

Laminating Oligomers used for Optically Transparent Adhesion to Glass

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Abstract

New specialty oligomers were developed to increase adhesive performance in low viscosity UV/EB curable laminating adhesives for glass. Sample formulations will be discussed including refractive indices, transmissions, clarity and surface tensions of glass and adhesives, along with environmental conditioning of laminate structures. Adhesive testing results will also be covered.

Introduction

Due to the huge demand for transmission and clarity, an optically clear adhesive is required for many types of applications. The goal of this work was to design optically clear UV/EB curable lamination adhesives for all types of glass 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, UV energy, photoinitiator selection and various types of UV energy absorption will be covered.

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-bulb¹. Different bulbs emit different wavelengths of energy and therefore respond to the photoinitiators differently. The UV wavelength range is from 200 to 425 nm.

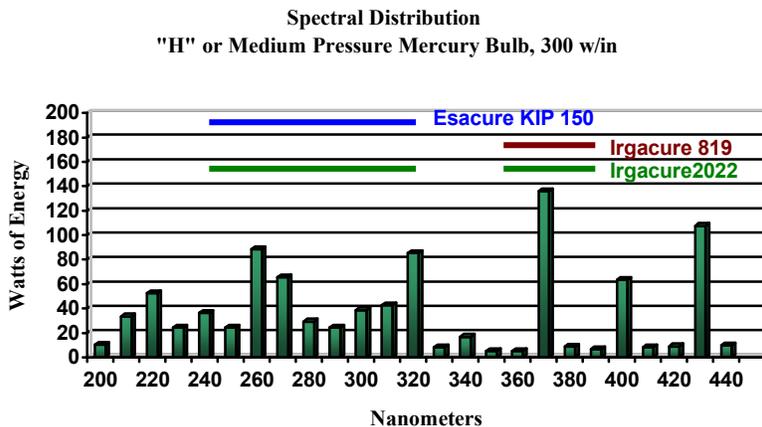
Three different photoinitiators listed in Table 1 show both the importance of photoinitiator and UV energy source. The photoinitiators chosen are Esacure[®] KIP150, Irgacure[®] 819 and Irgacure[®] 2022. Table 1 shows the chemistry and the absorbance of each photoinitiator.

Table 1 – Photoinitiators

Trade Name	Chemical Name	UV Absorbance
<i>Esacure KIP150</i>	Oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propanone]	240-320
<i>Irgacure 819</i>	Bis (2,4,6-trimethylbenzoyl)-phenylphospineoxide	360-390
<i>Irgacure 2022</i>	Bis (2,4,6-trimethylbenzoyl)-phenylphospineoxide (20%) and 2-hydroxy-2-methyl-1-phenyl ketone (80%)	240-320

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 1. An overlay for the three photoinitiators' UV absorption is also shown in the figure.

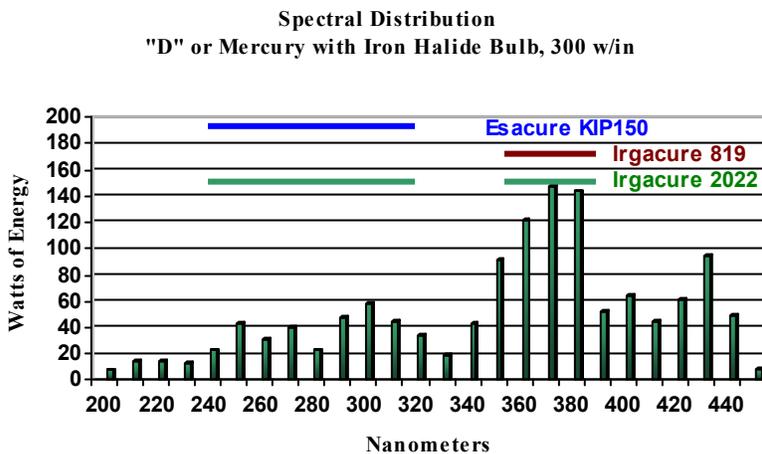
Figure 1



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 significant 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. The Irgacure[®] 2022 is a blend of the two photoinitiator types. From this, we see that all three photoinitiators can generate free radicals to initiate polymerization by using the H-bulb.

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 2. Different bulbs are used because the UV spectral output is shifted. As you can see from Figure 2 most of the UV energy is shifted to the 340-430 range with 350-380 the strongest. Various bulbs are being used because many of the plastics and glass used in laminations absorb the UV energy because of additives such as UV stabilizers.

Figure 2



The D-bulb has longer wavelength spectral output, 340-430 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 also activate the Irgacure[®] 819. Because the Irgacure[®] 2022 is a blend of the BAPO and α -Hydroxy Ketone type photoinitiator, it will generate free radicals sufficiently using the D-bulb.

Experimental

A new series of acrylated laminating oligomers were developed for UV/EB laminations of glass substrate. 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 Oligomers

Oligomer ID	Description	25°C Visc. (cps)	Ref Index	Tg-DSC (°C)
#1	Low Viscosity Acrylic Oligomer	95	1.5183	16
#2	Low Viscosity Acrylic Oligomer	35	1.4944	57
#3	Low Viscosity Acrylic Oligomer	150	1.4660	6

These three oligomers have a refractive index range of 1.46-1.52. The refractive index is important in optical laminations. The greater the difference between the substrates refractive index (glass) and the adhesive's refractive index, the greater the difference between the incident angle (light entering) and the refractive angle (light exiting). This is known as the bending of light according to Snell's Law:

$$N_i * \sin(A_i) = N_r * \sin(A_r)$$

Where:

N_i = refractive index of the medium the light is leaving

A_i = incident angle between the light ray and the normal to the medium to medium interface

N_r = refractive index of the medium the light is entering

A_r = refractive angle between the light ray and the normal to the medium to medium interface

Even the refractive index of glass varies according to the type of glass:

Glass	1.5171
Glass, Albite	1.4890
Glass, Crown	1.5170-1.5200
Glass, Flint	1.5800-1.8900

Our experiments used glass having a refractive index around the 1.49.

The three oligomers were mixed with 0.5% Irgacure[®] 2022 to evaluate each for adhesion characteristics for UV curable laminating adhesives on glass substrates. The procedure used for mixing the oligomer with the photoinitiator consisted of blending 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 the information for our actual curing unit when we had run the tests.

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

	UV-C	UV-B	UV-A	UV-V
J/cm ²	0.045	0.515	1.678	0.059
W/cm ²	0.102	1.396	4.544	0.043

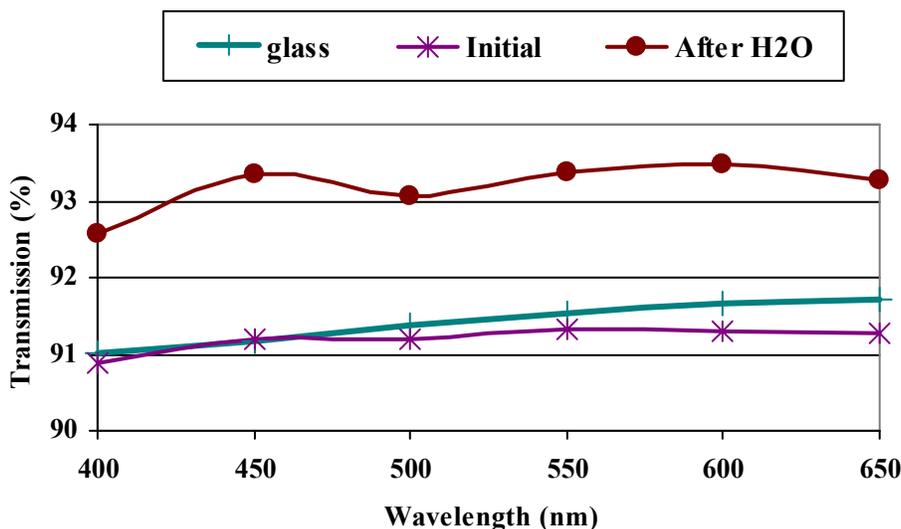
All three oligomers were evaluated for glass to glass adhesion. No surface preparation was done to the 0.040” thick glass prior to the lamination. UV-Visible Spectra were run on each of the samples. Half the samples were placed in boiling water for 15 minutes. After the samples were allowed to cool back down to room temperature, the UV-Visible Spectra was run again. Yellowness and haze were also measured on all the samples using a Hunter Lab Color Quest II. The final test run was to measure the strength of the 1”x1” lap shear joints at a crosshead speed of 0.5 inches/minute for both the initial and the samples exposed to the boiling water for 15 minutes.

Oligomer #1

Lap Shears were prepared using Oligomer #1 as described above with the addition of the photoinitiator. All samples were cured using a 600 WPI D-bulb at 25 FPM. The adhesive thickness for the 1”x1” overlap was 3 microns. This was one of the lower viscosity materials and a very low bond line thickness was obtained.

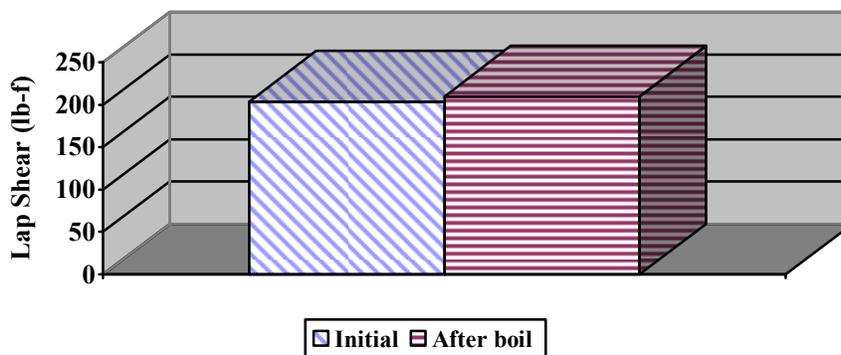
The UV-Visible transmission results are shown in Figure 3 for the first oligomer. The optical transmission of just glass is also shown as a reference. The transmission of the lamination initially is similar to the transmission of the glass. The UV-Visible transmissions improved for the glass lap shears that had been exposed to a boiling water bath for 15 minutes. This could be a result of the hot water cleaning the glass surface and therefore obtaining a better transmission.

**Figure 3: Oligomer #1
RI = 1.5183**



The yellowness and haze were also measured on both the before and after boiling water exposure. No significant difference was seen in these samples.

Figure 4: Oligomer #1 Lap Shear Results



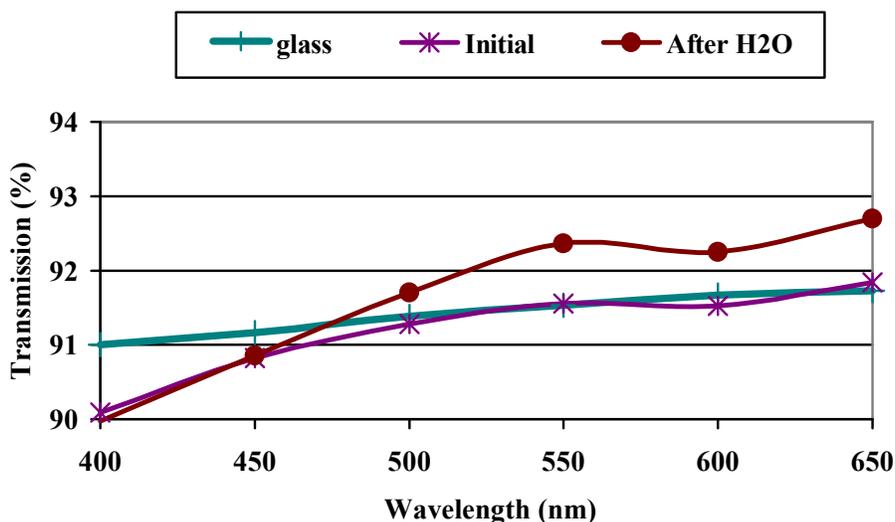
For the same set of samples, lap shear strength was measured on the initial and after the 15 minute exposure to boiling water. The results are shown in Figure 4. All lap shear samples broke glass rather than adhesive failure. Even after boiling water exposure the lap shears still broke glass.

Oligomer #2

The lap shear preparations for the second oligomer produced thicker adhesive layers. The average adhesive thickness for this oligomer was measured at 22 microns.

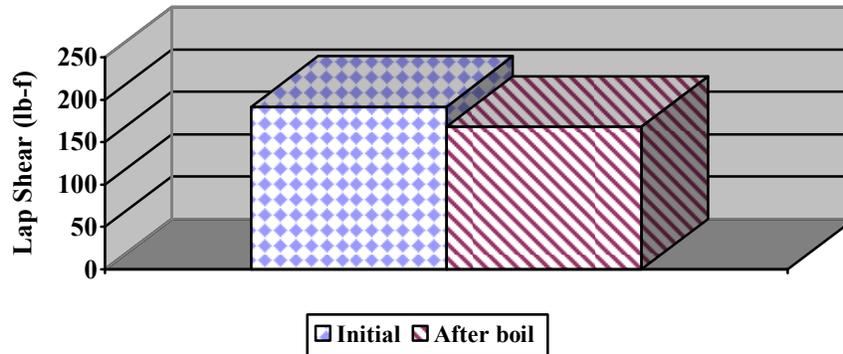
The UV-Visible transmission results are shown in Figure 5 for the second oligomer. Again, the optical transmission of glass is shown as a reference. And as seen in the previous sample, the initial UV-Visible transmission is similar to the glass with increased transmission after the samples were exposed to a 15 minute boiling water bath. Again this seems to be a cleaning effect of the glass.

Figure 5: Oligomer #2
RI = 1.4944



Again, the yellowness and haze were also measured on both the before and after boiling water exposure. No significant difference was seen in these samples.

Figure 6: Oligomer #2 Lap Shear Results



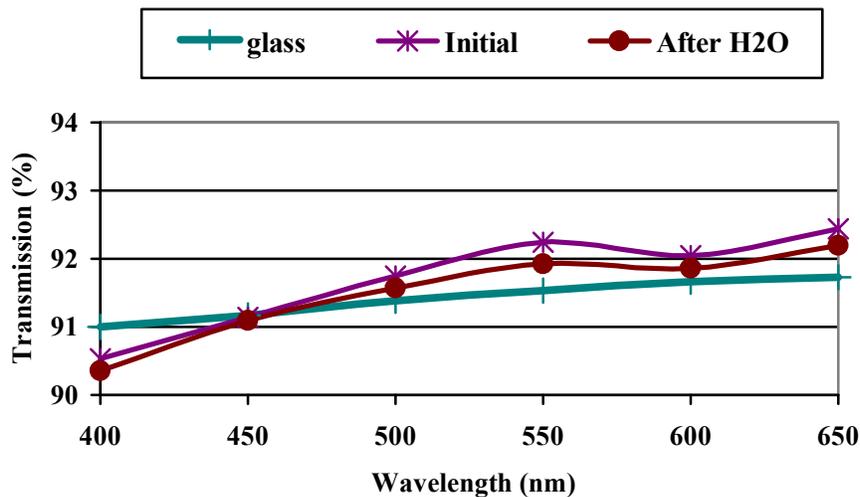
For this set of samples, the lap shear strength was measured on the initial and after the 15 minute exposure to boiling water. The results are shown in Figure 6. In all cases the glass lap shears broke glass rather than the adhesive failing. We also noted that all samples tested after the boiling water bath actually failed (broke glass) at a much lower strength than those samples that were not exposed to the boiling water.

Oligomer #3

The last oligomer evaluated also had relatively thin adhesive layers, measuring only 8 microns.

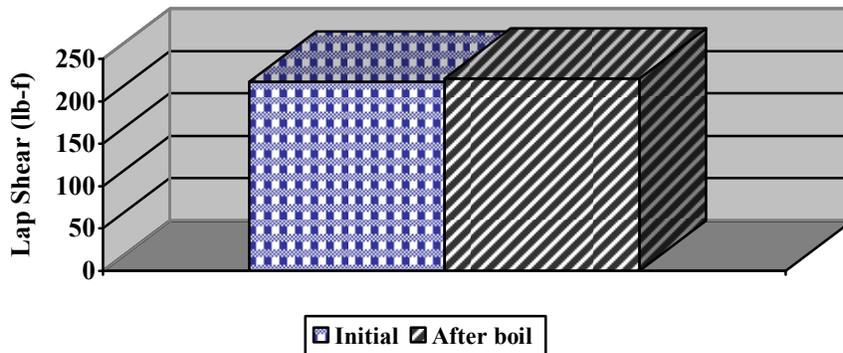
The UV-Visible transmission results are shown in Figure 7 for the third oligomer. Again, the optical transmission of glass is shown as a reference. As you can see, there is very little change from the glass to the laminate even after the 15 minute boiling water exposure.

**Figure 7: Oligomer #3
RI = 1.4660**



Again, the yellowness and haze were also measured on both the before and after boiling water exposure. No significant difference was seen in these samples.

Figure 8: Oligomer #3 Lap Shear Results



For this set of samples, lap shear strength was measured on the initial and after the 15 minute boiling water soak. The results are shown in Figure 8. In all cases the glass lap shears broke the glass while trying to separate the lamination rather than the adhesive failing. The same results were seen with the samples that had been exposed to the boiling water.

Conclusion

Over a hundred oligomers with varying chemistries were evaluated in this study. The above samples are great in all areas that we had tested for the initial and boiling water exposed samples. Some samples did give significant yellowing whereas other samples were extremely hazy, yielding transmissions in less than one percent. And then other samples that seemed good with clarity and yellowing simply fell apart in the boiling water bath.

The laminating oligomers presented have been identified for bonding glass to itself and still maintaining optical clarity after subjecting the lamination to boiling water for 15 minutes. No yellowing or hazing was seen in the samples and all UV-Visible transmissions remained nearly identical to the optical transmission of the glass. In most cases, the visible transmission actually improved after the samples had been subjected to boiling water. All initial and boiling water exposed samples presented produced lap shear laminations that actually broke the glass rather than the adhesive failing.

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