New Developmental UV-Curable Pressure Sensitive Adhesives

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Commercial interest in UV-curable pressure sensitive adhesives (PSA) continues to grow in recent years due to the potential for this technology to deliver better cure control, higher coating productivity, lower overall production cost, and lower VOC emissions. A number of UV-curable PSA (UVPSA) systems have been developed to meet the needs for different PSA applications. Those systems include UV-curable styrenic block copolymers,[1] cationic UV-curable epoxy-functional liquid rubbers,[2] acrylic polymers with grafted photoinitiator,[3] acrylic polymer/monomers syrups,[4] and various acrylated oligomers.[5] However, the UVPSA technology is still in its infancy stage and thus needs continuous improvement in several key areas including wider cure window, decreased sensitivity to air or moisture, more uniform cure for thick coating, and better adhesion/cohesion performance.

Conventional polyurethane has been widely used for many adhesive applications because of its good adhesion and high cohesion. Such a unique property is mainly a result of a two-phase microstructure of flexible polyurethane. Flexible polyurethane normally consists of both the hard segments (HS) and the soft segments (SS). The strong hydrogen bonding within the HS and the incompatibility between the SS and HS drive the formation of a two-phase structure where many nano-size hard phases are dispersed in a soft continuous domain.[6] By carefully designing the compatibilities, it is possible to have the UV-reactive components remain selectively with the HS micro-phase and the tackifiers to be miscible only with the SS domain. This two-phase UV-curable system is expected to offer several important advantages including better curability, less sensitivity to curing environment, and a higher adhesion performance.

This paper describes a new developmental UVPSA based on an acrylic urethane polymer that exhibits excellent UV curability, workable viscosity at warm-melt temperature (100-130°C), and good adhesion to both high- and low-surface energy substrates. By modifying the formulation, a wide range of UV-curable adhesives can be developed from this new technology to fit different industrial applications.

Experimental Section

Materials

The developmental UVPSA was typically made using a solvent-free warm-melt process. As a result, the final material is truly 100% solid without any solvent. A solvent-based acrylic PSA was used in this work for comparison purposes. This solvent-based PSA is a commercially available adhesive for high-performance tape applications.

Sample Coating

The coated samples in the lab were made using a ChemInstruments HLC-101 laboratory hot-melt coater. The UVPSA sample was preheated at ~120°C to remove any air bubbles in the material before coating. The typical temperature

setting for the hot-melt coater was ~130˚C for the top bar and ~100˚C for the bottom bar, respectively. The adhesive was coated on a silicone release liner to obtain the proper coat weight, cured to a desired degree using a Fusion UV system with two 600W/in H lamps, and laminated to a face stock such as PET film or Al foil. An appropriate speed (up to 300 ft/min) controlled the UV-cure energy density. The curing process was conducted at room temperature without nitrogen inerting.

Several industrial-scale coating trials were conducted with this new UVPSA. The first coating trial was conducted on a 60-inch wide hot-melt coater equipped with one bank of 600 W/in Fusion H-lamps. The coating was done at 100% lamp power at different cure speeds for the coat thickness of 1-8 mils. The temperature was set at ~121˚C for both the melt tank and slot-die head. The adhesive was cured in air without nitrogen inerting. The second coating trial was carried out on an 18-inch pilot coater equipped with two banks of 508W/in Eltosch lamps. The adhesive was coated at ~3.5 mils thickness and cured at several power rates (~20% to 100%). The cure property of the adhesive was also evaluated with or without nitrogen inerting.

Performance Testing

All performance testing was conducted in a constant temperature/constant humidity controlled room (23 ± 2˚C, 50 ± 5% relative humidity). An Enercom Instruments Ltd. weekly strip chart monitored the CTH consistency. All adhesion tests were done using the methods developed by the Specifications and Technical Committee of the Pressure Sensitive Tape Council. These methods include:

- 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^2).
- Peel adhesion was run on a Mass SP 2000 Slip/Peel Tester (Instrumentors Inc.), according to PSTC-101A on two different substrates, stainless steel and polypropylene panels. All panels were held at CTH for one hour prior to plating. One inch wide sample strips was applied to the panel and pressed using an auto-roller. The peel was measured at an Instron at a 180° angle at a speed of 12 in/min. The results were recorded in pounds per inch (lb/in).
- CTH shear strength was measured on a ChemInstruments 30 Bank Shear Tester with 2-Kg weights, according to PSTC-107A or alternatively ASTM D 3654, Section 9.4, Procedure A. One square inch of bonding area of the adhesive sample was applied to stainless steel panel and allowed dwell for 30 minutes at CTH conditions before hanging the weight.
- High-temperature shears were done on a ChemInstruments 8 Bank Shear Tester in the oven. Free adhesive films were laminated to 2 mils PET file and left for 72 hours at CTH conditions before testing. One square inch of bonding area of the adhesive sample was applied to stainless steel panel with a 4 lb roller and 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.

Viscoelastic Profile Measurement

Viscoelastic profile of the UV PSA samples was evaluated on a TA Rheometer, Model AR 2000, using 8 mm ETC parallel plates with a normal force control (no temperature gap compensation). Conditioning was conducted by inserting the specimen the sample holder and setting the gap (ca. 5000 µm) at room temperature, warming the specimen to 100°C at constant gap, and then cooling the specimen with normal force control (0.3 ± 0.1 Newton) to -50°C. The samples were evaluated over a temperature range of -50°C to +200°C at 3˚C per minute temperature ramp and at the frequency of 1 Hz and 0.025% controlled strain.

Results and Discussion

Physical Properties of UVPSA

This new UVPSA system is a clear and viscous liquid with Gardner color less than 3. Depending on

TABLE 1

Temperature dependence of viscosity for UVPSA 1

Temperature (˚C)	90	100	110	120	130	140
Melt viscosity (cps) (#5 spindle @ 50 rpm)	37,920	31,800	24,780	16,940	12,600	8,220

TABLE 2

Effect of shear rate on the viscosity of UVPSA 1

Spindle Speed (rpm)	2.0	4.0	5.0	10.0	20.0
Melt viscosity (cps) (#5 spindle @ 50 rpm)	15,250	14,750	14,600	14,250	14,150

TABLE 3

Adhesion comparison of UVPSA 1 and solvent-based acrylic PSA

Adhesion Performance	UVPSA 1	SB PSA
180˚ Peel on SS (20 min dwell)	4.1 lb/in	4.7 lb/in
180˚ Peel on SS (24 hr dwell)	4.4 lb/in	5.6 lb/in
180˚ Peel on PP (20 min dwell)	3.3 lb/in	1.0 lb/in (zipping)
180˚ Peel on PP (24 hr dwell)	4.8 lb/in	1.0 lb/in (zipping)
Shear at RT (1" x 1", 2Kg)	>167 hrs	70 hrs
Shear at 200˚F (1" x 1", 1 Kg)	>167 hrs	3 hrs
Before aging on polymeric PVC 180˚ Peel on SS (20 min dwell)	4.1 lb/in	4.9 lb/in
After 7 days at 70˚C on release liner 180˚ Peel on SS (20 min dwell) Retention	3.6 lb/in 88%	4.1 lb/in Peel 84%

the performance requirement and application, the adhesive formulation can be made in the forms of liquid material at room temperature or viscous material at warm melt temperature. UVPSA 1 is a warm melt formulation that was designed for high performance tape applications. Table 1 lists the melt viscosity of UVPSA 1 as a function of temperature, measured by using a Brookfield CAP 2000H at 50 rpm. In general, a hot melt is considered coatable if the viscosity is less than 50,000 cps. Based on the data in Table 1, UVPSA 1 should be easily coated at the temperature range 90-130°C. In the coating trial, the coating temperature was chosen at 120°C and the adhesive showed excellent coating quality in the speed range from 20-250 ft/min.

Table 2 shows the impact of the spindle speed (or the shear rate) on the melt viscosity of UVPSA 1 at 120°C. As expected, the melt viscosity of the adhesive was not very sensitive to the shear rate because the polymer chain is not long enough to form the chain entanglement. Conventional hot melt PSA, because of very high-molecular weight, normally show significant decreases in viscosity as the shear rate or coating speed increases. As a result, some adjustments in the slot die head may be needed for different coating speeds in order to get a consistent coating weight. Because of its comparatively low-shear thinning effects, this UVPSA is much easier to coat at the different coating speeds than conventional holt melt PSA. In the coating trial, 2-mil adhesive was successfully coated from 40-150 ft/min without any adjustment in the slot-die head.

Viscoelastic Properties of UVPSA

The PSA performance is closely related to the viscoelastic properties of the materials. Viscoelastic profiling provides a useful tool to characterize the PSA performance of UV-curable systems. For example, the modulus of an adhesive as a function of the temperature is a useful method to analyze how the cohesion strength and tack level change with temperature. At a given temperature, the higher the elastic modulus, the higher the cohesion strength, while the lower the loss modulus, the higher the tack level.

Figure 2 illustrates the viscoelastic profile of the uncured UVPSA 1. The uncured adhesive has a glass transition temperature at ~11.6˚C. The loss modulus is related to the visco-flow properties of the materials. The loss modulus increases quickly when the temperature is above the glass transition temperature, indicating that the uncured adhesive is a very viscous but flow-able liquid. After the adhesive was cured, the viscoelastic profile (Figure 3) showed much higher elastic modulus at temperatures above the glass transition temperature, which is a result of the crosslinking networks in the adhesive. The glass transition temperature also shifted to a higher temperature after cure. The UV cure

TABLE 4

UV-energy density dependence of adhesion performance of UVPSA 1

Cure Speed (ft/min) (600W/in, H bulb)	20	30	40	50	75	100	125	150
20 min Peel on SS (lb/in) *2 mil adhesive on 2 mil PET film*	4.5	4.4	3.8	3.9	4.4	4.5	4.9	4.7
24 hour Peel on SS (lb/in) *2 mil adhesive on 2 mil PET film*	4.6	4.4	4.9	5.3	5.0	5.1	5.6	5.5

TABLE 5

Effect of nitrogen protection on UV curability for UVPSA 1 (3.5 mil coat thickness)

Cure Speed (ft/min)*	24 hrs peel on SS (lb/in)		24 hrs peel on PP (lb/in		Shear at 200˚F (1kg/1 sq. in)	
	In N_2	In air	In N_2	In air	In N_2	In air
40	5.4	4.7	4.7	4.7	>160 hrs	>160 hrs
50	5.3	5.7	4.8	4.8	>160 hrs	>160 hrs
60	5.8	5.3	4.9	5.0	>160 hrs	>160 hrs
70	5.7	5.5	4.9	5.0	10 hrs	8 hrs
80	5.4	5.2	5.0	5.0	3 hrs	3 hrs

** Two UV bulbs (H_ga+ Ga) at total power of 400 W/cm or 1,016 W/in.*

converted some low- molecular weight components into the high-molecular weight network and therefore increased the glass transition temperature of the adhesive.

Typical Adhesion Performance

This new UV-curable system may be easily formulated to achieve a wide range of PSA performance. UVPSA 1 was designed to meet the high-performance requirement for industrial tape applications. A good PSA for high-performance tape applications should have the excellent adhesion to both high- and low-surface energy substrates as well as high cohesion strength at room and high temperatures.

Table 3 compares the adhesion performance of UVPSA 1 and a typical solvent-based acrylic PSA for industrial tape applications. UVPSA 1 was coated at 2 mil thickness on the release paper and then laminated to a 2 mil PET film after the adhesive was cured at ~500mJ/cm^2 (100 ft/min with two 600 W/in H lamps). Unlike typical solvent-based acrylic PSA, UVPSA 1 shows excellent adhesion not only on high-surface energy stainless steel (SS) but also on low-surface energy polypropylene (PP). The solvent-based acrylic PSA typically exhibits a very good adhesion to high-surface energy substrates, but only a marginal adhesion to low-surface energy substrates. In addition, UVPSA 1 can offer high cohesion strength at both room and high temperatures when it is cured appropriately.

UV-Curing Window

The strong dependence of adhesion performance on UV-cure energy density is one main concern for many UVPSA systems. The UV-cure window is quite narrow for these systems and thus the adhesion properties are a function of the UV-energy density or the cure speed. A higher UV-energy density can generate more crosslinked networks in an adhesive and therefore lead to higher cohesion and lower tack. A lower UV-energy density, on the other hand, can result in an adhesive with higher tack but lower cohesion. The adhesive, if under-cured, could continue to cure once exposed to UV light again and are not desirable for outdoor applications. If the adhesion performance is highly sensitive to the UV-energy density, it is very difficult for manufactures to be able to make a high-quality product with consistent performance. A good UV-curable PSA system needs to have a rather wider curing window in which the adhesion performance will be relatively stable and can meet the product performance specifications consistently under real manufacturing conditions.

In Table 4, the peel adhesion on stainless steel at a 2-mil coat thickness is showed as a function of the cure speed. The cure energy density was inversely proportional to the cure speed when the lamp power was not changed. Though the cure speed increased from 20 ft/min to 150 ft/min, the peel adhesion of UVPSA 1 was relatively constant. In other words, the cure window is quite wide for UVPSA 1 and the consistent adhesion properties can be achieved in a wide range of cure speed. One possible explanation for such a wide UV-cure window is that UVPSA 1 contains a very low level of curable functional groups and those groups are quite close to each other. As a result, those groups can quickly react with each other once exposed to UV

FIGURE 1

Viscosity vs. melt temperature of UVPSA 1

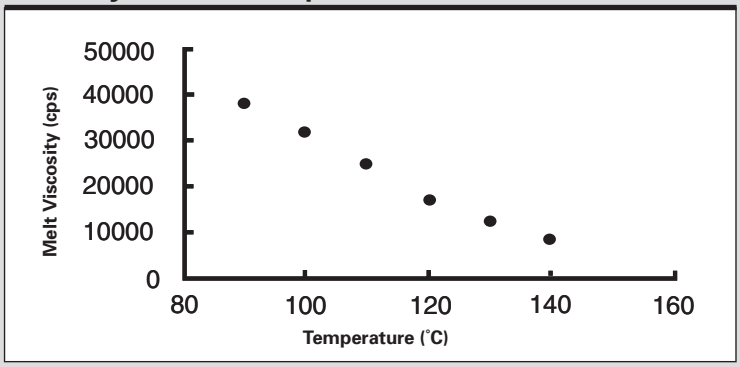
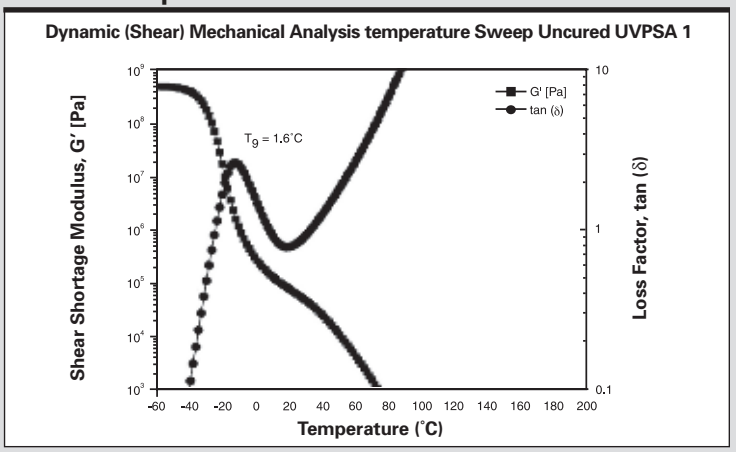


Figure 2

Viscolastic profile of uncured UVPSA 1



irradiation, and more exposing time or higher UV-energy density will not lead to significantly higher crosslinking density and cause a large change in the peel adhesion.

Effect of Oxygen on the Cure Reaction

It is well known that oxygen in air can inhibit or significantly slow the UV-cure reaction when a UV-curable system is based on the free radical chemistry. The inhibition effect of oxygen can occur on the adhesive surface as well as in the adhesive bulk due to the dissolved oxygen in the adhesive. As a result, most UV-curable PSA systems may require a nitrogen chamber to provide an oxygen-free environment for during cure. Such nitrogen inerting can eliminate the inhibition effect on the adhesive surface cure, but it may not prevent the inhibition impact of oxygen, which is already present in the adhesive bulk. This nitrogen inerting requirement will increase not only the production cost, but also the variables in the product quality control. The best solution is to develop a new UVPSA system that will be less sensitive to oxygen.

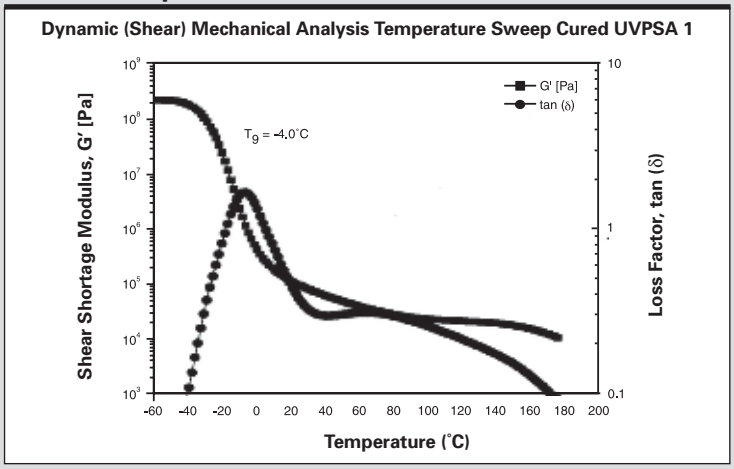
The present UV-curable system, possibly due to its unique composition, was found to be less sensitive to the oxygen and is easily cured without nitrogen inerting. Table 5 shows the adhesion properties of UVPSA 1 as a function of the cure speed under air and nitrogen. In this coating trial, the curing properties were evaluated in a lower coating speed range from 40-80 ft/min because of the thicker adhesive coating (3.5 mils) and lower lamp power (400 W/cm). At a given cure speed, the adhesive displayed similar adhesion peel on both high- and low-surface energy substrates, regardless of using nitrogen inerting or not. The same conclusion can be made from the results of the high-temperature shear. At high-cure speeds (70 and 80 ft/min) or low UV-energy density, both the adhesive samples, with or without nitrogen inerting, were insufficiently cured and showed similarly low shear at 200˚F. When the cure speed was lowered to 60 ft/min and below, all the samples were sufficiently cured to pass 160 hours shear target at 200˚F. Obviously, the oxygen in the air did not have much inhibition effect on the UV-cure process for this new adhesive.

Conclusion

A new UV-curable PSA system shows several important improvements over previous systems due to its unique chemistry and morphology. This new UVPSA exhibits excellent UV curability from low-coat weight to high-coat weight without nitrogen inerting. Consistent adhesive performance can be achieved over a relatively wide range of cure speed or UV-energy density. The adhesive can be easily coated at warm melt temperature (120˚C) and cured up to 8 mil thickness. Several coating trials consistently showed that this type adhesive can have good coatability, excellent UV curability, and a high

Figure 3

Viscolastic profile of cured UVPSA 1



adhesion performance. The high-adhesion performance includes excellent adhesion to both high- and low- surface energy substrates, high cohesion at room and high temperature, good plasticizer resistance, and thermal and UV stability. By tailoring the formulation to specific customer needs, this new UV-curable technology can offer a wide range of adhesives to fit with different industrial applications.

Acknowlegements

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The Carl Dahlquist Award is given to one speaker at each annual technical conference who, following the evaluation of judges panel, demonstrates the very best in research relating to adhesive tape technology. The award is named for innovator Carl Dahlquist who developed the Dahlquist criterion of tack. ◗

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