IMPACT OF ADHESIVE COMPOSITION AND DIFFERENTIAL CURE ON THE PERFORMANCE OF ACRYLIC ULTRAVIOLET LIGHT CURED HOTMELT ADHESIVES

Christopher M. Comer, Ph.D., Research Scientist, Bostik, Inc., Dublin, OH
Kelsey McGuire, Lab Technician IV, Bostik, Inc., Dublin, OH
Lars Kilian, Ph.D., R&D Director, Bostik, Inc., Dublin, OH

Introduction

UV cured hotmelt pressure sensitive adhesives (UV-HMPSA) are pressure sensitive adhesives that can be coated at 100% solids and cured with UV light. UV-HMPSA offer advantages to traditional solvent-based pressure sensitive adhesive (S-PSA) technology, such as higher coating speeds, minimal VOC emissions, small equipment footprint, and significantly lower initial capital investments (see Table 1 for a complete comparison with S-PSA). Therefore UV-HMPSAs offer tape manufacturers efficient and environmentally friendly alternatives to traditional S-PSA.

Table 1. Comparison of UV-HMPSA and S-PSA adhesives

Variable	UV-HMPSA	S-PSA
Raw materials	Acrylates, crosslinking monomer, photoinitiator, tackifiers, solvent (removed to make final product)	Acrylates, tackifiers, other additives, Al $(AcAc)_3$, solvent
MW	Low to medium	Medium to high
Crosslinking mechanism	Covalent via UV irradiation	Coordination (Al AcAc)
Solids	~100% (>99.5 wt%)	35-65%
Coating application methods	Slot die, spray	Reverse roll, slot die, knife over roll
Coating thickness	1-10 mil for Norrish Type I and Type II Photoinitiated crosslinking, highly dependent on formulation	0.8-5 mil
Coating speed	2 mils @400 FPM (depends on lights) 3 mils @300 FPM (depends on lights)	2 mils @ 60-120 FPM 3 mils @ 50-70 FPM
Coating speed limitations	Melting equipment, pumps, slot die, adhesive rheology	Lower explosion limits (LEL), oven driers, adhesive rheology
Thermal Oxidizer/incinerator	Not needed	Always needed
Equipment Footprint	Small	Large
Capital Investment (new equipment for converters)	Low-moderate	High

The basic building blocks of acrylic S-PSAs and UV-HMPSAs are similar. Each type of PSA is derived from the polymerization of acrylates that are initiated via a free radical initiator in a solvent such as ethyl acetate. Typical monomers include 2-ethylhexyl acrylate, *n*-butyl acrylate, methyl acrylate and acrylic acid. UV hotmelt PSAs have constraints based on product performance and adhesive processing that cause a deviation from the traditional solvent borne polymerization toolbox used to make S-PSA. These differences are due to the type of crosslinking chemistry employed to make the adhesives UV curable and the processing of the adhesives during the coating process, which is critically sensitive to molecular weight.

UV-HMPSAs cure through two main mechanisms which are radical and cationic photoinduced crosslinking reactions. For radical crosslinking of UV-HMPSAs, there are two main types of photoinitiators utilized, and they are shown in Figure 1. The first type of photoinitiator (Norrish type I or cleavage type) achieves an excited state triplet state when irritated with UV light[1, 2, 3]. Once the triplet state is reached, the molecule will relieve this excess energy by breaking a chemical bond within the molecule to form radicals. The radicals formed by cleavage can then react with unsaturation (e.g., polymer-bound acrylates) to form crosslinks. An example of this type of photoinitiator are α-hydroxyketones.

The second type of photoinitiator (Norrish type II or hydrogen abstraction) reaches an excited triplet state when irradiated with UV light, but instead of cleaving the molecule will abstract a hydrogen from either the same polymer or a neighboring polymer molecule[1,2,3]. Once the radical is formed, it can recombine with other radicals formed via the same process to form a crosslink or initiate polymerization/crosslinking through reactions with unsaturated molecules. Benzophenone is the standard example for type II photoinitiators and is extremely efficient.

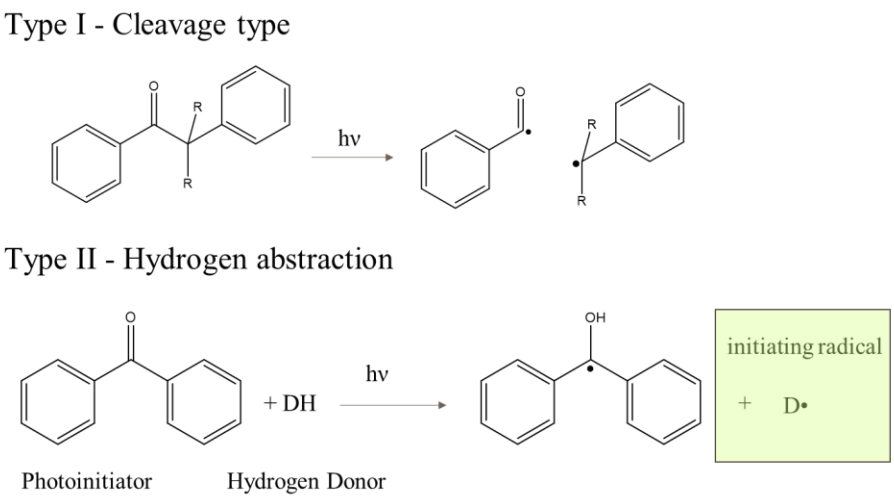

Figure 1. Examples of Norrish type I and type II photoinitiators.

The third type of photoinitiator is a photoacid generator. When irradiated, a photoacid generator reaches an excited state and will release very strong Brønsted acids and radicals[1, 2, 3]. Brønsted acids can initiate the ring opening reactions of epoxies and oxetanes. The radicals generated can also initiate crosslinking reactions of unsaturated molecules.

Instead of traditional metal ligand coordination bonds between carboxylic acid (from acrylic acid) and aluminum cations, UV-HMPSAs rely on covalent crosslinking mechanisms that are activated by UV light exposure. The state-of-the-art technology for crosslinking is typically one of three main mechanisms. The most prevalent in the industry is based on acrylic PSAs using a (meth)acrylate based benzophenone monomer in the polymer backbone[4]. When irradiated with UV light, the pendant

benzophenone, a hydrogen abstraction (Norrish type II) photo initiator, will abstract a hydrogen from a nearby polymer chain and form a radical that will combine with the newly formed radical on the polymer chain, thereby crosslinking the adhesive. Crosslinking is typically initiated most efficiently with UVC (200-280 nm) and UVB light (280-320 nm). A diagram of a generic polymer design and crosslinking is shown in Figure 2.

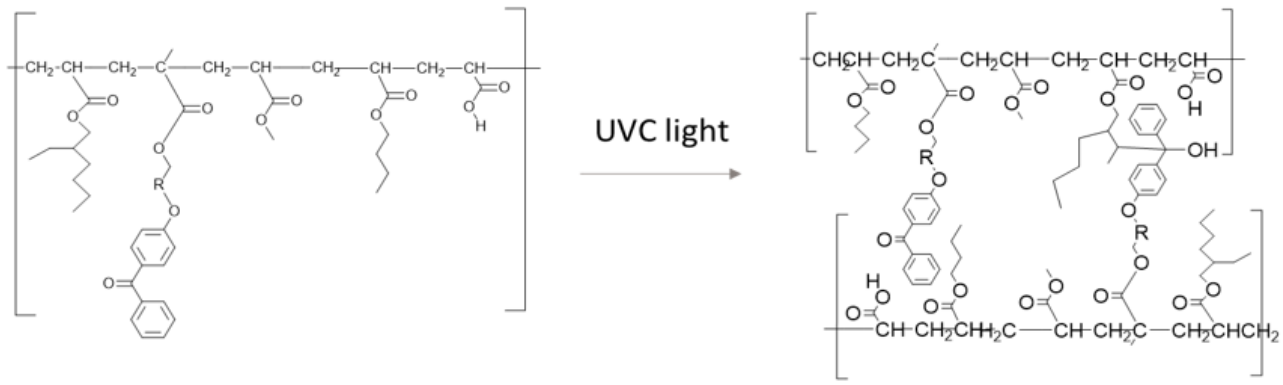

Figure 2. Illustration of the acrylic polymer with pendant Benzophenone and crosslinking after irradiation with UV light.

The second UV PSA technology is based on a pendant epoxy or oxetane functional group attached to the acrylic polymer chain[5]. A cationic photoinitiator is added to the formulation after the initial solvent-borne polymerization. When irradiated, the cationic photoacid generator will form a super acid that catalyzes a cationic polymerization to crosslink the UV-HMPSA. Cationic photopolymerizations are considered living polymerizations and allow for extended crosslinking reactions to occur even, after the light is turned off[1, 2]. The choice of cationic initiator and photosensitizers dictate the reactivity of the system to emission wavelength of the UV light.

The third UV PSA technology utilizes a traditional solvent borne polymer that is functionalized with the addition of a pendant double bond. After polymerization, a derivatization agent is reacted with the acrylic polymer to add a double bond to the polymer backbone as shown in Figure 3[6,7]. An example of this type of derivatization agent is the product of the reaction between 2-hydroxyethyl acrylate and isophorone diisocyanate. The derivatization agent consists of an acrylate and isocyanate functionality. The isocyanate functional group can react with carboxylic acid or hydroxyl groups on the acrylic polymer chain. A photoinitiator is added to the formulation and will initiate the crosslinking reaction of the acrylic double bonds when the adhesive is irradiated with UV light.

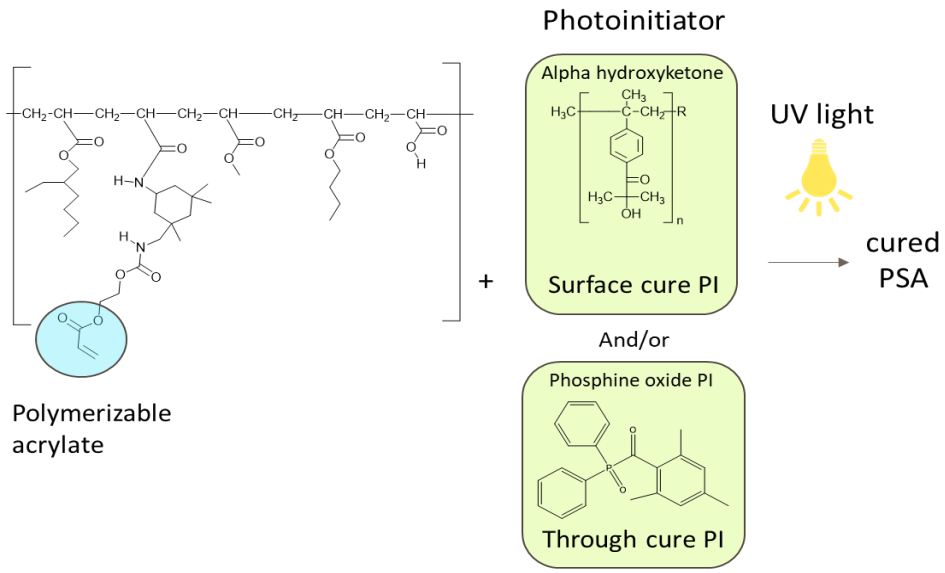

Figure 3. Acrylic polymer with pendant double bond and initiators to provide efficient surface and through cure of UVHMPSA samples.

UV light is absorbed by many materials typically used in UV-HMPSA formulations. Firstly, the photoinitiator absorbs UV light. For instance, benzophenone based crosslinking monomer absorb heavily below 300 nm[1,2]. The benzophenone functional group reacts efficiently and quickly with short wavelength light, but that reactivity is in competition with the absorption of light across the adhesive depth. Second, additives that have unsaturation or aromaticity, such as tackifiers, plasticizers, or pigments, absorb or block UV light. Therefore, the choice and concentration of these materials will have a significant impact on the extent of penetration of UV light through the thickness of the adhesive. Figure 4 demonstrates a model for this competition for UV light by typical PSA additives. Because of the competition for UV light by photoreactive chemistries and light absorbing additives, the penetration into an adhesive by UV light is dictated by the wavelength of light and composition of the adhesive. If the adhesive has limited materials that compete for light with the photoinitiator, the cure may be more uniform across the thickness of the adhesive. Addition of additives that absorb UV light or compete for the light required to activate photoreactive groups, limit the penetration of UV light through the sample and therefore limit the cure through the adhesive. An example of this competition for UV light and impact on cure is illustrated in Figure 5.

Absorption of light across the depth of the adhesive by photoreactive groups and additives reduces the effective the UV light penetration. Because short wavelength light (300 nm and below) is absorbed by many materials, it is the most impacted. Longer wavelength (300 nm and above) light will penetrate further into the adhesive. Photoreactive groups tend to react more efficiently with shorter wavelength light, but their crosslinking efficiency will be more consistent at greater depth with longer wavelength light. The reaction with longer wavelength of light requires more photons of light to get the same response as shorter wavelength of light[2]. The variation of cure across the thickness of the adhesive will be impacted by the adhesive formulation and UV light chosen to cure the adhesive. Hence, the viscoelastic properties at each surface are likely substantially different from each other when compared to a traditionally cured solvent-based adhesive, which will be more uniformly cured across the adhesive depth.

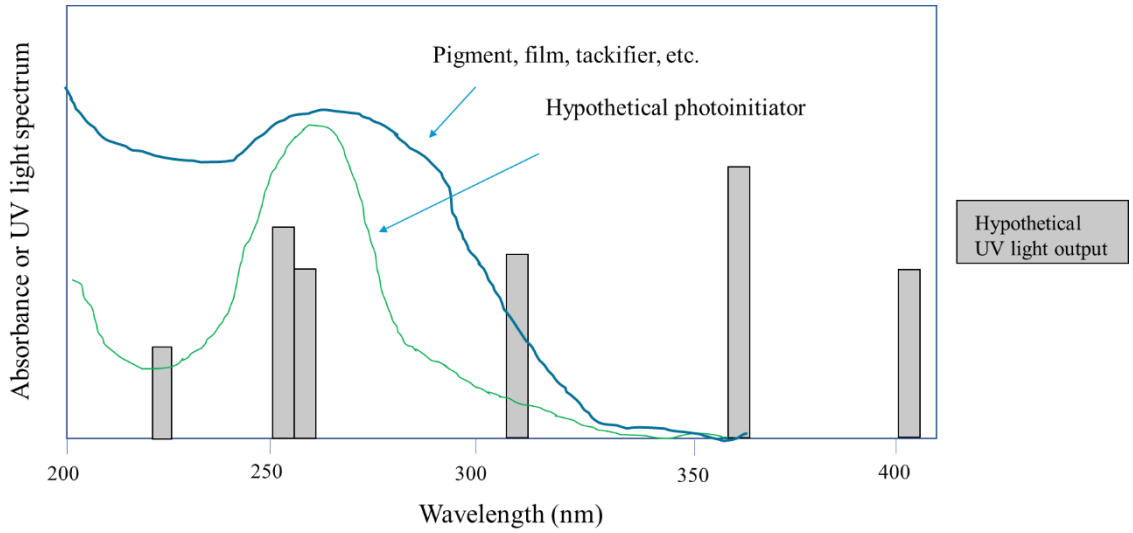

Figure 4. Illustration of a hypothetical UV light emission profile (similar to medium pressure mercury bulb), the UV absorption spectra of photoinitiators, and typical adhesive additives[2].

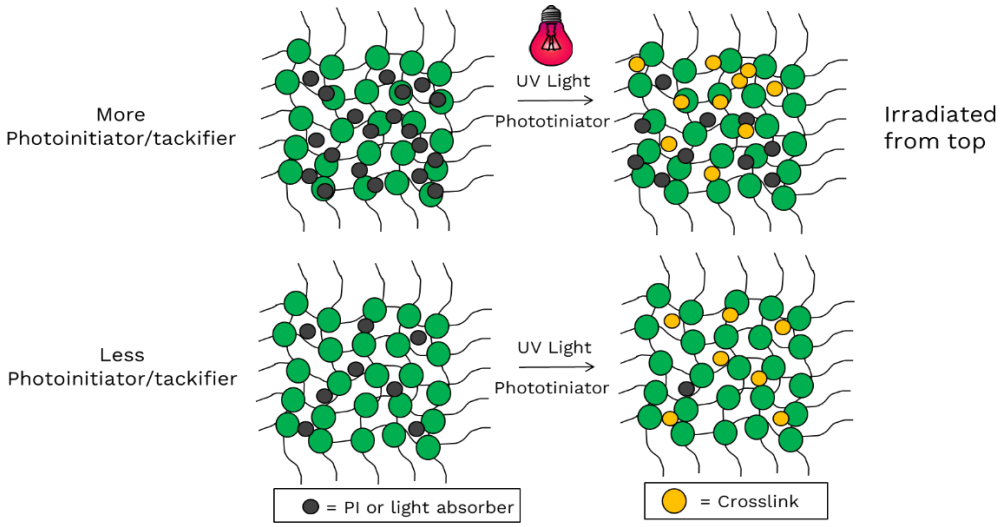

Figure 5. Illustration of the competition/absorption of UV light by photoreactive groups, additives and the impact on the penetration of light into the adhesive.

Additionally, the coating method utilized to create an adhesive coated product may also have an impact on the performance of the adhesive. In transfer-coating, you directly irradiate the adhesive surface, which is then laminated to the facestock. Therefore, adhesive performance is based on the adhesive response of the indirectly irradiated surface. Depending on the composition of the adhesive, the light that penetrates through the adhesive will be reduced, and therefore crosslink density will generally be lower at this surface than the directly irradiated surface. For adhesive samples that are direct-coated onto the facestock, the surface being tested for adhesive performance is the directly irradiated surface. The directly irradiated surface likely has a very high crosslink density when compared to the indirectly irradiated surface. The directly irradiated surface sees a large amount of UV light compared to the indirectly irradiated surface. Although the photoinitiator must overcome oxygen inhibition at the surface exposed to air, the high amount of UV light that the surface is irradiated with easily overcomes this limitation and a high crosslink density is the likely result.

The focus of this paper will be to show how the adhesive formulation, coating method, thickness, and UV light choice impact the adhesive performance of the adhesive. We will compare an $Al(AcAc)_3$ cured adhesive to the UV-HMPSA adhesive to show the variation in outcomes between the two types of curing mechanisms. The optical properties of the adhesive with regards to UV/Vis absorbance via UV/Vis spectroscopy of the UV-Base, UV-Tackified, and tackifier will highlight the interaction of light with the adhesive. Adhesive performance tests such as peel, loop tack, and shear will be used to probe the impact of cure at the surface and the cohesive properties of the adhesives. Williams Plasticity will be used to further probe cohesion, as it approximates the bulk modulus of each cured adhesive and is not impacted by surface effects such as wet-out. The combination of these test methods will highlight the design parameters to consider when formulating and curing a UV-HMPSA product.

Experimental methods

Materials

Acetone (HPLC grade), toluene (technical grade), ethyl acetate, aluminum acetoacetate ($Al(AcAc)_3$), 2,4-pentanedione, photometric grade chloroform, and rosin acid tackifier were purchased from commercial suppliers of laboratory and industrial chemicals. The UV-Base and UV-Tackified acrylic PSA samples were polymerized and formulated at Bostic, Inc. The UV-Base was formulated with a rosin acid tackifier to make UV-Tackified adhesive. The UVHMPSAs produced for this study utilize a type II or hydrogen abstraction process to crosslink polymers. $Al(AcAc)_3$ crosslinked samples were made by formulating UV-Base with a solution of $Al(AcAc)_3$ and 2,4-pentanedione mixed in toluene in a one to one ratio by weight. The aluminum solution was added to the UV-Base to achieve the desired weight percent aluminum based on solids.

Mylar® A (PET film) that is 0.002” thick and 11” x 14” and polycoated platinum cured release liner was sourced from industrial supplier of films and release liner. Stainless-steel panels with a bright annealed finish that were used for peel, loop tack, and shear were purchased from a test equipment supplier. H-Bulb (medium pressure mercury) or D-Bulb (Iron Doped Bulb) were purchased from an industrial supplier of UV lights and testing equipment.

UV/vis spectroscopy

Data were collected with an Agilent® Cary™ 100 UV-Vis spectrophotometer. Samples were diluted in photometric grade chloroform and analyzed in double beam mode with 10mm quartz cuvettes. Instrument performance tests were performed each day of analysis.

Radiometer measurement

UVC dose was measured using an EIT Powerpuck® II prior to UV curing to set the line speed of the conveyor and obtain the proper UVC light dose for each sample. The UVA, UVB, and UVC dose was recorded for each sample by placing the radiometer in the middle of the conveyor belt and running under the UV light at a specified speed. Representative data from radiometer measurements at each line speed will be documented in the results section.

PSA-coated film preparation

UV cured and $Al(AcAc)_3$ crosslinked UVHMPSA samples were solvated in ethyl acetate and coated onto polycoated kraft release liner or direct-coated onto corona-treated 2 mil PET film using a

Baker Bar. The bar was set to the wet film thickness appropriate for producing the desired dry film thickness of 2 or 5 mil PSA films. For 2 mil films, samples were air-dried for 15 min, and then samples were dried in a forced-air oven at 95 °C for 12 min. For 5 mil films, samples were air-dried for 30 min, and then samples were dried in a forced-air oven at 95 °C for 15 min. Immediately after oven drying, UV cured adhesive films were irradiated with either a H-Bulb (medium pressure mercury) or D-Bulb (Iron Doped Bulb) at the desired UVC dose (Measured with an EIT Powerpuck® II). Samples that were crosslinked with aluminum were not UV cured. Samples that were used for adhesive performance testing (peel, loop tack, and shear) are transfer-coated onto corona treated 2 mil PET film for testing by laminating at a 40 psi nip pressure. Adhesives that were direct-coated on to 2 mil PET were laminated to polycoated kraft release liner at 40 psi nip pressure prior to performance testing. All coated adhesive samples were allowed to equilibrate for 24 hr in a constant temperature and humidity room (23°C, 50% RH) before applications testing. The films for Williams Plasticity were left as free films and protected with a second weak release liner until testing.

Peel Testing

Peel testing was carried out in accordance with PSTC-101[8]. Stainless steel panels were cleaned with acetone and stored under constant temperature and humidity for at least 1 hour prior to use. 1" wide coated stock was bonded to the panels by rolling twice using an automated 4.5 lbs roller. After allowing the samples to dwell for 24 hr the samples were peeled at 180° at a rate of 12 in/min using an Instron® Model 4411 tensile tester with a 100 lb loadcell. Average peel values are reported in pounds per linear inch. Failure modes were recorded for each test. Failure modes are as follows: C – cohesive failure, A – adhesive failure, T – transfer failure, G - ghosting or a light/hazy deposit left on the panel after adhesive strip is removed, and NF – no failure. The percentage of each failure mode was also documented (*e.g.*, C5A5 is 50% cohesive failure and 50% adhesive failure).

Loop Tack

The loop tack testing was carried out in accordance with PSTC-16, Test method A[8]. Stainless-steel panels (6" x 2") were cleaned using acetone and stored under constant temperature and humidity conditions for 1 hr prior to use. An adhesive strip supported on 2 mil PET was prepared with the dimensions of 7" long and 1" wide. The Instron Model 4411 tensile tester crosshead speed was set at 12"/min speed. The minimum gap is set to 1" and the maximum gap is set to 4". The test fixture for mounting the stainless-steel plate at 90° to the upper clamp was mounted in the lower grip of the tensile tester. The release liner is removed from the sample and the sample is bent back to form a tear drop shape with the adhesive facing out and the ends of the sample being flush with each other. The ends of the sample are taped with a 1" wide piece of masking tape to secure the sample together. The taped end of the sample is then inserted into the upper grip of the tensile tester. The test panel is loaded into the bottom test fixture. The tensile tester is activated to begin test and lowers the sample to the minimum gap and then immediately begin moving upward. The maximum force required to remove the adhesive from the panel and failure mode is recorded. Failure modes are noted in peel testing procedure.

Static Shear

The static shear testing was carried out in accordance with PSTC-107[8], Procedure A. Stainless-steel panels (2" x 3") were cleaned using acetone and stored under constant temperature and humidity conditions for 1 hour prior to use. The coated stock was bonded to the panels with a 1" x 1" contact area and allowed to dwell for 15 min. The panels were then hung vertically (178°), and a 1 kg weight was attached to the film. The shear failure times were recorded in hours.

Williams Plasticity

Williams Plasticity is a method that determines the plasticity of high viscosity plastic materials, and the result is related to the materials bulk properties and not surface cure effects[9]. Adhesive free film samples are prepped and cured at the selected coat weight and cure conditions for both $Al(AcAc)_3$ and UV cured UVHMPSA samples as described previously. Two Williams Plastomers, model P-4 (physical testing equipment services) were placed in an incubator oven to equilibrate at 37.7°C for at least 1 hr prior to testing. A 4"x 4" piece of release liner was placed on a scale and tared. A 2-gram ball (±0.05 g) was formed by using your fingers to roll a ball from the adhesive free films and placed on the scale to check the weight. Hands should be washed prior to rolling the 2-gram balls of adhesive. Care was taken to minimize the entrapment of air in the balls. Two pieces of 4" x 4" pieces of release liner were placed between the plates of the Plastomer. The top platen was lowered and the Williams plastometer gage was set to zero gap. The two-gram balls were then placed in the incubator and allowed to equilibrate for 20 min at 37.7 °C. After 20 mins, each ball was centered between the top and bottom platen. The top platen is then lowered gently to compress the ball and allowed to dwell for 15 min. After 15 mins, the gap between the two plates is recorded. The gap is reported as the value for Williams plasticity in millimeters and is related to the materials bulk modulus. A small gap represents a low modulus material and a large gap a higher modulus material.

Results and Discussion

UV/Vis spectroscopy

In photopolymerization, it is traditional to match the absorbance spectra of the photoinitiator (or crosslinking monomer) with the spectral output of the UV light. In thin coatings or adhesives (<1 mil or 25 µm), this is an excellent approach to overcome oxygen inhibition, achieve efficient surface cure, and through-cure. Photoinitiators quickly react when irradiated with UV light that overlaps with the absorbance spectra of the photoinitiator[2]. In general, less light at these overlapping wavelengths is required to produce an efficient and fast photochemical reaction.

As coat weights increase, competition for light due to absorbance of UV light across the thickness of the adhesive occurs. UVC light is the most impacted and is absorbed within the first 10-15 µm of the adhesive[2]. Through-cure, cure across the depth of the adhesive, relies on longer wavelengths of UV light (UVA and UVB light) to initiate photopolymerization or crosslinking reactions. In order to initiate photochemical reactions with longer wavelengths of light, more light at those wavelengths is required to initiate a photochemical response[2]. Table 2 below provides a guide to the wavelength range for UVA, UVB, and UVC light[2].

Table 2. UV light wavelength range for UVA, UVB, and UVC light

Light	**Wavelength Range**
UVC	200-280 nm
UVB	280-320 nm
UVA	320-400 nm

The UV/Vis absorbance spectra of the crosslinking monomer, tackifier, and the two adhesive formulations, UV-Base and UV-Tackified, are shown in Figure 5. First, the crosslinking monomer has a high absorbance between 240 nm to 300 nm. UV-Base has a similar absorbance spectrum because the only chromophore in the adhesive is the crosslinking monomer. The absorbance of the highly-hydrogenated rosin acid tackifier at a concentration of 1 mg/ml has a broad absorption up to 330 nm. In

the UV-Tackified adhesive, the absorbance shifts to slightly higher wavelengths than the adhesive base, and this shift is due to the addition of the tackifier to the adhesive.

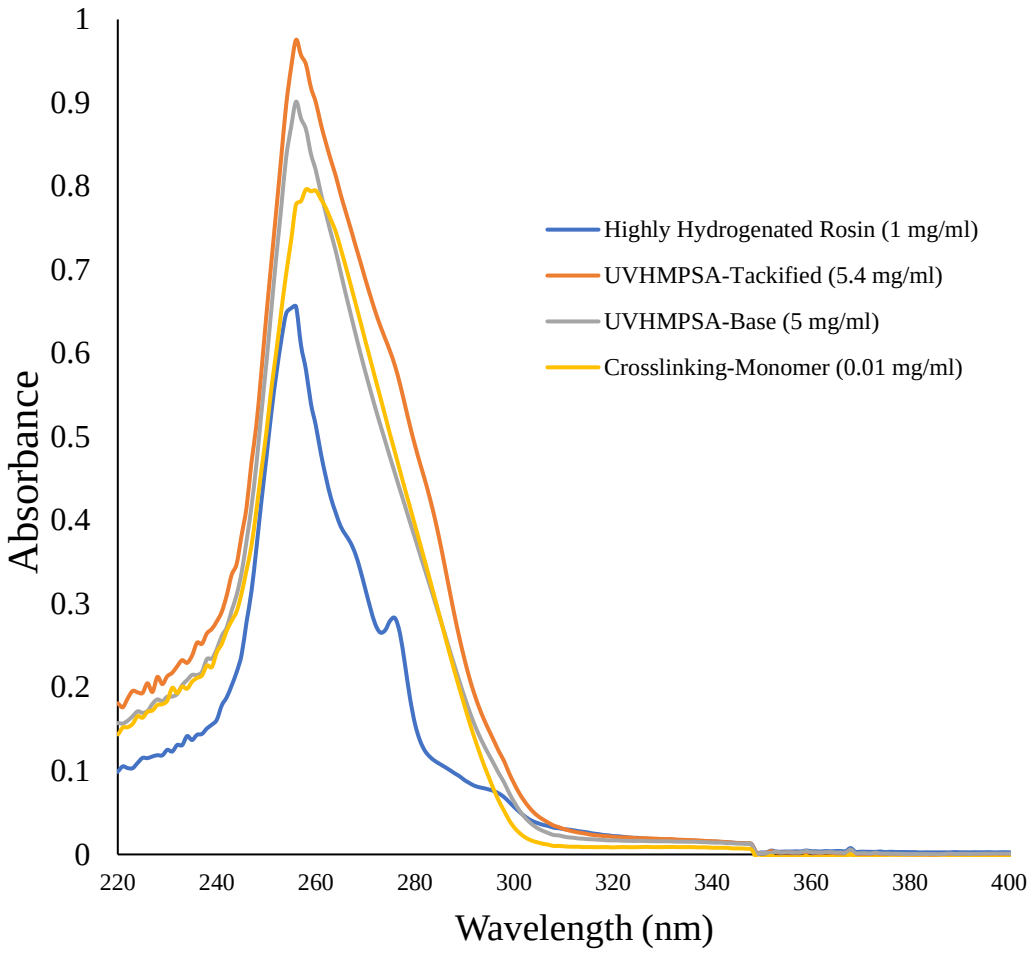

Figure 5. UV/Vis absorbance spectra of Tackifier, UV-Tackified, and UV-Base. All materials were dissolved in chloroform and diluted to obtain absorbances of less than 1.

As a point of reference, based on the Beer-Lambert law, an absorbance of 1 is equivalent to 10% transmittance[10]. An absorbance of 2 is equivalent to 1% transmittance. Therefore, it can be assumed that if the UV-Base and UV-Tackified are not diluted, the absorbance of short wavelengths of light will limit the depth of penetration of UVC light in to the adhesive at higher coat weights. Therefore, adhesives at higher coat weights, will rely on UVB and UVA light to efficiently cure across the depth of the adhesive. A minimum dose of UVC light at the surface of the adhesive may also be required to obtain good mechanical properties.

Radiometer UV Light Measurements

UV light output is traditionally measured using a radiometer. The UV dose or energy density is the amount of energy per unit of time applied to an area of the adhesive and is typically measured in mJ/cm^2. For this work, UV doses at several speeds were measured and kept consistent for each type of bulb or the thickness of the adhesive cured. For the work in this paper, representative UV light dose measurements are listed in Table 3 and Table 4 and will be referred to understand the amount of UVA,

UVB, and UVC light output by a specific lamp. UVC light output and line speed will be used as a reference and radiometer measurements typically have ±10% variation.

Table 3. Measured UV light output in UV dose (mJ/cm^2) for H-Bulb (Medium pressure mercury bulb) for UVA, UVB, and UVC light

Line setting (FPM)	**UVA Dose (mJ/cm^2)**	**UVB Dose (mJ/cm^2)**	**UVC Dose (mJ/cm^2)**
84	230	190	40
54	380	300	60
37	630	520	90
31	720	560	100
25	810	640	120

Table 4. Measured UV light output in UV dose (mJ/cm^2) for D-Bulb (Iron-doped bulb) for UVA, UVB, and UVC light

Line setting (FPM)	**UVA (mJ/cm^2)**	**UVB (mJ/cm^2)**	**UVC (mJ/cm^2)**
37	1030	340	41
31	1140	390	46
25	1400	470	57

It should be noted that at the same line speed when compared to the H-Bulb, the D-Bulb will output about ~50% less UVC light, ~25% less UVB light, and ~60% more UVA light when compared to the H-Bulb.

Peel Performance

UV-Base. For the initial analysis and point of comparison, the UV-Base was formulated with 0.3%, 0.5%, and 0.7% $Al(AcAc)_3$ based on the solids. These solvated adhesive samples were then coated and dried in a similar fashion to all of the UV cured hotmelt PSA samples presented in this paper. $Al(AcAc)_3$ crosslinked samples were not cured with UV light. The dry coat weight was 5 mil. Figure 6 shows that when the adhesive is transfer-coated or direct-coated, the peel strength decreases as the concentration of $Al(AcAc)_3$ crosslinker is increased. The difference in peel strength between transfer-coated and direct-coated adhesives is minimal.

Since $Al(AcAc)_3$ is distributed evenly throughout the adhesive[11], the results shown in Figure 6 illustrate that this even distribution of crosslinking density across the adhesive leads to consistent peel performance between direct and transfer-coated samples. Under these crosslinking conditions, the release liner being used in these studies does not appear to impact peel response significantly.

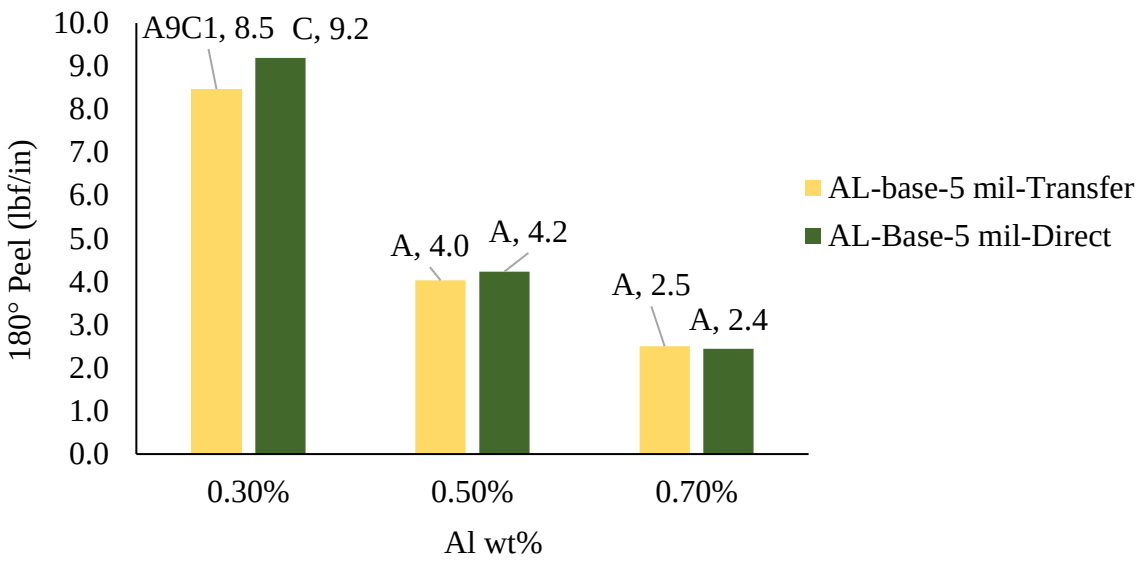

Figure 6. Peel performance of aluminum crosslinked UVHMPSA adhesives at 5 mil.

In this study, the potential for differential cure resulting from UV photocrosslinking was probed at adhesive thicknesses of 2 and 5 mil. The results of peel values of the UV-Base coated at 2 mil and cured with UV light (H-Bulb) are shown in Figure 7. At this coat weight, the peel difference is minimal at all UV doses, with transfer-coated material having a slightly higher peel value than direct-coated adhesive.

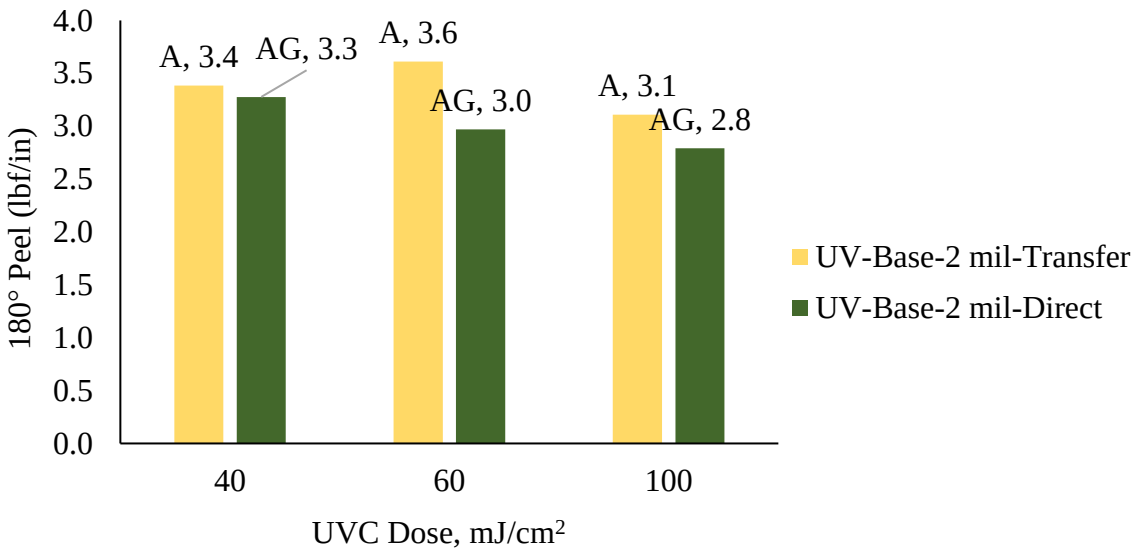

Figure 7. Peel performance of UV-cured UV-Base adhesive at 2 mil, cured with 40 (84 FPM), 60 (54 FPM), and 100 mJ/cm^2 (31 FPM) UVC light.

The results of peel values of UV-Base coated at 5 mil and cured with UV light (H-Bulb) are shown in Figure 8. At each UVC dose, the peel difference between transfer and direct coating is 1 to 1.5 lbf/in different. The direct-coated adhesives demonstrate a lower peel value at each UVC dose. This indicates that the surface being directly irradiated with UV light may have a higher cure/modulus than the side of the adhesive that does not get irradiated directly. At higher coat weights, there are more

chromophores to absorb UV light and reduce the amount of shorter wavelength light that penetrates through the adhesive. Because shorter wavelength light is more effective at activating the crosslinking molecule, less cure/crosslinking may occur across the depth of the adhesive. Additionally, the adhesive failure mode of peel adhesion for transfer-coated material was accompanied by adhesive ghosting (G). Ghosting is defined by a haze left behind after a peel test and may indicate a lower degree of crosslinking at the surface that was not irritated directly.

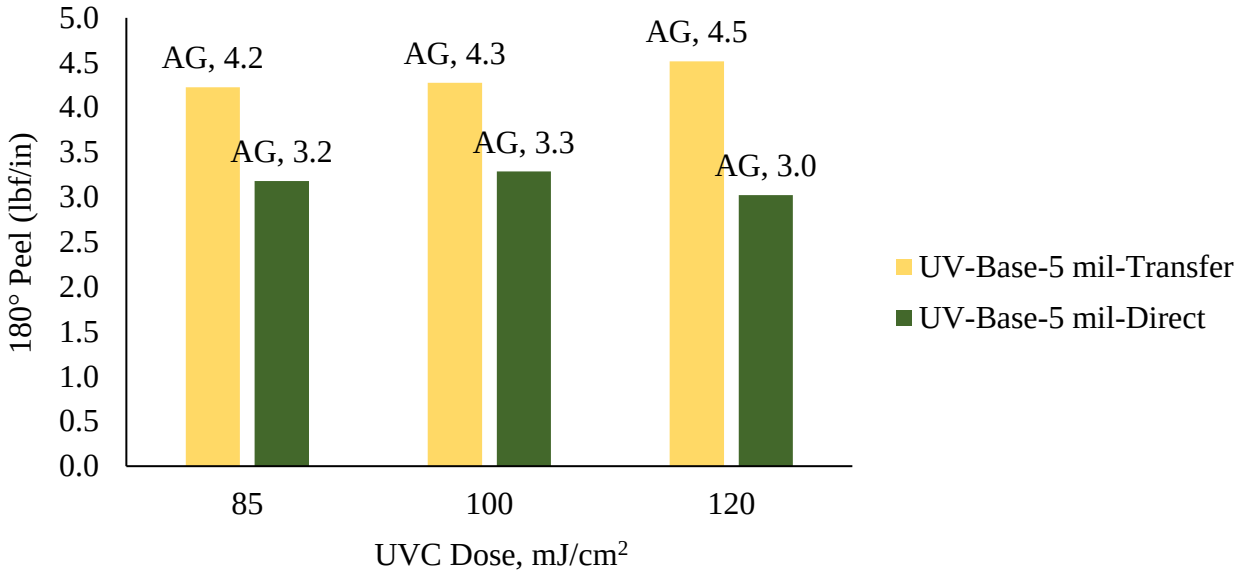

Figure 8. Peel performance of UV cured UV-Base adhesive at 5 mil cured with 85 (37 FPM), 100 (31 FPM), and 120 mJ/cm^2 (25 FPM) UVC light irradiated with a H-Bulb.

The results of peel values of UV-Base coated at 5 mil and cured with UV light (D-Bulb) are shown in Figure 9. At each UVC dose, the peel difference between transfer and direct coating is 0.2 to 0.5 lbf/in different. Compared to the results from the H-Bulb, the consistency of peel value at the irradiated surface and indirectly irradiated surface is improved. Additionally, the failure at the surface was observed to be adhesive only, without ghosting.

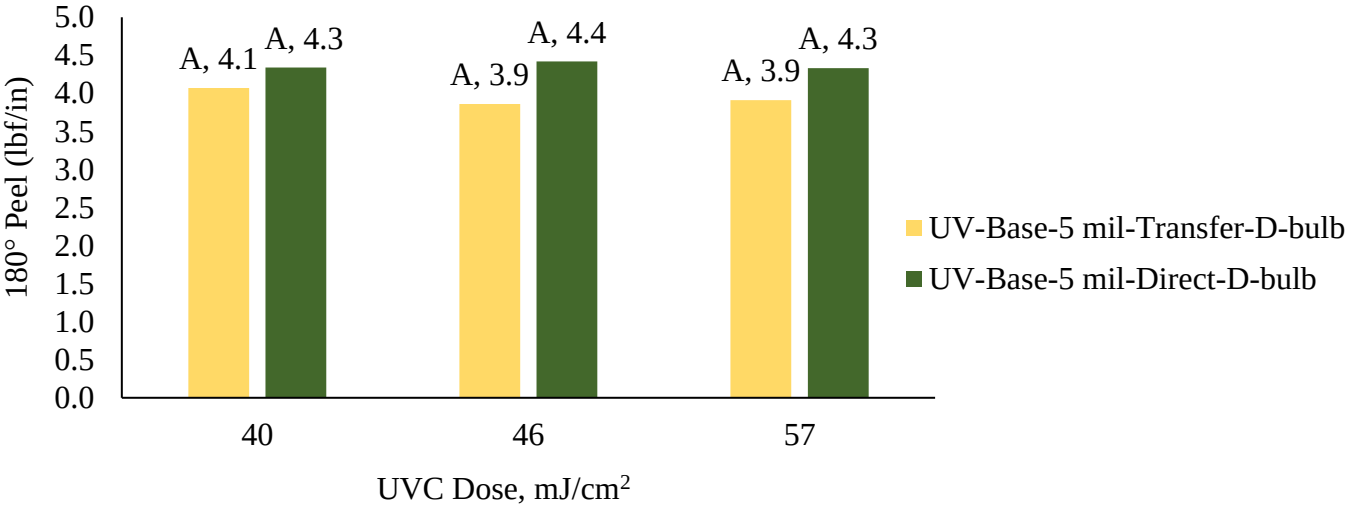

Figure 9. Peel performance of UV cured UV-Base adhesive at 5 mil cured with 40 (37 FPM), 46 (31 FPM), and 57 mJ/cm^2 (25 FPM) UVC light irradiated with a D-Bulb.

Because the D-Bulb has a UV light output with a high amount of UVA light compared to UVC light, it is hypothesized that the cure across the thickness of the adhesive can be altered when compared to curing with an H-Bulb. With less UVC light, the surface that is directly irradiated may crosslink less when compared to an H-Bulb. Surface cure is influenced by the ability of radicals generated by irradiation to overcome oxygen inhibition at the surface. The crosslinking monomer responds more efficiently to UVC light and therefore reacts more quickly with higher amounts of UVC light. The degree of crosslinking at the surface of the adhesive is impacted by the amount of UVC light output by the UV lamp chosen to cure the adhesive. UVA and UVB light penetrate through the adhesive to a greater extent, because they are less impacted by absorbance of the crosslinking monomer. In order to initiate the crosslinking reaction, more UVA/UVB light is required. Because oxygen inhibition is less in the bulk adhesive when compared to the surface, UVA and UVB light can effectively crosslink the adhesive below the first 5-10 microns (1). Therefore, alteration of the UV light output of the lamp may be an effective way of changing the performance of UV cured acrylic adhesives by balancing cure at the surface and across the thickness of the adhesive.

UV-Tackified. Addition of tackifier increases the UV absorption of the adhesive. Increased UV light absorption may have an impact on the penetration of light and the wavelength of light that can penetrate through the bulk of the adhesive. The results of peel values of UV-Tackified coated at 2 mil and cured with UV light (H-Bulb) are shown in Figure 10. Peel values for direct and transfer-coated material are similar and generally both decrease in peel strength with higher UVC doses. As previously seen in the UV-Base, the trend in peel adhesion is similar. Therefore at 2 mil thickness, the impact of cure across the adhesive is minimal.

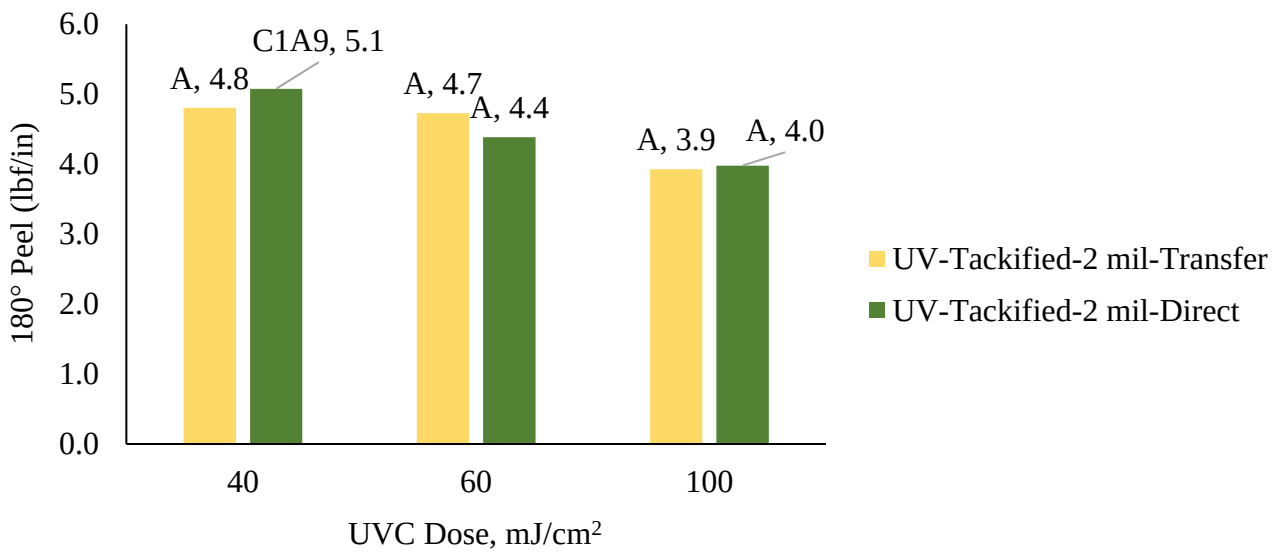

Figure 10. Peel performance of UV cured UV-Tackified adhesive at 2 mil cured with 40 (84 FPM), 60 (54 FPM), and 100 mJ/cm^2 (31 FPM) UVC light.

The results of peel values of UV-Tackified coated at 5 mil and cured with UV light (H-Bulb) are shown in Figure 11. Peel values between transfer-coated adhesive and direct-coated adhesive have a large differential. At 85 mJ/cm^2 UVC dose (37 FPM), the differential is approximately 4 lbf/in. At 120 mJ/cm^2 (25 FPM), the differential is 6.3 lbf/in.

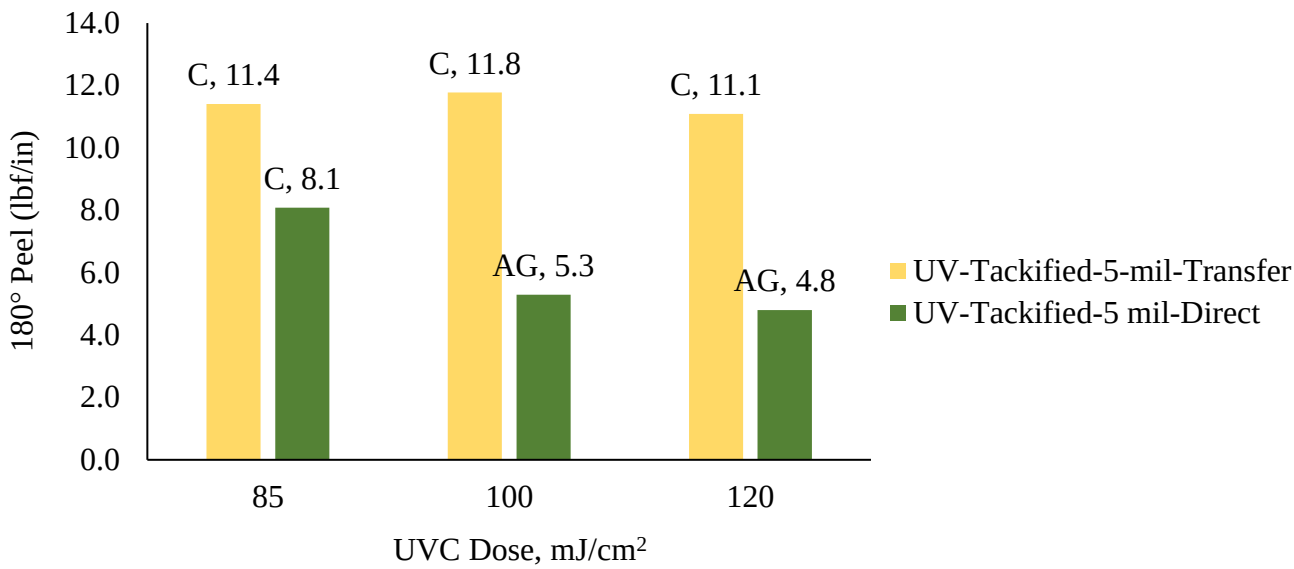

Figure 11. Peel performance of UV cured UV-Tackified adhesive at 5 mil cured with 85 (37 FPM), 100 (31 FPM), and 120 mJ/cm^2 (25 FPM) UVC light irradiated with a H-Bulb.

The results of peel values of UV-Tackified coated at 5 mil and cured with UV light (D-Bulb) are shown in Figure 12. At 40 mJ/cm^2 UVC light (37 FPM), the peel is almost identical when comparing transfer and direct-coated material. As the dose is increased, the differential adhesive between the transfer and direct-coated samples increased to a maximum of approximately 4 lbf/in. As the UVC dose is increased, the surface cure of the direct-coated adhesive likely increases leading to a decrease in peel value. Through-cure is also slightly improved as the failure mode of the adhesive is cohesive with an increase in peel strength in the transfer-coated adhesives at higher UVC doses. Direct-coated adhesives failure modes also transition from cohesive failure at 40 mJ/cm^2 UVC light to 90% adhesive failure at 57 mJ/cm^2 UVC light.

If 5 mil thick UV-Tackified adhesives are compared when cured with the D-Bulb vs. the H-Bulb, it becomes clear that the spectral output of the UV lamp has an impact on the adhesives characteristics. The H-Bulb gives more cure at the surface of the adhesive but appears to have less cure through the thickness of the adhesive leading to high peel levels at every UVC dose. Surface cure is indicated by the drop in peel strength of the direct-coated samples. The D-Bulb gives less cure at the surface, but may provide better through cure across the adhesive. With the D-Bulb, slight improvements in through cure may occur at higher UV doses based on the slight increase in peel strength of the samples cured with a higher UVC dose. Based on peel test results, the D-Bulb offers a better balance of peel strength between the two types of coating methods.

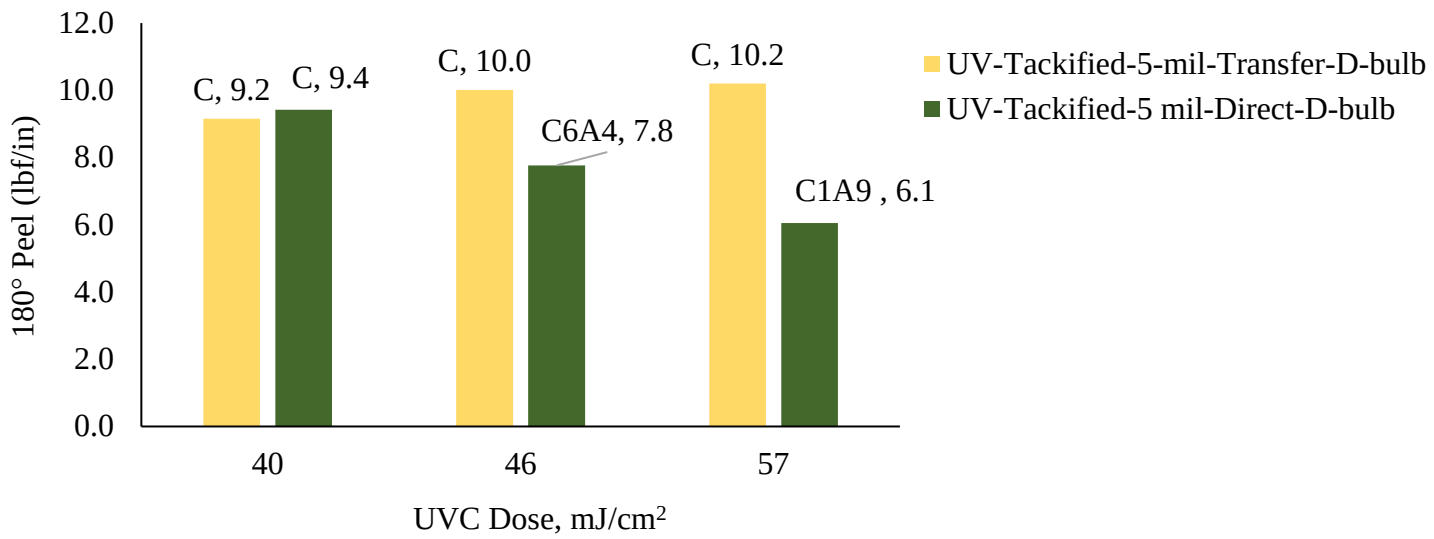

Figure 12. Peel performance of UV cured UV-Tackified adhesive at 5 mil cured with 40 (37 FPM), 46 (31 FPM), and 57 mJ/cm^2 (25 FPM) UVC light irradiated with a D-Bulb.

Loop Tack

UV-Base. Loop tack highlights the ability of an adhesives ability to quickly flow, wet-out, and adhere to a surface. Increasing crosslink density in an adhesive will generally increase the storage modulus and decrease wet-out. Results for loop tack tests are shown in Figure 13 for $Al(AcAc)_3$ crosslinked adhesives. The loop tack decreases with increasing amounts of $Al(AcAc)_3$ crosslinker in the adhesive. The loop tack also is consistent when comparing direct and transfer-coated adhesive samples. The consistent loop tack for each sample highlights the homogeneous/uniform nature of the $Al(AcAc)_3$ crosslinking technology. Increasing the amount of aluminum crosslinker in the adhesive demonstrates that wet out/modulus are impacted as expected.

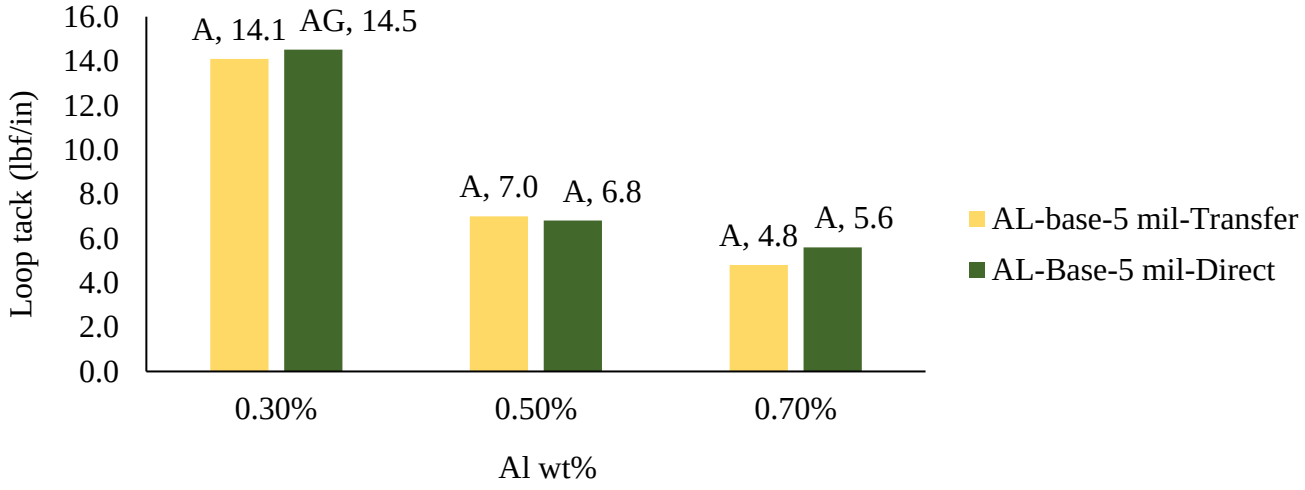

Figure 13. Loop tack performance of aluminum crosslinked UVHMPSA adhesives at 5 mil with 0.3, 0.5, and 0.7 wt% $Al(AcAc)_3$ crosslinker.

Results for loop tack tests are shown in Figure 14 for the UV-Base coated at 2 mil coat weights and cured with a H-Bulb at various UVC doses. As with peel data, the loop tack results are consistent when comparing transfer to direct coating. Loop tack slightly decreases with higher UV doses. At 2 mil coat weight of the UV-Base, the cure differential from transfer coat to direct coat was minimal.

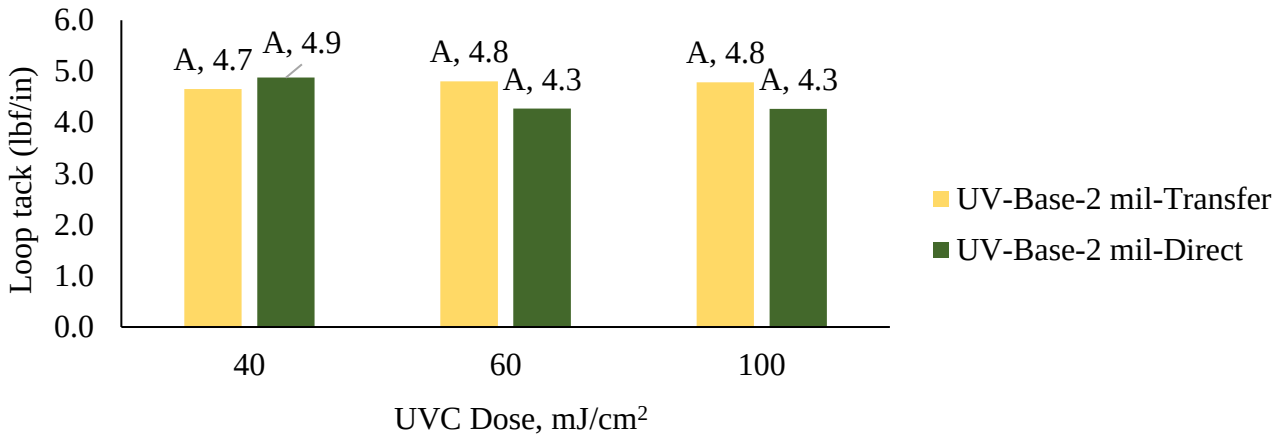

Figure 14. Loop tack performance of UV cured UV-Base adhesive at 2 mil cured with 40 (84 FPM), 60 (54 FPM), and 100 mJ/cm^2 (31 FPM) UVC light.

Results for loop tack tests are shown in Figure 15 for UV-Base coated at 5 mil coat weights and cured with a H-Bulb at various UVC doses. As with peel data for UV-Base at 5 mil coat weights, the loop tack differential between direct and transfer-coated samples increases when compared to the 2 mil coat weight samples. The differential increases with increased UVC dose. For transfer-coated adhesives, there is a slight increase in loop tack with increased UVC dose. For direct-coated samples, the loop tack value decreases with increased UVC dose. High UVC doses at the surface of the adhesive likely lead to higher cure/modulus at the surface and slower wet out for the loop tack test. Higher UVC doses only have a slight impact on loop tack of transfer-coated adhesives which indicates only modest improvements in through cure across the adhesive.

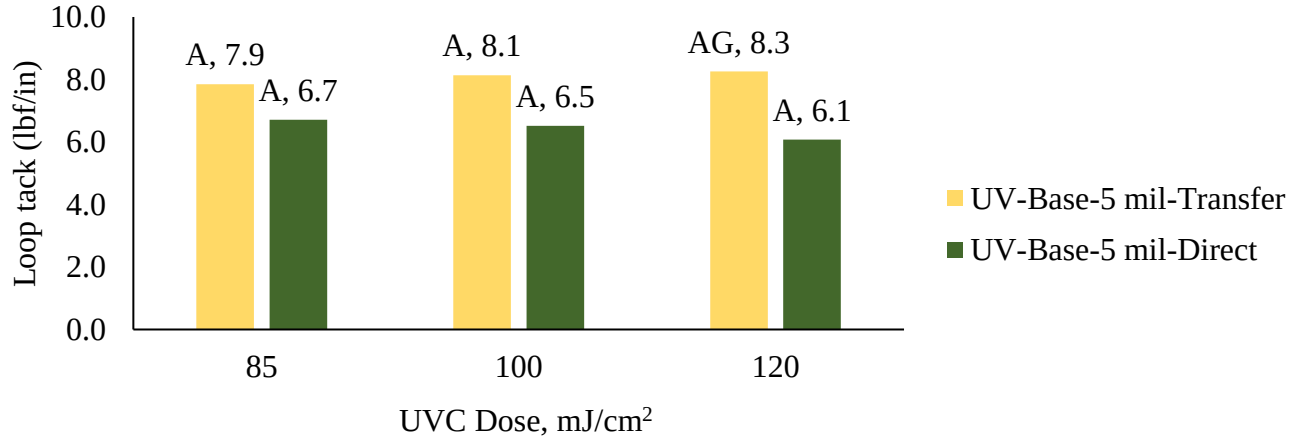

Figure 15. Loop tack performance of UV cured UV-Base adhesive at 5 mil cured with 85 (37 FPM), 100 (31 FPM), and 120 mJ/cm^2 (25 FPM) UVC light irradiated with a H-Bulb.

Results for loop tack tests are shown in Figure 16 for UV-Base coated at 5 mil coat weights and cured with a D-Bulb at various UVC doses. Similar to peel data, the loop tack results show minimal

difference between direct and transfer-coated adhesives. The D-Bulb with less UVC light and more UVA/UVB light appears to provide a more even cure across the adhesive based on loop tack and peel results.

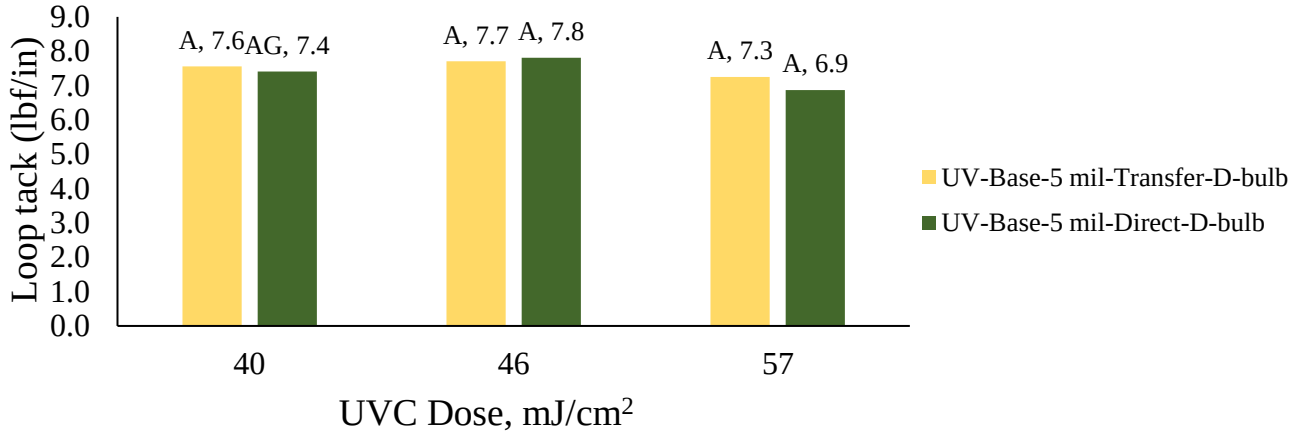

Figure 16. Peel performance of UV cured UV-Tackified adhesive at 5 mil cured with 40 (37 FPM), 46 (31 FPM), and 57 mJ/cm^2 (25 FPM) UVC light irradiated with a D-Bulb.

UV-Tackified. Results for loop tack tests are shown in Figure 17 for UV-Tackified coated at 2 mil coat weights and cured with a H-Bulb. Similar to peel test results, the addition of tackifier appears to have minimal impact on loop tack of direct and transfer-coated material at lower coat weight.

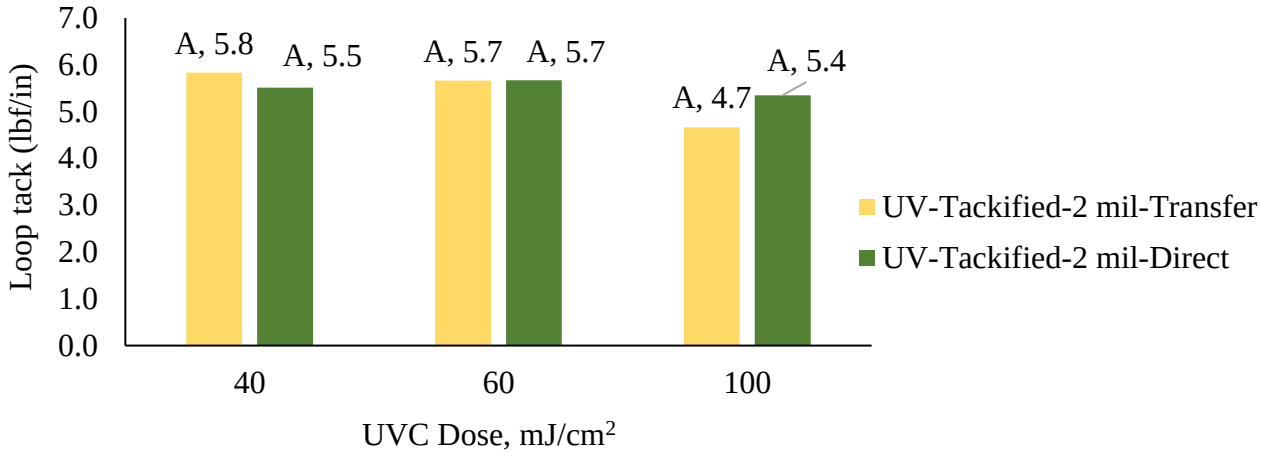

Figure 17. Loop tack performance of UV cured UV-Tackified adhesive at 2 mil cured with 40 (84 FPM), 60 (54 FPM), and 100 mJ/cm^2 (31 FPM) UVC light.

An increase in the coat weight of the UV-Tackified will decrease the transmission of UV light through the thickness of the adhesive. Results for loop tack tests are shown in Figure 18 for UV-Tackified coated at 5 mil coat weights and cured with a H-Bulb. As with peel test results, the difference in loop tack between direct coating and transfer coating increases significantly with higher UVC doses at 5 mil coat weight. Transfer-coated materials loop tack decreases slightly with higher UVC doses. Over the dose range studied, the directed coated adhesives have a sharp drop in loop tack when

compared to transfer-coated material. A loop tack differential of 0.9 to 2.5 lbf/in occurs over the UVC dose range studied.

The sharp change in loop tack demonstrates that the surface irradiated with UV light directly likely has a higher crosslink density. Therefore, the directly irradiated surface shows a different viscoelastic response when compared to the surface that is not directly irradiated. The high amount of UVC light that irradiates the surface efficiently crosslinks the surface of the direct-coated adhesive. As the light penetrates the adhesive, UV light is absorbed by the crosslinking monomer and tackifier. Therefore, lower UV doses penetrate across the adhesive. The absorption of UV light leads to less crosslinks across the adhesive from top (irradiated directly) to bottom (not irradiated). Reducing the UVC light and increasing the UVA/UVB light may lead to a balancing of the loop tack and reduce or eliminate the difference in tack values.

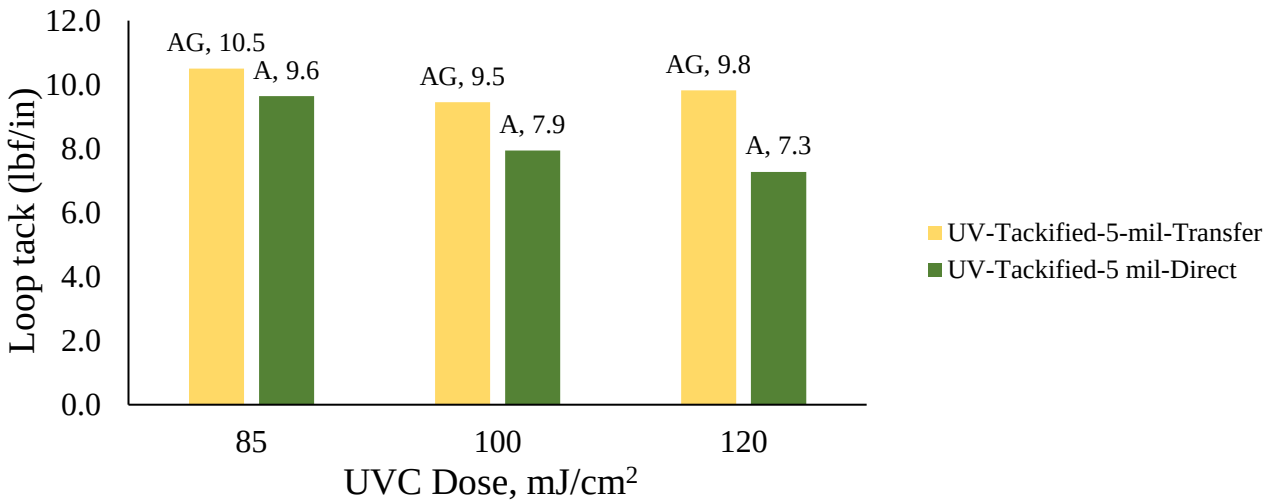

Figure 18. Loop tack performance of UV cured UV-Tackified adhesive at 5 mil cured with 85 (37 FPM), 100 (31 FPM), and 120 mJ/cm^2 (25 FPM) UVC light irradiated with a H-Bulb.

Results for loop tack tests are shown in Figure 19 for UV-Tackified coated at 5 mil coat weight and cured with a D-Bulb. A maximum of a 2 lbf/in differential are shown over the dose range studied. In general, the transfer-coated adhesives have a higher loop tack than the direct-coated material. The loop tack differential indicates that even with manipulation of the UV light spectral output a differential in the crosslink density and therefore the viscoelastic nature of the polymer still exists.

Comparison of the peel and loop tack results of the UV-Base and UV-Tackified adhesives when irradiated with the H-Bulb and D-Bulb illustrate the impact of additional chromophores on the cure of UVHMPSAs and the absorption of UV light across the adhesive. When the UV-Base was irradiated with the D-Bulb, peel strength and loop tack differences were minimized, compared to the outcomes of comparable H-Bulb irradiations. The UV-Tackified adhesive did have a decrease in the differential at all UVC doses, but equal performance of transfer and direct-coated adhesives was not achieved. Results show that the manipulation of the UV spectral output does impact the overall properties of the surface of the adhesive, but the crosslink density is likely never as homogeneous as aluminum crosslinking in traditional solvent PSA cure.

Additionally, the particular tackifier used in this study also introduces a small molecule that likely reduces crosslink density by providing a low molecular weight species for the crosslinking monomer to react with in the adhesive. The choice of tackifier is critical in obtaining good performance with minimal impact on crosslink density due to absorption of light, unsaturation, or labile proton that can be easily abstracted by the crosslinking monomer.

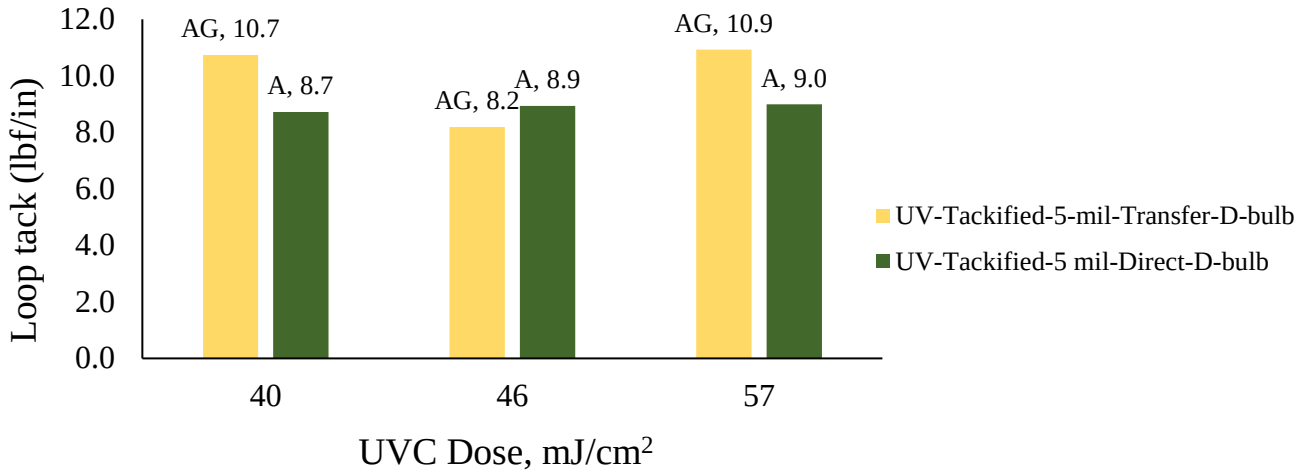

Figure 19. Loop tack performance of UV cured UV-Tackified adhesive at 5 mil cured with 40 (37 FPM), 46 (31 FPM), and 57 mJ/cm^2 (25 FPM) UVC light irradiated with a D-Bulb.

Static Shear

UV-Base. Results for static shear tests are shown in Figure 20 for Al(AcAc)$_3$ crosslinked adhesives at 5 mil coat weight. The static shear increases with increasing amounts of Al(AcAc)$_3$ crosslinker in the adhesive. Additionally, the static shear demonstrates similar failure modes and has consistent values for both transfer and direct-coated samples. At 0.7 wt% Al(AcAc)3, the shear samples did not fail (NF) over 628 hr, and the test was ended.

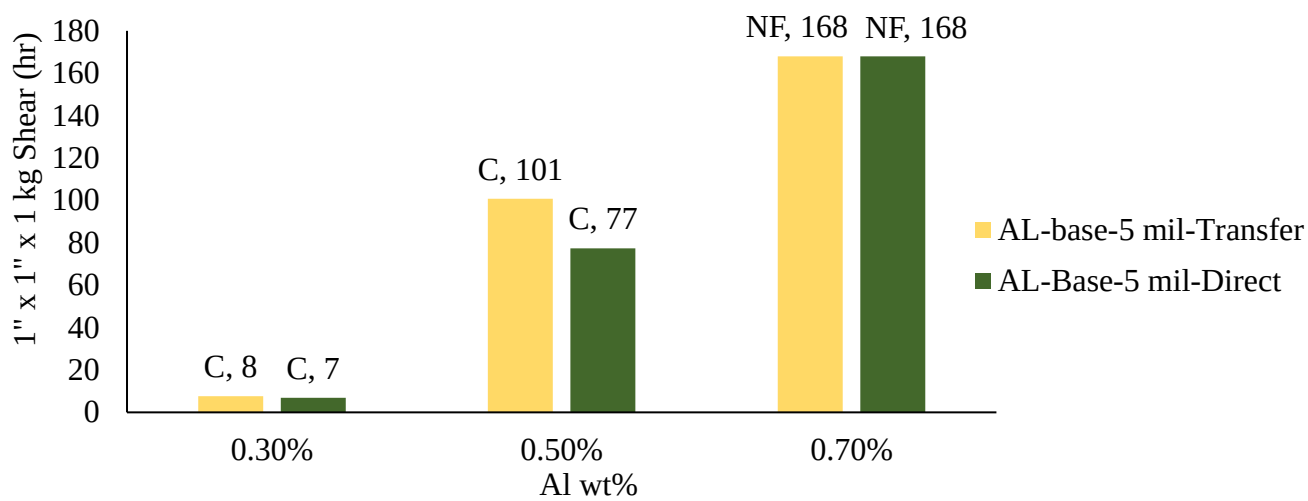

Figure 20. Static shear performance of aluminum crosslinked UV-Base adhesives at 5 mil with 0.3, 0.5, and 0.7 wt% Al(AcAc)$_3$ crosslinker.

Results for static shear tests are shown in Figure 21 for UV-Base crosslinked adhesives at 2 mil coat weight and cured with an H-Bulb. Shears increase from 40 to 60 mJ/cm^2 UVC dose. The failure mode of transfer-coated adhesives remains cohesive for each UVC dose. At 60 mJ/cm^2 the failure mode of the direct-coated adhesive is 70% adhesive failure. When the dose is increased to 100 mJ/cm^2, the shear value decreases for both the direct-coated and transfer-coated adhesives. The change in failure

mode at the surface of the adhesive is due to the high UVC dose at the surface of the adhesive which leads to poor wet out during the shear test.

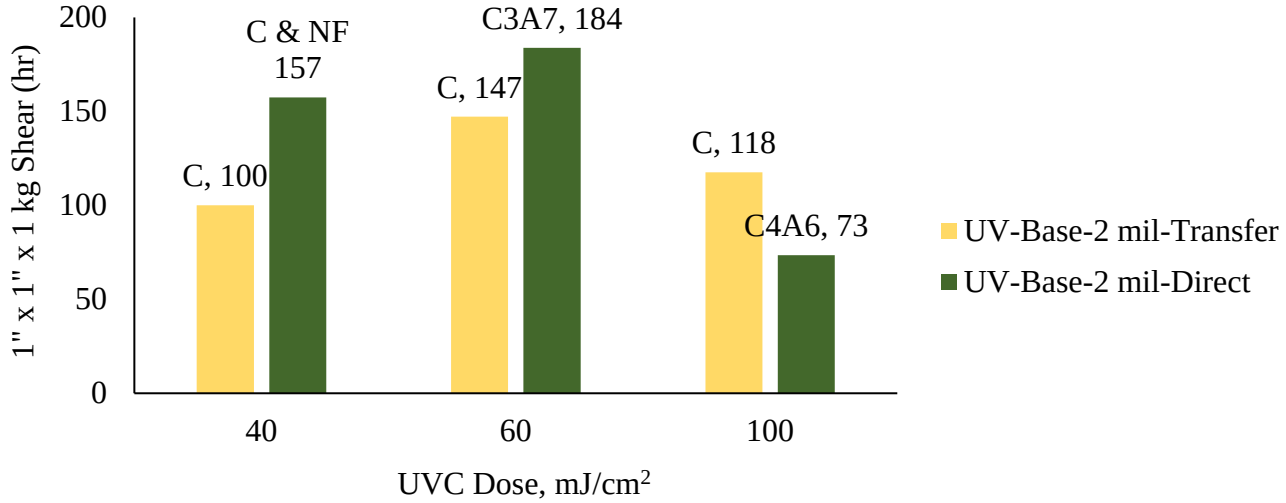

Figure 21. Static shear performance of UV cured UV-Base adhesive at 2 mil cured with 40 (84 FPM), 60 (54 FPM), and 100 mJ/cm^2 (31 FPM) UVC light.

For UV-Base an increase in the coat weight and UV dose required for cure, leads to a dramatic shift in shear values when comparing transfer and direct-coated adhesive. Results for static shear tests are shown in Figure 22 for UV-Base crosslinked adhesives at 5 mil coat weight and cured with an H-Bulb. Transfer-coated adhesives fail cohesively, but direct-coated adhesives fail adhesively at every UVC dose. Direct-coated adhesives are also lower in shear than transfer-coated adhesives. The dramatic difference for direct-coated adhesives is attributed to the high UVC dose at the surface. The high UVC dose at the directly irradiated surface leads to a high modulus at the surface and poor wet out of the stainless-steel surface. Therefore, the mixed failure-mode of static shear test can be misleading when relying on shear only as a measure of the cohesive strength of the adhesive.

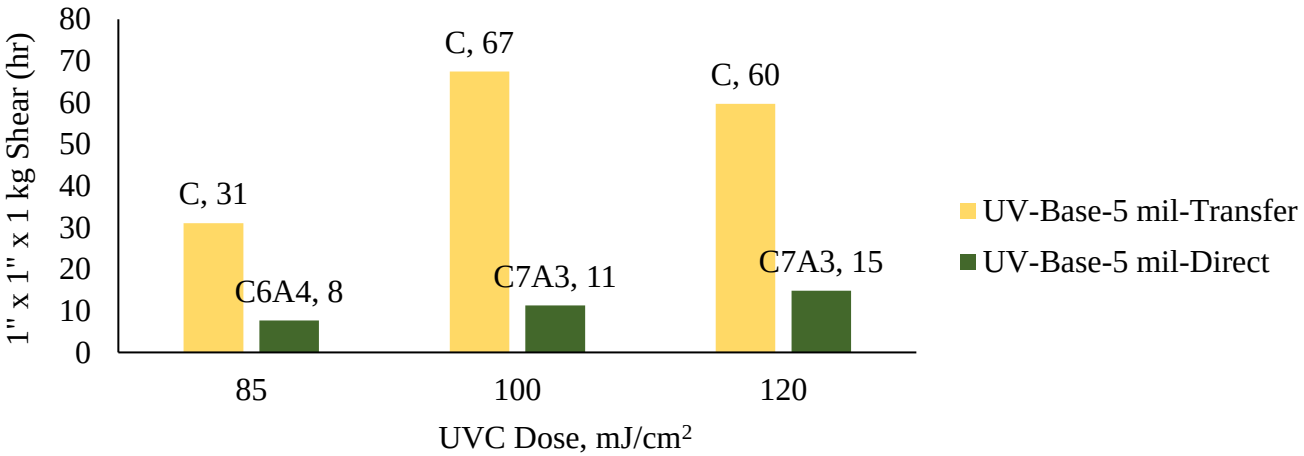

Figure 22. Static shear performance of UV cured UV-Base adhesive at 5 mil cured with 85 (37 FPM), 100 (31 FPM), and 120 mJ/cm^2 (25 FPM) UVC light irradiated with a H-Bulb.

For UV-Base cured with the D-Bulb, the shear results are similar to 5-mil UV-Base cured with the H-Bulb (see Figure 23). Even with the lower amount of UVC light, the direct-coated samples still have a high amount of adhesive failure leading to low shear values. The shear values for transfer-coated adhesive are like the H-Bulb cured adhesives. These results show that with the UV-Base, the surface cure does have an impact on the wet out of surfaces and viscoelastic properties of the surface.

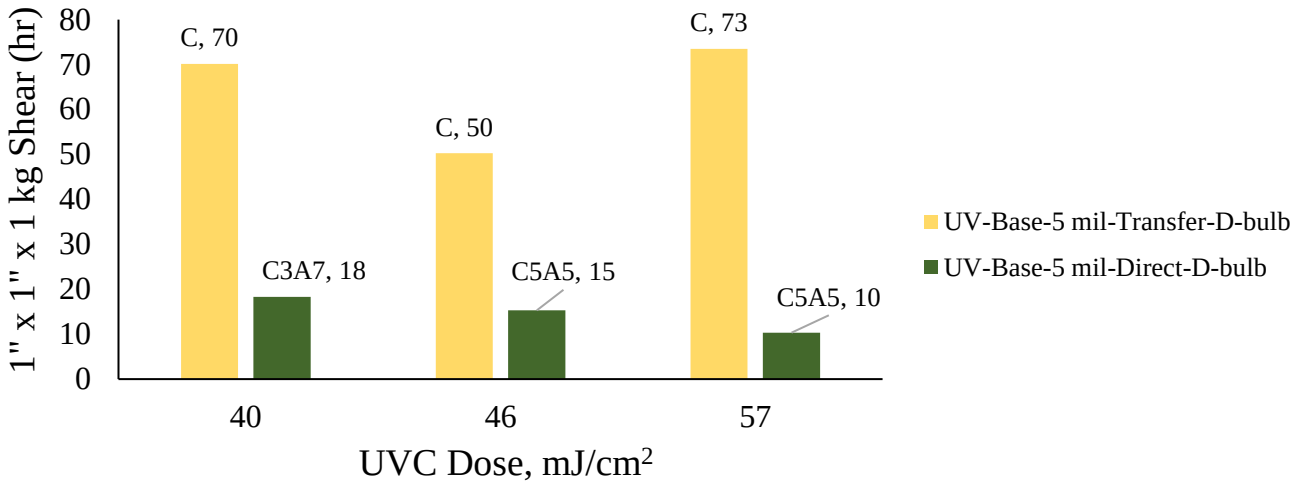

Figure 23. Static shear performance of UV cured UV-Base adhesive at 5 mil cured with 40 (37 FPM), 46 (31 FPM), and 57 mJ/cm^2 (25 FPM) UVC light irradiated with a D-Bulb

UV-Tackified. Tackifier added to the UV-Base adhesive impacts the surface cure and cure through the bulk of the adhesive. Results for static shear tests are shown in Figure 24 for UV-Tackified adhesives at 2 mil coat weight and cured with the H-Bulb. Shears for direct-coated adhesive are higher than transfer-coated material. When compared to the UV-Base, the shears are higher and in many cases for direct-coated adhesives never failed (shears were removed after 628 hr). Failure mode of both transfer coat and direct-coated adhesives was cohesive. Addition of the tackifier improved wet-out at the surface of the adhesive enough that wet-out occurred efficiently for direct-coated samples and shear values exceeded even the UV-Base values for direct-coated samples. Transfer-coated UV-Tackified shear values were on average less than shear values for UV-Base samples. The reduction in shear is typically expected for samples formulated with a tackifier. The high shear values for the direct-coated adhesives when compared to transfer-coated adhesives indicate that through cure may be impacting the results.

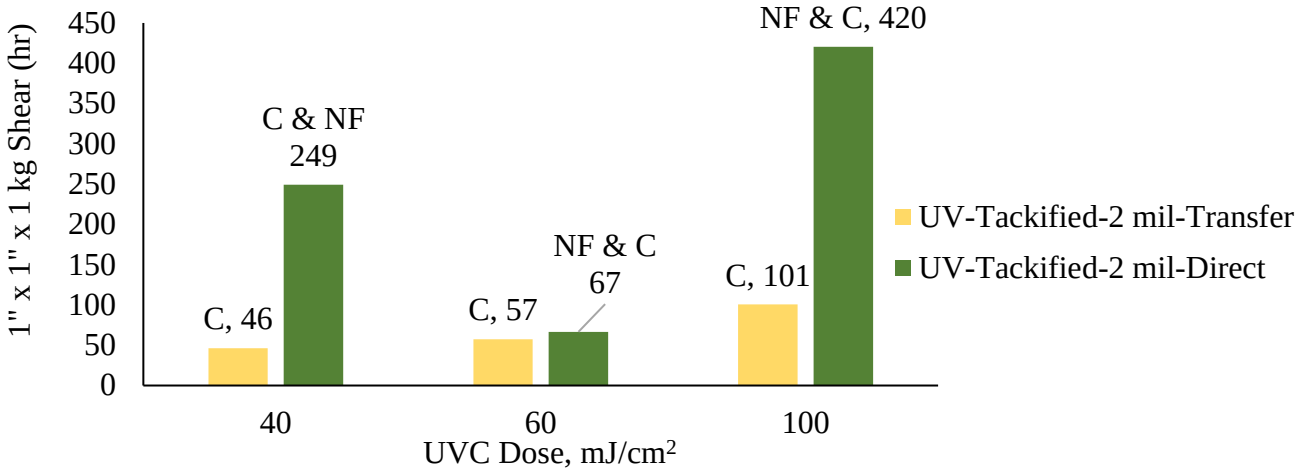

Figure 24. Static shear performance of UV cured UV-Tackified adhesive at 2 mil cured with 40 (84 FPM), 60 (54 FPM), and 100 mJ/cm^2 (31 FPM) UVC light. Note: sample cured at 60 and 100 mJ/cm^2 had two samples that did not fail (NF) after 628 hr.

The results for UV-Tackified coated at 5 mil coat weight and cured with the H-Bulb are shown in Figure 25. Like the 2-mil coated UVHMPSA-Tackifed samples, the direct-coated material shear outlasts the transfer-coated adhesives. Failure mode is cohesive for all samples, with the exception of the direct-coated adhesive cured with 120 mJ/cm^2. As the UVC dose is increased, the difference in direct-coated and transfer-coated adhesives increases until the failure mode changes to a mix of cohesive and adhesive failure at 120 mJ/cm^2. The direct-coated shears change drastically over the dose range studied, and this indicates that the directly irradiated surface is changing due to increased UV light exposure. Limited gains in through cure may be occurring, but the shear value for transfer-coated samples remains consistent across the studied dose range.

Transfer-coated adhesive is irradiated at the surface and then transferred to the PET facestock. Therefore, the adhesive surface being tested is not directly irradiated. The test surface for transfer-coated materials likely has a lower crosslink density than the surface of the direct-coated adhesive. Because this surface has a lower crosslink density, the modulus is likely lower. Lower modulus may lead to a thin weak layer of adhesive at the stainless-steel surface and therefore lower shear values due to the lower modulus at that surface (less chain entanglement and more flow at the surface).

If the static shear results of the 5-mil UV-Tackified are compared to the 5-mil UV-Base results, there are some noticeable differences. First, the direct-coated shears for the UV-Tackified samples are failing cohesively, versus a mix of cohesive and adhesive failure for UV-Base at 5-mil coat weights. The mixed failure mechanisms of the UV-Base indicate poor wet-out of the stainless-steel plates by the UV-Base and lower shear values result. A longer dwell time before hanging shear weights on the samples may make the data more reproducible and more accurate shear value for the UV-Base. UV-Tackified samples generally show higher shear values when direct-coated than the UV-Base.

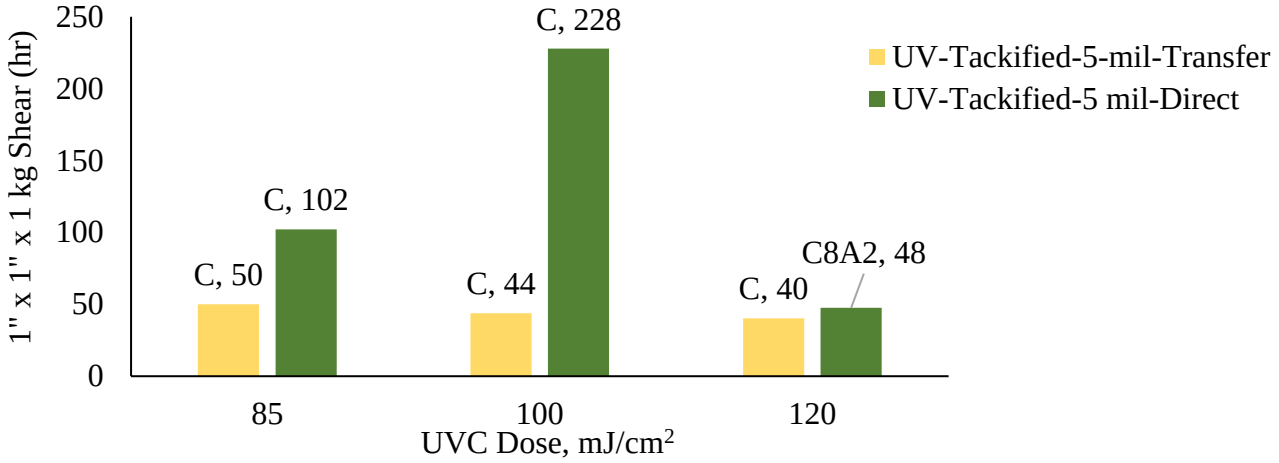

Figure 25. Static shear performance of UV cured UV-Tackified adhesive at 5 mil cured with 85 (37 FPM), 100 (31 FPM), and 120 mJ/cm^2 (25 FPM) UVC light irradiated with a H-Bulb.

The results for UV-Tackified coated at 5 mil coat weight and cured with the D-Bulb are shown in Figure 26. Over the dose range studied, the direct-coated adhesives shear values rose with increased UV dose. Transfer-coated adhesives have a slight increase in shear value over the dose range. All samples failed cohesively. When compared to results from the H-Bulb irradiated samples, the shears for transfer-coated adhesives have comparable shear values while direct-coated adhesives are slightly lower.

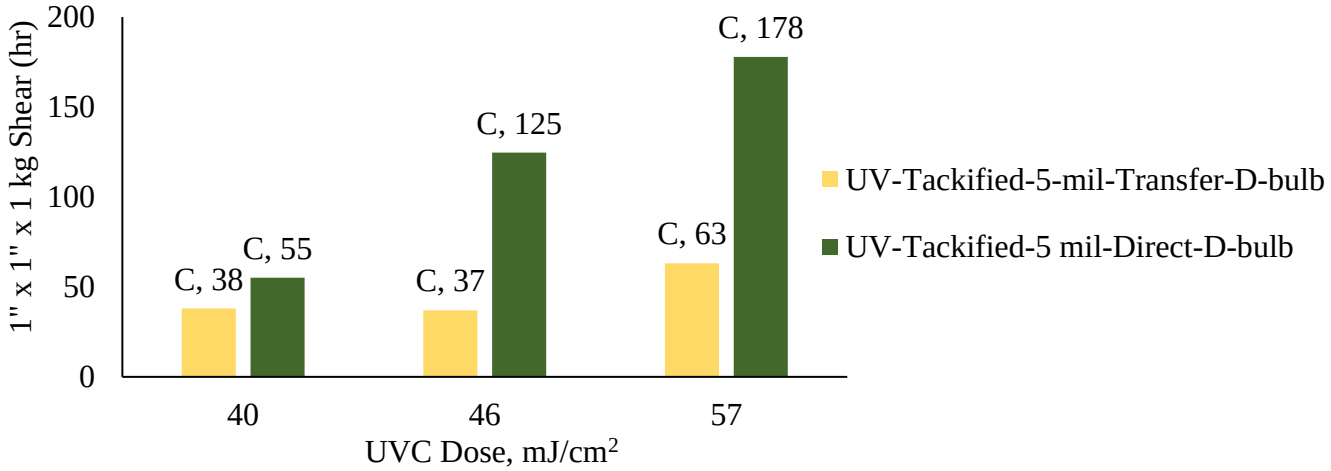

Figure 26. Static shear performance of UV cured UV-Tackified adhesive at 5 mil cured with 40 (37 FPM), 46 (31 FPM), and 57 mJ/cm^2 (25 FPM) UVC light irradiated with a D-Bulb.

Williams Plasticity

UV-Base. Williams Plasticity is an indirect measure of the storage modulus of an adhesive and is not impacted by surface effects (*i.e.*, wet-out/flow). The results of all UVHMPSAs are shown in Figure 27. As a base line, the Williams Plasticity of the 5 mil samples with 0.7 wt% $Al(AcAc)_3$ are similar to values demonstrated by 2 mil coat weight UV-Base when cured with the H-Bulb. The Williams Plasticity of the 5 mil samples with 0.5 wt% $Al(AcAc)_3$ are similar to Williams Plasticity values demonstrated by 5 mil coat weight UV-Base when cured with the H-Bulb or D-Bulb.

As previously shown, the properties such as peel, loop tack, and static shear of UV cured samples respond differently than the $Al(AcAc)_3$ crosslinked samples. Although each type of light used to cure 5 mil thick samples yields a similar Williams Plasticity to $Al(AcAc)_3$ crosslinked samples, the performance characteristics that rely on both viscoelasticity and surface effects (peel, loop tack, and shear), yield different results. The H-Bulb cured samples have a high differential in peel, loop tack, and shear at all UVC doses for UV-Base samples. The D-Bulb has a smaller differential in peel and loop tack values for UV-Base samples, but still has substantial differential in shear.

The difference in these performance characteristics while having similar Williams Plasticity values indicates that the samples cured with light likely have a differential modulus across the thickness of the sample. A differential modulus across the adhesive is highlighted by the sensitivity of shear tests of UV cured samples to fail with mixed cohesive/adhesive failure (direct-coated/testing the irradiated surface) and the large differential in loop tack. All $Al(AcAc)_3$ crosslinked UV-Base samples failed cohesively, even when peel and tack values decreased to substantially lower values than UV light-cured adhesives. The cohesive failure with $Al(AcAc)_3$ crosslinked samples demonstrates that cure is homogenous across the sample. The mixed mode failure of UV cured samples demonstrates a higher modulus at the surface that was directly irradiated (and tested) compared to the surface that was not directly irradiated.

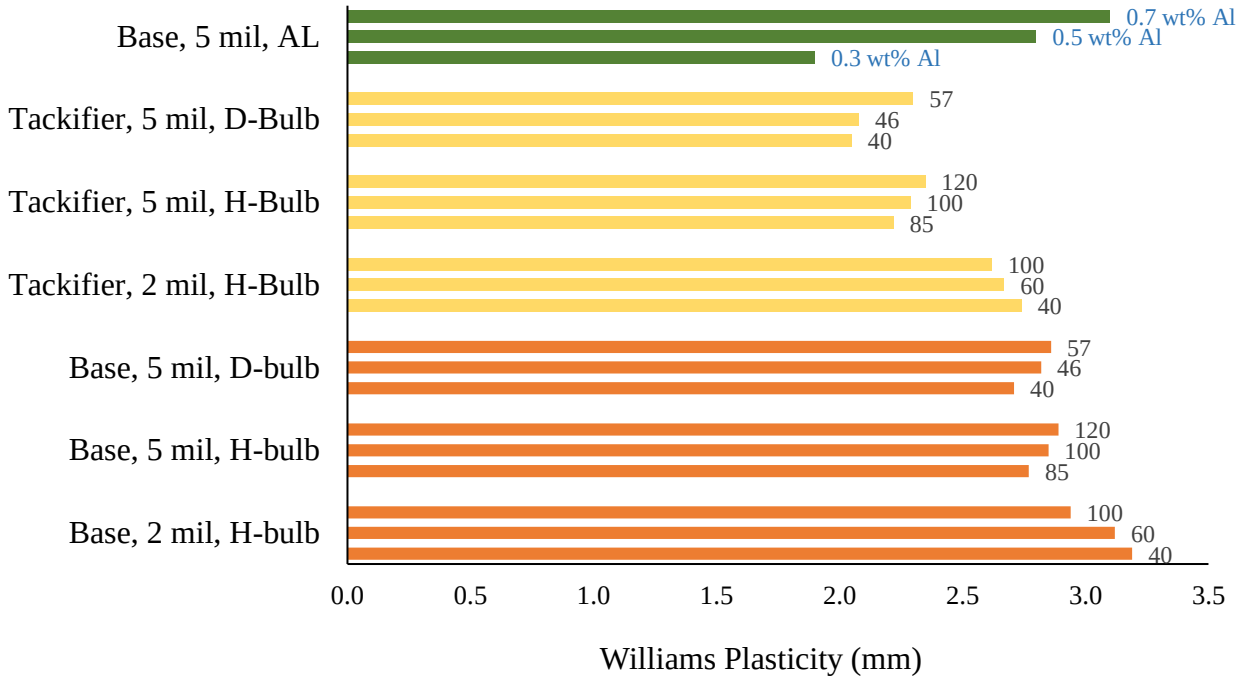

Figure 27. Williams Plasticity of UV-Base and UVHMPSA-tackified samples. Numbers at the end of the columns are UVC dose (mJ/cm^2) or $Al(AcAc)_3$ weight percent.

UV-Tackified. The UV-Tackified samples coated at 2 mil coat weight demonstrate the highest Williams Plasticity. Increasing the coat weight leads to a lower Williams Plasticity result. UV-Tackifed samples cured with the H-Bulb at 5 mil coat weight have slightly higher Williams Plasticity values than samples cured with the D-Bulb. Because 2 mil samples have a higher WP than the 5 mil thick samples, the cure across the samples is not homogenous at the dose ranges chosen for this study. The absorbance of UV light across the thickness of the adhesive makes this condition difficult to overcome with the types of UV lights chosen for this study without over-curing the surface. Lights that only output

UVB/UVA light might be a better choice to help facilitate less cure at the surface and more even cure across the thickness of the adhesive. Oxygen inhibition and therefore weakness at the surface that is directly irradiated may occur or a very high UV light exposure may be required to get adequate cohesive strength.

Conclusion

During this work, it was shown that the adhesive formulation, adhesive thickness, coating method, and type of UV light all impact the adhesive properties of UV-HMPSAs. First, it was shown that if UV-Base was cured with a traditional $Al(AcAc)_3$ crosslinking mechanism, similar adhesive properties were observed for both direct and transfer-coated adhesives. Consistent performance with both coating methods illustrates that the cure with $Al(AcAc)_3$ was uniform across the adhesive and that the release liner does not have a substantial impact on the surface of the adhesive.

In general, UV-HMPSAs cured with the H-Bulb demonstrate a different adhesive performance for peel, loop tack, and shear when comparing the directly irradiated (direct-coated) and indirectly irradiated (transfer-coated) surfaces. An increase in thickness and addition of additives that absorb UV light increased the variance in performance for each coating method. A difference in crosslink density at each surface due to varied light exposure likely leads to different viscoelastic response during testing. Cohesive strength was increased with higher UVC dose, but shear failure mode transitioned to mixed adhesive/cohesive failure, resulting in less consistent results. In the future a longer dwell time may improve results.

Irradiation of the adhesives with a D-Bulb at the same line speeds as the H-Bulb, lead to an adhesive with more consistent performance for each coating method. At the same speed, the D-Bulb typically emits less UVC light and more UVA light, which led to a more balanced cure through the adhesive over the dose range studied. Williams Plasticity showed minimal difference between samples irradiated with the H-Bulb and D-Bulb. The Williams Plasticity result highlights the fact that performance differences are likely related to a varied crosslink density across the adhesive thickness, which can be tuned by the spectral output of the UV light used to cure the adhesives.

The results of this study highlight the differences between traditional solvent-based pressure sensitive adhesives and UV-HMPSAs that need to be considered when evaluating UVHMPSAs compared to traditional solvent-based PSAs. An understanding of the UV-HMPSA formulation and interaction with light will allow for a thoughtful process to be designed for curing the adhesive to obtain the desired performance. Additionally, UVHMPSAs performance can be adjusted to manipulate the UV-HMPSAs crosslink density and therefore the viscoelastic performance.

References

1. Green, W. Arthur. *Industrial Photointiators.* Boca Raton : Taylor & Francis Group, 2010. 978-1-4398-2745-1.
2. Edinburgh Insturments. *Blog The Beer Lambert Law.* [Online] March 21, 2023. https://www.edinst.com/blog/the-beer-lambert-law/.
3. Johnston, John. *Pressure Sensitive Adhesive Tapes - A Guide to Their Function, Design, Manufacture, and Use.* Northbrook, IL : Pressure Sensitive Tape Council, 2003. 0-9728001-0-7.
4. *Test Methods for Pressure Sensitive Adhesive Tapes, 17th edition.* Northbrook, IL : Pressure Sensitive Tape Council, 2000.
5. Gerd Rehmer, Andreas Boettcher, Michael Portugall. *Benzophenone Derivatives and Their Preparation. 5264533* USA, November 23, 1993.

6. Yuxia liu, Peter Palasz, Charles W. Paul, Paul B. Foreman. *Cationic UV-Crosslinkable Acrylic Polymers for Pressure Sensitive Adhesives. US 8796350 B2* United States, August 5, 2014.
7. Fouassier, J.P. *Photoinitiaton, Photopolymerization, and Photocuring: Fundamentals and Applications.* Cincinnati, Ohio : Hanser/Gardner Publications, Inc., 1995. 1-56990-146-5.
8. Terry E. Hammond, Xiaochuan Hu. *Ultraviolet Radiation Curable Pressure Sensitive Acrylic Adhesive. 8735506 B2* USA, May 27, 2014.
9. Terry E. Hammond, Xiaochuan. *Ultraviolet Radiation Curable Pressure Sensitive Acrylic Adhesive. 9475968* USA, October 25, 2016.
10. Dietliker, Kurt. *A Compilation of Photointiators: Commercially Available for UV Today.* Edinburgh : SITA Technology Limited, 2002. 947798676.
11. *The Plasticity of Rubber and Its Measurements.* Williams, Ira. 4, Akron, OH : American Chemical Society, 1924, Industrial and Engineering Chemistry, Vol. 16.

Acknowledgements

Thank you to Nicholas Kelley for assisting with the production of UV-HMPSAs. Thank you to Mark Stuart (UV/Vis Absorption analysis and sample prep) and Bethany Staggemeier (UV/Vis Absorption analysis and sample prep) for their efforts. Additionally, I would like to thank Patrick Eaton and Lars Kilian for many discussions on the interesting ideas outlined in this paper and assistance with editing.