

Basic Concepts Of Liquid Energy Curable PSA's

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1. Targets

This report reflects Rahn's continuing work to provide applicable starting formulas to our customers. Also included is a study of different tackifying resins.

2. Summary

The PSA starting point formula offers the following properties at a film thickness of 0.5 mil.:

- Peel Strength of 2.90 lb/in
- Loop Tack of 1.80 lb/in²
- Shear Strength of 604 minutes at room temperature
- Viscosity of 3215 cps

This formulation adheres well to the following substrates:

- Plastic
- Metal
- Glass
- Paper/Board

The formulation can be readily modified as described in Section 7.

PRESSURE SENSITIVE ADHESIVE **STARTING POINT FORMULA**

Nr.	Component	Supplier	Amount	Remarks
1	Urethane B/MA	RAHN	14.0%	Urethane Acrylate
2.	Urethane A/MA	RAHN	16.0%	Urethane Acrylate
3	TR-A/MA	RAHN	36.0%	Sat. Polyester/M22
4	TR-B/MA	RAHN	12.0%	Sat. Polyester/M22
5	DPGDA	Various	1.0%	DPGDA
6	EOEOEA	RAHN	14.0%	EOEOEA
7	LTM	RAHN	4.0%	Initiator
8	PMP	RAHN	2.0%	Initiator
9	Stab A	RAHN	1.0%	Inhibitor
	TOTAL AMOUNT		100.0%	

TEST RESULTS

Viscosity: 3215 cps

Tg -23 Degrees C

Test Samples made with #5 Drawdown Rod (0.5 mil/12.8 μ)

Reactivity: 15 fpm x 2 passes
1x300 wpi bulb (0.420J/cm²)

Peel Strength: 2.90 lb/in

Loop Tack: 1.80 lb/in²

Shear Strength: 604 min.

* 100 gram sample available from Rahn Corporation

*Starting Point Formula not for sale

3. Introduction

A liquid radiation curable PSA is comprised of four essential components – elastomer, tackifier, diluent, and photoinitiator. The elastomeric component in this case is a combination of a monofunctional and a difunctional aliphatic urethane acrylate oligomer. The high molecular weights and glass transition temperatures (Tg) of well below ambient temperature allow the oligomer component to offer elastic like properties at room temperature, enabling the adhesive to be extended or compressed upon pressure. Its deformability under light pressure allows it to conform to and wet out a substrate (measured as the internal tack of the system). Upon adhesive removal from that substrate, its elasticity allows it to extend greatly before separating, giving the adhesive good peel and adhesion properties.

The tackifying component of this adhesive is a saturated polyester co-resin. Its function is twofold. Generally speaking, the resin has a much lower molecular weight and higher Tg than the oligomer. This difference allows the elastomer greater mobility in the system, maximizing both its deformability under light pressure and its elastic behavior during adhesive removal. The higher glass transition temperature of the tackifying resin brings the overall adhesive Tg to a value necessary to achieve PSA properties. Typically a pressure sensitive adhesive's Tg ranges from -25C - +5C, although this is merely a suggested range that can be altered when certain properties must be achieved such as a high Shear Adhesion Fail Temperature (SAFT) value. In general, the higher the overall Tg of an adhesive, the greater the cohesive strength and high temperature shear results and the lower the tack and deformability properties.

Besides acting a diluent, the reactive monomer plays a role similar to the tackifying resin, allowing for greater deformability of the adhesive due to its low molecular weight, and depending on the monomer, adding its own flexible behavior to an adhesive. The Tg of the monomer also assists in defining the overall Tg of the adhesive system. Monofunctional monomer Tg's can range from -54C (EOEOEA) to +88C (IBOA). For example, a high IBOA content influences the Tg to a point that the oligomer content would need to be much greater than the tackifier amount to offset the Tg of

the IBOA. Upon replacement of the IBOA with EOEOEA, the co-resin content could be increased to compensate for the Tg reduction.

Finally, the photoinitiator's role is vital as it dictates the manner of cure that the adhesive undergoes. A high surface cure photoinitiator will tend to increase shear properties, but destroy the tack of the system. A great through cure product may leave the surface very tacky but exhibit poor cohesive strength due to the surface not being as well crosslinked, resulting in poor shear properties. A good balance of cure properties is important in maintaining proper pressure sensitive adhesive attributes, which is what this starting point PSA study attempts to consider.

4. Experimental

The following trial series were carried out during the study:

- Test Series 1: A tack stability study is run on the existing PSA starting point formulation that was established in Lab Report No. US 02002. The loop tack is examined on samples that are subjected to room temperature and accelerated aging to determine their stability properties.
- Test Series 2: Based on the results from Test Series 1, two oligomers cut in a monofunctional urethane acrylate monomer are evaluated in a base formulation for their inherent PSA properties. Also examined is the ratio between the oligomers and the tackifying co-resin in the adhesive. Samples are tested for viscosity, peel strength, shear strength, and loop tack. The degree of cure for each tested sample is relative to maximizing the shear strength value for the respective formula. All corresponding tests are cured to that degree.
- Test Series 3: Using the best resulting formula from Test Series 2, slight alterations are administered to the formulation and their effects are examined. The same testing procedure is used as in Test Series 2.
- Test Series 4: Several photoinitiators are evaluated separately and as blends. Their ratios are altered to maximize their efficiency and optimize the PSA starting point formula. The same testing procedure is used as in Test Series 2.
- Test Series 5: The optimized formulation is used as a base for a tackifier resin study. Standard commercial products are evaluated for compatibility and performance. Resin types tested include polyesters, rosin esters, hydrocarbons, terpene phenolics, gum rosins and tall oil rosins. A ladder study is also executed on Rahn's polyester resins to examine their different effects on performance. The same testing procedure is used as in Test Series 2.
- Test Series 6: A tack stability study is executed on the PSA starting point formulation to determine its performance over time. Upon completion of this study, the PSA starting point formulation is finalized.

LEGEND OF PRODUCTS USED:

Chemical Name

Report Shorthand

Monomers:

Isobornyl acrylate	IBOA
2-(2-Ethoxyethoxy) ethyl acrylate	EOEOEA
Dipropylene glycol diacrylate	DPGDA
GENOMER* 1122	
2-Acrylic acid, 2-(((butylamino)carbonyl)oxy)ethyl ester (Monofunctional urethane acrylate)	Monomer A

Oligomers:

GENOMER* 4188/M22 Monofunctional aliphatic urethane acrylate diluted in 25% Monofunctional urethane acrylate monomer	Urethane A/MA
GENOMER* 4269/IBOA Difunctional aliphatic polyester urethane acrylate diluted in 25% Isobornyl acrylate	Urethane B/IBOA
GENOMER* 4269/M22 Difunctional aliphatic polyester urethane acrylate diluted in 25% Monofunctional urethane acrylate monomer	Urethane B/MA

Tackifying Resins:

GENOMER* 6043/M22 Modified saturated polyester resin diluted in 15% Monofunctional urethane acrylate monomer	TR-A/MA
Co-Resin 02-819/M22 Modified saturated polyester resin diluted in 35% Monofunctional urethane acrylate monomer	TR-B/MA
GENOMER* 6083/M22 Inert resin diluted in 35% Monofunctional urethane acrylate monomer	TR-C/MA

Photoinitiators:

Dimethylhydroxyacetophenone	DMHA
Liquid photoinitiator blend	LTM
2-Methyl-1-(4-(methylthio)phenyl)-2-morpholino-propan-1-one	PMP

Stabilizer:

Polymerization inhibitor in acrylic acid ester	Stab A
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5.1 Test Series 1 (Tack Stability Study)

	1	2	4	5	7	8
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Urethane B/IBOA	47	0	47	0	47	0
Urethane B/MA	0	47	0	47	0	47
TR-A/MA	34	34	34	34	34	34
IBOA	7.5	7.5	0	0	15	15
EOEOEA	7.5	7.5	15	15	0	0
DMHA	3	3	3	3	3	3
Stab A	1	1	1	1	1	1
TOTAL	100	100	100	100	100	100
Loop Tack (lb/in ²)						
Day 1	2.94	4.14	4.1	2.27	0.77	1.54
RT – Day 2	2.55	3.47	2.13	2.47	0.11	1.02
RT – Day 7	2.01	2.57	2.3	2.26	0.29	0.97
RT – Day 42	1.65	2.22	2.46	2.03	0.25	1.20
% Decrease	44%	46%	40%	11%	68%	22%
Heat Aged (60°C)						
Day 7	1.95	2.34	2.80	2.05	0.07	0.90
% Decrease	34%	44%	32%	10%	91%	42%

Interpretation

From this evaluation of tack stability, it is evident that IBOA is the cause of severe tack depreciation over time. Despite offering initial high values for tack and peel, the larger the amount of IBOA in a formulation, the greater the decrease in tack values. Formulations wherein the difunctional urethane acrylate, Urethane B was diluted in Monomer A, a monofunctional urethane acrylate monomer, seemed to offer the best tack retention performance. Oligomers diluted with Monomer A are designated with an MA after the resin code. Already being a standard dilution for Rahn, the remainder of this study will use Monomer A as the diluent of choice.

5.2 Test Series 2 (Oligomer/Co-Resin Ratio)

	1	2	3	4	5	6	7	8	9	10
Urethane B/MA	0	27	0	24	77	50	50	0	0	28
Urethane A/MA	78	49	50	27	0	27	0	0	28	0
TR-A/MA	0	0	27	26	0	0	27	77	49	49
EOEOEA	15	17	16	16	16	16	16	16	16	16
DMHA	6	6	6	6	6	6	6	6	6	6
Stab A	1	1	1	1	1	1	1	1	1	1
TOTAL	100	100	100	100	100	100	100	100	100	100
Test Results										
Viscosity (cps)	2827	2814	2631	2148	3150	2865	2283	3064	2557	2618
Peel Strength	2.08	2.16	2.52	1.81	1.26	1.68	1.40	1.83	2.46	2.41

(lb/in)										
Loop Tack (lb/in ²)	1.27	1.07	1.43	0.97	0.62	0.85	0.42	1.86	1.48	1.10
Shear Strength (min)	146	185	106	86	75	58	365	26	80	524

Interpretation

The two oligomers and the tackifying co-resin, Urethane B/MA, Urethane A/MA, and TR-A/MA, were examined respectively as the sole oligomer/resin, and in combination with the others. The elastomer/resin ratio (oligomer/tackifying resin) is optimized in Sample 10. At this ratio, the elastomer provided adequate mobility in the finished adhesive, resulting in good surface deformability and high tack properties. This also allows for greater adhesive extension prior to separation from the surface, providing higher peel values. Since shear results are a reflection of the cohesive strength of the adhesive, the difunctional Urethane B offers good shear properties while maintaining tack and peel characteristics. It can be seen that the monofunctional Urethane A raises tack values, but does not contribute much to the shear properties of the adhesive. The TR-A, having no functionality, causes shear values to decrease rapidly when used alone. Another interesting observation is the viscosity performance of Samples 5, 8, and 10. When used by themselves, Urethane B and TR-A offer viscosities over 3000 cps, but by adding them together, the viscosity falls to 2618 cps. This is due to the lower molecular weight of the co-resin allowing the Urethane B greater mobility in the liquid adhesive.

5.3 Test Series 3 (Variations)

	1	2	3
Urethane B/MA	15	15	15
Urethane A/MA	13	13	13
TR-A/MA	50	46	46
DPGDA	0	0	1
EOEOEA	15	15	14
DMHA	6	10	10
Stab A	1	1	1
TOTAL	100	100	100
Test Results			
Viscosity (cps)	2568	2078	2054
Peel Strength (lb/in)	1.76	2.12	2.04
Loop Tack (lb/in ²)	2.25	1.54	1.08
Shear Strength (min)	322	371	1125

Interpretation

Test Series 3 was based upon Sample 10 in the last test series. Slight variations were made to improve test results. Urethane A was added to improve the tack values and DMHA was increased to enhance cure response. DPGDA was added at 1% to improve the crosslink density and cohesive strength, drastically improving the shear strength properties.

5.4 Test Series 4 (Photoinitiator Study)

	1	2	3	4	5	6
Urethane B/MA	16	16	16	16	16	16
Urethane A/MA	14	14	14	14	14	14
TR-A/MA	48	48	48	48	48	48
DPGDA	1	1	1	1	1	2
EOEOEA	14	14	14	14	14	13
DMHA	6	0	0	3	0	0
LTM	0	6	0	0	4	4
PMP	0	0	6	3	2	2
Stab A	1	1	1	1	1	1
TOTAL	100	100	100	100	100	100
Test Results						
Viscosity (cps)	2634	2346	3124	2768	2558	2746
Cure Speed (# of passes)	6	3	7	7	4	4
Peel Strength (lb/in)	1.73	2.12	1.05	1.72	2.36	1.71
Loop Tack (lb/in ²)	1.76	0.97	2.55	2.42	2.17	1.95
Shear Strength (min)	853	645	16	97	152	191

Interpretation

Test Series 4 illustrates the performance of several different photoinitiators and their subsequent blends on this adhesive system. The total photoinitiator percentage is set to 6%. The DMHA offers a good balance of PSA properties. The PMP exhibits high tack and very low shear properties due to its lower surface cure tendencies, especially when using a medium pressure Hg bulb. The LTM offers excellent cure speeds with the Hg bulb, providing a high degree of cohesive bonding within the adhesive as well as very high shear strength properties. A 2:1 of LTM and PMP, exemplified in Sample 5, offers the best balance of properties. The drawback with using the LTM and PMP is the tendency for a slight yellowing effect to occur in the finished adhesive. If non-yellowing is a final criteria, this blend should be avoided and DMHA should be used. A 2% addition of DPGDA was also examined. The resulting system became too crosslinked and not elastic enough, exhibiting a zippery effect during adhesive removal.

5.5 Test Series 5 (Tackifier Compatibility Study)

Since compatibility of tackifying resins with elastomers is a fundamental issue, common tackifying resins were examined with respect to our particular oligomers and formulation. The majority of resins tested were not compatible with the system tested. The following chart illustrates the general trends for resin compatibility with Urethane A and Urethane B.

Tackifying Resin	Urethane A/Urethane B
Hydrocarbon Resins	Incompatible
Rosin Esters	Moderate Compatibility
Gum Rosins	Incompatible

Tall Oil Rosins	Incompatible
Terpene Phenolic Resins	Compatible
Polyester Resins	Compatible

The incompatibility occurs between the tackifying resin and the aliphatic urethane acrylates used. Blends of monomer and tackifying resin were produced successfully in each case, but upon combination with the urethane acrylates, the incompatibility ensued. In many cases, this incompatibility was only evident after application and cure of the adhesive on a transparent film. The result was usually a cloudy, hazy or separated sample with extremely slow cure combined with very poor tack and shear performance.

Certain rosin esters showed limited compatibility, exhibiting only a slight haze and some degree of acceptable physical properties. The only consistently compatible products with good performance were terpene phenolic resins and Rahn's polyester co-resins, the latter exhibiting the greatest balance of physical properties.

Test Series 5.5.1

	1	2	3	4	5	6	7	8	9	10	11	12
Urethane B/MA	14	14	14	14	14	14	14	14	14	14	14	14
Urethane A/MA	16	16	16	16	16	16	16	16	16	16	16	16
TR-A/MA	48	36	24	12	0	0	0	0	0	12	24	36
TR-B/MA	0	0	0	0	0	12	24	36	48	36	24	12
TR-C/MA	0	12	24	36	48	36	24	12	0	0	0	0
DPGDA	1	1	1	1	1	1	1	1	1	1	1	1
EOEOEA	14	14	14	14	14	14	14	14	14	14	14	14
LTM	4	4	4	4	4	4	4	4	4	4	4	4
PMP	2	2	2	2	2	2	2	2	2	2	2	2
Stab A	1	1	1	1	1	1	1	1	1	1	1	1
TOTAL	100	100	100	100	100	100	100	100	100	100	100	100
Viscosity (cps)	3367	3358	3106	2867	2745	2829	2955	2934	2793	3113	3116	3215
Cure Speed (fpm x passes)	15x4	15x2	15x1	15x1	25x1	25x1	25x1	25x1	25x1	15x1	15x2	15x2
Peel Strength (lb/in)	2.65	3.16	4.31	3.92	3.16	3.03	3.02	2.58	2.83	2.75	2.54	2.90
Loop Tack (lb/in ²)	1.60	0.34	0.42	0.26	0.20	0.24	0.59	0.93	1.53	1.65	1.28	1.80
Shear Strength (min.)	194	228	668	1049	1485	5353	1052	914	324	202	661	604

- **Interpretation**

Three products stand out as the optimum performance resins depending on end product requirements. The TR-A/MA exhibits good tack properties while maintaining good peel values, but lower shear properties than the other polyesters examined. The TR-B/MA exhibits the best overall balance of PSA

properties. Its peel, tack and shear strengths are all good and its larger molecular weight offers excellent internal cohesiveness resulting in very low residuals on substrates. In addition, it shows good cure response. The TR-C/MA offers superior shear and peel properties with good cure response, but it does exhibit low tack values. Blending polyester resins to make a dual tackifier resin system seems to work very well for specific properties. The optimum blend in this formulation is Sample 12, which includes a 3:1 ratio of TR-A/MA to TR-B/MA.

One point that also requires discussion is how the degree of cure effects PSA properties. Insufficient cure will result in an adhesive with high tack and low shear properties; excessive cure can result in the opposite. Depending upon the desired result, consistent cure levels must be established and maintained during the production process. To illustrate this point, the following table exhibits the performance versus cure for two samples from the previous table.

	Sample #7		Sample #9	
Cure Speed (fpm)	25	15	25	15
Peel Strength (lb/in)	3.02	3.69	2.83	2.80
Loop Tack (lb/in ²)	0.59	0.15	1.53	0.30
Shear Strength (min.)	1052	5162	324	3013

It is evident from these values that the degree of cure plays an important role in the formulating and production of radiation curable PSA's. Care must be taken by a formulator to optimize all properties with respect to the cure parameters of the application equipment.

As discussed earlier, the glass transition temperature of each component plays a role in the overall PSA Tg. The following is a list of each raw material's Tg in Degrees C.

Raw Material	Tg (Degrees C)
IBOA	+88
EOEOEA	-54
DPGDA	+104
Monomer A	-5
Urethane A	-14
Urethane B	-24
TR-A	-15
TR-B	+8
TR-C	+55

5.6 Tack Stability Study

	1	2	3	4
Previous Code	5.5.1.1	5.5.1.5	5.5.1.9	5.5.1.12
Urethane B/MA	14	14	14	14
Urethane A/MA	16	16	16	16
TR-A/MA	48	0	0	36
TR-C/MA	0	48	0	0
TR-B/MA	0	0	48	12
DPGDA	1	1	1	1

EOEOEA	14	14	14	14
LTM	4	4	4	4
PMP	2	2	2	2
Stab A	1	1	1	1
TOTAL	100	100	100	100
Loop Tack (lb/in2)				
Day 1	1.46	0.20	1.26	1.78
RT – Day 7	1.42	0.20	1.32	1.74
% Decrease	2.7	0	0	2.3
Heat Aged (60°C)				
Day 7	1.54	0.23	1.21	1.86
% Decrease	0	0	4.0	0

As a final step, a tack stability study was executed to ensure the stability of the starting point formula's properties. Additional samples examined contained TR-A/MA, TR-C/MA, and the TR-B/MA as the sole tackifying resins. No adhesive sample approached the tack instability exhibited in the IBOA containing samples from Test Series 1. The margin of error in this Loop Tack Test is relatively high as there is inevitable variability in adhesive film thickness, especially at a low coat weights. The starting point formula, Sample 4, did not exhibit any tack stability problems in this test and remains the adhesive of choice.

6. Test Methods

6.1 Application

All tested samples are applied to a 2 mil clear polyester film by a #5 applicator rod, which lays down a theoretical wet film thickness of 0.5 mil (12.8 μ).

6.2 Curing

An American Ultraviolet C12/300 UV lamp unit set at 300 WPI with a medium pressure Hg bulb is used for curing all tested samples. The belt speed was 15 FPM for all testing (each pass equals ~ 0.208 J/cm²) unless signified differently.

6.3 Peel Adhesion of Pressure Sensitive Tape

This test is carried out in accordance with the procedure outlined in Test Method A of PSTC-101 (Pressure Sensitive Tape Council: Test Methods For Pressure Sensitive Adhesive Tapes 13th Edition). Each test is a 180° peel test carried out using a Zwick Z010 tensile tester. No variation is made to this test method except that each sample is produced individually as there is no tape roll to sample from. No conditioning is done to the tape and testing is accomplished within 5 minutes of curing.

6.4 Shear Strength of Pressure Sensitive Tape

This test is carried out at room temperature according to the procedure outline in Test Method A of PSTC-107. Testing is done using a ChemInstruments HT-8 Shear Tester. No variation is made to this test method except that each sample is produced individually as there is no tape roll to sample from. No conditioning is done to the tape and testing is accomplished within 5 minutes of curing.

6.5 Loop Tack of Pressure Sensitive Tape

This test is carried out in accordance with Test Method A of PSTC-16. Testing is done using a Zwick Z010 tensile tester. No variation is made to this test method except that each sample is produced individually as there is no tape roll to sample from. No conditioning is done to the tape and testing is accomplished within 5 minutes of curing.

6.7 Viscosity

The viscosity is tested using a Bohlin CS-10 cone and plate type viscometer. A 4/40 cone is used and a temperature of 25+/-1°C maintained.

7 Suggestions For Formulation Alterations

From this study, there are certain trends that may assist a formulator in altering any PSA properties needed for their particular application. The basic properties are listed, with recommendations for improving upon them.

7.1 Peel Strength Increase

- Increase low Tg monomer with respect to high Tg monomer
- Increase tackifying co-resin (TR-C/MA and TR-B/MA)
- Increase Urethane A/MA
- Decrease Urethane B/MA
- Decrease high Tg monomer (IBOA**)

7.2 Shear Strength Increase

- Increase functionality (Urethane B/MA, multifunctional monomers)
- Increase high Tg monomer (IBOA**)
- Increase tackifying co-resins TR-C/MA and TR-B/MA
- Decrease tackifying co-resin TR-A/MA
- Decrease low Tg monomer (EOEOEA, Monomer A, 2-Ethyl Hexyl Acrylate)

7.3 Tack Increase

- Increase tackifying co-resin TR-A/MA
- Increase Urethane A/MA
- Decrease functionality
- Decrease system Tg
- Decrease tackifying co-resins TR-C/MA and TR-B/MA
- Decrease Urethane B/MA
- Decrease high Tg monomer (IBOA**)
- Add plasticizer (benzoates)

7.4 Steel Residual Decrease

- Increase Urethane B/MA
- Use EOEOEA instead of 2-Ethyl Hexyl Acrylate
- Increase IBOA**
- Increase tackifying co-resin TR-B/MA
- Decrease tackifying co-resin TR-A/MA
- Decrease 2-Ethyl Hexyl Acrylate
- Decrease Urethane A/MA
- Use EOEOEA instead of 2-Ethyl Hexyl Acrylate
- Use additives (organosilicones or silicas)

7.5 Viscosity Decrease

- Increase low molecular weight monomer (EOEOEA, IBOA**, Monomer A, 2-Ethyl Hexyl Acrylate)
- Heat product during application
- Decrease oligomer
- Decrease tackifying resin

7.6 Cure Speed Increase

- Increase photoinitiator
- Increase system functionality (oligomer, multi-functional monomers)
- Increase dosage of UV
- Increase # of UV bulbs
- Use fast curing photoinitiator (LTM)
- Decrease tackifying co-resin (especially TR-A/MA)
- Decrease low functional monomer
- Decrease methacrylate use

**Tack stability may be compromised with use of IBOA.

8 Conclusion

The pressure sensitive adhesive starting point formula serves as a basic reference tool for formulators. This formula can be readily modified to specific applications. The concept of this study is to not only offer the formulator a functional PSA formulation, but to provide an insight into the methods of altering certain properties that will enable a desired endpoint. It is evident that the delicate relationships between the oligomers, co-resins, different types of monomers and photoinitiators must be perfectly balanced in order to achieve a functional and optimized pressure sensitive adhesive.

9 References

1. Pressure Sensitive Adhesive Tapes. John Johnston, PSTC, 2000.