

MOVEMENT BETWEEN BONDED OPTICS

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INTRODUCTION

Controlling the movement of bonded optical parts depends, in large measure, on the properties of the adhesives used. Common issues include both shrinkage during cure and expansion during thermal excursions. Designers have historically had to limit their designs to optics whose thermal range fell below the then-available “high” glass transition temperature (T_g) epoxies; i.e., operating below the adhesive’s T_g . However, many of today’s optical devices employ even higher operating temperatures and require greater resistance to environmental conditions. The common minus 50°C to plus 200°C microelectronic test operating range challenges even classical “High T_g ” optical epoxies.

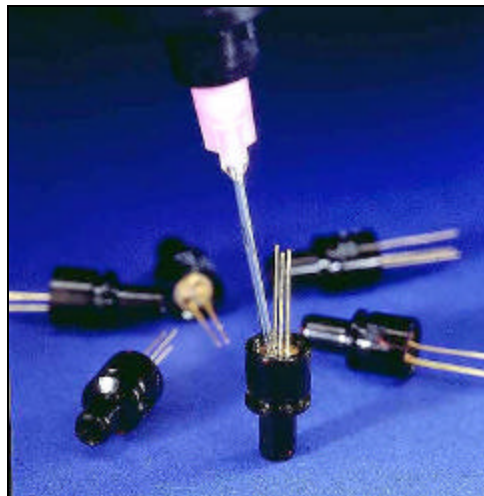
The NO SHRINK™ family of Optical Positioning adhesives features low total movement between bonded parts either on cure or when the optical device is thermally cycled. NO SHRINK™ products are based on novel, patent-applied-for technology. This technology was incorporated into light curing urethane-acrylics to create products with thermal characteristics that are different from those of older technology adhesives.

Table 1. Dimensional changes (measured at 25°C)

Adhesive OP-60-LS	Adhesive OP-64-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)
$T_g \sim 50^\circ\text{C}$	$T_g \sim 125^\circ\text{C}$

“Rules of thumb” for comparing epoxy resins are not accurate for comparing other resins or other resins with epoxies. Novel NO SHRINK™ UV and visible light curing adhesives exhibit less total movement over a temperature range *regardless of the T_g* . NO SHRINK™ is designed to help the optical designer by offering new solutions to control relative parts movement over the thermal range of optics.

Figure 1. VCSEL potting; a typical use for NO SHRINK™ positioning adhesive



LOW SHRINK LIGHT CURING ADHESIVES (LCA)

In traditional formulations, fillers are added to adhesives to reduce shrinkage during cure. While useful to control shrinkage-on-cure, fillers do not necessarily reduce further dimensional change due to elevated operating temperatures. The NO SHRINK™ adhesive family uses new technologies to achieve both the unique feature of minimal shrinkage during instant UV cure AND the ability to resist shrinkage and expansion when heated. This level of low shrinkage and resistance to further movement with heat has not been observed with other positioning adhesives until now. Table 2 compares the linear shrinkage of NO SHRINK™ adhesives to their precursors.

Table 2. Linear shrinkage*, after UV cure and after 120°C thermal excursion

Adhesive	Linear Shrinkage, After UV Cure	Linear Shrinkage, After UV Cure AND 120°C, 24 hours
<i>Prior Filler Technology:</i>		
OP-60	0.6 %	1.0 %
OP-61	0.8 %	1.6 %
<i>No Shrink Technology:</i>		
OP-60-LS	< 0.1 %	< 0.1 %
OP-61-LS	< 0.1 %	< 0.1 %
OP-63-LS	< 0.1 %	< 0.1 %
OP-64-LS	< 0.1 %	< 0.1 %
OP-65-LS	< 0.1 %	< 0.1 %
OP-66-LS	< 0.1 %	< 0.1 %

*Linear Shrinkage Test Method. DSTM D-102 is the DYMAX Standard Test Method used to measure linear shrinkage and is derived from ASTM D-2566-86. This test method is also similar to SPI-ERF 12-64, "Method of Test for Linear Shrinkage of Epoxy Casting Resins During Cure."

Linear shrinkage is determined by curing a 10-inch bar of adhesive and measuring the change in length after cure. The UV cured shrinkage bars may be additionally heated in an oven at a given temperature and length of time to observe further dimensional change. After heating, the shrinkage bars are allowed to cool to room temperature before the final measurement is taken.

POLYMER MOVEMENT AND PHASE TRANSITIONS

The optical designer needs adhesives to join optical components and needs to avoid adhesives that may have alignment problems over the thermal operating range or over the lifetime of the device. This section hopes to aid the optical designer in understanding the polymeric properties that are often used as guidelines in predicting product life. The properties of thermal expansion and contraction and phase transitions are reviewed. Equally important is understanding how these properties are measured.

All unstressed materials expand and contract with temperature. The Coefficient of Thermal Expansion, CTE, is the proportionality constant that assumes a linear increase in expansion for a linear increase in temperature. The CTE is only valid over a limited temperature range. If a material undergoes a phase change, then movement is no longer linear. All materials used in optics (glass, metal, and polymers) have more than one solid phase. Each solid phase has its own CTE. Because the phase changes of glasses and metals usually occur outside the operating temperatures of optical devices, we usually list a single CTE for glasses and metals.

Table 3 compares the room temperature CTE of glass, semiconductors, metals and polymers. The CTE of organic polymers is much higher than other materials. Thus, as the temperature increases, the polymer is expected to expand much more than the other optical components. To minimize motion and thermal alignment problems, polymers with a low CTE have been traditionally selected for bonding and positioning optics.

Table 3. Physical and thermal properties of materials used in optical and electronic components and devices (need source book)

Component Materials	Material Type	CTEx 10 ⁶ in/in/°C
Glass, Soda Lime	Glass	2.8
Glass, e-glass	Glass	9.0
Silicon	Optical Semiconductor	2.3
Germanium	Optical Semiconductor	5.9
Galium Arsenide (GaAs)	Optical Semiconductor	6.0
AMTIR-1	Optical Semiconductor	12
Aluminum	Metal	22.4
Copper	Metal	16.4
Gold	Metal	14.1
Lead	Metal	30
Silver	Metal	18
Solder	Metal	28
Tin	Metal	19.9
Typical Adhesive Polymers		
Epoxy	Polymer	45-100
Urethane	Polymer	60-250
Silicone	Polymer	200-1000

Polymers are often defined by two phases. A rigid crystalline phase and a rubbery elastic phase. Each phase has its own CTE. The CTE for the crystalline phase is called “alpha 1” The CTE of the elastic phase is called “alpha 2”. The temperature between these two phases is called the glass transition temperature, T_g . Polymers undergo nonlinear motion in region of the glass transition temperature. This is a reversible phase change. No chemical bonds are broken in going from the crystalline to the elastic phase. (See Figure 2.)

GLASS TRANSITION TEMPERATURE AND MELTING

There are misconceptions about the glass transition temperature. Confusion arises because most people are more familiar with thermoplastic polymers than thermosetting polymers. Thermoplastic polymers can melt and reflow when heated. The melting point is phase transition between the solid rubber state and the liquid resin state. Thermoplastics are typically not used with high performance optical devices because the device would fall apart above the melting point of the plastic. Polymers consist of long linear molecules called polymer chains. The linear polymer chains of thermoplastics have no (or few) bonds between. The products become solids at room temperatures because the chains are very long and too tangled to move without heating. Thermoplastic adhesives like most hot melt adhesives, solvent-based adhesives, and water-based adhesives can melt and flow.

Thermosetting polymers “cross-link” in the process of becoming a solid. Cross-links are extra chemical bonds between the linear polymer chains. These extra links are chemical anchors that prevent thermosetting polymers from melting. Thermosetting polymers can never be heated to a temperature where they flow like a liquid. Thermosetting polymers can be heated to temperatures where they are pliable or prone to creep when stressed. Thermoset adhesives like epoxies, urethanes, silicones, rubbers and all light curing adhesives cross-link to cure. *THERMOSETTING ADHESIVES CANNOT MELT AND FLOW.* There is no flow of a thermoset above its glass transition. Optical devices requiring permanent fixturing are only constructed with thermosetting adhesives. DYMAX UV and visible light curing adhesives are thermoset plastics when cured.

MEASURING THE GLASS TRANSITION TEMPERATURE

Differential Scanning Calorimetry (DSC) is a common method to determine T_g . DSC is frequently also used as a quality control tool to verify that the manufactured epoxy resin cures at the right temperature. DSC measures the energy the polymer absorbs or emits as it is heated. All deviations from linear heating indicate either a chemical reaction or phase change. Plastics can undergo many thermal reactions when heated. Only one of these reactions is the glass transition. Many other energetic peaks can show up on DSC spectra, including additional cross-linking, other chemical reactions, melting of additives, evaporation or sublimation of unreacted components, combustion of the polymer or unreacted components, and 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 single peak between the two peaks.

DSC is also used to measure the T_g of a cured adhesive. DSC tends to give high values for the glass transition (see Table 4). For an epoxy, the endothermic glass transition tends to be a relatively large, energetic DSC peak. This peak will shift depending upon the cure cycle of the epoxy. Highly crystalline and highly cross-linked polymers tend to have very energetic glass transitions. The more energetic the transition, the more rearrangement and motion of the polymer chains required to go from a crystalline orientation to an elastic domain.

Table 4. Data comparison of leading optical epoxy supplier vs. selected No Shrink™ UV curing adhesives

	Glass Transition (T_g)		CTE ($\times 10^{-6}$) (by TMA)	CTE ($\times 10^{-6}$) (by TMA)	CTE ($\times 10^{-6}$) (by TMA)
	(by DSC)	(by TMA)	Alpha 1	Alpha 2	-45 to 200
Optical Adhesives					
High T_g positioning “Red” Epoxy (heat cured at 150°C)	120°C*	95°C**	56.0	139.0	87.0**
Commercial UV Curing Epoxy	116°C*	57°C*	58.0	156.0	110 (estimated)
OP-61-LS Positioning Adhesive	Over 120°C	65°C	27.0	121.0	74.0
OP-65-LS Positioning Adhesive	None detected	125°C	27.0	66.0	50.0
OP-4-20632 In Light Path Adhesive	NM	100°C	45.0	105.0	90

NM = Not measured * Published values ** Tested value

However, since the most important property of interest to designers is movement and not heat absorption, TMA is the favored test method for optical design. In Table 4 above, the CTE from -45°C to +200°C is a measure of the TOTAL MOVEMENT, regardless of T_g over a wide operating temperature range. The smaller the number, the smaller the movement between parts.

Thermal Mechanical Analysis (TMA). TMA uses a stylus to measure contraction and expansion of the polymer as it is cooled and heated. A plot of this movement against temperature shows CTE, α_1 and α_2 and T_g as an inflection point (Figure 2). The TMA curve directly measures total movement (Y axis) over any chosen temperature range (X axis).

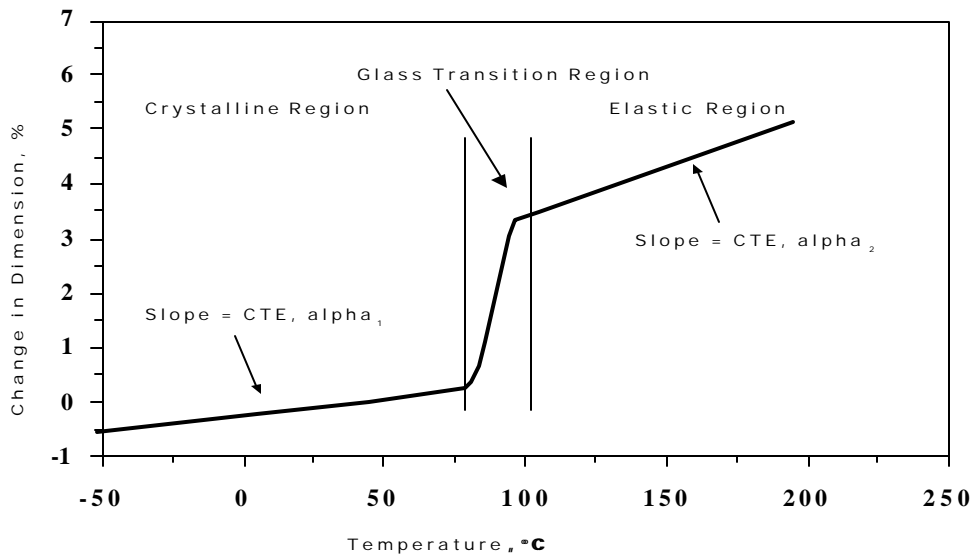


Figure 2. TMA curve measures motion with temperature, CTE of crystalline and elastic phases and glass transition temperature

Some polymers undergo energetic, large dimensional changes at the T_g . Urethane and acrylic polymers used in DYMAX light curing adhesives tend to have weak, small dimensional changes through the T_g . T_g is a temperature. T_g is not a measurement of movement.

COMPARISON OF DSC AND TMA T_g VALUES

As listed in Table 4, a one-component UV optical epoxy reports a T_g of 116°C by DSC but only 57°C by TMA. TMA only measures movement with temperature. If the TMA only sees two domains of linear expansion, then the T_g is right between the two domains. (See Figures 3 and 4.)

Does T_g Always Tell Me Something Useful?

“Rules of thumb” for comparing epoxy resins are not accurate for comparing other resins or other resins with epoxies. The T_g of light-curing and activator-curing acrylic adhesives used in rugged automotive applications range from -60°C to +70°C. The T_g of epoxies used in these same automotive applications tends to run from +50°C to +100°C. The T_g of silicones in these same applications ranges from -100°C to 40°C. Clearly T_g is characteristic of the adhesive and not a measure of performance.

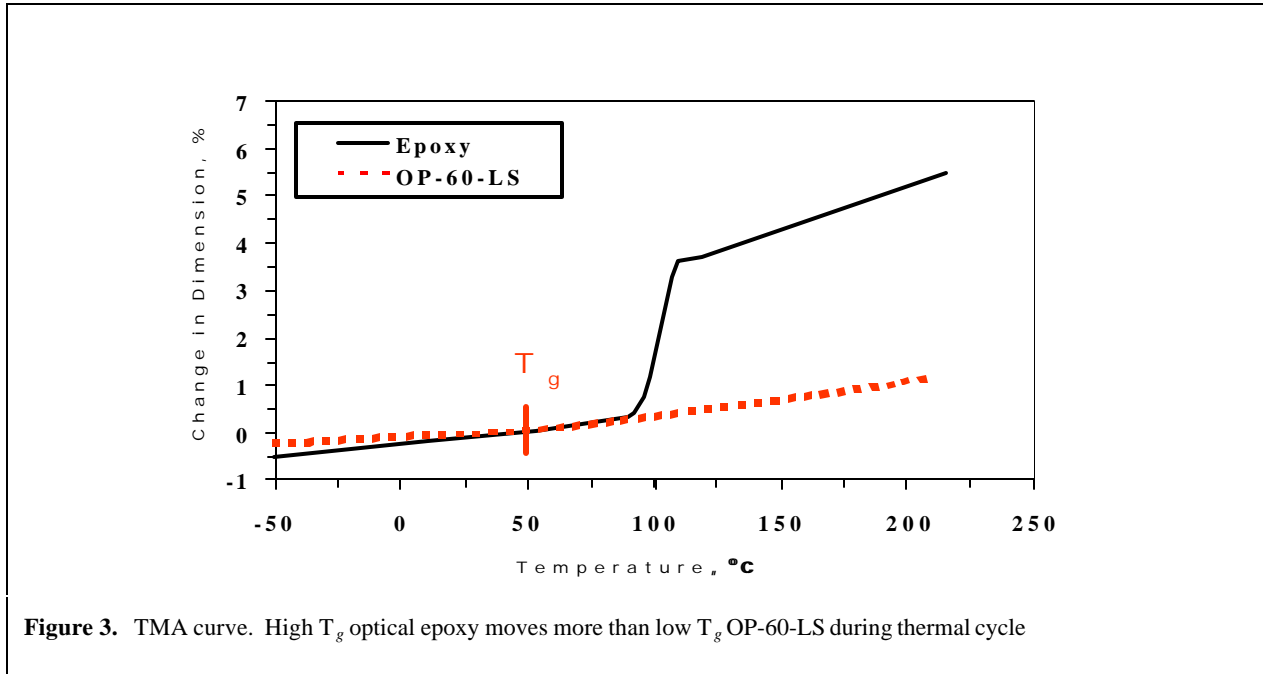
Due to the proprietary nature of most adhesives formulations, most people are unaware how unique and complex adhesive can be. Adhesives are complex mixtures. They are not pure polymers. As such, they do not obey the laws of pure polymers.

T_g can be misunderstood. Optical designers require near perfect alignment under all operating conditions. Everyone wants a product that stays where you put it, cures quickly and “never moves a microinch” from where it cures. So when an adhesive is needed that does not move a microinch, instead of asking, “How much does it move when you cure it and will it move a micro inch in my application ...” they may ask instead, “What’s the T_g ?”. This a fair question, but it may not provide the answer. Why? Because the T_g does not mean the same thing when its measured differently (see the DSC and TMA discussions above) and it may not give you a good basis for comparing movement between different adhesive families.

For example, compare two adhesives. DYMAX OP-60-LS with a T_g of 50°C compared to that of a leading epoxy with a DSC T_g of 120°C. If we play by the (epoxy) “rules,” then we assume the high T_g epoxy moves less under

thermal cycling than does the OP-60-LS. Rather than assuming the answer, we measure the motion of two cured adhesive films by TMA. The films were both roughly 1,000 nm thick. The change in dimension is plotted as a percent of the thickness is plotted to account for the small difference in film thickness. The TMA plot is shown in Figure 3. The data shows:

1. When cooled to -40°C the Dymax OP-60-LS contracts less than the epoxy
2. When heated to 100°C the Dymax OP-60-LS expands the same amount as the epoxy
3. The epoxy moves more in going through the T_g than it does over the rest of the curve.
4. The T_g motion of the OP-60-LS is negligible when measured on the same scale.
5. The total motion of the OP-60-LS from -40 to 200°C was 1%. The epoxy moved 7%.
6. The T_g of the epoxy was much higher than that for OP-60-LS.



To review, T_g is only a characteristic temperature. The glass transition temperature is neither an indicator of movement nor of performance. OP-60-LS contains a proprietary mixture of ingredients designed to minimize movement.

WHEN IS T_g MEANINGFUL?

Comparing T_g 's among adhesives is useful but only if the adhesives are of extremely close composition. Some applications really do require high T_g . Applications prone to part creep at higher temperatures require high T_g adhesives. For a thermosetting adhesive, creep is negligible below the T_g . Above the T_g , the adhesive is softer and more prone to deformation and strain. Usually the proper joint design will fix this problem. Figure 4 shows three possible joint configurations. Regardless of the T_g of the adhesive, the second design and (even better) third design will minimize alignment problems from thermal creep. These designs will also minimize part shift during adhesive cure.

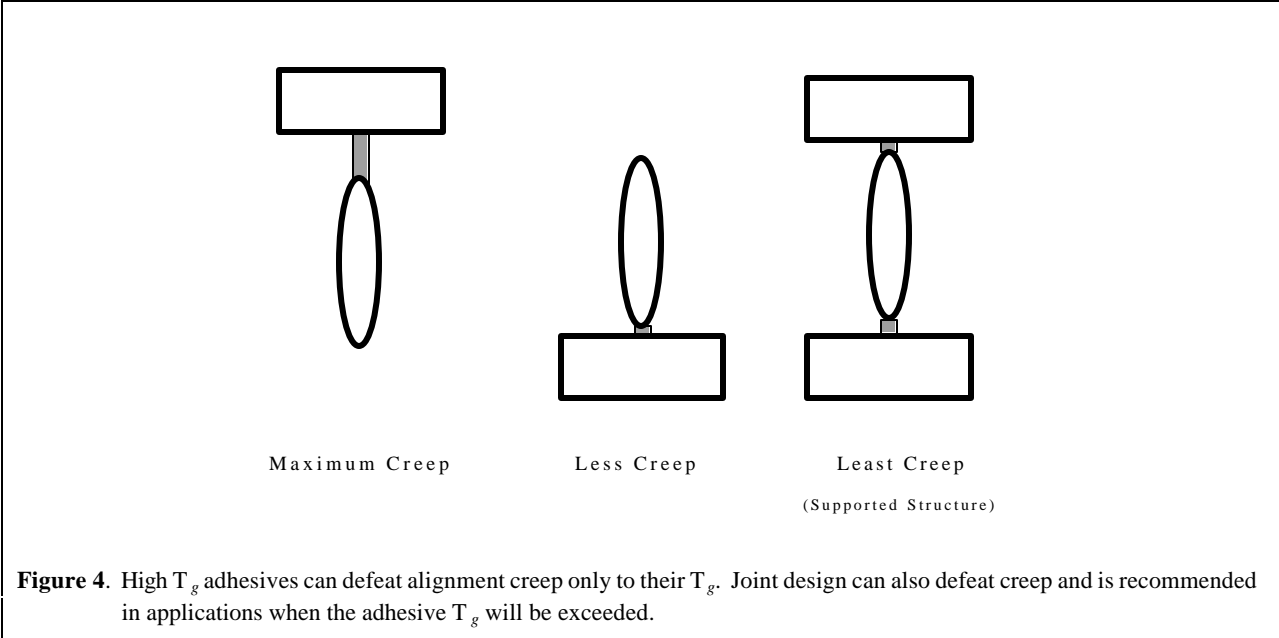
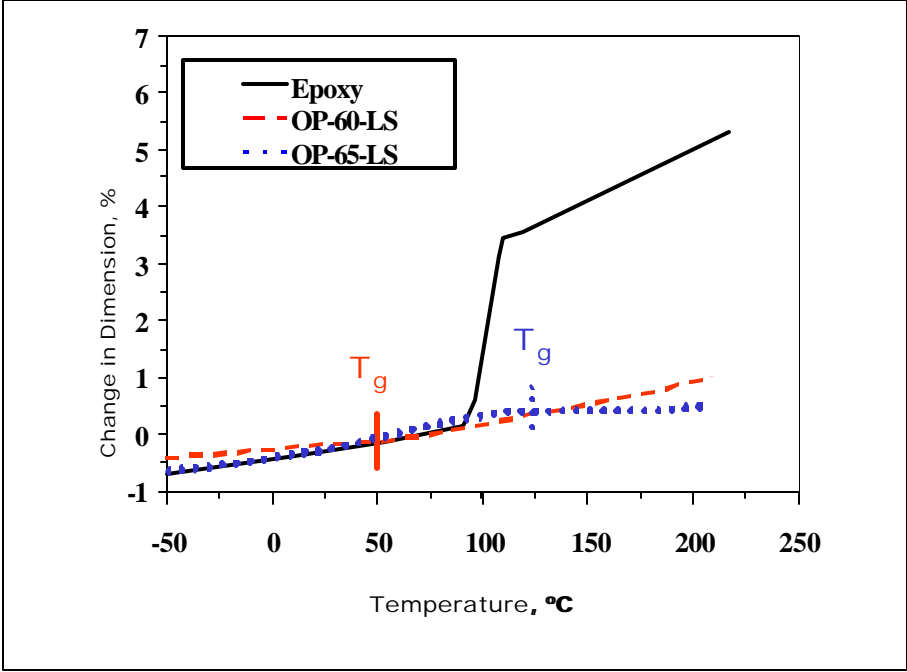


Figure 4. High T_g adhesives can defeat alignment creep only to their T_g . Joint design can also defeat creep and is recommended in applications when the adhesive T_g will be exceeded.

Because designers need high T_g adhesives for high temperature applications that lack support, DYMAX has recently invented a line of new high T_g UV curable adhesives. The TMA in Figure 5 below demonstrates OP-65-LS has a T_g of 125°C, the same contraction at -40°C as the optical epoxy and an even lower total motion from -40 to 200°C than even OP-60-LS.

Figure 5. High T_g OP-65-LS compared to OP-60-LS and a commercial epoxy



SUMMARY

This paper discusses the movement in bonded optics that can be a result of adhesive bonding. Some of these effects can be delayed for days, weeks or even months as some epoxies and “first generation” UV adhesives complete their cure cycles. New technology DYMAX Optical Adhesives that are designed to minimize movement while producing durable bond lines. Complete cures in seconds can enhance productivity and allow “on-line” quality control inspection.

The NO SHRINK™ family is opaque and not recommended for use in the light path. A range of T_g 's is available from 50°C to 125°C. NO SHRINK™ adhesives adhere to a variety of substrates and are listed in Table 5. Higher T_g products have lower specific adhesion.

Table 5. DYMAX NO SHRINK™ adhesives

NO SHRINK[®] Adhesive	T_g (°C)	Recommended Substrates
Higher Specific Adhesion		
OP-60-LS	50	Plastics, Glass, Metals
OP-61-LS	65	Metals, Plated Metals, Glass, Ceramics
OP-63-LS	60	Plastics, Glass
Lower Specific Adhesion		
OP-64-LS	118	Metal, Glass, Ceramics
OP-65-LS	125	Plastics, Glass, Metals
OP-66-LS	110	Glass, Ceramics, Plastics, Metals

For a discussion of the effects of stress is also available. See “*The Effect of Stress on Bonded Optics*”, Andrew Bachmann, Dr. John Arnold and Nicole Langer, October 1, 2001, Dymax Corporation.

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