NEW DEVELOPMENTS IN UV CURABLE LAMINATING ADHESIVES – FORMULATING FOR ENHANCED ADHESION AND SERVICE PROPERTIES

By Michael Bailey
TS&D Manager, Adhesives and Sealants, Advanced Materials
Sartomer Americas

Abstract

UV curable laminating adhesive use has grown in applications ranging from flexible packaging to complex electronic assemblies. This presents quite a challenge in terms of delivering formulations that provide adhesion to a variety of substrates while simultaneously meeting the demand for continuous improvement in service environment performance. This paper will describe the development of laminating adhesive oligomers and formulating strategies that give formulators the ability to keep pace with the ever evolving end-use performance requirements.

Introduction

Laminating adhesives find use in converting operations such as roll to roll and sheeting of flexible packaging and labeling products. These products can be used in food, medical, industrial and transportation applications that require bonding to a variety of substrates including plastic films, foil or metallized film, and paper or paperboard. More recently, they have found use in electronic applications including DVD's, high quality displays, and solar panels that require enhanced adhesion to flexible and rigid plastics, metals and glass, as well as improved durability for longer service life.

Although UV curable laminating adhesive material costs are generally higher than solvent-based and waterborne adhesives, they provide many benefits to the end-use product manufacturer including 1) reduced emissions due to low VOC and 100% reactivity 2) energy and production cost savings due to elimination of thermal or extended ambient temperature drying steps and 3) a reduction of waste due to the unlimited shelf life of the formulation that allows for continuous re-use versus two-component adhesive technologies. In terms of performance, the proper selection of UV curable materials provides strong adhesion to a variety of substrates at low adhesive thickness, faster curing and resistance to both physical stresses and harsh environmental conditions.

The most common UV curable laminating adhesives are referred to as "dry" laminations which means they have no tack after curing. The key challenge for UV curable laminating adhesives is to deliver enough energy to cure the adhesive, sandwiched between two substrates,

and achieve strong bonding. Generally, this requires one of the substrates be transparent. However, many factors such as additives in the substrate, orientation of the substrate and surface treatments on the substrate can affect clarity. Therefore, it is important to match the photoinitiator (PI) to the energy output of the UV lamps in use and the transparency of the substrate being cured through.

In this paper, we will discuss the components of a UV curable laminating adhesive formulation, the role each component serves in the processing and application of the adhesive, and the effect each component has on reactivity and final cured adhesive performance properties. Specifically, we will discuss the effect acrylate oligomer and monomer type, functionality, molecular weight and ratio has on adhesion and share how these factors can affect longer term durability based on UV, temperature and humidity exposure testing.

Experimental

Low cost UV cure adhesive formulations for low end, high volume packaging or labeling applications generally consist of inexpensive acrylate monomers, non-reactive resins such as acrylic polymers or hydrocarbon resins, and low cost photoinitiators. However, the objective of the experimental design studies discussed here is to provide formulators strategies to consider when developing UV cure laminating adhesives exhibiting stronger bonds and higher performance for more demanding applications. To achieve stronger bonds and higher performance, other specialty acrylate functional monomers and some specialty acrylate functional oligomers are added in addition to or in place of the non-reactive resins.

Five different design studies described below were conducted to evaluate the effect of acrylate monomer and acrylate oligomer type, functionality, molecular weight and ratio on adhesion to various film laminations. The five studies included the following:

1) Monomer Selection Effect on Adhesion
2) Oligomer Selection Effect on Adhesion
3) Oligomer/Monomer Blend Effect on Adhesion & Application Viscosity
4) Oligomer/Mixed Monomer Effect on Adhesion & Application Viscosity
5) High Performance Oligomer Effect on Adhesion after Environmental Exposure

In order to understand the full influences of acrylate functional monomers and acrylate functional oligomers the formulations tested did not contain any inert resin modifiers or any specialty adhesion promoters. The basic UV cure laminating adhesive formulations used in these studies are described in Table 1 below. Photoinitiator concentration and energy cure conditions were adjusted accordingly to match the substrate.

Table 1. Basic UV Cure Laminating Adhesive Formulation

Components	Level
Oligomers	30% to 70%
Monomers	70% to 30%
Photoinitiators	1% to 3%

Sample Preparation

All components of the formulations tested were blended overnight at low shear to make sure they were fully mixed. Solid photoinitiators were pre-dissolved in the monomer component with low heat and low shear prior to mixing in the oligomer. Formulation viscosity was measured in cP at 25°C using a Brookfield Digital RVT Viscometer following ASTM D2196 test method. 8" x 12" laminations were prepared by wire-wound rod drawdown method on the 1st film and pressing the 2nd film on top using a 5 lb roller to a controlled thickness. The laminations were then cured using the selected cure conditions described below and equilibrated for 72 hours at 25°C and 50% RH prior to testing.

Testing

The cured 8" x 12" laminations were cut to 1" wide strips for measuring T-peel adhesion following ASTM D8176 test method on an Instron Model 5543 Tensile Tester.

Separately, free films of the adhesive formulations were prepared using the drawdown method to the desired thickness. Curing conditions were the same as for the T-Peel adhesion specimens and the cured free films were equilibrated for 72 hours at 25°C, 50% RH prior to testing. Glass Transition Temperature (T_g) was measured using TA Instruments Model Q800 Dynamic Mechanical Analyzer. Tensile properties of the free adhesive films were measured using the Instron tensile tester described above following ASTM D882 test method.

Durability for the high performance oligomer study was evaluated by measuring T-Peel Adhesion before and after three different environmental exposure conditions as follows:

1) QUV Weatherometer ASTM D4329-05 cycle B
2) Cincinnati Environmental Chamber @ 85°C/85% RH
3) Cincinnati Environmental Chamber Freeze-Thaw cycle (20 hrs @ 85°C/85% RH; 2 hrs @-40°C).

Materials

Table 2. Film Substrates Used for Adhesion Testing

Film Type	Supplier	Description
Linear Low Density Polyethylene (LLDE)	ExxonMobil	
Polyethylene Terephthalate Polyester (PET1)	Teijin Films	Melinex 813; 45 gauge pretreated 1 side
Optically Clear PET Film (PET2)	Teijin Films	XST6578 optically clear; 100 gauge

Table 3. Acrylate Monomers Tested for Adhesion Study 1 (LLDPE:PET1)

Monomer	Description	Eq. Wt. (MW./Funct.)	Surface Tension (Dynes/cm)	Tg by DSC (◦C)
A	Alkane Diacrylate	99	34	64
B	Alkane Diacrylate	113	36	32
C	Cycloaliphatic Monoacrylate	156	36	-15
D	Alkane Monoacrylate	184	28	-54
E	Alkoxylated Monoacrylate	188	32	-54
F	Aromatic Monoacrylate	192	39	5
G	Cycloaliphatic Monoacrylate	208	32	88
H	Alkoxylated Cycloaliphatic Monoacrylate	272	33	-51
I	Alkoxylated Aromatic Monoacrylate	280	39	-24

Formulation : 99% Monomer, 1% BAPO photoinitiator
Cure Conditions : 1 pass, 600wpi D lamp @15 fpm
Adhesive Thickness ~ 5 mils

Table 4. Acrylate Oligomers Tested for Adhesion Study 2 (PET2)

Oligomer	Description	Eq. Wt (MW/Funct.)	Tg by DSC (◦C)
A	Low Viscosity Epoxy Acrylate	230	13
B	Epoxy Acrylate	750	51
C	Aliphatic Polyester Urethane Acrylate	~1,900	-33
D	Aliphatic Hydrophobic Acrylate	~2,000	-41
E	Aliphatic Polyester Urethane Acrylate	~5,000	NA
F	High Elongation Polyether Urethane Acrylate	~ 8,000	-54

Formulation: 99% Oligomer, 1% BAPO photoinitiator
Cure Conditions: 1 pass 600wpi D lamp, 300wpi V lamp @30fpm
Adhesive Thickness ~ 9 mils

Table 5. Oligomer/Monomer Blends Tested for Adhesion Study 3 (PET2)

Oligomer	Description	Viscosity @25◦C (cP)
A	High MW Polyester UA /Monomer Blend	2,000
B	Moderate MW Polyester UA/ Monomer Blend	500
C	Polycarbonate UA/ Monomer Blend	7,000
D	Moisture Resistant UA/ Monomer Blend	200
E	High Elongation Polyether UA/ Monomer Blend	600

Formulation: 51.2 parts Oligomer, Low, Med, High T_g (6.2/17/24.1 parts), 1.5 parts TPO PI
Cure Conditions: 1 pass 600wpi D lamp @15 fpm
Adhesive Thickness ~ 9 mils

Table 6. Oligomer/Mixed Monomer Blends for Adhesion Study 4 (PET2)

Oligomers	Description
A	Polycarbonate-Based Urethane Acrylate
B	High MW Polyester-Based Urethane Acrylate
Monomers	**Description**
A	Alkoxylated Monoacrylate
B	Cycloaliphatic Monoacrylate
C	Alkane Monoacrylate
D	OH Functional Monoacrylate
E	Cycloaliphatic Monoacrylate
F	Alkoxylated Cycloaliphatic Monoacrylate

Formulation: 50 parts Oligomer, 25 parts Monomer 1, 25 parts Monomer 2, 1 part BAPO
Cure Conditions: 1 pass 600wpi V lamp @50 fpm
Adhesive Thickness ~ 5 mils

Table 7. High Performance Oligomers Tested for Durability Study 5 (PET2)

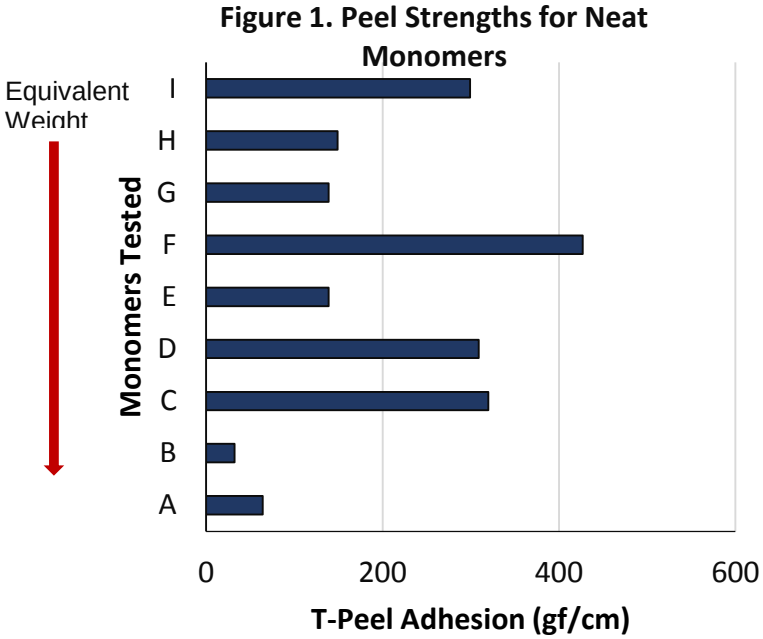
Oligomer	Description	Viscosity at 60°C, cps
A	High MW Polyether UA (HMWPetUA)	20,000
B	Moderate MW Polyester UA (PestUA)	4500
C	High MW Polyester UA (HMWPestUA)	16,000
D	Moisture-Resistant Polyester UA (MRUA)	5600
E	Moderate MW Polycarbonate UA (PCUA2)	26,000
F	Polycarbonate UA (PCUA1)	22,500

Formulation: 51.2 parts Oligomer, Low, Med, High T_g (6.2/17/24.1 parts), 1.5 parts TPO
Cure Conditions: 1 pass 600wpi D lamp @15 fpm
Adhesive Thickness ~ 9 mils

Results:

Study 1. Monomer Effect on Adhesion

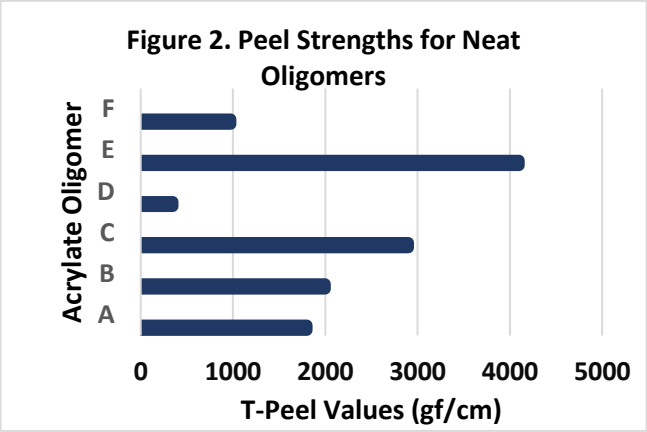
The objective for this study was to evaluate the influence of monomer backbone chemistry, glass transition temperature (T_g), and acrylate equivalent weight on adhesive strength for an LLDPE:PET1 lamination. Even though the T-Peel strengths for monomers alone are not very high, the results in Figure 1 do show significant differences between them. Monoacrylate monomers (F) and (I) exhibit higher adhesive strength due to the rigid aromatic backbone. Conversely, low T_g, low surface tension alkane monacrylate (D) and cycloaliphatic monoacrylate (C) also yield good adhesive strengths. These results are believed to be due in part to their ability to both wet and swell the individual film surfaces to form a pseudo interpenetrating network (IPN) during curing. The results of this study also demonstrate that lower equivalent weight diacrylate monomers (A) and (B) yield weaker adhesive bonds due to increased crosslinking which contributes brittleness and shrinkage.



Study 2 Oligomer Effect on Adhesion

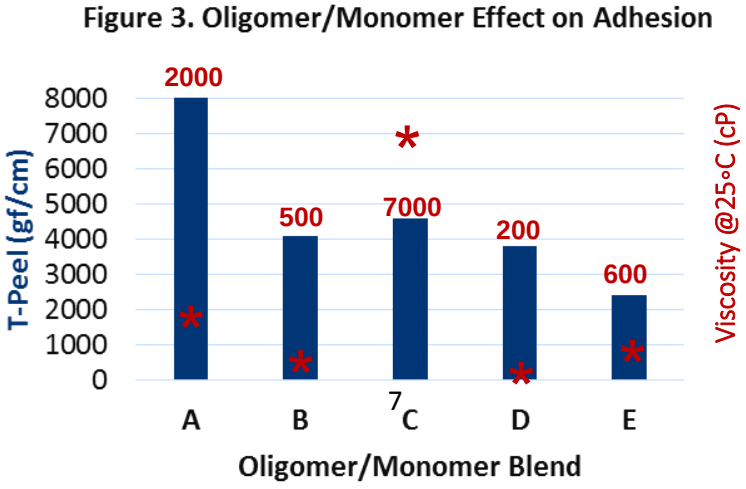
The objective of this study was to evaluate the influence of acrylate oligomer backbone type, T_g and equivalent weight on adhesive strengths. The T-Peel strengths in Figure 2 demonstrate that oligomer addition to an adhesive for a higher performance PET2:PET2 lamination significantly improves adhesion and cohesive strength. In particular, polyester-based urethane acrylate (UA) oligomers (C) and (E) exhibit the highest T-Peel strengths due to the

combination of high molecular weight and moderate T_g which adds some stiffness. However, higher molecular weight, low T_g UA oligomers yield weaker adhesion due to the soft backbone. Higher T_g epoxy acrylate oligomers (A) and (B) exhibit moderate T-Peel strengths due to the aromatic backbone contribution but epoxy acrylates in general exhibit lower toughness and poorer film wetting than high molecular weight UA's.



Study 3. Oligomer/Monomer Blending Effect

The previous studies showed that low T_g monoacrylate monomers and higher molecular weight, moderate T_g urethane acrylate oligomers offer higher T-Peel adhesive strength. In this study, the effect of combining high weight urethane acrylate oligomers with monoacrylate monomers having good substrate wetting and a range of T_g's on T-Peel adhesive strength and adhesive viscosity is studied. The T-Peel strengths plotted in Figure 3 demonstrate again that T-Peel adhesion is strongly influenced by the backbone chemistry and molecular weight of the urethane acrylate oligomer. Polyester-based oligomer (A) and the polycarbonate-based oligomer (C) exhibit stronger bonding but also exhibit higher viscosities at a 50/50 ratio of oligomer to monomer which may limit their use in certain adhesive application processes. The moderate molecular weight and moderate T_g urethane acrylate (B) exhibits a good balance of peel strength and application viscosity suitable for roll to roll processes.



Study 4. Oligomer/Mixed Monomer Effect

In order to optimize oligomer/monomer combinations to meet the desired viscosity in combination with the high adhesive strength required for higher performance applications, we evaluated a moderate T_g polycarbonate-based urethane acrylate oligomer (A) and a new high MW, low T_g polyester-based urethane acrylate oligomer (B) developed for higher performance UV curable pressure sensitive adhesives (PSA's). The two oligomers were blended with low viscosity monoacrylate monomer combinations (Monomer 1/Monomer 2) varying in surface tension, molecular weight and water resistance. The T-Peel values plotted in Figure 4 show blends with Oligomer (B) exhibits much higher average peel strengths and blends containing the high T_g cycloaliphatic monoacrylate monomer (E) exhibit the highest average T-Peel values.

A more significant observation shown in Table 8 below was that certain monoacrylate monomer combinations at a 50/50 Monomer 1/Monomer 2 ratio containing monoacrylate monomer (E) yield a synergistic increase of > 4X in peel strength compared to the individual monoacrylate monomers alone. The increase in T_g and elongation observed with the cycloaliphatic monoacrylate (E) component in the formulation contributes to the higher adhesive strengths but also increases the formulation viscosity. Formulation viscosities can be lowered by reducing the Oligomer B loading to 40% and varying the ratio of the cylcloaliphatic monoacrylate (E) and the secondary monoacrylate to maintain similar adhesive strengths.

Figure 4. Monomer Effect on Adhesion

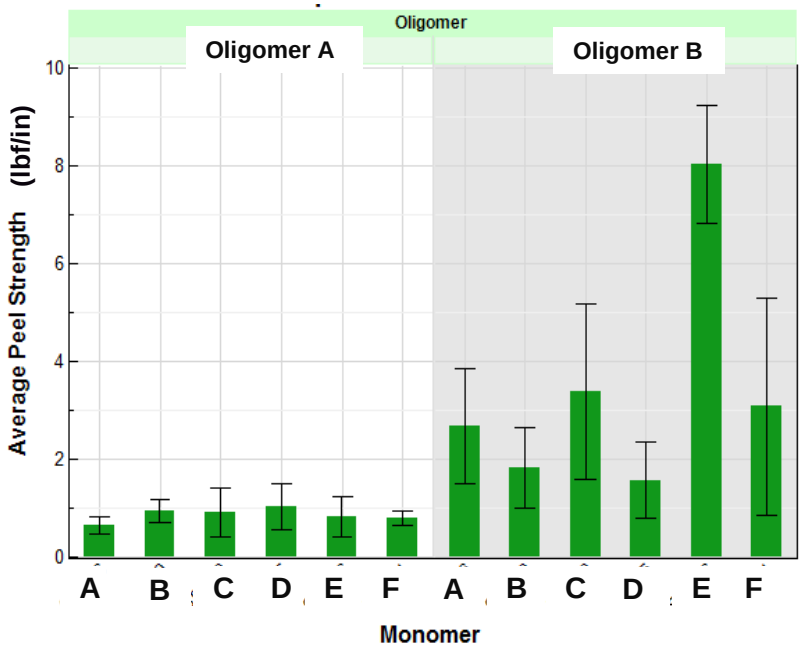


Table 8. Summary of UA Oligomer Mixed Monomer Blend Performance

Formulation (Olig B/Mon1/Mon2)	Viscosity @25◦C (cP)	Tg by DMA (◦C)	Elongation (%)	T-Peel Adhesion (lbf/in)
B/A/A	827	-25.0	44	0.8
B/C/C	NT	-13.0	39	1.9
B/F/F	3,000	-40.0	270	1.0
B/E/A Good	1,350	-3.0	380	5.7
B/E/C Better	1,900	-16.0	45	8.7
B/E/F Best	3175	-10.0	570	9.7

Study 5. Environmental Exposure Effect on Adhesion

In this study, the objective was to utilize the formulating strategies detailed in the previous studies to develop high performance UV cure laminating adhesives for electronic applications such as high resolution displays and energy efficient solar panels. The formulations tested are based on both commercial UA adhesive oligomers and new UA oligomers developed specifically for these more demanding applications. Figure 5 below shows the change in T-Peel strength after exposure to the three environmental conditions listed. In general, UV cure laminating adhesives based on polyester-based and polycarbonate-based UA oligomers provide better durability than polyether-based UA oligomers due to their water sensitivity. The results show that higher molecular weight UA oligomers exhibit the highest initial T-Peel strengths but they exhibit poorer resistance to environmental stresses (i.e., UV, temperature and moisture) due to reduced crosslink density in the cured adhesive.

The oligomers that exhibit the best overall resistance to environmental exposure are two of the newly developed electronics adhesives, Polycarbonate-based UA PCUA1 (F) and Moisture-resistant Polyester-based UA MRUA (D). Figures 6 and Figure 7 show the minimal changes observed in peel strengths after 2000 hours exposure for these two oligomers. The polycarbonate-based UA exhibits a higher initial peel strength but the moisture resistant polyester-based UA exhibits better overall retention of adhesive strength performance.

Figure 5. High Performance Oligomer Effect on Adhesion
500 Hours Exposure

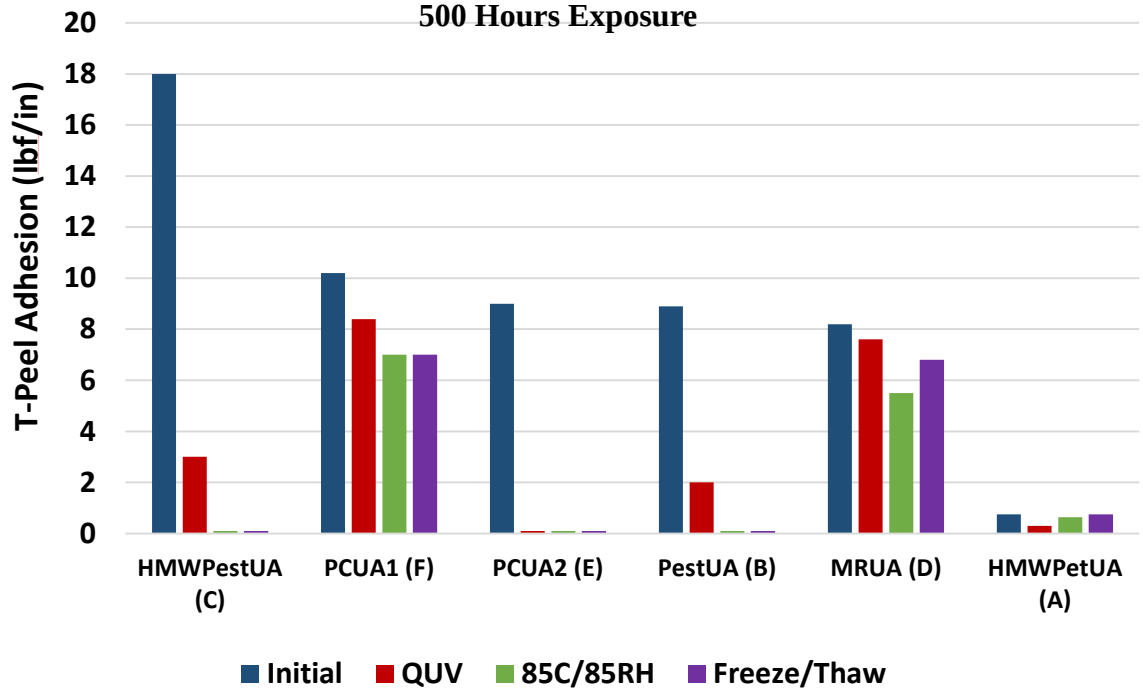


Figure 6. Polycarbonate UA Durability

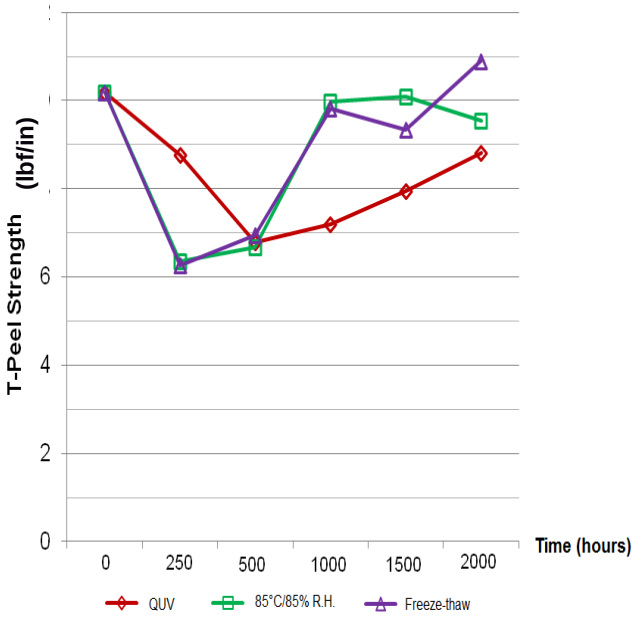
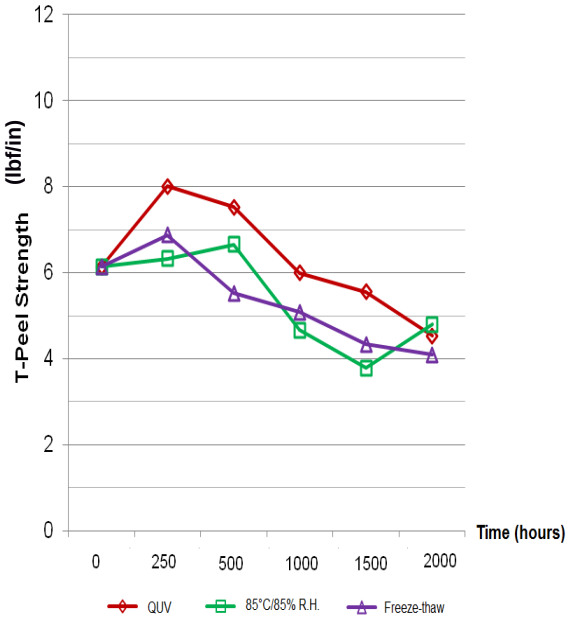


Figure 7. Moisture Resistant UA Durability



Conclusion:

The key takeaway from the five lab studies discussed is the wide array of UV curable laminating adhesive materials available to formulators versus conventional solvent-based and waterborne technologies. These materials provide a substantial toolset for tailoring properties for higher performance applications. This toolset provides for bonding to a variety of substrates and enables the formulator to create complex, cured polymeric systems offering a broad range of adhesive strength and service life durability. Influencing factors for peel strength include monomer and oligomer functionality, backbone chemistry and molecular weight. The key challenge to formulating success is finding the appropriate combination of materials that work together to provide:

- the target application viscosity
- the correct surface tension for good substrate wetting
- fast curing with minimal shrinkage
- a balance of strength and flexibility

Generally, the studies presented here show that low viscosity, low functionality acrylate monomers can provide application viscosity adjustment, enhanced adhesion through bonding at the surface of the substrate and synergistic behavior when blended with other acrylate functional monomers and oligomers. Sartomer monoacrylate monomers are good examples of monomers with these features.

Additionally, the studies show that higher molecular weight urethane acrylate oligomers having polyester and polycarbonate backbones provide high peel adhesion strengths and can be formulated with hydrophobic monomers to provide bond retention under environmental stresses encountered in both electronics and automotive applications. Newly developed urethane acrylate oligomers from Sartomer are good examples of oligomers which offer these features.

References

1. Joshua M. Oliver, Influences on Barrier Performance of UV/EB Cured Polymers, UV&EB 2010 Technology Expo and Conference.
2. Jin Lu, High Performance Materials for Laminating Adhesives, RadTech 2014 Technology Expo and Conference.

Acknowledgment

The author would like to thank the Sartomer Adhesives & Sealants R&D Platform group's work led by Jin Lu and my Technical Service & Development colleagues William Wolf and Ronald Wlodyga for their application work.