

# Pressure Sensitive Adhesives with Reactive Components Added

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## Introduction

Pressure Sensitive Adhesives (PSAs) are used in Construction, Aerospace, Packaging, and many other applications. They are used because they are able to bond dissimilar surfaces with the ease of use not available with other types of adhesives. In addition to bonding properties, PSAs can display good UV resistance, transparency, and can be tailored to achieve a wide balance of adhesive and cohesive properties. However, a limitation in the utility of PSAs is the inherent strength of these viscoelastic materials as defined by the Dalquest Criteria. This limitation can be overcome by adding reactive components to a PSA matrix to increase performance for applications which require higher strength. The interaction between the reactive components and the PSA matrix as well as the ensuing properties will be the subject of this paper.

## Background

### Acrylic Pressure Sensitive Adhesive Technology

When considering an acrylic PSA design strategy, factors which influence performance include:

- Monomer Composition of the Acrylic Backbone
- Functionality on the Acrylic Backbone
- Polymer Molecular Weight and Branching
- Crosslinking
- Formulation

*Effect of monomer composition* - Choice of base monomer for an acrylic PSA will influence hydrophobicity, glass transition temperature (T<sub>g</sub>), and moisture and oxidative resistance of the polymer backbone. Some common low T<sub>g</sub> base monomers include 2-ethylhexyl acrylate, isooctyl acrylate and butyl acrylate. These “soft” base monomers are typically the most abundant monomers by weight in an acrylic PSA formulation and are responsible for the inherent tackiness of the PSA.

Modifying medium T<sub>g</sub> monomers include Methyl and Ethyl Acrylate, Vinyl Acetate, and Isobutyl Acrylate. High T<sub>g</sub> modifying monomers include Isobornyl Acrylate and t-Butyl Methacrylate.

*Functional Groups* - Carboxylic acid or hydroxyl functionality can be incorporated into the adhesive backbone during the polymerization by utilizing acrylic acid or hydroxyethyl acrylate monomers respectively. Acrylic acid is a high T<sub>g</sub> monomer that, in addition to increasing cohesive strength, provides a polar moiety for bonding to polar substrates like metals. Hydroxyethyl acrylate is also a polar monomer, but has a moderate T<sub>g</sub>. Both acrylic acid and hydroxyethyl acrylate provide sites for crosslinking. Additional functional groups that can be incorporated during polymerization include epoxy and anhydride.

*Polymer Molecular Weight and Branching* - Generally, increasing molecular weight improves cohesive strength while reducing peel adhesion. For a given composition, the molecular weight distribution of the acrylic polymer must be optimized to obtain maximum performance. Higher T<sub>g</sub> compositions require a relatively low molecular weight in order to maintain the ability to wet a surface. Softer compositions require higher molecular weight in order to display adequate cohesive strength.

A polymer with a high degree of branching will display higher adhesion while maintaining an equivalent cohesive strength compared with a polymer with a more linear backbone. This can be attributed to the additional chain ends, which aid in the ability to wet a surface.

*Crosslinking* - Crosslinking increases cohesive strength, temperature and solvent resistance. The improvement in strength comes at the expense of adhesion. The crosslinking can either be covalent or ionic (metal chelate). The former imparts better temperature resistance and the latter is convenient as crosslinking is accomplished upon solvent removal without the need for additional heat.

*Formulation* - Acrylic PSAs can be further formulated with tackifiers, fillers, and antioxidants to enhance properties. Tackifiers can increase adhesion especially to non-polar surfaces. This improved adhesion comes at the expense of cohesive strength. Fillers can provide increased thermal conductivity or flame resistance.

The above discussion outlined factors that influence PSA performance by influencing the adhesive's surface energy and polymer architecture. The next section of the paper will discuss PSA rheology, specifically bulk viscoelastic properties.

## Bulk Viscoelastic Properties of PSAs

It is known that the performance of Pressure Sensitive Adhesives (*e.g.* peel, tack, shear) depends strongly on bulk viscoelastic properties. The viscoelastic properties of an adhesive polymer can be studied by dynamic mechanical analysis (DMA) where a sinusoidal force (stress  $\sigma$ ) is applied to the adhesive material over a displacement (strain) which is typically in the linear viscoelastic region. From these stress-strain measurements, the modulus of the adhesive is obtained. As will be discussed below, the frequency of the applied stress and temperature of the sample are important considerations in predicting PSA performance. A suitable instrument to perform a DMA analysis would be a Rheometrics Mechanical Spectrometer (RMS-800).

The bulk viscoelastic properties can be defined as a combination of two moduli: the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ). Under an applied stress, the storage modulus measures the stored energy, representing the elastic recoverable portion, and the loss modulus measures the energy dissipated as heat, representing the viscous portion.

It has been established that measuring  $G'$  and  $G''$  at  $10^{-2}$  and  $10^2$  radians/sec at room temperature provides the appropriate information to predict peel, tack, and shear performance.<sup>1</sup> This frequency span can be used to construct a viscoelastic window to compare different PSAs. The window is constructed by plotting four points on a log-log crossplot of  $G'$  and  $G''$ .<sup>2</sup> These four points are: 1)  $G'$  at  $10^{-2}$  rad/sec and  $G''$  at  $10^{-2}$  rad/sec, 2)  $G'$  at  $10^2$  rad/sec and  $G''$  at  $10^{-2}$  rad/sec, 3)  $G'$  at  $10^{-2}$  rad/sec and  $G''$  at  $10^2$  rad/sec, 4)  $G'$  at  $10^2$  rad/sec and  $G''$  at  $10^2$  rad/sec. A viscoelastic window is shown in Figure 1.

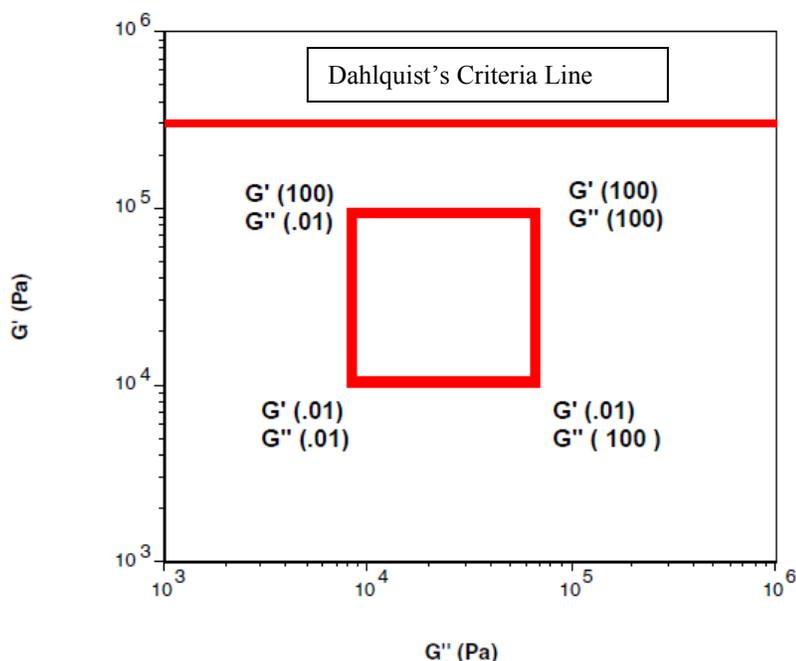


Figure 1: Construction of a Viscoelastic Window

The placement and size of the viscoelastic window on the cross-plot predicts PSA performance as elegantly described in reference 1. For the current discussion, the important feature is that the viscoelastic window must be below the Dahlquist Line (Figure 1) in order to function as a PSA at room temperature. This requirement in the magnitude of the storage and loss moduli, which is low enough for the adhesive to form a bond, is the basic limitation of the strength of a pressure sensitive material. However, if a PSA is applied in state where its modulus is below the Dahlquist line and transforms to a higher modulus after application, this strength limitation is overcome.

## PSAs With Reactive Components added

Acrylic polymers with reactive oligomers have been discussed previously.<sup>3</sup> These materials display enhanced properties and will be compared to the new materials under discussion. The Acrylate-Oligomer PSA displays very high strength but still obeys the Dahlquist Criteria. An example of an oligomer containing PSA is shown below:

### Acrylic Polymer With Reactive Oligomer Example

55% Acrylic Base Polymer

25% Terpene phenolic Tackifier (Softening Point 110-120°C)

20% Reactive Oligomer (Silyl-Terminated Polyether)

The above example was modified with a reactive epoxy material to increase strength. The reactive epoxy is latent until cured via a photo catalyst. Upon activation of the catalyst with ultraviolet light, the PSA exhibits a degree of “open time”, which allows the adhesive to be applied while its modulus is below the Dahlquist Line. Within 24 hours, full strength is attained. An example of an Epoxy containing PSA is shown below. Note the modifications from the above example:

### Acrylic Polymer With Reactive Epoxy Example

Acrylic Base Polymer

Terpene phenolic Tackifier (Softening Point 110-120°C)

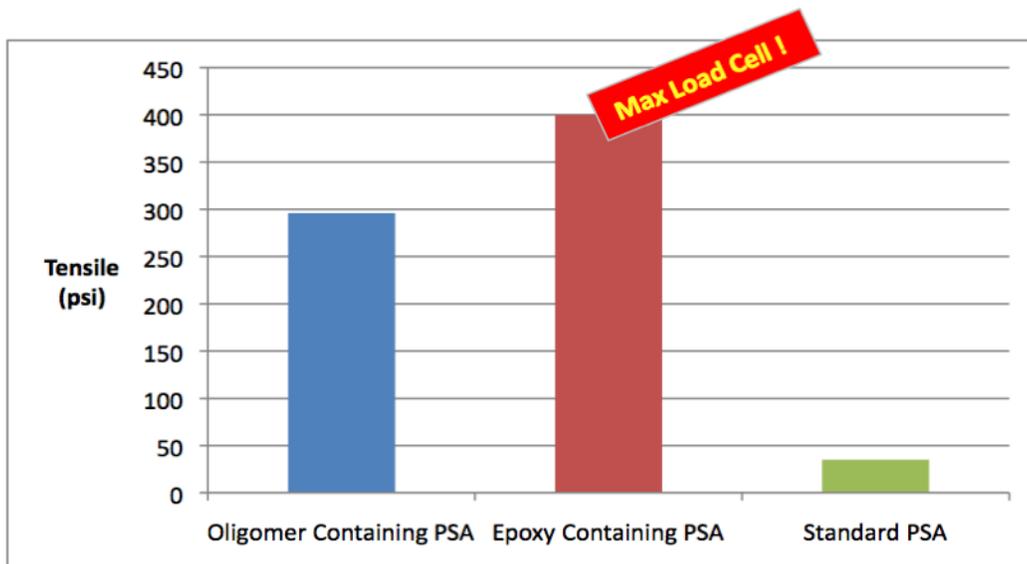
Reactive Oligomer (Silyl-Terminated Polyurethane-Modification)

Reactive Epoxy Component (Modification)

Epoxy-Silane Coupling Agent (Modification)

Photo Catalyst (Modification)

The above examples will be compared to a standard acrylic PSA in a tensile test to determine relative strength:



As can be seen, the PSA with the reactive oligomer displays enhanced tensile strength relative to a standard PSA (300 lbs. versus 35 lbs.). The adhesive with the reactive epoxy component provides the greatest strength, which reached the maximum tensile strength of the load cell of the tensile tester (>400 lbs). A PSA can be formulated to bond in a normal fashion after UV exposure and, depending on epoxy loading, attain strengths not associated with PSAs.

## **FUTURE WORK**

A large degree of formulation latitude exists between the acrylic polymer backbone composition, oligomer choice, and reactive epoxy loading. In addition to high tensile properties, enhanced resistance to various solvents and oils, current work is being directed towards resistance to aviation fluids for aerospace applications. This is being accomplished by the use of specialty designed oligomers designed to be resistant to these fluids and combining them with acrylic PSA polymers.

## **CONCLUSIONS**

It has been demonstrated that the ease of bonding of a PSA can be coupled with the strength associated with higher strength adhesives. This is accomplished by allowing the PSA to bond in a relatively soft state and cure after application.

## **APPENDIX**

### Tensile Testing

-The PSAs were applied to a 1 inch X 6 inch X 0.130 inch aluminum sheet as 2 mil transfer films. A second sheet of aluminum of the same dimensions was laminated to the PSA containing sheet in a manner to create a 1 inch by 1 inch overlap. Note: The epoxy-containing sample was exposed to UV light before lamination.

-The laminates were tested on an MTS tensile tester 24 hours after lamination.

-Results reported in pounds/square inch.

## **REFERENCES**

1. E.P Chang, J. Adhesion, **34**, 189, (1991)
2. Curable Optically Clear Pressure Sensitive Adhesives, E.P. Chang and Daniel Holguin, TECH XXVI, May 2003.
3. Acrylate-Polyether Based Pressure Sensitive Adhesives , Mike Zajackowski, TECH XXX, May 2007.

## **ACKNOWLEDGEMENTS**

I would like to thank the Avery Dennison Adhesive Center of Excellence Research Team, especially Kyle Heimbach for the synthetic work and the development of an aviation fluid resistant PSA. Also, a special thanks to E.P. Chang for his inspiring work.