Kirk-Othmer Encyclopedia of Chemical Technology.

ACRYLIC ESTER POLYMERS, 2-CYANOACRYLIC ESTER POLYMERS

The polymers of the 2-cyanoacrylic esters, more commonly known as the alkyl 2-cyanoacrylates, are hard glassy resins that exhibit excellent adhesion to a wide variety of materials. The polymers are spontaneously formed when their liquid precursors or monomers are placed between two closely fitting surfaces. The spontaneous polymerization of these very reactive liquids and the excellent adhesion properties of the cured resins combine to make these compounds a unique class of single-component, ambient-temperature-curing adhesives of great versatility. The materials that can be bonded run the gamut from metals, plastics, most elastomers, fabrics, and woods to many ceramics.

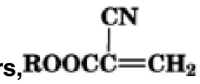
The utility of these adhesives arises from the electron-withdrawing character of the groups adjacent to the polymerizable double bond, which accounts for both the extremely high reactivity or cure rate and their polar nature, which enables the polymers to adhere tenaciously to many diverse substrates.

The polymers first synthesized (1, 2) were reported to be clear glassy resins. This original work involved a thermal polymerization, and it was not until the early 1950s that scientists at Eastman Kodak discovered the rapid room-temperature cure and excellent adhesion of these materials quite by accident. While determining the refractive index of a freshly prepared monomer, they discovered that the glass prisms of the refractometer had become tightly bonded. Further work led to the discovery that many other substrates became bonded in the same manner. This resulted in the commercialization in 1958 of Eastman 910, the first in what would become a large family of 2-cyanoacrylic ester adhesives. At present, a number of manufacturers in the United States, Europe, Japan, and elsewhere market extended lines of these adhesives all over the world. Some of the major producers and their trademarks include Loctite (Prism and Superbonder), Toagosei (Aron Alpha, Krazy Glue), Henkel (Sicomet), National Starch (Permabond), Sumitomo (Cyanobond), Three Bond (Super Three), and Alpha Giken (Alpha Ace, Alpha Techno).

1. Physical Properties

The physical properties of the monomers must be discussed along with those of the cured polymers because consideration of one without the other presents an incomplete picture. The 2-cyanoacrylic ester monomers are all thin, water-clear liquids with viscosities of $1-3\ \mathrm{mPa{\cdot}s(=cP)}$. Although a number of the esters have been prepared and characterized, only a relative few are of any significant commercial interest, and, of those, the methyl and ethyl esters by far predominate. The physical properties of the principal monomers are included in Table 1.

The base monomers are too thin for convenient use and therefore are generally formulated with stabilizers, thickeners, and property-modifying additives. The viscosities of such formulated adhesives can range from that of the base monomer (for wicking grades) to thixotropic gels with viscosities of $20,000$ to $50,000\ \mathrm{mPa{\cdot}s}$ (=cP) for larger gaps. The liquid products are characterized by sharp, lacrimatory, faintly sweet odors, except for several recent variants. The substitution of an alkoxyalkyl ester side chain for the normal alkyl group renders these products nearly odor free as well as slightly less effective as adhesives.

Table 1. Properties of Common Cyanoacrylate[a] Monomers, 

	R							
Property	Methyl	Ethyl	Isopropyl	Allyl	n-Butyl	Isobutyl	Methoxyethyl	Ethoxyethyl
molecular formula	$C_5H_5O_2N$	$C_6H_7O_2N$	$C_7H_9O_2N$	$C_7H_7O_2N$	$C_8H_{11}O_2N$	$C_8H_{11}O_2N$	$C_7H_9O_3N$	$C_8H_{11}O_3N$
CAS Registry Number	[137-05-3]	[7085-85-0]	[10586-17-1]	[7324-02-9]	[6066-65-1]	[1069-55-2]	[27816-23-5]	[21982-91-8]
odor	very sharp, lacrimatory		⟵ sharp acrylic odor, lacrimatory ⟶				⟵ virtually odorless ⟶	
viscosity, mPa·s (=cP)	2.2	1.9	2.1	2.0	2.1	2.0	2.6	5.0
density, g/cm^3	1.10	1.05	1.01	1.05	0.98	0.99	1.06	1.07
boiling point, °C	48–49	54–56	53–56	78–82	83–84	71–73	96–100	104–106
at kPa[b]	0.33–0.36	0.21–0.40	0.27–0.33	0.80	0.40	0.25–0.29	0.35–0.44	0.67
refractive index, n_D, 20°C	1.4406	1.4349	1.4291	1.4565	1.4330	1.4352		1.4470
heat of polymerization, kJ/mol[c]	57.7	58.1	67.8	63 ± 4	63 ± 1	66.9		
flash point, °C	83	83		82	85	93		130

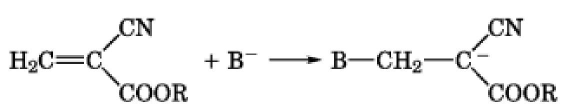
[a] Alkyl cyanoacrylates or alkyl 2-cyano-2-propenoates.
[b] To convert kPa to mm Hg multiply by 7.5.
[c] To convert kJ to kcal divide by 4.184.

The outstanding characteristic of the 2-cyanoacrylic esters is their high reactivity. The liquid monomers and adhesives will polymerize nearly instantaneously via an anionic mechanism when brought into contact with any weakly basic surface. Even the presence of a weakly basic substance such as adsorbed surface moisture is adequate to initiate the curing reaction. The adhesives cure very rapidly and are potentially hazardous skin bonders because of the presence of moisture and protein in the skin. The adhesive bonding process is accomplished by placing a small drop or bead on one surface and quickly bringing the mating part in contact with light pressure and holding it in place for a period of several seconds to several minutes. The rapid polymerization will cause rapid fixturing and adhering of the mating parts. As one might expect, conditions of low humidity and/or acidic groups on the surface can slow or inhibit the cure reaction.

2. Polymerization

The basic polymerization reaction is described by the following equations.

Initiation



Propagation

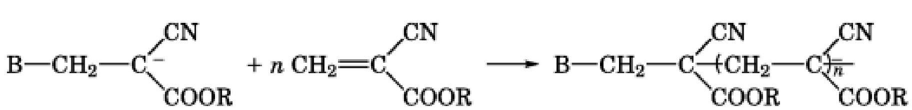
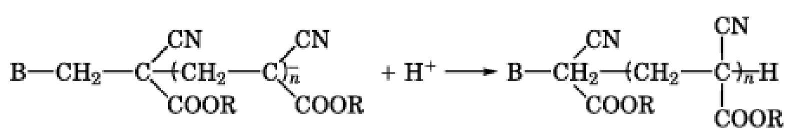


Table 2. Cured Bulk Properties of Common 2-Cyanoacrylic Esters

	Monomer type							
Property	Methyl	Ethyl	Isopropyl	Allyl	Butyl	Isobutyl	Methoxyethyl	Ethoxyethyl
softening point, °C (Vicat)	165	126	154	78	165	197		52
melting point, °C	205		179			192	165	103
refractive index, n_D, 20°C	1.45	1.45	1.45			1.26	1.4	1.48
dielectric constant[a] at 1 MHz	3.34	3.908	3.8	3.3	5.4			
dissipation factor[a] at 1 MHz			2.04	0.02				
volume resistivity, MΩ·mm		3×10^{15}	9×10^{12}	7×10^{14}	5.37×10^{9}			
tensile strength[b], steel–steel, MPa[c]	31	27.6	20.7			20.4	24.5	30.3
elongation, %	<2	<2	<2	10		<2		
flexural modulus[d], MPa[c]	3400	2069		1752				
hardness (Rockwell)	M 65	M 58	R 18					

[a] ASTM D150.
[b] ASTM D638.
[c] To convert MPa to psi multiply by 145.
[d] ASTM D790.

Termination



The reaction proceeds until all available monomer has reacted or until it is terminated by an acidic species. The gel point in these *in situ* polymerizations, as represented by the time of fixture, occurs within several seconds on strongly catalytic surfaces such as thermoset rubbers to several minutes on noncatalytic surfaces.

When the surface conditions are acidic or the ambient humidity is low enough to affect the cure significantly, a surface accelerator may be used to promote the reaction. Available from most manufacturers, these basic solutions may be dip, wipe, or spray applied. Recently, new additive chemistry has been developed that accelerates the cure under adverse conditions without the need for a separate accelerator.

The bulk physical properties of the polymers of the 2-cyanoacrylic esters appear in Table 2. All of these polymers are soluble in *N*-methylpyrrolidinone, *N,N*-dimethylformamide, and nitromethane. The adhesive bonding properties of typical formulated adhesives are listed in Table 3.

The cured polymers are hard, clear, and glassy thermoplastic resins with high tensile strengths. The polymers, because of their highly polar structure, exhibit excellent adhesion to a wide variety of substrate combinations. They tend to be somewhat brittle and have only low to moderate impact and peel strengths. The addition of fillers such as poly(methyl methacrylate) (PMMA) reduces the brittleness somewhat. Newer formulations are now available that contain dissolved elastomeric materials of various types. These rubber-modified products have been found to offer adhesive bonds of considerably improved toughness (3, 4).

The structure–property relationships for the lower cyanoacrylic ester polymers generally indicate that cure rates, tensile strength, tensile shear strengths, and hardness vary inversely with increasing ester chain length and that glass-transition temperatures (T_g) and adhesive bond service temperatures decrease with increasing ester chain lengths.

Table 3. Adhesive Bond Properties of 2-Cyanoacrylic Esters with Metals and Various Polymeric Materials

	Ester type					
	Methyl	Ethyl[a]	Butyl	Isobutyl	Methoxyethyl	Ethoxyethyl
set time, s						
steel	20	10	30	20	15	5
aluminum	3	10	5	20	15	5
nitrile rubber	5	3	5	5	5	3
neoprene rubber	5	3	5	5	5	3
ABS	20	10	20	20	5	3
polystyrene	20	10		20		20
polycarbonate	20	10	20	20	60	20
PMMA	10	5		10		15
PVC	5	3	2	5		10
nylon	30	15		30		10
phenolic resin	5	3	30	5	25	5
bond strength[b], kPa[c]						
steel	206	172	151	96	206	165
aluminum	186	158	151	96	138	117
ABS	48	48	96	48	48	48
polystyrene	34	34	83	34		34
polycarbonate	69	69	90	69		41
PMMA	48	48	62	41		48
PVC	96	96	62	83	55	69
nylon	76	76	62	34		41
phenolic resin	69	76	90	62	62	55

[a] Set times for allyl esters are similar to those for ethyl esters, as are bond strengths to steel, aluminum, ABS, PS, and PC.
[b] According to ASTM D1002.
[c] To convert kPa to psi multiply by 0.145.

Several special-property cyanoacrylic esters that offer variations on the general theme are also available. Allyl esters give bond properties similar to the ethyl or isopropyl esters, but are reported to cross-link by a free-radical mechanism through the allyl group, providing increased thermal resistance. This reaction is very sluggish and requires long exposures at high temperatures to proceed. The alkoxyalkyl esters, several of which are now commercially available, are practically odorless because of the inclusion of an alkoxy group on the ester side chain. These modifications also impart slightly reduced adhesive performance.

3. Manufacture and Processing

The cyanoacrylic esters are prepared via the Knoevenagel condensation reaction (5), in which the corresponding alkyl cyanoacetate reacts with formaldehyde in the presence of a basic catalyst to form a low molecular weight polymer. The polymer slurry is acidified and the water is removed. Subsequently, the polymer is cracked and redistilled at a high temperature onto a suitable stabilizer combination to prevent premature repolymerization. Strong protonic or Lewis acids are normally used in combination with small amounts of a free-radical stabilizer.

The above batch process has undergone numerous refinements to improve yields, processing characteristics, purity, and storage stability, but it remains the standard method of manufacture for these products. Recently a continuous process has been reported by Bayer AG (6) wherein the condensation is carried out in an extruder. The by-products are removed in a degassing zone, and the molten polymer, mixed with stabilizers, is subsequently cracked to yield raw monomer.

Adhesives formulated from the 2-cyanoacrylic esters typically contain stabilizers and thickeners, and may also contain tougheners, colorants, and other special property-enhancing additives. Both anionic and free-radical stabilizers are required, since the monomer will polymerize via both mechanisms. The anionic stabilizers that have been reported include acidic gases such as NO, SO_2, SO_3, BF_3, and HF (7–9). Strong protonic acids such as the aliphatic and aromatic sulfonic acids (10), and even strong mineral acids, have been used at low concentrations. Combinations of nonvolatile strong acids with gaseous stabilizers (11) have demonstrated synergistic improvements.

Although the anionic polymerization mechanism is the predominant one for the cyanoacrylic esters, the monomer will polymerize free-radically under prolonged exposure to heat or light. To extend the usable shelf life, free-radical stabilizers such as quinones or hindered phenols are a necessary part of the adhesive formulation.

4. Economic Aspects

Production of the 2-cyanoacrylic ester adhesives on a worldwide basis is estimated to be approximately 2400 metric tons. This amounts to only 0.02% of the total volume of adhesives produced but about 3% of the dollar volume.

Because of the high costs of raw materials and the relatively complex synthesis, the 2-cyanoacrylic esters are moderately expensive materials when considered in bulk quantities. Depending on the quantity and the specific ester or formulation involved, the prices for cyanoacrylic ester adhesives can range from approximately $30/kg to over $1000/kg. For these reasons, as well as several technical factors related to handling and performance, cyanoacrylic ester adhesives are best suited to small bonding applications, very often where single drops or small beads are adequate for bonding. In such cases the cost of the adhesive becomes inconsequential compared to the value of the service it performs, and these adhesives become very economical to use.

5. Specifications and Standards

A wide variety of adhesives based on the cyanoacrylic esters are now available worldwide. Product distinctions are based on ester type and specific performance attributable to that ester, formulation, viscosity, and cure speed. A number of special performance grades have appeared that maximize performance in specific areas, sometimes quite significantly. Adhesive grades are now available with improved thermal resistance; improved peel strengths, impact resistance, and toughness; and low odor, low blooming characteristics. New formulations contain cure additives that reduce the sensitivity of cure to acidic surfaces and low atmospheric humidity. More recently, surface primers have been introduced that have dramatically improved bond strengths to traditionally hard-to-bond surfaces such as polyolefins and other low energy polymers.

The adhesives are routinely tested for specific performance and compliance to many user specifications with different requirements. Government purchases are covered in the Mil Standard A-46050C (12).

6. Analytical and Test Methods

The routine compositional and functional testing done on the adhesives includes gas chromatographic testing for purity, potentiometric titrations for acid stabilizer concentrations, accelerated thermal stability tests for shelf life, fixture time cure speed tests, and assorted ASTM tests for tensile shear strengths, peel and impact strengths, and hot strengths.

7. Health and Safety Factors

The 2-cyanoacrylic esters have sharp, pungent odors and are lacrimators, even at very low concentrations. These esters can be irritating to the nose and throat at concentrations as low as 3 ppm; eye irritation is observed at levels of 5 ppm (13). The TLV for methyl 2-cyanoacrylate is 2 ppm and the short-term exposure limit is 4 ppm (14). Good ventilation when using the adhesives is essential.

Eye and skin contact should be avoided because of the adhesive's rapid tissue-bonding capabilities. In case of eye or skin contact, the affected area should be flushed with copious amounts of water. Especially with eye contact, the bonded area should not be forced apart, since this will produce more damage than the initial bonding. Medical attention is recommended. Soaking in warm water will gradually weaken and release the bond. Contact through clothing may produce a rapid exotherm and the clothing involved should be flooded with water. Efforts to pull the involved clothing away may result in skin damage.

The cured 2-cyanoacrylic ester polymers are relatively nontoxic. Oral doses of 6400 mg/kg failed to kill laboratory rats. Mild skin irritation was observed with guinea pigs, but there was no evidence of sensitization or absorption through the skin (15).

Both the liquid and cured 2-cyanoacrylic esters support combustion. These adhesives should not be used near sparks, heat, or open flame, or in areas of acute fire hazard. Highly exothermic polymerization can occur from direct addition of catalytic substances such as water, alcohols, and bases such as amines, ammonia, or caustics, or from contamination with any of the available surface activator solutions.

8. Uses

The combination of fast room-temperature cure and excellent adhesion to numerous substrates makes the adhesives of the 2-cyanoacrylic esters a natural choice in the assembly of small close-fitting parts in a number of diverse market areas. Some of the market segments served by these versatile materials include automotive, electronic, sporting goods, toys, hardware, morticians, law enforcement, cosmetics, jewelry, and medical devices. Although they are not approved for use in the United States, their strong tissue bonding characteristics have led to their use as chemical sutures and hemostatic agents in other countries around the world.

The diverse nature of the cyanoacrylate adhesives applications illustrates vividly that there is no truly typical application. The number of applications in which these adhesives are used is being expanded daily as technological improvements continue to broaden their capabilities.

Examples of some of the current uses for these adhesives include retention of automotive gaskets, weather stripping, side trim, and wiring harnesses; athletic shoes; swim masks; shotgun recoil pads; arrow feathers; dolls and doll furniture; circuit board component mounting and wire tacking; and lipstick tube and compact mirrors. Medical devices include balloon catheters and tubing sets; the adhesives are used by morticians to seal eyes and lips.

Law enforcement agencies make use of the volatility and reactivity of the vapors to develop fingerprints not retrievable with conventional methods.

The new technical developments have made possible quick bonding to woods, papers, and porous surfaces. Polyolefins, which comprise approximately 50% of the U.S. thermoplastic production, are now bondable with the cyanoacrylic ester adhesives. These new capabilities are sure to provide for continued market growth in the years ahead.

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