Polyurethane Dispersion Based Pressure Sensitive Adhesives

P. Cranley, E. Cork, C. Esneault, A. Chavez, B. Erdem
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ABSTRACT

The first patented pressures sensitive adhesives (PSA) were derived from natural rubber for bandages back in 1850. Recent developments in the use of polyurethane dispersions (PUDs) to replace natural rubber in non-allergenic examination gloves have sparked interest in their evaluation in PSAs [1].

New continuous PU dispersion technology has allowed the creation of novel PUDs based upon polyether polyols and methylenediphenyl-diisocyanate (MDI). These PU dispersions are solvent free, high solids (50-60 wt %), and have submicron sized particles and excellent stability. The PUDs from this process have been found useful for designing PSAs with properties ranging from removable to high shear strength.

In this presentation, the versatility of these new dispersions formulated with waterborne tackifiers and other PSA additives will be demonstrated. Physical property and rheological data from the evaluation of a variety of PUD formulations will be discussed with focus on the material science of the design and formulation of pressure sensitive adhesives.

INTRODUCTION

We are studying the use of waterborne polyurethane dispersions (PUDs) for use in adhesive applications. These dispersions are solvent free and based upon high MW polypropyleneoxide polyols and methylenediphenyl-diisocyanate (MDI) so they exhibit low temperature elastomeric properties.

This paper will outline how the properties of adhesive films based on these dispersions are modified by standard PSA additives.

HISTORY

Pressure Sensitive Adhesives date back in the US patent literature to the 1850’s, where they were used as self-sticking bandages [2]. From their earliest days they were based upon natural rubber; since then, almost every elastomer and plastomer has been evaluated in PSAs. Minnesota Mining and Manufacturing, now 3M, developed tape in the mid 1920’s and since then a wide variety of PSA products are now on the market. New applications, such as postage stamps, crystal clear labels and envelope closures, are being developed each year.

Pressure Sensitive Adhesives can be applied in a variety of forms, for example solvent, water, hot melt and calandered. New applications for the outstanding properties of solvent based PSAs are still appearing. However, long term trends in the industry have been forcing the reduction of solvent-based PSAs in favor of hot melt and waterborne PSAs to eliminate Volatile Organic Compound (VOC) emissions and to improve economics and speed application.

TESTING

The three most common tests of PSA performance are Tack, Peel and Shear. There are a number of different techniques for each outlined by ASTM or the Pressure Sensitive Tape Council (PSTC).
Tack can be measured by rolling a steel ball across the surface of the adhesive until it comes to a stop. Alternatively, the Loop Tack procedure uses an Instron tensile tester to press a loop of tape lightly onto a steel substrate and then slowly pull it away, measuring the force. Finally, the Polyken Probe procedure presses the flat end of a small stainless steel cylinder against the PSA surface and slowly removes it at 90 degrees to the surface, measuring the force.

Peel is also measured with an Instron tester, pulling at 90 or 180 degrees angle to the substrate.

Shear tests are very slow tests, which reflect the creep tendency of the PSA over long time periods. In a shear test, the tape is adhered to a steel coupon and a 1-2 kg weight is hung on the tape thus applying a force parallel to the substrate. The time it takes for failure is a reflection of the shear strength. If the temperature is ramped slowly to accelerate the test, a Shear Adhesion Failure Temperature (SAFT) can be measured.

RHEOLOGY

Polymer rheology is the most important property of a pressure sensitive adhesive [3]. Flow behavior allows the adhesive to wet any substrate under slight pressure and determines how much resistance to peel or shear force it possesses upon de-bonding.

A PSA is typically permanently and aggressively tacky and will form a measurable bond under hand pressure alone.

Figure 1. Understanding PSA Properties via DMTA

It has sufficient cohesive strength so it will not fail cohesively, but will always fail adhesively or by substrate failure and it will resist creep under a shear load. PSA adhesives do not need to heed the “like dissolves like” rule, their viscoelasticity, combined with weak Van der Waals forces are sufficient to overcome differences in polarity between adhesive and substrate.

Material Scientists have defined the rheological profile of a PSA for various applications. The G’ or modulus, at room temperature must be below $10^6$ Dynes/cm$^2$ [4]. Room temperature modulus correlates negatively with tack. The Tg generally needs to be between -10 and +10 C in order to have significant peel strength at room temperature, although lower temperature applications and removeable PSAs require lower Tgs.

Figure 1 illustrates a typical rheological/temperature scan of a PSA. Using time-temperature superpositioning, the same scan can be obtained by measuring storage modulus vs. shear frequency. The peel strength test (12 inches/min, 25C) is fast enough that the shear on the polymer (~435 rad./sec.) causes the polymer to act like it is at a cooler temperature, resulting in a larger modulus and peel strength. [3]. The faster the modulus rises as temperature is reduced below 25C, the larger the resulting peel strength up until brittle failure limits. Tack measurements, on the other hand, tend to correlate negatively with the modulus at 25C. Finally, shear testing, being a very low frequency creep test, tends to correlate positively with modulus at 80-90C.

One can immediately see the tradeoffs inherent in PSA formulation. To get high tack and high shear requires a very flat rubbery plateau in the region between 25-90C. High temperature resistance also requires a modulus that remains high at the highest possible temperature. This is difficult for hot melt applied PSAs, but much easier for dispersion based PSAs

FORMULATION

The formulator’s approach to a PSA is to blend elastomers, tackifiers, plasticizers and other additives to achieve the properties needed. The elastomer contributes cohesive strength, a flat rubbery plateau and a low Tg. The tackifier (a solid, glassy, low MW plasticizer soluble in the elastomer) increases the Tg of the elastomer/tackifier blend while simultaneously decreasing room temperature modulus and thus increasing tack. Finally, a low freezing point liquid plasticizer allows lowering modulus.
independently of Tg. Thus a formulator can move around in this space using three basic components to target all the PSA applications.

**Tackifiers**

The effect of a tackifier is to increase the resulting Tg of the soluble blend of the elastomer and the resin, and to reduce the modulus at room temperature to improve tack.

It may however cause the modulus at higher temperatures to drop excessively, reducing shear strength. For label applications, high tack is required but shear strength is not as important since labels only have to support themselves, a very small shear load. A tape, on the other hand, must have a high shear resistance and high elevated temperature resistance to hold boxes together under high shear forces, long storage times and sometimes elevated storage temperatures found in warehouses.

Figure 2 describes the rheological behavior of a Dow experimental polyurethane dispersion (PUD). The modulus at every temperature is much higher than commercial acrylic PSA latex, reflecting the internal hydrogen bonding, and great cohesive strength of polyurethane polymers. In order to get the PUD polymer to be tacky at ambient temperatures, we need to lower its modulus. Over the rest of this paper we will investigate four ways to achieve this: 1. Tackifiers, 2. Plasticizers 3. PSA blending; and 4. PUD polymer modification.

In Figure 3, the effect of adding commercial rosin ester tackifiers to the Dow Experimental PUD is illustrated. Aquatac* 5527 is a 27 degree softening point tackifier which has the effect of lowering the modulus at all temperatures because its Tg (-30 C Tg by DSC) is very similar to the Tg of the PUD. On the other hand, Aquatac 6080A, a tackifier with an 80 C softening point (41 C Tg by DSC), also reduces room temperature modulus however another Tg transition is now seen above room temperature. This suggests it is incompatible with the PUD such that two Tgs result rather than a mixed Tg somewhere in between that of the PUD and that of the Tackifier. At 60 % levels of Aquatac 5527, the modulus at 25C is below 10^6 and indeed this formulation has a measurable tack. The acrylic control is shown for reference. * Aquatac is a tradename of Arizona Chemical.

**Plasticizers**

Plasticization of the Dow Experimental PUD can be accomplished by low molecular weight glycol plasticizers such as MPEG 350. These materials lower modulus at all temperatures, however these glycol materials may be too volatile or water-soluble to remain permanently some PSA applications. These materials can however be used in small amounts as coalescing agents to accelerate film formation so as to speed the development of final polymer properties. The effect of a more permanent benzoate ester plasticizer, Benzoflex** 9-88 is shown in Figure 4 formulated with the Dow Experimental PUD.

![Figure 2. DMTA of Dow PUD vs. Acrylic Emulsion PSA.](image2)

![Figure 3. Effect of Rosin Ester Tackifiers on PUD.](image3)
Figure 4. Benzoate Ester Plasticized PUD

The modulus is lowered at all temperatures above the plasticizer Tg and the flatness of the rubbery plateau is improved at this level of addition. This plasticizer level alone is not sufficient to achieve tack at ambient temperatures. By blending both tackifiers and plasticizers, we can lower the modulus to achieve tack as will be shown later.

**Benzoflex is a tradename of Velsicol Chemical

Latex Blending

Another formulation option is to add other PSA latex to manipulate the rheology appropriately. Figure 5 illustrates the effect of adding various amounts of UCAR*** 9569 to the Dow Experimental PUD. One effect seen is the increase at low levels of PUD addition in high temperature modulus and a little more flattening of the modulus vs. temperature curve. This may result in improved peel, temperature, shear resistance and SAFT if the formulator can compensate for the resultant loss of tack by other formulating means.

Four PSA formulations are shown in Table 1, using the principles discussed so far [5]. In addition to plasticizers and tackifiers, surface active additives and thickeners are added to get proper wetting of the mylar film. As shown in the table, a wide range of PSA properties can be achieved by traditional PSA formulations at the hands of skilled formulators. Thus, the study of rheology is a valuable tool to help the formulator achieve the range of PSA properties needed.

*** UCAR is a tradename of the Dow Chemical Co.

Figure 5. Effect of Acrylic Latex on PUD

Polymer Modification

Finally, the chemistry of the polyurethane dispersion can also be manipulated in many ways to achieve a range of PSA properties. Commercial PUD cross-linkers, such as emulsifiable isocyanates can be added to the emulsion by the formulator to increase modulus, and heat resistance of the resultant PSA. In addition, by changing the chain extender and the polyol composition of the PUD, the rheological performance of the PUD can be manipulated as well. In this way a variety of PSA properties and applications can be achieved using polyurethane chemistry. By combining both chemistry and formulation science, a PUD can be designed for any PSA market application.

EXPERIMENTAL MATERIALS

Table 2 lists the experimental materials used in this study.

SUMMARY

In summary, the modulus of this Dow Experimental PU dispersion is too high to be inherently pressure sensitive in an unformulated state. Various traditional PSA additives are useful in reducing this modulus. Plasticizers are more efficient in modulus reduction than are tackifiers. Both the compatibility and softening point of the tackifier must be taken into account to achieve success.
Table 1. PUD Based PSA Formulation [5]

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tr>
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<td>32</td>
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<td>35</td>
<td>38</td>
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<tr>
<td>Snowtack 765A (Tackifier)</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>62</td>
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<td>Aquatac 6025 (Tackifier)</td>
<td>3</td>
<td>5</td>
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<td>Surfynol 465 (Surfactant)</td>
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<tr>
<td>Surfynol SE-F (Surfactant)</td>
<td>--</td>
<td>--</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Citroflex 2 (Plasticizer)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3</td>
</tr>
<tr>
<td>Acrysol 6038 (Thickener)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>Peel (pli)</td>
<td>2.47 Z,C</td>
<td>2.67 Z,C</td>
<td>1.48 AF</td>
<td>3.2 AF</td>
</tr>
<tr>
<td>Tack (grams)</td>
<td>91</td>
<td>44</td>
<td>396</td>
<td>234</td>
</tr>
<tr>
<td>Shear (hours)</td>
<td>&gt;120.6</td>
<td>102.9 C</td>
<td>&gt;102.8</td>
<td>173</td>
</tr>
</tbody>
</table>

AF=Adhesive Failure, C=Cohesive Failure, z=Zippiness or Slip-Stick

Table 2. Experimental Materials used in Study

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<tr>
<th>Name</th>
<th>Type</th>
<th>Class</th>
<th>Supplier</th>
<th>Tg (in C)</th>
<th>Soft. Pt. (in C)</th>
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<td>PU</td>
<td>Dow</td>
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<tr>
<td>Aquatac 5527</td>
<td>Tackifier</td>
<td>Rosin Ester</td>
<td>Arizona Chemical</td>
<td>-30</td>
<td>27</td>
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<tr>
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<td>Tackifier</td>
<td>Rosin Ester</td>
<td>Arizona Chemical</td>
<td>34</td>
<td>80</td>
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<tr>
<td>Aquatac 6025</td>
<td>Tackifier</td>
<td>Rosin Ester</td>
<td>Arizona Chemical</td>
<td>N/A</td>
<td>25</td>
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<tr>
<td>Piccotex LC-55WK</td>
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<td>Hydrogenated Aromatic Resin</td>
<td>Eastman Chemical</td>
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<td>MPEG 350</td>
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<td>Polyglycol</td>
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<td>Surfynol 465</td>
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<td>Nonionic</td>
<td>Air Products</td>
<td>N/A</td>
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<tr>
<td>Surfynol SE-F</td>
<td>Surfactant</td>
<td>Nonionic</td>
<td>Air Products</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Benzoflex 9-88</td>
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<td>Velsicol Chemical</td>
<td>-40</td>
<td>N/A</td>
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<td>Dow</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
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<td>Tackifier</td>
<td>Rosin Acid</td>
<td>Nobel</td>
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</table>

The combination of tackifiers and plasticizers are effective in achieving the necessary modulus reduction. Also, the blending of lower modulus acrylic dispersions is useful to achieve modulus modification.

The modification of the polymer backbone using traditional polyurethane chemistry or external cross-linkers can also be used to achieve specific PSA properties. Based on these studies, it is our belief that polyurethane dispersions will soon find a more significant place among the many waterborne polymers being used in the PSA industry.

REFERENCES
**BIOGRAPHIES**

**Paul E. Cranley, Development Leader**

Paul received a B.S. in Chemistry from Xavier University in 1971 and a MS in Chemistry and a MBA from the University of Kentucky in 1974. He started with Dow in 1974 and spent the last 28 years in a variety of R&D roles in the development of new products for the Specialty Chemical, Epoxy and Polyurethane Businesses in Michigan, Connecticut and Texas. He is currently a Development Leader responsible for exploring new business and new product opportunities targeted for Polyurethane Adhesive, Sealant, Coatings and Elastomer Markets.

**Elizabeth Cork, Research Chemist**

Elizabeth received a B.S. in Chemistry from Purdue University in 2001. She began her career with Dow R&D in June 2001 as a participant in the Research Assignments Program (RAP). In her first year at Dow, she has worked with the Analytical Separations, Custom and Fine Chemicals, Polyurethanes, and Fabricated Products R&D Laboratories.

**Calvin Esneault, Development Leader**

Calvin Esneault obtained a B.S. from Nicholls State University in 1969 and a M.S. in Physical Chemistry from the University of New Orleans in 1976. He was a pilot in the U.S. Air Force. In 1976 he joined Dow Chemical has held research assignments in product development for addition, condensation, and block copolymers. He is a member of Dow Corporate Research in Materials Science and is an inventor on 10 U.S. patents.

**Alejandra Chavez, Development Engineer**

Alejandra received a B.S. in Chemical Engineering from the University of New Mexico in 1999. She started at Dow in the Research Assignments Program, where she rotated throughout and gained a broad understanding of various Dow functions and technologies. She is now working in Polyurethanes R&D and is responsible for servicing accounts and development needs of Coatings, Adhesive, Sealant, and Elastomer customers.

**Bedri Erdem, Research Specialist**

Bedri received a B.S. in Chemistry and M.S. in Physical (Polymer) Chemistry from Karadeniz Technical University, Trabzon, Turkey. He received his Ph.D in Polymer Science and Engineering from Emulsion Polymers Institute of Lehigh University in 2000. He started to his industrial career at Dow Polyurethanes R&D, working in various new business development programs including aqueous polyurethane dispersions. His area of expertise also includes various aspect of colloidal science.
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