NEW OLIGOMERS DESIGNED TO ENHANCE FORMULATING UV/EB PRESSURE SENSITIVE ADHESIVES

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Introduction

Pressure sensitive adhesives (PSAs) are found in hundreds of products that consumers use every day. Masking tape, packaging tape, note pads, and labels are just a few of today’s most popular PSA applications.

Traditionally, chemists have used solvent borne formulations, which are based on modified rubber chemistry, to develop high-performance PSAs. But because of the increasing number of environmental regulations restricting or eliminating the use of solvents, chemists are beginning to turn to low-VOC, fast-curing ultraviolet (UV) and electron beam (EB) systems.

The Economics of UV/EB Technology

Economic concerns are the main driving force behind the adoption of UV/EB technology. As covered by Elias\textsuperscript{1}, the economic factor can be broken into three main areas:

\begin{itemize}
  \item \textit{Increased Sales}: With a UV/EB system, faster production speeds are achieved – often leading to an increase in sales.
  \item \textit{Reduced Production Costs}: Costs usually go down due to the resulting increase in productivity, as well as the decrease in energy requirements, reduction in waste and down time, easy clean-up, and smaller amount of factory space required (because no drying ovens are needed).
  \item \textit{Simpler Environmental Compliance}: UV/EB technology requires minimal or no state and federal clean-air operating permits, no new compliance assurance monitoring equipment, and reduced record keeping requirements.
\end{itemize}

In Table 1 the market expectations are shown for various types of pressure sensitive adhesives. Removable adhesives are used in applications where the PSA will be removed from the surface. Sheet stock includes labels of various sorts. And, general-purpose industrial adhesives are higher-performance adhesives.

<table>
<thead>
<tr>
<th>Peel (ASTM D903-95)</th>
<th>Removable</th>
<th>Sheet Stock</th>
<th>GP Industrial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel – 30 min, pli</td>
<td>0.5</td>
<td>2.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Peel – 24 hours, pli</td>
<td>1.2</td>
<td>3.0</td>
<td>5.0</td>
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<tr>
<td>Peel – 1 wk @ 70°C, pli</td>
<td>1.5</td>
<td>3.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Peel – 3 wk @ 70°C, pli</td>
<td>1.75</td>
<td>3.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Tack, g (ASTM D2979)</td>
<td>225</td>
<td>500</td>
<td>800</td>
</tr>
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</table>
The Development of New Raw Materials

For more than fourteen years, the work done in UV/EB-cure PSAs has shown the types of structures for both the oligomers and monomers that will produce an acceptable UV/EB curable PSA\(^2\text{-}^9\). Initial work yielded the best monomers to achieve low odor and low viscosity UV/EB curable PSA's\(^2\). Optimizing the tackifier and oligomers T\(_g\) to yield the best UV/EB-cured PSA performance\(^3\), followed by optimizing the oligomer structure\(^4\text{-}^9\), lead chemists in a positive direction for UV/EB-curable PSA development. These studies have shown that excellent 180° peel strengths can be obtained with acrylate terminated oligomers with molecular weights ranging from one thousand to six thousand and glass transition temperatures ranging from minus seventy four degrees centigrade up to thirteen degrees centigrade.

One of the greatest difficulties of this work was dissolving the hydrocarbon resins into the monomers and yielding a stable mixture. After fully studying the processing conditions, stabilizers, and antioxidants available, a fully stable process and new products were developed.

Sartomer chemists applied this technology and designed new oligomers specifically for pressure sensitive adhesives. The new oligomers eliminate the need for the addition of solid tackifying resins. This is beneficial because the addition of tackifier into a monomer system is not only time-consuming, but also requires a heated resin vessel, which smaller operations usually do not have. Because of this, the new oligomers will make it easier for the small player to enter the marketplace by mixing simple blends to yield an end PSA that meets their needs. The new oligomers also make the development of smaller niche markets possible. Finally, they enable formulators to develop UV/EB-cured PSAs for traditional markets as well (i.e., removable adhesives, tapes, labels, etc.).

The following study investigates new low-viscosity tackifying oligomers designed to simplify the formulation of UV/EB-curable pressure sensitive adhesives. Viscosity, 180° peel adhesion, tack, and SAFT were all run to help better understand performance of the oligomers and the formulated pressure sensitive adhesives.

Discussion – New Tackifying Oligomers

New tackifying oligomers were designed with varying monomers to obtain best possible performance. Each of these tackifying oligomers was then formulated into a PSA. The photoinitiator used in this study was Sarcure\textsuperscript{®} 1135, which is a liquid blend of three photoinitiators: 2,4,6-trimethyl benzoyldiphenylphosphine oxide, oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl] propanone], and methylbenzophenone derivates. Table 2 shows the formulations used in this study.

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN3210</td>
<td>Aromatic Urethane Acrylate</td>
<td>19.0</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>CN3003</td>
<td>Tackifying oligomer w/ EO NPA</td>
<td>74.0</td>
<td>79.0</td>
<td>79.0</td>
</tr>
<tr>
<td>PRO6858</td>
<td>Tackifying oligomer w/ IBA</td>
<td>79.0</td>
<td>79.0</td>
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<tr>
<td>PRO6859</td>
<td>Tackifying oligomer w/ Alk NPA</td>
<td>79.0</td>
<td>79.0</td>
<td>79.0</td>
</tr>
<tr>
<td>SR504</td>
<td>Ethoxylated Nonyl Phenol Acrylate</td>
<td>5.0</td>
<td>5.0</td>
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<tr>
<td>Sarcure 1135</td>
<td>Photoinitiator blend</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Viscosity</td>
<td>cps @ 77°F</td>
<td>800</td>
<td>435</td>
<td>445</td>
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</table>
The pressure sensitive adhesive formulations were cast using both a #10 and #40 wire wound rod applying directly onto the surface 2.0-mil Mylar film. The cured thicknesses were measured at 0.4 +/- 0.1 mils for the #10 rod and 1.3 +/- 0.1 mils for the #40 rod. The adhesive was cured by ultraviolet light using a 300-watts/inch mercury vapor lamp at 700 mJ/cm². This was tested using an IL 390B Light Bug radiometer. Then the samples were covered with Rhodia release liner.

The sheets were allowed to dwell for 48 hours at 72°F and 50 percent relative humidity before any testing was done on them. The samples were cut into one-inch strips at the time of testing.

The peel adhesion was run as per ASTM D903-98 at an angle of 180° and a speed of 12 inches per minute. The samples were applied to the standard micro-finish stainless steel panels using a 4½-pound PSTC roller. The samples were allowed to dwell for 15 minutes for the initial samples. Four to six samples per adhesive per condition were tested and averaged.

The tack was run as per ASTM D2979-95 using a ChemInstruments Probe Tack Tester, Model PT-500. The surface of the probe comes into contact with the adhesive, dwells for one second and is pulled away. Five samples per adhesive were run and averaged.

The shear adhesion failure temperature (SAFT) was run as per ASTM D4498-95. One square inch of adhesive contact was applied to the standard stainless steel panel and was then placed in an oven starting at 25°C. A 500-gram weight was then applied. The temperature was raised by 5°C every ten minutes. The point at which the sample fails was recorded. The limiting temperature on the oven was 225°C. The Mylar film will fail at 245-250°C. Three samples per adhesive were run and averaged.

### Tackifying Oligomer Comparison

All the above formulations (A, B, and C) contain an aromatic urethane acrylate to give the PSA better peel adhesion and tack. This oligomer is high in molecular weight.

![Figure 1: Tackifier Oligomer Comparison](image)

We tested these three formulations for 180° peel adhesion. These results are shown in Figure 1. The 180° peel adhesion was also run with industrial grade Scotch Tape, #02-030 that has an adhesive
thickness of 1.5 mils. The minimum requirements for a removable PSA and sheet stock PSA are shown on the graph. All the formulations meet the 180° peel adhesion requirement for the removable PSA, but only Formula B and C meet the requirement for sheet stock PSAs.

As you can see from Figure 1 results, the Isobornyl acrylate based tackifying oligomer (Formula B) and the Alkoxylated nonyl phenol acrylate based tackifying oligomer (Formula C) yielded better results than the standard Ethoxylated nonyl phenol acrylate tackifying oligomer (CN3003 in Formula A). Previous studies have shown that Isobornyl acrylate improves peel adhesion in radiation curable PSAs, but it is normally avoided due to its higher odor. Formula C contained an Alkoxylated nonyl phenol acrylate that appears to also improve peel adhesion. Both Formula B and C perform similar to the industrial grade Scotch Tape, #02-030 for the 180° peel adhesion.

Next the tack was tested on the same formulated PSAs and the Scotch Tape. These results are shown in Figure 2. Again the minimum requirement for the tack is shown for a removable PSA, sheet stock PSA and industrial grade PSA. Formula A and a thicker applied Formula B meet the requirements for a removable PSA. The thicker applied Formula B actually qualifies for sheet stock PSA.

As you can see in Figure 2, the Isobornyl acrylate based tackifying oligomer in Formula B yielded the best tack results at a thickness of 1.3 mils. The Alkoxylated nonyl phenol acrylate found in Formula C yielded PSAs with minimal tack. None of these formulated PSAs decreased their tack with heat aging.

The Shear Adhesion Failure Temperature (SAFT) was also run on these three formulations. No significant information was gained from the testing. The trend of an increase in adhesive thickness to increase the SAFT was seen in all three formulations. But for the most part, the SAFT was less that 125°C for all three of these formulations.

**Discussion – Activated Urethane Acrylate Oligomers**

A variety of urethane acrylate oligomers were made more reactive for thick cure PSA applications. These were evaluated in the same manner as above, but using the formulations shown in Table 3. These three formulas will be compared to Formula A above.
<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRO6863</td>
<td>Aromatic Urethane Polyether Acrylate</td>
<td>19.0</td>
<td></td>
<td></td>
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<tr>
<td>PRO6864</td>
<td>Aliphatic Urethane Polyether Acrylate</td>
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<tr>
<td>Viscosity</td>
<td>cps @ 77°F</td>
<td>1000</td>
<td>425</td>
<td>410</td>
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</tbody>
</table>

The urethane oligomer in Formula A (CN3210) is a high molecular weight aromatic polyester urethane acrylate. The molecular weights of the urethane acrylates are similar in formula A, D and E. The main difference when comparing Formula A to D is that the urethane backbone in CN3210 (Formula A) is made using polyester polyol whereas in PRO6863, the urethane is made using a polyether polyol. The urethane in Formula F (PRO6865) has a similar backbone (aliphatic urethane polyether based) as formula E (PRO6864), but has half the molecular weight of the urethane in Formula E due to a shorter chain length of the polyether polyol. So this will show a direct comparison of molecular weight.

### Oligomer Structure Comparison

When comparing Formula A to Formula D in Figure 3 below, the only difference in the backbone of the aromatic urethane oligomer is the polyester (CN3210 – Formula A) compared to the polyether (PRO6863 – Formula D). It appears that this particular polyether improves the 180° peel adhesion of the formulated PSA. Again the 180° peel adhesion requirements for a removable PSA and sheet stock PSA are shown on the graph. All formulas meet the requirements for removable PSA, except for Formula F (lower MW oligomer). Formula D actually qualifies for sheet stock PSA.

When comparing Formula D (aromatic urethane) and Formula E (aliphatic urethane) all would be similar except for the isocyanate. The aromatic yielded higher 180° peel adhesion when compared to the aliphatic urethane.
The only difference in Formula E and F is the molecular weight of the polyether polyol used to make the aliphatic urethane acrylate oligomer. The oligomer in Formula F is roughly half the molecular weight of the oligomer in Formula E. We see that by reducing the molecular weight of the polyether polyol (Formula F), the 180° peel adhesion is greatly affected. None of these formulated PSAs yielded a high 180° peel adhesion when compared to industrial grade Scotch Tape, #02-030.

Figure 4 shows the results of the tack for the same set of formulated PSAs. Again when comparing Formula A to Formula D, the difference in the backbone of the aromatic urethane oligomer is the polyester (A) compared to the polyether (D). Now the higher tack results are seen in Formula A, the aromatic urethane polyester acrylate (CN3210).

The comparison shown in Figure 4 between Formula D (aromatic) and Formula E (aliphatic) shows a much higher tack in the aliphatic urethane.

![Figure 4: Oligomer Structure Comparison](image)

But when the molecular weight of the urethane acrylate is cut in half (Formula F), the tack is reduced greatly. None of these have a high enough tack required for an industrial PSA.

**Summary of Study Findings**

When looking for alternatives for the Ethoxylated nonyl phenol acrylate in the CN3003 tackifying oligomer, the Isobornyl acrylate based tackifying oligomer performs with greater 180° peel adhesion and higher tack, especially in the thicker (1.3 mil thick) pressure sensitive adhesive. The SAFT did not appear to be affected by using the Isobornyl acrylate to replace the Ethoxylated nonyl phenol acrylate.

When comparing three urethane acrylate oligomers with similar molecular weight, but different backbones (aromatic isocyanate vs. aliphatic isocyanate and polyesters polyol vs. polyether polyol), differences between the chemistries were noted. The aromatic polyether yielded higher 180° peel adhesion but lower tack when compared to its polyester equivalent (Formula D vs. Formula A). The aromatic urethane yielded higher 180° peel adhesion, but lower tack than its aliphatic urethane counterpart (Formula D vs. Formula E). And when we reduced the molecular weight of the aliphatic urethane polyether acrylate, we noted that both the 180° peel adhesion and tack are reduced greatly (Formula E vs. Formula F).
What’s Next for Formulators?

Now is the time for forward-looking formulators to prepare to meet the future demands of this fast-growing market. As shown by the statistics presented earlier, many are already producing UV/EB PSAs and the numbers will continue to grow as more and more formulators realize the benefits of this technology – including simplified formulation, increased cost-efficiency, and easier environmental compliance.

To help formulators ease the transition from solvent borne to UV/EB systems, progressive raw material suppliers are continually working to develop new products such as the three tackifying oligomers discussed in this article. These exciting product and technology developments will make UV/EB-cure PSAs an increasingly viable option for formulators worldwide.

References

Deborah Smith received her BS in chemistry from Rider University in New Jersey. Since joining Sartomer in September 1998, she has been working in the Application Department focusing on UV/EB curable adhesives. Prior to Sartomer, she worked numerous years in coatings, adhesives and sealants in both synthesizing and formulating a variety of end use products. Debbie synthesized oligomers and formulated UV curable coatings for the flooring industry. Prior to that, she had formulated two part structural urethane adhesives and one part urethane sealants for the automotive industry.