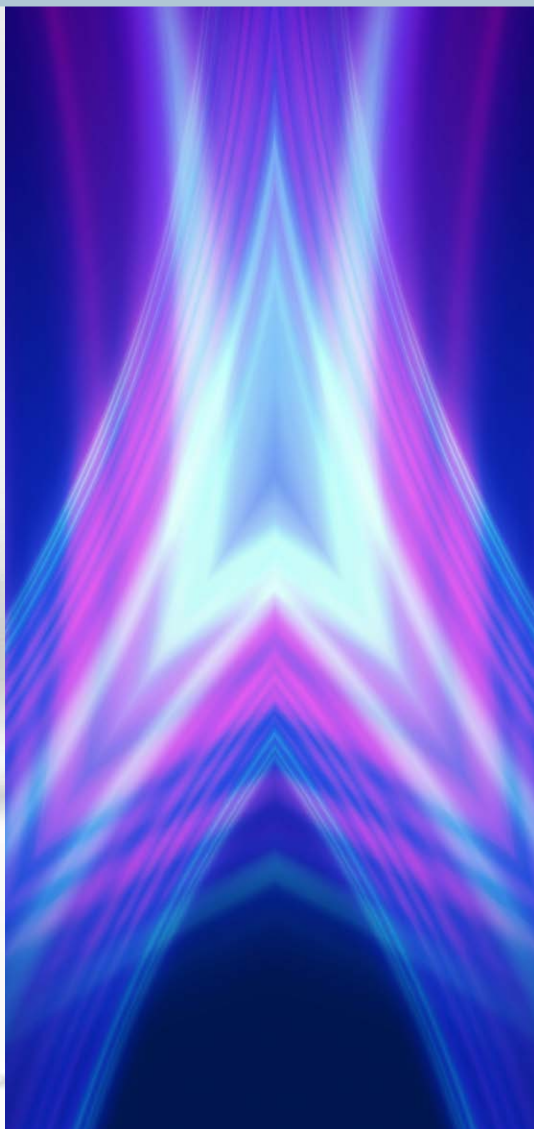
Henkel Adhesive Technologies

LOCTITE®

NOVEL LED-CURE ***FLEXIBLE BONDERS***

Gavin Haberlin, Zachary Bauman, Hermann Handwerker, Thomas Silva, Martin Smyth



Contents

Abstract

As part of a light cure adhesive innovation program, Henkel has developed two new LED-curable adhesives, LOCTITE® AA 3951TM and LOCTITE® AA 3953TM. These new adhesives cure rapidly, with a combination of high flexibility and high strengths on many diverse plastic substrates. This paper details that combination of new properties, while maintaining all other product attributes commonly associated with light curing acrylic (LCA) polymers.

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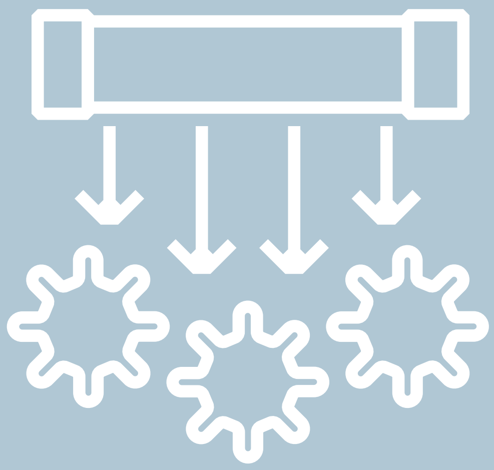


Background

UV and visible light curing of acrylate adhesives is a technology that continues to grow due to its favourable industrial applicability. Rapid curing, broad substrate adhesion, flexibility, and fluorescent detectability make light cure acrylics the first consideration for high speed automated bonding operations.

Due to advances in curing technology, light cure acrylates are being cured by LED systems instead of traditional bulb-based systems with increasing frequency. This trend will continue in the market due to the several advantages of LED over mercury arc and metal halide UV Lamps. LED’s are 60 – 80% more energy efficient than conventional UV lamps. They are lower in cost and provide an increased longevity with more consistent output. In addition, they do not contain mercury or produce ozone. Innovation in LED systems continue to lower the cost and increase the output of film and adhesive curing systems year by year. LED’s are becoming the new standard for curing so it is no surprise that the adhesives exhibited in this project were designed to be fully compatible with the most common LEDs on the market. Since, the LED technology is a recent development, many of the previous generation products do not have the same compatibility.

One of the major challenges with new substrates being introduced into the market is the introduction of extremely soft and low surface energy thermoplastic elastomers (TPEs). Typical light curing adhesives have shown poor performance on many of these substrates for two reasons: lack of adhesion and lack of flexibility. Lack of adhesion inherently causes issues with bonding, however and sometimes just as important, a low tensile modulus and a high elongation allows adhesives to stretch in the bond-line and decentralizes the peel forces. Peel is the most aggressive type of force for any adhesive and is common in flexible bonding applications. In an example case of the combination of a rigid and a flexible material, the adhesive has to “moderate” the different material behaviours under load. For such applications, a high elongation before break is a very beneficial property for an adhesive and generally correlates to higher assembly strengths.

Additionally, many of these TPEs are being chosen for tubing assemblies which require a low viscosity adhesive to be able to wick into tight diametrical gaps. The issues presented to adhesive formulators is that adhesion and low viscosity often need to be sacrificed to achieve flexibility. However, the new light- curing adhesive products presented in this paper have achieved a high degree of flexibility without sacrificing the other two properties.

Discussion

Henkel has developed two new, LED-cure flexible LCA bonders. To fill several market needs, multiple viscosities were required for different gaps in flexible junctions. LOCTITE® AA 3951 and LOCTITE® AA 3953 are 150 and 450 cP, respectively. In addition to the high strength and flexibility in these low viscosity products, each of these products are optically clear, fluorescent and present good depth of cure.

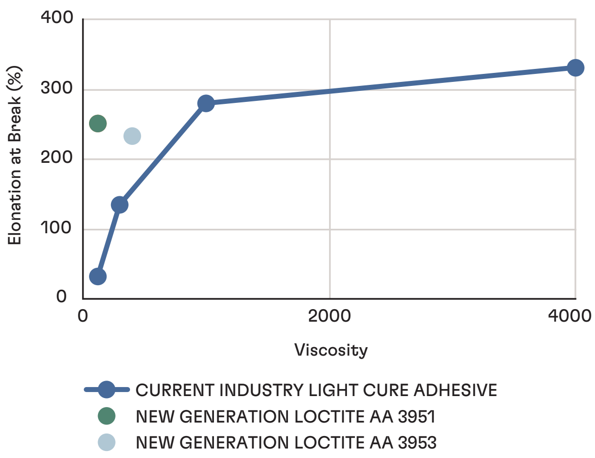
High elongation & low viscosity

One unique characteristic of these new LCA adhesives is high elongation in combination with low viscosity. Previous grades have shown a dependency of the flexibility on the viscosity as illustrated in *Figure 1*. For higher viscosity grades a higher degree of flexibility was achieved. By contrast, for low viscosity acrylics, only a certain elongation was possible to achieve.

The new performance combinations of LOCTITE® AA 3951 and LOCTITE® AA 3953 allows the use of highly flexible acrylics in applications requiring low viscosity, e.g. in small parts or in narrow gap designs. This gap design is common in applications where solvent welding is being replaced.

Figure 1

% Tensile elongation at break vs. viscosity (cP)
Comparison of elongation vs. viscosity and previous generation light-cure grades



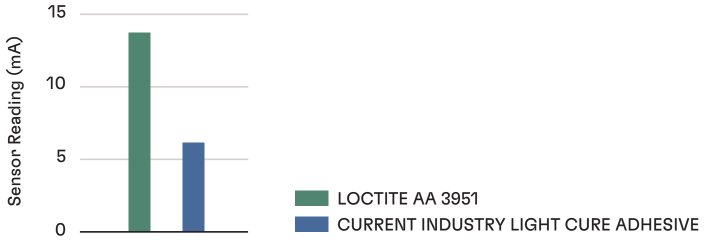
Fluorescence

Fluorescence offers customers, particularly with automated lines, the opportunity to quickly and easily confirm if product has been applied correctly to the mating parts. Colourless products without fluorescence do not have the required contrast to be detected on a high-speed production camera. Using a medium standard on the SICK camera, the following results were obtained.

This increased fluorescence performance displayed in *Figure 2*, aids in the detection, allowing for the use of less-expensive detectors; or enabling the detection of very small product quantities present in exceedingly narrow bond gaps.

Figure 2

Fluorescence magnitude with a SICK camera (medium standard)



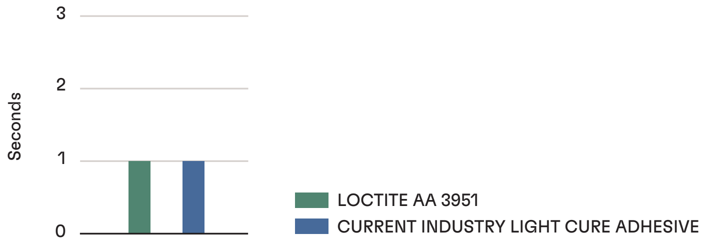
Fixture times

The fixture time is a commonly used indicator for the cure speed of light-cure products. The test entails bonding thin glass slides at different cure intervals until the bond is strong enough to break the glass when pull testing. Excellent fixture times on glass slides were achieved at less than 1 second cure at 405 nm and extremely low light intensity *(Figure 3)*. 405 nm compatibility is a must for new generation products as visible LED's are now the curing equipment of choice due to efficiency, penetration, and speed.

LOCTITE® AA 3951 maintains a high speed even while fluorescing at a magnitude of 2 or more times the previous generation. Increased fluorescence is a challenge for cure speed because fluorophores absorb the same wavelengths of light as the photoinitiators and are known to reduce cure speed.

Figure 3

Fixture time on glass slides, LED flood, 10 mW/cm² at 405 nm



Surface cure

For light cure acrylics the surface cure is affected by the oxygen inhibition. Prior to LED bulbs, full spectrum bulbs were traditionally used, which emit visible light (400 nm – 420 nm), UVA (315 nm – 400 nm), UVB (280 nm – 315 nm), and, most importantly, UVC (100 nm – 280 nm). Visible and UVA light penetrates well into the adhesive and through the transparent substrates and provides cure through a bond-gap. The UVC wavelength has low penetration and is primarily absorbed at the adhesive surface.

This creates a high concentration of free radicals to overcome oxygen scavenging at the air-exposed surface interface. With LEDs, this path of wavelength combination is no longer possible, as LEDs emit one wavelength only. Therefore, when curing with LED, the surface cure must be fulfilled by the UVA (365 nm) or visible light (405 nm) wavelength only. *Figure 4* shows how LED surface tack was improved versus previous generations.

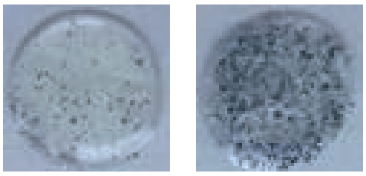
At 100 mW/cm^2 for 10 seconds, the silicon carbide particles cannot be brushed off the cured drop of LOCTITE® AA 3921 due to its tacky surface layer. In contrast, the new flexible bonder retains fewer silicon carbide particles. At 500 mW/cm^2 for 20 seconds, LOCTITE® AA 3951 no longer retains the silicon carbide while the previous generation still displays signs of a tacky surface.

Figure 4 shows how LED surface tack was improved versus previous generations.

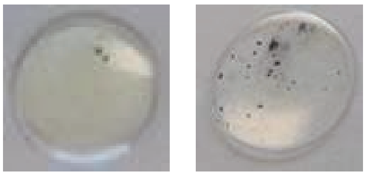
Figure 4

Surface tack testing using 80 grit silicon carbide powder
LOCTITE® AA 3951 (left), current industry light cure adhesive (right)

405 nm LED at 100 mW/cm^2 for 10 seconds



405 nm LED at 100 mW/cm^2 for 10 seconds



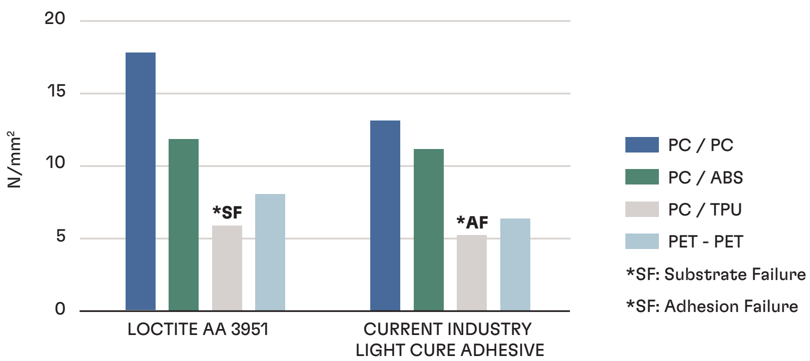
REGID REQUIREMENTS – *FLEXIBLE* DESIGN

Adhesion strength

Our new entrants to the LCA market consistently offer improved results across a variety of plastics, when compared of previous generation adhesives. *Figure 5* shows increase adhesion performance on ABS, PC, PET, and TPU.

Figure 5

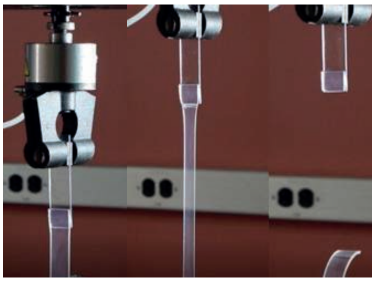
Lapshear (Adhesive shear) strengths on various substrates



It is worthy to note that the new adhesive was able to reach substrate failure of the TPU *(see Figure 6)*, while the previous generation grade did not.

Figure 6

Shear adhesion test using LOCTITE® AA 3951
Resulting in substrate failure of the TPU (still frames are chronological left to right)



Conclusion

The timely arrival of this project has been a great opportunity to ensure Henkel's position as the leading supplier in the light cure adhesives market, especially at a time when the market is rapidly commercializing highly elastic TPE blends which may include TPU, TPO, SEBS, PEBA, Polyesters, or combinations thereof. The high elongation and low viscosity of LOCTITE® AA 3951 and LOCTITE® AA 3953 allow tight fitting flexible parts to be bonded with ease.

Visible LED compatibility ensures that users will obtain fast cure times, with good surface cure, using state of the art curing systems designed for high speed automated lines. All these attributes tie together to create a high value package that is desirable to manufactures in medical, electronics, aerospace, consumer goods and beyond.

Appendix

ABS: Acrylonitrile butadiene styrene plastic Adhesive failure: A term used to describe an adhesive bond failure in which the interface between the adhesive and the substrates delaminates.

Fluorescence: A property of a material that characterizes absorption of light in one spectrum and emission in a different spectrum. The wavelength of light absorbed and emitted is determined by the energy of the photons as it correlates to the difference in energy levels between the excited state and the ground state.

LED: Light-emitting diode

LCA: Light-curing acrylic adhesive

Oxygen inhibition: A phenomena of radical cure polymer chemistries in which oxygen in the atmosphere diffuses into a curing resin and scavenges free radicals needed to crosslink the polymer. This leads to a layer of uncured material that is less than 0.1 mm thick on the surface of any resin exposed to the atmosphere.

PC: Polycarbonate plastic

PEBA: Polyether block amide. A type of thermoplastic elastomer.

PET: Polyethylene terephthalate plastic

SEBS: Styrene ethylene butadiene styrene Substrate failure: A term used to describe an adhesive bond failure in which the substrates bonded fail internally prior to interface between the adhesive and the substrates.

Tensile elongation: A material property that describes the average amount of deformation that a material can undergo prior to failure.

Tensile modulus: A material property that describes the rigidity of a material. It is determined by the stress strain curve during tensile testing and is often considered the slope of this curve. Different calculation techniques are required to obtain this number as not all stress strain curves are linear.

TPE: Thermo-plastic elastomer. A plastic with elastic properties that can be melted for processing.

TPO: Thermo-plastic olefin. A type of thermoplastic elastomer that usually has a very lower surface energy.

TPU: Thermo-plastic urethane. A type of thermoplastic elastomer.

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