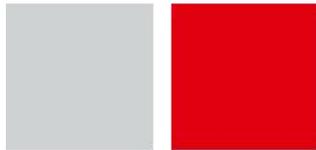


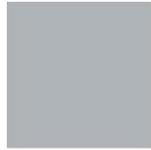
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Innovations in Hybrid Structural Instant Adhesive Technologies

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Abstract

Over the last century, adhesive use has become increasingly popular over other assembly methods for structural design. To meet the demands of the latest product designs and manufacturing processes, new adhesives are continually being formulated. Current cyanoacrylate and epoxy technologies have proved to be valuable in today's largest manufacturing companies. Despite the many advantages, each technology still has its disadvantages that limit the materials and situations in which it is used. The recent advancement in hybrid adhesive technologies has allowed manufacturers to overcome limitations by increasing manufacturing speeds and assembly durability. New structural instant adhesives, hybrids of epoxy and cyanoacrylate technologies, can be used to meet the demands of present and future production requirements.

Introduction

Cyanoacrylates are one-part, room-temperature-curing adhesives.

They have excellent adhesion to most substrates, including metals, plastics, elastomers and porous substrates. When pressed into a thin film between two surfaces, cyanoacrylates cure rapidly to form a rigid thermoplastic.

Cyanoacrylates undergo anionic polymerization in the presence of moisture, a weak base, which is present in trace amounts on virtually all surfaces. As the acid stabilizers present in the formula are neutralized by the moisture, rapid polymerization occurs [1].

Adhesive fixture strength is achieved in just seconds, and full strength occurs in 24 hours. Along with the rapid room-temperature cure, cyanoacrylates are solvent-free and have a wide range of viscosities. They have excellent bond strength in shear and tensile mode.

Cyanoacrylates however, have limited gap-filling capabilities, with a maximum cure-through gap of about 0.25 mm. When fully cured, cyanoacrylates are very brittle and have low impact strength. They also have poor resistance to polar solvents. With some cyanoacrylates, blooming – or the white haze that can form on the assembly around the bond line – may occur. Blooming occurs when

cyanoacrylate monomer volatilizes, reacts with moisture in the air, and then settles on the part as a white dust.

Cyanoacrylates are commonly used in the medical industry to bond medical tubing, endoscopes and catheters. They can also be used in general assembly, including bonding dissimilar substrates and hard-to-bond plastics, wire tacking and O-ring bonding.

Epoxies are one- or two-part structural adhesives that cure at room temperature. Two-part epoxy systems have a resin and a hardener that polymerize when mixed together to form thermoset polymers. One-part pre-mixes that utilize a heat cure are also common. Epoxies bond a variety of substrates and shrink minimally upon cure. These adhesives have high cohesive strength and toughness, as well as very good heat and environmental resistance. They have excellent depth of cure and can fill large gaps.

Though epoxies are a great choice for many structural applications, they still have their disadvantages. Mainly, epoxies have long fixture times that tend to be much slower than other chemistries. Typical fixture times for epoxies range from 15 minutes to 2 hours. Though heat can be used to accelerate the cure, the temperature limitations of the

substrates, such as plastics, must be considered. During cure of a two-part system the reaction can also exotherm, which again can be problematic for highly sensitive parts.

Epoxies are often used on metals and easy-to-bond plastics for structural bonding. Examples include electric motors, wire bonding, name plates, speakers, small engines and potting applications such as printed circuit boards. They can be used in many manufacturing areas such as aerospace, electronics, automotive and medical industries.

Advancements

Today's industry production requirements are forever demanding new and improved adhesive technologies. To meet these demands, companies such as Henkel have produced hybrid structural instant adhesives – for example, Henkel's LOCTITE 4090 (referred to as cyanoacrylate/epoxy hybrid). This is a two-part curable composition consisting of (1) a cyanoacrylate curing component and a cationic catalyst; and (2) a second part composed of a cationic curable epoxy, wherein when mixed together the cationic catalyst initiates cure of the epoxy component [2]. This two-part, room-temperature-curable system bonds to a variety of substrates including plastics, metals and elastomers. This hybrid is a high-viscosity gel adhesive with a 1:1 mix ratio. The product is clear at no gap to a light yellow color with larger gaps. Because it is a two-component mixture, the risk of blooming that can occur with a cyanoacrylate is greatly reduced. It has a 3-to-7-minute fixture time at 1 mm gap. This hybrid formulation combines the most critical attributes of a cyanoacrylate – fast fixture

time and substrate versatility – with the advantages of using a structural epoxy: high bond strength; temperature, environmental and impact resistance; and the ability to fill gaps up to 5 mm.

Strength

In regard to shear strength, epoxies perform very well with most types of metal. Epoxies do fall short, however, when a customer expects the same range of shear strength of different types of plastics. Combined with the cyanoacrylates' ability to bond to many plastics and elastomers, hybrid structural instant adhesives have overcome this problem and provide more consistent shear strength values for a range of materials.

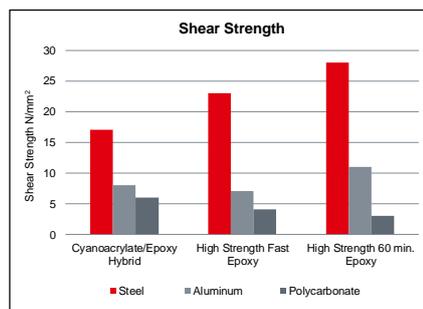


Figure 1. Shear strength: a Cyanoacrylate/Epoxy Hybrid vs. other typical epoxies on multiple substrates.

Speed

Typical fixture speeds for cyanoacrylates can range from 5 seconds to 90 seconds, depending on the composition of the adhesive and the substrate on which it is applied. Epoxies tend to have much longer fixture times (hours vs. seconds). Even with the help of additives, the fastest fixture times are typically around 8 to 15 minutes. Hybrid structural instant adhesives have adapted the speed of a cyanoacrylate, allowing for a zero gap fixture time of less than 180 seconds, and 3-to-7-minute fixture times for gaps ranging from

1 mm to 5 mm. This is a slightly longer fixture speed compared with instant adhesives, but it is still faster than the fastest epoxies. Fixture speed is the most important feature for customers in their final assembly lines, where fast removal of parts on the line allows for more parts to be assembled per hour.

Versatility

Longtime users of adhesives know that there are not many options when bonding elastomers. Instant adhesives are among the few adhesives that will accomplish the job. But with the help of hybrid adhesives, more structural assemblies that need to fill a gap, as well as bond dissimilar or difficult-to-bond substrates, can be bonded with structural instant adhesives solutions.

Typical epoxies are not suggested when bonding olefins such as polypropylene or rubbers such as nitrile. Table 1 captures the range of materials that a hybrid adhesive can bond, and that shear strength is achievable even on those materials not designed for adhesive use.

Typical Performance of Cured Material Adhesive Properties

Cured for 168 hours @ 22°C (72°F)
Shear Strength, Lap Shear Strength, ISO 4587:

	N/mm ²	(psi)
Steel (grit blasted)	17	(2,420)
Aluminum	7.6	(1,100)
Aluminum (etched)	13	(1,900)
Zinc dichromate	9.1	(1,320)
Stainless steel	15	(2,120)
ABS	5.2	(750)
Phenolic	3.2	(460)
Polycarbonate	6.9	(1,000)
Nitrile	0.7	(100)
Wood (oak)	4.8	(700)
Epoxy	9.1	(1,320)
Polyethylene	0.5	(72)
Polypropylene	0.6	(87)

Table 1. Typical shear strengths of a Cyanoacrylate/Epoxy Hybrid on different substrates [3].

Impact Resistance

Structural assemblies often require not only high tensile strength, but high impact resistance as well. Solenoid pumps, power brake systems and prosthetics are just a few examples where there are high-impact joints. In the past, cyanoacrylates were not suggested for these types of applications because they are so brittle. One impact can cause cracks that propagate throughout the cyanoacrylate bond line and result in adhesive failure. Hybrid structural instant adhesives incorporate epoxy performance properties to triple the impact resistance of that seen with a generic cyanoacrylate.

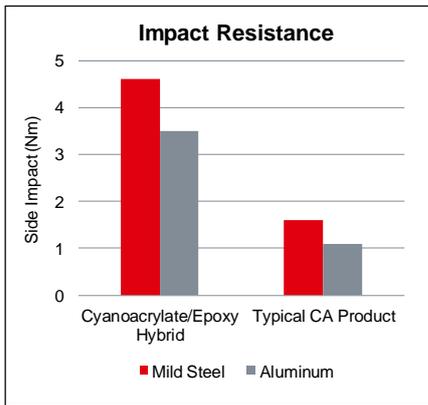


Figure 2. Typical impact resistance of a Cyanoacrylate/Epoxy Hybrid vs. a generic cyanoacrylate.

Heat and Humidity Resistance

Generic epoxies and cyanoacrylates have average heat resistance ranges of 82°C to 121°C (180°F to 250°F). Above these temperatures, epoxies can lose up to 75% of their initial strength and cyanoacrylate bonds tend to fall apart. Hybrid structural instant adhesives have been designed to overcome these temperature limits to meet the demand of higher-performing adhesives.

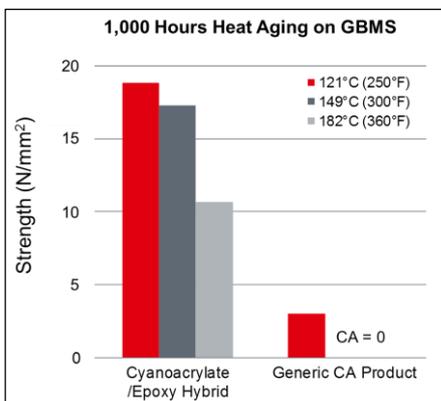


Figure 3. Heat resistance of a Cyanoacrylate/Epoxy Hybrid vs. a generic cyanoacrylate on grit-blasted mild steel.

Figure 3 shows a heat aging study that compares the bond of grit-blasted mild steel (GBMS) using a cyanoacrylate/epoxy hybrid and a generic cyanoacrylate. These parts were bonded at room temperature

and brought up to the temperatures shown for 1,000 hours before being brought back to room temperature and tested for shear strength. The generic cyanoacrylate had a mediocre performance when held at 121°C (250°F), but failed to hold the GBMS together at 149°C (300°F) and 182°C (360°F). The hybrid adhesive had excellent strength retention at 149°C. Even at 182°C, a temperature above the recommended value, it was still able to retain over half the strength of the 121°C test. Heat resistance becomes important for adhesives in applications involving electromechanical systems or motors.

Similar concerns are true for cyanoacrylates when they are exposed to high humidity or moisture. Cyanoacrylates tend to break down when exposed to high-humidity situations for long periods of time. Hybrid structural instant adhesives overcome this hurdle due to the epoxy portion of the adhesive. Even after exposing the bond line to 65.5°C (150°F) and 95% relative humidity for 1,000 hours, the hybrid adhesive still retained 62% of its initial shear strength. The moisture resistance of hybrid adhesives makes them an excellent choice for assemblies used in outdoor applications where exposure to rain and sunshine are common.

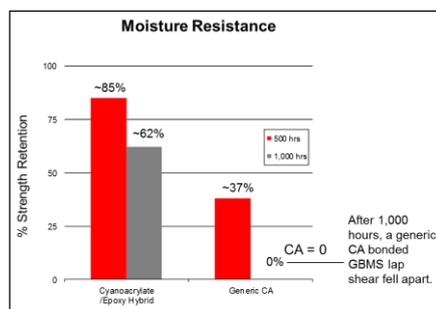


Figure 4. Lap shears of grit-blasted mild steel were bonded and then exposed to 65.5°C (150°F) and 95%

relative humidity for the times shown. The lap shears were then pulled apart and the % of the original strength is shown for both the Cyanoacrylate/Epoxy Hybrid and a typical cyanoacrylate product.

Chemical and Solvent Resistance

Epoxies often have excellent chemical resistance. Epoxies and cyanoacrylates are typically unaffected by non-polar solvents like gasoline and motor oil, but when it comes to polar solvents such as acetone and isopropanol, cyanoacrylates perform poorly. Hybrid structural instant adhesives have adapted the chemical resistance attribute of epoxies to produce a bond that is highly resistant to gasoline, motor oil, ethanol, isopropanol, water and more.

Chemical/Solvent Resistance				
Aged under conditions indicated and tested @ 22°C (72°F)				
Environment	°C	% of initial strength		
		100 h	500 h	1,000 h
Water	22	90	75	70
Water	60	80	55	55
Motor oil	40	120	130	130
Unleaded gasoline	22	95	100	105
Ethanol	22	85	90	90
Isopropanol	22	100	100	95
Water/glycol 50/50	87	50	5	5
98% RH	40	85	70	70
95% RH	65	95	85	65

Table 2. Chemical and solvent resistance of a Cyanoacrylate/Epoxy Hybrid [3].

Gap-Filling Capabilities

While epoxies tend to fill a large gap, especially when applied in multiple steps, cyanoacrylates do not. When cyanoacrylates cure, the adhesive relies on the surface moisture on a substrate to neutralize the acidic stabilizer in the adhesive to initiate polymerization. With large gaps, there is too little surface moisture for the large amount of acidic stabilizer present, resulting in poor or incomplete

curing. This limits cyanoacrylates' gap-filling capabilities to an average of 0.25 mm maximum. Gap filling is an important design consideration, especially with structural assemblies where gases or liquids are present. Hybrid structural instant adhesives that can fill a gap up to 5 mm open up another realm of applications where cyanoacrylates were once not typically considered for use.

Uses and Applications

Hybrid structural instant adhesives are technological breakthroughs suitable for a broad range of applications. They demonstrate the greatest benefit in applications where the combination of speed, toughness, moisture resistance and gap filling is required. These adhesives are suitable for technologies where outdoor use, UV protection and low blooming is needed. They also provide a solution when standard cyanoacrylates prove to be too brittle and a high temperature resistance is required. Structural applications that require the bonding of multiple substrates including metals, plastics, elastomers and rubber will benefit from the use of these hybrid technologies.

Some application ideas include electric motors, textile machines, railway and rail cars, and marine applications where good moisture resistance is needed, such as saunas and hot tubs. Other areas include light assemblies such as LED luminaries and outdoor lighting housings. Hybrid structural instant adhesives can also be used with electronic components such as antennas and loudspeakers; in sporting goods, modern furniture, jewelry, prostheses and plastic tanks; and in general and vehicular maintenance and repair.

Conclusion

The development of hybrid structural instant adhesives will assist manufacturers in overcoming common adhesive problems. Using a cyanoacrylate epoxy hybrid technology, companies can make assemblies with a wide range of materials. These assemblies will be able to handle harsher chemicals, higher heat and other environmental conditions not typically supported by adhesives, and for production at a faster rate than ever before.

Now that the adhesive industry is bridging the gap between cyanoacrylate and epoxy adhesives, engineers, design teams, companies and manufacturers have an option for a better-performing structural adhesive that allows for high-production volume demands.

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3. LOCTITE 4090 Technical Data Sheet. July 2014.

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