

Methylene Malonates and Cyanoacrylates: Energy-Efficient, High-Performance Sustainable Adhesive Systems*

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Abstract

More robust and eco-friendly adhesive options are growing in demand. Monomer-based adhesive systems provide an alternative to solventborne adhesives residentially and industrially used. The systems discussed here include cyanoacrylates and methylene malonates. Although not typically used for woodworking, novel one-part cyanoacrylate formulations have been developed for millwork applications offering improved sustained strength and durability. Mechanical and environmental testing highlight the feasibility of using one-part cyanoacrylate systems in lieu of traditional solventborne wood glues or two-part cyanoacrylate adhesives. Similar to cyanoacrylates, methylene malonates provide supplementary environmental resistance that increases the range of overall industrial application.

Truly new millwork and wood-based composite adhesives have been few and far between. Sirus has developed innovative adhesives designed to minimize energy consumption from the manufacturing of wood products by eliminating energy input, providing rapidly polymerizing systems, and eliminating solvent use. In turn, end users can optimize valuable resources allowing for the production of products at a potentially faster rate. Currently, these adhesives encompass a one-part cyanoacrylate (CA) formulation that supports a wide range of millwork applications and demonstrates the benefits of using rapidly curing, one-part, solvent-free adhesive systems. These adhesives are monomer based and 100 percent reactive. Formulated variations allow for a range of convenient handling times, increased toughness, and increased durability without compromising the ultimate mechanical performance.

CA adhesives have long been used in industrial, medical, and household venues because of their rapid polymerization and post-cure properties. By general classification, a CA monomer is an acrylic resin that rapidly polymerizes anionically in the presence of base, forming long, strong polymer chains that bond adjacent substrates together. More commonly known as “super glue,” it has traditionally been used in applications involving plastics and metals. Conversely, one-part CA wood adhesives provide an alternative to traditional polyvinyl acetate (PVA) wood glues through their improved cure profile and to traditional two-part CA adhesives through their sustained ultimate strength. This combination of properties allows for the fast cure performance of a super glue as well as the ultimate functionality of a PVA wood glue. Suggested coverage is lower in comparison to competitive recommendations of about 82.4 g/m².

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Similarly, methylene malonates are molecules that embody the formula shown in Figure 1a, where R1 and R2 represent a wide variety of substituents or side-chains. The overall chemistry and behavior of methylene malonates are analogous to CA monomers; e.g., they both cure anionically. On the other hand, methylene malonates possess improved environmental resistance for enhanced product application compared with traditional CA monomers. This chemistry also suggests the potential synthesis of monomers specifically designed for a given application, e.g., adhesives, inks, sealants, stains, coatings. Similar compounds have been investigated since 1886 without notable synthetic improvement (Perkin 1886, Bachman and Tanner 1939, Ballesteros and Roberts 1990, Feely and Boekelheide 2003). Because of the apparent reactivity, the initial synthetic difficulty stemmed from mediating catalytic activity and eventual monomer degradation (Kunichika et al. 1972, Hamper et al. 1999). Using a novel synthetic process, previous issues preventing commercially viable monomers have been resolved (Chen et al. 2012; Malofsky et al. 2012, 2013). In addition to methylene malonates, methylene acetyl acetonates and methylene beta-diketones have been synthesized (see Figs. 1b and 1c). The synthesis of methylene malonates and associated monomers will not be discussed here. These monomer platforms provide a plethora of variability with derivatized resin development that translate to appealing features and benefits, e.g., high-speed and zero-energy polymerization, tailored solvent and thermal resistance, and increased product life.

In light of the changing industrial regulatory landscape, the demand for more efficient, environmentally friendly, high-performance adhesive systems is rising. Solvent-free adhesives provide a wide range of application and performance properties that will surpass these shifting standards. In general, there are a variety of appealing characteristics when using monomer-based systems such as cyanoacrylates or methylene malonates: they are formaldehyde-free, eliminate or diminish energy and solvent use,

provide significant increases in production speeds and full cure properties, and have diverse functionality for general- and focused industrial applications.

Both solvent- and waterborne systems are commonly used in industry for large-scale applications representative of wood-based composite and millwork venues. Consequently, appreciable amounts of energy are sometimes required to remove solvents and/or thermally cure the adhesive. Substantial improvements have been made in shop-based machinery creating a safer work environment and permitting valuable, time-saving automation capabilities. These processes, however, are often dependent on a particular adhesive system and application methods that prevent expanding automation into the assembly of wood-based products. Moreover, there are a range of technological chemical disadvantages; e.g., amino resins, which are typically sensitive to wood buffering, can be hydrolytically unstable, have very limited pot-lives, and may have a low hot-press moisture tolerance. Additionally, typical PVA wood glues have substantial drying times owing to water absorption and evaporation that can bottleneck production capabilities. Even though PVA wood glues are typically waterborne, they still contain considerable volatile organic compounds that can be problematic as air regulations become stricter. Each concern beckons for a more robust adhesive option.

There are a variety of wood product applications in which controlled, ambient cure systems can be used to provide notable benefits. For example, speed is a critical criterion especially in solid wood assemblies by finger and edge jointing. These systems may eventually be used in structural applications where heat and environmental resistance are required. Currently, finger joints for structural applications often use relatively expensive resorcinol formaldehyde adhesives and/or radio frequency heating to cure bond lines. Methylene malonates would provide desirable environmental resistance and zero-energy cure capabilities. Additional applications include the manufacture of plywood, the production of particleboard (PB) and oriented strand board (OSB), in laminates and overlays, and in glulam and laminated veneer lumber (LVL). Current methodologies use high-heat input for plywood, PB, and OSB production. Methylene malonate adhesives have tailorable bond strength properties and would fit well into these scenarios enabling significant reduction of heat input while still allowing for relatively adequate surface densification. Additionally, because of the current high temperature requirements, steam and pressure build in the panel necessitating even longer press time in some scenarios. Methylene malonate technology would also facilitate the manufacture of wood composite products at higher moisture contents. Prior studies illustrate the potential to shorten press time by nearly 38 percent and/or reduce press temperature by 20°C using alcohol- and ester-modified phenol-formaldehyde resins. According to these evaluations, the most effective phenol-formaldehyde modification incorporated ethyl malonate and yielded adequate mechanical bonding with reduced press time and temperature (Mirski et al. 2008, 2011). Reduction of heat input has equally appealing benefits in laminates, overlays, glulam, and LVL. Third-party validation by Life Cycle Associates suggests a zero-heat cure savings of 23 trillion Btu in the United States for wood bindings and composites, and over 128 trillion Btu globally. In summary, methylene malonate

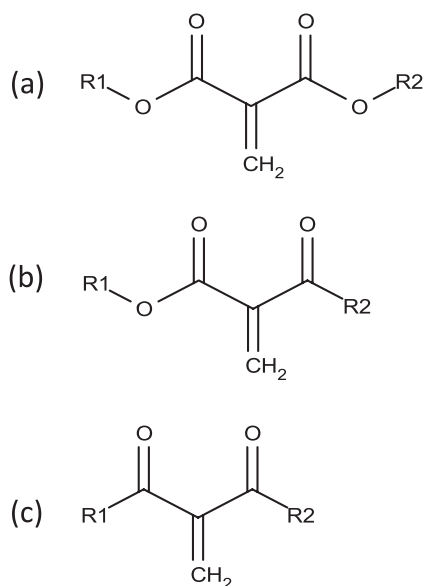


Figure 1.—Methylene malonate monomer platforms where R1 and R2 represent a wide variety of substituents or side-chains: (a) methylene malonate, (b) methylene acetyl acetonate, and (c) methylene beta-diketone.

adhesives offer the potential to eliminate heat input through ambient cure mechanisms, significantly improve resistance capabilities, and be tailored for structural applications.

Materials and Methods

The performance of one-part, formulated CA wood adhesives was assessed using specimens prepared from flat-sawn domestic and exotic wood species (free of knots, heartwood, etc.). Seven replicates to a sample set were prepared for each scenario. Unless otherwise indicated, five sample sets were prepared for each evaluation described below. Averages and subsequent standard deviations were calculated and reported where applicable. Lap shears were prepared using the following dimensions for each wood species: 10.16 by 2.54 by 0.635 cm. The procedure required roughly 0.1 g of adhesive, after which the lap shears were clamped with a 2.54-cm overlap. Using this method, the fixture or set time was assessed on domestic and exotic wood species after clamping. Fixture time is defined here as the minimum time for a set of bonded lap shears with a 2.54-cm overlap to withstand a 0.1 N/mm² force for 10 seconds. Additionally, using the specimen design described above, the tensile shear strength was evaluated at various time intervals on an assortment of domestic wood species. All reported tensile shear results were collected using a 5969 Universal Testing System made by Instron (Norwood, Massachusetts) and Bluehill v.3.24 software. ASTM D3163-01 was used to evaluate tensile shear strength with modifications to specimen preparation outlined above (ASTM International 2014).

A variety of environmental conditions were evaluated. Bonded white oak lap shears were tested after aging at 82°C for 60 days using a Sheldon VWR Scientific 1535 forced-air laboratory oven (Cornelius, Oregon). Additionally, the thermal resistance of methylene malonates was assessed at 121°C on cold rolled steel lap shears (10.16 by 2.54 by 0.16256 cm) supplied by Q-Lab (Columbus, Ohio). The test range was from 1 to 70 hours using a VWR symphony 414004 forced-air laboratory oven incubator (San Dimas, California). Accelerated aging was performed using an Arrhenius relationship for the temperature dependence of monomer reaction rates (Sundberg 1998, Rodriguez-Aragon and Lopez-Fidalgo 2004). ASTM D1002-10 was used to evaluate the tensile shear strength of rigid metal lap shears (ASTM International 2010).

Manufactured cabinet doors were cycled between low humidity (20% relative humidity [RH] at 43.3°C) and high humidity (70% RH at 48.9°C) for 28 days using an EZT-570i Cincinnati Sub-Zero environmental chamber (Cincinnati, Ohio). These cycling conditions were recommended

for this application because they represent extreme internal household environments finished products might encounter. Additionally, these conditions sufficiently stress the joints and door panels relative to internal dimensional stress. Performance was then evaluated according to resultant gap formation and bond failure on at least 20 cabinet doors for each scenario reported below.

Water and thermal resistance was evaluated using a soak test developed for hardwood and decorative plywood using the solid wood lap shear dimensions described above for tensile shear testing (American National Standards Institute/Hardwood Plywood and Veneer Association [ANSI/HPVA] 2009). Specimens were submerged in water at 24°C ± 3°C for 4 hours and then dried at 50°C for 19 hours using a VWR symphony 414004 forced-air laboratory oven incubator. Specimens were cycled three times using these conditions and tensile shear strength was evaluated.

The manufacturers and brands of alternative adhesives have been omitted to prevent commercial bias or conflict. The manufacturer of control PVA emulsions used in these evaluations classifies them according to ANSI/HPVA Type I and II water resistance methods. Type I glues are considered to have superior water resistance to Type II glues. Type I and II notations are used to distinguish the grade of PVA glues used in this study.

Results and Discussion

Table 1 shows the tensile shear strength of one-part CA wood adhesives in comparison to two-part CA products and both types of PVA emulsions. This table highlights the tensile shear strength as a function of time leading to full cure. These one-part CA wood adhesives build and maintain full cure strength (greater than 7.6 MPa) within 10 to 30 minutes of clamping. Alternative two-part CA products require the use of an activator to elicit rapid bonding. Activated, commercial CA wood adhesives initially build comparable strength but quickly drop between 1.4 and 3.4 MPa within 10 to 30 minutes. If not controlled, activation of CA monomer can lead to performance deficiencies. A two-part, or activated, system is difficult to mediate and overwhelming chain propagation is expected. Uncontrolled polymerization will subsequently diminish performance strength as shown here and result in brittle failure modes. A secondary activator is unnecessary when speed is not required; however, without a commercial activator, initiation of two-part CA adhesives is dependent on wood moisture content. Because of wood moisture variability, the adhesive does not often build the desired strength. On the other hand, PVA wood glues provide desirable mechanical strength and adequate durability. Unfortunately, full cure

Table 1.—Cure study comparing one-part CA adhesives with commercial products using domestic white oak lap shears.^a

Adhesive	Tensile shear strength (MPa)					
	5 min	30 min	1 h	4 h	16 h	24 h
One-part CA (short)	5.63 ± 0.80	7.51 ± 0.42	8.04 ± 0.76	8.28 ± 0.32	8.23 ± 0.82	8.19 ± 0.81
One-part CA (medium)	5.59 ± 0.74	7.59 ± 0.52	9.07 ± 0.68	9.35 ± 0.85	9.31 ± 0.43	9.28 ± 0.55
One-part CA (long)	1.22 ± 0.84	5.53 ± 0.87	8.02 ± 0.46	9.16 ± 0.86	8.99 ± 0.83	9.13 ± 0.36
Two-part CA (#1)	4.42 ± 0.25	5.64 ± 0.23	5.61 ± 0.67	4.69 ± 0.29	4.62 ± 0.73	4.01 ± 0.27
Two-part CA (#2)	6.56 ± 0.17	7.46 ± 0.62	8.63 ± 0.42	6.24 ± 0.21	5.76 ± 0.54	5.81 ± 0.43
Type I PVA emulsion	0.33 ± 0.25	3.43 ± 0.74	5.68 ± 0.53	7.09 ± 0.57	8.98 ± 0.47	9.03 ± 0.86
Type II PVA emulsion	0.87 ± 0.22	4.16 ± 0.82	6.26 ± 0.53	7.87 ± 0.53	9.46 ± 0.58	9.41 ± 0.69

^a CA = cyanoacrylate; PVA = polyvinyl acetate.

can require 8 to 24 hours for typical formulations. Although some commercial PVA formulations set rapidly, subsequent water absorption and evaporation can result in localized dimensional stresses in the wood around the joint delaying successive machining procedures until the joint equilibrates.

By taking advantage of techniques used in industrial CA products, one-part CA wood adhesives have been formulated to provide convenient handling times without compromising ultimate mechanical strength. Figure 2 shows the tensile shear strength of one-part CA wood adhesives in comparison to two-part CA products and both types of PVA emulsions on various wood species. The ultimate strength is comparable in each scenario. Because of the dynamic substrate properties of wood, some variation in strength from species to species is expected. However, one-part CA wood adhesives surpass two-part CA products and both types of PVA emulsions in ultimate performance. In comparison, speed is not diminished for one-part CA wood adhesives and they perform equally well on exotic and oily woods without necessitating typical surface treatment (see Table 2).

Common concern regarding adhesives is long-term performance. White oak lap shears with one-part CA wood adhesives, a two-part CA product, and both types of PVA emulsions were bonded and accelerated aging was simulated at 82°C. Figure 3 illustrates the aging durability of one-part CA wood adhesives in comparison to alternative wood glues. Over the span of 60 days (roughly 5 y), each adhesive lost varying amounts of strength. The one-part CA wood adhesives ultimately performed better than the commercial two-part CA product and both types of PVA emulsions. To assess adhesive performance under dimensional stresses induced by the wood as a result of environmental conditions, bonded hard maple lap shears were treated using ANSI/HPVA Type II water resistance conditions and the subsequent tensile shear strength was evaluated. Figure 4 shows that the one-part CA (medium) formulation nearly matches the performance of a Type I PVA emulsion and all one-part CA products perform better than a Type II PVA emulsion. All one-part CA formulations performed better than the polyurethane wood adhesive, which is advertised to have superior resistance properties. These results are illustrative of the water resistance performance inherent in these one-part CA products.

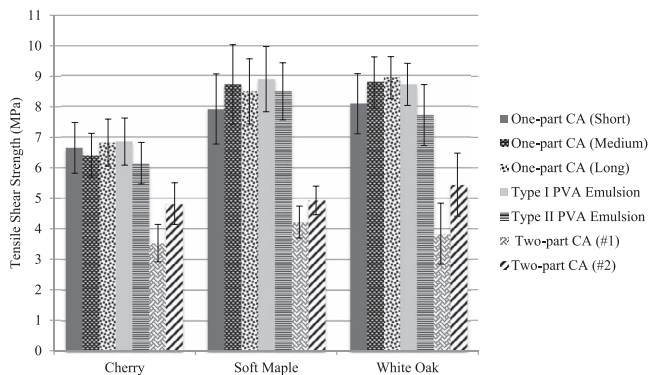


Figure 2.—Tensile shear strength comparison of one-part CA wood adhesives to commercial wood glues on domestic wood species. Results shown at 24 hours after bonding and clamping. CA = cyanoacrylate; PVA = polyvinyl acetate.

Table 2.—Fixture time using a variety of domestic and exotic wood substrates conditioned at 50 percent relative humidity.

Substrate	Fixture time (s)		
	One-part CA (short) ^a	One-part CA (medium)	One-part CA (long)
African mahogany	20	25	30
Aromatic cedar	15	30	180
Cedar	30	60	75
Cherry	15	30	180
Clear pine	10	15	60
Douglas fir	5	15	30
Hard maple	5	15	60
Mahogany	15	45	60
Soft maple	10	15	60
Poplar	5	20	25
Purple heart	15	30	30
Red oak	10	60	90
Rosewood	15	30	90
Walnut	5	30	90
White oak	15	30	90

^a CA = cyanoacrylate.

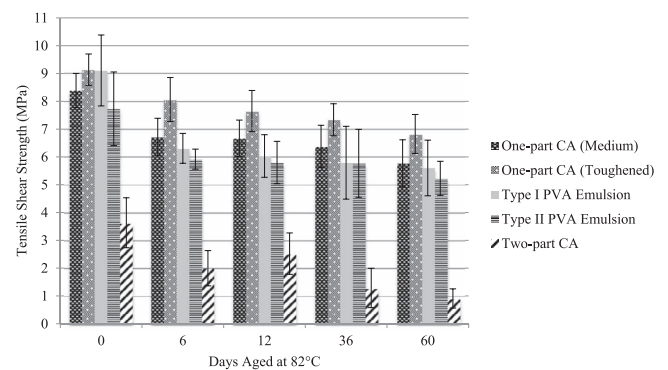


Figure 3.—Tensile shear strength of bonded white oak lap shears aged for 60 days at 82°C. CA = cyanoacrylate; PVA = polyvinyl acetate.

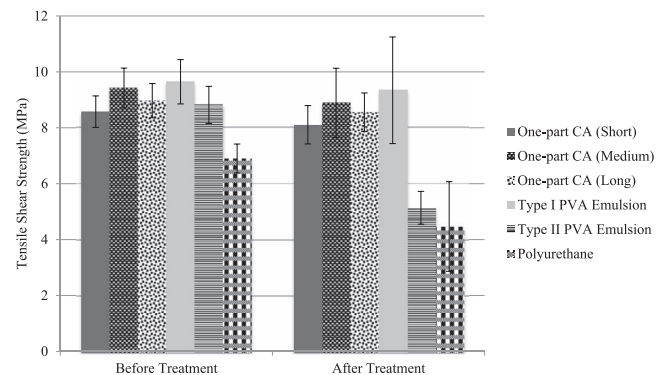


Figure 4.—Water resistance of bonded hard maple lap shears using American National Standards Institute/Hardwood Plywood and Veneer Association Type II soak and temperature cycling conditions. CA = cyanoacrylate; PVA = polyvinyl acetate.

To assess performance in a manufacturing scenario, unstained and unfinished commercial cabinet doors were assembled using a Type II PVA emulsion and one-part CA wood adhesives. The doors were made from domestic cherry and hard maple. These doors were assembled using industrial manufacturing procedures; they were clamped for about 5 minutes under hydraulic pressure, sanded, shaped, and then tested using the cycling conditions discussed above for 28 days. Figures 5 and 6 show the joint gap formations that meet repair criteria and doors with one or more gaps that are beyond repair. Repair is permissible if the gap fell between 0.00762 and 0.0254 cm. Cabinet doors with one or more joint gap formation larger than 0.0254 cm were discarded. It was observed that resultant gap formation was dependent on humidity. At low humidity, a gap formed at the inner corner of each door. At high humidity, a gap formed at the outer corner of each door, suggesting moderately high stresses under cycling. Prior to conditioning, the number of joints to be repaired or doors to be discarded was low. At low humidity, the percentage of joints to be repaired for each adhesive rose significantly. However, nearly 90 percent of the doors assembled with the Type II PVA emulsion have gaps greater than 0.0254 cm after high humidity cycling. This test represents an extreme aging scenario to assess overall adhesive performance. Even under these conditions, however, less than 10 percent of the

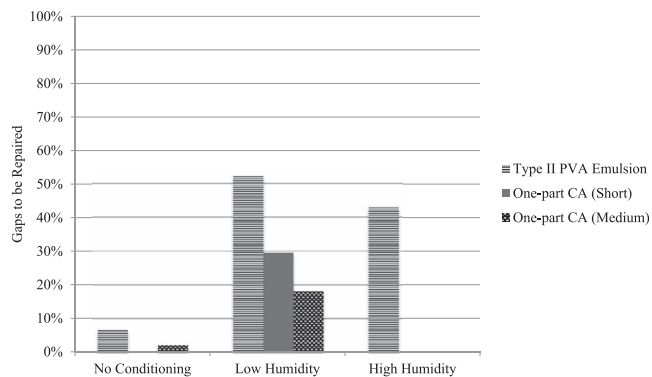


Figure 5.—Percentage of gaps to be repaired following humidity cycling. Repair is permissible if the gap fell between 0.00762 and 0.0254 cm. PVA = polyvinyl acetate; CA = cyanoacrylate.

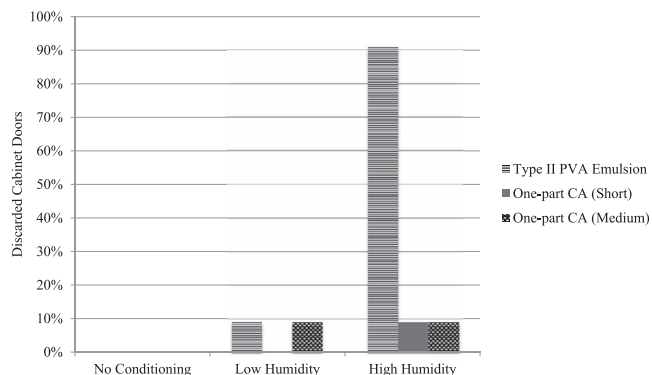


Figure 6.—Percentage of cabinet doors that had one or more gap formation beyond the permissible threshold (0.0254 cm) following humidity cycling. PVA = polyvinyl acetate; CA = cyanoacrylate.

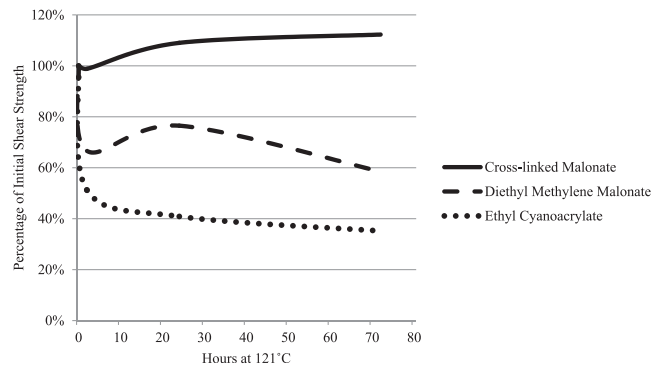


Figure 7.—Thermal resistance of various monomers at 121°C for 72 hours.

doors assembled using one-part CA wood adhesives were discarded. These results show significant advantages versus the resulting 90 percent failure using the Type II PVA emulsion and suggest competitive, dynamic manufacturing improvement possibilities.

As discussed, methylene malonates are comparable to CA in terms of some cure properties but provide additional, unmatched performance possibilities. Figure 7 depicts the thermal resistance of a cross-linked methylene malonate, diethyl methylene malonate, and ethyl CA monomer at 121°C over a period of 72 hours. At 72 hours and 121°C, ethyl CA lost 60 percent of its tensile shear strength on cold rolled steel compared with results before aging. In comparison, diethyl methylene malonate lost 40 percent. The cross-linked methylene malonate, on the other hand, increased nearly 10 percent under the same conditions. The cross-linked malonate performance illustrates intriguing possibilities regarding formulated products and a wide range of tailored application scenarios. Methylene malonate polymers appear to be environmentally, biologically, and/or metabolically compatible with living organisms as evidenced by peer-reviewed clinical research articles spanning nearly 20 years (Lescure et al. 1994, Le Visage et al. 2004, Felt-Baeyens et al. 2006, Breton et al. 2008). Furthermore, methylene malonates do not react when in contact with skin offering improved ease-of-handling.

Conclusions

Although not yet commonly used, monomer-based adhesive systems, such as cyanoacrylates and methylene malonates, provide manufacturing cost reduction opportunities, such as high cure speeds without energy input, increased production speed, automation, and solvent elimination. In addition, cyanoacrylates and methylene malonates can enable improved manufacturing and product opportunities via improved ultimate strength, ease-of-use, and/or environmental resistance. As the need for versatile wood adhesives increases, so will the demand for formaldehyde-free monomer-based systems. Methylene malonate platforms enable transformative energy efficiency and provide critical material benefits by delivering a high-speed, zero-energy ambient cure scenario. These adhesives will dramatically accelerate manufactured assembled and decorated goods while simultaneously reducing costs, capital equipment requirements, and environmental impact.

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