Environmentally Friendly Tackifying Oligomers for Formulating Radiation Curable Pressure Sensitive Adhesives

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Introduction

Is green technology the answer, but are raw material limitations making formulating difficult? Is SARA 313 products a concern to your company? These are some of the issues to be addressed in a new series of acrylated tackifying oligomers developed for formulating UV/EB curable pressure sensitive adhesives (PSAs). Emphasis will be given to all types of adhesive performance such as removable adhesives, sheet stock and general purpose industrial pressure sensitive adhesives. Test results include 180° peel adhesion, tack, and Shear Adhesion Failure Temperature (SAFT). Various example formulations of UV curable PSAs showing comparisons to adhesive thickness versus performance along with commercial products will be covered.

For over fourteen years, the work done 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 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 evaluate and identify non-SARA 313 monomers for designing tackifying oligomers. Most of the monomers used previously in radiation curable PSAs were listed in Section 313 of SARA Title III by the EPA, i.e. 2 (2-Ethoxy Ethoxy) ethyl acrylate (SR256) and Ethoxylated Nonyl Phenol Acrylate (SR504) and are less desirable. It seems that the chemical industry's goal is to reduce the use of chemicals and compounds listed under this government regulation. These new non-SARA 313 UV curable tackifying oligomers are evaluated for 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. Since UV cured PSAs instantaneously meet the fully cured solvent and water based PSAs, then the goal for the UV PSA is to meet the final requirements of the finished product.

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. Table 1 will be used and referenced in evaluating the various PSAs discussed in this paper.

Table 1 – Market Expectations

	Removable	Sheet Stock	GP Industrial
Peel, pli (ASTM D903)	1.75	3.5	6.0
Tack, g (ASTM D2979)	225	500	800

Test Methods

The pressure sensitive adhesive formulations were cast using both #10 and #40 wire wound rod applying directly onto the surface 2.0-mil PET film. The cured thicknesses were measured at 1.0 to 3.0 mils. Adhesive thickness will also be discussed in the various sections. 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. The measured integrated energy was 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 (2004) 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 D2979-01 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 D4498-00. 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 for the oven is 225^{o}C. The Mylar film will fail at 245-250^{o}C. Three samples per adhesive were run and averaged.

Tackifying Oligomers

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

This stabilized technology was applied and new tackifying oligomers are being designed specifically for radiation curable 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 technology, the new tackifying oligomers make it easier for 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 started by comparing the solubility of various monomers with hydrocarbon resins. Then a stabilized tackifying oligomer was developed and tested for standard PSA properties. Finally the new tackifying oligomers were formulated into various PSAs by addition of a urethane acrylate oligomer and photoinitiator to the tackifying oligomer.

Three new tackifying oligomers were developed that are non-SARA 313 listed products. All three of these products have a medium softening point hydrocarbon resin (115°C S.P.) incorporated into the backbone of the oligomer which seems to be the more desired product. Table 2 shows the product description and viscosity of these new products. These new products are also higher viscosity than previous tackifying oligomers to yield greater formulating flexibility.

Table 2 – Tackifying Oligomers

ID #	Product	Description	Viscosity (cps @ 25°C)	Color	Density	Refractive Index
1	CN3010	**Medium softening point**	36,500	7	0.99	1.54
2	CN3011	**Medium softening point**	59,250	7	0.99	1.54
3	CN3012	**Medium softening point**	24,650	7	1.00	1.54

Experimental – Formulated PSAs

Each of the three new tackifying oligomers was formulated into both a higher and lower viscosity UV curable PSA by addition of a urethane acrylate oligomer, photoinitiator and then diluting with additional monomer to formulate the lower viscosity PSA. The formulation is shown in Table 3. Each of the formulations were drawn down using both #10 and #40 wire wound rod to achieve two different adhesive thicknesses for performance testing.

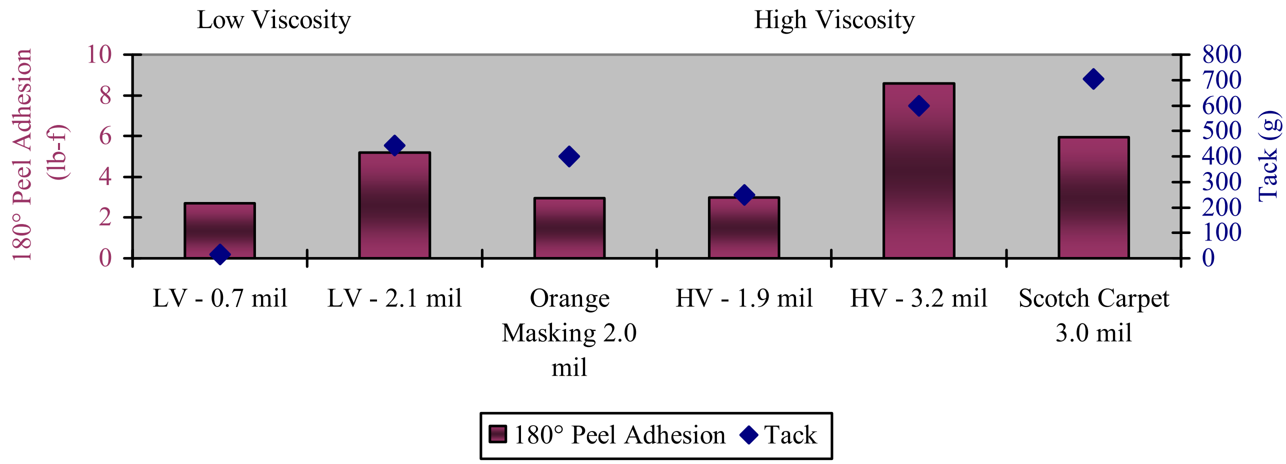
Table 3: Formulation for UV PSA

Chemical	High Viscosity	Low Viscosity
Tackifying Oligomer	83	71.2
Monomer		11.8
CN9004 – urethane acrylate oligomer	15	15
Esacure KTO46 photoinitiator	2	2

Experimental – CN3010 Tackifying Oligomer Formulation

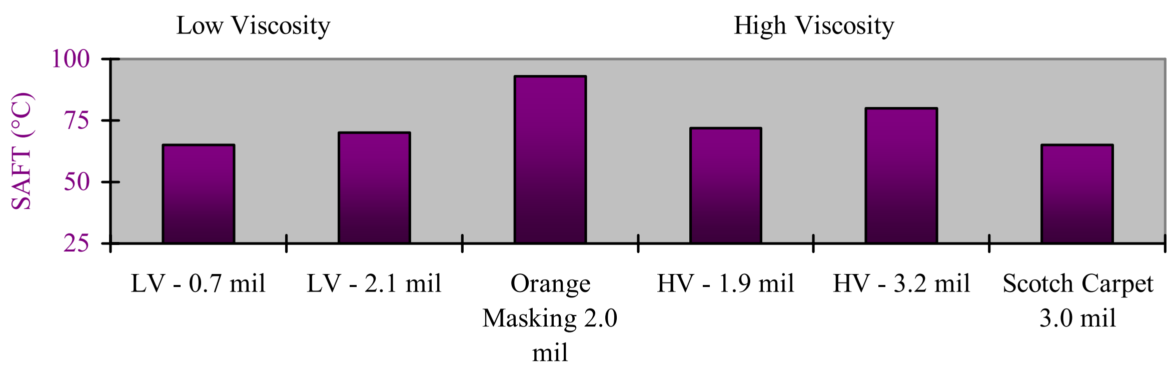
The first set of formulated UV curable PSA uses the CN3010 as the tackifying oligomer. The monomer used to reduce the viscosity in the low viscosity PSA is SR440, Isooctyl Acrylate. The high viscosity PSA had a measured viscosity of 22,250 cps at 25°C using a Brookfield Viscometer; whereas, the low viscosity PSA was measured at 2,785 cps. These PSAs were then prepared into cured products at two different adhesive thicknesses and then evaluated for 180° Peel Adhesion, Tack and SAFT. The results for 180° Peel Adhesion and tack are shown in Figure 1 with comparison to two commercial products: Orange Masking Tape and Scotch Carpet Tape, code 139NA.

Figure 1: Formulated PSA with CN3010
180°Peel Adhesion & Tack



As with most PSAs, when the adhesive thickness is increased, the 180° Peel Adhesion, tack and SAFT are also increased. This is easily seen when comparing the two different application thicknesses for the two formulated UV cured PSAs.

Figure 2: Formulated PSA with CN3010
SAFT

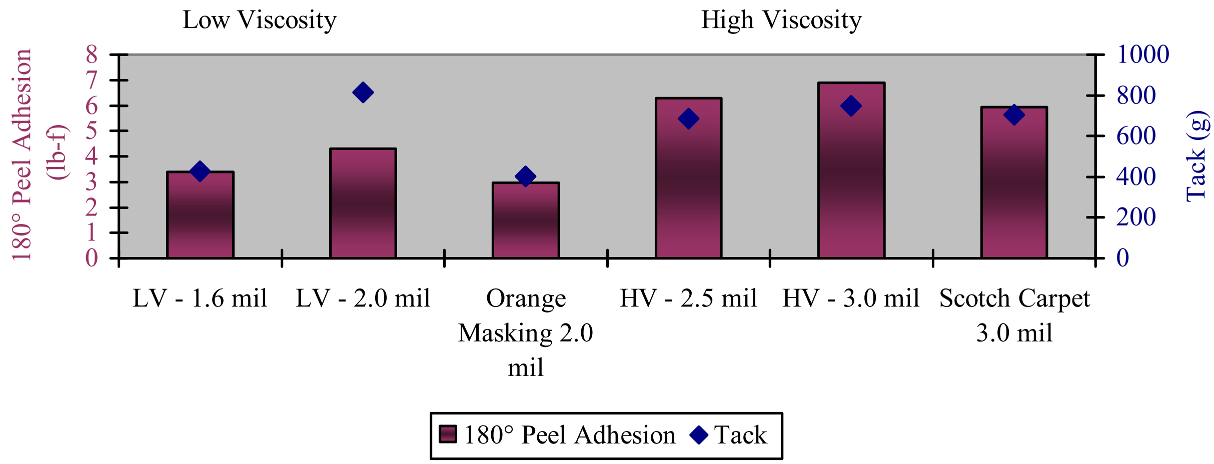


As shown in Figure 2, the adhesive thickness does play a role in the SAFT results. The Orange Masking Tape has a slightly higher SAFT than any of the formulated UV cured PSAs, but the Scotch Carpet Tape is lower than any of the experimental formulations.

Experimental – CN3011 Tackifying Oligomer Formulation

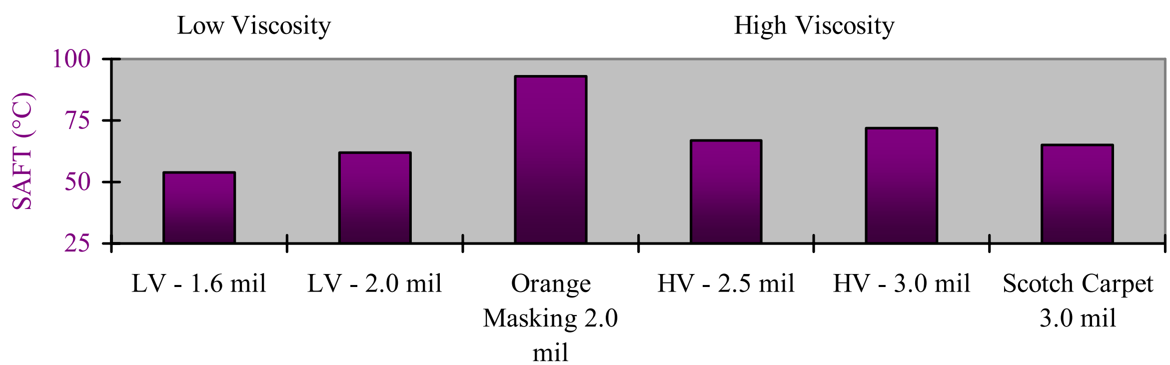
The second set of formulated UV curable PSA uses the CN3011 as the tackifying oligomer. The monomer used to reduce the viscosity for this series is SR335, Lauryl Acrylate. The high viscosity PSA has a measured viscosity of 28,650 cps at 25°C using a Brookfield Viscometer; whereas, the low viscosity PSA was measured at 3,875 cps. These PSAs were then prepared in the same fashion as the previous UV cured PSAs and then evaluated for 180° Peel Adhesion, Tack and SAFT. The results for 180° Peel Adhesion and tack are shown in Figure 3 with comparison to two commercial products: Orange Masking Tape and Scotch Carpet Tape.

Figure 3: Formulated PSA with CN3011
180°Peel Adhesion & Tack



When looking at these formulated PSAs, the performance of the low viscosity #10 rod (1.6 mil adhesive thickness) UV cured PSA is similar to the Orange Masking Tape, but lower adhesive thickness to achieve similar results. A similar trend was seen with the high viscosity formulation, again using the #10 rod to achieve a 2.5 mil adhesive thickness to achieve comparable results to the Scotch Carpet Tape.

Figure 4: Formulated PSA with CN3011
SAFT

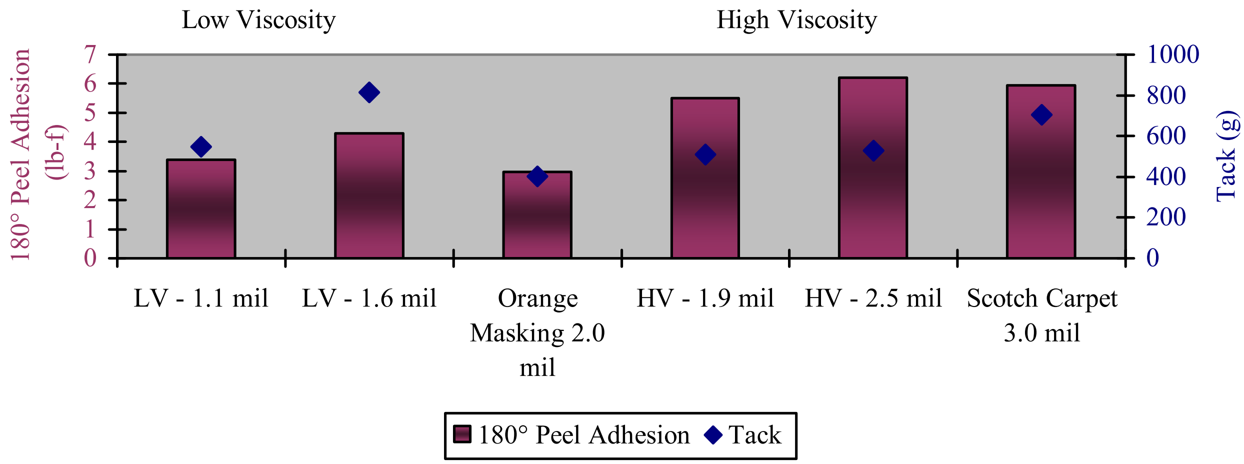


In this set of data shown in Figure 4, the Orange Masking Tape has a higher SAFT than any of the formulated UV cured PSAs. The Scotch Carpet Tape is has a similar SAFT to the two high viscosity experimental formulations.

Experimental – CN3012 Tackifying Oligomer Formulation

The final set of formulated UV curable PSA uses the CN3012 as the tackifying oligomer. The monomer used to reduce the viscosity in the low viscosity PSA is SR484, Octyl/Decyl Acrylate. The high viscosity PSA had a measured viscosity of 17,500 cps at 25°C using a Brookfield Viscometer; whereas, the low viscosity PSA was measured at 2,325 cps. And again, these PSAs were then prepared into cured products at two different adhesive thicknesses and then evaluated for 180° Peel Adhesion, Tack and SAFT. The results for 180° Peel Adhesion and tack are shown in Figure 5 with comparison to the same two commercial products: Orange Masking Tape and Scotch Carpet Tape.

Figure 5: Formulated PSA with CN3012
180°Peel Adhesion & Tack



The low viscosity material seems to have a higher peel adhesion and tack than the commercial product being compared with (Orange Masking Tape). The higher viscosity formulated PSA is very strong even at lower adhesive thickness although it is being compared to the Scotch Carpet Tape (3.0 mil adhesive thickness).

Figure 6: Formulated PSA with CN3012
SAFT

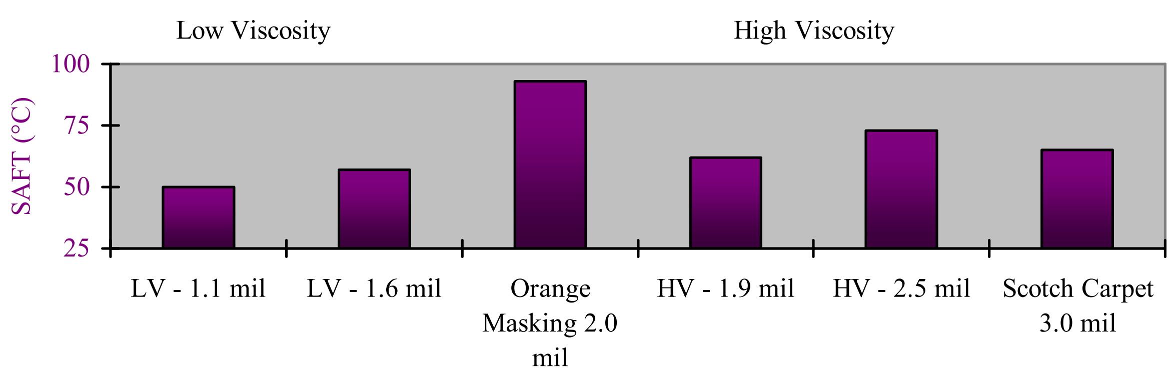


Figure 6 shows the SAFT results. The Orange Masking Tape has a much higher SAFT than any of the formulated UV cured PSAs, but the Scotch Carpet Tape is similar to the UV cured higher viscosity experimental formulations, even though the experimental PSAs are lower in adhesive thickness.

Conclusion

A variety of both tackifying oligomers and formulated UV curable PSAs have been demonstrated to achieve similar properties as commercially available products. Increasing the adhesive thickness will increase the 180° Peel Adhesion, tack and SAFT of an adhesive. In all the cases, it appeared that more monomer in the formulation to reduce viscosity increases the tack when comparing similar adhesive thicknesses.

The CN3010 high viscosity formulated PSA obtained very high 180° Peel Adhesion, tack and SAFT results; similar to the commercial Scotch Carpet tape tested having the same adhesive thickness.

Formulated high viscosity CN3011 also yielded high 180° Peel Adhesion, tack and SAFT and was also very similar to the commercial Scotch Carpet tape we tested.

The CN3012 proved also to be a great candidate for a PSA used in a sheet or label application. Most of the commercial products that we evaluated were much lower in 180° Peel Adhesion than all of these UV products.

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. These tackifying oligomers also offer the flexibility of using these types of materials that are not regulated under SARA 313.

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