond.[10]

The next example used the same base polymer and is transposed to a high-performance type PSA. The 180° peel strength (ASTM D3330) off stainless steel after a 15 minute and 24 hour dwell is reported along with room temperature (ASTM D3654) and 65°C static shear in Table 4.

Table 4: Adhesion Data for the Unreacted Transposable Adhesive Vs. the Transposed Adhesive

	180^o Peel on Stainless Steel (pli)		**8.8 lb/in^2 Static Shear on Stainless Steel (Min)**	**5 lb/in^2 65^{o}C Static Shear on Stainless Steel (Min)**	
Dwell Time	**15 Min**	**24 Hour**		**Min**	**Slip (mm)**
Unreacted Transposable	1.97	2.38	8.55 Adhesive	78.5 Adhesive	Failure
Transposed (Immediate)	4.34 Stain	4.47 Stain	10,000+	5300+	0
Transposed (24 Hr Open Time)	3.80 Stain	3.91 Stain	10,000+	n/a	n/a

As reported, the peel adhesion more than doubles after the thermal activation of the epoxy polymerization. Not only does the peel adhesion double, but also the shear dramatically increases. This is unique because typical PSAs have a balancing effect when talking about peel and shear. This effect shows that, as there is an increase in either peel or shear, typically the other property decreases. The enhancements of adhesion and cohesion properties that the transposable adhesive exhibits are also present when the open time (time after application but before epoxy activation) is changed from immediate to 24 hours. Similar adhesion data between these preactivated dwell times suggests this transposable tape system has long/stable open time. This property allows users to apply, remove, and reapply the tape before activation, which makes a permanent bond at the user's will. In addition to increased adhesion, temperature resistance increases with transposition and is supported by the 65^{o}C shear data included in table 4. Resistance to temperature makes these tapes attractive for automobile applications under the hood or any application where the adhesive has to withstand high temperatures without degrading.

For example 2, the transposition was thermally activated at 140^{o}C for 15 minutes. These conditions may not be acceptable for some applications. To find the limits of the thermal activation, an experiment was conducted using hot roll lamination on 8 mil Aluminum lap shear samples. The rate of the hot roll and the pressure were held constant at 12 in/min (0.30 m/min) and 110 psi respectively, and the temperature of roll was changed. After the samples were transposed via the hot roll lamination step, lap shear peak load was measured to quantify the level transposition. This lap shear data can be found in Table 5 below.

Table 5: Tensile Strength Vs. Hot Roll Temperature

Temperature (^{o}F)	**Control (Room Temp)**	**300^{o}F**	**350^{o}F**	**400^{o}F**
Peak Load (lbf)	52.80	99.00	252.80	252.85

The data reported is just one example of conditions in which the transposable adhesive was successfully transposed. The level of cure of the activatable epoxy polymerization will be dependent on the substrate and its thickness, and the pressure, speed, and temperature of the hot roll lamination steps. The exact limits of the cure would have to be experimentally found for any given application. For this given construction and hot roll laminator settings, a temperature of 350^{o}F was sufficient heat to fully transpose the adhesive. The fact that 400^{o}F yielded the same tensile strength as 350^{o}F suggests that the max tensile strength (100% cure of epoxy) is roughly 252 lbf.

The final example to be discussed is an adhesive that transposes from a removable adhesive to a general purpose PSA using the same base polymer as the previous two examples, and differs only by the amount of epoxy added to the system. The adhesion data is reported in Table 6 below.

Table 6: Adhesion Data for the Unreacted Transposable Adhesive Vs. the Transposed Adhesive

	180^{o} Peel on Stainless Steel (pli)		**8.8 lb/in^{2} Static Shear on Stainless Steel (Min)**	**5 lb/in^{2} 65^{o}C Static Shear on Stainless Steel (Min)**	
Dwell Time	**15 Min**	**24 Hour**		**Min**	**Slip (mm)**
Unreacted Transposable	1.04	1.31	3.05 Adhesive	2655 Adhesive	Failure
Transposed (Immediate)	2.16 Stain	2.30 Stain	10,000+	5300+	0
Transposed (24 Hr Open Time)	2.29 Stain	2.51 Stain	10,000+	n/a	n/a

Comparable to example 2, the peel adhesion doubles and the cohesion strength dramatically increased, supported by the room temperature and 65^{o}C shear. Also observed is the enhanced performance independent of the open time as expected from the results of the previous example.

Revisiting the viscoelastic windows mentioned as the qualification of the types of adhesives before and after transposition, example 3 was examined by DMA. A frequency sweep was conducted in which the performance window was constructed for the unreacted PSA and the transposed PSA. The resulting viscoelastic windows were found and displayed in Figure 3.

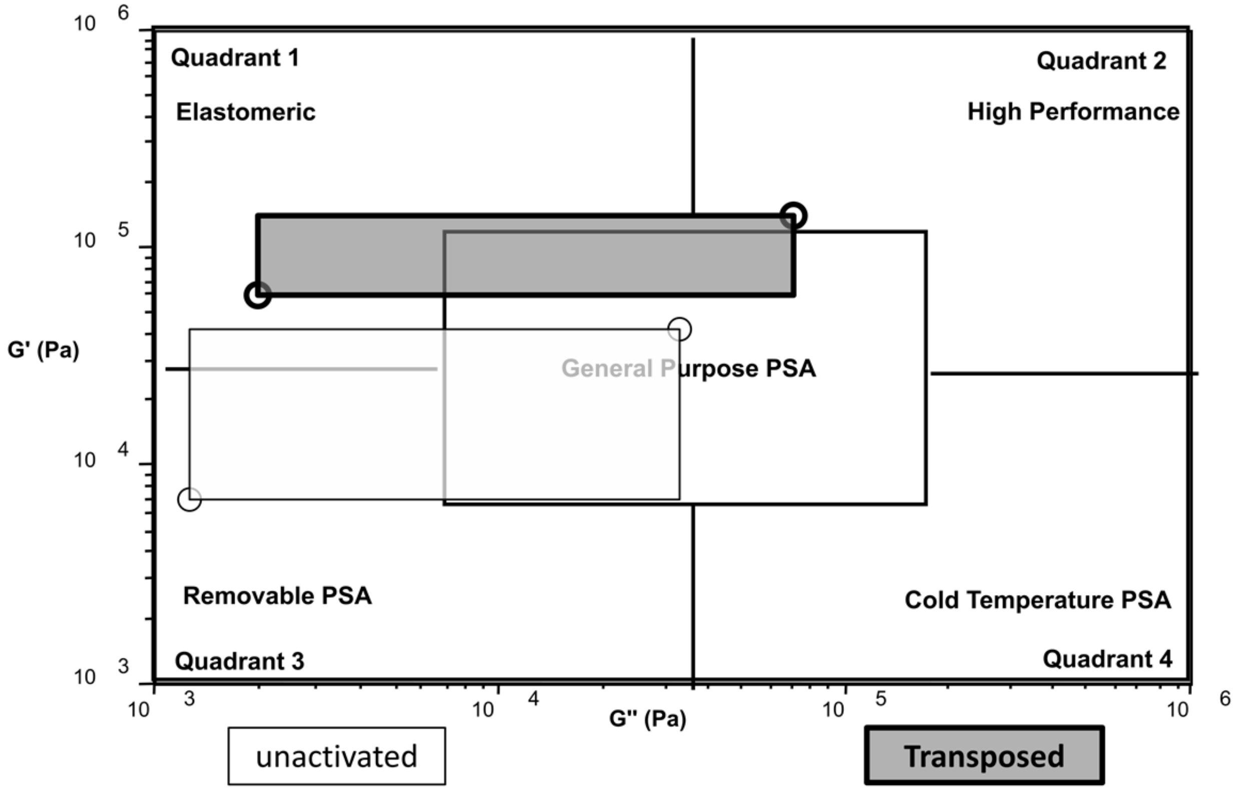

Figure 3: Viscoelastic Windows Measured for Example 3 Before and After Transposition

As seen in figure 3, the performance window was shifted from the removable quadrant to the general purpose region of the overall viscoelastic window plot. Thus, the transposition from one PSA state to another was evident by adhesion performance and analytical techniques.

Higher temperature resistance was included in the adhesion data, but chemical resistance is another property that can also be improved by transposition. To expand on this concept, resistance to Skydrol™ was evaluated. Skydrol™ is an aviation hydraulic fluid consisting of phosphate esters that is known to degrade polyacrylate elastomers and PSAs.[11] The need for a PSA which resists degradation by this fluid has been an area of focus for the tapes/adhesive industry. The 8 mil Aluminum 1”x1” lap shears were again used to qualify the transposable adhesive examples 2 and 3 before and after being soaked in Skydrol™ at 65°C for 16 hours and are shown in Table 7.

Table 7: Skydrol™ Resistance Lap Shear Data

	CONTROL		**EXAMPLE 2**			**EXAMPLE 3**		
Transposed	no	no	no	yes	yes	no	yes	yes
Soak	no	yes	no	no	yes	no	no	yes
Tensile								
Peak load (lbf)	69	40	29	373	357	36	350	377
Modulus (psi)	4.02e^{6}	2.17e^{6}	2.25 e^{6}	1.65e^{7}	1.68 e^{7}	3.36 e^{6}	1.57 e^{7}	1.54 e^{7}

The tensile data reported in Table 7 provides two key pieces of information:

1. The % increase in peak load and modulus for the two examples when being transposed.
2. The % decrease in peak load and modulus for the adhesives after the Skydrol™ soak

These numbers are shown below in Table 8.

Table 8: Percent Increase in Peak Load and Modulus after Transposition, in Addition to % Decrease in Peak Load and Modulus after Skydrol™ Soak

Process	**Measurement**	**Control**	**Example 2**	**Example 3**
Transposition	% Increase in Peak Load	-	439%	310%
	% Increase in Modulus	-	405%	292%
After Soak	% Decrease in Peak Load	43%	4%	-2%
	% Decrease in Modulus	46%	-8%	2%

The degradation of the transposed adhesives was significantly better than the base adhesive, which nearly degraded to 50% of its original strength. In comparison, the transposed adhesives degraded <5% if they did not increase in strength. (Note: a negative number for the decrease in peak load or modulus designates that the values increased) For the cases in which there was an increase in value, we conclude that the percent increase is within the error of the test.

It was observed that example 3, which had higher epoxy loading, had a lower increase in strength, which is opposite to expectations. To confirm this response to epoxy loading, the storage modulus was measured by a DMA temperature sweep of both examples before transposition. It was expected that higher epoxy loading should result in a lower storage modulus before transposition and a higher storage modulus after transposition. Figure 4 shows the resulting storage modulus curves for the temperature sweeps and verifies this prediction.

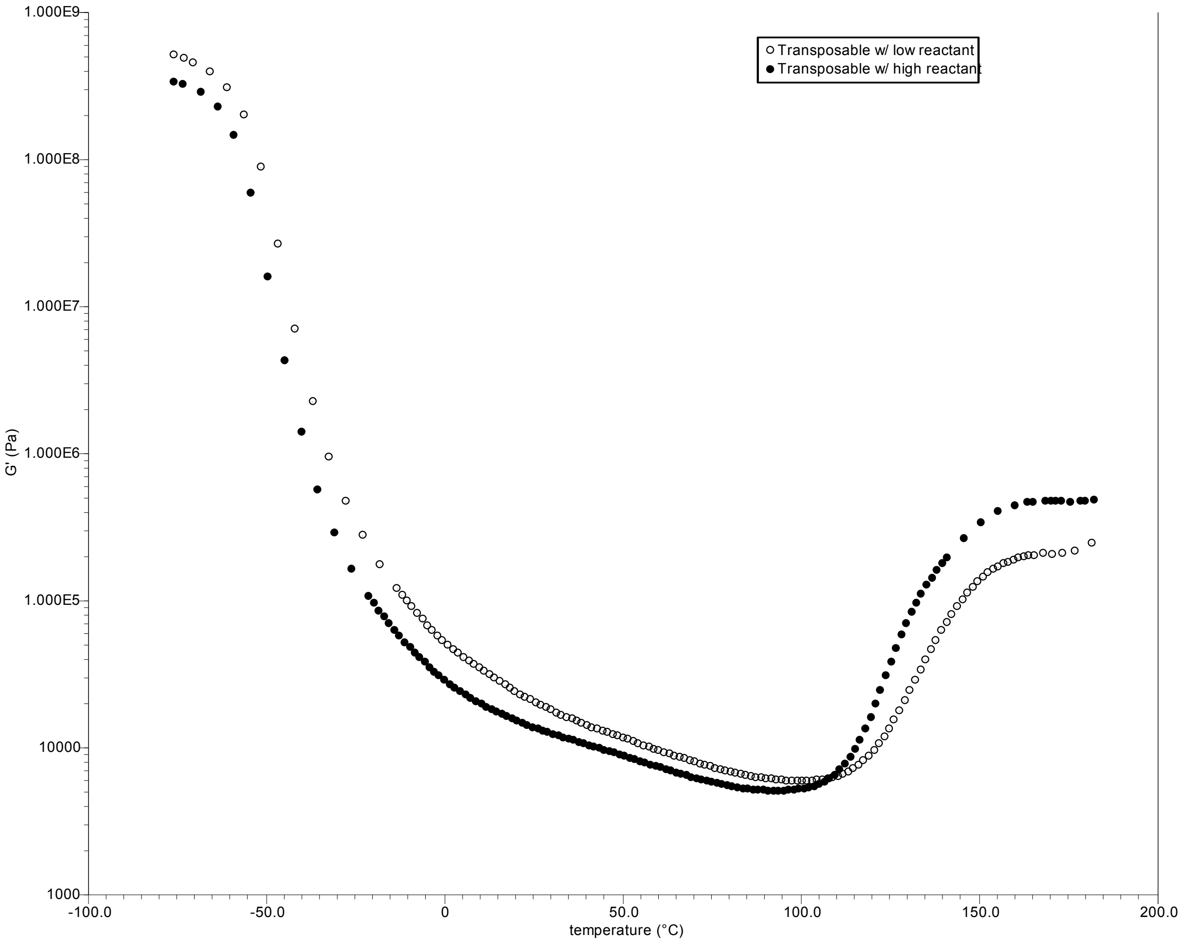

Figure 4: Storage Modulus Vs. Temperature for Examples 2 and 3

The curve that is filled in represented the example with higher loading of epoxy. As expected, the storage modulus is lower compared to its lower epoxy loaded example before transposition and higher strength after transposition. This data confirms what was expected, but contradicts the lap shear data in table 7. The contradiction in the lap shear data was attributed to errors in the lap shear test. Potential causes are lack of adhesion over the entire 1”x1” surface due to flexibility of the 8 mil Aluminum and possible volume contraction during transposition, leading to lack of adhesion over the entire test area resulting from the lack of flexibility of the Aluminum.

Conclusion

Transposable adhesives were characterized physically and analytically by proving a shift of a base adhesive’s performance window as a function of storage and loss moduli. The benefit of the shift in performance window was found to be 2-3x increase in peel strength in addition to dramatic increases in cohesive strength after application. The resulting transposed adhesive exhibited enhanced temperature and chemical resistance versus the non-transposed counterpart. It was demonstrated that the transposition process is activated by precise temperatures or UV exposure to yield a tape construction that can be manufactured and applied with long open times before being transposed to high strength or structural adhesive. In tape applications, this is advantageous over traditional two-part structural adhesives due to the lack of applicator guns and controlled bond lines.

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Acknowledgments

I would like to thank my team of coworkers in Mill Hall, Pennsylvania at the Avery Dennison Adhesives Center of Excellence for their insight and hard work to help generate all the concepts and data:

Mike Zajaczkowski, Eric Bartholomew, Nathan Brown, Sudhir Hublikar, Bobbi-Jo Shortledge, Adam Karstetter and Jennifer Lofton