New Low Cost Acrylated Tackifying Oligomers Designed to be used in Formulating Radiation Curable Pressure Sensitive Adhesives

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Abstract

Due to the ever-rising cost of raw materials, new low cost acrylated tackifying oligomers have been developed for formulating UV/EB curable pressure sensitive adhesives. All types of adhesive performance such as removable adhesives, sheet stock and general-purpose industrial pressure sensitive adhesives will be emphasized. Test results include 180° peel adhesion, tack, and Shear Adhesion Failure Temperature (SAFT). A comparison to standard commercial products will be covered.

Introduction

Pressure sensitive adhesives are found in many everyday applications: masking tape, packaging tape, note pads, and many different types of labels make up a small list of applications. Solvent borne PSA formulations traditionally based upon modified rubber chemistry are now being challenged by low VOC, fast curing systems such as ultraviolet (UV) and electron beam (EB) cured PSAs.

For over fourteen years, the work at Sartomer has shown the types of structures for both the oligomer and monomer that will produce an acceptable UV/EB curable PSA[1-13]. Initial work yielded the best monomers to achieve low odor and low viscosity UV/EB curable PSA's[1]. Optimizing the tackifier and T_g to yield the best UV/EB cured PSA performance[2] followed by optimizing the oligomer structure[3-6] lead us in a positive direction for UV/EB curable PSA development[7-13]. These studies have shown that excellent peel strengths have been 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.

The goal of this work was to demonstrate a cost effective UV curable PSA with quality performance as measured by 180° Peel Adhesion, Tack and SAFT.

Market Expectations

Table 1 shows the typical market expectations for various types of pressure sensitive adhesives. UV curable PSAs are at full strength immediately after cure; therefore, our comparison is based upon the fully cured water and solvent based PSAs (3 weeks at 70°C).

Removable adhesives are used in applications where the PSA will be removed from the surface. Usually a clean surface after removal is required with this type of adhesive. Sheet stock includes tapes

and labels of various sorts. Again, usually a clean surface after peel is required. General-purpose industrial adhesives are higher-performance adhesives. Because these types of PSAs are not usually removed, the mode-of-failure is not as important. This table will be used in evaluating the various PSAs.

Table 1 – Market Expectations

Peel (ASTM D903)	**Removable**	**Sheet Stock**	**GP Industrial**
Peel – 3 wk @ 70°C, pli	1.75	3.5	6.0
Tack, g (ASTM D2979)	225	500	800

Test Methods

The pressure sensitive adhesive formulations were cast using #40 wire wound rod applying directly onto the surface of 2.0-mil PET film. The cured thicknesses were measured at 2.0 +/- 0.1 mils, unless indicated differently. The samples were then laminated to a Rhodia release liner. The adhesive was cured by ultraviolet light using two 300-watts/inch-mercury vapor lamp at 700 mJ/cm^2 measured using an IL 390B 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[14] D903-98 at an angle of 180^o and a speed of 12 inches per minute. The samples were applied to standard micro-finish stainless steel panels using a 4½-pound PSTC roller. The initial samples were allowed to dwell for 15 minutes. Four to six samples per adhesive per condition were tested and averaged.

The tack was run as per ASTM D2979-01 using a Chem Instruments 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 tested and averaged.

The shear adhesion failure temperature (SAFT) was run as per ASTM D4498-00. One square inch of adhesive contact was applied to the standard stainless steel panel and then placed in an oven starting at 25^{o}C. A 500-gram weight was 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 tested and averaged.

Tackifying Blends

One of the greatest difficulties of this work through the years was properly dissolving the hydrocarbon resin into the monomers and yielding a stable mixture. After fully studying the processing conditions, a fully stable mixing process was developed for these new products.

This stabilized technology was applied and new tackifying oligomers were designed 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.).

This study compares new commercial tackifying blends that are lower in cost. Table 2 shows the product description and viscosity of these new products. The pricing is shown as a general range of price for the products. High softening point tackifiers yield PSAs with a higher 180° Peel Adhesion, but lower tack. Also a higher softening point tackifier usually yields better Shear Adhesion Failure Temperatures (SAFT), as well. Low softening point tackifiers have a higher tack, which is more desirable in certain applications.

Table 2 – Low Cost Tackifying Oligomers

Product	Description	Viscosity (cps @ 25°C)	Price
CN3007	**Low softening point**	15,000	$
CN3008	**Medium softening point**	100,000	$$

Pricing Key: *$* *$1.00-1.99/lb*
$$ *$2.00-2.99/lb*

Experimental – Formulated PSAs

To achieve a desired pressure sensitive adhesive an acrylated oligomer needs to be formulated with a tackifying oligomer. A variety of urethane oligomers were evaluated into a simple formulation and then tested for performance. The formulation used for the evaluation is shown in Table 3.

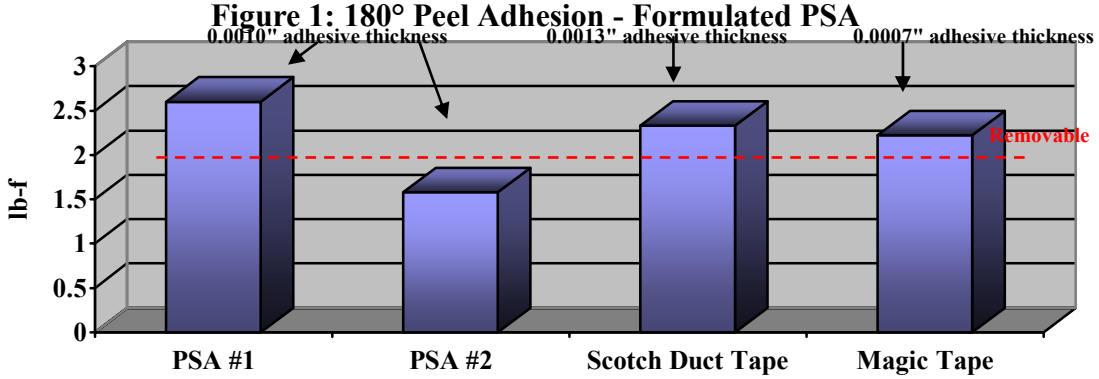
Table 3 – Sample PSA Formulations

Trade Name	Chemistry	Price	PSA #1	PSA #2
CN3007	Tackifying oligomer	$	60	
CN3008	Tackifying oligomer	$$		60
CD9087	Alkoxylated Phenyl Acrylate	$$	22	22
CN9002	Aliphatic Urethane Acrylate	$$$$	15	15
Esacure KIP 100F	Photoinitiator	$$$$	2	2
Formulated Cost:			$$	$$
Viscosity (cps @ 25°C)			1,350	2,250

Pricing Key: *$* *$1.00-1.99/lb*
$$ *$2.00-2.99/lb*
$$$ *$3.00-3.99/lb*
$$$$ *greater $4.00/lb*

The results shown in Figure 1 are a comparison of the formulated pressure sensitive adhesives shown in Table 3. Each of the UV PSAs was prepared with an adhesive thickness of 1 mil. Also included are two commercially available 3M products that are sheet type PSA tapes: Scotch Duct Tape (1.3 mil), code 131NA and Magic Tape (0.7 mil). The adhesive thickness is different on both of these types of tapes. Again the UV PSAs being tested have an adhesive thickness of 1.0 mil.

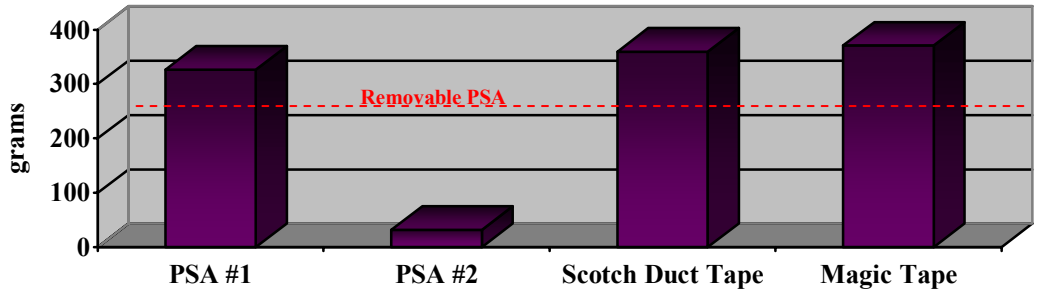
Figure 1: 180° Peel Adhesion - Formulated PSA



Formulated PSA #1 with a 1.0 mil adhesive thickness is in the same range as the two commercial 3M products. Formulated PSA #2 is slightly lower than the removable adhesive requirements.

The next graph shows the results for the tack on the same two tackifying oligomers compared to the same commercial tapes. The results are shown in Figure 2.

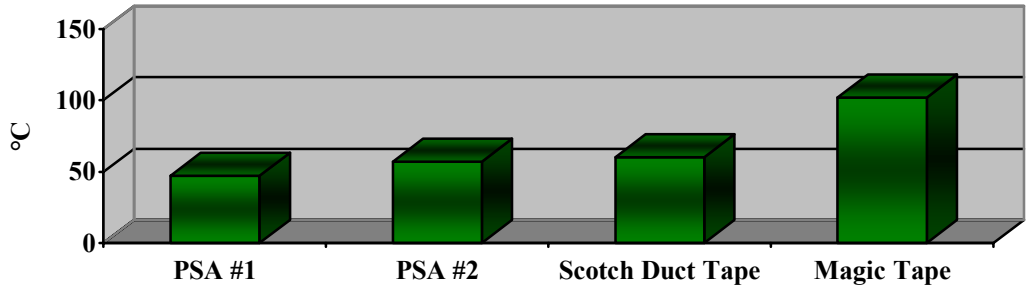
Figure 2: Tack - Formulated PSA



Formulated pressure sensitive adhesive #1 is similar in tack to the commercial products. The formulation made with CN3008 (formula #2) seemed to have low tack. But in some cases this is beneficial.

The Shear Adhesion Failure Temperature (SAFT) test was originally designed to find the heat failure temperature in shear of hot melt adhesives. Now most pressure sensitive adhesives of all types tend to test for shear adhesion failure temperatures. The results will help define the failure temperature where the adhesive fails in shear mode. The results for the above tested pressure sensitive adhesives are shown in Figure 3.

Figure 3: SAFT - Formulated PSA



The SAFT varies on products based upon their use. Formulated PSA #2 is similar to the Duct Tape evaluated.

Experimental – Oligomer structure, T_g and resin softening point versus SAFT

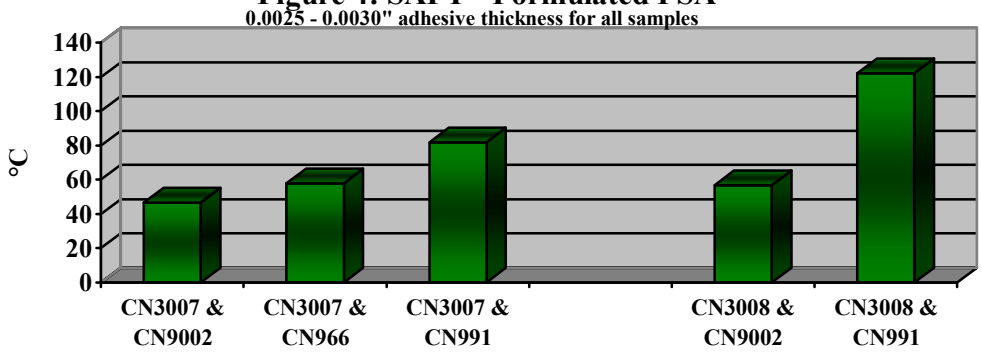
Years ago numerous studies relating chemical backbone, T_g and PSA performance[4] were performed. Just as important as the oligomer structure is the softening point of the hydrocarbon resin. The CN3007 is a low softening point resin (80-90°C) whereas the CN3008 is a mid-range softening point resin (110-120°C). In similar formulations including pricing to the ones shown in Table 3, CN991 and CN966 was exchanged for the CN9002 oligomer. Table 4 shows the physical comparison between these oligomers all having similar backbones. The table is arranged in order of increasing Tg rather than increasing molecular weight.

Table 4 – Oligomer Comparison

Oligomer	Backbone	MW	Tensile	Elong	1% Mod	T_g
CN9002	Aliphatic Urethane	Medium	184	116	292	-33 °C
CN966	Aliphatic Urethane	High	151	136	169	-8.1 °C
CN991	Aliphatic Urethane	Low	5380	79	19,400	33 °C

Figure 4 shows the comparison in these oligomers into the same formulations containing both the CN3007 and CN3008. First looking at the CN3007 based PSAs, the SAFT increases as the T_g of the oligomer increases. But when comparing the same two oligomers using the CN3008, the SAFT is higher. This is due to the CN3008 being a higher softening point resin than the CN3007.

Figure 4: SAFT - Formulated PSA

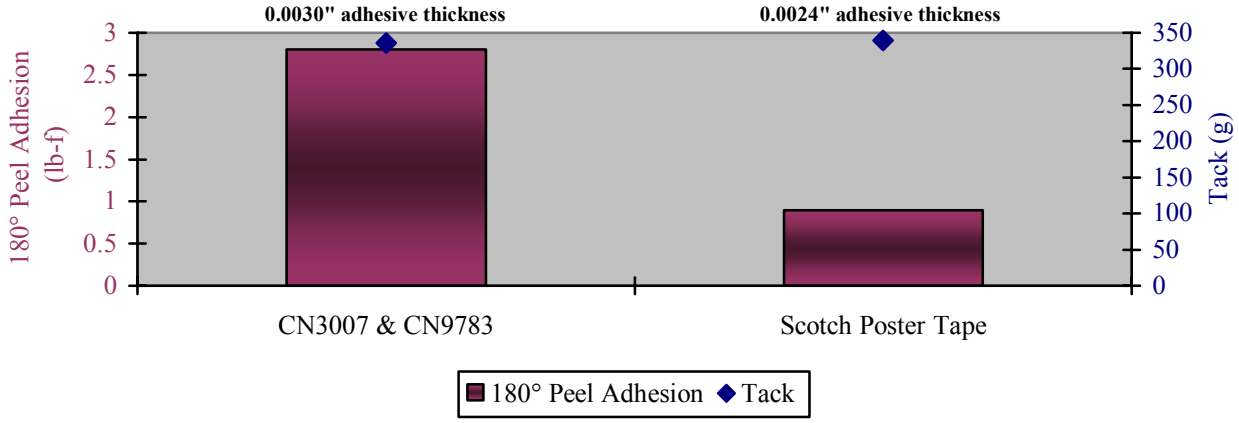


Experimental – Transfer PSA

Transfer tapes are used for various laminations such as name plates and product assembly applications. They consist of an unsupported adhesive coating applied over a silicone coated release liner. With radiation curing, the transfer adhesive is made in-line eliminating the need for ovens to dry traditional solvent-based and water-based adhesives. These radiation curable adhesives could easily be pattern coated, cured and then slitted in the uncoated area producing free edges and eliminating legging or lifting between layers.

This final set of data shows that the CN3007 when formulated with the CN9783 produces a suitable transfer adhesive. Again the formulation used including pricing is the same as shown in Table 3, except that CN9783 is the oligomer. This PSA, even though it works well as a transfer adhesive has higher 180° Peel adhesion when compared to the removable Poster tape. This type of PSA would be better suited to a more permanent label type application where you need to transfer the PSA onto a substrate such as nameplates or product assembly applications.

Figure 5: Transfer PSA
180°Peel Adhesion & Tack



Conclusion

A variety of formulated UV curable PSAs have been demonstrated to achieve similar properties as commercially available products. CN3007 formulated with the CN9002 yielded similar tests results to Scotch Duct tape, except that the duct tape has a thicker adhesive coat weight when compared to the UV PSA.

When trying to design a UV curable PSA, not only is the molecular weight and T_g of the oligomer important, but also the softening point of the resin is crucial in designing the best PSA for your requirements.

When formulating with the CN3007 we found many UV PSA formulations that created the perfect transfer PSA. The only example of a commercial transfer tape was the Scotch Removable Poster Tape. Our formulated UV cured transfer PSA yielded higher peel adhesion than the Poster tape, but similar tack.

UV curable pressure sensitive adhesives can be designed to meet current demands by properly formulating the reactive chemistry to ultimately replace current water based and solvent based technology.

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