Formulating Goals of Energy Curable

Pressure Sensitive Adhesives

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1. Introduction

In a continuously expanding worldwide market for Pressure Sensitive Adhesives (PSA's), there are specific trends that appear to be occurring. Environmental pressures are causing industries to turn their collective backs upon solvent technologies of the past, and accept the solventless systems of the present and future. Converters initially began using hot-melt PSA systems, which offered no volatile components, accelerated process times, and a dramatic reduction in cost and required space needed to operate the tunnel ovens of the past.

However, there are limitations inherent to hot-melt PSA's, such as insufficient high temperature resistance and low chemical resistance, which are due to the thermoplastic nature of the hot-melt adhesives. To combat these issues, the molecules in a PSA need to have crosslinking tendencies, which bring about the necessity of Energy Curable adhesives. Ultraviolet (UV) radiation energy or Electron Beams are used to initiate the chemical process that results in the three-dimensional cross-linked network of monomers and oligomers. These Energy Curable adhesives can be either Hot-Melts or Room Temperature Liquids. RAHN USA has done extensive work studying the tendencies and developing Starting Point Formulations for the latter of these two adhesive types. The following paper delves into the basics of formulating these adhesives with a specific end property in the mind of the formulator.

2. Components

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 –25°C to +5°C, 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 as 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 –54°C (EOEOEA) to +88°C (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.

3. End Properties

The tack of a pressure sensitive adhesive describes the ability of that system to conform to and wet out upon a given substrate with only minimal external force being applied. An adhesive with high tack will wet out and "stick" efficiently to a respective substrate, while low tack will cause poor immediate adhesion. Each pressure sensitive adhesive is unique, and each takes a specific amount of time to completely wet out upon a substrate. Tack is measured using many different methods, although each can be looked at as a specific adhesion test, with well defined methods of application to a test surface, external pressure applied, precise geometry, and removal rate. RAHN uses the Loop Tack Test for this purpose; however, other laboratories successfully employ such techniques as the Rolling Ball Test, the Quick Stick Test, or the very subjective, yet widely practiced, Finger Appeal Test, which has far too many variables to accurately measure tack.

Adhesion of a pressure sensitive adhesive refers to the measure of amount of force required to remove the respective adhesive from a specific substrate. Three components are involved in this process. The first being the extension of the adhesive itself, the second part involves the deformation of the PSA backing substrate during the removal process, and the third and final step being the actual separation of the adhesive from the substrate surface. An Adhesion or Peel Test attempts to standardize the involved variables by utilizing the same backing, same adhesive film

thickness, same applied substrate, and same removal rate. The adhesive tapes are generally removed at either a 90º or 180º angle, with consistency in testing being of the utmost importance.

The Shear property of a pressure sensitive adhesive relates to the cohesive strength of the respective system. A shear force is applied to a controlled area of a pressure sensitive adhesive tape that has been applied to a standard substrate. Initially, a trapezoidal distortion occurs in the adhesive, until a point is reached at which the adhesive fails either cohesively or adhesively. This failure is reported differently depending upon the type of shear test being administered. A Static Shear Test involves a standard force being applied to the test sample, and the adhesive failure is reported as the time it takes for failure to occur. A Dynamic Shear Test involves a force being applied to the PSA tape at a specific rate of speed (typically 0.25mm/0.01" per minute). The PSA Dynamic Shear Value is reported as the peak force required to cause adhesive failure.

Another type of Shear Test involves the testing of a sample under heated conditions. A Shear Adhesion Failure Test (SAFT) is a Static Shear Test administered to a PSA sample under increasing thermal conditions, typically 1ºC or 2ºC per minute. The recorded SAFT value is the temperature at which the adhesive fails. Another standard thermal test involves a Static Shear Test done at a respective constant temperature, such as 80ºC. The Shear Value reported would be the time required for adhesive failure at the respective elevated temperature.

4. Factors Influencing Properties

The properties of pressure sensitive adhesives are influenced by certain factors. Each component in a formulation plays a very important role in determining the end properties of that respective adhesive. Even slight alterations in a formulation can drastically affect the adhesive's performance.

The tack property is affected mainly by the crosslink density or functionality of the adhesive. A lower crosslink density will generally result in a higher tack value. This will allow the adhesive greater flexibility and assist in its conforming to and wetting out upon substrates. Most radiation curable PSA's consist of inert and monofunctional products with very limited exceptions of di and trifunctional components. Another vital component of tack involves the Glass Transition Temperature (Tg) of the adhesive. As a general rule, the lower the overall Tg, the higher the tack value will be. A typical PSA will be have a Tg of between -25ºC and +5ºC, with the lower Tg products having increased tack performance. Another method of increasing the tack property is to add flexibilizers to the adhesive, such as benzoate plasticizers, which assist in the conformation of the adhesive.

The Adhesion property is a balance between tack and shear performance. Low Tg products that have good cohesive properties exhibit high peel performance. These are typified by large molecular weight urethane acrylates with mono or difunctionality and low Tg's between -10ºC and -30ºC. The larger molecular weight assists with the cohesion attributes of the adhesive. Low Tg monomers, like Isodecyl Acrylate, are also beneficial to enhanced peel properties rather than high Tg monomers, such as Isobornyl Acrylate. Finally, increasing the content of inert tackifying resins generally benefits the adhesion performance, by maximizing the elasticity of the elastomeric component.

The Shear performance of a PSA illustrates the cohesion of the system. The fundamental method of enhancing the shear property is to increase the crosslink density of the adhesive. This is accomplished by increasing the functionality of the system's components. In addition, an increase of

the overall Tg of the adhesive will assist in achieving this goal. By utilizing higher Tg tackifying resins, diluents or oligomers the shear values of a PSA will rise significantly. These trends also hold true for the heat resistance property of an adhesive, resulting in increased SAFT values.

5. Specific Formulations

5.1 - Product List

Oligomeric Component

A) URETHANE ACRYLATE 1
Monofunctional Aliphatic Urethane Acrylate Oligomer cut in 2-Ethyl Hexyl Acrylate (Tg = -16ºC)

B) URETHANE ACRYLATE 2
Difunctional Aliphatic Urethane Acrylate Oligomer cut in monofunctional Aliphatic Urethane Acrylate (Tg = -15ºC)

C) POLYESTER ACRYLATE 1

Trifunctional Polyester Acrylate Oligomer (Tg = +28ºC)

D) OLIGOAMINE 1
Difunctional Amine Acrylate (Tg = -45ºC)

Tackifying Component

E) TACKIFYING RESIN 1
Inert Modified Polyester Resin cut in Aliphatic Urethane Acrylate monomer (Tg = -18ºC)

F) TACKIFYING RESIN 2
Inert Modified Polyester Resin cut in monofunctional Aliphatic Urethane Acrylate monomer (Tg = +12ºC)

Diluent Component

G) EOEOEA
2-(2-Ethoxyethoxy) Ethyl Acrylate Monomer (Tg = -53ºC)

H) IDA
Isodecyl Acrylate Monomer (Tg = -60ºC)

Photoinitiator Component

I) PHOTOINITIATOR 1

Proprietary liquid photoinitiator blend with Absorption Peaks at 253 and 368 nm

5.2 – Formulations

A) High Tack UV Curable PSA

Product	%
URETHANE ACRYLATE 1	18.0
TACKIFYING RESIN 1	56.0
2-(2-Ethoxyethoxy) Ethyl Acrylate (EOEOEA)	22.0
PHOTOINITIATOR 1	4.0
TOTAL	**100.0**
Test Results	
Viscosity (cps)	1,500
Loop Tack (Lb/in2)	**3.49**
Peel Strength (Lb/in)	2.54
Static Shear Strength (Hr)	1.25
Static Shear Strength @ 80ºC (Hr)	0.0

The high tack of this formulation derives from the low functionality and Tg's of the products included. The URETHANE ACRYLATE 1 is monofunctional and when combined with 2-EHA it offers exceptional elastic properties which are ideal for PSA's. The TACKIFYING RESIN 1, an inert resin cut in a monofunctional aliphatic urethane acrylate monomer, is being utilized as a low Tg (-18ºC) Tackifying Resin. In addition, the diluent component is 2-(2-Ethoxyethoxy) Ethyl Acrylate, which is monofunctional and has a Tg of -53ºC. The low Tg and crosslinking combination of this PSA offers very high tack performance, but very limited cohesive characteristics, which is evident in the low Shear Value and negligible heat resistance.

B) High Peel UV Curable PSA Formulation

Product	%
URETHANE ACRYLATE 1	53.0
TACKIFYING RESIN 2	25.0
Isodecyl Acrylate (IDA)	14.0
OLIGOAMINE 1	4.0
PHOTOINITIATOR 1	4.0
TOTAL	**100.0**
Test Results	
Viscosity (cps)	9,925
Loop Tack (Lb/in2)	1.60
Peel Strength (Lb/in)	**6.86**
Static Shear Strength (Hr)	Indefinite
Static Shear Strength @ 80ºC (Hr)	24.0

To obtain higher peel properties, the URETHANE ACRYLATE 1 content is maximized for its elastic characteristics. This enables a large extension of the adhesive during removal which provides strong adhesion in a PSA. Inert TACKIFYING RESIN 2 is incorporated as the Tackifying Resin which exhibits a higher Tg, +12ºC, than the TACKIFYING RESIN 1. In addition, the difunctional OLIGOAMINE 1 is incorporated to add a degree of crosslinking. The combination of increased crosslinking, Tg, and elasticity of the adhesive brings about the improvement in Peel performance.

C) High Shear/SAFT UV Curable PSA Formulation

Product	%
URETHANE ACRYLATE 1	52.0
URETHANE ACRYLATE 2	22.0
POLYESTER ACRYLATE 1	4.0
Isodecyl Acrylate (IDA)	14.0
OLIGOAMINE 1	4.0
PHOTOINITIATOR 1	4.0
TOTAL	**100.0**
Test Results	
Viscosity (cps)	9,700
Loop Tack (Lb/in2)	1.20
Peel Strength (Lb/in)	4.19
Static Shear Strength (Hr)	**Indefinite**
Static Shear Strength @ 80ºC (Hr)	**Indefinite**

To maximize the Shear and temperature resistance performance of a PSA, the objective is to increase the crosslink density and overall Tg of the adhesive. This is accomplished by replacing the inert Tackifying Resin with a difunctional aliphatic URETHANE ACRYLATE 2, and adding 4% of a trifunctional POLYESTER ACRYLATE 1. The increased crosslinking and Tg negatively affects the Tack property, but greatly enhances the characteristics that are targeted. Using Isodecyl Acrylate as the diluent also works very well for higher temperature resistance than EOEOEA.

D) Well Balanced UV Curable PSA Formulation

Product	%
URETHANE ACRYLATE 1	40.0
URETHANE ACRYLATE 2	10.0
TACKIFYING RESIN 2	25.0
OLIGOAMINE 1	3.0
Isodecyl Acrylate (IDA)	18.0
PHOTOINITIATOR 1	4.0
TOTAL	**100.0**
Test Results	
Viscosity (cps)	5,900
Loop Tack (Lb/in2)	1.70
Peel Strength (Lb/in)	6.40
Static Shear Strength (Hr)	Indefinite
Static Shear Strength @ 80ºC (Hr)	Indefinite

This final formulation offers nicely balanced PSA performance, with exceptional adhesion and shear properties. This is done by reincorporating TACKIFYING RESIN 2 to allow the oligomeric component to maximize its elastic characteristics and to decrease the crosslink density, which act to increase the Peel and Tack properties, while still maintaining excellent Shear and heat resistance.

6) Test Methods

a. Application

All tested samples are applied to a 2 mil clear polyester film by a #20 applicator rod, which lays down a theoretical wet film thickness of 2 mil (51.3 μm).

b. 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 30 fpm (9.14 m/min) for all testing (each pass equals ~0.320 J/cm2) unless signified differently.

c. 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.

d. 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.

e. 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.

f. 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°C (+/- 1°C) maintained.

7) Conclusion

The pressure sensitive adhesive starting point formulas serve as a basic reference tool for formulators. These formulations can be readily modified to specific applications. The concept of this study is to not only offer the formulator functional PSA formulations, 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.

8) References

A. *Pressure Sensitive Adhesive Tapes. John Johnston, PSTC, 2000.*
B. *Pressure Sensitive Adhesive (PSA) Starting Point Formulation – Lab Report US02008. Des Roches/Murphy, RAHN USA Corp., 2003.*
C. *Test Methods For Pressure Sensitive Adhesive Tapes – 13th Edition. Pressure Sensitive Tape Council, 2000.*