APPENDIX I – GLASS TRANSITION TEMPERATURE (T_g)

Knowledgeable scientists disagree on the usefulness of different T_g measurement techniques. However, the Optical Industry is most interested in **motion**. DSC does not measure movement, but a “thermal event”. It has long been assumed that, at last for epoxies, this was associated with other properties that may be evident around a Glass Transition Point. In addition, DSC peaks shift with cure conditions. DSC peaks are easy to misinterpret and should not be the sole decision criteria for movement on temperature. **<u>For these reasons, we no longer use DSC to measure glass transition temperatures</u>.**

(1) DSC stands for Differential Scanning Calorimetry. DSC detects “extra” thermal absorptions/emissions from a plastic (cured adhesive) as it is heated. Plastics can undergo many thermal reactions when heated. Only one of these reactions is the glass transition, i.e., the temperature at which the polymer strands realign from a crystalline state to an elastic state. Many other energetic peaks do show up on DSC spectra including, additional chemical reactions, solids melting, amorphous reorganizations to a crystalline state. These other DSC peaks can interfere with the glass transition peak. Interfering peaks can hide the glass transition or combine with the glass transition to produce a peak between the two reactions.

DSC is the oldest and least expensive thermal analysis technique. Some companies continue to use DSC because it has been widely used for epoxy in the past. DSC <u>tends to give higher values</u>. Epoxy companies use DSC as QC tool to verify the thermal cure reaction occurs within a specified range. Epoxy companies also use the DSC to measure the T_g of the cured adhesive. For an epoxy, the endothermic glass transition is a large, energetic DSC peak. This peak will shift depending upon the cure cycle of the epoxy. For a urethane, silicone, or acrylate, the glass transition peak is often a very weak DSC peak that can be lost in the noise. The glass transition peak of OP-63 was hidden in the noise. OP-63 has several DSC peaks above 100°C. These peaks were misinterpreted to represent the glass transition. The chemical structure of OP-63 is very different from another Dymax resin. If fully cross-linked, the chemical structure contains elements that could push the glass transition anywhere from 130ºC to 220ºC. As we found from other work, this system does not fully cross-link with UV or thermal exposure.

(2) TMA stands for Thermal Mechanical Analysis. TMA directly measures motion as a sample is heated. There can also be an abrupt change of shape (motion) when a polymer goes from a crystalline to a more amorphous state--this is the glass transition. In addition to the glass transition, TMA analysis yields the CTE of the cured resin.

Table 1: Adhesive changes both on cure and after thermal excursions

Adhesive OP-60-LS	Adhesive OP 61-LS
< 0.1% (during UV Cure)	< 0.1% (during UV Cure)
< 0.1% (after 24 hr, 120°C)	< 0.1% (after 24 hr, 120°C)

Epoxies tend to have large dimensional changes at the T_g. A resilient adhesive can exhibit smaller TOTAL MOVEMENT than epoxies regardless of T_g, depending on individual formulations. Figure 1, below compares a high T_g epoxy and a high T T_g UV adhesive measured on <u>different scales</u> in order to make a visual comparison. However, the scales of the two adhesives are vastly different; the UV expanding far less that the epoxy.

Figure 2 compares filled adhesives as measured on the <u>same scale</u>. Both UV adhesives display much lower total movement despite one of the adhesives having a “lower T_g” than the Epoxy.

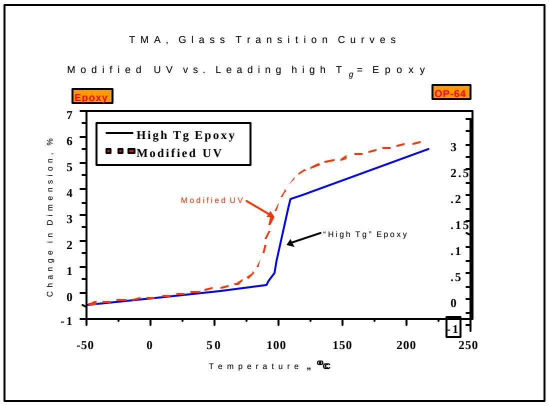


Figure 1

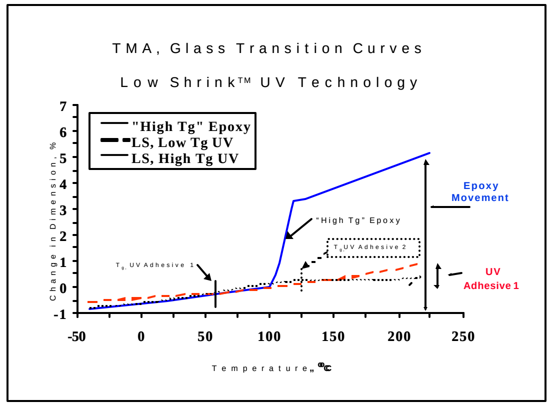


Figure 2

The following below compares published data from a leading optical epoxy supplier compared to selected UV adhesives. The highest T_g is found by DSC.

Looking at the final column, the CTE from -45ºC to +200ºC is a measure of the TOTAL MOVEMENT, regardless of T_g over the operating temperature range. The smaller the number, the smaller the movement.

Table 2: Data comparison of leading optical epoxy supplier vs. selected UV adhesives

	Glass Transition (T_g)		**CTE**	**CTE**	**CTE****
Optical Adhesives	**(by DSC)**	**(by TMA)**	**Alpha 1**	**Alpha 2**	**-45 to 200**
Popular "High Temperature Epoxy" for Fiber Optics (heat cure at 150ºC)	120ºC*	90ºC**	56.0	139.0	87.0**
UV Curing Epoxy	116ºC*	57ºC*	58.0	156.0	110(est.)
Filled UV Acrylic 1*	Over 120°C	65ºC	27.0	121.0	74.0
Filled UV Acrylic 2*	None detected	54ºC	27.0	66.0	50.0
Filled UV Acrylic 3*	NM	125ºC	71.0	5.0	52.0

NR = Not reported
* Published values
** As tested in our laboratories.
** A measure of the total movement over the thermal operating range of some optical devises.

APPENDIX II - CURING LAMP CONSIDERATIONS

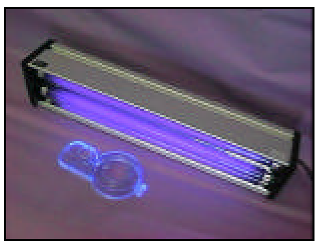
Ultra Violet, Visible, and Combined UV Visible Curing Lamps

UV adhesives evolved in the late 70's and early 80's for optics from polyester based curing chemistry that began as early as about 1940. Mercaptoesters and acrylic modified epoxies began being used for photonics in the late 70's. These so called first generation optical UV curing adhesives are typically placed for several hours under low intensity UV lights, commonly called black lights. With some adhesives, though not with Cellux™ Modified Acrylics, black light cure can rake hours, overnight, or even longer, exposures.

Older generation UV adhesives do not develop full properties for weeks after UV exposure (refer to manufacturers Data Sheets). Low intensity lights (black light) shown in Figure 1, while being very low in cost, do not produce the rapid complete cures needed for today's high speed assembly requirements.

Figure 1:

LOW INTENSITY LIGHTS FOR SLOW CURE



Black Light
(minutes to hours)

HHL-400
Low Intensity Spot Lamp
(for visible cure formulations)

Choosing the right curing lamp for the application can be critical to obtaining maximum productivity and cure properties. Ideally, the light frequency and intensity of the selected lamp should match the curing chemistry of the adhesive. Other factors to consider include determination of desired throughput (whether batch or continuous process), and matching the lamp "footprint" with the area to be bonded. The optimum shape or pattern of light emitted by a lamp for any specific application is called its "footprint", and depends upon the size and geometry of the bond area and other process recommendations.[5]

UV curing lamps are typically categorized as follows:

- **Spot** - Spot source lamps with light guides are typically used for curing small areas, or areas where light needs to be directed through partially obstructed areas that can not be easily reached.
- **Flood** – Flood sources offer a large cure area but generally lower light intensity. They emit less heat as well, and are usually the product of choice for bonding heat sensitive plastic parts. The large area of flooded light also is useful for curing many parts at once. Floodlights may be fitted over a conveyor or turntable for continuous product assembly.
- **Focused Beam** – Similar in configuration to a flood lamp, the focused beam lamp concentrates light energy into a beam, (typically 1" x 6"), generating intensity higher than that of a flood. Focus beam lamps may also be used over a conveyor for continuous processing.

The lamps shown in Figure 2 represent a range of high speed curing equipment suitable for optical assembly applications from the Dymax Corporation.

Figure 2: Moderate intensity lamps for fast cure

Many applications require only lower intensity curing lamps. Bonding between surfaces, one of which allows light to pass, is one of the applications where resin may be effectively cured with lower intensity, lower cost lamps. Most UV formulations are capable of curing within 1 to 30 seconds through clear glass or plastic parts under lower intensity lamps. Because the inhibiting effect of oxygen is not present, cures are relatively fast. Bond lines are usually fairly thin - 0.001 to 0.125 inches.

Table 1: Typical adhesive and coating cure rates with a range of UV curing lamps

Lamp/Type	**Moderate Intensity UV Flood 2000-EC**	**Higher Intensity UV Flood 5000-EC**	**High Intensity UV Spot PC-3Ultra**	**Very High Intensity UV Spot 3010-EC**	**Conveyorized Beam 2 x 1200-EC High Intensity**	**Conveyorized Electrodeless Lamps**
Spectral Output of Lamps (nanometers)	300-500	200-500	200-500	200-500	200-500	200-500
Nominal Intensity (mW/cm^2)	20-60	175-225	1,000-2,000	1,800-5,000	225-275	1,700 – 2,000
Typical Adhesive Cure Rate						
(UV/Visible Cure Adhesive)						
Between Surface Cures (Glass)	1-4 sec	1-3 sec	<1-2 sec	≤ 1 sec	3-5 feet/min	5-20 feet/min
On Surface Cures*	40-240 sec	10-40 sec	2-10 sec	1-5 sec	1-3 feet/min	3-10 feet/min
(UV Cure Adhesive)						
Between Surface Cures (Glass)	2-6 sec	1-4 sec	1-3 sec	≤ 2 sec	2-4 feet/min	5-15 feet/min
On Surface Cures	30-600 sec	20-50 sec	3-5 sec	1-3 sec	1-2 feet/min	1-10 feet/min

Ranges represent the fastest and slowest cure times of Dymax formulations under the stated lamps.

*Some formulations never achieve a dry surface cure, though most do. The time range stated represents the fastest to the slowest curing products.

APPENDIX III - ADHESIVES AVAILABLE TO THE OPTICAL ENGINEER

Adhesive can be the best, most cost effective method of joining components. Adhesive issues can include material handling (shelf life/proper mix ratio/pot life); long cure times often at high temperature; application and dispensers; and environmental concerns. Single component, light curing Aerobic Acrylic Adhesives are designed to reduce problems and maximize for both batch and continuous production processes. With improved performance these new generation adhesives are replacing many traditional adhesives. Table 1. provides a quick comparison of typical adhesives used in Photonics.

Table 1. Adhesives for optical applications

Adhesive	**Aerobic Acrylic Adhesive**	**UV Mercaptoester**	**Epoxy**	**RTV Silicone**	**Cyanoacrylate**
Cure Mechanism	UV or visible light	UV light	2-part mix or frozen	Moisture	Moisture
Typical Properties	Resilient - hard to very flexible	Resilient – hard to very flexible	Very hard and brittle	Very flexible and soft	Hard and brittle
Time To Full Cure	Tack in seconds Full cure in minutes	Pre-cure in seconds Post cure for minutes Post bake	Minutes to hours	Hours	Seconds
Odor	Low	Pungent	Low	Low	Pungent
Storage	1 year, room temperature	4-6 months refrigerated	Various	1 Year	4-6 months refrigerated

Light curing Aerobic Acrylic Adhesives - offering a wide range of options

A tough, resilient urethane polymer backbone gives Aerobic Acrylic Adhesives high strength, toughness, and resiliency as well as a range of properties from rigid to flexible, from very hard to very soft, depending on the formulation. Formulations can come in a range of viscosities, from thin wicking grades to thixotropic gels. These adhesives cure "on demand", allowing the operator to position the lens before affecting cure. UV curable resins can be cured with UV light only. Light curing Aerobic Acrylics, some termed "Ultra Fast™", cure with UV or visible light and offer the benefit of being able to cure even through UV blocked plastic, such as polycarbonate, polystyrene, and polymethylmethacrylate (acrylic). Multi-Cure® formulations offer the ability to cure with heat as a secondary cure method, permitting cure in a shadowed area.

Light curing Aerobic Acrylate Adhesives cure by a free radical polymerization as depicted in Figure 1 below. Cure is generally complete within a few seconds though optimum glass adhesion may take longer due to the slower reaction rate of adhesion promoting additives.

Figure 1. Free Radical Polymerization

>C=C< + R• → R-C-C•	Free Radical Initiation
R-C-C• + >C=C< → R-C-C-C-C•	Chain Extension
R-(-C-C-)$_n$-C=C< or R-(-C-C-)$_n$-C-C-R	Termination

UV curing mercaptoester

Long a "standard" in optical assembly, thiol-ene polymer (a.k.a. mercaptoesters) systems can yield sealants or adhesives that range from hard to soft. Some formulations contain solvents and may be flammable. Initiated by UV light, thiol-enes cure by an addition mechanism as shown in Figure 2. Most commercial literature indicates that a significant amount of time is required for cured properties to fully develop. Post cures of at least one week at 50ºC (122ºF) are frequently required according to conventional literature.

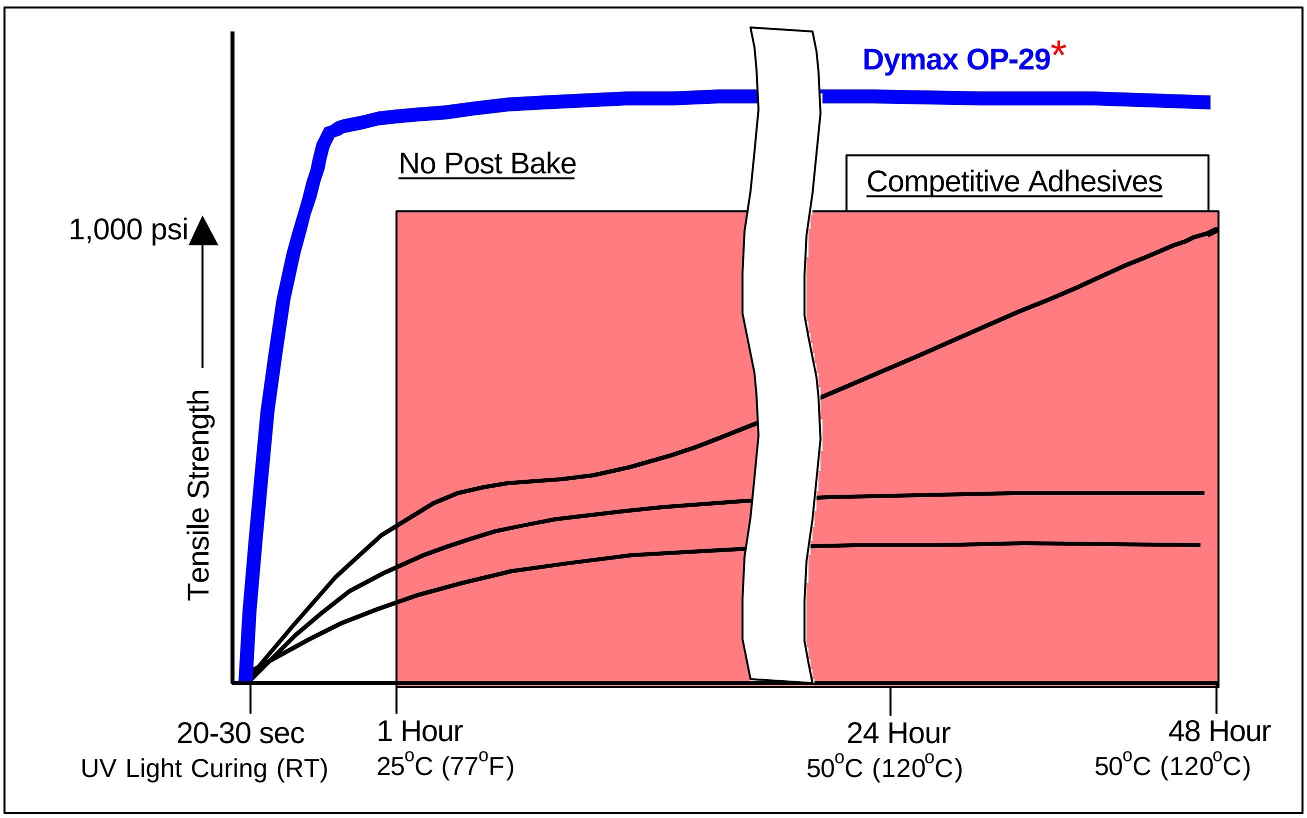
Figure 2: Mercaptoester polymerization

>C=S< + R+ → R-C-S+	Addition Reaction Initiation
R-C-S+ + >C=S< → R-C-S-C-S+	Chain Extension
$R\text{-}(\text{-}C\text{-}S\text{-})_n\text{-}C{=}S<$ or $R\text{-}(\text{-}C\text{-}S\text{-})_n\text{-}C\text{-}S\text{-}R$	Termination

Both the Anaerobic Acrylic Adhesives and the mercaptoesters cure upon exposure to UV light though the cure chemistries are different. Does this difference in composition then, result in a difference in performance? Laboratory testing of these two types of UV curing products in conjunction with a review of published literature has shown some significant distinguishing features.

Figure 3 below shows a significant increase in both the speed of cure and strength of the Aerobic Acrylic Adhesives compared with the mercaptoester based adhesives.

Figure 3: Compression strength versus time following UV cure



During UV cure, adhesion promoters become part of the polymer matrix, which after cure, can react with the glass surface to show a 10-200% increase in compressive strength. This increase is due to a secondary cure mechanism that forms strong covalent bonds directly to the silicone atoms in the glass. See Figure 6 for more information.

Epoxies

Typically used when induced stress or speed of cure are not important, epoxies can provide durable, rigid structures for high temperature applications. There are a wide variety of systems. Typically, epoxies fall into one of three categories; two-component systems, one-component heat cure systems, and one-component frozen systems. However, all present processing problems, ranging from limited pot life and slow cure to special storage. Two-part epoxies typically require 24 hours for full cure. Heat curing types, whether premixed, frozen or a true single component grade, usually requires exposure to 120º - 150ºC heat.

UV curing epoxies

While similar in properties to heat curing epoxies, UV curing epoxies are typically lower in adhesive strength, especially to glass and metal. Older types of UV epoxies actually "bond" parts by forming a vacuum between closely matched surfaces upon cure. Their greatest advantage is low shrinkage and good thermal stability. UV curing epoxies cure as fast or faster than other UV curing adhesives in very thin layers. However, their depth of cure is very limited and that coupled with lower adhesion has tended to limit their use in many assembly applications. Lower durability is frequently observed.

Figure 4. Epoxy and UV epoxy polymerization

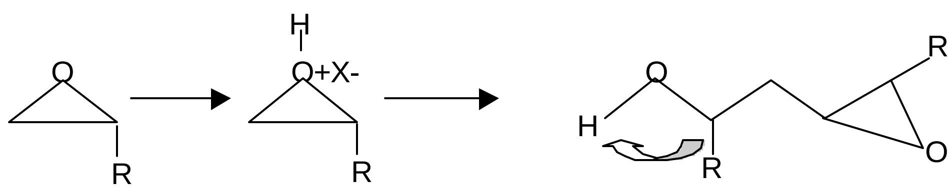


Table 2: Cure time comparisons of Aerobic Acrylic Adhesives and epoxy systems

	UV Aerobic Acrylic adhesives	**2-Part Epoxy**	**1-Part Thermal Cure Epoxy**	**Frozen 1-Part Epoxy**
Speed of Cure to 0.125"	15-30 seconds	10-50 minutes	15 min - 2 hours @ 100 -150ºC.	3 hour thaw; 10-50 minutes
Time to Reach Full Strength	20 minutes	24 hours	Heat time + cool down	24 hours
Pot Life	Unlimited	5-60 minutes	Days @ room temperature	10-50 minutes @ RT

Silicones

Silicones have a highly flexible polymer backbone and are usually used in gasketing and sealing applications. Two-part mix silicones cure in a few minutes while one part "RTV" types need controlled humidity and many hours to many days to cure fully. There are a few types of UV curing silicones. Most are used as release agents. Other types on the market are simply mixtures of UV curing acrylics and RTV silicones. As with other RTV types, full cures require long exposures to humidity. Most RTV silicones give off other chemicals on cure (outgassing) which may fog or even damage precision optical components.

Cyanoacrylates (CA's)

Rigid and brittle CA's (superglues) cure in seconds upon contact with the moisture that is naturally absorbed on almost all surfaces. Some plastics require priming. Many CA's effloresce on cure, resulting in a "frosting" effect that can effect both appearance and the clarity of optical components. Though depending on it for cure, CA bond lines are quite sensitive to and degrade with exposure to too much moisture. Most CA bonds are not shock resistant.