High and Matched Refractive Index Liquid Adhesives for Optical Device Assembly

Taro Kenmochi
Kyoritsu Chemical
Chiyodaku, Tokyo, Japan

Abstract
There is an increase in the number of optical sensors and cameras being integrated into electronics devices. These go beyond cell phone cameras into automotive sensors, wearables, and other smart devices. The applications can be lens bonding, waveguide imprinting, or other applications where the adhesive is in the optical pathway. To support these various optical applications, new materials with tailorable optical properties are required. There is often a mismatched refractive index between plastic lenses such as PC (Poly Carbonate), COP (Cyclo Olefin Polymer), COC (Cyclo Olefin Copolymer), PMMA (Poly Methyl Methacrylate), and UV curable liquid adhesive. A UV curable liquid adhesive is needed where you can alter the refractive index from 1.470 to 1.730, and maintain high optical performance as yellowness index, haze, and transmittance. This wide range of refractive index possibilities provides optimized optical design. Using particular plastic lens must consider how chemical attack is occurring during the process. Another consideration is that before the UV curable liquid adhesive is cured, chemical raw component can attack the plastic lens which then cracks and delaminates. We will also show engineering and reliability data which defined root cause and provided how optical performance is maintained under different reliability conditions.

Introduction
High and matched refractive index liquid adhesives are strongly required in several electronics devices. The application can be lens bonding, waveguide imprinting, and other applications where the liquid adhesives are in the optical pathway. When liquid adhesives are selected, there is often occurring mismatched refractive index and not obtained optical performance between liquid adhesives and engineering plastic lens. We introduce a liquid adhesive with important supported data as follows(1) what is risk about lamination structure and adhesive thickness(2) High refractive index liquid adhesive's optical performance data, (3) Comparison refractive index between liquid adhesive's refractive index and optical plastic lens, (4) what are the causes when the plastic leas undergoes chemical attack, (5) how to solve oxygen inhibition.

This data helps to support when you select plastic lens and make optical design.

<u>Lens structure, lens size, and adhesives' thickness provide different risk.</u>
There is often occurring technical issues which is void and delamination after the lamination process. Both void and delamination is caused by the process and the adhesive's property. Void issue is solved by how the process is optimized. On the other hand, adhesive's property is related to viscosity and wettability to solve the void issue.

If there is a void at the center part, it is difficult to reduce the void because the adhesive is already cured, and void is unable to move to the edge part. Therefore, one of solution for reducing void is the vacuum process. However, with the vacuum process it is necessary to consider investment and to take care of the substrate. Thus, air lamination is another solution. The delamination issue is becoming tricky because appearance is similar from the chemical attack issue. Delamination is often occurring at the edge part because its part is made of a thin layer after lamination process especially curved lens lamination.

Adhesive's property which is tensile modulus, elasticity, and tan delta have an effect on delamination; in addition, lens structure and size also relate to delamination. If the delamination issue is needed to be solved by adhesive, it is necessary to find optimized tensile modulus, elasticity, and tan delta. These properties are related to adhesives oligomer and monomer even fillers also are affected. Void and delamination is caused both process and adhesive's property, and we need to find out optimized process condition and optimized adhesive's property.

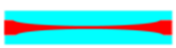
Haze is another technical issue; however, haze occurs after reliability during high temperature and high humidity testing. Haze always appeared at the edge part, and haze is growing to the active area. Adhesive is attacked by moisture and absorbed. If the adhesive's structure does not prevent hydrolysis performance, the cured adhesive starts to degrade easier. In addition, there is another key consideration that the edge part is cured completely, or oxygen inhibition is influenced. If oxygen inhibition is affected, there is tackiness at the edge which is easier to absorb moisture under the reliability test. Therefore, haze is dependent on the adhesive's property. From experience voids, delamination, and haze can occur at the edge, center, and by random. It is explained for *Table 1- What is risk dependent on lens structure, lens size, and adhesive thickness.* Before lens lamination is evaluated, this table will help to prevent each technical issue and prepare which evaluation is needed.

Table 1- What is the risk depends on lens structure, lens size, and adhesive thickness

High risk	Medium	Low risk

Lens Structure	Lens size (Diameter)	Adhesive thickness (umt)	Void					
			Edge part		Center part		Random	
			T=0	T=REL	T=0	T=REL	T=0	T=REL
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	High risk	Medium	Medium	Medium	High risk
	> 30.0 mm	20.0 ~	Medium	High risk	Low risk	Low risk	Medium	High risk
	> 30.0 mm	50.0 ~	Medium	Medium	Low risk	Low risk	Medium	High risk
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	Medium	Low risk	Low risk	Medium	High risk
	> 30.0 mm	20.0 ~	Medium	Medium	Low risk	Low risk	Medium	High risk
	> 30.0 mm	50.0 ~	Medium	Medium	Low risk	Low risk	Medium	High risk
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	Medium	Low risk	Low risk	Medium	High risk
	> 30.0 mm	20.0 ~	Medium	Medium	Low risk	Low risk	Medium	High risk
	> 30.0 mm	50.0 ~	Medium	Medium	Low risk	Low risk	Medium	High risk

Lens Structure	Lens size (Diameter)	Adhesive thickness (umt)	Delamination					
			Edge part		Center part		Random	
			T=0	T=REL	T=0	T=REL	T=0	T=REL
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	Medium	Medium	Medium	Medium	Medium
	> 30.0 mm	20.0 ~	Medium	Medium	Medium	Medium	Medium	Medium
	> 30.0 mm	50.0 ~	Medium	Medium	Medium	Medium	Medium	Medium
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	Medium	Medium	Medium	Medium	Medium
	> 30.0 mm	20.0 ~	High risk	High risk	Medium	Medium	Medium	Medium
	> 30.0 mm	50.0 ~	High risk	High risk	Medium	Medium	Medium	Medium
	3.0 ~ 30.0mm	10.0 ~ 20.0	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	20.0 ~	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	50.0 ~	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk

Lens Structure	Lens size (Diameter)	Adhesive thickness (umt)	HAZE					
			Edge part		Center part		Random	
			T=0	T=REL	T=0	T=REL	T=0	T=REL
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	20.0 ~	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	50.0 ~	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	20.0 ~	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	50.0 ~	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	3.0 ~ 30.0mm	10.0 ~ 20.0	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	20.0 ~	Medium	High risk	Low risk	Low risk	Low risk	Low risk
	> 30.0 mm	50.0 ~	Medium	High risk	Low risk	Low risk	Low risk	Low risk

High refractive index liquid adhesive's optical performance data

There is refractive index liquid adhesive's optical performance data in terms of transmittance, yellowness index, and haze compared at T=0 and reliability test under high temperature and high humidity, and UV exposure test T=500hrs. When cured adhesive is exposed to the reliability test, optical performance data is shown to have no large change number from T=0 with even refractive index not changing significantly. When yellowness index shows a number more than 1.0, it is a cosmetic issue because it is easier to find coloration visually. There is data which is shown for the cured adhesive's transmittance between 350nm to 800nm. Transmittance data provides how the cured adhesive is changed after the reliability condition.

Haze data provides how the cured adhesive became hazed which is easier at high temperature and high humidity because the cured adhesive absorbs moisture. Moisture is low molecular weight which penetrates easier into the cured adhesives; as a result, the cured adhesive's polymer and moisture is swelled and shows haze. There is experience if the cured adhesive which is already in high temperature and high humidity testing, is in a dry heat condition, the haze result is improved because absorbed moisture is released to the outside. If haze is only occurring at the edge and not grow on the active area, transmittance is maintained.

Refractive index cured adhesive needs to maintain high optical performance data even after the reliability condition, the adhesive layer's thickness becomes critical in design because the adhesive thickness becomes as large as 300um thickness, optical performance has gotten worse because the adhesive's area of contact to the external atmosphere which is attacked by a lower humidity under the reliability test. Liquid adhesive needs to survive not only high temperature and high humidity test but also the UV exposure test because the UV exposure test gives high temperature, wavelength, and oxygen. These three factors affect the adhesive's yellowness.

If there is a structured laminate together, three factors affect yellowness at the edge, and active area is prevented because of the lamination structure. Therefore, optical performance is impacted by two big factors which is optical design of the structure as sandwich or coating, and reliability test as high temperature and UV exposure test. There is a result when the high refractive index liquid adhesive is cured, in terms of how it offers optical performance data. This data is shown in Table-1: Refractive index liquid adhesive's optical performance data. Figure 1 shows Optical performance of transmittance result for cured adhesive sample A and B. Figure 2 shows Optical performance of yellowness index and haze data.

Table 2- Refractive index liquid adhesive's optical performance data

		Cured Adhesive A	Cured Adhesive B
Refractive index (589nm) after curing		~1.700~	~1.617~
Adhesive thickness		10umthickness	10umthickness
Transmittance (%) at 400nm	T=0	99.57 %	99.86%
Transmittance (%) at 400nm	T=500hr 60 degC/90%	99.46%	99.75%
Transmittance (%) at 400nm	T=500hr ASTMD 4459	97.70%	97.40%
Yellowness index	T=0	0.10	0.05
Yellowness index	T=500hr 60 degC/90%	0.11	0.05
Yellowness index	T=500hr ASTMD 4459	0.97	0.77
Haze	T=0	0.02	0.01
Haze	T=500hr 60 degC/90%	0.11	0.07
Haze	T=500hr ASTMD 4459	0.05	0.04
Refractive index (589nm)	T=500hr 60 degC/90%	1.699	1.617
Refractive index (589nm)	T=500hr ASTMD 4459	1.706	1.617

Figure 1- Optical performance of transmittance result for cured adhesive sample A and B

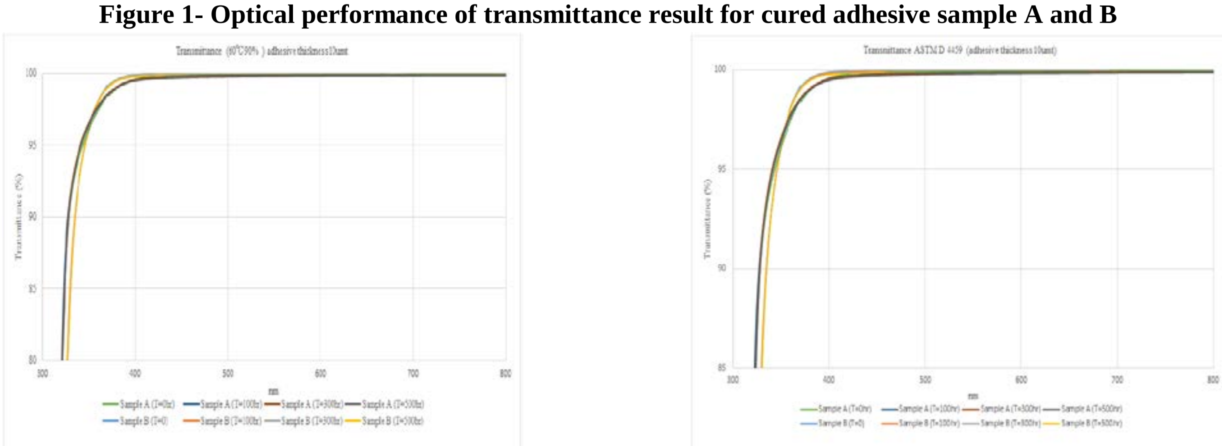
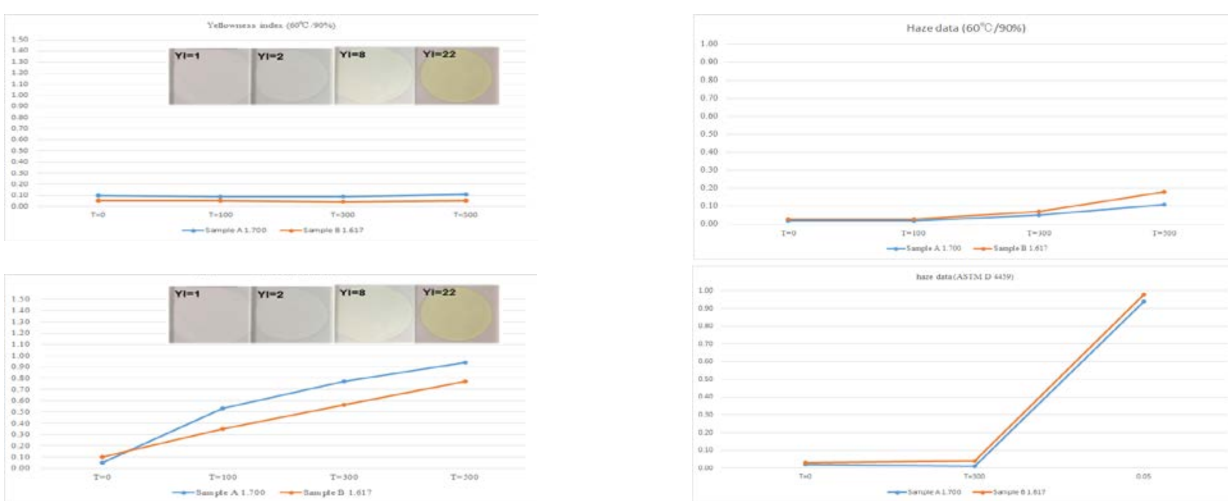


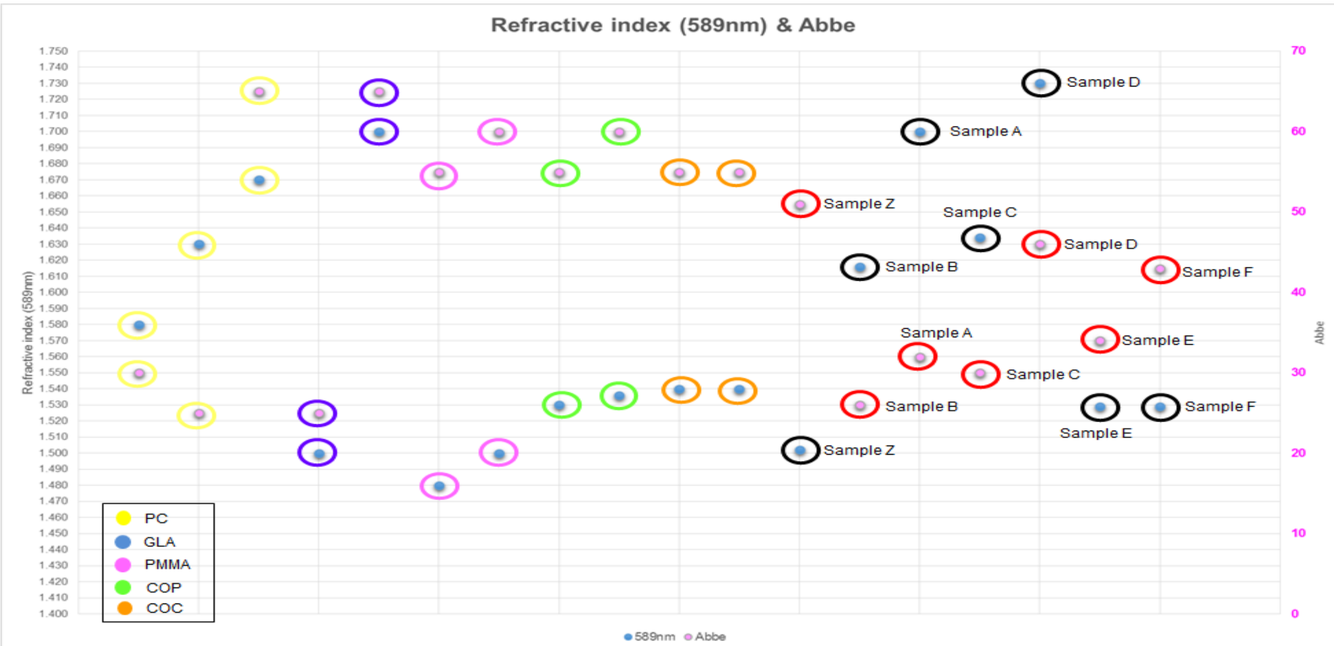
Figure2- Optical performance of yellowness index and haze data



Comparison between refractive index liquid adhesive's performance and optical plastic lens

Before optical devices are assembled, it is necessary to consider what liquid adhesives and optical lens have in terms of different optical characteristics. There is often occurring optical mismatch especially refractive index and abbe number. Therefore, there is supporting data which is shown where cured adhesive is plotted in terms of optical lens's characteristics, which is referred to in Figure 3- comparison refractive index and abbe at 589nm by cured adhesive and optical lens. Optical plastic lens's refractive index needs to match cured adhesive's refractive index because if there is a large mismatch refractive index between cured adhesive and optical lens, the optical path is influenced. For instance, there can occur interface fringes. If there is a range of refractive index in the liquid adhesive such as 1.470 to 1.730, it contributes to easier optical design.

Figure 3 - Refractive index liquid adhesive's optical performance data (GLA is Glass in Figure image)



What is the cause when the plastic lens has less chemical attack?

Optical design and refractive index of the liquid adhesive is fixed into the optical device; however, there is a critical consideration in terms of the optical lens having chemical attack from the liquid adhesive. When there is found to be chemical attack during the process, it is necessary to set and do design of engineering again because the liquid adhesive is necessary to be fine-tuned or a new adhesive developed. Liquid adhesive considers raw chemical composition and how each composition prevents swelling into optical lens and composition of polarity. We introduce how we have measured to check for chemical attack and there are two different validation measurements as follow in Table 3- measurement process for chemical attacking of optical lens. Comparing measurement method, A and B, measurement method B is stricter because the optical lens is bent which is caused by stress. The stress part is easier to swell the raw chemical composition and for chemical attack to occur. There is design of engineering data which is shown how the optical lens, Poly Carbonate and Poly Methyl Methacrylate, has chemical attack occurring as shown in Figure 4 and 5- DOE test result Optical lens versus Liquid adhesive.

Table 3- Measurement process flow for chemical attack

	Measurement method A	Measurement method B
Process 1	Preparation of silicone spacer and optical lens	Preparation for particular size of optical lens
Process 2	Dispense liquid adhesive on optical lens plate	Optical lens is bent and maintain the bend
Process 3	Lamination by air	Dispense liquid adhesive on bent optical lens at center
Process 4	Hold and stay at room temperature	Hold and stay at room temperature in dark room
Process 5	UV cure 6,000mJ/cm2	Check for chemical attack (appearance)
Process 6	Heat anneal 120 degC x 30min	
Process 7	Check for chemical attack (appearance)	

Figure 4- DOE test result Optical lens (Poly Carbonate) versus Liquid adhesive

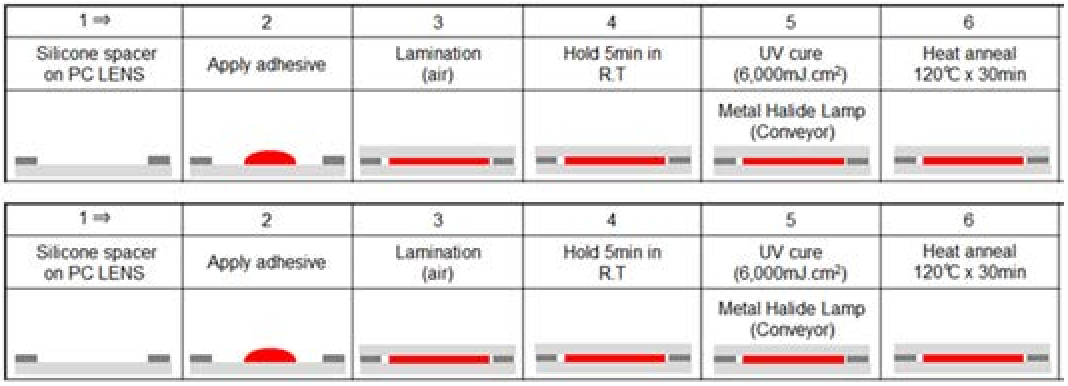
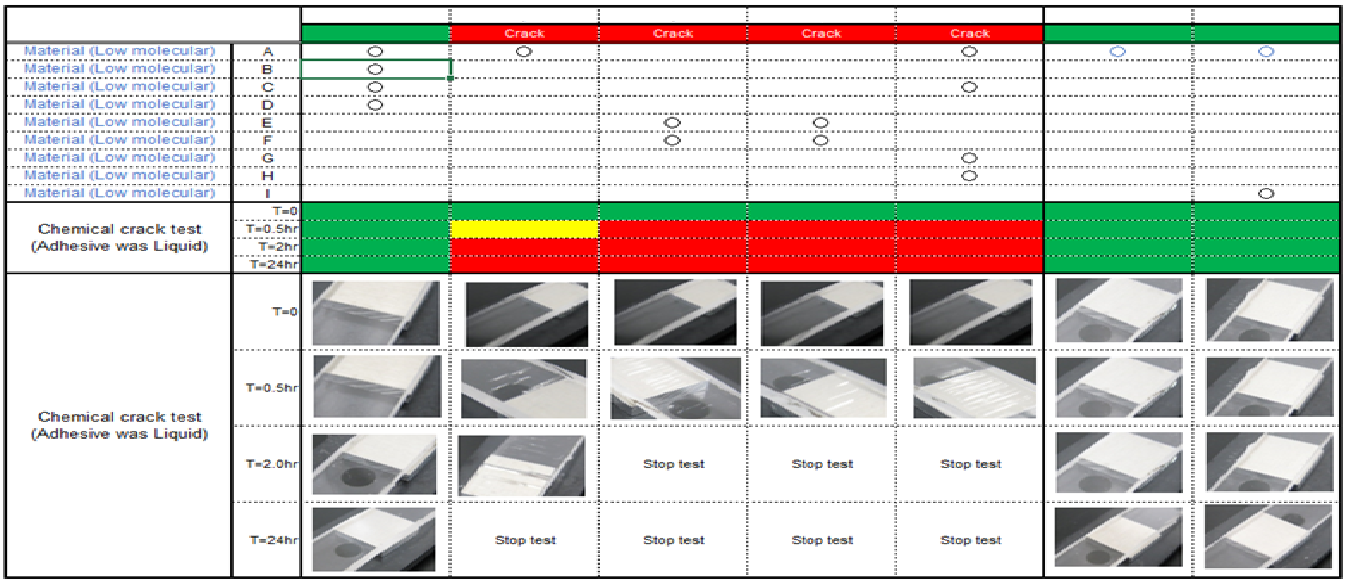


Figure 5- DOE test result Optical lens (Poly Methyl Methacrylate**) versus Liquid adhesive**



DOE test results from Figure 4- DOE test result Optical lens (Poly Carbonate) versus Liquid adhesive indicates how long the liquid adhesives is able to stay on the plastic lens before the UV cure process. This result indicates that the liquid adhesive is able to contact for less than five minutes. If the liquid adhesive stays on the optical plastic lens more than five minutes, chemical attack will occur and the part will show haze. This result offers as to how process flow and time needs to be controlled which impacts productivity. In addition, measurement method B as indicated in *Table 2- measurement process flow for chemical attack, and Figure 5- DOE test result Optical lens (Poly Methyl Methacrylate) versus Liquid adhesive* is provided a much stricter test. The Poly Methyl Methacrylate lens is bent, and the liquid adhesive swells easier into the lens. The key point is that which chemical composition swells into the optical lens easier. High molecule material does not attack and swell into the optical lens. On the other hand, low molecule material swells into the optical lens especially if the optical lens has already been scratched. This is the same occurrence as when germs attack into a wound. Inspection of the optical device's appearance after the cured process will show haze. It is difficult to determine haze caused by chemical attacking or delamination. Both chemical attacking and delamination is similar in appearance as haze; however, if the optical lens has chemical attack before the UV cure process, this is not delamination.

How to solve oxygen inhibition in the process

This is related to technical issues from haze. Oxygen inhibition is difficult to determine because adhesive's cure reaction is already completely. Some acrylate liquid adhesives are attacked by oxygen during the cure process; however, oxygen inhibition appears as surface tackiness. There is data on how acrylate adhesive prevents tackiness which occurs from oxygen. This data explains how UV curable acrylate adhesive has oxygen inhibition from different UV lamps. UV LED365nm lamp exposes a single wavelength; however, other UV lamps are able to expose several wavelengths which range from short to long wavelength. Those wide range wavelengths prevent oxygen inhibition. There is often confusion because FTIR measurement shows that the cure reaction is completed; however, the surface has tackiness. Therefore, it is important to know if oxygen inhibition has occurred, but the reaction is completed. There is data which is shown in *Figure 6- FTIR measurement for UV curable acrylate adhesive*, and *Figure 7- How to check surface tackiness.* The data for Figure 6 and Figure 7is able to be compared because design of engineering data is used for the same UV curable acrylate adhesive.

Figure 6- FTIR measurement for UV curable acrylate adhesive

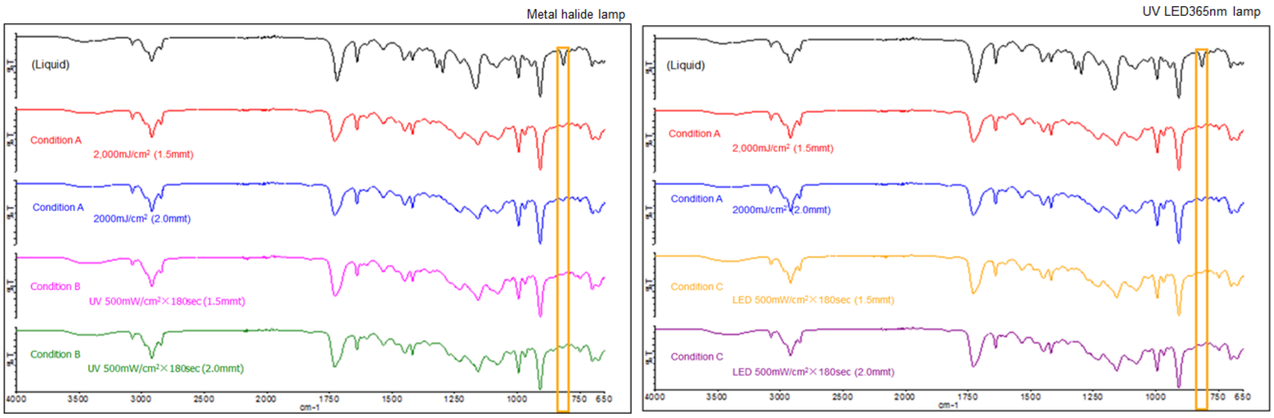


Figure 7- How to check surface tackiness

Test	Product	Lamp type	UV intensity	Cure time	Results
①	Acrylate	UV-LED(365nm)	50mW/cm2	60sec	Tackiness
②	Acrylate	UVNT Lamp	50mW/cm2	60sec	More no tackiness
③	Acrylate	High mercury	50mW/cm2	60sec	No tackiness
④	Acrylate	Metal halide	50mW/cm2	60sec	No tackiness

Summary/Conclusions for high and matched refractive liquid adhesive

There are several sets of data shown which covers the lens lamination process, selection of liquid adhesives, and technical solutions. Using high refractive index liquid adhesive has limitations and tradeoffs for the adhesive's performance. There is no one way on how to solve the tradeoff of the adhesive's performance however, if there are basic oligomer and monomers which are able to solve the tradeoffs, liquid adhesives have the opportunity to make very high refractive index liquid adhesive, and maintain current processability.