Formulating a UV-Cure Pressure Sensitive Adhesive for PVC Foam Tapes and Converting an Oven-dry Water-Borne Material Using an LED Lamp Cure System

Brian Chambers, Director Research & Development, Novagard Solutions, Cleveland, Ohio

Introduction

Materials that cure upon exposure to actinic radiation are extremely fascinating. Formulating these systems is both challenging and rewarding. While the chemistry is fairly simple, these systems must be designed within the scope of a rather complex exposure condition. Product development and raw material selection must consider the full array of the process variables to achieve maximum performance. There is a balance between the chemistry and the physics that must be observed to provide full functionality to these systems.

Novagard Solutions is a full line sealant, coating and adhesive manufacturer located in sunny Cleveland, Ohio. The company offers a wide range of products into a multitude of markets. Built on a foundation of PVC foam tape, the original business quickly expanded into other chemistries. Now while Novagard continues to produce PVC foam tape we also market a full line of silicone based materials, including single-component, moisture cure RTVs, two-component platinum-catalyzed materials and UV curing formulations. Additionally, Novagard produces silicone-based, non-curing products for grease and dielectric applications.

For nearly forty (40) years Novagard has manufactured PVC foam tape. Originally the company was called Foam Seal, Inc. Today Foam Seal remains as a tradename for a broad range of polyvinyl chloride (PVC) products. With over a dozen distinct formulations covering an extensive density and performance range these products still provide an extremely cost effective sealing solution to many different applications. Large 56 inch wide logs varying in gauge (thickness) from 1/32" to over 1" may be slit at the converter to different widths and sold by the roll, or die-cut into a variety of shapes. These products may be sold as standalone materials, or should the final application require, they may be coated subsequently with a pressure-sensitive adhesive (PSA).

Most water-borne pressure sensitive adhesives (PSA's) perform poorly on flexible PVC foam tapes. Plasticizers from the PVC migrate into the PSA which softens the resin and reduces the overall adhesive strength. This lack of plasticizer migration resistance impacts the shelf stability of the foam tapes and limits the potential applications for these products. Solvent based PSA's generally perform better; however, the use of solvents is often problematic and in many instances even prohibited.

The principle challenge presented to the Novagard R&D group over two years ago was to provide an adhesive with the superior performance characteristics necessary to pass the rigorous automotive standards. As the project progresses it is evident that there are opportunities for several different compositions dependent upon the different application needs. Because Novagard already produces a variety of UV cure silicone products it is a natural extension to consider a UV curing solution. 100% solids, UV-cure materials often may be formulated with properties and performance similar to solvent-based compounds. Formulating the product in-house provides the opportunity to build the plasticizer resistance into the resin, monomer and tackifier combination. Proper raw material selection is essential to produce superior performance. Original formulations using a traditional mercury-vapor lamp system performed well but the excess heat scorched the foam surface. The relatively low T_g of the PVC necessitates the use of an LED curing lamp.

This article describes the laboratory experiments conducted to develop the adhesive and evaluate performance. Additionally it follows the scale-up and then the full-scale implementation of the entire process on the main production line, documenting the challenges and victories associated with each step of the execution.

Methods and Experimentation

The composition of most pressure sensitive adhesives (PSAs) includes resin, tackifier and some blend of rheology modifiers. A UV curing PSA is basically no different. Formulating these systems begins with the selection of a palette of raw materials from which an experimental design may be developed. Like the varying colors of paint this raw material palette typically will contain a variety of different chemistry types, a range of polymer molecular weights and full complement of additives which will modify the behavior of the base materials. The formulator, or artist if you will, must blend these materials precisely to create the final composition. Usually this is an iterative process; blend ingredients, coat and cure the system, test performance…repeat.

While plasticizer migration resistance is the primary goal, there are many different performance parameters that must be considered. Viscosity and general "coat ability", cure speed, cure depth, tack, peel adhesion strength, ease of manufacture and a host of other conditions must be designed into the final product. The Novagard team began by examining several resin/monomer combinations, and multiple different tackifier chemistries.

For UV curing materials the resin ultimately will be a blend of urethane acrylic oligomers and monomers, which act as reactive diluents to reduce viscosity. While there are several important considerations, perhaps the most important criteria is the T_g of the system. For a material to perform as a pressure sensitive adhesive the T_g must fall between approximately –30ºC and 10ºC. A material that is too hard (i.e. high T_g) will not have the tack necessary to perform; a material that is too soft (i.e. low T_g) will not have enough strength to perform. The Fox equation (1) provides the means to adequately predict T_g of a multi-component blend.

Fox Equation

$$1/T_g = W1/T_g1 + W2/T_g2 + W3/T_g3$$

Where: WX is weight fraction of component X and

T_gX is glass transition temperature of component

The Fox equation assumes complete miscibility of the components, which is generally the case for most acrylic oligomer/monomer blends. For this project several different urethane oligomers from Rahn USA were selected. **Table 1** provides a description of each oligomer. Four acrylic monomers also outlined in **Table 1** yield the appropriate T_g while simultaneously being capable of dissolving the different tackifiers. The process begins by developing several different blend ratios of monomer and oligomer to verify compatibility and viscosity of the compositions. It was found that the monomers and oligomers chosen are miscible at all levels, and that the viscosity of the final blends will vary widely based upon the specific combination. Ethoxylated (4) nonyl phenol acrylate is the fastest curing monomer; both the isodecyl acrylate and the 2-(2-ethoxyethoxy) ethyl acrylate are much slower curing, but they better solvate tackifiers yielding lower viscosity formulations.

Table 1 – Oligomers and Monomers (Courtesy Rahn USA)

Name	**Description**	**F(x)**	**Tg (ºC)**	**Viscosity (cps @ 25C)**
Genomer 4188/EHA	Aliphatic urethane acrylate	1	-16	120,000
Genomer 4217	Aromatic urethane acrylate	2	-35	100,000
Genomer 4269/M22	Aliphatic urethane acrylate	2	-15	55,000
03-849	Polyester acrylate	3	28	20,000
Genomer 3414	Polyester acrylate	3	-17	4,500
Genomer 6043/M22	Modified polyester resin	n/a	-18	30,000
Ethoxylated (4) nonylphenol acrylate	NP(EO)4A (CAS no. 50974-47-5)	1	-28	100
Isodecyl acrylate	IDA (CAS no. 1330-61-6)	1	-60	7
2-(2-ethoxyethoxy)ethyl acrylate	EOEOEA (CAS no. 7328-17-8)	1	-53	10
Isobornyl acrylate	IBOA (CAS no. 588-33-5)	1	80	10

There is one significant difference between a UV curing PSA and other types of PSA systems, when exposed to actinic radiation these formulations are transformed from liquids to viscoelastic solids. However, for this transformation to proceed the formulation must contain a free radical photoinitiator. It is the photoinitiator that reacts with the UV radiation to generate free radicals, which in turn initiate the polymerization. The mechanisms of free radical generation are beyond the scope of this article. While there are a multitude of photoinitiators from which to choose, a versatile and efficient photoinitiator for acrylic systems is Irgacure® 1173 from BASF. Initially, the

Novagard team used a standard mercury vapor lamp system to generate the UV light. This worked well for the preliminary trials where the various formulations were simply coated on aluminum weighing dishes to quickly evaluate cured physical properties. However, as described later in this article, problems developed when the team started coating actual PVC foam samples.

Perhaps the most important ingredient for improving tack, adhesive strength and plasticizer migration resistance is the tackifier resin. Tackifiers may compose as much as 40 percent, or higher, of the total adhesive. These chemical compounds are usually blends of various resins, often derived from plant sources; however, synthetic tackifiers and chemically-modified resins are extremely popular. They are typically lower molecular weight materials with relatively high glass transition temperatures, or softening points. In adhesive formulations, tackifiers function as polymer modifiers and therefore compatibility with the monomer/oligomer composition is critical. Compatibility is determined by chemical make-up, molecular weight, molecular weight distribution (polydispersity) and solubility parameters. There are predominately three main types of tackifiers: rosin esters and their derivatives, terpenes and modified terpenes, and hydrocarbon resins both aromatic and aliphatic. Each of these types may be further sub-divided by softening point, chemical modification, and melt viscosity.

At the start of the project, the team at Novagard selected approximately 10-12 different tackifiers based upon the different chemistries, a range of softening points and most importantly based on recommendations from the various vendors. Several of the tackifier chemistries are quickly rejected based on poor solubility in the monomers. Because of their highly polar nature the polyterpenes in theory offer better adhesion and better plasticizer migration resistance; however their poor solubility rendered them unusable. A partially hydrogenated rosin ester also had poor solubility and was eliminated from the study; however, highly hydrogenated rosin esters of similar composition showed excellent compatibility and made nice low viscosity solutions when dissolved in monomer. After the initial screening the team selected six (6) tackifier candidates to proceed in the study. **Table 2** outlines the chemistry and some of the physical properties for these materials.

Table 2 – Tackifier Resins

Designation	Chemistry / Description	Softening Point* (^{o}C)	Solubility
RE1	Highly hydrogenated glycerol ester of wood rosin	80-88	Excellent
RE2	Highly hydrogenated pentaerythitol ester of wood rosin	95-103	Good
AR1	Aromatic hydrocarbon resin	110-120	Good
TP1	Terpene phenolic resin	109-114	Excellent
TP2	Terpene phenolic resin	120-126	Excellent
TP3	Terpene phenolic resin	122-128	Good

*Ring and Ball test method

When the project first started there was considerable controversy in the market regarding the viability of UV-LED lamp systems. At that time, Novagard had virtually no experience with LED lamp systems; the silicone products all require a medium-pressure, mercury vapor lamp to cure properly. Novagard experimented briefly with LED lamps and the silicone products with very little success. Because of solubility considerations the choice of photoinitiators in a silicone formulation is limited. Those that are soluble in silicone are fairly unresponsive to longer wavelength emitting LED lamps. The debate on the viability of UV-LED lamps mostly focused on the lower output power. Additionally, it was rumored that the nearly monochromatic spectral output at longer wavelengths causes poor cure response of most coatings, particularly relating to surface cure.

In spite of these perceived short-comings, because of the relatively low T_g (approximately 80^{o}C) of PVC the Novagard team saw no alternative but to try UV-LED curing. Original PSA formulations using a traditional mercury-vapor lamp system performed adequately but the excess heat scorched the foam surface. Even at the fastest line speeds the heat still damaged the foam surface. In some instances, particularly with the lower density foams, the surface was burnt so badly that it made the product unusable. The PSA formulations appeared to cure fine; however, because the foam integrity was compromised, regardless of the adhesive type the failure always occurred within the foam at extremely low performance. The team contacted several different LED lamp manufacturers and ran multiple trials, but in the end, the laboratory opted to invest in an 8W Phoseon FireJet™ FJ200.

With the Phoseon lamp system fully operational, the team now focused their attention on formulating a functional adhesive. The LED system operates much cooler, no longer scorching the PVC foam surface. Allowing the team to coat and cure directly on the PVC foam; testing the various formulas in the actual application. Representatives from Phoseon informed the Novagard scientists that their experience shows that the success of their LED lamp systems is nearly always dependent upon selecting the appropriate material. The lamp and the material must be matched closely to maximize performance. In most instances the lamp manufacturer and the material supplier rarely work in unison. However, Novagard is not the average UV curing consumer. Formulating the product in house gives Novagard the advantage of working through the entire value stream, from raw materials through the finished product. This unique position allows Novagard to work closely with two principal vendors, Rahn USA for raw materials and Phoseon for LED curing expertise, to quickly blend and test different permutations to achieve the perfect match.

The first task is to achieve maximum cure – from surface to full depth. Initially, the coating thickness was limited to a maximum of 2 mils (0.002"). As the top, open surface eventually becomes the bonding interface, adequate cure is essential. Oxygen inhibition at the surface is of primary concern. The photoinitiator(s) selection is critical. However, the photoinitiator is only part of the equation. Monomer selection is also important. The degree of cure is evaluated using a combination of adhesive shear strength and heat aged peel adhesion.

Table 3 – Adhesive Performance

	Formula #1	**Formula #2**	**Formula #3**	**Formula #4**
Monomer type (see Table1)	EOEOEA	NP(EO)4A	EOEOEA	NP(EO)4A
Tackifier type (see Table 2)	RE1	RE1	RE1	RE1
Resin	Oligomer Blend	Oligomer Blend	Oligomer Blend	Oligomer Blend
Photoinitiator	Irgacure 1173	Irgacure 1173	Irgacure 819	Irgacure 819
Viscosity (Brookfield)	350 cps	5,500 cps	350 cps	5,700 cps
Shear Strength (minutes)	No Cure	No Cure	35	180
Initial Peel Adhesion (pli)	No Cure	No Cure	1.75	4.25
Heat Aged Adhesion (pli)	No Cure	No Cure	0.50	2.00

*Coated at 5.2 grams/s.ft. on PVC foam. Cured with lamp height adjusted to 12.5 mm from surface of PSA and line speed set at 3 meter/min.

Table 3 clearly demonstrates the importance of monomer and photoinitiator selection. Irgacure® 1173 from BASF is a versatile and efficient photoinitiator for acrylic systems; however, while it works well with a standard mercury-vapor lamp system it does not perform well with LED curing. The maximum absorption spectrum does not match the spectral output of the LED lamp. This wavelength mis-match limits the number of free radicals generated on exposure regardless of lamp intensity. Irgacure® 819 from BASF absorbs at longer wavelengths, which is a much closer match to the LED lamp system. Yet, while the photoinitiator absorption is a better match, Formula #3 and Formula #4 indicate that if the monomer reactivity is not precisely adjusted the PSA still will not perform.

Once the details of UV LED curing were settled, the next step in the development process is to evaluate different combinations for plasticizer migration resistance. In early stages of development, the principal goal was to build an automotive grade adhesive capable of passing stringent automotive specifications. Early experiments determined that the choice of tackifier resin predominately dictates performance. As mentioned earlier in this article, six (6) different tackifiers were selected for additional screening. As is often the case when formulating products, the team faced yet another series of compromises; tackifiers with higher softening points had better resistance, but yielded PSA formulations with higher viscosity. Also, tackifiers with higher polarity showed improved resistance but also were more difficult to solvate and yielded higher viscosities. The trick is to strike the perfect balance of properties.

Implementation

Once the Novagard development team had a working formulation the project moves to the implementation phase. The process begins with several mini-line trials. Novagard owns and operates a 1/6th scale replica of the main production line specifically for pre-production trials and sample preparation. Maximum allowable width on the mini-line is 18"; however, for convenience we keep the width at 12". The operation of the mini-line is virtually identical to the main line with the exception of the adhesive coater station. **Figure 1** and **Figure 2** depict the two styles of coater heads.

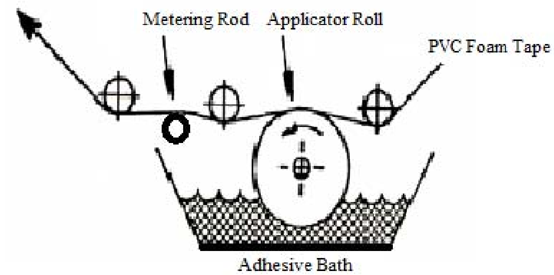

Figure 1. Wire-wound Metering Rod Technology

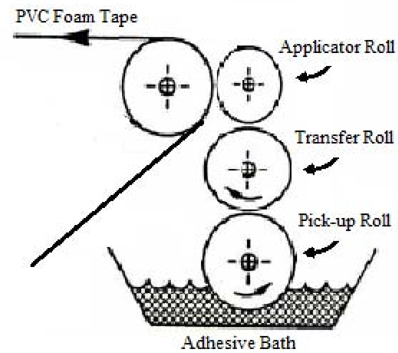

Figure 2. Modified Reverse Gravure

The mini-line is equipped with a wire-wound metering rod (Meyer Rod) coating station as shown in **Figure1**. The mainline has the modified reverse gravure coater (**Figure 2**). For "proof of concept" experimentation it seemed that the type of coater station is irrelevant, provided we could achieve an adhesive thickness of at least 2 mils (0.002") in a uniform application. This improves upon hand-coated samples where it is virtually impossible to get perfectly smooth coatings. Initially, two 8W 150mm Phoseon Firejet^{TM} lamps were mounted in-line, side by side approximately 3 meters from the coater station. Lamp height is fixed so the gap between emitting window and the surface of the foam was varied by changing foam thickness. Line speeds varied between 3 meters/min to 6 meters/min (10 feet/min to 20 feet/min). At higher line speeds the 8 watt lamps do not adequately cure heavier coat weights. To evaluate cure, an 8W lamp is mounted next to a 12W lamp for the final few trials. As with the laboratory experiments, the degree of cure is evaluated using a combination of adhesive shear strength and heat aged peel adhesion. The mantra "coats – cures –sticks" still echoes through the halls at Novagard Solutions today.

Twenty-six (26) months from the very first laboratory mix the Novagard team finally moves to a main-line trial. As one can imagine, breaking in to an extremely busy production schedule for experimental line trials is an exceptionally challenging operation…but absolutely essential. The co-ordination of efforts grows exponentially as the number of departments involved increases. The team at Phoseon graciously designed and built a temporary mounting bracket and loaned Novagard a total of 6 – 150mm 12W Firejet^{TM} lamps yielding nearly 36" of width, which is the minimum operating width on the main production line. Again, the lamp height is fixed. Lamp intensity and lamp on/off is manually controlled. While the mini-line trials were all essentially "proof-of-concept", the goal of main line trial is to determine actual production feasibility and begin to justify the significant investment dollars. Will the product "coat – cure - stick" under conditions that actually replicate real-world manufacturing.

Beyond the formulation, there are several key processing parameters that need to be closely controlled for success. The trial design covered multiple substrates, multiple foam types and multiple gauges (thickness) of foam. Beyond running the foam line and coating/curing adhesive, the adhesive mixing process also requires experimentation. New mixing equipment is part of the investment. Determining appropriate vessel size and mixer configuration are critical for success as the addition sequence, the incorporation time and the blade design all contribute to ultimate PSA performance. An entire day and the full Foam Seal production staff dedicated to UV cure PSA. The trial runs nearly flawlessly; a total success by any measure - a tribute to the entire team.

Again, our partners at Phoseon go back to work designing and manufacturing the fully integrated lamp system. Through all of the experimentation, the team determines that two (2) banks of 12W air-cooled lamps best fits the production needs. A second bank of lamps provides some redundancy in the operation and assures full cure at maximum coating thickness and maximum line speed potentials of 20-25 meters/minute (65-80 feet/minute). Lamp height is fully adjustable between 0 and 50 mm (2"). Lamp intensity and lamp on/off are linked to line movement to accommodate variations in speed and periodic start/stops associated with log changes. The Phoseon team rose to the challenge and delivered a unique, one-of-a-kind UV LED lamp station on time and on budget.

Conclusion

The next time you go to Home Depot® or Ace Hardware and buy a roll of weather-stripping to seal that drafty bedroom window take a closer look at the adhesive, there is a pretty good chance that product is UV LED cured in sunny Cleveland, Ohio. Or take a look under the hood of your new Chevy Corvette, there just might be some UV LED cured PSA there too. Surprisingly, PVC foam tape is everywhere in literally hundreds of applications, and the radical idea (pun intended) of UV curing the PSA has upped the performance bar.

Formulating a UV cure pressure sensitive adhesive, building the product from scratch and designing ultimate performance properties is both challenging and rewarding. Critical to success are the partnerships formed during the nearly three (3) year development cycle. The Product Specialists at Novagard continue to perfect the process and the products.