New UV/EB Curable Laminating Oligomers Specially Designed for Transparent Adhesion to Rigid Plastic substrates

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Abstract

New specialty oligomers were developed to increase adhesive performance in low viscosity UV/EB curable laminating adhesives. Sample formulations laminating various metals, glass and semi-rigid plastic substrates will be discussed including refractive indices and surface tensions of substrates and adhesives, and environmental conditioning of laminate structures. Substrates will include various metal sheets, glass panels, PC, PMMA, Acrylic, PET, ABS, Polystyrene, and other engineered plastics.

Introduction

Plastics have been around for many years. In 1927 Otto Rohm and Otto Haas attempted to prepare sheets of polymethyl acrylate by pressing between two sheets of glass[1]. This produced a superior safety glass to the previous which contained cellulose nitrate. Then in 1935, Rohm & Haas produced polymethyl methacrylates (PMMA) naming it Plexiglass. Plexiglass proved to be transparent, strong and tough, finding its place in the cockpits of military aircraft. Today, Plexiglass is used in place of glass in airplanes, automobiles, light fixtures, signs and household appliances. DuPont also introduced its own polymethyl methacrylates product under the name Lucite. When formed into a clear rod, Lucite can direct light. Because of this ability, Lucite is used in medical applications. In 1942, DuPont introduced polyacrylonitrile fibers (Orlon). Acrylonitrile-butadiene-styrene (ABS) copolymer was used first in the manufacture of luggage in 1948. Then in 1966 ABS was used on the exterior surfaces of helicopters.

Polycarbonate was first developed in 1953 by Dr. Daniel Fox, a GE chemist[2]. Since the discovery by Dr. Fox, polycarbonate has been used in so many applications from Astronaut's helmets to all types of transportation and everyday life in general. By the late 1960's, polycarbonate sheets were developed which began the lamination of polycarbonate sheets. Laminated polycarbonate sheets are being used to make various types of signage, greenhouses, and impact and bullet-resistant laminations including windows for buses, trains, and planes.

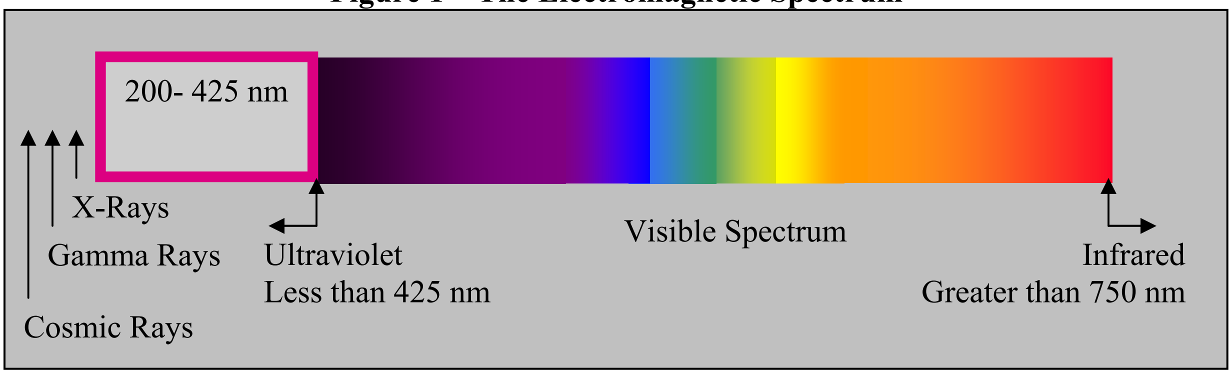
Due to the huge demand on clarity, an optically clear adhesive is required for these types of applications. The goal of this work was to design optically clear UV/EB curable lamination adhesives for all types of rigid plastic laminations. Moisture absorption also plays a key roll in the overall clarity of the laminations. UV transmission is the best method to study the laminates performance.

Prior to reviewing the adhesion tests, the electromagnetic spectrum, UV energy, photoinitiator selection and various types of absorption will be covered.

Electromagnetic Spectrum and Photoinitiator Selection

Previously, studies have been done to determine the correct photoinitiator for three different UV energy lamp sources – H-bulb, D-bulb, and V-bulb[3]. Different bulbs emit different wavelengths of energy and therefore respond to the photoinitiators differently. The UV wavelength is from 200 to 425 nm as shown in the electromagnetic spectrum in Figure 1.

Figure 1 – The Electromagnetic Spectrum



Two different photoinitiators are shown to understand both the importance of photoinitiator and UV energy source. The photoinitiators chosen are Esacure® KIP150 and Irgacure® 819. Table 1 shows the chemistry and the absorbance of each photoinitiator.

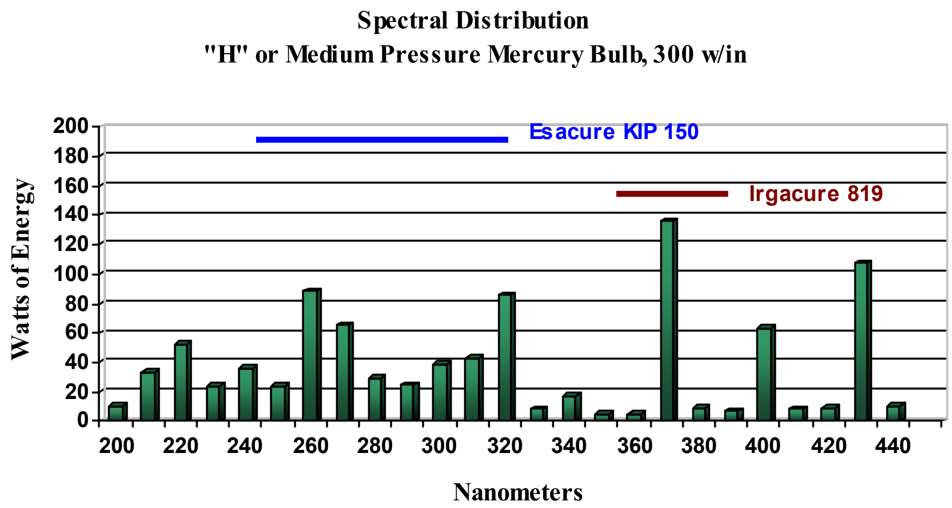
Table 1 – Photoinitiators

Trade Name	Chemical Name	UV Absorbance
Esacure KIP150	Oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl] propanone]	240-320
Irgacure 819	Bis (2,4,6-trimethylbenzoyl)-phenylphospineoxide	360-390

The most common bulb used for curing in the UV industry is a medium pressure mercury bulb, or H-Bulb. The typical spectral distribution emitted from an H-bulb is shown in Figure 2. An overlay for the two photoinitiators UV absorption is also shown in the figure.

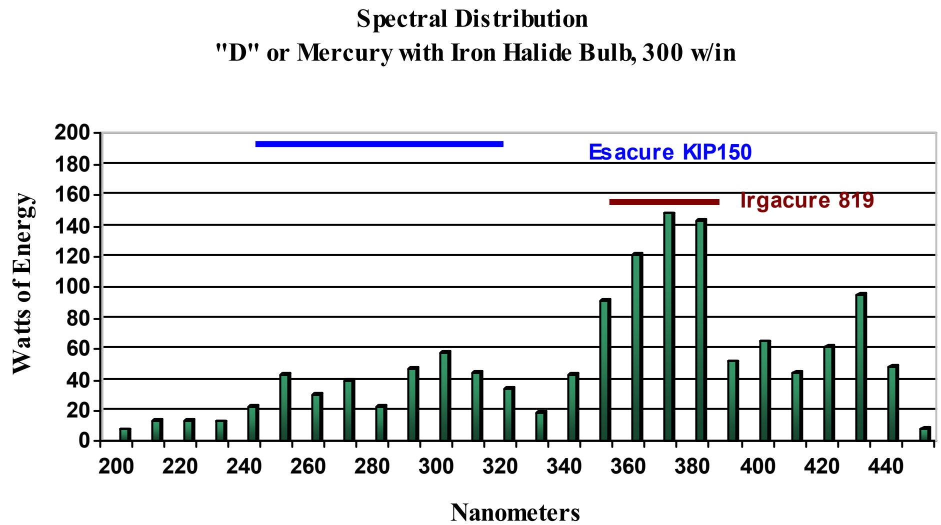
The majority of the spectral distribution for the "H" bulb shows most energy is in the 210-320 nm range. There are also a few peaks at 370, 400 and 430 nm. The Esacure KIP150 is designed primarily as an H-bulb or mercury lamp photoinitiator. However, the Irgacure ® 819 will also work with the H-bulb because it has a UV absorbance in the 370 nm peak area.

Figure 2



Another common bulb being used in the industry is the iron halide additive in the mercury bulb, or D-bulb. The spectral output of this bulb is shown in Figure 3. Different bulbs are used because the UV spectral output is shifted. As you can see from Figure 3 most of the UV energy is shifted to the 340-440 range. Various bulbs are being used because many of the plastics used in laminations absorb the UV energy. In most cases UV energy in the 200-350 nm range is being absorbed by the various plastics. Therefore, if using the H-bulb, very little of the UV energy penetrates the outer film to activate the photoinitiator and ultimately cure the adhesive.

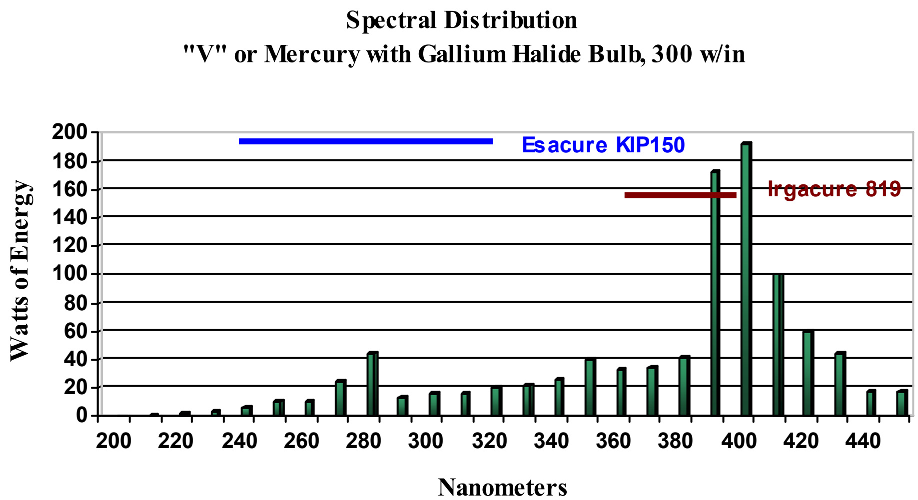
Figure 3



The D-bulb has a much wider range of spectral output, 340-440 nm, and also tends to provide very intense UV energy. Even at the lower end of the spectrum (250-320 nm) a fairly intense energy is measured, yielding an output suitable for some mercury-type cure photoinitiators. The D-bulb will activate the Irgacure® 819. The D-bulb also works very well for curing through most clear films and even some opaque films due to the higher energy output (340-440 nm).

The final common bulb used for UV cure is the gallium halide additive in the mercury bulb or V-bulb. The spectral output of the V-bulb is shown in Figure 4. The UV energy is shifted even closer to the visible spectrum with the V-bulb. Now most of the UV energy is in the 390-430 nm range.

Figure 4



By looking at Figure 4, it is obvious that the spectral output is quite different than the H-bulb and even more toward the visible spectrum than the D-bulb. Where the H-bulb was near the 200-340 nm range of the UV spectrum, the V-bulb is near the visible end of the spectrum, 390-430 nm and is very intense UV energy over a very small spectral output. Because of this type of spectral distribution, only a few of the photoinitiators responded with the V-bulb. The V-bulb will activate Irgacure 819. Again, the V-bulb also cures through most films, due to its near visible UV spectral output (390-430 nm).

Experimental

A new series of acrylated laminating oligomers were developed specifically for UV/EB laminations of various rigid substrates. As shown in Table 2, the three new oligomers were evaluated for physical performance characteristics, as well as various laminating adhesive qualities. To achieve cured film properties, the oligomers were each mixed with 5% Oligo (1-Hydroxy-2-Methyl-1-4(1-methylvinyl) Phenyl Propanone), also known as Esacure® KIP 150 photoinitiator.

Table 2 – Physical Properties

ID	Trade Name	Description	Visc. (cps)	Surf. Tens.	Ref Index	Tensile* (psi)	Elong.* (%)	Mod.* (psi)	Tg-DMA
Olig 1	**CN3108**	Low Viscosity Specialty Oligomer	850	40.6	1.512	49	80	181	24.8
Olig 2	**CN3109**	Aliphatic Urethane Acrylate Oligomer	525	39.2	1.503	86	62	276	16.5
Olig 3	**CN3110**	Low Viscosity Specialty Oligomer	600	37.1	1.475	61	49	375	22.0

* Tensile, elongation, and modulus were run on 5.0 mil UV-cured films mixing 5% Esacure® KIP 150 photoinitiator.

The three oligomers were evaluated neat on various types of rigid plastic, glass and metal to determine what they contributed to the overall adhesive. To do this test, each oligomer was mixed with 0.5% Irgacure® 819 (Bis (2,4,6-trimethylbenzoyl)-phenylphosphineoxide) to evaluate each oligomer as a major component in an energy curable laminating adhesive. The Irgacure® 819 was chosen because previous studies[4,5] have shown that it performs best on film laminations because certain plastics absorb the UV energy below the 380 nm, the Irgacure® 819 will be activated when using a Fusion P-600 D or V bulb.

The procedure used for mixing the oligomer with the photoinitiator consisted of blending the two at 50°C for 30 minutes. All the laminations were cured using a 600 WPI D-bulb at 25 FPM. Table 3 shows the measured UV energy using a UV Power Puck. All UV curing equipment is different. This is formation is shown as our actual curing conditions.

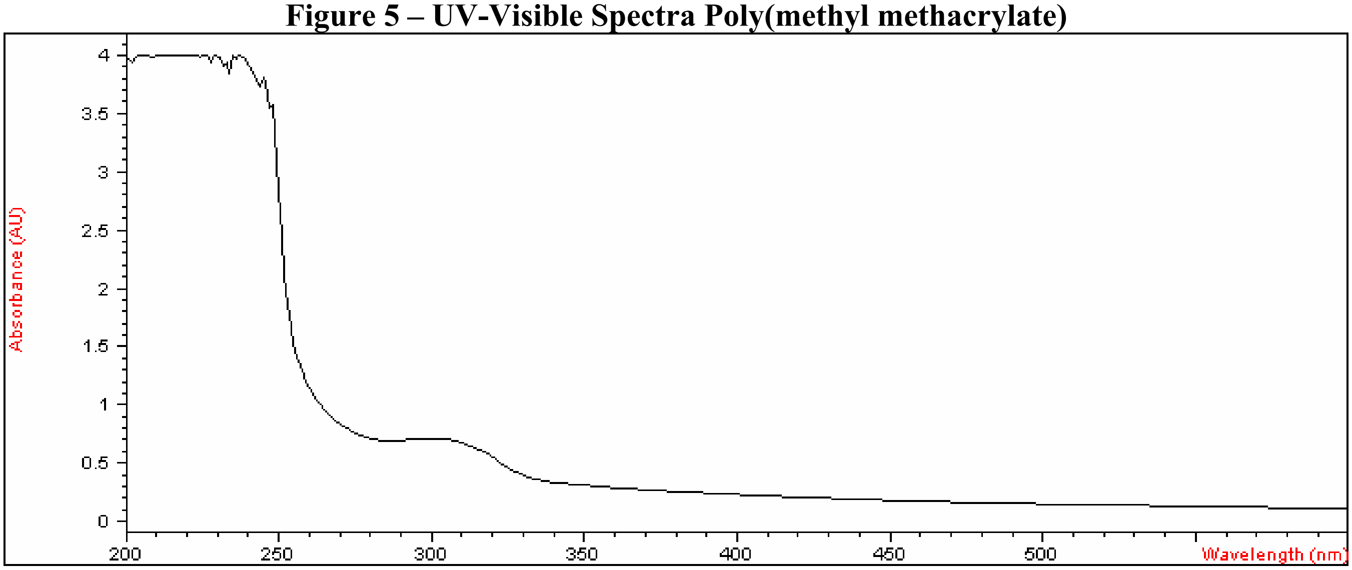
Table 3 – UV Power Puck, 600 WPI D-bulb at 25 FPM

	UV-C	UV-B	UV-A	UV-V
J/cm^2	0.052	0.430	1.772	1.390
W/cm^2	0.134	1.249	5.000	3.956

Poly(methyl methacrylates) – PMMA

The PMMA discs were relatively thin at 0.026" having a surface tension of 38. An UV-Visible absorbance spectrum was run on the PMMA to determine absorbance of the UV energy. The spectrum is shown in Figure 5. The PMMA absorbs very little UV energy above 270 nm. Therefore any type of UV energy, i.e. H-bulb, D-Bulb or V-bulb should sufficiently cure through the PMMA.

Figure 5 – UV-Visible Spectra Poly(methyl methacrylate)

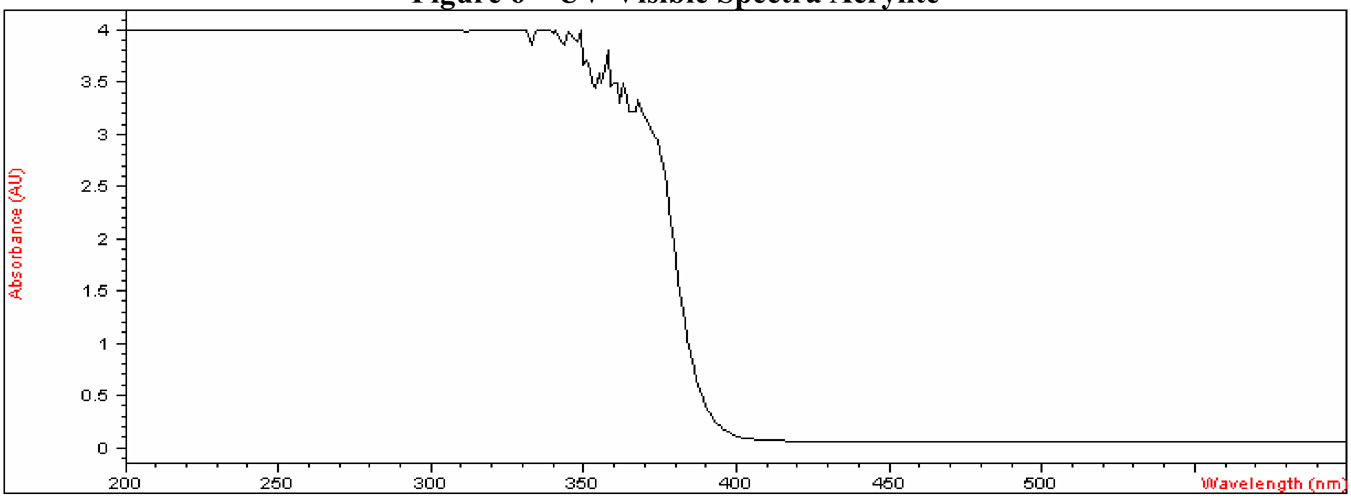


All three of the laminating oligomers were evaluated on the PMMA. Because the PMMA substrate was discs rather than sheets, lap shears could not be prepared. Instead, a few drops of the adhesive were applied to one edge of the disc and then UV cured. All three of these laminating oligomers, Oligomer #1-3, either deformed or broke the PMMA disc when trying to separate the two discs after cure.

Acrylic

There are many grades of acrylic used in laminations. First we ran UV-Visible absorbance spectra on Acrylite® Acrylic sheets (surface tension of 34). The results are shown in Figure 6. By looking at the absorbance spectra, the UV energy less than 390 nm will be absorbed. This is very different from the above sample of the PMMA disc. In this case, you should use the V-bulb to sufficiently cure the adhesive through the Acrylite sheet.

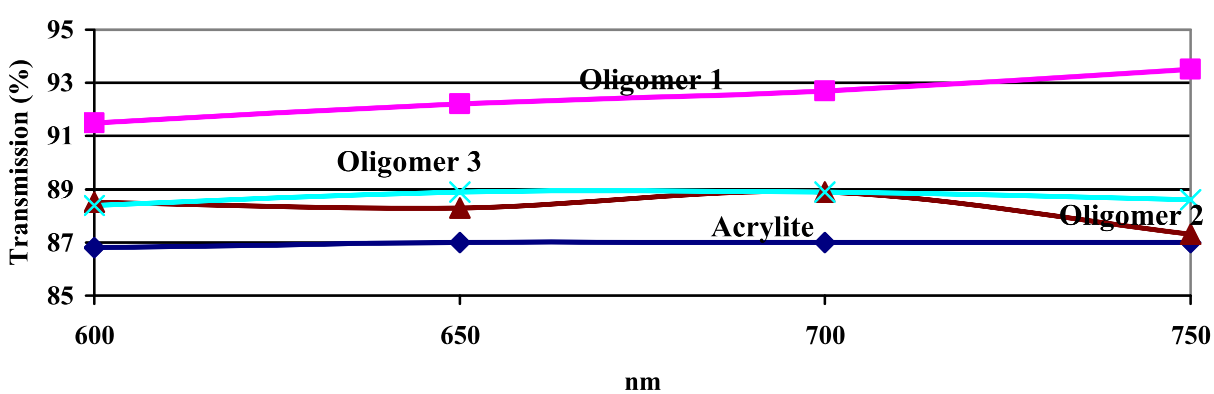
Figure 6 – UV-Visible Spectra Acrylite



We took the three laminating oligomers using the Acrylite substrate, prepared 1"x1" overlap lap shears with a 2.0 +/- 0.1 mil adhesive thickness and cured them using a 600 WPI D-bulb at 25 FPM. The lap shears were pulled at 0.5 in/min on an Instron. All three of these laminating oligomers actually broke the Acrylite substrate using 165-190 pounds force when trying to separate the lamination.

An evaluation of the transmission was also studied for these laminations using a UV-Visible Spectrophotometer. The results are shown in Figure 7. All three of the oligomers actually increased the percent transmission of the light through the Acrylite, Oligomer #1 (highest refractive index oligomer) increases percent transmission the most.

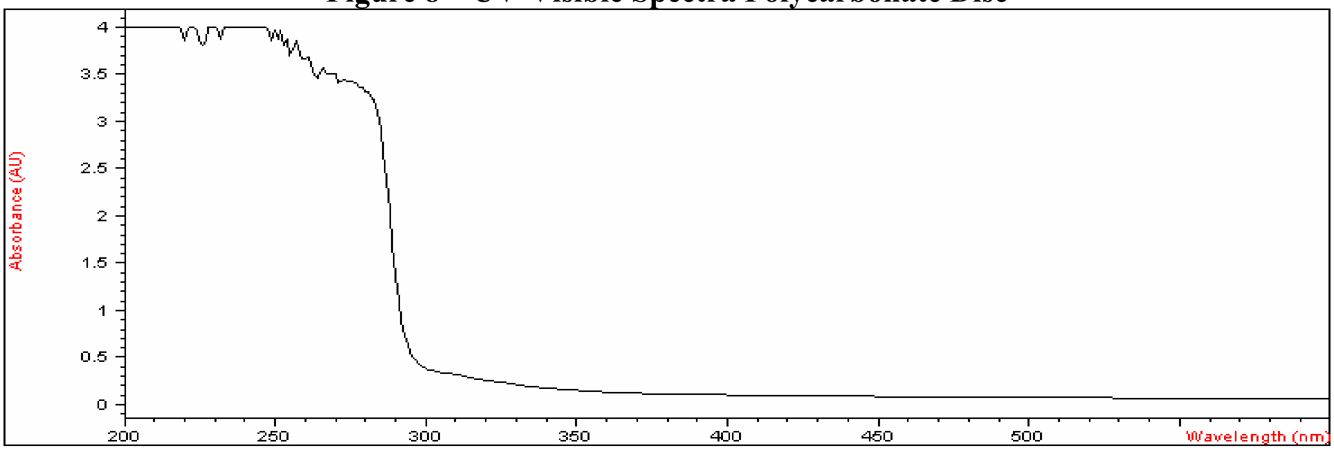
Figure 7: UV-Visible Transmission Acrylite samples



Polycarbonate

There are many grades of polycarbonate used in laminations. We ran UV-Visible absorbance spectra on two different types of polycarbonate substrates used for this test. The first shown in Figure 8 is a simple polycarbonate disc used in DVD laminations (surface tension 38). By looking at the absorbance spectra, the UV energy less than 280 nm will be absorbed, but greater than 280 nm UV energy will be transmitted through the polycarbonate.

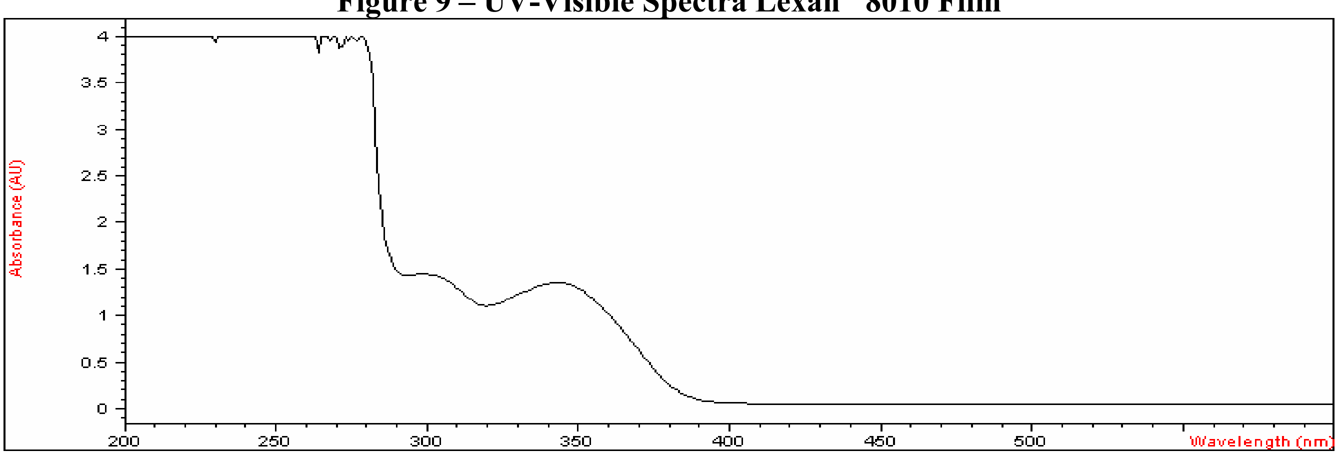
Figure 8 – UV-Visible Spectra Polycarbonate Disc



We tested each of the laminating oligomers on the PC disc. Similar to the PMMA disc, we took a few drops of the laminating oligomer with photoinitiator and cured in place using a 600 WPI D-bulb at 25 FPM. All three of these laminating oligomers, Oligomer #1-3, either deformed or broke the PC disc when trying to separate the two discs after cure.

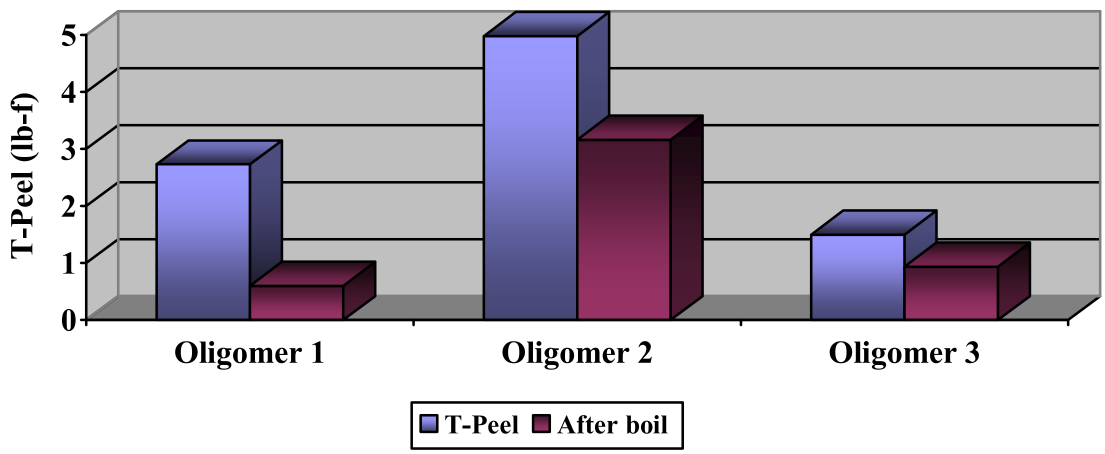
The next UV-Visible absorbance spectrum, Figure 9, is Lexan® 8010 Film. This type of polycarbonate film offers high temperature resistance, excellent dimensional stability as well as good printability without pretreatment making it the ideal product for multi-layer printing[6]. The absorbance spectrum begins to follow the same absorbance as the PC disc, but the additives in the polycarbonate further absorb the UV energy. These additives are absorbing some of the UV energy in the 280-380 nm range. Above the 380 nm range, very little UV energy is absorbed.

Figure 9 – UV-Visible Spectra Lexan® 8010 Film



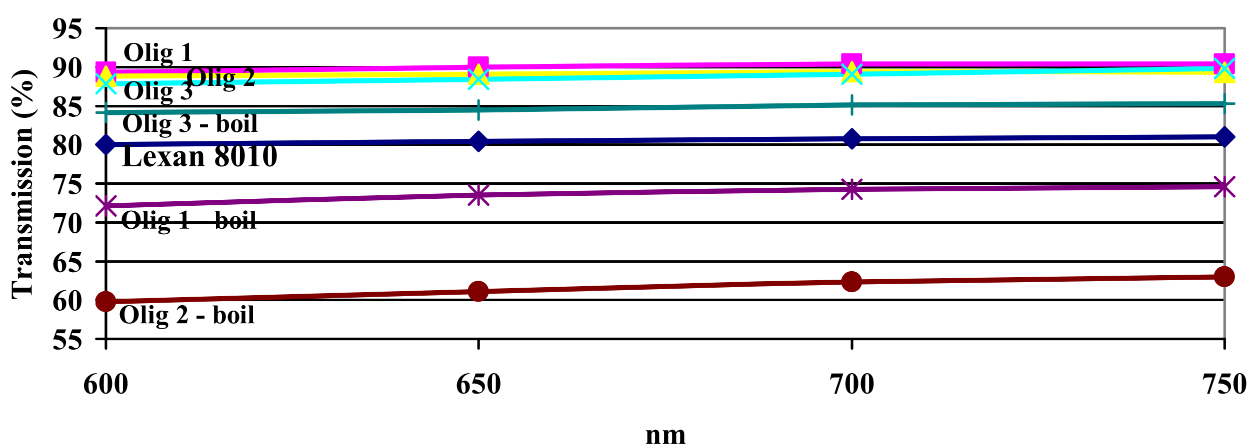
The Lexan 8010 PC is a flexible film with a thickness of 0.010 inch. Instead of testing in a lap shear, we made 1”x4” laminations using 1.0 +/- 0.1 mils adhesive thickness and then pulled apart as a T-Peel lamination test. The results for the average peel values are shown below in Figure 10.

Figure 10: Lexan 8010 PC T-Peel



Oligomer #2 not only produced high T-peel values for the original lamination, but also still had high strength after exposure of 15 minutes in boiling water. We also ran UV-Visible transmission spectra on all of these samples both before and after exposure to boiling water. These results are shown in Figure 11.

Figure 11: Transmission Lexan 8010 PC samples

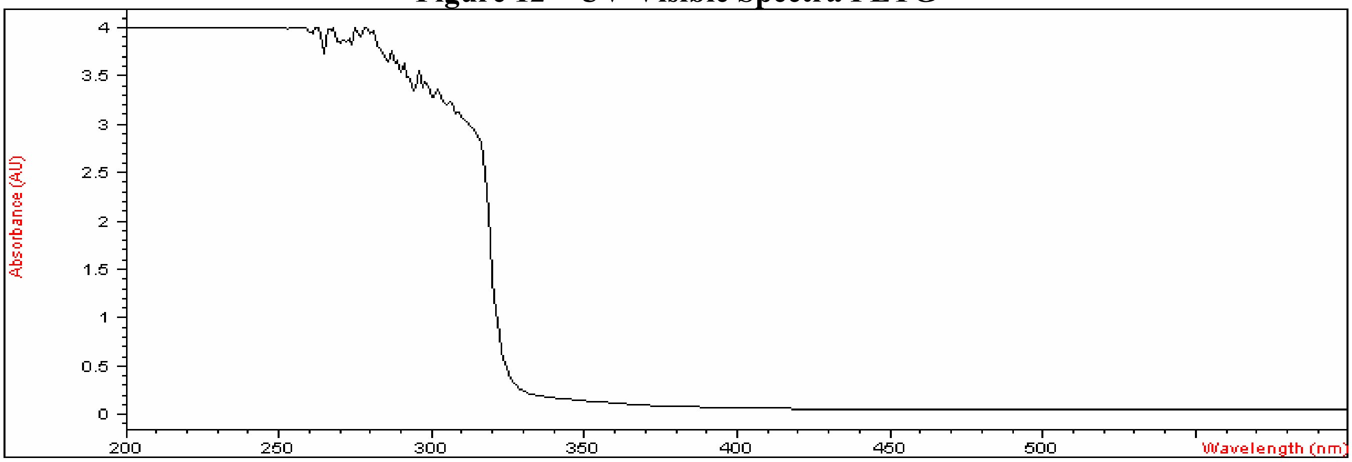


The Lexan 8010 sheets that were not laminated had around an 80% transmission in the visible spectra. After laminated with the UV cured oligomers, all the laminations had a higher transmission than the single piece of Lexan 8010. But only one of the samples, Oligomer #3 maintained a high (84-85%) transmission even after exposure to boiling water for 15 minutes.

Polyethylene Terephthalate (PET)

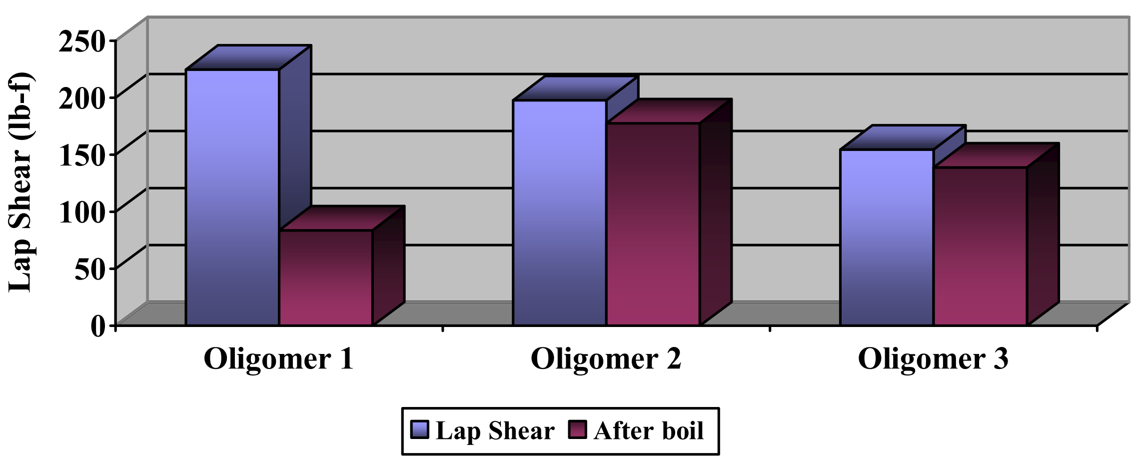
There are many grades and types of polyethylene terephthalate (PET) used in laminations. We used a glycol modified version (PETG) having a surface tension of 32 for this testing. We also looked at the UV-Visible absorbance spectra shown in Figure 12. By looking at the absorbance spectra, most of the UV energy less than 330 nm will be absorbed and greater than 330 nm will be transmitted through the PETG.

Figure 12 – UV-Visible Spectra PETG



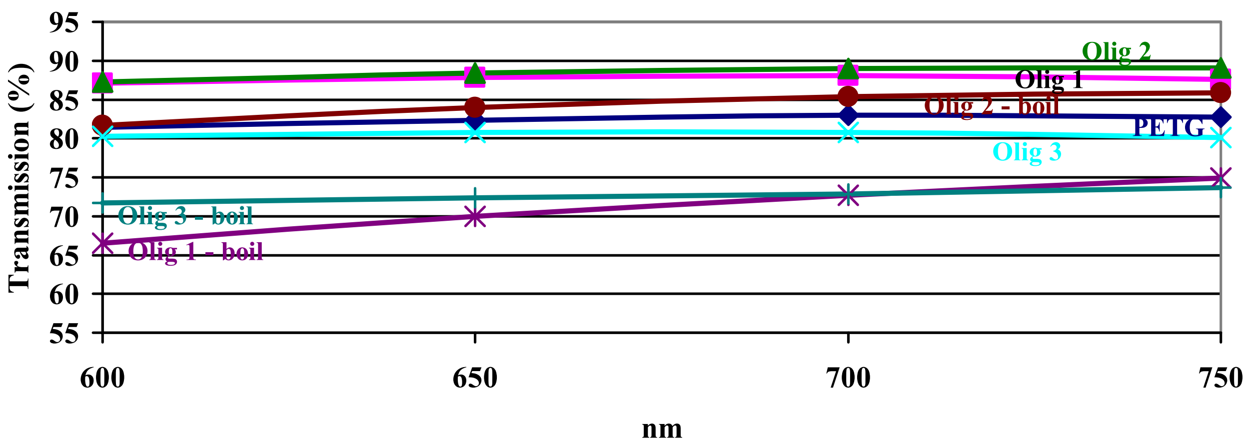
All three of the oligomers were cured as lap shears using a 2.0 mil adhesive thickness. The results are shown in Figure 13. Oligomer #1 maximized the load cell at 225 pounds without breaking the lap shear joint. But after exposure to the boiling water, Oligomer #1 did not perform as well as the other two oligomers. Oligomer #2 yielded very high lap shear strength before it broke the PETG. Even after boiling water for 15 minutes, Oligomer #2 still broke the PETG for Lap Shears. Oligomer #3 also broke the PETG during the initial lap shears, but failed slightly lower in strength with adhesive failure after the boiling water soak.

Figure 13: PETG Lap Shear



Again the UV-Visible transmission spectra were run on all of these samples. The results are shown in Figure 14. The PETG by itself yielded a transmission of around 82-83% in the 600-750 nm range. Both Oligomer #1 and #2 had higher transmission as the laminate, but only Oligomer #2's transmission was higher than the base PETG (82%) both before (87%) and after boiling water soak (83%). Oligomer #2 also had the best lap shear strength.

Figure 14: Transmission PETG samples



Other Plastic Substrates

Many other plastic substrates were evaluated, but the additional data is being presented in Table 4 rather than additional figures. None of these substrates were clear to UV cure through; therefore, each was bonded to the clear Acrylite Acrylic sheets.

All three of these laminating oligomers performed well on the styrene. The thinner styrene actually broke with all three of the oligomers when running the lap shear test.

In many cases, Oligomer #2 seems to yield higher lap shear strengths. But Oligomer #1 seems to be the best for laminating ABS.

Table 4 – Various Plastic Lap Shear Results

Plastic	Type	Surf Ten	Thickness	Adh Thick	Olig 1	Olig 2	Olig 3
Styrene	PS	36	0.040	0.030	**111**	**115**	**109**
Dow Styron	High Impact PS	36	0.125	0.025	123	195	160
GE Valox	Polyester	36	0.125	0.020	152	159	136
GE Noryl	PPO/Nylon	34	0.100	0.030	147	172	162
Solvay Sequel	TPO	32	0.125	0.050	86	86	71
ABS	ABS	34	0.025	0.020	**165**	172	156
Bayer Lustran	Auto ABS	42	0.100	0.030	*204*	164	130

BOLD = indicates that substrate broke during lap shear test.
Italics = indicates machine maximized load cell parameters without breaking.
Dark Shading = indicates best results in set

Metal Substrates

Many metal plaques were tested again using the Acrylite Acrylic so UV curing would be possible. The results are shown in Table 5. Some very high lap shear strengths were achieved with these laminating oligomers. With the metals, Oligomer #1 seems to perform best with most of these metal substrates tested. But in many tests, all three oligomers yielded nearly identical results.

Table 5 – Various Metal Lap Shear Results

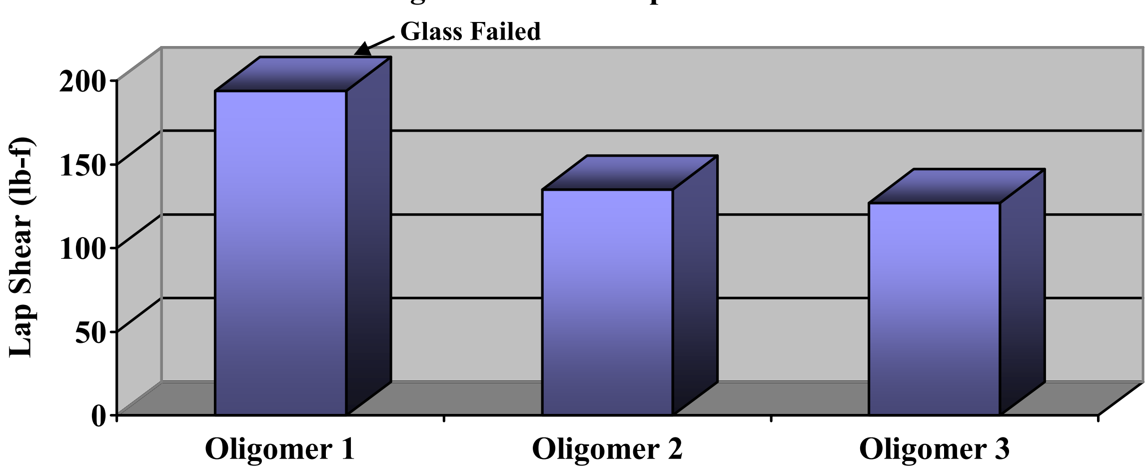
Metal	Adhesive Thick	Oligomer 1	Oligomer 2	Oligomer 3
Brass	0.020	122	94	105
A136 Chrome	0.020	187	188	220
Smooth Steel	0.040	168	158	145
Primed Steel	0.020	215	205	205
A36 Mill Finish	0.020	159	125	114
R46 Dull Steel	0.015	150	99	134
R46I Dull Steel	0.020	174	181	172
DT36 Tin Plate	0.015	163	189	176

Dark Shading = indicates best results in set

Glass

All three of the laminating oligomers were evaluated for glass to glass adhesion. The results are shown in Figure 15. The adhesive was applied at 0.030" thickness. No surface preparation was done to the 0.080" thick glass prior to the lamination. Oligomer #1 actually shattered the glass when the lap shears were pulled apart.

Figure 15: Glass Lap Shear



Conclusion

Unless you have the transmission/absorbance spectra for the type of substrate that you are using, the preferred UV energy source is the D or V bulb. A preferred photoinitiator for the lamination is Irgacure 819 due to it's absorbance in the 360-390 nm range.

The easiest way to summarize all the plastics, metal and glass results is by identifying the top two laminating oligomers as shown in Table 6. In many instances, all three oligomers performed equally or two of the oligomers performed equally.

Table 6: Oligomer Performance Summary

Metal	Oligomer 1	Oligomer 2	Oligomer 3
PMMA	Excellent	Excellent	Excellent
Acrylite Acrylic	Excellent	Good	Good
Polycarbonate	Excellent	Excellent	Excellent
Lexan 8010		Excellent	Good
PETG	Good	Excellent	Good
Styrene	Excellent	Excellent	Excellent
Dow Styron		Excellent	Good
GE Valox	Good	Excellent	
GE Noryl		Excellent	Good
Solvay Sequel	Excellent	Excellent	Good
ABS	Excellent	Good	
Bayer Lustran	Excellent	Good	
Brass	Excellent		Good
A136 Chrome	Good	Good	Excellent
Smooth Steel	Excellent	Good	
Primed Steel	Excellent	Good	Good
A36 Mill Finish	Excellent	Good	
R46 Dull Steel	Excellent		Good
R46I Dull Steel	Good	Excellent	Good
DT36 Tin Plate	Good	Excellent	Good
Glass	Excellent	Good	Good

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