

## **New Approaches for Radiation Curable Pressure Sensitive Adhesives**

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### **ABSTRACT**

Radiation curable pressure sensitive adhesives (RC-PSA's) research is actively ongoing in Surface Specialties, Inc. (UCB). Market and technical drivers include high productivity, good processing flexibility, low processing temperature, low or zero VOC, and the potential to achieve high performance on par with solventborne technology.

A new generation of RC-PSA's has been developed based on the results of multiple technical approaches. The new RC-PSA resins are acrylated urethane oligomers/polymers, in which the backbone comprises a block copolymer of several functional building blocks. The RC-PSA formulations based on the new synthetic resins have shown two advantages: workable viscosity and a good balance between tack, peel strength and shear strength.

Synthesis, formulation and evaluation work of these RC-PSA materials will be described in this presentation. The data on major PSA performance parameters are presented in comparison with the performance of commercial solvent-borne PSA and UV-PSA products.

### **Introduction**

Commercial interest in radiation curable adhesives continues due to the potential for this technology to deliver immediate cure, higher overall production output, and lower energy consumption, reduced floor space occupied with work-in-progress and low or no VOC emissions. However, to usurp those currently well-entrenched technologies such as solvent-based, water-based as well as hot-melt adhesives, radiation curable adhesive technology must demonstrate an exceptional balance of adhesive performance without introducing new concerns and shortcomings. Moreover, it must do so at a cost that, together with its benefits, provides added value to the end-user. This is truly a formidable challenge.

The viscoelasticity of an adhesive refers to the balance of both flow (viscous property) and stiffness (elastic property). As such viscoelasticity governs macromolecular flow, deformation, resistance to deformation and energy dissipation and therefore impacts both the bonding and debonding aspects of adhesion<sup>(1)</sup>.

Conventional polyurethane elastomers have proven to be very successful and versatile for adhesive applications. The polyurethane backbone, which contributes flexibility and hydrogen bonding, exhibits exceptional adhesion, heat resistance and toughness. Although many factors may be involved, there appear to be two main factors, inherent molecular structure and crosslink density, that play a critical role in determining adhesion performance.

Flexible polyurethane elastomers consist of mainly two segmented structures: long and flexible polyol chains, "soft segments", and relatively short rigid polyurethane/polyurea linkages, "hard segments". The characteristic properties of the resultant elastomer depend largely upon secondary or hydrogen bonding of polar groups in the polymer chains. Hydrogen

bonding in the hard segments is strong, causing the hard segments to agglomerate into domains within structures having long flexible chains. A two-phase microstructure consisting of hard and soft segments is formed<sup>(2)</sup>.

As a measure of crosslink density of cured conventional polyurethane network, the average equivalent weight per branch point in the crosslinked polymer network, designated as  $M_c$ , will typically vary from 2,000 for an elastic material to about 25,000 for a very soft material. Therefore, conventional soft, flexible, high-elongation polyurethanes are mainly linear in structure and possess a relatively low degree of branching<sup>(2)</sup>.

The expectation for RC-PSA technology was historically very optimistic: radiation curable adhesives would grow rapidly, and penetrate solventborne and waterborne as well as hot melt PSA markets. However, these ambitious growth forecasts never fully materialized. As a technical point, this is because the balance between viscous and elastic properties, or the balance of molecular weight and crosslink density (measured by  $M_c$ ), or ultimately, the balance of tack, adhesion and cohesion in these radiation curable systems, was never well-controlled.

As Ozawa and co-workers<sup>(3)</sup> indicated, the balance of the adhesive and the cohesive strength within the cured coating is critical to the performance of the RC-PSA, and the UV (ultraviolet light) or EB (electron beam) energy must be delivered to the wet film in a controlled and efficient fashion. Based on DSC (differential scanning calorimetry) and DCA (dynamic contact angle) analysis, probe tack and peel adhesion decreased monotonically with an increase of storage moduli  $E'$  and loss moduli  $E''$  for all non-UV and UV cured blends while their holding power was higher. It was shown that modulus values and glass transition temperatures ( $T_g$ ) of these blends after UV irradiation were higher than those before UV irradiation. In short, the deformation energy of UV cured blends was reduced by the curing process. In general, radiation curable formulations, due to viscosity/handling considerations of high molecular weight oligomers, which impart flexibility and elongation, need to be diluted with low molecular weight, therefore low viscosity monomers. These monomers may have mono-, di-, tri- or higher functionality. Oligomers usually contain at least two terminal (meth)acrylate groups, which upon curing/copolymerizing/crosslinking with monomers become branch points. As monomer functionality increases  $M_c$  and elongation at break decrease, whereas tensile strength,  $T_g$ , and hardness increase. .

On other hand, when the absolute number of double bonds (functionality of monomers/oligomers) in the formulation is reduced in order to suppress the excess crosslinking, the radiation curing may proceed locally, and the network is not fully formed. This results in failure to obtain sufficient cohesion strength as a whole.

In addition to viscoelastic properties, surface energy (tension) of the PSA materials is another critical factor for adhesion performance.

## **Experimental Section**

### **1. Overview**

Three commercial PSA products were used as benchmarks for comparative purposes. The first one, designated Benchmark 1, is a solvent-based PSA product that is very popular in the current high performance PSA market, and the second and third, designated Benchmark 2 and 3 respectively, are two commercially available UV-curable hot-melt PSA products.

All synthesized resins were screened for compatibility with tackifier, UV reactivity, and general performance as pressure sensitive adhesives.

Most of the synthesized resins were compatible with a variety of tackifier systems including rosin and rosin derivatives, hydrocarbon (both aromatic and aliphatic) tackifier resins, as well as terpene resins, from 15 to 80 parts per hundred (phr) based on resin solids. Likewise, most resins were cured with 1 phr photoinitiator using two, 600-watts per inch (W/inch) Fusion UV lamps at 150 fpm ( $300 \text{ mJ/cm}^2$ ) using nominal adhesive film thicknesses of 2 mil.

Since the base resins were typically synthesized in organic solvent, all initial formulation work was done in the solvent. For selected resins, the solvent was stripped and the base resin was blended with tackifier, photoinitiator, and additives.

## 2. Formulation

The formulation preparation was done with a SpeedMixer™ Model DAC 150 FVZ from FlackTek, Inc. (Landrum, SC), manufactured by Hauschild Engineering, Hamm, Germany.

A typical formulation procedure is summarized below:

- 1) Weigh synthesized resin into 100 g disposable cup (#501-221 from FlackTek), add Tackifier 1, mix at 3,000 rpm for 3 minutes (“3K3m”).
- 2) The mixing step may be repeated for several times as necessary for homogeneous mixing.
- 3) Weigh Tackifier 2 if necessary and mix as in steps 1 and 2.
- 4) Weigh photoinitiator and mix to form a homogeneous solution.
- 5) Sample is then drawn down to form a 2 mil film.

Some base resins (solvent-stripped) could be mixed with tackifier, photoinitiators, and additives in the SpeedMixer and coated with a ChemInstruments HLC-101 laboratory hot-melt coater. Other base resins were mixed with a Ross Model DPM-1Qt Double Planetary Mixer with High Viscosity “HV” blades, and then coated, cured, and hand laminated as described above

## 3. Test Sample Preparation

All tapes for PSA evaluation were prepared by adhesive transfer.

The uncured, liquid PSA was drawn down on release paper (Loparex Poly Slik 111/120, Apeldoorn, the Netherlands, roll No. W03180672), and UV cured as described above.

Drawdowns were made by Gardco Automatic Drawdown Machine, 12-in stroke with a Braive Instruments adjustable Bird applicator, the typical film thickness was 2 mil.

The cured adhesive on release paper was warmed in a  $70^\circ \text{C}$  oven for 30 minutes, and then held under vacuum to evacuate for 1 hour. The adhesive side exposed to the UV radiation was laminated with polyester film (Pilcher Hamilton Corp, 200 gauge, and control no. 787- 7222) using two double passes of an 8-inch hard rubber roller (5.03 Kg with handle held horizontally). The laminate was trimmed, and cut into 1 inX7 in strips. The films were left for

24 hours at CTH (constant temperature and humidity) conditions. All testing was done from the side of the adhesive not exposed to UV radiation.

Adhesive film thickness was determined by non-destructive testing with a ChemInstruments (Fairfield, OH) Micrometer MI-1000, which was calibrated before each set of measurements. Film thickness values were reported as the average of five measurements each on three randomly selected strips and recorded to 0.01 mil precision.

#### 4. Screening

Screening involved the determination of 1) physical compatibility of tackifier with the resin, 2) UV cure reactivity, and 3) general suitability for a pressure sensitive adhesive. If the resin was incompatible with tackifiers, or if a first-pass formulation gave extremely low tack or shear strength, the evaluation was stopped.

#### 5. Performance Testing

All performance testing was conducted in a constant temperature/constant humidity controlled room held at  $23 \pm 2$  °C,  $50 \pm 5\%$  relative humidity. CTH consistency was monitored by an Enercom Instruments Ltd. (Toronto, ON, Canada) weekly strip chart. Test methods developed by the Specifications and Technical Committee of the Pressure Sensitive Tape Council (Glenview, IL), Eighth Edition, were utilized.

- a) Loop tack was measured with a ChemInstruments LT-500, AmeTeck, according to standard procedure on stainless steel substrate, by method PSTC-16B. Results are reported in pounds per square inch (lb/in<sup>2</sup>).
- b) Peel testing was run on a Mass SP 2000 Slip/Peel Tester (Instrumentors, Inc., Strongsville, OH), according to PSTC-101A on four different substrates: Stainless steel, Ford clearcoat (R10CG060Z), Chrysler clearcoat (CSRC8002E), and GM clearcoat (RK8148GEN4AC). The automotive clearcoated panels were pretreated by gently wiping the panel with isopropanol and the stainless steel panels were prepared by wiping with MEK. All panels were held at CTH for 1 hour prior to plating. One inch PSA sample strips were applied to the panels with a 4 Lb. roller and tested with an Instron at a 180° angle at a speed of 12 in/minute. The results were recorded in lb/in<sup>2</sup>.
- c) CTH Shear Strength was measured on a ChemInstruments 30 Bank Shear Tester with 1-Kg or 2-Kg weights, according to PSTC-107A or alternatively ASTM D 3654, Section 9.4, Procedure A. The samples were prepared as described above. 1 X 1 in<sup>2</sup> samples were applied to stainless steel panels. Samples dwelled for 30 minutes at CTH conditions before hanging the weights (1 Kg/2 Kg). The panels were prepared as described above. All results were recorded in hours. Failure mode was also specified.
- d) High Temperature Shears  
Free films were laminated to aluminum facestock and left for 24 hours at CTH conditions. 1 x 1 in<sup>2</sup> samples were applied to both stainless steel and aluminum panels with a 4 lb. roller. The stainless steel panels with MEK and the aluminum panels with isopropanol were prepared. They dwelled under CTH for 24 hours before placing the samples in the 93°C oven. After conditioning in a 93°C oven for one hour, 1 Kg weights were hung on the samples and the results were recorded in hours.

6. Rheology of cured PSA samples was evaluated on a TA Rheometer, Model AR 2000, using 8-mm ETC parallel plates with normal force control (no temperature gap compensation). Best results were obtained using samples prepared by rolling  $\frac{1}{4}$  in strips of cured, conditioned adhesive film to a diameter of ca. 8 mm which were then placed in the rheometer fixture. Conditioning was conducted by inserting the specimen and setting the gap (ca. 5000 $\mu$ m) at room temperature, warming the specimen to 100 °C at constant gap, and then cooling the specimen with normal force control ( $0.3 \pm 0.1$  Newton) to -70 °C. At this point the specimen was trimmed, if necessary, to the diameter of the 8 mm fixture diameter, before cooling to the test starting temperature of -100 °C. Samples were conditioned then evaluated over a temperature range of -100 °C to +200 °C at 3 °C per minute temperature ramp, using a rheometer frequency of 1 Hz and 0.025% controlled strain.

## **Results and Discussion**

### **Base Resins**

Currently, activity to develop the next generation of RC-PSAs is ongoing in R&D laboratories of Surface Specialties Inc. (UCB). Based on careful investigation and study of the shortcomings of previously developed UV-PSA technologies, very promising results have been obtained via multiple technical approaches. New RC-PSA base resins have been successfully synthesized in the R&D laboratories of UCB. The resins are generally linear or semi-linear, acrylated urethane oligomers/polymers, in which the backbone comprises random block-copolymer of several functional building blocks. One of these functional blocks brings many intrinsic PSA properties while another block brings good elasticity, low T<sub>g</sub>, and good hydrolysis resistance. Other blocks are utilized to adjust resin properties including hydrophobicity/hydrophilicity, compatibility to tackifiers, surface tension and etc. The new RC-PSA formulations based on the synthesized resins have shown two advantages: workable viscosity under warm-melt conditions and a good balance between tack/peel strength/shear strength.

The major objective of UCB's RC-PSA project is to develop a method to make a new, backbone-extended urethane (meth)acrylate oligomer/polymer. Additionally, several other objectives of this project are listed below:

- a) Provide adhesive compositions that are radiation curable (curable with actinic or ionizing radiation such as ultraviolet light or electron beam irradiation);
- b) Provide adhesive compositions with high, or 100% solids contents;
- c) Provide adhesive compositions that have high adhesion performance on par with solvent-bone adhesives to various substrates after cure;
- d) Provide adhesive compositions that have high UV-cure speed.

### **Performance**

#### 1. Processability and Coatability of Formulations

The coatability of the formulations was determined by rheology studies.

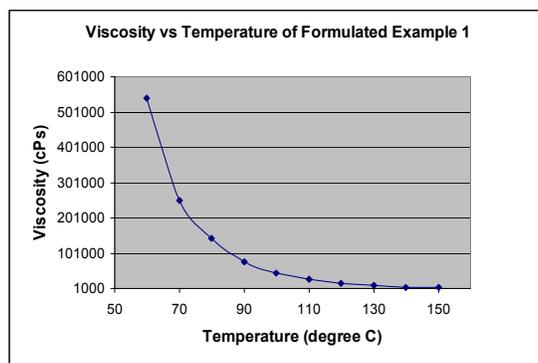
A series of urethane (meth) acrylate oligomers/polymers have been synthesized in the R&D laboratories of UCB. Generally, the radiation curable adhesive oligomers/polymers ("resins") were synthesized in an organic solvent and were received as a 60% solution. Based on these resins, a variety of formulations have been made. Solvent was stripped off

from the resin or formulation at 80°C and at 50-200 mbar vacuums. After solvent-stripping, the formulated PSA materials show viscosities that typically depend upon the molecular weight of the base resins, composition of the formulation, and the temperature of the coating process (see **Figure 1**), as well as the shear rate. PSA performance is also closely related to the MW of the base resins as well as the formulations. In general, a viscosity of 20,000 cP or less is considered a coatable viscosity. **Table 1** shows two formulations with significantly different viscosities, and the viscosity is temperature dependent.

**Table 1**  
**Temperature Dependent Viscosity of RC-PSA Formulations**

Temperature (°C)	60	70	80	90	100	110	120
Formulated Example 1 ( 1000cPs)	540	250	143	75	45	27	14
Formulated Example 2 ( 1000cPs)	N/A	N/A	5.4	N/A	N/A	N/A	0.76

**Formulated Example 1** represents a case where the base resin is high in molecular weight, and the viscosity of the formulation is very high. **Figure 1** illustrates that the viscosity of Formulated Example 1 reduced significantly as the temperature was elevated. The coating temperature must be elevated to 120 °C to attain coatability. In contrast, **Formulated Example 2** represents a case where the base resin is lower in molecular weight, and therefore, the material is coatable at 80°C or even lower temperature. In the presented studies, the viscosity values of most of formulations are intentionally controlled to fall in the range between these two extreme cases.



**Figure 1**  
**Viscosity vs. Temperature of Formulated Example 1**

## 2. Thermal Stability of Synthesized Oligomers/Polymers

The thermal stability of radiation curable resins under warm melt process conditions is an important product parameter. Unintended thermal polymerization (gelation) often causes quality problems in radcure applications. In general, the thermal stability of a radiation curable resin system is determined by measuring the viscosity of a sample after aging the sample at an elevated temperature for a specified period of time. Two commonly used procedures in the radiation curable resin area report results as the percent viscosity change or pass/fail.

- 1) A viscosity change of  $\leq 20\%$  after 7 days at 140 F (60°C) is considered passing,  $>20\%$  is considered failing.
- 2) A viscosity change of  $\leq 100\%$  after 2 days at 200 F (93.3°C) is considered passing,  $>100\%$  is considered failing.

In PSA applications, thermal stability becomes even more important because the coating process is carried out at elevated temperatures, for example 120 °C. **Table 2** lists results of thermal stability tests at 60 °C, 93 °C, and 120 °C. The results suggest that **Formulated Example 2** sustains a viscosity increase that would be considered acceptable at 93 °C, and at 120 °C for at least 24 hours.

**Table 2**  
**Thermal Stability of a RC-PSA Formulation (Formulated Example 2)**

Temperature (°C)	Viscosity-Change (%)	Pass/Fail
60	< 5.0% (after 7 days)	Pass
93	< 20.0% (after 2 days)	Pass
120	< 60.0% (after 24 hours)	Pass

### 3. UV/EB Curing Window

The strong dependence of PSA performance on UV/EB cure dose in many UV-PSA products is a concern. High UV/EB dose can impart high crosslinking density, therefore higher network build up, and ultimately, higher elasticity. This could provide higher cohesion (shear strength) but lower tack and peel strength. In contrast, lower UV/EB cure dose generates lower crosslinking density; and consequently, higher tack and adhesion (peel strength) but lower cohesion (shear strength). The dependence of PSA performance can be highly sensitive to UV/EB cure dose. Variations in UV/EB cure dose, which are possible in many cases, could cause inconsistent performance. UCB's RC-PSA formulations appear to show good PSA properties in a wide UV/EB cure window. **Table 3** below lists adhesion properties of **Formulated Example 3** as a function of UV dose.

**Table 3**  
**UV Dose Dependence of PSA Performance of Formulated Example 3**

UV dose(mJ/cm <sup>2</sup> )	170	265	340	500	680	1000
Corresponding Line speed ( feet/minute) (600W/in, 2xH bulb)	300	200	150	100	150x2	100x2
Peel (24 hours) (lb/in)	6.0	5.5	5.2	4.4	4.5	4.5

With UV dose of 170 mJ/cm<sup>2</sup>, **Formulated Example 3** showed higher peel strength, 6.0 lb/in. In contrast, with slightly higher UV-dose, 265 mJ/cm<sup>2</sup>, **Formulated Example 3** showed slightly lower peel strength, 5.5 lb/in. As UV-dose approached to 340 mJ/cm<sup>2</sup>, the adhesives appear to reach maximum cure. Beyond 340 mJ/cm<sup>2</sup>, peel strength and shear strength showed no significant changes upon UV-dose increase, even as UV-dose approaches 1,000 mJ/cm<sup>2</sup>. This performance feature contrasts with common “over-cure” problems, and suggests that the performance of **Formulated Example 3** may not vary significantly over a wide UV cure-dose window.

Moreover, differences in PSA performance caused by surface-cure and through-cure are another concern for UV-PSA applications, particularly, for thick film application of 5 mil (125 μm) and higher thickness. Polyken probe tack measurements demonstrate that **Formulated Example 3** shows good homogeneous cure. The adhesive surface directly exposed to UV radiation with a UV dose of 600 mJ/cm<sup>2</sup>, and the surface against the stock-film which was not directly exposed to UV radiation exhibit similar probe-tack properties (see **Table**

4). This suggests that the surface facing to UV and the surface not facing to UV-radiation achieve a similar degree of UV cure.

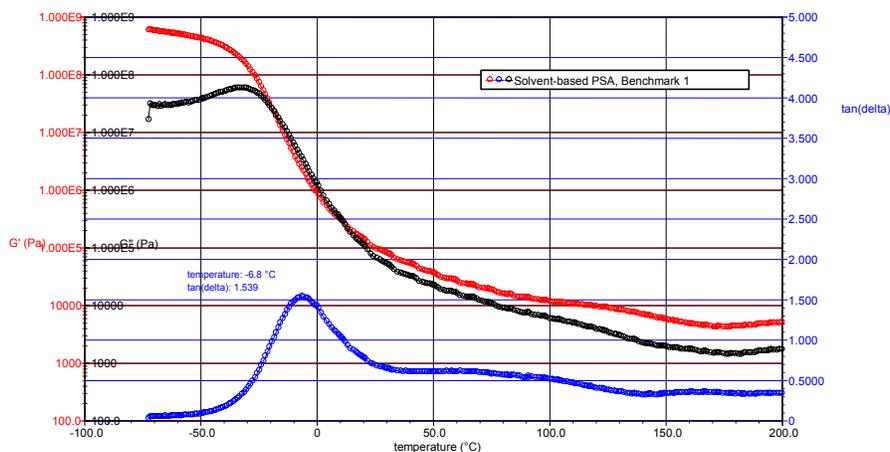
**Table 4**  
**Polyken Probe Tack of Different Surfaces of Adhesives**

	Directly exposed to UV	Not direct exposed to UV
Adhesive Thickness	5.0 mil	5.0 mil
Sample 1	798 (gram)	827 (gram)
Sample 2	771 (gram)	816 (gram)
Sample 3	802 (gram)	763 (gram)
<b>Average</b>	<b>790 (gram)</b>	<b>802 (gram)</b>

#### 4. Rheology Behavior

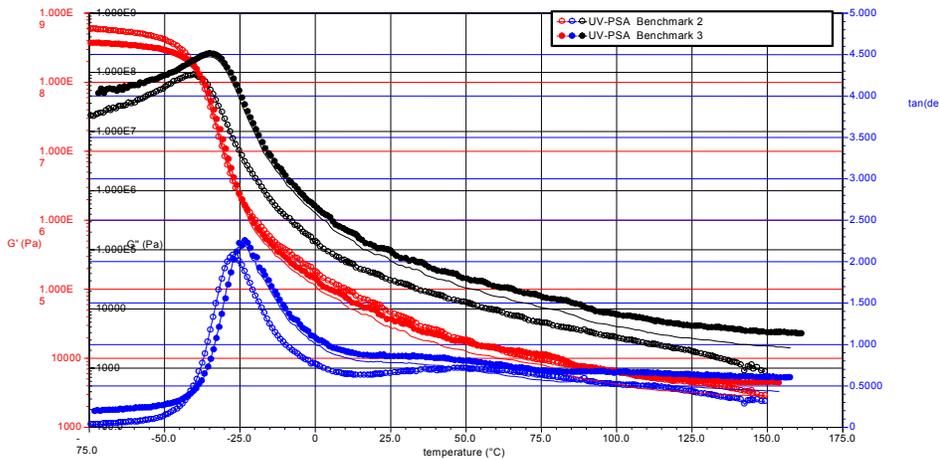
Rheology studies have utility as a screening tool to determine whether resins or formulations are suitable for PSA applications. The dependence of modulus of the materials on the temperature was determined. The modulus include storage (shear) modulus (upper curve in **Figure 2-5**), loss (adhesive failure) modulus (middle curves in **Figure 2-5**) as well as loss  $\tan(\delta)$  (loss modulus/storage modulus, bottom curves in **Figure 2-5**). The dynamic measurement temperature range spans the glassy state at low temperature, the glass transition range with strong decrease of both storage and loss moduli, and a temperature range where both storage and loss moduli decrease more gradually as temperature increases above Tg. Just above the glass transition range, the viscoelastic behavior is governed by polymer entanglements. The gradual decrease in both storage and loss moduli over a broad temperature range is typical for a polymer with a very broad molecular weight distribution. The pronounced increase of loss modulus is due to increasing deformation with increasing temperature. The decrease of loss modulus at higher temperature is associated with the debonding process. The ability of a polymer to dissipate energy usually has a maximum in the glass transition range, and decreases at higher temperature. Tack maximum is related to the glass transition temperature while other parameters such as molecular weight and crosslinking density etc. also influence the maximum.

**Figure 2** illustrates the rheology curve of Benchmark 1 which shows the rheological behavior of a typical high performance solvent-based PSA product.

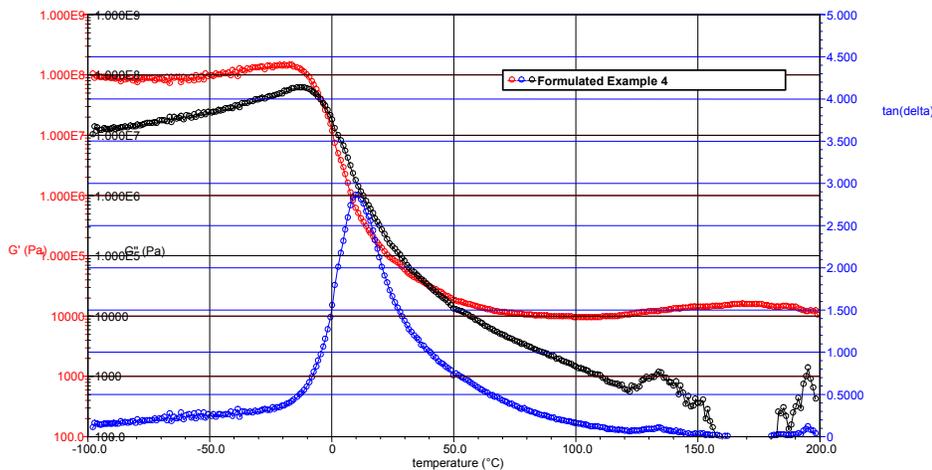


**Figure 2**  
**Rheological Behavior of Benchmark 1(Solvent-Based PSA)**

**Figure 3** shows the rheological curves of two UV-cured PSA products as Benchmarks 2 and 3. The low values of storage moduli for both Benchmark 2 and 3 at elevated temperature (> 100 °C) may indicate low shear strength at a high temperature.



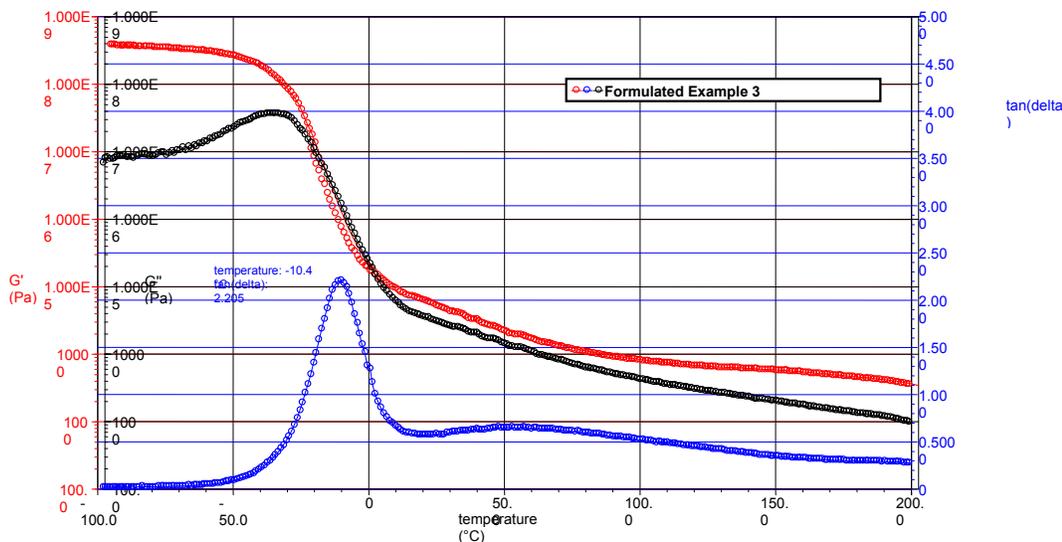
**Figure 3**  
Rheological Behavior of UV-Cured Benchmarks 2 and 3 (UV-PSA)



**Figure 4**  
Rheological Behavior of UV-Cured Formulated Example 3

**Figure 4** shows the rheological curves of the UV-cured **Formulated Example 4**. The high value of loss  $\tan(\delta)$  (ca. 3.1) may imply that the formulation has high tack value. The slightly high  $T_g$  (ca. 20°C) of the formulation could detract the performance of tack and peel strength. Importantly, unstable loss modulus at elevated temperature 120 °C and above strongly indicates poor PSA performance at high temperature.

**Figure 5** shows the rheological curves of the UV-cured **Formulated Example 3** which is similar to that of Benchmark 1. The rheological similarity implies possible similar adhesion performance while the higher  $\tan(\delta)$  value from **Figure 5** suggests a higher tack value of **Formulated Example 3** (see **Table 3** and **4**).



**Figure 5**  
**Rheological Behavior of UV-Cured Formulated Example 3**

## Conclusion

RC-PSA research is actively ongoing at UCB. Overall, high productivity, good processing flexibility, relatively low processing temperature, low or no VOC emissions, and also approaching high performance of solvent-borne technology are demonstrated as potential advantages brought by RC-PSA's.

New urethane (meth) acrylate oligomers/polymers as base resins have been developed and synthesized in UCB's R&D laboratories. Based on these resins, a new generation of warm-melt RC-PSA materials has been formulated. This new generation of PSA materials is curable by either EB or UV irradiation.

RC-PSA materials can be formulated to 100% solids content while providing workable coating viscosity. Most importantly, RC-PSA materials provide the potential to achieve high PSA performance on par with solventborne PSA's, in addition to their high cure speed and broad cure window.

## References

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