Flexibility Improvement of Light-Curable Cyanoacrylate Adhesives

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Introduction

Cyanoacrylate (CA) adhesives are one-part, instant adhesives that can be cured at room temperature to form rigid thermoplastics [1]. They are generally cured in the presence of trace amount of moisture found on applied substrates, and known for their extremely fast curing speed, ease of use and excellent adhesion to a wide variety of substrates. Despite many attractive features, CA adhesives have certain limitations, such as blooming/frosting on bonding parts, limited cure through large gaps, and slow fillet cure [1]. Light-curable CAs known as Flashcure® Adhesives were developed in the late 1990's to overcome such limitations, allowing these single component adhesives to cure in seconds when exposed to light at appropriate wavelength and providing superior adhesion to a wide variety of substrates including elastomers, rubbers, plastics and metals after curing [2]. With their secondary shadow cure mechanism, light-curable CAs eliminate blooming and enable larger cure-through-gap (CTG) capability, providing combined benefits from both light-curable acrylic and conventional CA technologies. But CA adhesives, including Flashcure® technology, still have challenges when applied to flexible parts due to their rigidity after curing. Recently, a series of flexible CA adhesive products such as Loctite® 4902, 4903 and 4902FL were introduced. These products provide a significant improvement on flexibility while still maintaining the advantages of instant adhesives, which make them suitable for tube bonding applications in the assembly of medical devices [3].

In this work, efforts made to improve the flexibility of light-curable CA adhesives are summarized. Results from this study show that high flexibility can be achieved while light-curable benefits are maintained.

Experimental

Materials

All raw materials used in this work, such as CA monomers, stabilizers, photo-initiators, diluents, etc., are commercially available and purchased directly from external suppliers. No further processing was applied to these raw materials. All CA adhesive samples were prepared with about 25% by weight of plasticizers, 0.5% by weight of photo-initiator, and balanced with ethyl CA monomers, stabilizers and metallocene. The adhesive samples were prepared by uniformly mixing the required ingredients at room temperatures until a homogenous liquid is achieved.

Tensile Properties

Tensile properties of CA adhesive samples were determined according to ISO 527-3 [4]. To prepare testing specimens, a transparent mold was first filled with liquid CA adhesives, then cured under Ultra-violet (UV) light at an intensity of 100 mW/cm^2, measured at 365 nm wavelength, for 30 seconds per each side of the mold. After the curing, the mold was removed, and a piece of cured film of flexible light curable CA with thickness ranging from 0.025 to 0.034 inches was formed and cut into strips in the size of 6.0 inches by 0.25 inches for testing.

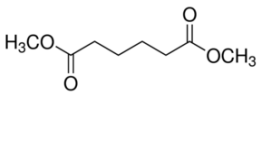
Bonding Strength, Light Cure Condition

Bonding strength of CA adhesive samples was tested on UV-transparent polycarbonate blocks according to ISO 13445. During this test, a pair of blocks were bonded by the adhesive, then cured for 2s under a Loctite® 405 nm LED Flood System at an intensity of 1.7 W/cm^2, measured using a Loctite® UV-Visible Radiometer. After curing, the specimen was tested by an Instron equipment.

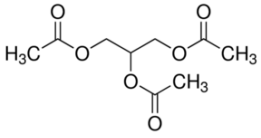
Results and Discussion

In general, to increase the flexibility of an adhesive one should incorporate into the adhesive a reactive resin or a non-reactive component such as plasticizers. These two strategies have been applied in flexible CA adhesives, in which a CA monomer with a longer alkyl chain replaces partial amount of ethyl CA monomer and a plasticizer is also added to adjust the flexibility of cured adhesives [3]. While there are many plasticizers commercially available for use in adhesives [5], some of which have been used in CA adhesives[6], many widely-used plasticizers such as phthalates are being phased out or banned due to health and safety hazardous issues [7-10]. In this study, seven non-hazardous plasticizers, shown in Figure 1, were used to formulate CA adhesive samples captured in Table 1.

Figure 1. Chemical Structures of Plasticizers Used in This Study

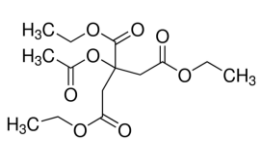


Dimethyl adipate

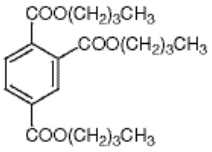


Triacetin

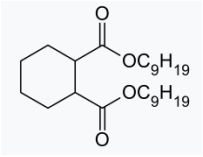
Dibutyl sebacate



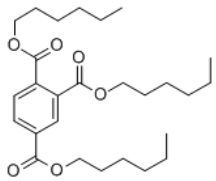
Acetyl triethyl citrate



Morflex 540



Hexamoll DINCH



Morflex 560

Table 1. CA Adhesive Samples

	Sample # /Amount (wt.%)						
Materials	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**
Ethyl CA/Stabilizer/Additive	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Trimethylbenzoyldiphenylphosphine oxide	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Dimethyl adipate	25						
Triacetin		25					
Acetyl triethyl citrate			25				
Dibutyl sebacate				25			
MORFLEX 540					25		
HEXAMOLL DINCH						25	
MORFLEX 560							25

Samples #1 to #7 were composed of 25 wt.% of one plasticizer and the same type and amount of stabilizer, photo-initiator reagent, etc. All the samples were balanced with ethyl CA monomer to reach 100 wt.%.

Samples #1 through #7 were then tested for curing speed and mechanical properties, results from which are summarized in Table 2. For a light-curable adhesive, the primary cure mechanism is polymerization initiated by exposure to UV/visible light. One common method to measure the primary cure speed is tack-free time. From Table 2, one can see that all these seven samples can achieve a tack-free surface within 2 to 6 seconds after exposure to a UV light, showing a comparable curing speed to the standard light-curable CA compositions. In general, the plasticizers function as diluents and do not participate in reactions. Thus, if a plasticizer is compatible with CAs, with 25 wt.% loading, their impact on radiation-curing speed is limited.

Table 2. Summary of Testing Results of CA Adhesive Samples

Sample #	**Tack free time**, s	**Appearance after curing**	**Elongation at break,** %	**Bonding Strength (Psi)**
1	6	Transparent	35	702
2	5	Transparent	125	1474
3	4	Transparent	53	1636
4	2	Opaque	5.6	863
5	5	Slightly opaque	1.8	2112
6	3	Opaque	3.7	1151
7	3	Opaque	1.6	1191

The typical appearance of a light-curable CA adhesive after radiation curing is a transparent and colorless solid. For the above seven CA adhesive samples investigated, after the curing, three of them (Samples #1 to #3) gave a transparent look. The other four samples turned into different extend of opaque appearance. For examples, Samples #4, #6 and #7

appeared largely opaque, while Sample #5 showed only a small portion of opaque area after curing. Comparing the appearance of these light-curable samples before and after the curing, one can see that, though some plasticizers are miscible well with CA monomers, their compatibility with polycyanoacrylate polymer is limited. As a result, a phase separation likely occurs during polymerization, which leads to a translucent or opaque cured product after the curing.

Effectiveness and efficiency of plasticizers are a function of plasticizer structure [4,9]. The poor compatibility of some studied plasticizers with polycyanoacrylate polymer may be linked to two factors. The first one is the molecular weight (MW) of the plasticizer used. As it can be seen, the cured samples that remained transparent are generally made with a plasticizer having lower MW, such as Sample #1 made with dimethyl adipate. On the other hand, the opaque cured samples are resulted from formulas made with higher MW plasticizers, such as Sample #7 made with Morflex 560. This indicates that the effectiveness of plasticizers decreases for high MW plasticizers [9], especially after the curing, where a phase separation between the polymer and plasticizer likely occurs. Another aspect that impacts the compatibility of plasticizers with CA before and after the curing is polarity. Generally, to achieve good compatibility, polar plasticizers should be used with polymers containing polar groups. The smaller the distance between the polar groups along the polymer chain, the higher the plasticizer polarity must be to overcome the forces between the polymer molecules. It is known that ethyl cyanoacrylate is a monomer with high polarity. Therefore, it is relatively easy to understand that Sample #3 made with acetyl triethyl citrate shows more transparency than Sample #4 with dibutyl sebacate after the curing. Though these two plasticizers have similar molecular weight, the chemical structures shown in Figure 1 demonstrate that dibutyl sebacate, with a linear and long alkyl chain, is less polar as compared with acetyl triethyl citrate that is formed with a branched and asymmetric structure and more ester groups. This also explains why Sample #7 is opaquer than Sample #5 after the curing.

To further understand the impact of plasticizers on mechanical performance of cured CAs, these samples were cured into films and tested for tensile properties. As can be seen from Table 2, the cured films from Samples #1, #2 and #3 provided higher elongations at break (ranging from 35% to 125%), which indicates that those three plasticizers are very effective on increasing the flexibility of cured CA adhesives. On the other hand, a lower elongation at break (<6%) was observed in Samples #4 to #7. The tensile property results of cured films align well with the appearance observation. Due to the phase separation of Samples #4 to #7 during the curing, the film specimens made from those samples were “patchy” and not homogeneous. With the presence of “weak” spots across much of the film, the testing specimens made from these samples tended to break easily at low elongation stress.

The adhesion property of these seven samples were tested by using polycarbonate block substrates, results of which are shown in Table 2. As expected, the reaction products of the samples show block shear strength on polycarbonate of 700 ~ 2100 psi, lower than that from standard CA adhesives due to the plasticizing effect. Apparently, these plasticizers showed different impact on adhesion. To balance the bonding strength and flexibility of cured products, proper selection of plasticizers in the appropriate amounts should be made to formulate CA adhesive samples.

Summary and Conclusions

In summary, different plasticizers were evaluated for their effects on the performance of light-curable CAs. The study demonstrated that the compatibility of plasticizers with light-curable CA adhesives both before and after light curing should be considered for achieving stable and flexible products. Plasticizers with lower molecular weight and higher polarity were found to be more compatible with CAs and effective in increasing flexibility of light-curable CA adhesives. Flexible light-curable CAs can be formulated by incorporating selective plasticizers to achieve high flexibility while maintaining light-curable benefits, such as fast tack-free time and desirable bonding strength.

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
3. Ling Li, Joseph B. Schulz, Zheng Lu, Andrew Scott, "Cyanoacrylate Compositions", US Patent 9,528,034 B2
4. ISO 527-3:2018 "Plastics — Determination of tensile properties — Part 3: Test conditions for films and sheets".
5. Mustafizur Rahman, Christopher S. Brazel, "The Plasticizer Market: An Assessment of Traditional Plasticizers and Research Trends to Meet New Challenges", *Progress in Polymer Science* 2004, 29, 1223-1248
6. George Wypych, "Plasticizer Use and Selection for Specific Polymers", *Handbook of Plasticizer,* edited by George Wypych, Elsevier 2017, 333-483
7. John D. Meeker, Sheela Sathyanarayana, Shanna H. Swan, "Phthalates and Other Additives in Plastics: Human Exposure and Associated Health Outcomes", *Philosophical Transactions of The Royal Society B* 2009, 364, 2097-2113
8. Rolf U. Halden, "Plastics and Health Risks", *Annual Review of Public Health* 2010, 31, 179-194
9. Pasquale Ventrice, Domenica Ventrice, Emilio Russo, Giovambattista De Sarro, "Phthalates: European Regulation, Chemistry, Pharmacokinetic and Related Toxicity", *Environmental Toxicology and Pharmacology* 2013, 36, 88-96
10. Britt E. Erickson, "Regulators and Retailers Raise Pressure on Phthalates", *Chemical & Engineering News* 2015, 93(25), 11-15
11. Edmund H, Immergut, Herman F. Mark, "Principles of Plasticization", *Advances in Chemistry* 1965, 48, 1-26