

**Cationic UV-Curable Hot Melt Pressure Sensitive Adhesives**  
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**Abstract**

Epoxidized block copolymers were used as the base polymer to formulate UV-curable hot melt pressure sensitive adhesives (HMPSA). The ratio of epoxy to mono-alcohol groups is shown to be critical to optimizing the balance of peel, tack, and shear. Low levels of mono-ol produce cured adhesives with low extensibility and low peel. Too high a level of mono-ol results in a weak adhesive with poor shear resistance. The optimal level of epoxy / mono-ol is 2.5 - 1.5 for the systems studied. Formulation latitude was enhanced by replacing high molecular weight mono-ols with lower molecular weight rosin alcohol. This switch permits lower levels of mono-ol to be used (on a weight basis) thus reducing cost and largely delinking control of the cure chemistry (epoxy / mono-ol ratio) from formulation physical properties. To obtain reproducible properties, careful control of moisture exposure is shown to be critical. Release liners are optimally dried to below 4% moisture prior to use. Higher moisture levels in the liner leads to an undercured surface layer, which reduces shear holding power. This weak layer is not detectable by conventional spectroscopic or rheological characterization. Properly cured formulas can be cured at high line speeds (>500 fpm with a 3 bulb system) even when coated at 5-10 mils thick, provide high heat/shear resistance, and adhesion to both polar and non-polar surfaces.

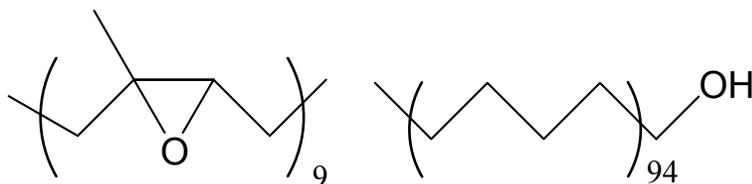
**Introduction**

Industrially, UV and e-beam cure of pressure sensitive adhesives is almost entirely via free radical chemistry. Cationic curable systems have been proposed by Kraton™ (1). They have prepared diblock copolymers of isoprene and butadiene. By weight the isoprene end is about 10-15% of the molecule. This end of the molecule is polymerized first followed by the butadiene portion. A hydroxyl end group is formed by reaction with a suitable capping agent such as ethylene oxide. Selective hydrogenation saturates the butadiene block thus converting it into an ethylene/butylene block, while leaving the isoprene end unsaturated (2). Subsequent epoxidation of these unsaturated groups leads to 9 epoxy groups per molecule (670 g/equiv.), but all in this minor block. The overall molecular weight of this epoxidized diblock (Ep/Di) is about 6000 Da (see Figure 1). It has an epoxy/OH ratio of about 9/1.

Cured by itself, Ep/Di produces a stiff rubbery product. Typically Kraton™ recommends combining this material with a 4200 Da ethylene/butylene mono-ol (EB-OH), tackifier, and a cationic photoinitiator such as a triaryl sulfonium or iodonium salt. As in any cationic polymerization, alcohols serve to cap growing chains while regenerating the active acid species. Mono-ols provide branches

and a looser network structure. Diols provide crosslinks, as does the Ep/Di. The EB-OH mono-ol liquid functions to lower the epoxy/mono-ol ratio and also serves as a diluent, much like oil in a conventional hot melt PSA. We have explored methods to increase formulation flexibility (and reduce cost) through separating these two functions. Using as little as 5% rosin alcohol (292 Da) one can optimize the epoxy/mono-ol ratio (to provide the desired cured network structure), and use standard tackifiers and mineral oil to optimize the formulation Tg (3). This approach is far more flexible and also allows the incorporation of saturated block copolymers to form true hot melt materials.

Cationic systems offer many advantages over conventional free-radical systems: fast line speeds, low dependence on UV dose, thick film cure (>10 mils), and no oxygen inhibition. However, cationics are quenched by moisture or base, and do not complete their cure for up to several days. In this study we explore how these issues can manifest themselves and methods to ensure reproducible processes using cationic HMPSAs.



Epoxidized  
Isoprene  
Block

Hydrogenated  
Butadiene  
Block

**Figure 1: Epoxidized Diblock (Ep/Di) Base Polymer from Kraton™ (L207)**

### General Procedures

Gel content was determined by weighing a piece of cured film, extracting the film in cyclohexane overnight, removing the swollen extracted film gel, drying the film, and comparing the dried weight to the theoretical percentage of ingredients in the formula that can participate in the curing process.

All adhesive testing (peel, tack, shear, and SAFT) was conducted on films transferred to 2 mil corona-treated PET, bonded to the substrate (usually polished stainless steel) with two passes of a 4.5 lb roller at 12 in/min. Wet out time prior to testing was 20 minutes for peel and SAFT, 15 min for shear.

SAFT was determined on a 1 inch x 1 inch square bonded to stainless steel. This bond was then placed in an oven at room temperature and a 1 kg or 0.5 kg weight was hung from the sample. The temperature was ramped up quickly to 120°F and then subsequently at 1°F/minute. The temperature of failure was noted. Each reported value is an average of 4 samples.

Shear was conducted in a similar manner to SAFT, except that the oven was equilibrated to the desired temperature prior to placing the samples in the oven. Time to failure was noted.

Peel was determined on 1 inch wide strips pulled at 180 degrees and a speed of 12 inches/min. Each reported value is the average of 3 measurements. Probe tack was conducted using a Texture Analyzer (TA-XT2i) and a stainless steel probe. Maximum force on retraction was recorded. Each reported value is an average of 5 measurements. Loop tack was measured with a TMI tack tester.

Moisture content in release liners was determined following the general guidelines of TAPPI method T412 om-94. A 4 inch x 4 inch square was cut from the center of the release roll about 10 layers deep. The outside two bottom and top layers were removed from the stack and it was placed into a preweighed 250 ml Ehrlenmeyer flask. The flask was covered with aluminum foil and weighed. The weight of the paper was 6-12 grams. The flask was placed in an oven at 250°F and the aluminum foil was removed. The samples were allowed to dry for a total of 2.5 hours (at which time they had reached constant weight). Before reweighing the samples were allowed to cool in a dessicator.

## **Results and Discussion**

### **A. Epoxy / Mono-ol Ratio**

Initial formulas contained no alcohol groups, besides the group on the other end of Ep/Di. These adhesives were slightly rubbery with poor extensibility. When immersed in cyclohexane, their free swell was only about 80% (weight gain). Finger tack was poor and peel values were marginal (4-5 lb/in at 5 mils thickness). Extensibility was improved by loosening the cured network through the addition of rosin alcohol. As shown in Table 1, reducing the epoxy/mono-ol ratio increased peel and tack. Even at 1.0 epoxy/mono-ol ratio a cured network was formed, with 300% free swell, but shear at 200F (even at 1 inch x 1 inch with 500g) was very poor. Depending on the formulation and end use properties desired, it was found that ratios from 2.5 to 1.5 are useful, and exhibit free swell values of 150-200%.

**Table 1: Effect of Epoxy / Mono-ol Ratio on Peel, Tack and Shear**

	Epoxy / Mono-ol Ratio <sup>a</sup>			
	2.4	2.0	1.75	1.5
<b>Peel</b> (lb/in) 20 min dwell, S.S.	3.6	4.8	5.4	6.2
<b>Probe Tack</b> (g)	346	397	453	474
<b>Shear</b> (hrs) 200°F, 2.2 psi (1/2"x1"x500g)	>95	>121	>121	>121

a- The same base formula was used in each case and the mid-block T<sub>g</sub> of the adhesive was kept constant. This range of epoxy/mono-ol covers only a 2 part shift in formula. All adhesive films were 5 mils thick.

## B. Humidity During Cure

A developmental cationic HMPSA, 34-646A was melted down in an ITW hot melt tank at 200°F and then coated via a 6 inch wide slot head onto release paper at an adhesive thickness of 5 mils. The coating passed through an Aetek 400 watt/in H-bulb and then was nipped to another release paper. Both release papers were obtained from Enterprise. The adhesive was coated to the release paper with a tighter (harder) release (T3070) and nipped to an easy release liner (P1000). Both silicone coatings are thermal cured addition systems that employ platinum catalysts. The line speed was 60 ft/min and the UV power was 50%.

The transfer tapes made on the coater were cut from the roll immediately and allowed to cure as sheets under dry (in a dessicator) or standard (23°C/50%RH) conditions. The time to fully cure this cationic-initiated adhesive is roughly 3 days. All properties were measured after at least 5 days of post cure time.

As shown in Table 2, the conditions under which the samples are cured is important. Dry conditions produce slightly higher gel fraction, but significantly higher SAFT. Peel and probe tack are not affected. This adhesive and others of this type are very hydrophobic and are manufactured and applied at high temperature, thus there is essentially no chance of water being present in the adhesive. However, water is present in the release liner. While the adhesive will absorb very little water, the surface of the adhesive can be affected significantly. Undercure at the surface of the adhesive can produce a weak undercured outer layer on the PSA, which could be responsible for the low SAFT. The observed

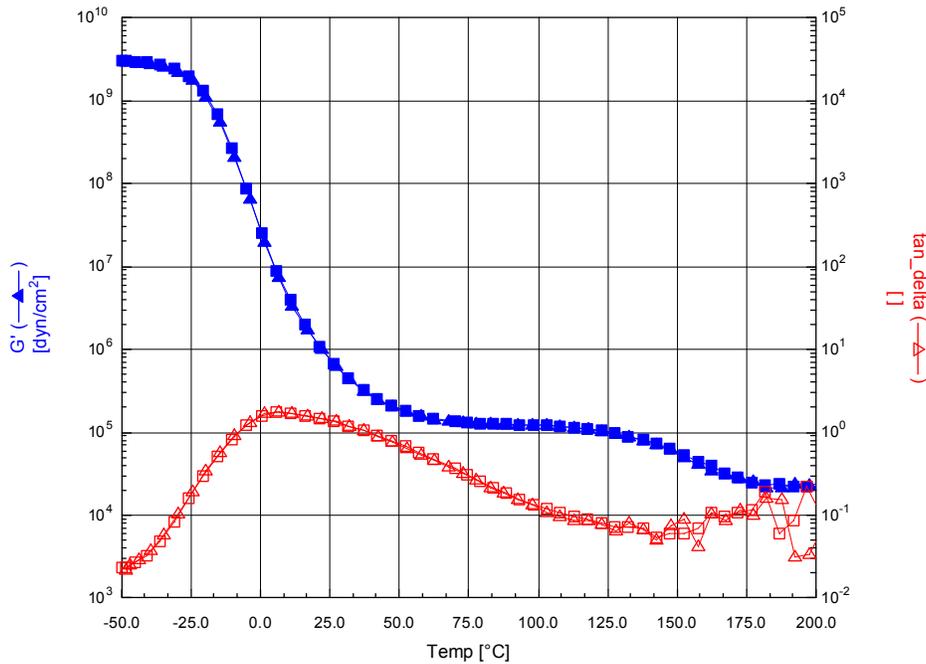
failure mode - adhesive (i.e. failure at the adhesive/steel interface) with ghosting (residue on the steel panel) - is consistent with this hypothesis.

**Table 2: Effect of Atmospheric Moisture During Cure on Properties**

Sample	Batch	Moisture Content of Liner (%)		Curing Conditions	Gel Content (%)	SAFT (°F)	Peel (lb/in)	Probe Tack (g)
		Easy Release	Hard Release					
1	-35	4.4 <sup>a</sup>	4.8 <sup>a</sup>	Dessicator	72.1	282	7.5	501
2	-35	4.4 <sup>a</sup>	4.8 <sup>a</sup>	23C/50% RH	69.3	238	7.4	466
3	-71	4.4 <sup>a</sup>	4.8 <sup>a</sup>	Dessicator	70	>350	6.9	467
4	-71	4.4 <sup>a</sup>	4.8 <sup>a</sup>	23C/50% RH	68.4	262	7.2	480

a - moisture content of liners as-received

RDA (Rheometrics Dynamic Analysis) was conducted on cured films (samples 3 and 4) as described below. The overall level of cure was virtually identical as determined by this bulk method (see Figure 2). However, the SAFT was much lower on the adhesive cured at 50% RH. Again, this indicates a thin undercured layer at the surface may be responsible for the low SAFT.



**Figure 2: Lack of Effect of Atmospheric Moisture During Cure on Bulk Adhesive Properties as Determined by RDA. Triangles are sample 3 and squares are sample 4.**

**C. Moisture Content in Release Liner**

In a tape production environment, particularly for large rolls of tape, the adhesive will complete its cure under conditions where little additional moisture can enter. Thus the moisture in the release liner itself, not the environment is the primary issue. To simulate a production environment, rolls of transfer tape were made as before, but with release liners containing various levels of moisture. Rolls of release liner were conditioned at various temperatures and humidities to obtain these different levels of moisture in the paper. In one case the liner was misted with water and then partially dried and rewound. After conditioning, these liners were immediately placed in a double bag of polyethylene film (2 layers, each 4 mils thick). The tapes made on these liners were similarly double-bagged so as to post-cure without any subsequent moisture loss or gain.

As shown in Table 3, the moisture content of the liner has a dramatic effect on the SAFT of the adhesive. Again failures were adhesive (at the steel/adhesive interface) not cohesive (through the adhesive layer). Clearly the lower the moisture content the better. However, somewhere below 5% moisture SAFT values jump up dramatically to useful levels for high performance industrial tape (>250°F). Thus extreme drying of the paper, or the use of hydrophobic film liners may not be necessary. We are recommending moisture level be maintained below 4% to obtain typical SAFT values.

**Table 3: Shear Adhesion Failure Temperature (SAFT) vs. Moisture Content of Liners (tapes stored in PE bags during post cure)**

Moisture Content of Liner (%)		SAFT (°F)
Easy Release	Hard Release	
4.4 <sup>a</sup>	4.8 <sup>a</sup>	298
4.4 <sup>a</sup>	4.8 <sup>a</sup>	298
4.4 <sup>a</sup>	8	185
4.3 <sup>b</sup>	5.2 <sup>b</sup>	281
7 <sup>c</sup>	6.2 <sup>c</sup>	182
1.7 <sup>d</sup>	1.6 <sup>d</sup>	345

a - moisture content as-received  
b - moisture of roll conditioned for 16 days at 23C/50% RH  
c - moisture of rolls conditioned for 16 days at 23C/90%RH  
d - moisture of rolls dried two days in an oven at 220F.

#### D. Methods to QC Material On-Line

The delayed cure of these materials is a concern for tape manufacturers. They do not want to wait 3 days before testing what they are making. Therefore we explored methods to distinguish good from bad material shortly after UV exposure. Fortunately we had on hand an early batch of 34-646A (batch -34) which was known to deliver low SAFT values even though it did cure. The process to make -34 did not provide adequate dispersion of the cationic photoinitiator (UVI 6974), which is known to be critical to providing high levels of performance (1).

This “poor-marginal” performing batch of adhesive was compared to two later batches produced in the same reactor, but with improved dispersion of the photoinitiator (-1 and -71). These three batches were run under identical conditions and tested after 1 hour by three methods: probe tack, peel, and shear. The results and test details are displayed in Table 4.

**Table 4: Potential In-Line QC Tests - Conducted 1 Hour After UV Exposure.**

	Bad Batch	Good Batches	
	-34	-1	-71
<b>Probe Tack (g)</b>	308 (cohesive) <sup>b</sup>	339 (adhesive) <sup>b</sup>	327 (adhesive) <sup>b</sup>
<b>Peel (lb/in)</b> 20 min dwell, S.S.	6.7 (transfer/cohesive) <sub>b</sub>	8.7 (transfer) <sup>b</sup>	8.8 (transfer) <sup>b</sup>
<b>Dynamic Shear (lbs)<sup>a</sup></b> 1"x1" film between S.S., 0.5 in/min	9	51	46
<b>SAFT (°F)</b> - after full cure (5 days)	195	298	298

a- Maximum force upon pulling panels apart in shear at 0.5 in/min (20 min dwell after bonding).

b-cohesive = failure through the adhesive layer

adhesive = failure at the adhesive/steel interface

transfer = adhesive transfer to the steel surface from the PET backing

#### E. Adhesive Properties Under Proper Cure Conditions

Using the principles outlined in section A, low moisture paper liners, and sealing the tapes in plastic bags during final post cure, we have produced tapes with the properties shown in Table 5. Heat resistance is far superior to non-UV hot

melts, which exhibit SAFT values only ~190°F and shear hold at 200°F of only minutes. Peel values are somewhat lower than conventional hot melts, but comparable to the best acrylics on steel, while offering superior adhesion on polyolefins, as would be expected based on their hydrophobic character.

**Table 5: Adhesive Properties of Cationic UV-HMPSAs**

	UV3010		UV3020	
	2 mil	5 mil	2 mil	5 mil
Peel (lb/in)				
S.S., 20 min dwell	4.6	5.9	5.6	7.1
S.S., 1 wk	5.3	6.7	5.8	7.2
S.S., 1 wk (95°F + 95%RH)	5.0	5.3	5.6	~7.1
HDPE, 20 min	3.2	4.3	3.6	4.6
HDPE, 1 wk	4.0	4.4	3.9	4.9
Shear (hrs)				
2 psi (1/2"x1"x500g), RT	>262	>167	NA	NA
4 psi (1/2"x1"x1kg), RT	>48	>48	>138	>75
8 psi (1/2"x1/2"x1kg), RT	5	7	>138	12
2 psi (1/2"x1"x500g), 200°F	>168	>165	>120	>134
SAFT (°F)				
2 psi (1"x1"x1kg), 1°/min	>300	>300	275	265
1 psi (1"x1"x500g), 1°/min	>300	>300	340	>300
Loop Tack (oz/in <sup>2</sup> )				
S.S., RT	54	62	37	71
Probe Tack (g)				
	310	530	350	600

## Conclusions

Epoxy/Mono-ol ratio is critical to optimizing PSA properties. For the systems studied, a ratio of 2.5-1.5 provided high peel, tack, and shear. Rosin alcohol and oil can serve as a more versatile and less expensive alternative to 4200 Da EB-OH.

Liners need to be dried to less than 4% moisture to avoid an undercured surface layer. Tapes produced should not be exposed to high humidity during post-cure or adequate network formation may not be achieved.

Lap shear measurements immediately after coating the adhesive can be a useful predictor of whether the tape has been adequately initiated and will post cure fully. This technique should make it possible to provide rapid on-line QC measurements despite the lengthy post-cure of cationic systems.

Cationic formulas have been developed with properties suitable for high performance, thick film, industrial tapes.

## **References**

1. "Kraton Liquid™ Polymer/Solid Polymer Hybrid UV Cure Adhesives with Stable Peel Strength", by J. R. Erickson, J. K. L. Schneider, and L. M. Kegley, presented at the Pressure Sensitive Tape Council Annual Meeting, 2002.
2. "Crosslinked Epoxy Functionalized Polydiene Block Polymers and Adhesives", J. R. Erickson, US patent 5,491,193, 2/13/96.
3. "Radiation Curable Adhesive", C. W. Paul, WO03002684, 1/9/03.