Success Secured with LOCTITE®

New Highly Flexible Cyanoacrylates: LOCTITE® 4902™ and LOCTITE® 4903™

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Abstract

Speed and flexibility have always been known to be a trade-off for adhesives. Current cyanoacrylates, light cure acrylics, hot melt adhesives, two-component silicones and polyurethanes can provide either flexibility and/or relatively fast fixture speeds. In most cases, however, there exists a trade-off with shear strengths, adhesive cost, ease of dispense, or ability to cure at all (i.e., bonding opaque substrates with a light cure acrylic). Henkel has developed two LOCTITE® instant adhesives that offer high flexibility and fast fixture speed while maintaining high strength on a majority of substrates. Thorough testing of LOCTITE® 4902™ and LOCTITE® 4903™ has confirmed that these new formulations perform equally, if not better, in standard cyanoacrylate categories such as fixture speed, shear strength, and heat aging. Testing has also proven that while maintaining these desired performance parameters, the new formulations have also increased sealing reliability on common flexible substrates.

Introduction

Speed and flexibility have always been known to be a trade-off for adhesives. Cyanoacrylates are considered to be some of the fastest and strongest adhesives available but those properties also lend themselves to a rigid, brittle end product. Light cure acrylics are one-component adhesives that provide fast fixture times and very good adhesion and are also available in highly-flexible formulations. The obvious caveat when considering a light cure acrylic, however, lies in the necessity for a transparent bond line and the need for light cure equipment. Hot melt adhesives can be flexible, but by definition need heated dispensing equipment, which rules out their use in applications with heat-sensitive substrates. While two-component silicones can provide flexibility with relatively fast fixture speeds, the shear strengths obtained on most substrates never surpass 500 psi. Henkel has developed two LOCTITE® instant adhesives that also offer high flexibility and high strength on a majority of substrates.

Cyanoacrylates Background

Cyanoacrylates, often referred to as “instant adhesives,” are considered to be one-part, room-temperature curing adhesives. When pressed into a thin film between two surfaces, the moisture present on the bonding surfaces causes the cyanoacrylate to cure rapidly and form a rigid thermoplastic. Cyanoacrylates generally provide excellent adhesion to most substrates and typically fixture within 10 to 30 seconds. First patented in 1957 by Eastman Kodak, the instant adhesive known today as LOCTITE® QuickSet® 404® was soon sold to Loctite Corporation in 1960. Over the years, improvements have been made to this line of cyanoacrylates to provide premium performance. Rubber-toughened cyanoacrylates were developed to offer higher impact resistance and peel strength. Thermally resistant cyanoacrylates offer excellent bond strength retention after exposure to temperatures as high as 250°F for thousands of hours. Surface-insensitive cyanoacrylates offer rapid fixture times and cure speeds on acidic surfaces such as wood or dichromated metals; surfaces that are known to hinder performance of cyanoacrylates. Low odor/low bloom cyanoacrylates minimize the potential for a white haze to occur around the bond line and prevent aesthetic issues in sensitive applications. Light curing cyanoacrylates utilize proprietary photo-initiators to

cure the adhesive in seconds when exposed to light of the appropriate wavelength while still maintaining the humidity-curing abilities for opaque areas.

Highly Flexible Cyanoacrylates

Benefits of using cyanoacrylates include, but are not limited to, excellent adhesion to most substrates, fast fixture times, high shear strengths and high tensile strengths. Due to their one part, easy-to-dispense nature, cyanoacrylates lend themselves easily to automation on production lines. One key limitation noted earlier is the brittle, rigid nature of the thermoplastic that is formed once the cyanoacrylate is cured. One common metric for flexibility of an adhesive is the percent elongation of a bulk sample of material. On average, the percent elongation of bulk cyanoacrylate material tends to be no more than a couple percent, whereas highly-flexible adhesives such as silicones regularly achieve percent elongations higher than 100%. Why is flexibility important when it comes to cyanoacrylates? Where bonded components are subjected to bending loads, flexible instant adhesives reduce localized stress concentration and encourage homogeneous deformation of parts. The highly flexible cyanoacrylates have much lower durometer hardness and modulus than typical cyanoacrylates. These features are particularly useful on flexible substrates that may tear due to the stress concentration that a more rigid cyanoacrylate would create; also referred to as the fillet creating a "knife edge."

To achieve the flexibility desired in these new highly-flexible cyanoacrylates, a novel ethyl/octyl monomer combination was used as the chemical backbone of the LOCTITE® 4902™ and LOCTITE® 4903™ adhesives. This monomer combination allowed for enhanced performance compared to standard cyanoacrylates with regards to strength in flexible bond lines. The increased flexibility and lower durometer hardness yields to exceptional resistance to leaks and excellent sealing capabilities. All the while, LOCTITE® 4902™ and LOCTITE® 4903™ have proven to maintain the speed, strength, and ease of use desired with standard cyanoacrylates. Both products have also acquired ISO-10993 certification for use in the medical device industry.

LOCTITE® 4902™, LOCTITE® 4903™ Performance

Testing for benchmarking data of the new formulations could be grouped into two categories: standard cyanoacrylate testing and specific application testing. The standard cyanoacrylate testing included shear strength tests, fixture speed tests, heat resistance tests, and elongation testing of bulk material. To get a better sense of the sealing capability and on-part flexibility of the new formulations, specific application testing also needed to be performed. This testing included leak testing of plastic tube/fitting combinations before and after applying rotational stress to the bond line.

Standard Cyanoacrylate Testing

Four basic tests were performed to compare physical properties of LOCTITE® 4902™ and Loctite® 4903™ to other "non-flexible" cyanoacrylates on the market: fixture speed, shear strength, heat aging, and bulk elongation. It was found that the new highly flexible formulations performed equally or better than the comparative formulations, which included a standard cyanoacrylate, a rubber-toughened cyanoacrylate, a high-temperature rubber-toughened cyanoacrylate, and an early generation flexible cyanoacrylate.

Fixture speed is defined as the time it takes for an adhesive to cure enough to be able to support a three kilogram weight for five seconds using a one square inch bond overlap. In the testing performed, the fixture time was tested on acrylonitrile butadiene styrene (ABS), polycarbonate (PC), and steel lap shears. **Figure 1** shows the results. It can be

seen that the LOCTITE® 4902™ and LOCTITE® 4903™ produced fixture times of less than 20 seconds on each substrate – with fixture times less than 10 seconds on the two plastic types tested.

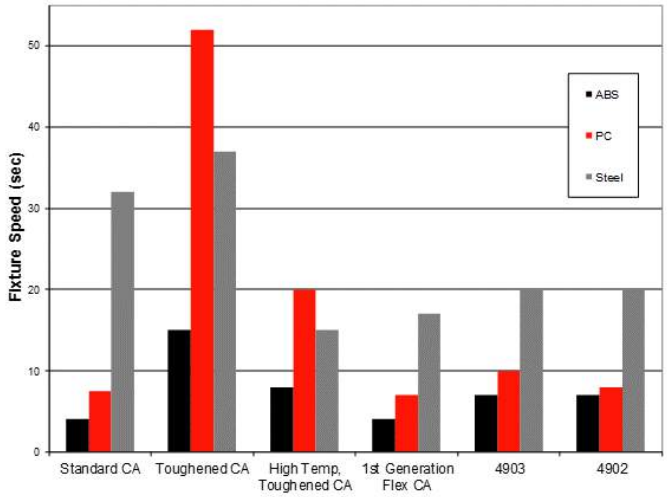

Figure 1 – Fixture speed of cyanoacrylates on various substrates.

Shear strength was tested on the same three substrate types as the fixture speed testing. Once bonded and cured for 24 hours, the substrates were pulled apart on an *Instron*® physical properties tester at a speed of 0.05 in. per minute. It can be seen in **Figure 2** that the LOCTITE® 4902™ and LOCTITE® 4903™ developed strengths of at least 1,500 psi on each substrate tested including strengths over 2,000 psi on ABS. LOCTITE® 4902™ and LOCTITE® 4903™ also displayed the highest overall bond strengths to polycarbonate of all adhesives tested, although it should be noted that no data was generated for the high- temperature rubber toughened cyanoacrylate for that substrate.

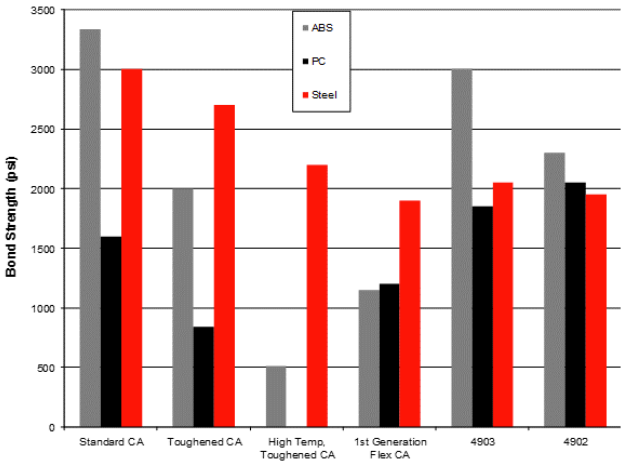

Figure 2 – Shear strengths of cyanoacrylates on various substrates.

A common concern among users of cyanoacrylates is the long term, high-temperature resistance of the adhesive. In general, cyanoacrylates are not considered "high-temperature" adhesives. For this testing, lap shears were bonded in the same manner as the shear strength testing. The samples were then placed into ovens at 80°C and 100°C for 500 hours. Upon completion of aging, the samples were then pulled apart using the same method as the shear strength testing. Figure 3 shows that LOCTITE® 4902™ and LOCTITE® 4903™ were able to maintain well over 80% of their initial strength after aging at 80°C and well over 60% of initial strength after aging at 100°C. The results of

this testing proved that the new highly flexible formulations were able to perform at an equivalent level to other high performance cyanoacrylates on the market.

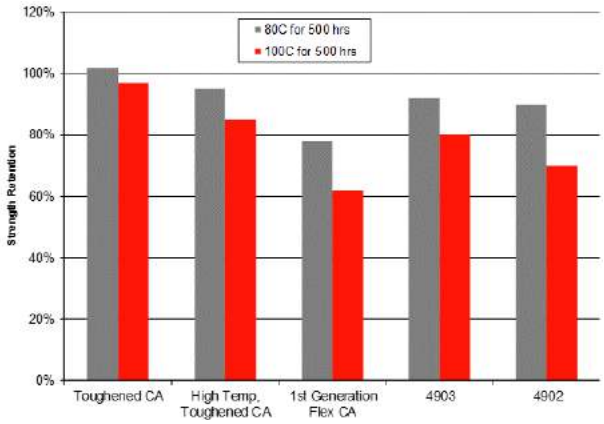

Figure 3 – Heat aging stability of cyanoacrylates for 500 hours of aging.

The final round of standard cyanoacrylate testing performed was the percent elongation of bulk samples of product. To perform percent elongation testing of material, the adhesive was dispensed and cured into a thin film. The film was then cut into "dog bones" of set lengths for testing on the *Instron*® physical properties tester. The "dog bone" samples were pulled apart until failure and the percent elongation was calculated. **Figure 4** shows the lack of "flexibility" of the common cyanoacrylates and the high level of flexibility of the novel highly flexible formulations used for LOCTITE® 4902™ and LOCTITE® 4903™. None of the comparative formulations of cyanoacrylates achieved greater than 20% elongation, while LOCTITE® 4902™ and LOCTITE® 4903™ have been found to regularly achieve percent elongations higher than 100%.

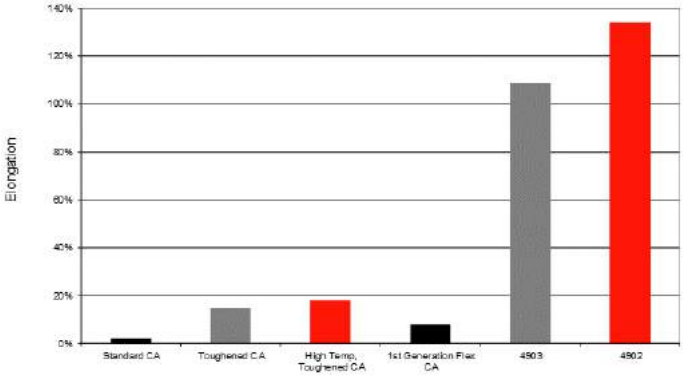

Figure 4 – Bulk elongation properties of various cyanoacrylates.

Specific Application Testing

To better showcase the drastically improved level of flexibility of LOCTITE® 4902™ and LOCTITE® 4903™ over current formulations of cyanoacrylates, testing specific to flexible applications needed to be performed. A novel test method was chosen to quantify the improvement in on-part flexibility of the new products: leak testing of plastic tube/fitting combinations before and after applying rotational stress to the bond line and rotational testing where the same tube/fitting combinations were rotated on a horizontal axis until failure.

Figure 5 – Example of PVC tubing and PVC Y-fitting.

The leak testing was performed on three substrate combinations: soft PVC tube with PC Y-fitting, soft PVC tube with ABS Y-fitting, and soft PVC tube with PVC Y-fitting. An example of a test sample can be seen in **Figure 5**. In each case, the adhesive was applied onto the outside diameter of roughly the last centimeter of tubing. The Y-fitting was then slid over the tubing using a rotating motion to ensure 360° coverage within the bond line. Once the assemblies were cured for 24 hours, the Y-fittings were sealed and the loose end of the tubing was connected to an air supply. The samples were then pressurized to 20 psi for 10 seconds and held underwater to indicate any leaking in the bond line. The same test specimens were then placed under rotational stress for two minutes using a modified LOCTITE® RB10 Rotary Table, and once again, subjected to the leak testing. **Figure 6** shows the results of the testing. It can be seen that LOCTITE® 4902™ and LOCTITE® 4903™ were the only samples that passed testing after rotational stress was applied to the bond lines.

No Stress	Toughened CA	High Temp, Toughened CA	1st Generation Flex CA	4903	4902
PC Fitting / PVC Tube	Fail	Fail	Fail	Pass	Pass
ABS Fitting / PVC Tube	Pass	Pass	Pass	Pass	Pass
PVC Fitting / PVC Tube	Pass	Pass	Pass	Pass	Pass

Slight Rotational Stress – (2 minutes @55 rpm - Rotary Table)

PC Fitting / PVC Tube	Fail	Fail	Fail	Pass	Pass
ABS Fitting / PVC Tube	Fail	Fail	Fail	Pass	Pass
PVC Fitting / PVC Tube	Fail	Fail	Fail	Pass	Pass

Figure 6 – Results from leak testing before and after light rotational stress was applied to fittings.

Conclusions

Speed and flexibility have always been known to be a trade-off for adhesives. Cyanoacrylates have always proven to be some of the fastest and strongest adhesives available, but those properties also lend themselves to a rigid, brittle end product. Henkel has brought to market two new LOCTITE® products that maintain the desirable properties of common cyanoacrylates available today, while simultaneously providing the flexibility desired by manufacturers. Thorough testing of LOCTITE® 4902™ and LOCTITE® 4903™ has confirmed that these new formulations perform equally, if not better, in standard categories such as fixture speed, shear strength, and heat aging.

Testing as also proven that while maintaining these desired performance parameters, the new formulations have also increased sealing reliability on common flexible substrates.

References

1. P. J. Courtney, C. Verosky, Advances in Cyanoacrylate Technology for Medical Device Assembly.