

# Novel Polymer Design for Radiation Curable PSAs

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**Abstract:** A new acrylic urethane polymer, comprised of a unique mixture of structurally different polyols and isocyanates, provides significant improvement in the high temperature performance of pressure sensitive adhesives. This new polymer, in combination with other functional monomers and oligomers, can be formulated with various tackifiers and other additives to provide a solvent-free and radiation curable product that offers tack, adhesion and high temperature cohesive strength when applied to high surface energy substrates (stainless steel) as well as low (polypropylene). The invented technology targets primarily the high performance tape market.

## Introduction

UV-cure technology in pressure sensitive adhesives (PSA's) became actively pursued in the early 70's. Since that time, different types of polymerizations initiated by UV energy have been developed that include the cross-linking of acrylic syrups, building the photoinitiators on the polymer chain, and the cationic cure of epoxy-functional block copolymers. These technologies have attracted the attention of the PSA market because of three major advantages relative to traditional waterborne and solventborne products: lower converting costs, flexible processing, and environmental friendliness. Moreover, these UV-cure technologies can also offer significant performance improvements in comparison with waterborne and solventborne products. However, like any technology, these UV-curable PSA's have encountered their own technical and financial challenges: 1. the capability to provide good adhesion to both low and high surface energy substrates; 2. simultaneously exhibiting excellent high temperature shear performance and good adhesion to low surface energy substrates; 3. obtaining consistent performance over a broad UV curing range; 4. obtaining good through-cure for thick PSA films; and 5. reasonable cost to the general PSA market. Overcoming these challenges became the technical missions for the Cytec PSA research group in its plan to develop new and cost-effective UV curable PSA's for the high performance tape market.

One of the leading UV PSA technologies is solvent-free acrylic syrup. The formation of an adhesive film involves subjecting to radiation in the near-UV region<sup>1</sup> an acrylate-containing polymerizable mixture that includes monomers, oligomers, and/or polymers. This syrup technology can produce films with traditional PSA performance. However, the process requires protecting the syrup from oxygen (by flooding the curing line with nitrogen) and usually the curing speed is slow. Most important of all, this technology has been patented and used captively; therefore, it is not available to most tape manufacturers. A more recent development employs photoinitiators that are part of a polymerizable, organic structure.<sup>2,3,4</sup> In this way, the photoinitiator is covalently bound to the polymer backbone, ensuring cross-linking and chain branching rather than oligomer formation. This technology can be very effective in preventing the migration of the photoinitiator after coating and prior to irradiation, a common problem with non-polymeric initiators. However, the poor mobility of the initiator, a consequence of its large size, severely reduces efficiency of UV-initiated cross-linking. The results is

greatly reduced polymer cohesive strength. Finally, UV-initiated cationically cured epoxy systems can provide excellent PSA performance, but these products tends to suffer poor heat and moisture aging.<sup>5</sup>

The UV PSA technology developed by Cytec employs the formation of an acrylated urethane hybrid, different from those previously reported and targeting improvement against all five of the described challenges.

## **Experimental Methods**

### ***Polymer formulation***

The acrylic urethanes formulation is performed at elevated temperatures after the urethane condensation polymerization has been completed.

### ***Film preparation***

The formulated UV PSA's can be made into PSA films according to the following method: the liquid products were preheated in the reservoir of a laboratory hot melt coater (Cheminstruments HLCL-1000) at approximately 110 °C and coated onto a silicone release liner (LOPAREX RP 12). The film thickness was controlled by adjusting the gap between the coating bars. The coated adhesive films were then cured in air by UV irradiation using a laboratory UV curing line (Fusion DRS 120 NQ equipped with an H-bulb) at UV radiation dosages from 20 to 250 mJ/cm<sup>2</sup>. The UV exposure was measured using radiometers, either UVICURE Plus II from EIT-IM or ILT 393 from International Light. The cured film was finally laminated to one of three substrates: a release liner, Mylar film (PET), or Al metal film. The choice depended upon the performance test needs.

The 2-mil solventborne adhesive films, used for comparison performance testing, were made in the lab by producing a drawdown, followed by 15 min air drying. The air dried films were cured in a 90°C oven for 5 minutes. The 5-mil solventborne adhesive films were prepared by overlaying two films that had been air dried and that produced 2.5 mil films after drying. These double-thickness films were then cured in a 90°C oven for 5 minutes. The heat cured films were then laminated to the appropriate substrate in the same manner as described above for UV PSA film.

### ***Adhesive performance test methods***

The cured films were evaluated by measurement of the peel, room temperature shear, and high temperature shear, using published adhesive tests<sup>8</sup>:

Peel Adhesion-PSTC 101

Room Temperature Shear Resistance-PSTC-107

High temperature Shear Test – Modified PSTC-107. A standard shear test with the panel hung in a temperature controlled 93°C and 150°C oven.

## **Polymer backbone design and synthesis**

It is well known that an inverse relationship usually exists between changes in adhesive and cohesive strength for a PSA product: loss of adhesion usually accompanies cohesion strength improvement, and

vice versa. Therefore, significantly improving both adhesion and cohesion strengths for a PSA is a very tough technical challenge. A new design for a polymer resin was necessary. The approach taken by Cytec for the new polymer design included the choice of urethane-acrylate hybrid chemistry, design of a polymer with microstructure alternation, and careful optimization of the polymer molecular weight.

### ***Choice of the hybrid chemistry***

Among many polymer architectures considered, the marriage of an appropriately designed urethane backbone bearing pendant acrylate functionality was chosen. This backbone structure is known to offer excellent film flexibility and toughness. The primary challenges facing the use of urethane-acrylic hybrids in a pressure sensitive adhesive were improvement of high temperature shear resistance without sacrificing room-temperature performance, and compatibility towards a variety of adhesive additives, ensuring broad and straightforward formulation possibilities.

### ***Key raw material selection***

Several key factors were considered when choosing the raw material for the urethane polymerization:

1. Molecular weight
2. Compatibility with the reactant mixture
3. Polarity
4. T<sub>g</sub>
5. Chemical stability (heat, weathering and others)

To avoid an impractically large experimental design, it was decided to focus the synthesis work based upon three principles: first, identify the use level for each key reactant; second, identify the proper molecular weight distribution so as to form a functional cross-link network and retain good coating properties; and third, optimize the product composition with respect to the compatibility between polymer and formulation components. A series of polymers were made and formulated into final products using several composition models based upon these principles. The result was a product that achieved excellent coatability, good adhesion and cohesion properties at room temperature, and excellent product composition compatibility.

### ***Polymer microstructure alternation design***

The new polymer models selected from the above work showed some promising PSA performance features. However, the balance between room temperature and high temperature performance was not yet ideal. A different approach to solving this problem was taken: the adhesive characteristics were evaluated against changes in the microstructure of the polymer, while leaving the composition and molecular weight of the polymer unchanged.

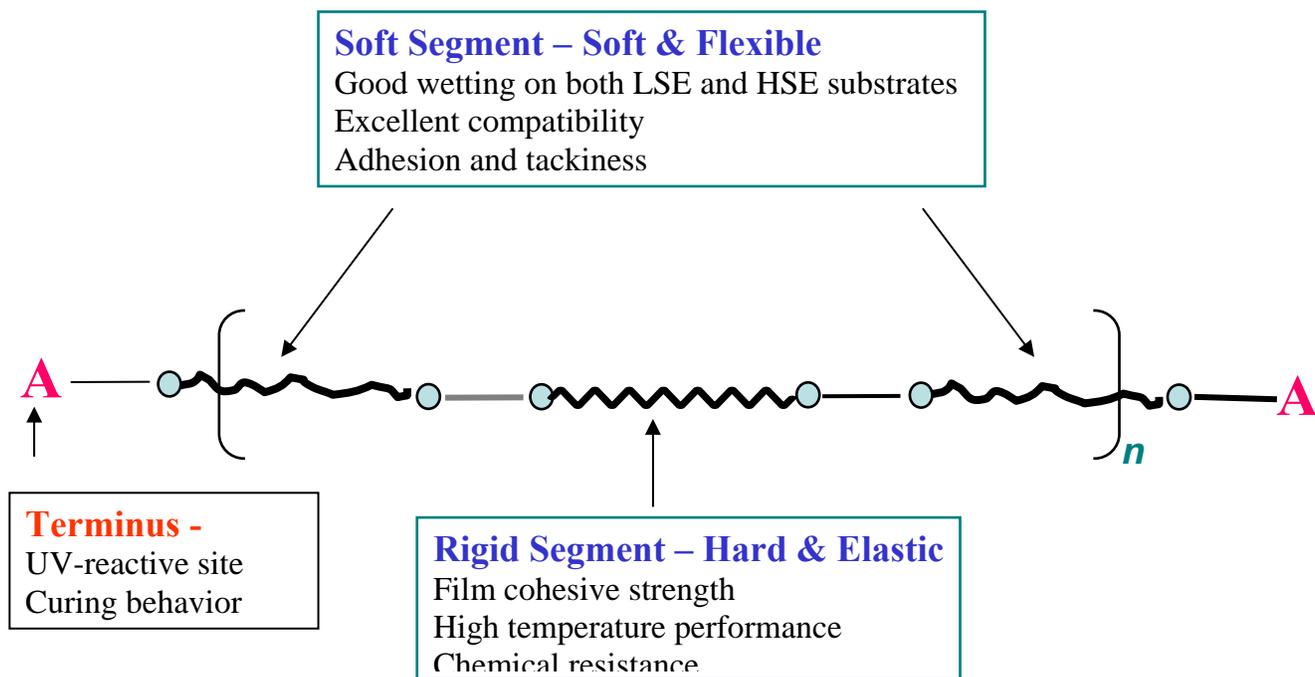
Several polymer structure models were built for this next study and their PSA performance characteristics are listed in Table I. All of the polymers are made with similar molecular weight. The compositions of the soft and the hard polymers are made with the same compositions as the soft and hard segments respectively in the invented polymer described in the Figure 1. The soft polymer model can offer excellent adhesion but lacks cohesive strength; the hard polymer model possesses excellent elasticity for cohesive strength but lacks adhesion and tack; the physical blend of soft and hard polymers offers excellent room temperature performance but could not provide acceptable high temperature performance. By contrast, the specially designed hybrid polymer made by purposely alternating the

polymer microstructure with soft and hard segments offers balanced performance and superior individual performance in these standard adhesive tests.

**Table I. Polymer Structure versus PSA Performance**

Performance	Soft	Hard	Blend	GMR 8020-02
93 °C Shear, Kg/in <sup>2</sup> (minutes)	9	151	166	>3000
30 min. Peel (lb/in)	4.07	1.39	4.35	4.35
Room Temp. Shear, 2 Kg/in <sup>2</sup> (hours)	107	> 336	> 336	>336

A representation of the structure of this specially designed polymer is shown in the Figure 1:



**Figure 1. Structure of the invented polymer**

The structure listed in the Figure 1 contains several critical features: 1. position of the soft and hard segments; 2. relative quantities of soft and hard segments; 3. the linear structure of the polymer; and 4. the network structure designed to be built by UV-initiated cross-linking.

### ***Polymer molecular weight study***

The molecular weight of the hybrid urethane acrylate plays a critical role in defining the product physical properties. For a UV-curable PSA, once the cross-linking functionality is placed on the termini of the polymer, the polymer molecular weight strongly influences the crosslinking density and the formation of the network, both directly influencing the adhesive peel and shear balance. The size of the polymer also dominates its rheological properties, significantly affecting the wetting and coating capabilities of the product. A series of polymers of different molecular weights was prepared by manipulating the stoichiometry among the reactants while the polymer structure remained virtually unchanged. The high temperature shear performance was chosen to guide optimizing the polymer chain length since the high temperature shear depends on both the adhesive and cohesive properties of the polymer. However, there is a limit: the high viscosity inherited from the high molecular weight can cause problems in typical coating operations. Therefore, the polymer molecular weight in this study was optimized so as to achieve both excellent adhesive performance and a commercially acceptable viscosity range at coating temperature.

### **Product formulation design**

Once the polymer structure and molecular weight were defined, the challenge was to optimize the formulation. Formulation components are added to achieve or influence necessary product attributes and their relative compositions adjusted to minimize the deterioration of properties and to prevent new problems from arising. The technical targets for the formulation work were:

1. Good rheological profile leading to superior wetting, flow, and leveling so the product is coater-friendly
2. Acceptably broad curing window so the adhesive can achieve consistent performance without a highly constrained coating operation
3. Good through-cure performance (discussed below) on films of thickness greater than 2 mils. Many applications in the tape market require thick, free films and UV PSA can easily and reproducibly achieve these high film thicknesses
4. Commercially viable curing speed with no requirement of inert gas such as nitrogen

The formulated product of the invented hybrid polymer is called GMR 8020-02. Figure 3 illustrates the viscosity/temperature profile for GMR 8020-02. Given this viscosity profile, GMR 8020-02 can be coated at 110 - 115°C at line speeds greater than 500 ft/min.

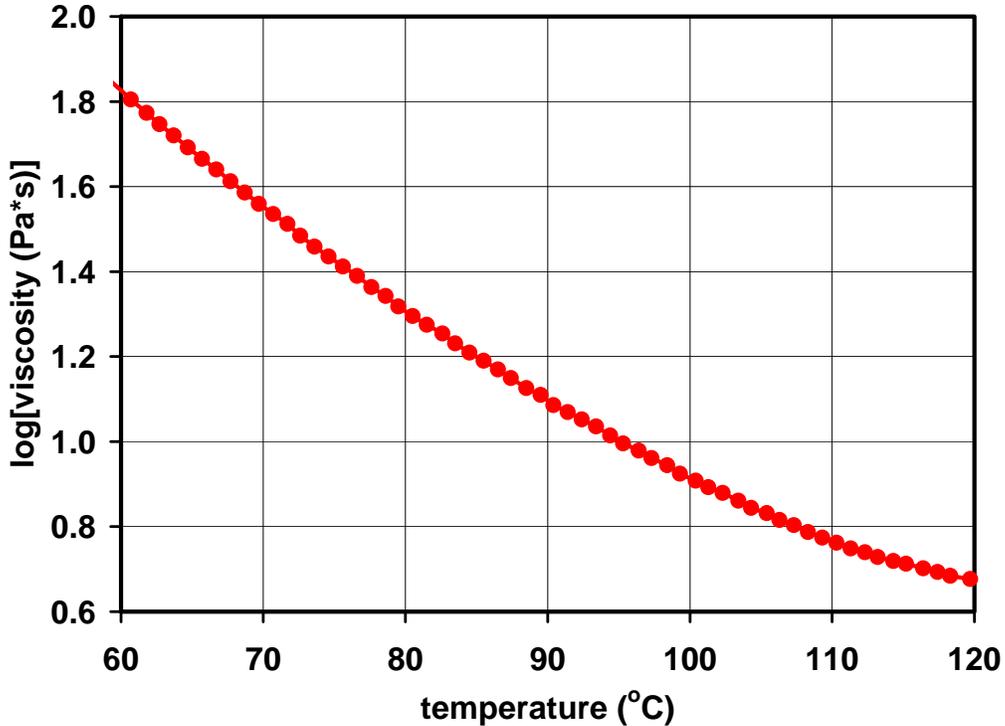
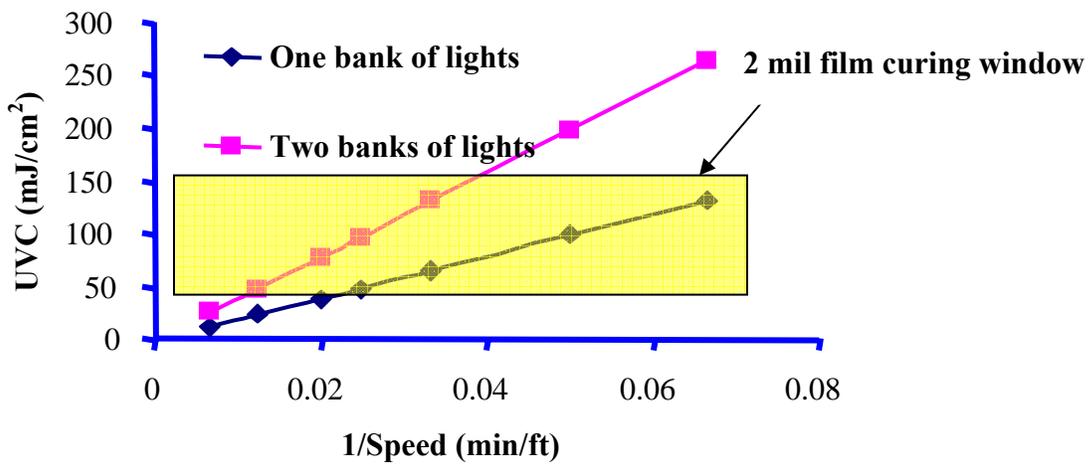


Figure 3. GMR 8020-02 log[viscosity]-temperature profile.

## Product UV curing characteristics

### *Curing speed*

The photoinitiator composition has been optimized considering several curing performance requirements: curing efficiency, the balance between through-cure and surface cure for thick films, and consistent performance over reasonably broad curing ranges. Selecting the proper type of UV lamp such that it matches the UV active components absorptions of GMR 8020-02 is also important.<sup>9</sup> Efficient curing is achieved by the use of a properly tailored combination of photoinitiators. Figure 4 is a plot of UV radiant energy per square centimeter emitted by a single Fusion H-Bulb, measured using a UVC (wavelength < 280 nm), radiometer on a moving coating web, against the reciprocal of the coating web speed. The highlighted band in Figure 4 indicates an appropriate curing range for GMR 8020-02; in particular, a 2 mil thick film can be cured over a broad UVC exposure range, from 40 mJ/cm<sup>2</sup> to 150 mJ/cm<sup>2</sup>. Films cured within this range display consistent adhesive performance characteristics.



**Figure 4. UVC light energy vs. reciprocal of coating speed**

***Curing window***

Figure 5 summarizes the performance results of cured 2 mil films of GMR 8020-02 over a range of UVC energy exposures. Both peel and room temperature shear tests were used to evaluate the balance of adhesion and cohesion properties of the product. As shown in Figure 5, a 2 mil film achieves excellent room temperature shear with as little as 30 mJ/cm<sup>2</sup>, and its performance is improved at higher UV exposure levels. The 5 mil film can also offer good room temperature shear performance across a broad UVC curing range from 75 mJ/cm<sup>2</sup> up to 400 mJ/cm<sup>2</sup>. The 5 mil shear times are lower than those of a 2 mil film because shear times decrease with increasing film thickness at constant cohesive strength, a commonly observed phenomenon for PSA's.

## GELVA<sup>®</sup> GMR AX 8020-02

### UV Energy vs. Performance

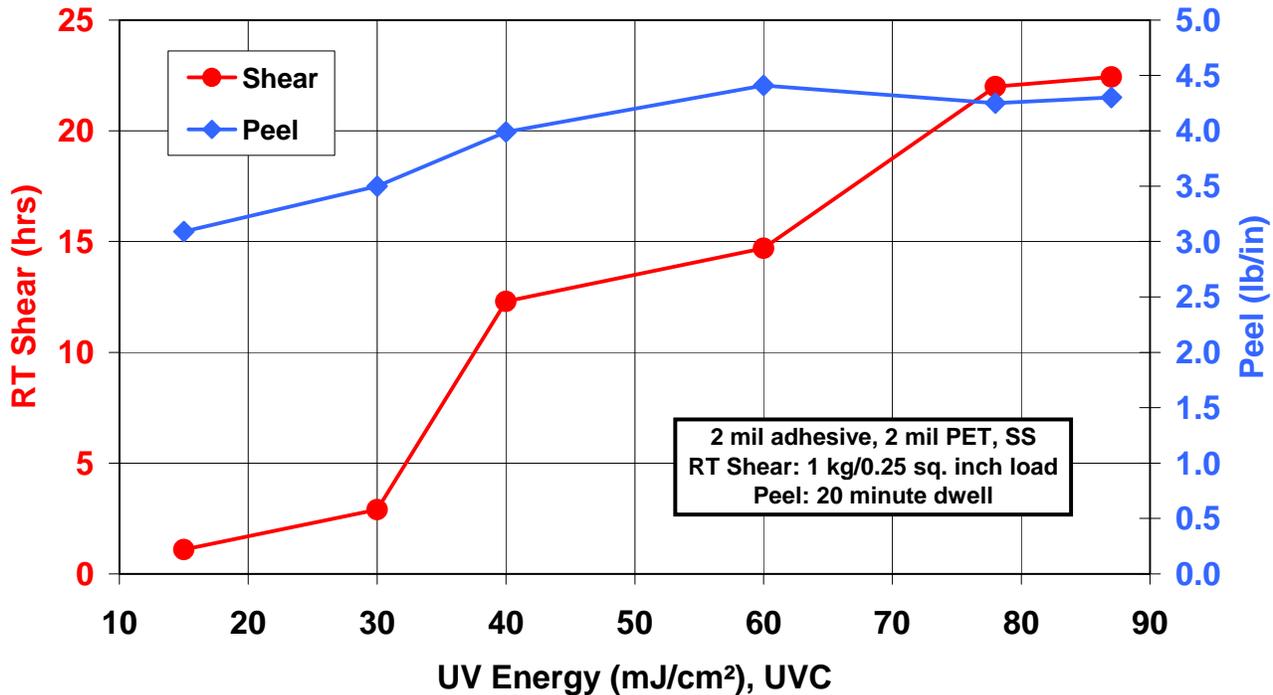


Figure 5. GMR 8020-02 performance versus UVC curing energy at 2 mil thickness

### *Product through-cure*

In order that both sides of a cured film can offer the same PSA performance, the film should be cured evenly and completely across the thickness of the film. This is called through-cure. Figure 6 shows a representation of a film being cured under UV light. The Beer–Lambert law (Equation 1), an empirical relationship that relates the absorption of light to the properties of the material through which the light is traveling, describes the mathematical relationship between the absorbance ( $A$ ), the film thickness ( $b$ ), and the concentration of the substance ( $c$ ). This equation is appropriate for an absorbing compound in a non-absorbing solution. In a complex system like a UV PSA, one can express the sum of the products  $\epsilon c$  for all of the components in the adhesive as a constant, Equation 2. [ $\alpha$  is then the sum of the products  $\epsilon c$  for the individual species in the whole mixture ( $\sum \epsilon_i c_i$ ).] Equation 2 succinctly describes the difficulty with preparing thick films: the thicker the film the more light will be absorbed by the adhesive and its formulation components. Thus, the bottom of the film receives only a fraction of the light received by the top.

$$A = \epsilon bc \quad \text{Equation 1}$$

$$A_t = \alpha b \quad \text{Equation 2}$$

$A$  is the absorbance for an individual component

$\epsilon$  is a constant for an absorber in the film of a given component at a particular wavelength

$b$  is film thickness

$c$  is the concentration of the molecule

$A_t$  is the total absorbance for the entire film

$\alpha$  is a constant for an homogenous material of a given composition, comprised of many different absorbing species

Achieving good through-cure for thick UV PSA film was the result of first choosing a cocktail of photoinitiators that responds to a wide portion of the light available from commercial UV bulbs. Once accomplished, the formulating components were chosen and optimized to minimize the overall absorptivity ( $\alpha$ ) of the adhesive. The designed reduction of  $\alpha$  was achieved through management of the UV absorption profile of all the components except the photoinitiators. For GMR 8020-02 the result was efficient use of both short and long wavelength UV light, contributing to the observation of both rapid line speeds and identical adhesive properties on the top and bottom of the film. This combination of approaches yielded excellent through-cure even for films 10 mil thick. Figure 7 presents the performance results of GMR 8020-02 for both 2 mil and 5 mil films. There is no difference between the peel values measured from the top and bottom of the cured films, regardless of the surface energy of the substrate. The small differences between any top-bottom pair is within the reproducibility of the test method.

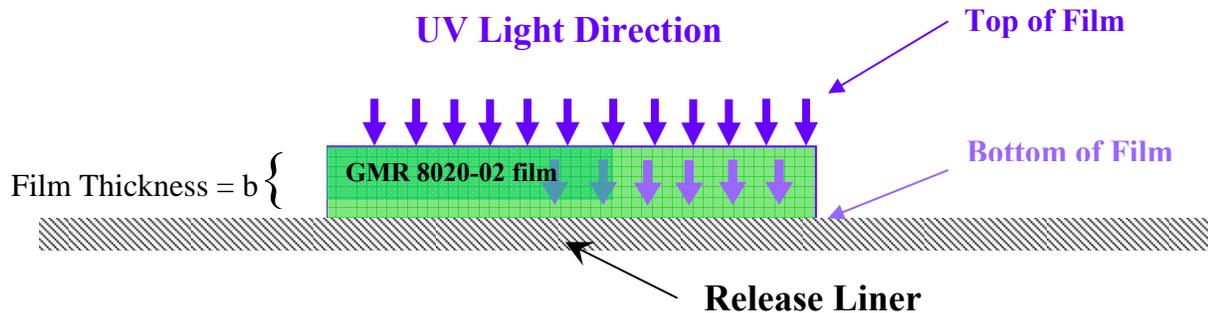
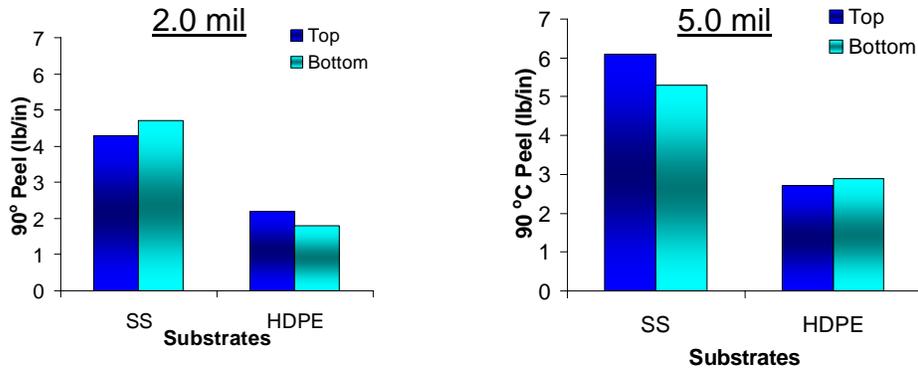


Figure 6. GMR 8020-02 film being cured under UV light



**Figure 7. 2 mil and 5 mil GMR 8020-02 film through-cure evaluation.**

### Overall Product Performance

To better assess the performance improvement of GMR 8020-02 versus solventborne and current UV PSA products, a comparison study was performed among GMR 8020-02, a commercial solventborne adhesive (SB PSA), and the current leading UV PSA product. The SB PSA was designed for the high performance tape market. The leading UV PSA product offers excellent adhesion to both low and high surface energy substrates while maintaining reasonable shear strength at both room and high temperature.

Table 2 lists the peel strength comparison among these three products. Both the market leading UV PSA and the GMR 8020-02 display excellent peel results for all tested substrates, while SB PSA demonstrates excellent peel on only the high polarity substrates.

**Table 2. 90° Peel evaluation of 2 mil adhesive film using aluminum backing**

Substrate Type	Market leading UV PSA	SB PSA	GMR 8020-02
Stainless Steel (SS), lb/in	6.5 T/A	4.9 A	4.3 A
Polypropylene (PP), lb/in	5.7 A/Z	1.5 A/Z	5.5 A
High density Polyethylene (HDPE), lb/in	1.69 A/T	0.5 A	2.26 A
ABS plastic, lb/in	5.1 A/Z	2.1 A/Z	5.5 A

Note: the letters in the table denote failure modes; those with slashes indicate more than one failure mode: A = adhesive, C = cohesive, T = transfer, Z = zipping.

Table 3 details the shear performance data for both 2 mil and 5 mil films of these three products. GMR 8020-02 shows overall excellent room temperature shear (these tests were aborted at 280 hours, prior to failure). The market leading UV PSA product shows less cohesive strength than either of the other two products, regardless of thickness.

**Table 3 Room temperature shear times, 2Kg/in<sup>2</sup> (Hours)**

Film Thickness	Market leading UV PSA	SB PSA	GMR 8020-02
2 mil	51 C	>280	>280
5 mil	70 C/T	>280	>280

Note: Values such as > 280 record the hang time at the point when the test was aborted. No failure mode can be assigned to these tests.

The high temperature shear results listed in the Table 4 show the same trend found in the room temperature shear results. Both SB PSA and GMR 8020-02 have shown excellent high temperature shear while the market leading UV PSA has not.

**Table 4. High temperature shear times, 1Kg/in<sup>2</sup> (Hours)**

Temperature	Market leading UV PSA	SB PSA	GMR 8020-02
93°C, Kg/in <sup>2</sup> (hours)	< 2.5 C	>50	>50
150°C, 0.5Kg/in <sup>2</sup> (hours)	2.5 C	>167	>167

Note: Same as Table 3.

Combining the data from Tables 2, 3, and 4, it can be claimed that Cytec's new UV PSA, GMR 8020-02 can offer better overall performance with a balance of both excellent adhesive and excellent cohesive strength. The product also passes the cold adhesion performance test specified by UL696.

## Conclusions

A new UV PSA product, GMR 8020-02, has been developed using a new polymer structure incorporating an alternating microstructure. This polymer has been formulated to meet the demanding needs of the high deposition tapes market and other applications. The product offers excellent adhesion when applied to plastic and other low surface energy substrates while maintaining solid performance on high surface energy substrates. GMR 8020-02 raises the performance bar by significantly improving room temperature adhesion while simultaneously increasing cohesion in comparison with many high performance solventborne products and current commercially available UV PSA products. Excellent coatibility, fast line speeds, complete curing under air, and broad curing window make GMR 8020-02 a high yield, robust product with low converting costs for many applications, particularly high performance tapes.

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