

Advances in Light Curing Adhesives

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ABSTRACT

This paper describes the development of a new family of light curing adhesives containing a new reactive additive previously not used in optical grade light curing adhesives. High performance properties, such as high T_g , previously not associated with light curing adhesives are obtained with the addition of functionalized cellulositics. Outgassing as low as 10^{-6} grams/gram has been observed based on headspace sampling. Other additives have lowered the shrinkage rates of positioning (edge bonding) adhesives from near 1% to less than 0.1% with fractional percentage movements over thermal range of -40°C to $+200^{\circ}\text{C}$.

Key words: Adhesive, UV Cure, Ultraviolet Light, Visible Light Cure, Acrylic, Epoxy, UV Epoxy, Bond, Cure, Cement, USP Class VI.

1. INTRODUCTION

UV curing adhesives have typically been considered lower performing than epoxies and other “classical” adhesive technologies. The reputation has been partially deserved because properties inherent in “first generation UVs” led to shrinkage on cure, stress and mismatch that have been difficult to control. High powered and overly complicated specialty UV curing systems have evolved in an attempt to “improve performance”.⁽¹⁾ The result can be unnecessary expense with little to no increase in effectiveness.

Figure 1 below illustrates the process efficiency and manufacturing cost control that is available from using this new adhesive technology coupled with more simple UV curing lamps. There is no need for complicated, overly expensive, or “programmable” UV or visible light sources. In a properly formulated adhesive, complete cure occurs quickly based upon a single exposure to metal halide curing lamps. Figure 15 (page 10), shows little effect on final properties such as shrinkage, as long as the formulations receive at least the minimum amount of light required for cure. Figure 2 shows precision optical assemblies, each constructed in a few seconds with a UV and/or visible light an Aerobic Acrylic Adhesive formulation.

Figure 1:

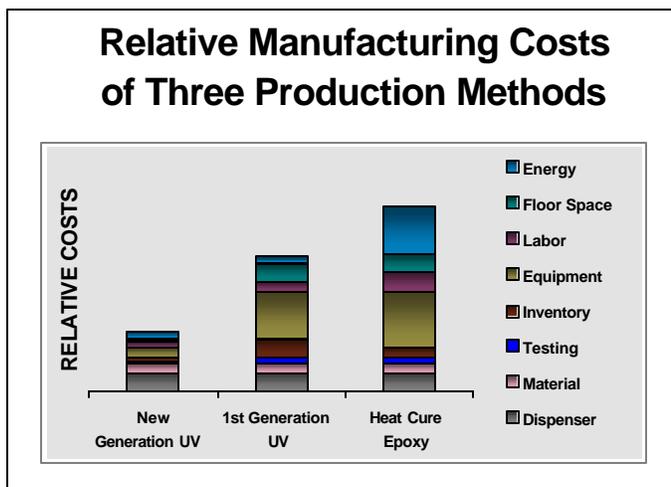
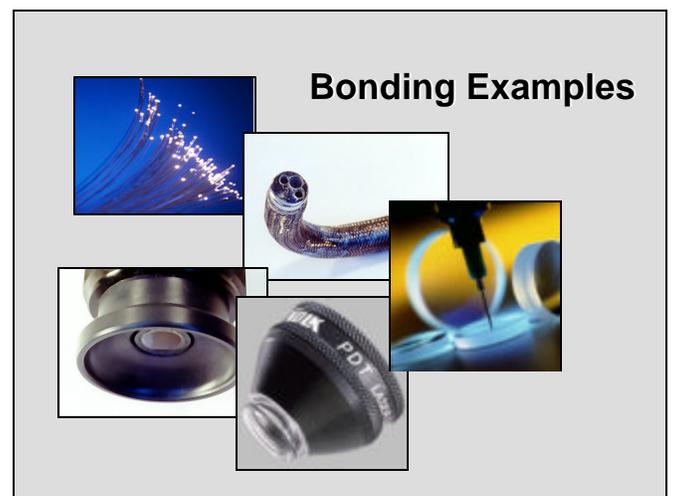


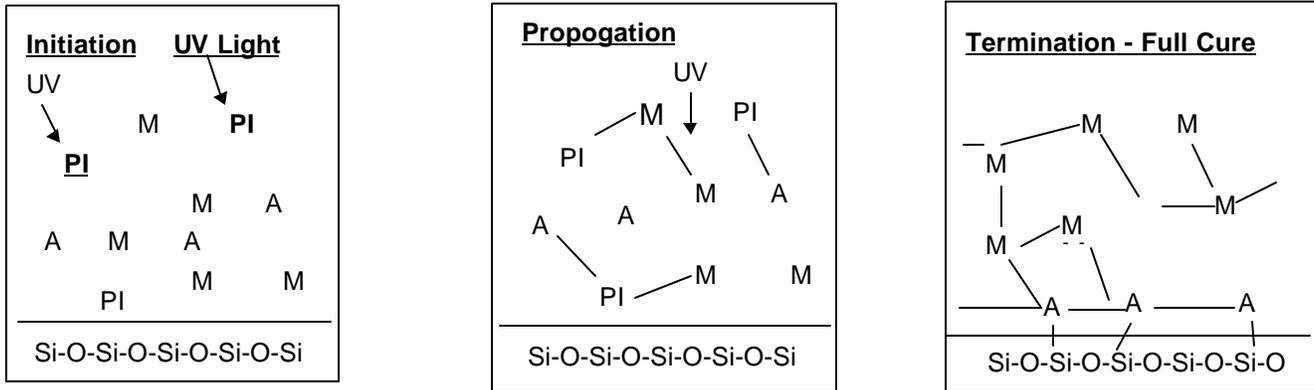
Figure 2:



2.2 Adhesion promoters

The final adhesion to glass and metal is developed by secondary reactions with adhesion promoters directly to the silicon atoms in the glass within 1-60 minutes, to gain a 10-200% increase in compression strength. Figure 5 is a non-rigorous schematic representation of the way adhesion is developed in acrylic polymerization.

Figure 5: Polymerization and adhesion to glass surface



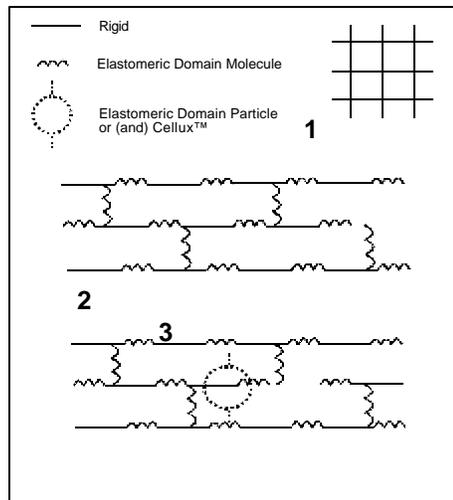
M = Monomer, A = Adhesion Promoter, PI = Photoinitiator

2.3. Elastomeric domains

Aerobic Acrylic Adhesives incorporate specific formulation strategies that lower modulus, incorporate the feature of elastomeric domains and various ingredients, both organic and inorganic, that combine to minimize bond line stresses. These adhesives are formulated with a different degree of cross-linking, which minimizes shrinkage.

Figure 6 illustrates different degrees of cross-linking and shows how strain relief mechanisms can be “programmed” into molecules to take up stress from cure by utilizing elastomeric domains. Properly selected, these domains can also lower Young’s Modulus and, thereby, bond line stress. The expressed modulus remains low while still showing high specific adhesion.

Figure 6: Elastomeric domains



#1 Represents the high degree of cross-linking and rigid bond lines typical of some early generation UV adhesives, epoxies and Anaerobic Adhesives

#2 Introduces the concept of elastomeric molecules and/or Cellux™

#3 Shows the addition of elastomeric domain fillers, the strategy followed in some Aerobic Adhesives

3. REASONS FOR OPTICAL ADHESIVE FAILURE

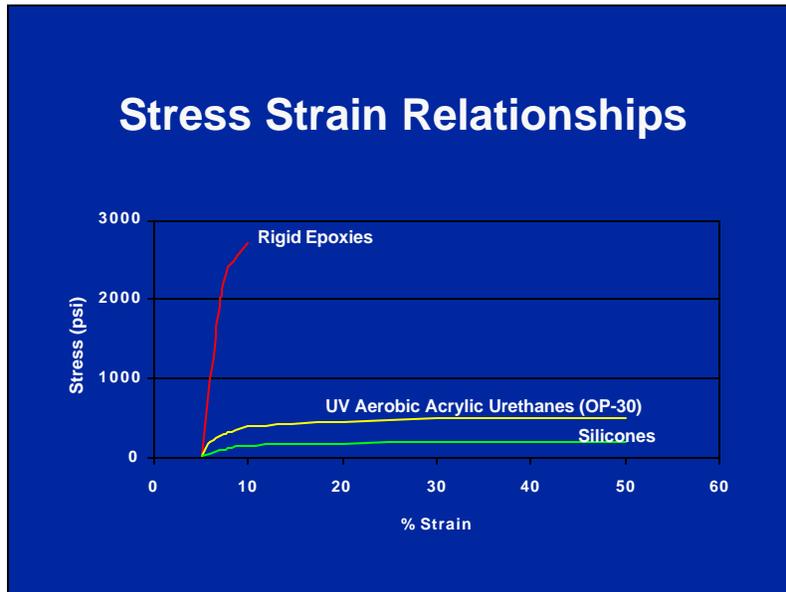
Several factors, most of them stemming from properties that are inherent in all cured adhesives and that are essentially independent of the curing process include:

- Polymer rigidity (modulus, elasticity)
- Bond line durability (polymer changes on aging)
- Shrinkage on cure (change in molecular bond length)
- Mismatches in CTE (T_g , α_1 , and α_2)
- Dimensional change on thermal excursion (average α_1 , α_2)

Stress, low durability and insufficient strength to prevent relative movement between parts are the main causes of optical adhesive failure. Stress, either from shrinkage on cure, aging, or thermal excursions causes birefringence in a lens. Overly rigid materials can have divergent thermal expansion coefficients both above and below the glass transition temperature that can result in significant relative movement between fibers even though the material has a “High T_g ”.

Figure 7 shows the stress strain relationships inherent between three different types of cured adhesive polymers. High modulus polymers such as epoxies tend to have a higher ratio of stress to strain⁽³⁾.

Figure 7:



In summary, stresses induced by an adhesive are controlled by the following “good practices”:

- Minimize the shrinkage on cure
- Lower the modulus of the cured adhesive polymer
- Place the T_g above or below the operating temperature of the optical device
- Chose polymers with a small T_g effect
- Select α_1 and α_2 to minimize relative movement over the operating thermal range

3.1 A simple test for detecting stress on cure

A simple test can be performed to identify stress that might develop during cure. First, place polarizers (such as plastic polarized sunglasses) on top of each other at 90° angles. Place the bonded optic between the two polarizers and illuminate with sunlight or a bright white light source. Induced stresses in the lens will be visible by its birefringence pattern.

3.2 Stress management in a curing adhesive

Delamination is frequently observed in precision fiber optic couplers. Equation (2) below shows that induced stress may exceed the strengths of both adhesive and substrates resulting in bond line delamination. The stress (σ) on cure arises from the change in length between monomer and polymer bonds. Stress on cure is shown in the simplified equation (1):

$$\sigma_{\text{shrinkage}} = (\text{Shrinkage}) \times \text{Modulus} \quad (\text{Equation 1})$$

Table 1 below indicates inherent factors that influence induced stress.

Table 1:

Polymer	Shrinkage on Cure (unfilled)	Modulus (psi)	Shrinkage on Cure (filled)	See Equation
Addition Epoxy	2-3%	100,000-1,500,000	-	(2)
Heat Cured Epoxy	2-5%	500,000-1,500,000	-	-
Acrylates	4-5%	35,000	-	(3)
Cellux™ Treated	1-4%	1,000,000	0.05-0.1%	(4)

Basically, the shrinkage on cure is but one factor leading to stress. As can be seen in the table, in materials of equal modulus, shrinkage is a major factor in lowering induced stress. However, even moderately shrinking adhesives will show a very much lower induced stress, if the modulus has been reduced from that common in a typical epoxy.

$$\text{(Filled)} \quad \sigma_{\text{shrinkage/epoxy}} = 0.01 \times 500,000 = 5,000 \text{ psi} \quad (\text{Equation 2})$$

$$\text{(Unfilled)} \quad \sigma_{\text{shrinkage OP 60-LS}} = 0.02 \times 35,000 = 700 \text{ psi} \quad (\text{Equation 3})$$

$$\text{(Filled)} \quad \sigma_{\text{shrinkage/x-376-41-A}} = 0.0075 \times 1,000,000 = 750 \text{ psi} \quad (\text{Equation 4})$$

4. CONTROLLING THERMAL STRESS

In addition to the above, bonding stress is typically created on thermal excursion. Epoxies and older generation UV adhesives can act as a source of stress relative to differences in coefficients of thermal expansion. If an adhesive and a substrate expand differently under temperature cycles, stress is created and stress in optical components creates stress birefringence and optical distortion. Birefringence stress creates polarization sensitive changes, which in many cases affects performance. High temperature curing of many epoxies can create stress on cool down to room (and lower) temperatures.

The durability of optical bonds is most strongly effected over the lifetime of a part by the thermal excursions which that part will experience. The expanded stress equation (5) shows that, while closely matching the CTE between the adhesive and the substrate lowers stress. However, matching CTEs is difficult to accomplish and not as effective in lowering stress as is controlling the modulus. Equation (5)³ describes the shear stress produced during thermal excursions between bonded substrates. Low modulus adhesives can be more effective in lowering stress than are closely matching CTEs.

$$\sigma_T = (\alpha_{\text{adh}} - \alpha_{\text{sub}}) * \Delta T * E_{\text{avg}} \quad (\text{Equation 5})$$

where,

σ_T	=	Shear stress due to adhesive bond
α_{adh}	=	Coefficient of Thermal Expansion of Adhesive
α_{sub}	=	Coefficient of Thermal Expansion of Substrate
ΔT	=	Temperature Range
E_{avg}	=	Average Modulus of the adhesive over the temperature range

Since the tensile strength of glass is around 1,000 psi and most structural adhesives 2-5,000 psi, the delaminating potential of stress induced during thermal excursion is shown in table 2.

Table 2: Glass to glass adhesive properties

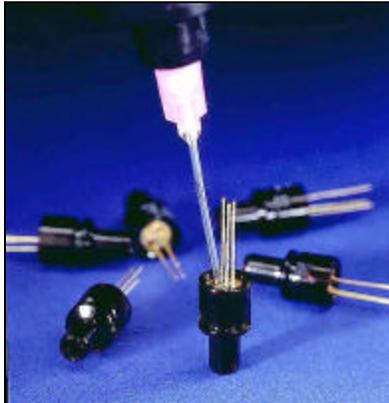
Property	Commercial Optical Epoxy	Commercial “General Purpose” Optical UV Acrylic	Commercial “Low Stress” Optical UV Acrylic
α_{adh}	80×10^{-6} in/in/ $^{\circ}$ C	200×10^{-6} in/in/ $^{\circ}$ C	200×10^{-6} in/in/ $^{\circ}$ C
a_{sub}	2.8×10^{-6} in/in/ $^{\circ}$ C	same	same
ΔT	-40 to 125 $^{\circ}$ C	same	Same
E_{avg}	550,000	35,000	3,000
$\sigma_{T calc.}$	7,000 psi	1,100 psi	100 psi

5. STRESS, MOVEMENT AND GLASS TRANSITION TEMPERATURE (T_g)

Controlling the movement of optical parts has become more critical with the development of optical and optoelectronic couplers, splitters and so forth. Historically, an epoxy with a T_g above the operating temperature of the construct has been the adhesive of choice. However, the operating temperature of some constructs today are requiring a -50° C - 200° C. operating range making even the classical “High T_g ” epoxies less effective.

New UV adhesives that exhibit less shrinkage on cure than most epoxies and show better control of movement over a temperature range, are now being widely used for positioning such as lens mounting, VSCSELs, V-groove attachment, and so forth.

Figure 8: VSCSEL potting



Minimizing shrinkage on cure has been discussed on page 5. However, Thermal Expansion, as measured by the Thermal Expansion Coefficient (CTE), is an equally important intrinsic property of polymers (adhesives) that affects relative movement between parts, and is particularly critical in fiber optic couplings.

In addition to strain (page 6), CTE affects relative parts movement. The CTE of a cured adhesive will change above and below that polymer’s T_g . Cross-linked epoxy adhesive polymers tend to show a well-defined T_g around which a physical size and shape can occur. The slope of the curves below and above the T_g are known as α_1 and α_2 .

As further discussed in Appendix I, some manufacturers report T_g measured by DSC (Differential scanning calorimeter.) However, DSC only detects a thermal change and may not represent “true” T_g . For example, the “Leading Epoxy” referred to herein reports a T_g of 120° C by DSC and about 95° C by TMA. A one-component optical epoxy reports a T_g of 116° C by DSC but only 57° C by TMA. Figure 9 compares the TMA Curve and T_g of a typical leading epoxy (tested by our outside laboratory) with a typical acrylic UV curing adhesive and Figure 10 shows the effect which Cellux™ and other additives can have on T_g .

Figure 9:

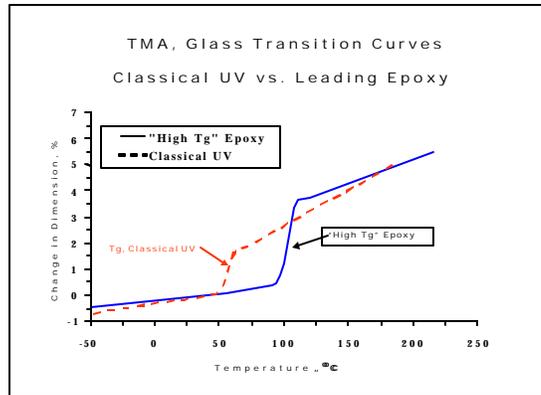
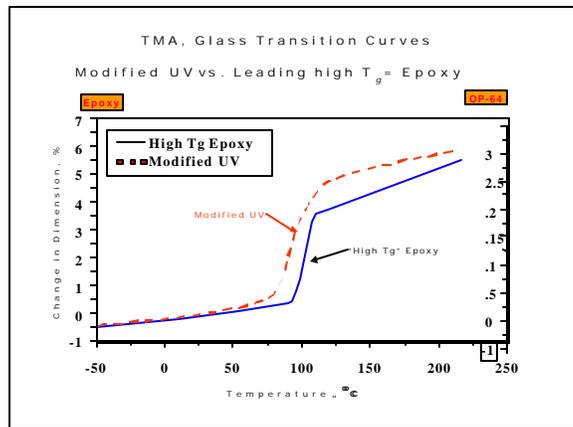


Figure 10:



Combining α_1 , α_2 and T_g gives the total movement that a polymer will have over a selected temperature range. The lower that movement, the lower will be the potential for relative movement between bonded parts

Figure 11 shows the overall effect of combining the new additives (see Equations number 3 and 4 on page 5). The total change in the TMA curve is affected more by the new formulations than a simple reliance of T_g data would suggest.

Figure 11:

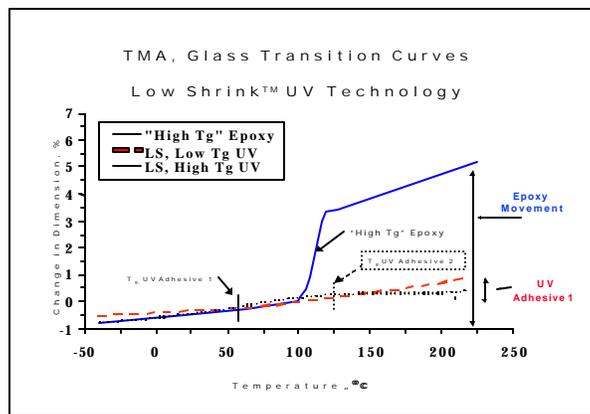


Table 3: Effect of T_g on expected movement over a -50°C to +200°C range

Filled, Positioning (Edge Bonding) Optical Adhesives			CTE	CTE	CTE**
Positioning Adhesives	T_g Reported (or by DSC)	T_g (by TMA)*	Alpha 1	Alpha 2	-45 to 200
Leading Optical Epoxy Cured for 1 hr @ 150°C	120°C	95°C	56.0	139.0	87.0
Formula of Equation (3) Page 5	110°C	65°C	27.0	121.0	74.0
Formula of Equation (4) Page 5	Not detected	54°C	27.0	66.0	50.0
X-431-11-A	130°C	98°C	71.0	5.0	52.0

* As tested in our laboratories.

** The thermal operating range of some optical devises.

Table 4: Linear shrinkage per ASTM D-2566⁽⁷⁾

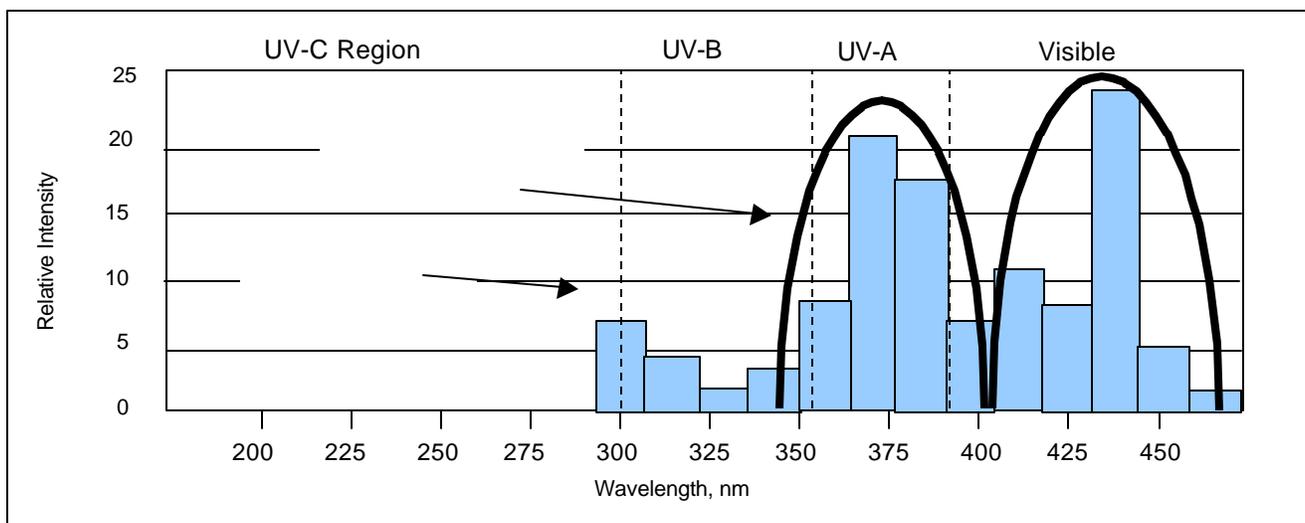
Adhesive OP-60-LS	Adhesive OP 61-LS
< 0.1% (during UV Cure)	< 0.1% (during UV Cure)
< 0.1% (after 24 hr, 120°C)	< 0.1% (after 24 hr, 120°C)

6. CURING WITH LIGHT

Aerobic Acrylic Adhesives are designed to be sensitive to those areas of the electromagnetic spectrum which allow the optimum combination of speed and depth of cure for assembly applications. Formulations that cure only with UV light are primarily triggered by longwave UVA spectrum. Formulations for bonding through UV inhibited surfaces, combine catalysts from both the UV and visible regions and generally produce faster and deeper cures.

The most efficient curing occurs when a curing lamp's spectral output is matched to the Lamda Alpha of an adhesive. If the absorption maxima of the adhesive should match the spectral output of the curing lamp, there is no need to use complicated, programmable, overly expensive UV lamps in an attempt to "make a UV adhesive work better". Figure 12 illustrates the optimum synergy between a properly tuned curing lamp and the intensity and wavelength that the adhesive needs for optimum cure.

Figure 12: Matching the lamp's spectral output with the absorption spectrum of the adhesive

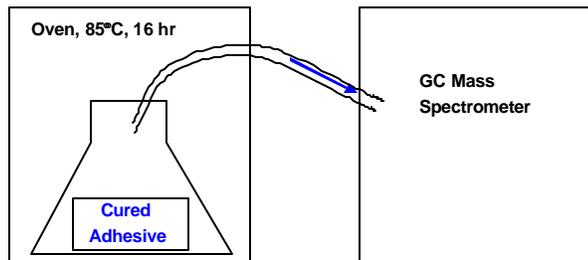


7. OUTGASSING

The high cross-link densities normally required for low outgassing typically produce overly rigid polymers that are not suited for durable bonding. One of the chief drawbacks to UV optical adhesives has been their relatively high outgassing. This has limited their use in sensitive applications where low outgassing is important, such as in the assembly of sealed lasers. The new cellulosic additives have the ability of substantially increasing cross-linking, which effectively “traps” volatile components within the adhesive matrix and lowers thermal outgassing.

Headspace sampling as illustrated in Figure 13 below has been used to detect outgassing as low to 10^{-6} grams/gram of adhesive used. Combined with lower shrinking rates, these formulations represent a new alternative in high performance bonding in areas where outgassing is critical.

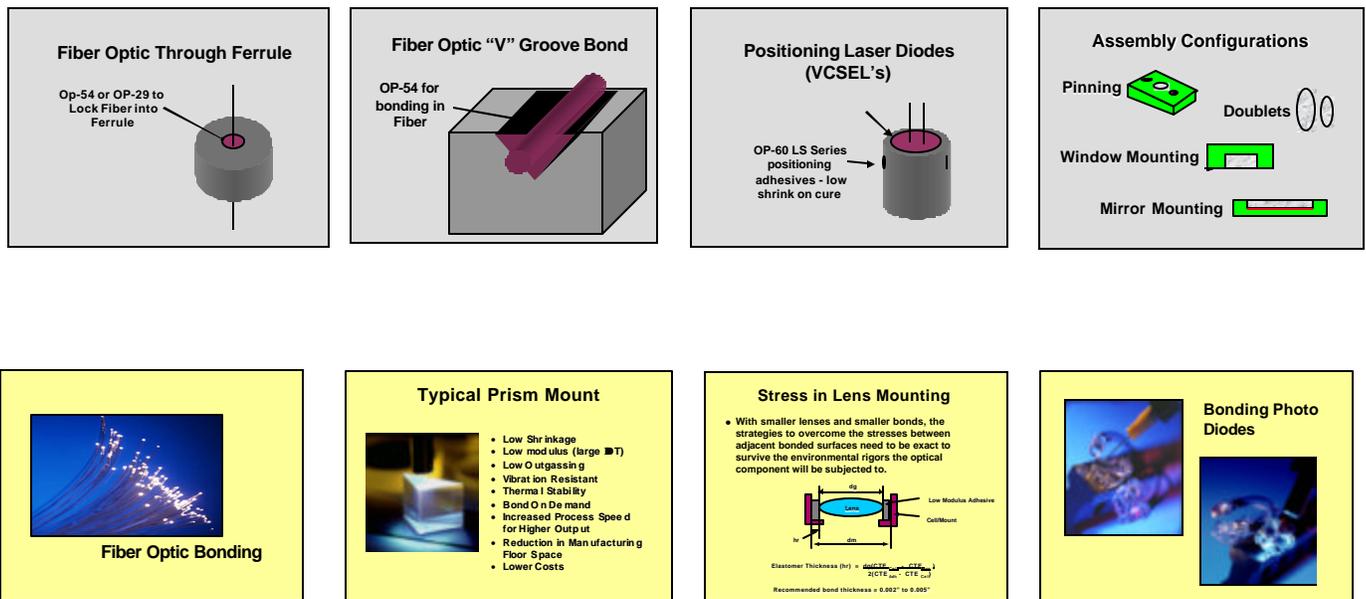
Figure 13: Outgassing: Headspace Analysis



7.1 Examples of commercial products utilizing these new adhesive formulations

The photographs in Figure 14 show various types of materials that are commercially bonded with these new high performance UV formulations. Both lenses, fiber optics, prisms, mirrors and other assemblies are rapidly bonded using production methods faster than other adhesives.

Figure 14:



7.2 Other design considerations

Glass to metal or plastic to metal bonding, in applications such as lens, prism, mirror mounting, ferrule bonding, or fiber optic tacking, require other adhesive characteristics. Viscosity, shrinkage, speed of cure, flexibility, and tensile strength can be critical to the success of an application. Modified UV acrylics are available that cure by UV light, visible light, heat, or a combination of these that offer advantages over slower curing epoxies. Termed Multi-Cure[®], these adhesives can cure with UV, visible light, activator, or heat for areas not able to receive light for curing. For example, a mirrored surface that blocks UV light from exposing all of the UV adhesive is still completely cured in seconds by pre-applying an activator solution.

Some applications require an adhesive that passes the biocompatibility standards established by USP Class VI and ISO 10993. Typically involving a medical device, these adhesives must be non-toxic when cured, as they will be coming in contact with human tissue or fluids. Applications may include imaging systems, endoscopic devices or lenses for ophthalmic surgical procedures. Modified UV Acrylics are commonly used in such applications where optically clear, USP Class VI adhesives are mandated.

7.3 Low shrinkage applications - pinning

Pinning applications, such as vertical-cavity surface-emitting lasers (VCSEL)⁶, require an extremely low shrinkage adhesive. As operators align optical components, the adhesive can already be in place. Once the proper alignment has been obtained, a spot curing system can focus a narrow beam of light to the adhesive with subsequent cure in seconds with very little movement upon cure. It is important to cure multiple bond sites simultaneously to avoid uneven shrinkage, even with the low shrinkage values. Modified UV/Visible Light Curing Adhesives⁷ maintain the component's position without moving over the life of the part, even through normal temperature cycling conditions.

While for most applications, the correct light source will play a significant role in the shrinkage of the adhesive, these special resins maintain low shrinkage over a wide light intensity range. Figure 15 shows the same approximate linear shrinkage regardless of the energy of the light source. The time of cure is, of course, different for different light intensities. Figure 16 depicts a typical prism mount.

Figure 15: % shrinkage vs. energy for OP-60

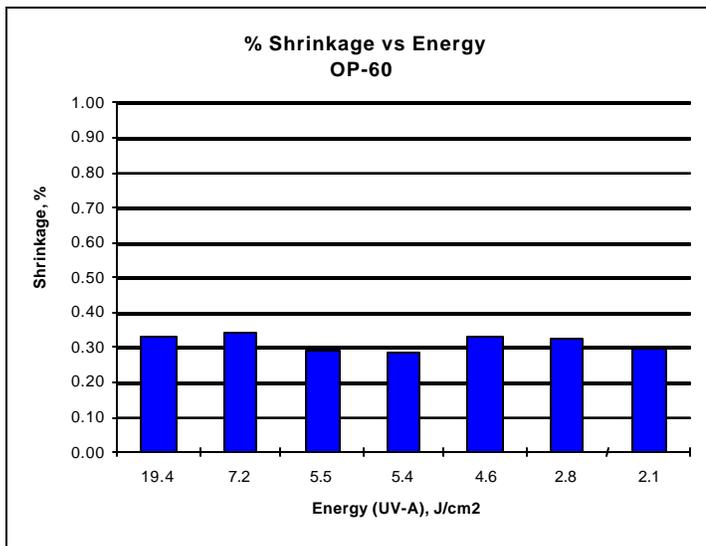
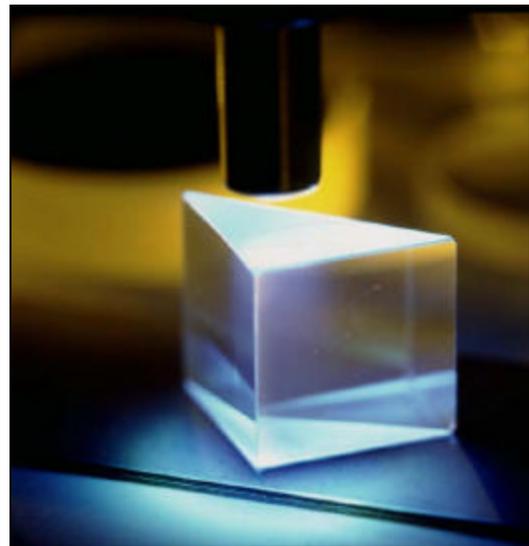


Figure 16: Typical prism mount



8. PHOTOCURING LIMITATIONS

Photocuring adhesives requires light transmission to the bond area to effect cure. Therefore one of the surfaces must be transparent or translucent enough to permit UV or visible light transmission. "Bridge bonding" is one technique used to bond completely opaque substrates. This is a technique whereby the adhesive is dispensed and cured in a bead over a joint and between two or more substrates. The use of Multi-Cure[®] techniques is another method to bond opaque surfaces. Only

through an evaluation of each new application, can a fair assessment be made for the practicality of implementing a light curing bonding process.

SUMMARY

New, additive modified UV and visible light curing adhesives have been described that, in many cases, can equal or surpass the performance of more classically used optical epoxies. Formulations that cure completely in seconds are available for testing. Understanding the functional differences between old and new generation UV or visible light curing adhesives permit the optical engineer to explore more efficient assembly processes which offer increased productivity, reduced cost, and improved product quality.

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Presented at SPIE, San Diego, CA, August 1, 2001. Paper # 4444-20 (due to space and time limitations the paper did not include the attached Appendices).