UV/EB CURABLE PSA's

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INTRODUCTION

Pressure sensitive adhesives (PSA's) have become a ubiquitous element in our society. Solvent-borne PSA formulations traditionally based upon modified rubber chemistry are now being challenged by low VOC, fast curing systems such as UV and EB cured PSA's. This paper describes both water-based and 100% solids UV curable PSA's and their properties. A new acrylate monomer, ethoxylated nonyl phenol acrylate, has great utility in the formulation of water-based PSA's.

THEORY

UV PSA systems are formulated to contain three major components: tackifier resins for peel strength and tack, monomers for Tg modification and viscosity control, and oligomers for shear performance. Two minor components are additives such as antioxidants and photoinitiators.

HISTORICAL

Previous studies (presented at Radtech '94, Low Cost UV Curable PSA's, Craig A. Glotfelter) have shown the effects of monomer content and tackifier properties on peel strength performance in UV PSA's. In summary, PSA performance was found to correlate to monomer content, system glass transition temperature (Tg), and tackifier softening point (as determined by ring and ball method). Tackifier resins having higher softening points will yield higher peel strengths.

PSA's described in this work have been evaluated by three test methods: rolling ball tack (RBT), 180 degree peel, and shear. Each of these test methods will be described in the results section. PSA's were prepared by a procedure developed in order to minimize premature polymerization.

While test methods described previously are sufficient for evaluating PSA performance, the formulator is well served to quantify adhesive properties during the conception and preparation of the particular adhesive. To this end, we have found the Fox equation[1] to be useful where:

$$1/Tg = W1/Tg1 + W2/Tg2 + W3/Tg3...$$

and $W1 + W2 + W3 = 1$ (W=weight fraction, T in degrees K)

The Tg of a multicomponent system can be determined via the Fox equation and subsequently related to adhesive performance (see Fig. 1). One can argue as to the accuracy of the Tg values derived via the Fox equation based upon empirically derived data, functionality of acrylate used, and the Tg of the non-reactive tackifying resin, nevertheless it was shown that the Tg is related to the performance of the adhesive formulation.

Figure 1
Adhesive Performance versus Tg

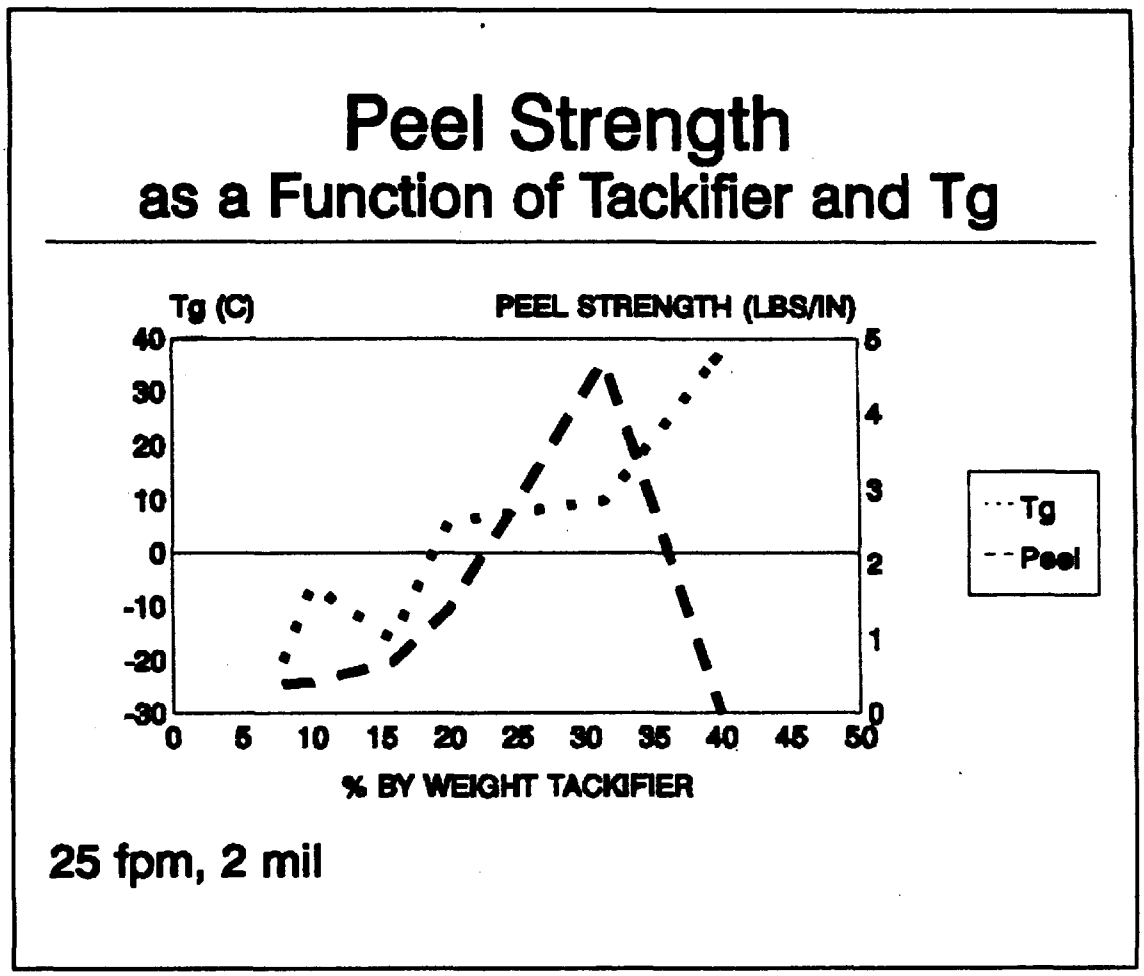

Table 1 describes the monomers evaluated and the compatibility of the monomer with the rest of the PSA formulation.

Table 1
Monomer Compatibility with PSA Formulation

Monomer	Description/Tg	Compatibility
isodecyl acrylate	non-polar/-45	no
ethoxylated nonyl phenol acrylate	polar/non-polar/15	yes
tridecyl acrylate	non-polar/-75	no
isooctyl acrylate	non-polar/-100	no
2 (2-ethoxyethoxy) ethyl acrylate	polar/-50	yes
aromatic epoxy acrylate	non-polar/?	no
aliphatic epoxy acrylate	polar/?	no

The polarity of the monomer played a large role in the relative compatibility within the PSA formulation, though it was surprising that the aromatic epoxy acrylate was not compatible.

PSA formulation 6 (see appendix i) was developed using 2 (2-ethoxyethoxy) ethyl acrylate and ethoxylated nonyl phenol acrylate as the monomer components.

SAMPLE PREPARATION AND TEST METHODS

100% Solids UV PSA's

Adhesive films were drawn down on 1 mil Mylar at a nominal thickness of 2 mils. The films were then cured at 7.6 mpm while being exposed to a single 300 W/inch Hg-arc medium pressure "D" type lamp. After curing, the films were allowed to equilibrate 24 hours in a 75 F, 50% R.H. atmosphere before testing.

Water-based UV PSA's

Adhesive films were drawn down on 1 mil Mylar at a nominal thickness of 2 mils. The films were then dried at 90 C for 5 minutes before UV curing. The films were UV cured by exposure to a single 300 W/in Hg-arc lamp on a conveyor running at 7.6 mpm. After curing, the films were allowed to equilibrate 24 hours in a 75 F, 50% R.H. atmosphere before testing.

Rolling ball tack testing was done using a stainless steel ball rolled down an inclined plane and onto the surface of the adhesive film. Test procedures were as per PSTC specifications.

The distance the ball travelled was recorded and compared to other readings. The test was carried out in triplicate and the average value reported.

Peel testing (180 degree) was performed using a peel/slip tester which was used to pull a 2.54 cm wide strip of adhesive coated Mylar from a stainless steel panel. The force in Newtons was recorded for triplicate runs and the average value in Newtons/100 mm was reported. All test procedures were carried out according to PSTC specifications.

Shear testing was performed by placing a one square inch section of a 7.5 cm long adhesive strip onto a stainless steel plate and suspending a 1 kilogram weight form the opposite end. The time required for the weight to be pulled away from the plate was recorded. Test procedures were as per PSTC specifications. Cheminstruments[2] equipment was used for all testing.

Values for rolling ball tack are listed in centimeters. Values for peel strength are listed in Newtons/100mm. Shear values are listed as time to failure

RESULTS

Several new UV PSA formulations were prepared based upon conclusions drawn from work presented at Radtech '94. Specifically, studies were done to assess the relative performance of photoinitiator systems, to assess the influence of monomer ratios, and to assess the performance of water-based UV PSA's. All UV PSA formulations are listed in Apendix i.

100% Solids UV PSA Formulations

Table 2 lists UV PSA formulations having varying ratios of 2 (2-ethoxyethoxy) ethyl acrylate to ethoxylated nonyl phenol acrylate. All other components and total monomer concentration were as reported for Formulation 6 in appendix i. The results reported are for 50 micron samples cured at 7.6 mpm using one 300 W/in Hg-arc lamp.

Table 2
UV PSA's with Varying Monomer Ratios

Formulation	ethoxylated nonyl phenol acrylate: 2 (2-ethoxyethoxy) ethyl acrylate	Rolling Ball Tack (cm)	Peel (N/100 mm)	Appearance after cure
6	1:1	30.5	96	clear
6-A	0.77:1	19.1	97	clear
6-B	0.35:1	3.2	75	cloudy
6-C	100% 2 (2-ethoxyethoxy) ethyl acrylate	10.16	85	sl. cloudy

Small changes in monomer ratio had little effect on peel strength but showed decreasing RBT values with decreasing concentration of ethoxylated nonyl phenol acrylate. Peel strength had a minimum value in formulation 6-B but recovered to near control values in formulation 6-C. A reduction in clarity was observed with decreasing content of ethoxylated nonyl phenol acrylate.

Table 3 lists adhesive properties for formulations having various photoinitiators. Commercial names for photoinitators are listed in the interest of brevity. Photoinitator concentrations were held constant as in Formulation 6. All samples were cured at 7.6 mpm using one pass under a single 300 W/in Hg-arc lamp.

Table 3
Effect of Photoinitiator on Adhesive Properties

Formulation	Photoinitiator	Rolling Ball Tack (cm)	Peel Strength (N/100mm)
6	Esacure KIP100F	30.5	96
6-D	Esacure KB1/ Irgacure 651	14.6	79
6-E	Darocur 1173	11.4	93
6-F	Benzophenone/ methyl diethanolamine	Did not cure properly	

Water-based UV PSA Formulations

New monomers such as ethoxylated nonyl phenol acrylate which are self-emulsifying have been integral in the development of water based UV PSA's. Table 4 lists the properties for water based UV PSA's that have been tested.

Table 4
Water-Based UV PSA Properties

Formulation	% Trifunctional	Rolling Ball Tack (cm)	Peel (N/100 mm)	Shear
W-3	5.0	30.5	27	1 hour
W-1	5.8	27.2	14	>550 hrs.
W-6	9.5	30.5	18	>550 hrs.

Overall performance of the water-based UV PSA's was not as good as the 100% solids formulations. However, there are factors such as other tackifiers and water dispersible oligomers yet to be evaluated. There is, as expected, a clear correlation between the amount of crosslinker, i.e. ethoxylated TMPTA, and the shear strength with shear strength increasing with increasing crosslinker. Generally speaking the relative proportions of the oligomer (crosslinker), monomers, and tackifier resin in the 100% solids UV PSA does not translate to the water-based UV PSA's.

EXPERIMENTAL

100% Solids PSA Preparation

To an appropriate sized resin kettle equipped with thermometer, condenser, air sparge, and mechanical stirrer were added the oligomer, monomer, inhibitor, and antioxidant. The mixture was heated with stirring and air flow to about 60 C after which the tackifier resin was added over a period of about 15 minutes. The tackifier was added in this manner to prevent clumping. The speed of stirring was increased as the tackifier was added. After the tackifier resin was added, the temperature was raised to about 80 C and maintained there until the tackifier resin was completely dissolved. Formulations containing higher amounts of tackifier resin may take up to 3 hours at 80 C to ensure solution of the tackifier resin. It is not recommended to raise the temperature of the PSA formulation over 80 C or to maintain the temperature at 80 C for longer than 4 hours. After the tackifier resin is dissolved, the temperature was lowered to 40 C and the photoinitiator was added. The PSA formulation was

mixed 15 minutes after the addition of photointiator, then bottled, making certain to leave a headspace equivalent to 1/4 the volume of the container.

Water-Based PSA Preparation

To an appropriate sized Ehrlenmeyer flask were added the ethoxylated nonyl phenol acrylate, aqueous tackifier, ethoxylated TMPTA and photoinitiator. The Erlenmeyer was stoppered and the contents were shaken vigorously for two minutes. The water was added and the contents were shaken vigorously for an additional two minutes. The resulting creamy emulsion was stable and able to be coated onto substrates.

CONCLUSIONS

1. Changing monomer ratios in 100% solids UV PSA's affects RBT values and coating clarity.

2. Peel strengths increase with tackifier content so long as Tg's are adjusted with monomers.

3. Shear durations increase with increasing cure and crosslinking and decrease with tackifier content in 100% solids PSA's. Shear values increase with ethoxylated TMPTA content in water-based UV PSA's.

4. Water-based UV PSA's generally do not performs well as 100% solids formulations, but are continuously developing.

BIBLIOGRAPHY AND REFERENCES

1. Billmeyer, Fred Jr. "Textbook of Polymer Science", 3rd Ed., Wiley-Interscience, New York, 1984.

2. Cheminstruments, 510 Commercial Drive, Fairfield, OH, 45014, Tel. 513-860-1597

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APPENDIX i

100% Solids UV PSA Formulations

Component	6	6-A	6-B	6-C
Urethane Oligomer	15.8	19	15.8	15.8
Tackifier resin	31.6	31.6	31.6	31.6
2 (2-ethoxyethoxy) ethyl acrylate	21.0	21.0	32.4	43.9
Ethoxylated nonyl phenol acrylate	22.9	19.7	11.5	-
MEHQ	0.08	0.08	0.08	0.08
Antioxidant	0.8	0.8	0.8	0.8
Photoinitiator	7.82	7.82	7.82	7.82
Peel Strength, lbs/in				
Appearance, postcure	clear	clear	cloudy	sl. cloudy

Water-based UV PSA's

Ingredient	W-1	W-3	W-6
Ethoxylated nonyl phenol acrylate	55/63.7%	55/55%	55/52%
Aqueous Tackifier (57% solids)	32/21.2%	56/32%	56/30.5%
Ethoxylated trimethylolpropane triacrylate	5/5.8%	5/5%	10/9.5%
Photo-initiator	8/9.3%	8/8%	8/7.5%
Water	10	10	10