LOCTITE 402

The Ultra-Performance Instant Adhesive.

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Industrial design and manufacturing engineers are constantly looking for innovative solutions that can enable new and improved designs, and advance overall manufacturing processes. Across many industries, the trend is toward smaller and higher performance devices. Smaller devices require innovative materials and assembly processes, combined with enhanced precision: fit more function into tighter spaces, and maintain or enhance performance of the end device. Such device designs can be a challenge from an assembly perspective, as well as for new performance requirements such as heat generation.

There are many assembly solutions available to engineers today, ranging from mechanical methods such as fasteners, to tapes, welding (ultrasonic, solvent) and adhesives. Each assembly method brings its own benefits and challenges. Table 1 provides an overview of the various assembly methods with their key benefits and challenges.

TABLE 1
Various Assembly Method Benefits & Challenges.

ASSEMBLY METHOD	KEY BENEFITS	KEY CHALLENGES
Mechanical Fastening	• Strong • Cost-effective • No curing • Join dissimilar materials	• Parts inventory • Challenge to automate • No sealing • Stress concentrated around fastener • Loosening over time
Ultrasonic Welding	• Easy to automate • Simple process • High strength • Speed	• Capital investment • System maintenance • Dissimilar materials • Hard-to-bond materials • Gap fill
Tape	• Cost • Immediate fixture • Join dissimilar materials	• Challenge to automate • Precise application • Hard-to-bond substrates
Adhesives	• Join dissimilar materials • Even stress distribution • Fill large gaps • Seal • Easy to automate • Join hard-to-bond materials	• Must be dispensed/applied • Curing required (some equipment) • Select formulas with lower temp resistance

Within the adhesives assembly category, there are several options including epoxies, hot melts, light cures, two-step acrylics and cyanoacrylates (or instant adhesives). Cyanoacrylate adhesives offer many advantages over other assembly methods, including but not limited to:

- Fast fixture
- Room temperature cure
- One-part, single component
- High-bond strength to a wide range of plastics, metals and elastomers
- High-bond strength to hard-to-bond materials (i.e., polyethylene, polypropylene)
- Easy/accurate dispensing

A few challenges exist for instant adhesives driven mainly by their thermoplastic nature: typical maximum operating temperature of 82 °C; gap fill maximum for high viscosity versions of 2.5 mm / 0.10 inch; inherent brittleness; and poor durability in wet environments.

Since their introduction over 50 years ago, cyanoacrylates have seen considerable formulation advancement with new tough and flexible variants, high temperature (up to 121 °C) formulas and even low-odor versions. The latest innovation combines the optimum performance characteristics of top instant adhesives into one new solution.

INTRODUCING LOCTITE 402

LOCTITE 402 is the latest product innovation from Henkel, featuring patented technology that pushes the boundaries of performance beyond that of standard ethyl cyanoacrylates. It is an ultra-performance instant adhesive, combining fast fixture and high strength, with best-in-class high temperature performance and improved durability in environmental conditions.

Fast fixture and high strength
LOCTITE 402 demonstrates fast fixture speed on a wide range of substrates including metals, plastics, rubbers, and porous materials such as paper and wood, comparing well to a typical surface insensitive adhesive as shown in Table 2.

TABLE 2
Fixture Speed of LOCTITE 402 and Typical Surface Insensitive on Various Substrates.

MATERIAL	LOCTITE 402	TYPICAL SURFACE INSENSITIVE
Mild Steel	20 s	20 s
Aluminum	< 5 s	< 5 s
Stainless Steel	30 to 45 s	20 to 30 s
Polycarbonate	< 5 s	< 5 s
ABS	< 5 s	< 5 s
PVC	10 to 20 s	5 to 10 s
Paper	5 to 20 s	< 5 s
Wood (Oak)	30 to 45 s	30 to 45 s
Leather	30 to 45 s	10 to 20 s
EPDM Rubber	< 5 s	< 5 s

LOCTITE 402 provides high bond strength on a wide range of metals and plastics (see Figure 1). In comparison to the typical surface insensitive adhesive, it excels on metals such as aluminum and stainless steel. LOCTITE 402 also has excellent lap shear strength on all plastics tested.

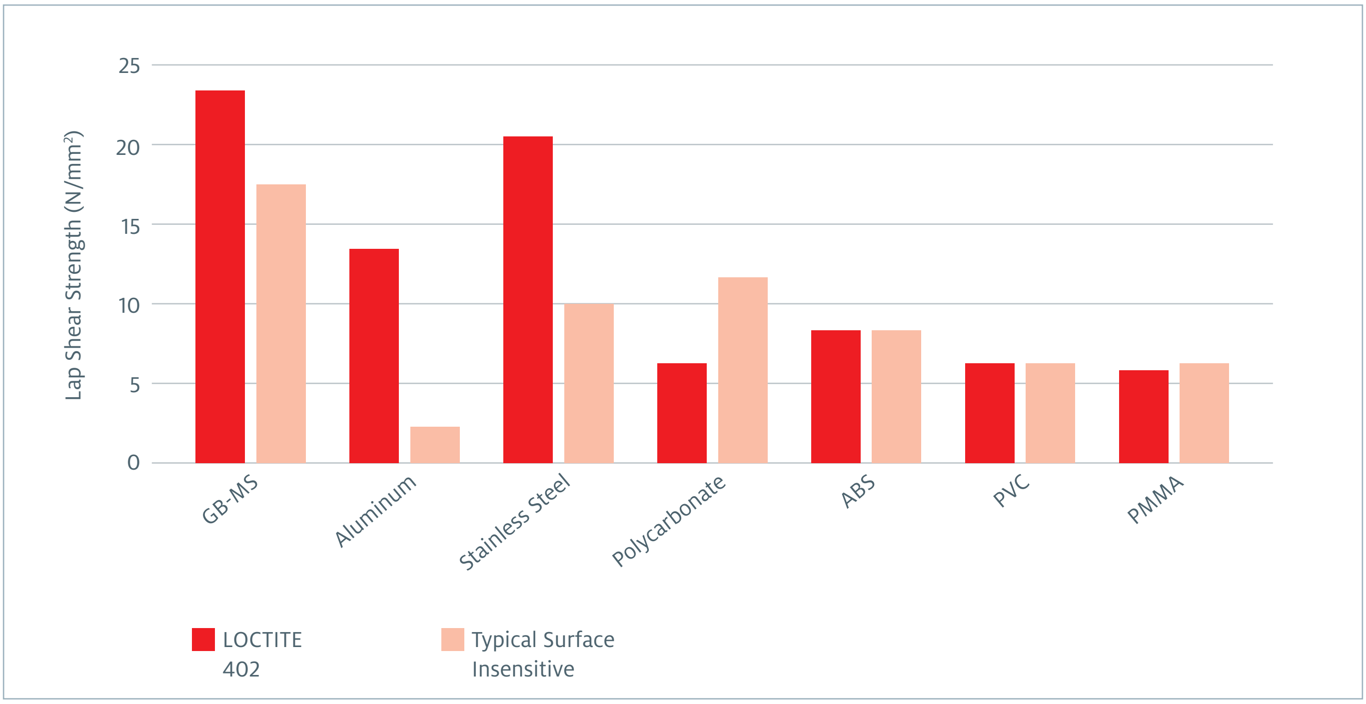

Figure 1
Lap shear strength of LOCTITE 402 and typical surface insensitive on various metals and plastics after seven-day room temperature cure.

Best-in-class, high-temperature performance

The safe operating temperature limit for cyanoacrylate adhesives is typically 82 °C. Up to now, poor thermal resistance has been a limiting factor in the use of ethyl-based instant adhesives in applications where the adhesive bond is exposed to high temperatures for extended periods of time. This poor thermal resistance is due to a combination of factors, including softening of the cured polymer at temperatures close to its glass transition temperature (Tg), and degradation of mechanical properties such as tensile shear strength due to depolymerization of the linear polymer. A comprehensive review was published in 2017.

One solution to this poor thermal resistance is the use of a cyanoacrylate monomer with the capability of forming a cross-linked polymer structure, such as allyl 2-cyanoacrylate. When heated to temperatures of approximately 150 °C or higher, cross-linking of the allyl cyanoacrylate linear polymer will occur via radical polymerization to give a thermally-resistant polymer. However, if cross-linking of the allyl polymer hasn't occurred, allyl-based instant adhesives suffer from the same poor thermal resistance as other cyanoacrylate polymers. Therefore, an additional processing step involving exposure at elevated temperatures of approximately 150 °C is required to impart this thermal resistance to adhesive joints bonded with allyl 2-cyanoacrylate. This additional processing step can add significant time and cost to the manufacturing assembly process.

LOCTITE 402 contains new patented technology developed by Henkel to overcome these limitations in high-temperature performance. LOCTITE 402 contains a mixture of ethyl and allyl cyanoacrylate monomers, combined with a patented additive package. This mixture of ethyl and allyl cyanoacrylate monomers enables LOCTITE 402 to be used in high-temperature applications like any other instant adhesive, without any additional processing steps. The ethyl cyanoacrylate monomer supports the initial heat performance of LOCTITE 402 at elevated temperatures, until the allyl monomer cross-linking reaction has taken place. The time required for this cross-linking reaction to take place is dependent on the exposure temperature.

There are three different thermal properties that are considered essential for overall heat durability: (i) hot strength; (ii) heat resistance over time at elevated temperatures; and (iii) hot strength after long periods of exposure to high temperatures. In the following sections, we will provide a discussion of each property, and demonstrate where LOCTITE 402 outperforms other instant adhesives.

Hot strength

Hot strength is the strength of the adhesive bond when measured at elevated temperatures. Cyanoacrylate polymers are classified as thermoplastic materials, which means that these polymers soften when heated to temperatures close to their glass transition temperature (Tg). The Tg values of some common cyanoacrylate esters are listed in Table 3.

TABLE 3

Glass Transition Temperature (Tg) Values of Common Cyanoacrylate Esters.[1]

CYANOACRYLATE ESTER	TG (°C)
Methyl	165
Ethyl	140 – 150
n-Butyl	90
B-Methoxyethyl	85
Allyl	130

Ethyl cyanoacrylate polymer has a reported Tg in the region of 140 – 150 °C, hence the polymer will start to soften and flow at temperatures approaching or above the Tg range. Bonded lap shear joints stored at, close to, or above this temperature, exhibit low strengths.
At temperatures above the Tg, the cyanoacrylate polymer begins to depolymerize, resulting in the loss of mechanical properties such as tensile shear strength.

Figure 2 shows the hot strength of LOCTITE 402 at elevated temperatures, compared to a typical surface insensitive adhesive and a typical high temperature instant adhesive, on stainless steel lap shears after curing for seven days at room temperature. In each case, a decrease in the lap shear strength of the bonded joint is observed as the environmental temperature is increased. At a temperature of 135 °C, the lap shear strength is approximately 3 N/mm² for the bonded adhesive joints.

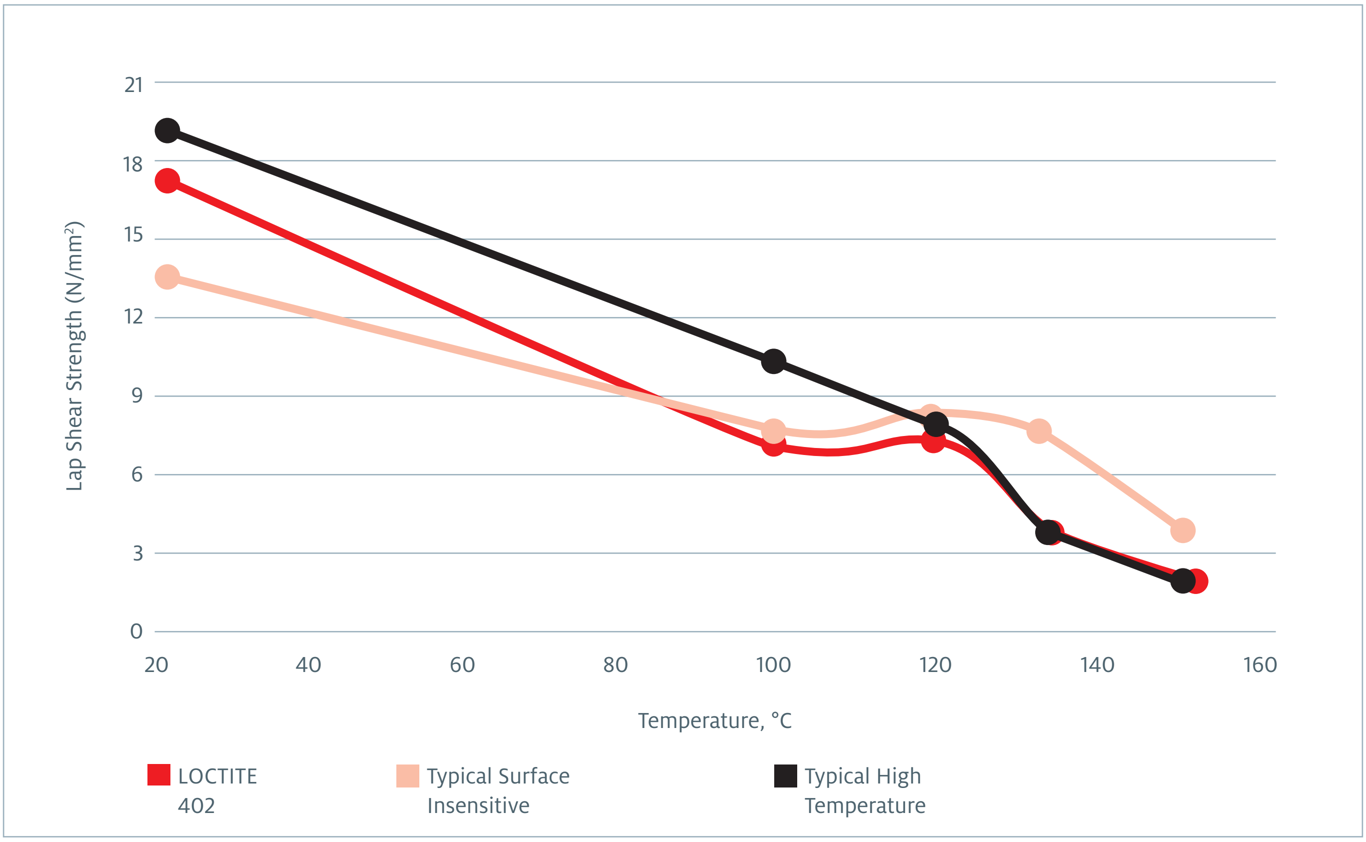

Figure 2
Hot strength of LOCTITE 402, typical surface insensitive and typical high temperature after curing for seven days at room temperature on stainless steel lap shears.

Heat resistance

Heat resistance refers to the ability of the cured adhesive in a bonded joint to maintain its initial room temperature bond strength when the bonded joint is exposed to long-term aging at elevated temperatures, but then returned to and tested at room temperature. The effect of heat weakens adhesion at the interface between the cyanoacrylate polymer and the bonded substrate. Typically, instant adhesives show rapid loss of bond strength when bonded joints are aged at temperatures far below their Tg.

The heat resistance of LOCTITE 402, typical surface insensitive and typical high temperature adhesives was determined after exposure to temperatures ranging from 100 °C up to 150 °C (see Figures 3 to 6). In all cases, stainless steel lap shears were used, and the bonded lap shears were cured for seven days at room temperature prior to high-temperature exposure.

After 1.000 hours of exposure at 100 °C, LOCTITE 402 maintains 79% of its initial strength (see Figure 3). The typical surface insensitive adhesive also performs well at this temperature, maintaining 59% of its initial strength, while the typical high temperature adhesive shows 29% strength retention.

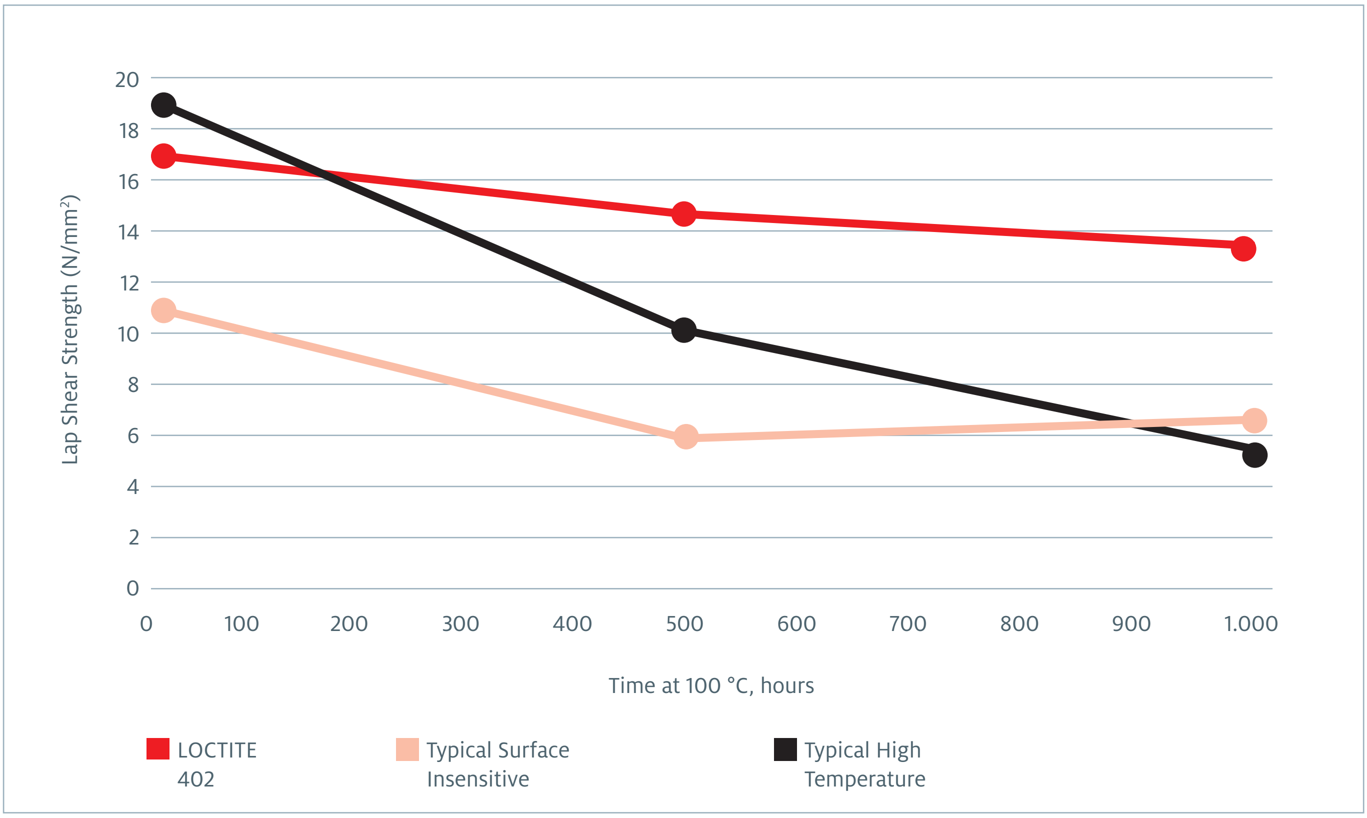

Figure 3

Heat resistance of LOCTITE 402, typical surface insensitive and typical high temperature over 1.000 hours at 100 °C on stainless steel lap shears.

Figure 4 shows the heat resistance of LOCTITE 402 over 1.000 hours at 120 °C, compared to typical surface insensitive and typical high temperature adhesives. Rapid loss of bond strength is observed for the typical high temperature adhesive. A lap shear strength of 3.9 N/mm^2 is maintained by the typical surface insensitive adhesive after 1.000 hours of exposure. In contrast, LOCTITE 402 maintains a lap shear strength of 6.5 N/mm^2 (or 38% of initial strength) after 1.000 hours of exposure.

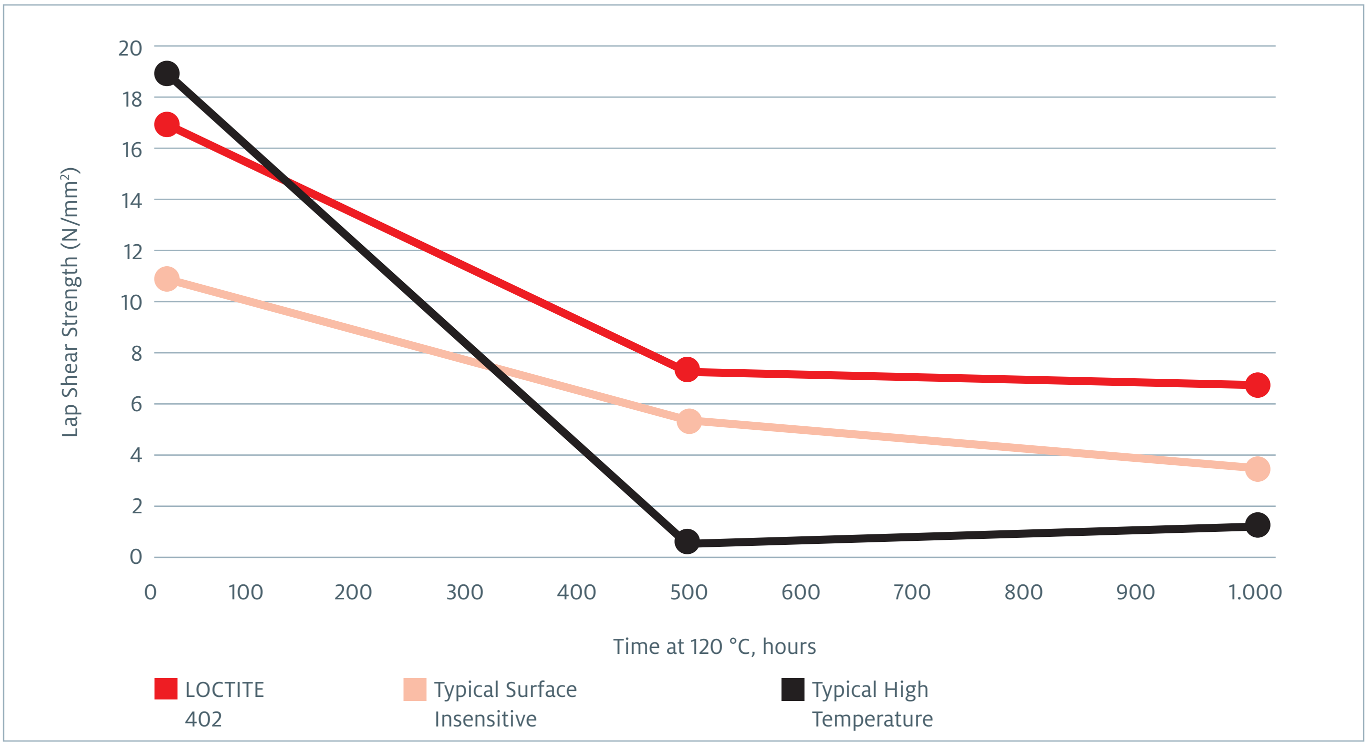

Figure 4
Heat resistance of LOCTITE 402, typical surface insensitive and typical high temperature over 1.000 hours at 120 °C on stainless steel lap shears.

As the temperature is increased further to 135 °C, the heat resistance performance of LOCTITE 402 becomes more evident (see Figure 5). After 1.000 hours of exposure at 135 °C, LOCTITE 402 maintains a lap shear strength of 11.3 N/mm² or 66% of initial strength. In contrast, the typical surface insensitive and typical high temperature adhesives show a rapid decrease in strength within 500 hours. After 1.000 hours of exposure, the typical surface insensitive and typical high temperature adhesives show zero strength, indicating that degradation of the linear polymer has occurred.

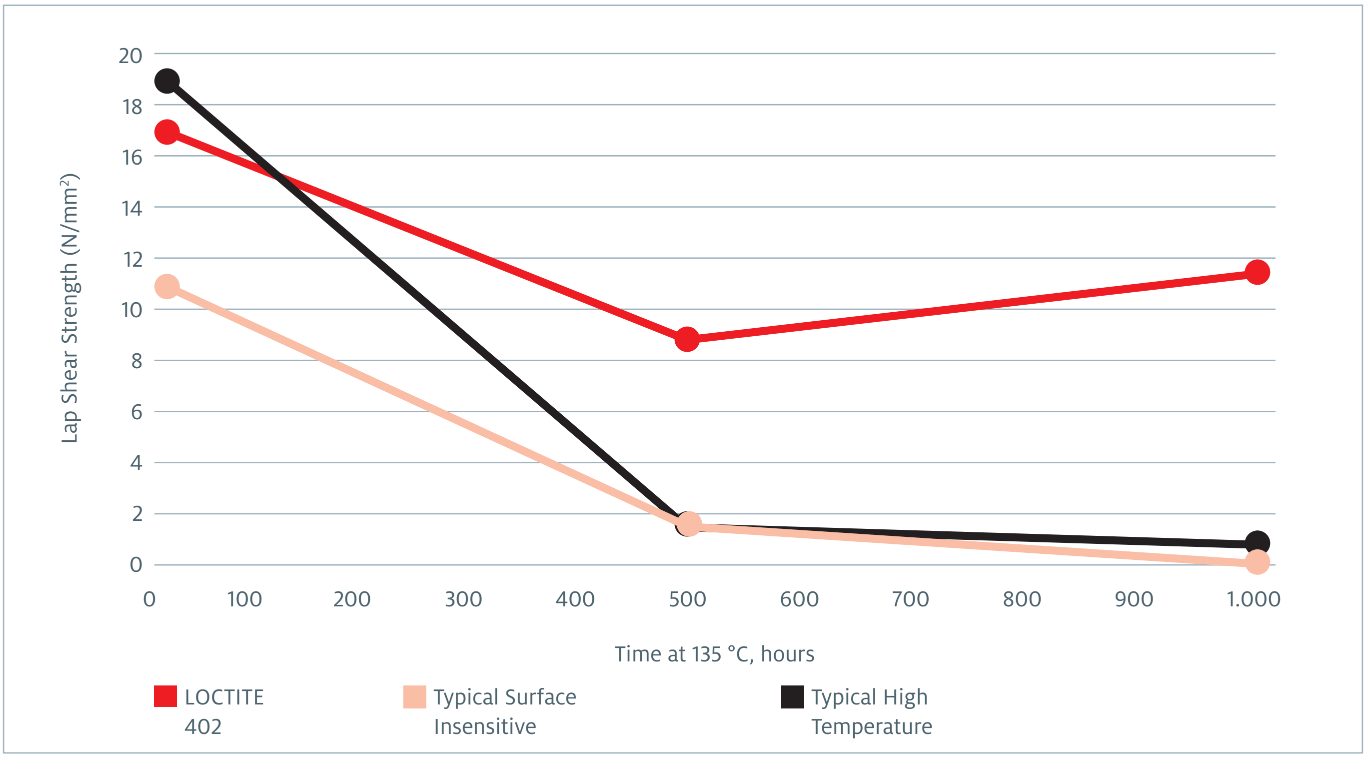

Figure 5
Heat resistance of LOCTITE 402, typical surface insensitive and typical high temperature over 1.000 hours at 135 °C on stainless steel lap shears.

The heat resistance of LOCTITE 402 is sustained when exposed to the highest temperature of 150 °C (see Figure 6). After 1.000 hours of exposure, LOCTITE 402 maintains 49% of its initial bond strength. In contrast, the typical high temperature adhesive drops significantly within the first 500 hours of exposure, maintaining only 9% of its initial bond strength. A more rapid loss of lap shear strength is observed for the typical surface insensitive adhesive, which has zero strength after 500 hours at 150 °C. This demonstrates that linear polymer degradation happens more quickly as the exposure temperature is increased.

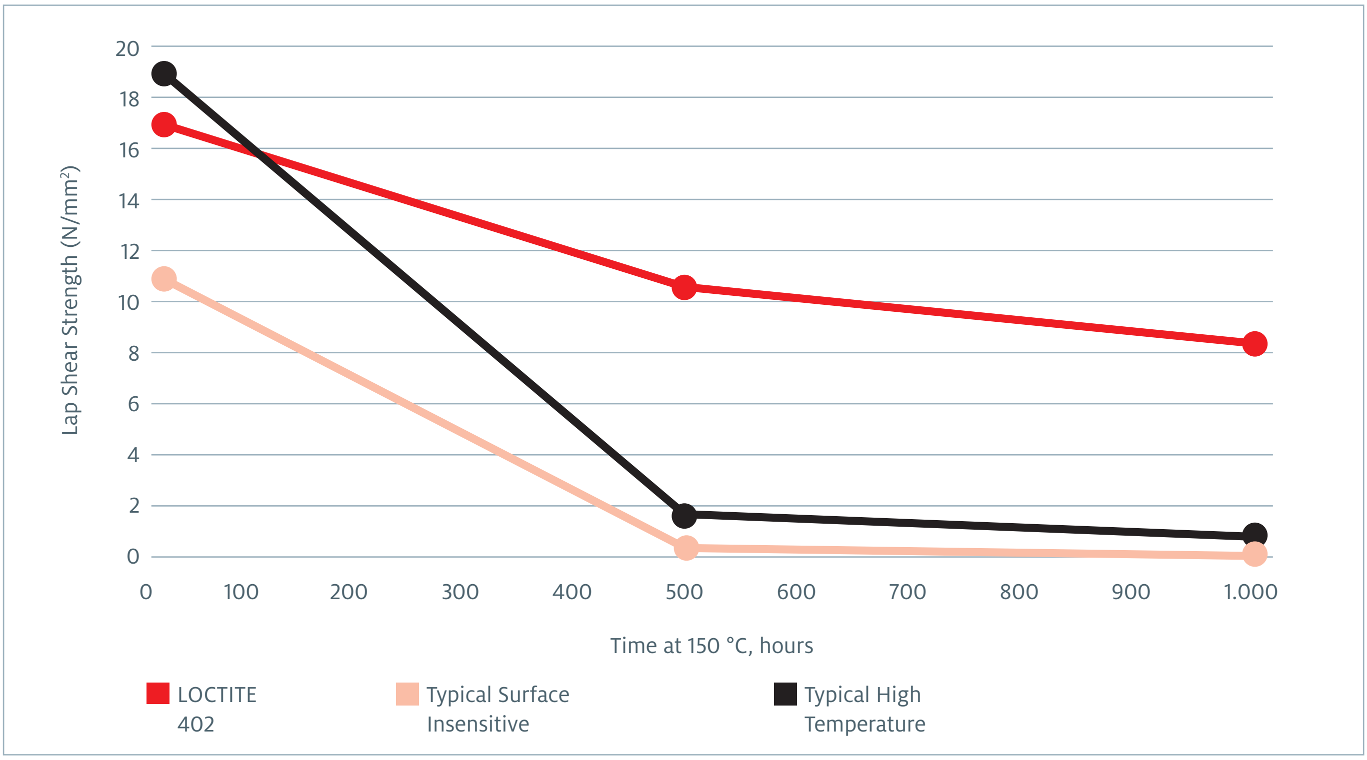

Figure 6
Heat resistance of LOCTITE 402, typical surface insensitive and typical high temperature over 1.000 hours at 150 °C on stainless steel lap shears.

Hot strength after long periods of exposure to high temperatures
The standout feature of LOCTITE 402 is its impressive ability to withstand high temperatures and to maintain its hot strength over long periods of exposure. Thus, LOCTITE 402 is the only instant adhesive capable of sustained high-temperature performance over time.

The hot strengths of LOCTITE 402, typical surface insensitive and typical high temperature adhesives after exposure to high temperatures were determined as follows:

- Stainless steel lap shears were bonded with either LOCTITE 402, typical surface insensitive or typical high temperature adhesives.
- After seven-day room temperature cure, the bonded joints were exposed to high temperatures of:
  - 100 °C
  - 120 °C
  - 135 °C
  - 150 °C
- After 500 and 1.000 hours of exposure at each temperature, the strength of the bonded lap shears was measured also at this temperature.

Figure 7 shows the hot strength at 100 °C for LOCTITE 402, typical surface insensitive and typical high temperature adhesives after exposure for long periods of time at this temperature. For LOCTITE 402, the hot strength increases from 7.8 N/mm² initially, up to 13.4 N/mm² within the first 500 hours of exposure. This increased hot strength is sustained over the next 500 hours of exposure at this temperature. The hot strength of the typical high temperature adhesive is constant at around 10 N/mm² over 1.000 hours of exposure. For the typical surface insensitive adhesive, the hot strength drops slightly down to 5.4 N/mm² after 1.000 hours of exposure.

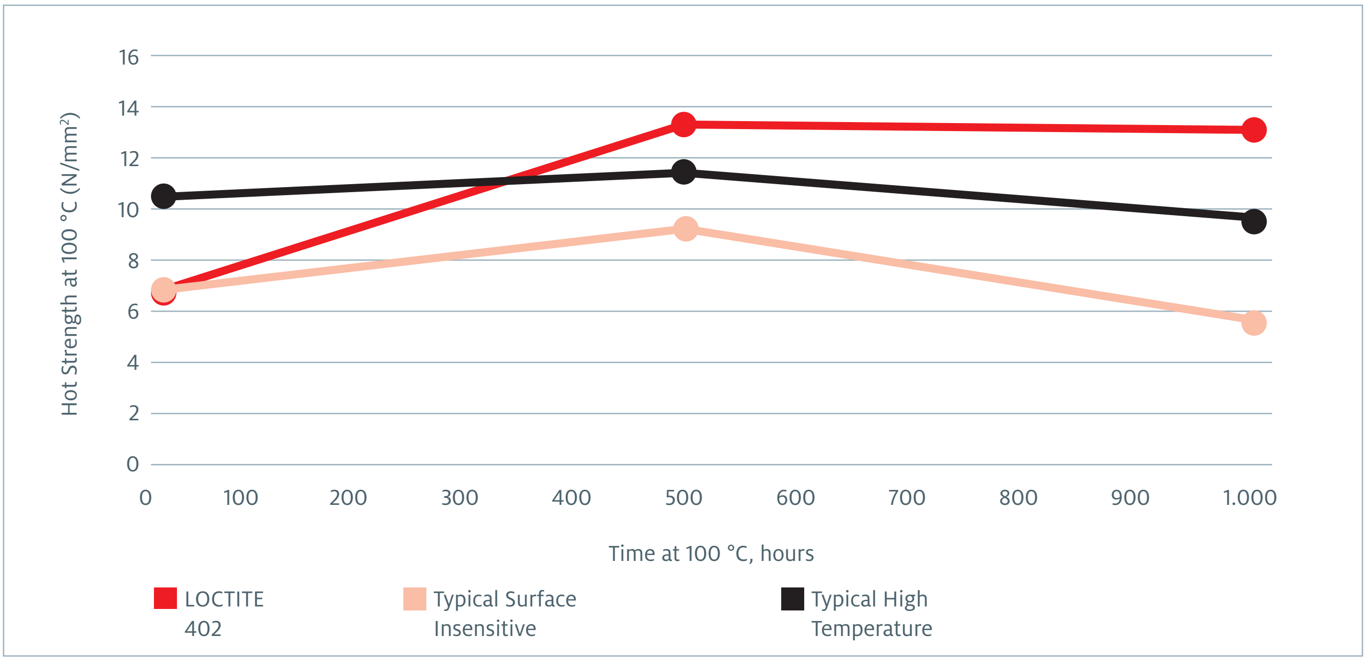

Figure 7
Hot strength at 100 °C of LOCTITE 402, typical surface insensitive and typical high temperature on stainless steel lap shears, after aging for up to 1.000 hours at 100 °C.

For LOCTITE 402, exposure at 120 °C results in a slight decrease in hot strength over 1.000 hours of exposure to 4.8 N/mm² (see Figure 8). A similar decrease in hot strength is observed for the typical surface insensitive adhesive over the exposure time, decreasing from 8 N/mm² to 3.9 N/mm² over 1.000 hours. This decrease in hot strength over time indicates that some degradation in the mechanical properties of the linear polymer is occurring. With that said, even after 1.000 hours of exposure at 120 °C, both products still have an adequate hot strength to provide performance in applications. In contrast, the hot strength for the typical high temperature adhesive drops to 0.7 N/mm² after 1.000 hours of exposure, which is not sufficient to provide performance in applications.

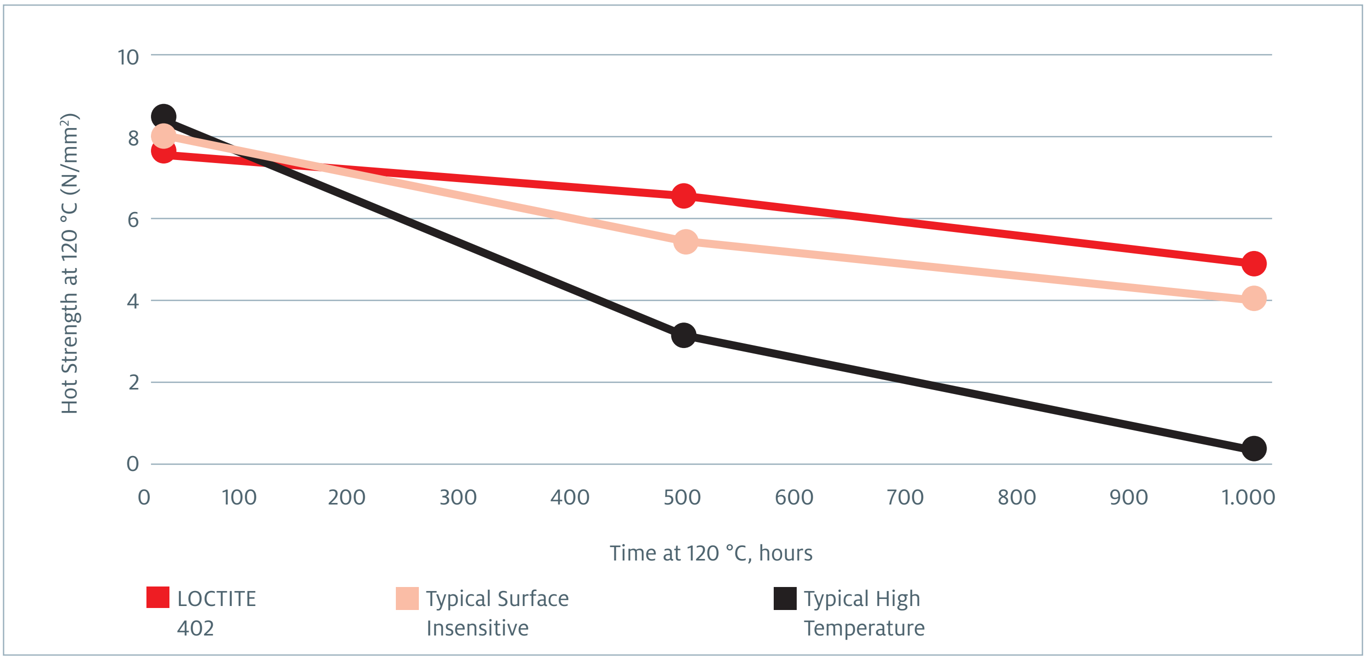

Figure 8
Hot strength at 120 °C of LOCTITE 402, typical surface insensitive and typical high temperature on stainless steel lap shears, after aging for up to 1.000 hours at 120 °C.

As the exposure temperature is increased further, the difference between LOCTITE 402 and the other two adhesives becomes more evident (see Figure 9). For the typical surface insensitive adhesive, the hot strength at 135 °C decreases over time. After 500 hours of exposure at 135 °C, the hot strength has dropped to 1.7 N/mm² which is not sufficient to provide performance in applications. By 1.000 hours, there is zero strength left, indicating that complete degradation of the linear polymer has occurred. For the typical high temperature adhesive, the hot strength declines to 1.4 N/mm² within 500 hours of exposure, but then stays at this level for the next 500 hours. Again, the hot strength of this adhesive over time is not sufficient to provide performance in applications. In contrast, after 1.000 hours of exposure at 135 °C, the hot strength of LOCTITE 402 is sustained at 3.8 N/mm². This sustained performance over time is due to the cross-linking of the allyl polymer, which provides excellent thermal performance.

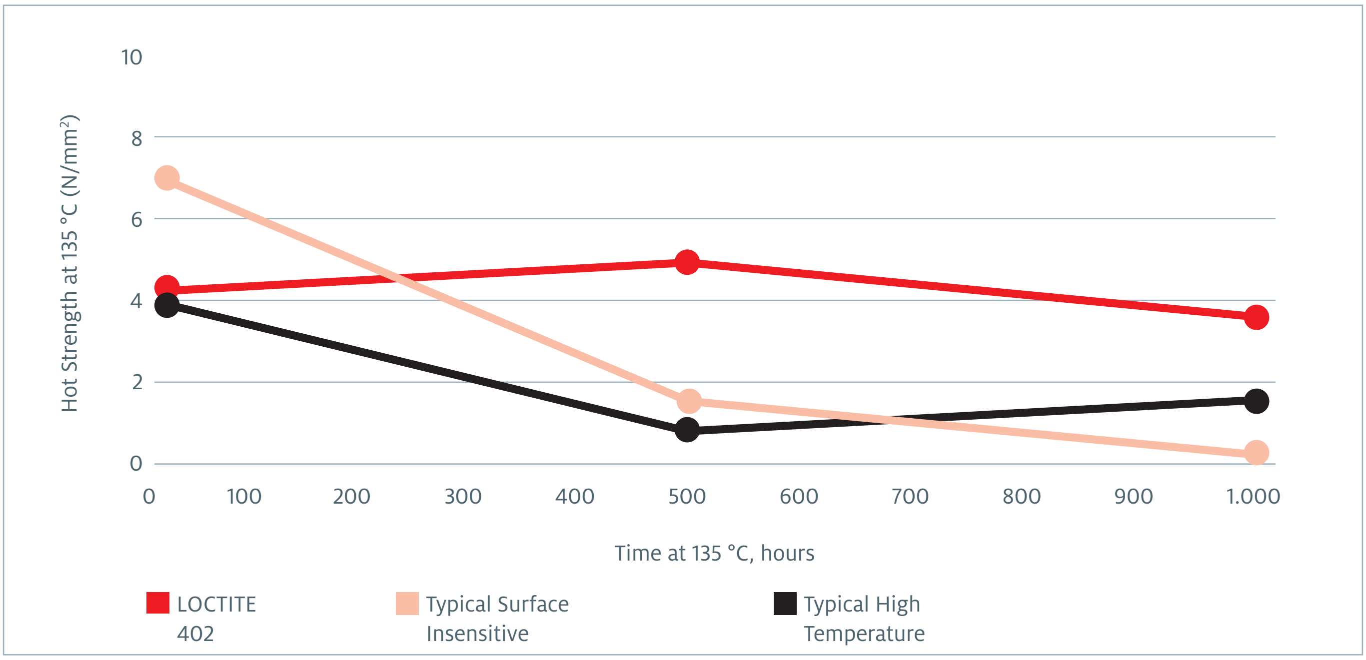

Figure 9
Hot strength at 135 °C of LOCTITE 402, typical surface insensitive and typical high temperature on stainless steel lap shears, after aging for up to 1.000 hours at 135 °C.

Increasing the exposure temperature to 150 °C accelerates the polymer degradation for the typical surface insensitive adhesive (see Figure 10). After 500 hours, the linear polymer has almost fully degraded. At 150 °C, the hot strength of the typical high temperature adhesive is 1.7 N/mm² initially and 0.9 N/mm² after 1.000 hours of exposure. Interestingly, the hot strength of LOCTITE 402 increases within the first 500 hours of exposure at 150 °C, up to 3.1 N/mm². This increased hot strength indicates that cross-linking of the allyl polymer has occurred, imparting excellent thermal performance to the bonded lap shears. Over the next 500 hours of exposure at 150 °C, the hot strength of LOCTITE 402 is sustained at a level that is adequate to provide performance in applications.

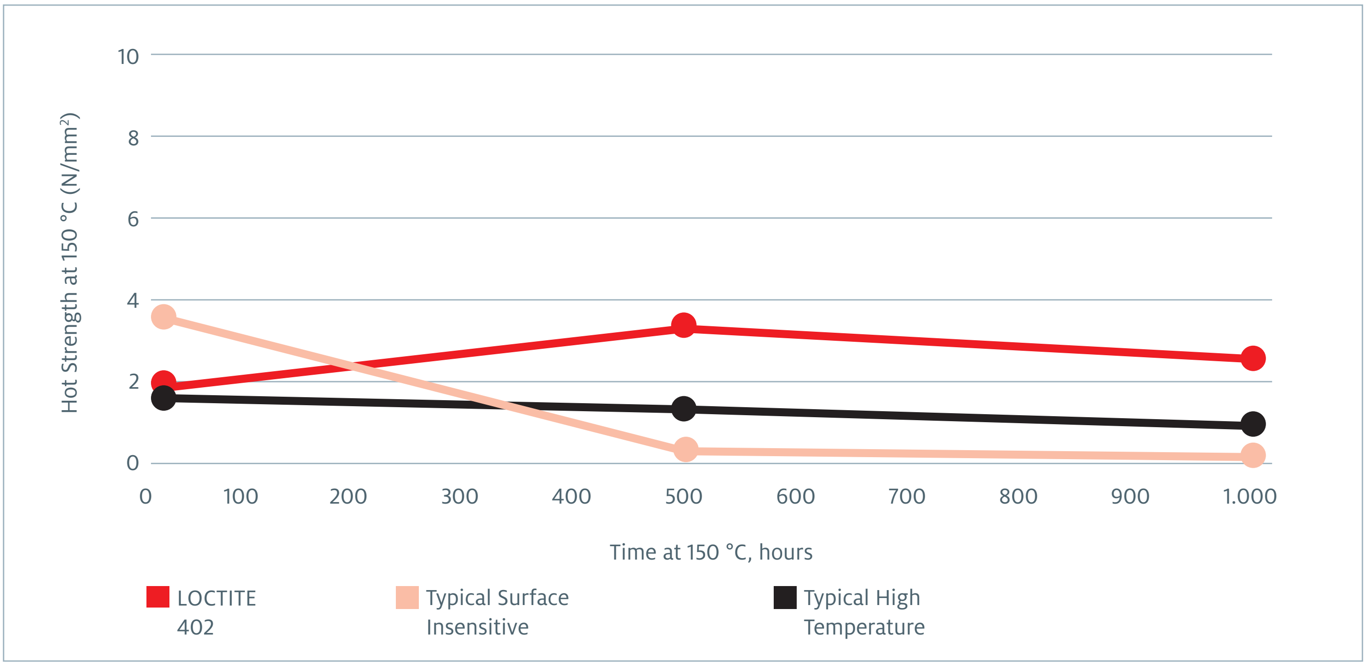

Figure 10
Hot strength at 150 °C of LOCTITE 402, typical surface insensitive and typical high temperature on stainless steel lap shears, after aging for up to 1.000 hours at 150 °C.

Summary of high-temperature performance

A summary of the overall high temperature performance of LOCTITE 402, the typical surface insensitive and the typical high temperature adhesives is provided in Table 4. Taking each of the three thermal properties into consideration, the recommended operating temperature for LOCTITE 402 is -40 °C to +135 °C. This is because the initial hot strength for LOCTITE 402 at 150 °C is 1.8 N/mm^2, which is slightly below what is considered adequate to provide performance in applications. If, however, initial hot strength at 150 °C is not a primary need for a particular application, then LOCTITE 402 may be suitable for applications at temperatures exceeding 135 °C. Trials with LOCTITE 402 are recommended for each individual application.

TABLE 4

Summary of High-Temperature Performance for LOCTITE 402, Typical Surface Insensitive and Typical High Temperature from 100 °C to 150 °C.

PRODUCT	TEST	100 °C	120 °C	135 °C	150 °C
LOCTITE 402	Typical High Temperature	Yes	Yes	Yes	No
	Heat Resistance Over 1.000 Hours	Yes	Yes	Yes	Yes
	Hot Strength Over 1.000 Hours	Yes	Yes	Yes	Yes
Typical Surface Insensitive	Initial Hot Strength	Yes	Yes	Yes	Yes
	Heat Resistance Over 1.000 Hours	Yes	Yes	No	No
	Hot Strength Over 1.000 Hours	Yes	Yes	No	No
Typical High Temperature	Initial Hot Strength	Yes	Yes	Yes	No
	Heat Resistance Over 1.000 Hours	Yes	No	No	No
	Hot Strength Over 1.000 Hours	Yes	No	No	No

Improved durability in environmental conditions

LOCTITE 402 also offers improvements in durability under various environmental conditions, compared to the typical surface insensitive adhesive. LOCTITE 402 demonstrates improved resistance at high temperature/humidity conditions, particularly as the temperature is increased. Figure 11 shows this improved performance after 1.000 hours aging at 40 °C/98% RH and 65 °C/95% RH.

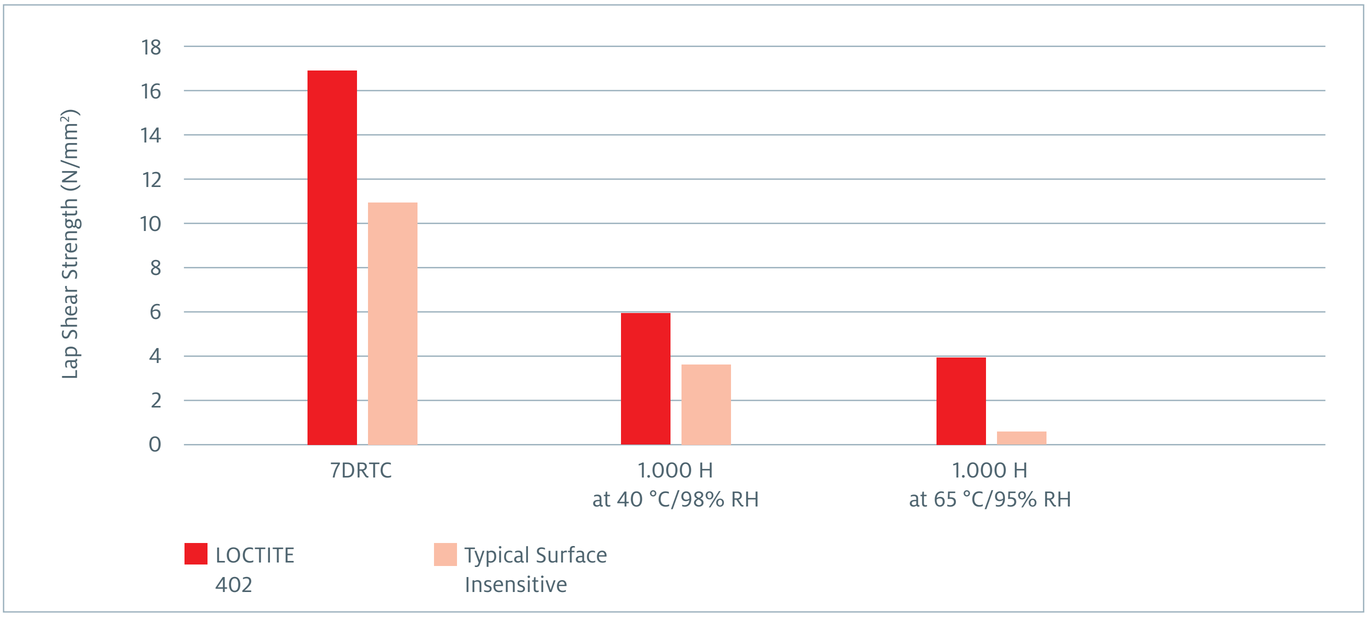

Figure 11

Lap Shear Strength (N/mm^2) for LOCTITE 402 and typical surface insensitive on stainless steel after 1.000 hours exposure at high temperature/humidity conditions.

LOCTITE 402 also excels in resistance to exposure of various solvents/media, including unleaded petrol, motor oil, isopropanol and ethanol, when compared to the typical surface insensitive adhesive (see Figure 12).

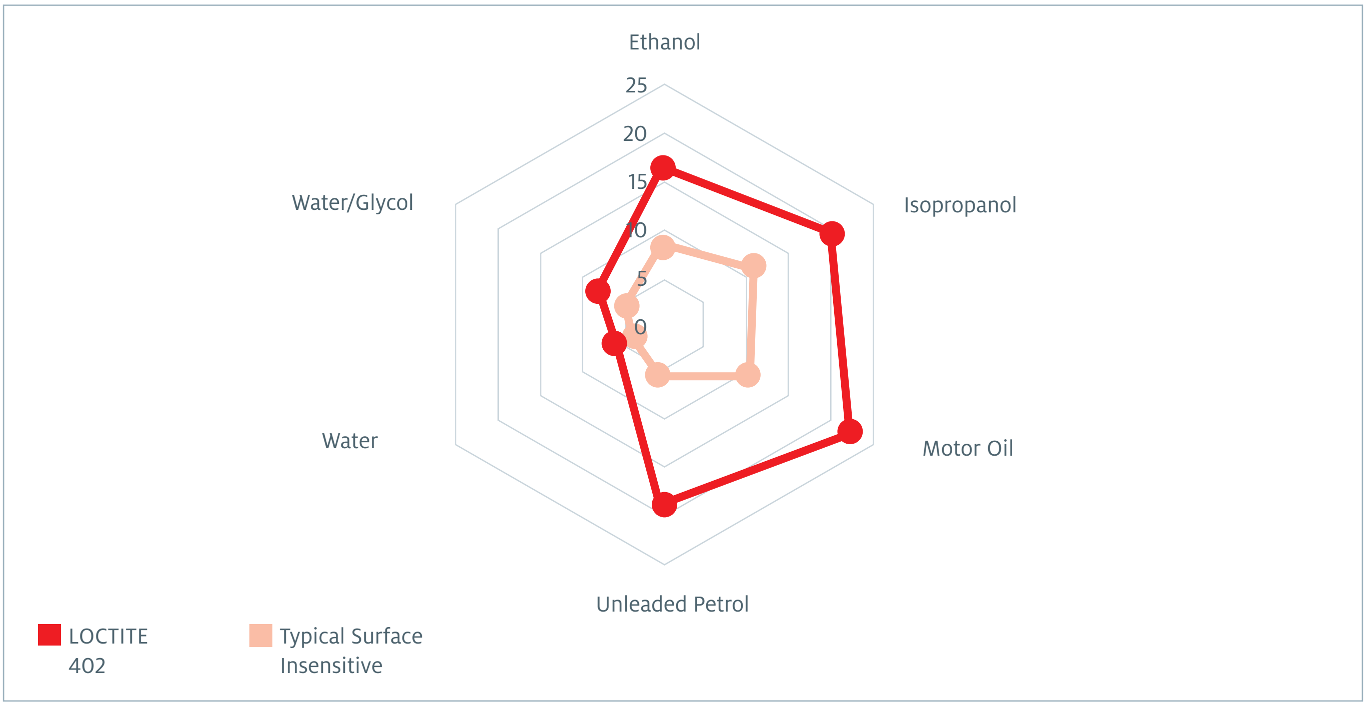

Figure 12
Lap Shear Strength (N/mm²) for LOCTITE 402 and typical surface insensitive on stainless steel after 1.000 hours environmental aging in various solvents/media.

CONCLUSION

Although many assembly methods are available to designers and manufacturers, instant adhesives in particular offer significant benefits well-aligned with the recent market demands of smaller, higher-performing and precision devices. LOCTITE 402 shows significant advantages over traditional cyanoacrylates, including sustained high-temperature performance and improved durability following heat/humidity – all while maintaining the key features for which instant adhesives are selected (one-part, fast fixture, substrate versatile).

LOCTITE 402 is the ultra-performance instant adhesive: fast, reliable and easy-to automate for precision assembly.

References

1. Cyanoacrylates: Towards High Temperature Resistant Instant Adhesives. A Critical Review, Barry Burns, Rev. Adhesion Adhesives, Vol. 5, No. 4, December 2017.

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