New Specialty Oligomers Developed to Increase Performance in UV Curable 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[1], the economic factor can be broken into three main areas:

- *Increased Sales:* With a UV/EB system, faster production speeds are achieved – often leading to an increase in sales.
- *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).
- *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.

The Growing International Market for UV/EB PSAs

In May of 2001, Frost and Sullivan issued a report summarizing the European adhesives market[2]. According to the report, the European Commission adopted the Solvent Emission Directive (SED) in 1999 to address the environmental challenges of using solvents in the production of finished goods. This new directive forced adhesive industries using organic solvents to find ways to meet new, stricter solvent emission targets. Under this new legislation, UV/EB-cured pressure sensitive adhesives are expected to do well in Europe because of their environmentally friendly technology.

Additionally, the United States UV/EB markets quoted the adhesives volume to be 2,500 MT (metric tons) in 2000, which accounted for 3 percent of the total UV/EB market. Of that market, pressure sensitive adhesives accounted for 350 MT, or 14 percent. That study did not include captive usage of UV/EB-curable pressure sensitive adhesives, which was estimated at 4,500 MT/year. From 1995 to 2000, the average growth rate of UV/EB-curable adhesives increased by 8 percent. The forecast for the year 2000 through 2005 is expected to be 8-10 percent, which is the largest growth forecasted among all UV/EB market areas[1].

Table 1 shows the market expectations 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 tapes and labels of various sorts. And, general-purpose industrial adhesives are higher-performance adhesives.

Table 1

Peel (ASTM D903-95)	**Removable**	**Sheet Stock**	**GP Industrial**
Peel – 30 min, pli	0.5	2.5	4.0
Peel – 24 hours, pli	1.2	3.0	5.0
Peel – 1 wk @ 70°C, pli	1.5	3.0	6.0
Peel – 3 wk @ 70°C, pli	1.75	3.5	6.0
Tack, g (ASTM D2979)	225	500	800

The Development of New Raw Materials

For more than thirteen years, the work done here at Sartomer in UV/EB-cure PSAs has shown the types of structures for both the oligomer and monomer that will produce an acceptable UV/EB curable PSA[3-10]. Initial work yielded the best monomers to achieve low odor and low viscosity UV/EB curable PSA's[3]. Optimizing the tackifier and T_g to yield the best UV/EB-cured PSA performance[4], followed by optimizing the oligomer structure[5-10], 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 mixing process was developed for these new products.

Sartomer chemists applied this technology and designed new tackifying oligomers specifically for pressure sensitive adhesives. These tackifying 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 tackifying oligomers make it easier for the smaller companies to enter the marketplace by mixing simple blends to yield an end PSA that meets their needs. The tackifying 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.).

To go along with these tackifying oligomers, two new highly reactive urethane oligomers have been developed to improve the PSA performance especially in thicker applications. If a thick PSA application were required, then a high level of photoinitiator or removal of oxygen would be required to get adequate through cure. These new oligomers can be cured in air with excellent cure and performance.

The following study starts with the investigation of the three low-viscosity tackifying oligomers designed to simplify the formulation of UV/EB-curable pressure sensitive adhesives. And then using the new highly activated oligomers to aid in the formulation of the UV cured PSAs. Viscosity, color, 180^o peel adhesion, tack, and SAFT were all run to help better understand performance of all the oligomers and the formulated pressure sensitive adhesives.

Discussion – Tackifying Oligomers

Three new tackifying oligomers were designed with varying degrees of tackifying softening point of the hydrocarbon resin incorporated within the oligomer. The physical properties of the tackifying oligomers are shown below in Table 2.

Table 2

Product	Description	Viscosity (cps @ 25°C)	Color (Gardener)	Density (lbs/gal)
CN3002	**High softening point**	200	6	8.68
CN3003	**Medium softening point**	170	6	8.68
CN3004	**Low softening point**	110	7	8.67

Each of these tackifying oligomers was then formulated into a PSA. The photoinitiator used in this study was Sarcure® 1135, which is a liquid blend of three photoinitiators: 2,4,6-trimethyl benzoyldiphenylphospine oxide, oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl] propanone], and methylbenzophenone derivates. In Table 3, the formulations used in this study are shown.

Table 3

Product	Description	A	B	C
CN973J75	**Aromatic Urethane Acrylate**	15.0	15.0	15.0
CN3002	**High SP tackifying oligomer**	83.0		
CN3003	**Medium SP tackifying oligomer**		83.0	
CN3004	**Low SP tackifying oligomer**			83.0
Sarcure 1135	**Photoinitiator blend**	2.0	2.0	2.0
Viscosity	cps @ 77°F	**1000**	**950**	**850**
Color	Gardener	**4-5**	**4-5**	**4-5**

The pressure sensitive adhesive formulations were cast using #40 wire wound rod applying directly onto the surface 2.0-mil Mylar film. The cured thicknesses were measured at 2.0 +/- 0.1 mils. The samples were then laminated to a Rhodia release liner. The adhesive was cured by ultraviolet light using a 400-watts/inch mercury vapor lamp at 700 mJ/cm^2. This was tested using an IL 390B Light Bug radiometer.

The sheets were then allowed to dwell for 30 minutes at 72^{o}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^o 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^{o}C. A 500-gram weight was then applied. The temperature was raised by 5^{o}C every ten minutes. The point at which the sample fails was recorded. The limiting temperature on the oven was 225^{o}C. The Mylar film will fail at 245-250^{o}C. Three samples per adhesive were run and averaged.

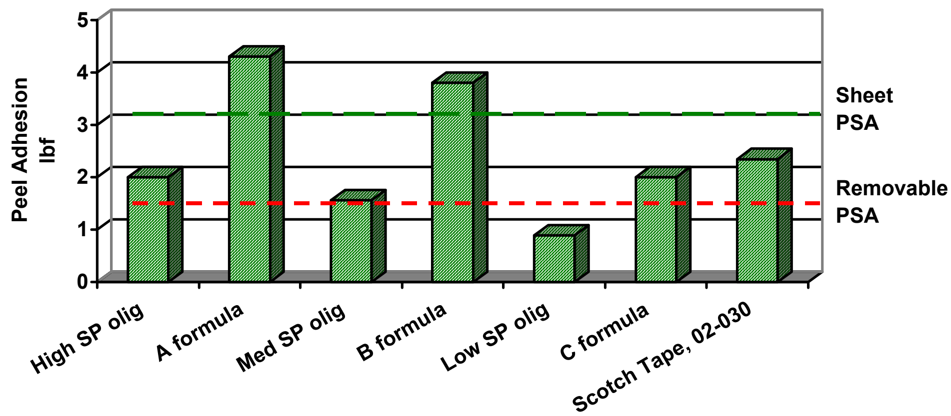
Tackifying Oligomer Comparison

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.

We tested these three formulations for 180° peel adhesion. These results are shown in Figure 1 on the following page. The 180° peel adhesion was also run on standard industrial grade Scotch Tape, #02-030. The 180° peel adhesion for each of the neat tackifying oligomers cured using 2% Sarcure 1135 photoinitiator is also included in Figure 1. All the formulated PSAs and base tackifying oligomers were tested at a 2.0 mil adhesive thickness. The Scotch Tape #02-030 was measured to be 1.5-mil adhesive thickness.

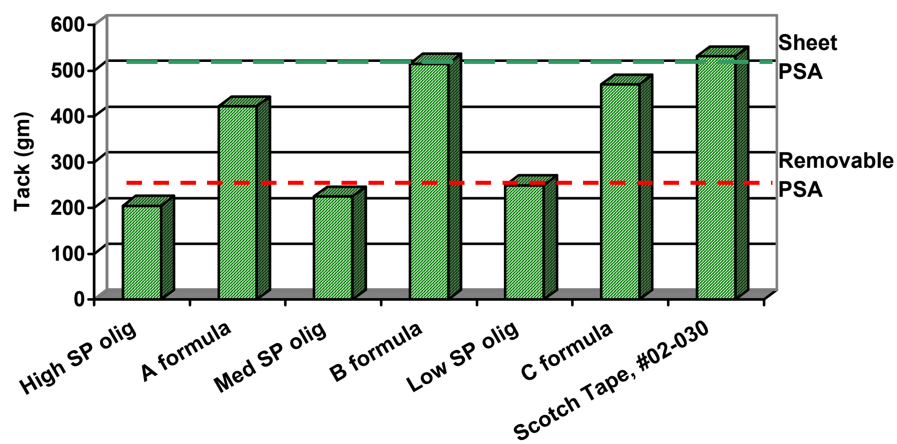
As you can see from the results in Figure 1, the addition of the urethane in the formulated adhesives improves the peel adhesion when compared to the neat tackifying oligomers. Also, we see that the formulated UV PSAs containing the urethane oligomer perform similar to the Scotch Tape, #02-030 for 180° peel adhesion.

Figure 1: Tackifier Oligomer Comparison
180° Peel Adhesion - Oligomer and Formulated PSA



Next the tack was tested on the formulated PSAs, the neat tackifying oligomers and the Scotch Tape, #02-030. These results are shown below in Figure 2.

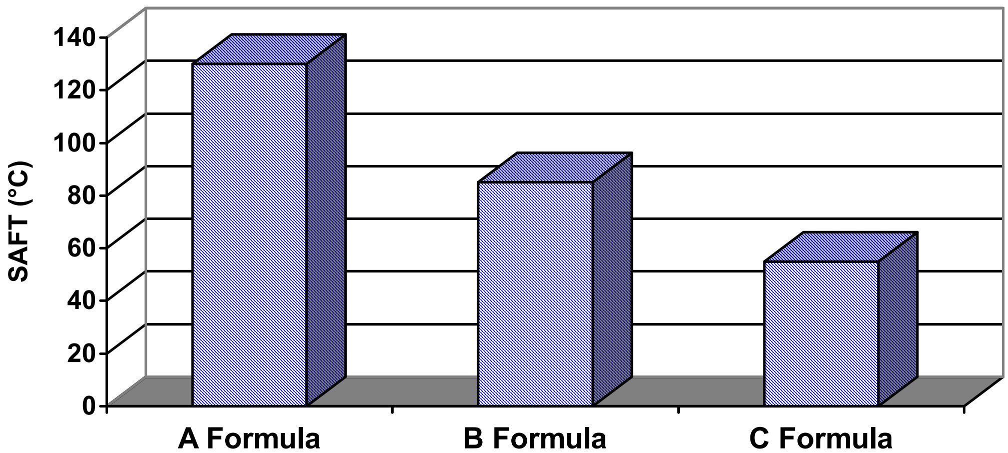
Figure 2: Tackifying Oligomer Comparison
Tack- Oligomer and Formulated PSA



As you can see in Figure 2, the addition of a urethane acrylate oligomer improves the tack over the neat tackifying oligomer. The tacks of the "B" and "C" formulated PSAs are similar to the tack of the Scotch Tape that was tested.

Finally, the shear adhesion failure temperature (SAFT) was measured on these three formulated PSAs. The tackifying oligomers were not included because a SAFT could not be run due to lack of strength of the cured PSA. The results for the SAFT are shown in Figure 3 on the following page.

Figure 3: Tackifying Oligomer Comparison
SAFT - Formulated PSAs



As the temperature of the softening point of the tackifying resin decreases, the SAFT also decreases. This is shown in Figure 3 above.

Activated Urethane Oligomers

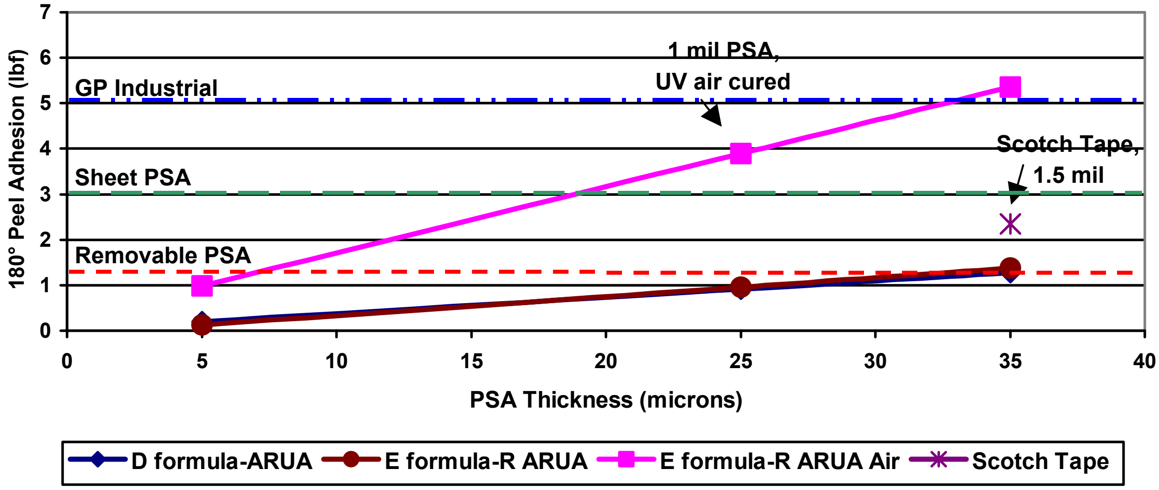
Next we took the high softening point tackifying oligomer (CN3002) and formulated using two high molecular weight urethane acrylate oligomers (CN973H85 and CN966H90) and compared these to the two new activated urethane oligomers (CN3210 and CN3211). These two new oligomers are similar in structure and molecular weight of their counterparts, but have been made more responsive for a faster cure. The formulation used for this comparison is shown below in Table 4. These four formulas are shown as a direct comparison in peel adhesion, tack and SAFT. The two aromatic urethane acrylates will be compared against each other, as well as the two aliphatic urethane acrylates will be compared.

Table 4

Product	Description	D	E	F	G
CN973H85	**Aromatic Urethane Acrylate (ARUA)**	15.2			
CN3210	**Activated Aromatic UA (R ARUA)**		17.2		
CN966H90	**Aliphatic Urethane Acrylate (ALUA)**			15.2	
CN3211	**Activated Aliphatic UA (R ALUA)**				17.2
SR504	**Ethoxylated Nonyl Phenol Acrylate**	2.6	0.6	2.6	0.6
CN3002	**High SP tackifying oligomer**	80.2	80.2	80.2	80.2
Sarcure 1135	**Photoinitiator blend**	2.0	2.0	2.0	2.0
Viscosity	cps @ 77°F	**700**	**700**	**750**	**750**
Color	Gardener	**4-5**	**4-5**	**4-5**	**4-5**

Originally we have been curing the UV cured PSAs through a clear release liner to limit oxygen inhibition to obtain better 180° peel adhesion. Formula E and G were both tested by curing with and without the release liner. All testing was done for the six samples at two various adhesive thicknesses, 0.5 and 1.0 mils.

Figure 4: 180° Peel Adhesion Formulated PSAs
Aromatic Urethane Acrylate based

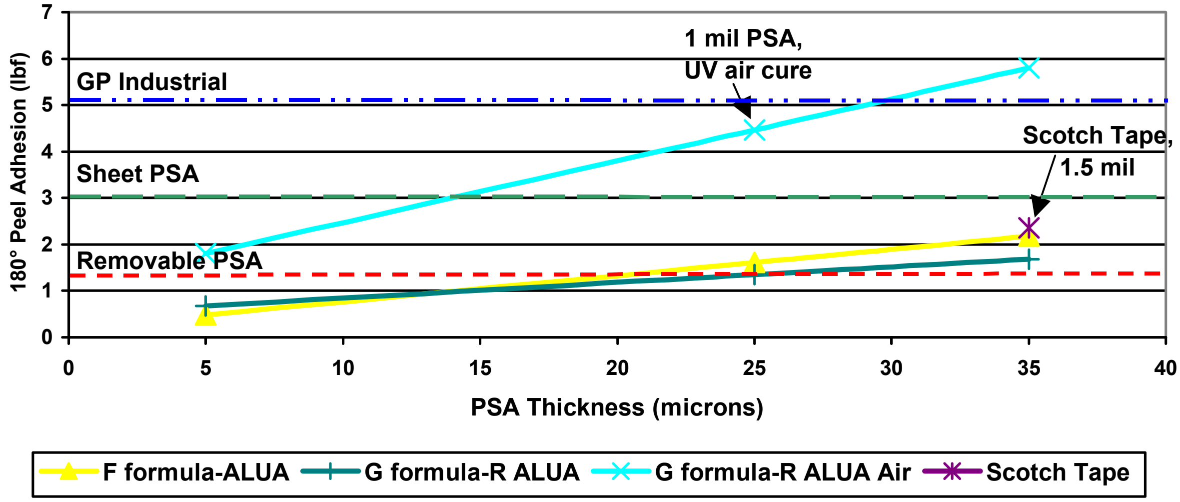


Key: ARUA = Aromatic Urethane Acrylate
R ARUA = Activated Aromatic Urethane Acrylate

Figure 4 compares all three tested PSAs for the aromatic urethane oligomers for 180° peel adhesion. Over 25 samples were evaluated for each formulated PSAs at the different adhesive thicknesses to obtain the 180° peel adhesion versus adhesive thickness as shown in Figure 4. You can see that the activated oligomers perform similar to their non-activated counterpart when both are cured underneath the release liner to reduce oxygen inhibition. But when the activated oligomer is cured in air, the 180° peel adhesion is greatly increased. As a comparison, 1.0 mil of this UV cured PSA yields around 3.95 pounds-force 180° peel adhesion whereas standard Scotch Tape, #02-030 which is 1.5 mils thick has a 180° peel adhesion of around 2.25 pounds-force. At the same 1.5-mil adhesive thickness, the activated oligomer formulated into the PSA has a 180° peel adhesion of 5.40 pounds-force. This is more than double that of the Scotch Tape, #02-030.

Figure 5, shown on the following page, has the same type of information as Figure 4, but it compares all the aliphatic urethane acrylate based PSA formulas with the adhesive thickness. Again, the activated aliphatic urethane acrylate when UV cured in air rather than under a release liner yielded a 1.0 mil PSA with a 180° peel adhesion of 4.5 pounds-force. Again, the Scotch Tape, #02-030 was around 2.25 pounds-force for the 180 ° peel adhesion using 1.5-mil thickness of the PSA. So if we looked at the 1.5 mil thick air cured activated aliphatic urethane oligomer, the 180° peel adhesion is around 5.8 pounds-force. The activated aliphatic urethane acrylate is getting even better results than it's counterpart – the activated aromatic urethane acrylate.

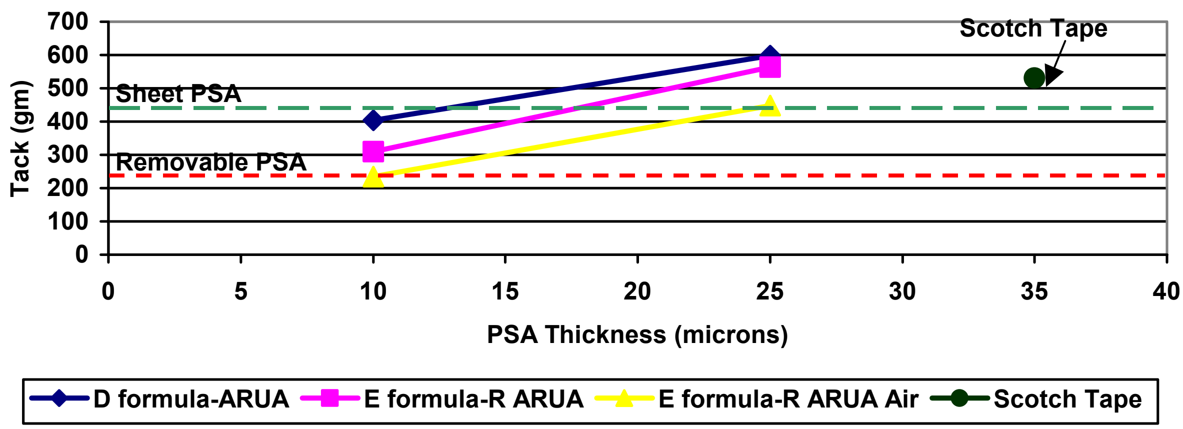
Figure 5: 180° Peel Adhesion Formulated PSAs
Aliphatic Urethane Acrylate based



Key: ALUA = Aliphatic Urethane Acrylate
R ALUA = Activated Aliphatic Urethane Acrylate

Figure 6 shows the tack results for both the normal and activated aromatic urethane acrylate at both 10 and 25-micron adhesive thickness. The activated urethane does have slightly lower tack results possibly due to better cross-linking within the polymer network. The 25-micron results are similar to the results for the scotch tape (530 gm), which has a coating thickness of 35-40 microns. All three of the PSAs at the 35-micron adhesive thickness would have better tack results than the Scotch Tape, #02-030.

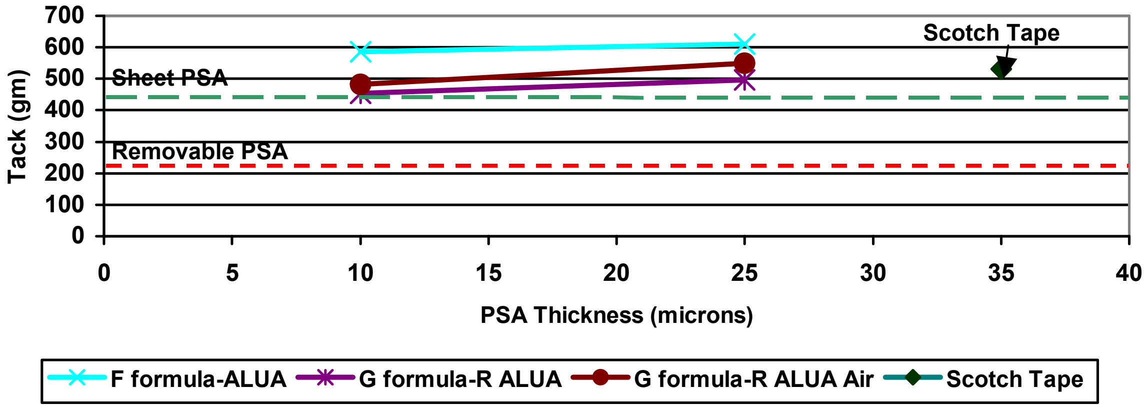
Figure 6: Tack - Formulated PSAs
Aromatic Urethane Acrylates



Key: ARUA = Aromatic Urethane Acrylate
R ARUA = Activated Aromatic Urethane Acrylate

Figure 7 shows similar results to Figure 6, but the aliphatic urethane acrylate PSA formulations are highlighted here. The normal “F” formulation that contains the CN966H90 again has the higher tack, probably due to the much better cross-linking seen in the more reactive systems. The adhesive thickness doesn’t appear to play as large of a factor in these formulations compared to the aromatic urethane acrylate formulation results (previous page). But again, even the test PSAs with a 1.0-mil thickness is comparable or better than the 1.5-mil adhesive thickness tack results for the Scotch Tape, #02-030.

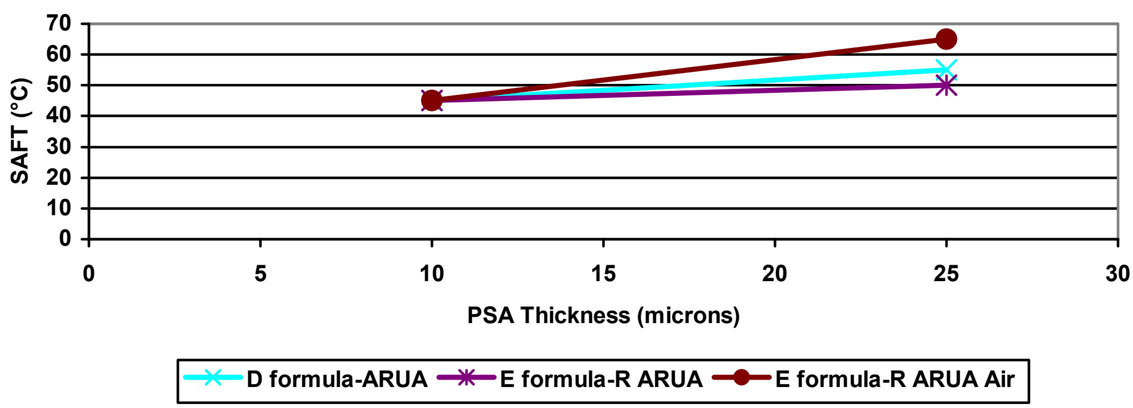
Figure 7: Tack - Formulated PSAs
Aliphatic Urethane Acrylate



Key: ALUA = Aliphatic Urethane Acrylate
R ALUA = Activated Aliphatic Urethane Acrylate

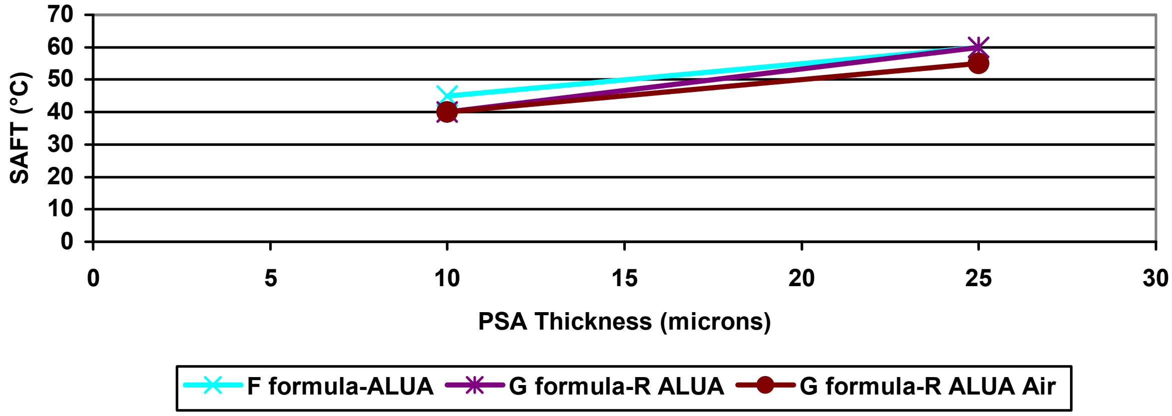
And finally, the Shear Adhesion Failure Temperature (SAFT) was measure on the above six formulations. All SAFT were run on aged samples, 6 month at room temperature. We’ve had numerous studies for fresh samples (as reported earlier in this report). First we’ll look at the effect of the aromatic urethane acrylate based PSAs. Figure 8 shows the results of the adhesive thickness versus the SAFT.

Figure 8: SAFT - Formulated PSAs
Aromatic Urethane Acrylate



It does appear that as you increase the adhesive thickness, the SAFT will also increase. It is very minimal in these results, which could be an indication of the age of the samples that were tested. It might also be an indication of the adhesive thickness. Since better SAFT has been reported at greater adhesive thicknesses (around 2.0 mil) with similar formulations then maybe a huge improvement is seen between 1.0 and 2.0 mils of adhesive thickness.

Figure 9: SAFT - Formulated PSAs
Aliphatic Urethane Acrylate



Key: ALUA = Aliphatic Urethane Acrylate
R ALUA = Activated Aliphatic Urethane Acrylate

Figure 9 shows the results of the SAFT for the aliphatic urethane based formulated PSAs. Again, the SAFT results are not as good as expected when compared to the 2.0 mil thick PSA of similar construction and cure. But in either case, there is an upward trend for the adhesive thickness versus the SAFT. And again, much higher SAFT has been seen with similar formulations that have not been aged and are much thicker, 2.0 mil adhesive thickness.

Summary of Study Findings

The highest softening point tackifying oligomer formulated into an UV-curable PSA yielded the highest 180° peel adhesion, slightly lower tack, and higher SAFT than the lower softening point tackifying oligomers. As the softening point of the tackifying resin is increased, the 180° peel adhesion and SAFT increase, whereas the tack decreases.

When comparing the activated urethane oligomers to their normal urethane acrylate oligomer, much improved 180° peel adhesion was found. The method of UV cure is important. This new faster to react oligomer performs better in air UV cure rather than being cured through release liner. We found these results in both the aromatic and aliphatic highly reactive urethane acrylates designed for PSA formulating. No adverse effects on tack or SAFT were seen with these new highly reactive oligomers. A much thinner adhesive application (1.0 mil) for these highly reactive urethanes formulated into UV cured PSAs can be used to achieve similar or better results than a commercially applied PSA (Scotch Tape, #02-030 at 1.5 mil thickness).

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 and the two new highly reactive urethane acrylate oligomers discussed in this article. These exciting product and technology developments will make UV/EB-cure PSAs an increasingly viable option for formulators worldwide.

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