UV-VIS initiated unlimited cure through cyanoacrylates

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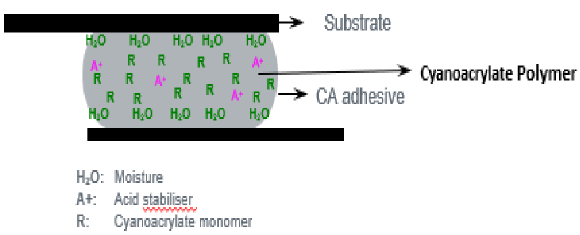
Introduction

Cyanoacrylate ("CA") adhesives are one-part, instant adhesives that can be cured at room temperature, without application of external energy to form thermoplastics adhesive bond. Cyanoacrylate monomers are generally polymerized due to trace amount of moisture present on applied substrates, (Scheme 1). Adhesives made from CA monomers are known for extremely fast curing speed, ease of use, and excellent adhesion to a wide variety of substrates.

Scheme 1. Cyanoacrylate Polymerization



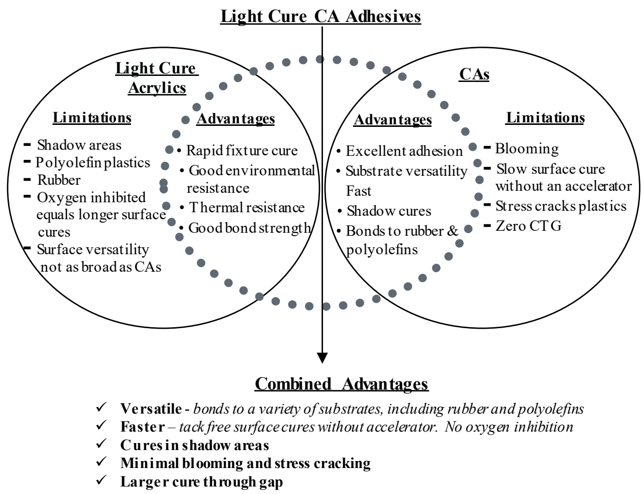
Though with many attractive features, CA adhesives have certain limitations, such as blooming/frosting on bonding parts, limited cure through large gap, and slow fillet cure [1]. Table 1 summarizes the benefits and limitation that CA adhesives can provide.

Table 1. Benefits and Limitations of CA Adhesives

Benefits	Limitations
• Excellent adhesion to wide variety of substrates • Substrate versatility • Rapid fixture • Simple cure mechanism • High bonding strength on metal and elastomers	• Blooming / frosting • Slow fillet cure without accelerator • Stress crack plastics • Limited gap cures

Light-curable CAs were designed and developed to overcome such limitations. These single component adhesives – sold under the tradename FlashCure®, cure in seconds when exposed to light at appropriate wavelength to provide superior adhesion to a wide range of substrates including elastomers, plastics and metals [2]. Due to secondary shadow cure mechanism, light-curable CAs minimize if not outright eliminate blooming and enable larger cure-through-gap (CTG) capability. Thus, combined benefits from both light-curable acrylic and conventional CA technologies are provided, seen in Scheme 2.

Scheme 2. Advantages of Light Curable CAs



Experimental

Preparation of CA Formulation

Unless otherwise specified, all CA formulations were prepared using a method modified from standard operation procedures for making Loctite® FlashCure® 4304.

Viscosity

Viscosity of CA formulation was measured at 25°C by using an Anton Paar MCR 301 rheometer equipped with a pair of Cone & Plate (50 cm diameter) at a shear rate of 100 s^{-1}.

Accelerated Shelf life stability

Thermal stability of CA was determined by aging at 82 °C for 7 days in aluminum tubes. A sample is considered to pass the test if it can still flow freely after aging.

Tack-Free Time

A Loctite® Zeta 7411-S UV flood system was used as a light source for tack-free time tests of the light-curable CA formulations. During this test, one drop of an adhesive was placed on a glass slide and cured under the Loctite® Zeta 7411-S UV flood system at an intensity of 30 mW/cm^2, measured using a Loctite® UV A/B Radiometer (item #1390323). The length of exposure time to achieve tack-free surface is recorded as tack-free time.

Bond Strength

Bond strength of CA formula was determined according to ASTM D1002–05 method, Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal) or ASTM D4501-01 Shear Strength of Adhesive Bonds between rigid substrates by the Block-Shear Method. Two type of substrates were used: grit blasted mild steel (GBMS) lap shears and transparent, medical grade polycarbonate (PC) blocks.

The specimens were bonded with a Flashcure® product. A total area of 0.5 in^2 (322.6 mm^2) was covered by the adhesive without any induced gap. For GBMS lap shears, the specimens were cured at ambient condition for 24 hours. For PC blocks, the specimens were cured for 10 seconds under a Loctite® Zeta 7411-S UV flood system at an intensity of 30 mW/cm^2, measured using a Loctite® UV A/B Radiometer. After curing, the specimens were tested using an Instron tensile tester at a crosshead speed of 0.08 inch/minute.

Results and Discussion

Table 2 listed the test results of three Flashcure® products, Loctite® 4304, Loctite® 4310 and Loctite® 4311. For comparison, the testing results of Loctite® 401, a conventional CA product, were also included.

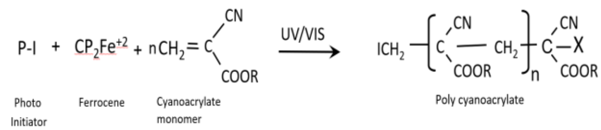
As can be seen from Table 2, the viscosity of Flashcure® products is available in a wide range. This will allow customers to meet different dispensing conditions. After being stored at 82°C for 7 days, all three products remained very stable, without obvious gelling. This will guarantee Flashcure® products to have a shelf life of at least 12 months, when stored under refrigeration condition.

Table 2. Example of a Sample Table and Table Caption

Product Name	Viscosity (mPa.s)	Thermal Stability (days)	Tack Free Time (s)	Bond Strength (N/mm^2)	
				GBMS	PC
Loctite® 4304	20	>7	5	17.7	15.2
Loctite® 4310	152	>7	3	14.6	17.9
Loctite® 4311	804	>7	4	16.8	17.3
Loctite® 401	90	>7	N/A	17.2	N/A

The three products were further evaluated for tack free time. As shown in Table 2, when exposed to UV light with an intensity of 30 mW/cm^2, all three products cured quickly, and the surface became tack free within 5 seconds. It is well-known that for conventional light-curable acrylic adhesives, the surface of adhesives can remain tacky even after long exposure to UV light. This is because light-curable acrylic adhesives are cured via photoinitiated free radical polymerization, and the presence of oxygen can significantly inhibit polymerization. On the contrary, Flashcure® products are cured via photoinitiated polymerization (Scheme 1), which is not inhibited by oxygen. As a result, the surface of Flashcure® adhesives shows a potential to reach unlimited cure through gap, tack free surface and non-blooming/Frosting on bonded assembly.

Scheme 1. Photoinitiated Polymerization



Conventional CA adhesives are known for their high adhesion strength on a wide range of substrates. Therefore, for Flashcure® products to receive positive market reception, they need to maintain this advantage of CA products. As can be seen from Table 2, all three products showed high bonding strength on GBMS and PC. Those results demonstrate that like conventional CA products, Flashcure® adhesives are also able to achieve good adhesion on different substrates such as metal and plastic.

It is also noteworthy to point out that GBMS is not a transparent substrate. The fact that all three Flashcure® products can reach bonding strength on GBMS similar to conventional CA products clearly demonstrates their efficient secondary curing mechanism. Even without light exposure, Flashcure® adhesive can still be cured by moisture-induced polymerization. On the other hand, when UV light is available and can penetrate the substrate, the adhesive can reach full strength in a much shorter time than conventional CA products. This will help overcome limitations from conventional CAs, such as blooming, stress cracking and limited gap-filling capability.

Conclusions

In summary, light-curable CA adhesives with different viscosities have been realized. These adhesives can be cured by either UV exposure or moisture-initiated polymerization and can reach high adhesion strength on a wide range of substrates. Such dual-cure mechanism will provide significant advantages over both conventional CA adhesives and conventional light-curable acrylic adhesives.

References

1. H. W. Coover, D. W. Dreifus, J. T. O'Connor, "Cyanoacrylate Adhesives", Handbook of Adhesives, edited by Irving Skeist, Springer, 1990, 463-477
2. Stan Wojciak, Shabbir Attarwala, "Radiation-Curable, Cyanoacrylate-Containing Compositions", US Patent 6,906,112 B1