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TECHNICAL NEWS

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34

Instant Adhesives
(Cyanoacrylate adhesives)
<Vol 2>

Introduction

As already described in Three Bond Technical News 21, instant adhesives are one-part solvent-free adhesives that cure rapidly through polymerization at room temperature. These adhesives are used in a wide range of applications across various industries as a result of their strong adhesive strength. However, instant adhesives includes some disadvantages: low resistance to heat, water, and impact.

Numerous patents and reports have been submitted on methods of improving these properties. This issue will introduce several studies addressing such methods and investigating the addition of new functions, with a special focus on modifications to the main component of instant adhesives, cyanoacrylate.

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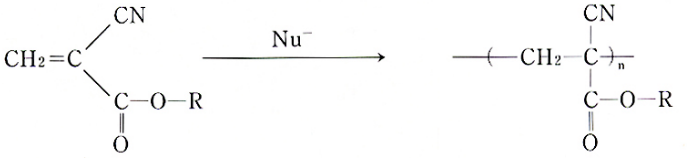
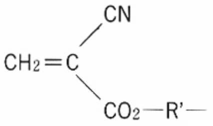
1. Overview

The main components of instant adhesives, 2-cyanoacrylate (2-cyanoacrylic acid ester), feature two strong electron attracting groups – the cyano group (–CN) and the carbonyl group (>C=O) – on a single carbon atom in the vinyl group (CH_2=C–). Thus, this substance reacts readily with relatively weak nucleophilic solvents (Nu^-) such as water and alcohol, curing through polymerization.



The main components of instant adhesives available on the market are mostly cyanoacrylates (alkyl 2-cyanoacrylates) having either a methyl group ($–CH_3$) or an ethyl group ($–C_2H_5$) as substituent (R). Attempts have been made to improve the properties of cyanoacrylates or to add new functions to them by changing this ester substituent (R) to various substituents or functional groups other than the alkyl groups. An overview of these efforts is shown below.

R	Improved properties, new functions
Groups such as CH_2=CHCH$_2$– and CH≡CCH$_2$–	Heat resistance
CH_2=CHCH$_2$–O–CH$_2$CH$_2$–	Heat resistance, flexibility
Groups such as CF_3CH_2–	Low refractive index
	Water resistance
Groups such as Me_3SiCH_2–	Heat resistance

2. Cyanoacrylates with unsaturated groups[1,2]

Cyanoacrylates are generally monofunctional monomers, and so the polycyanoacrylates that are produced by their polymerization are linear chain type thermoplastic polymers with correspondingly low heat resistance.

Therefore, it can be expected that crosslinking the linear chain type polymers will result in higher heat resistance. This assumption led to studies on the synthesis of cyanoacrylates with unsaturated groups and evaluation of the heat resistances of the resultant substances.

Heating a polymer after the cyanoacrylate has been cured by anion polymerization will induce thermal radical polymerization among the remaining unsaturated groups to produce a crosslinked polymer.

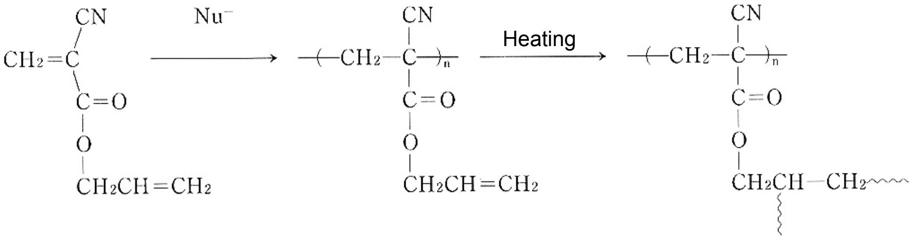
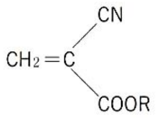


Table 1 shows various cyanoacrylates with unsaturated polymers and the associated heat resistance values.

Table 1. Cyanoacrylates with unsaturated polymers and adhesion heat resistance

 $CH_2=C(CN)COOR$		Shearing adhesive strength, N/cm^2 {kgf/cm^2}	
		Room temperature	After heating at 150°C for 24 hours
R	$CH_2=CHCH_2-$	1240 {126}	500 {51}
	$CH\equiv CCH_2-$	1670 {170}	400 {41}
	$CH\equiv CCH(CH_3)-$	1140 {116}	90 {9}
	$CH\equiv CCH(CH_2CH_2CH_3)-$	330 {34}	50 {5}
	CH_3-	1800 {183}	0 {0}
	CH_3CH_2-	1560 {159}	0 {0}
	$CH_3CH_2CH_2-$	930 {95}	0 {0}

As seen from the above, the introduction of unsaturated groups improved heat resistance. Furthermore, a decrease in adhesive strength and heat resistance was observed with an increase in the number of carbon atoms in a substituent (R).

Next, the changes in glass transition temperatures (Tg) with varied aging temperatures and times are shown in Fig. 1 for poly(allyl 2-cyanoacrylate, R: $CH_2=CHCH_2-$).

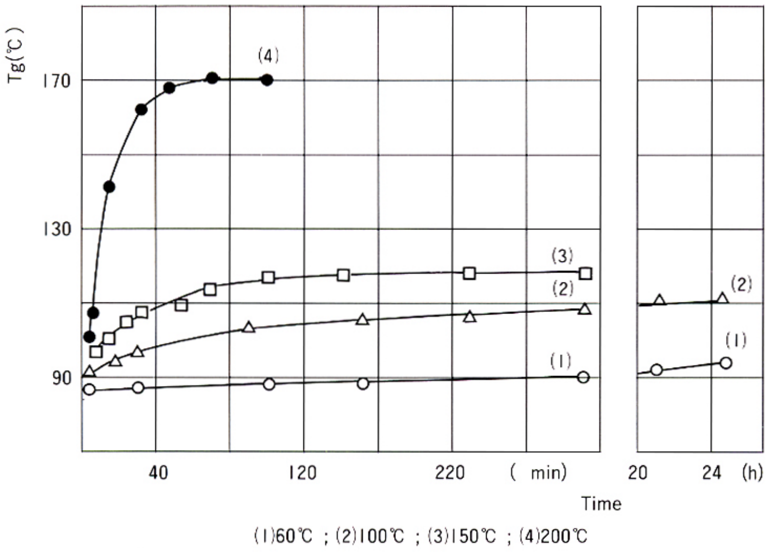


Figure 1. Changes in Tg with heating of poly(allyl 2-cyanoacrylate)

It can be seen here that the crosslinking of polymers induced by thermal treatment results in higher glass transition temperatures, which indicates that heat resistance was improved.

3. Aryloxy ethyl 2-cyanoacrylates[3)]

It is generally known that flexibility and impact strength may be improved by using the alcoxy ethyl group ($R'–O–CH_2CH_2–$) for the ester substituent (R). As described in the previous section, heat resistance can be improved by the introduction of unsaturated groups. Therefore, to obtain the combined effects of improved heat resistance and higher impact resistance, aryloxy ethyl 2-cyanoacrylate (AOECA, R: $CH_2=CHCH_2–O–CH_2CH_2–$) was investigated.

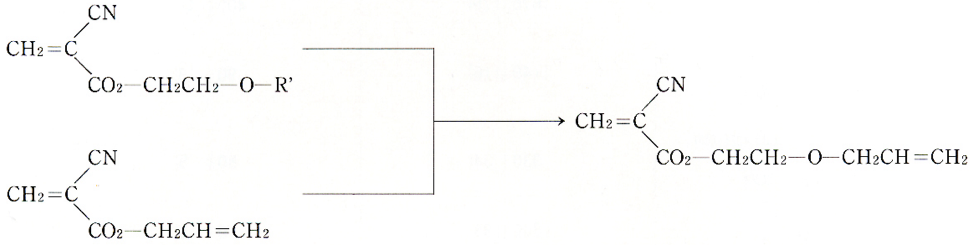


Table 2. Changes in impact strength by thermal treatment of AOECA

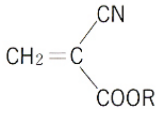
 $CH_2=C(CN)COOR$		Impact strength after thermal treatment kJ/m^2 {kgf•cm/cm^2}		
		20°C, 24 hours	100°C, 24 hours	150°C, 5 hours
R	$CH_3CH_2—$ (ECA)	3.8 {3.9}	2.2 {2.2}	1.2 {1.2}
	$CH_2=CHCH_2—$	5.9 {6.0}	4.1 {4.2}	1.6 {1.6}
	$CH_2=CHCH_2—O—CH_2CH_2—$ (AOECA)	5.5 {5.6}	3.0 {3.1}	2.4 {2.4}
	9:1 mixture of ECA/AOECA	7.6 {7.7}	3.6 {3.7}	2.7 {2.8}

Table 3. Decrease rate of unsaturated group after thermal treatment of poly AOECA and changes in glass transition temperature (Tg)

Thermal treatment conditions	Decrease Rate of unsaturated group ($CH_2=CH–$) (%)	Weight loss rate (%)	Tg (°C)
20°C, 24 hours	-	-	21
100°C, 24 hours	37.3	0.009	49
150°C, 5 hours	43.6	0.054	52

It can be seen that although the number of unsaturated groups is decreased by thermal treatment, there is no significant loss in weight. Thus it may be concluded that the decrease rate of unsaturated to the crosslinking rate. This bridging between polymer chains results in improved glass transition temperatures.

4. Fluoroalkyl 2-cyanoacrylates[4)]

The sheathed fiber optic cable has a core with refractive index n0, sheathed by a material with a refractive index of n1. Since light is reflected and contained inside the core, the refractive indices must satisfy the condition $n_0 > n_1$.

Generally, polymers of alkyl 2-cyanoacrylates have refractive indices n_D of 1.48-1.49. Therefore, when such materials are used for sheathing, the core material will be limited to polystyrene or polycarbonates with higher refractive indices (n_D = 1.59-1.60). The use of core materials with superior translucency–such as polymethyl methacrylate (n_D = 1.49) and quartz–thus becomes impractical.

Thus, to allow the use of such materials with relatively low refractive indices in cores, cyanoacrylates with low refractive indices were developed through the introduction of a fluoroalkyl group as the substituent.

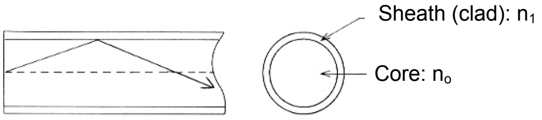
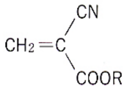
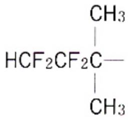
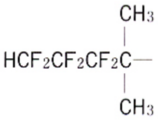
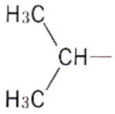


Figure 2. Structure of a fiber optic cable and transmission of light

Table 4. Refractive indices of fluoroalkyl 2-cyanoacrylate polymers

	Refractive index of polymer
CF_3CH_2-	1.439
$HCF_2CF_2CH_2-$	1.430
$HCF_2CF_2CF_2CF_2CH_2-$	1.407
 $HCF_2CF_2C(CH_3)_2-$	1.435
 $HCF_2CF_2CF_2C(CH_3)_2-$	1.421
CH_3-	1.4923
CH_3CH_2-	1.4868
 $(H_3C)_2CH-$	1.4898

5. Bis(2-cyanoacrylate)[5)]

C. J. Buck synthesized a bis (2-cyanoacrylate) having two cyanoacryloyl groups within a single molecule, and confirmed that the use of this monomer improved water resistance. In contrast to above-mentioned cyanoacrylates with unsaturated groups that require heat for crosslinking, the bis (2-cyanoacrylate) crosslinks simply by anion polymerization.

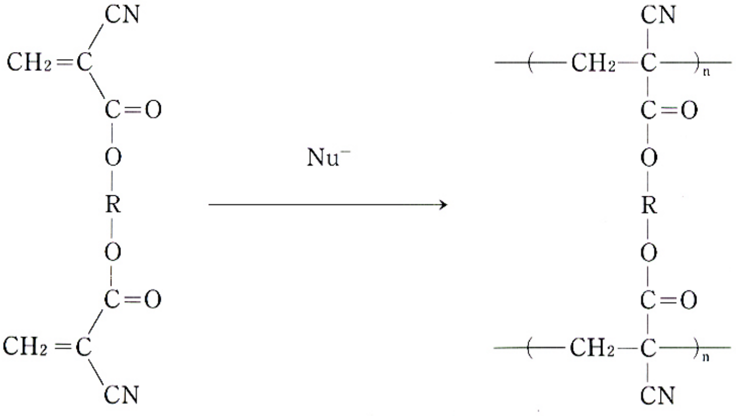
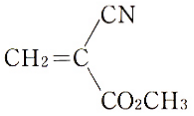
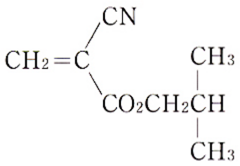


Table 5. Bond water resistance values of alkyl 2-cyanoacrylates mixed with ODBCA

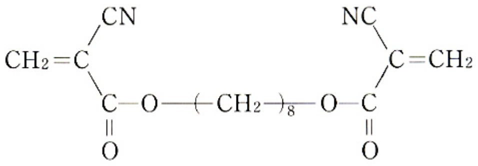
Immersion conditions	Shearing adhesive strength, N/cm^2 {kgf/cm^2}			
	IBC only	9:1 mixture of IBC/DBCA	MCA only	9:1 mixture of MCA/ODBCA
100°C in air, 1 day	349 {36}	420 { 43}	1794 {183}	1373 {140}
100°C in water, 1 day	352 {36}	558 { 57}	1140 {116}	1014 {103}
100°C in water, 7 days	360 {37}	431 { 44}	536 { 55}	794 { 81}



MCA



IBC

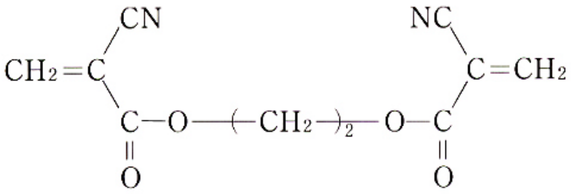


ODBCA

Table 6. Mixing ratio of EGBCA and IBC and adhesion water resistance

Monomer mixing ratio*, IBC/EGBCA	Tensile adhesive strength, N/cm^2 {kgf/cm^2}	
	100°C in water, 1 day	100°C in water, 7 days
100/ 0	4360 {440}	4720 {480}
99/ 1	4480 {460}	5590 {570}
98/ 2	4380 {450}	5350 {550}
96/ 4	5050 {520}	5970 {610}
94/ 6	5220 {530}	6390 {650}
90/10	5600 {570}	-
80/20	5750 {590}	-

* contains 72% of alumina as filler

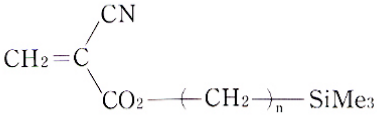


EGBCA

6. Cyanoacrylates containing silicon6)

Organic silicon compounds feature unique reactivity and distinctive physical properties derived from the properties of silicon (Si). Due to these properties, these compounds are widely used as reaction agents or as synthetic powder in synthetic organic chemistry and polymer chemistry. In particular, polysiloxane, due to its superior heat resistance and flexibility at low temperatures, has is widely used in several industries as a sealant or lubricant for component parts that are subject to high temperatures.

In contrast to such applications, we have focused on the unique properties of silicon, synthesizing a cyanoacrylate with silicon as the substituent (R), resulting in the production of a polymer with high heat resistance, particularly good stability at elevated temperatures.

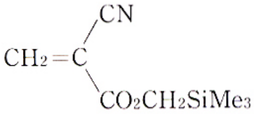


Trimethylsilyl alkyl 2-cyanoacrylate

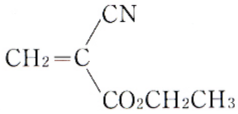
Table 7. Mixing ratios of cyanoacrylates containing silicon and alkyl 2-cyanoacrylates and adhesion heat resistance

SMCA/ECA mixing ratios	Shearing adhesive strength, N/cm^2 {kgf/cm^2}	
	Room temperature	150°C*
0/100	1260 {128}	50 {5}
20/80	1220 {124}	40 {4}
40/60	1100 {112}	50 {5}
60/40	1050 {107}	120 {12}
80/20	980 {100}	270 {28}
100/0	910 {93}	440 {45}

*) Measured at 150°C after heating at 150°C for 1 hour



SMCA

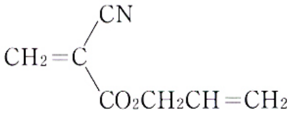


ECA

Table 8. Mixing ratios of cyanoacrylates containing silicon and cyanoacrylates with unsaturated groups and featuring high bond adhesion resistance

SMCA/ACA mixing ratios	Shearing adhesive strength, N/cm^2 {kgf/cm^2}	
	Room temperature	150°C*
0/100	1160 {118}	50 {5}
20/80	1160 {118}	130 {13}
40/60	1080 {110}	130 {13}
60/40	1010 {103}	310 {32}
80/20	980 {100}	410 {42}
100/0	910 {93}	440 {45}

*) Measured at 150°C after heating at 150°C for 1 hour

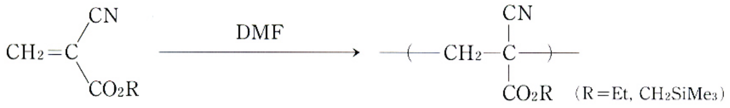


ACA

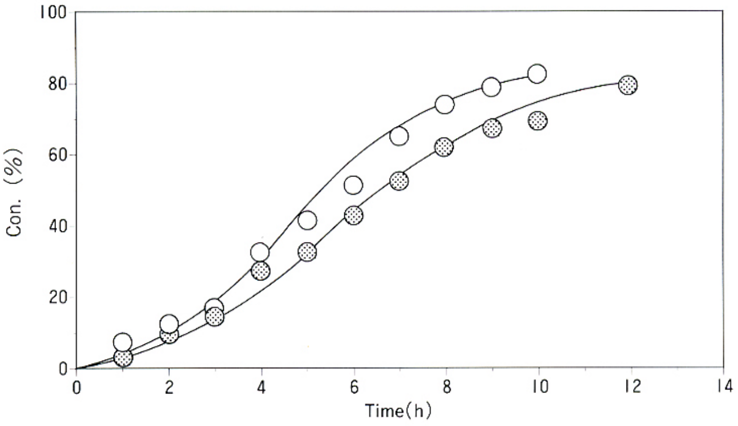
As described in the above section, the heat resistance of cyanoacrylates with unsaturated groups can be increased by thermal treatment to crosslink. However, to produce cyanoacrylates with practical heat resistance (Tg), the temperature and duration of the thermal treatment must be higher and longer, respectively, relative to the conditions of actual cyanoacrylate use (see Figure 1). Thus, if the bonded parts are heated under load conditions, these parts will peel because the heat resistance is insufficient (i.e. if the crosslinking is insufficient) to maintain the bond.

In contrast, polymers of cyanoacrylates containing silicon are inherently good at heat resistant, and so may be used for parts that will be subject to heating under load conditions.

Next, as for the polymerization speeds of cyanoacrylates containing silicon (curing speed), Figure 3 shows results that are measured in nitromethane by using DMF (dimethyl formaldehyde) as a polymerization initiator. The polymerization speed is slightly slower than that of the ethyl 2-cyanoacrylate (ECA) used as reference, which is assumed to be due to the steric hindrance caused by the trimethylsilyl group ($-SiMe_3$).



$$\mathrm{CH_2{=}C(CN)(CO_2R)} \xrightarrow{\mathrm{DMF}} \mathrm{-(CH_2-\overset{CN}{\underset{CO_2R}{C}})-} \quad (\mathrm{R{=}Et,\ CH_2SiMe_3})$$



Conversion curves at 70℃ in CH_3NO_2 [Monomer]= 1 mol/l,DMF=20mol%

○ ; Ethyl 2−cyanoacrylate (ECA)

▨ ; Trimethylsilylmethyl 2−cyanoacrylate (SMCA)

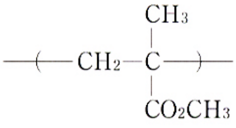
Figure 3. Polymerization speeds of cyanoacrylates containing silicon

Furthermore, Reichmanis et al.[7)] have reported that the use of poly(trimethylsilylmethyl methacrylate) as a positive photoresist will result in improved O_2RIE resistance, and similar effects are expected with cyanoacrylates containing silicon.

Table 9. Silicon content, oxygen pressure, and etching speed of polymers (Å/min)

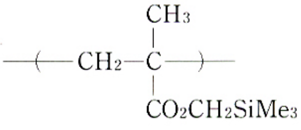
Polymer	Silicon content (in weight %)	Oxygen pressure	
		20 μm	100 μm
PMMA	0.0	3700	-
HPR-204*	0.0	1750	3250
P (SiMA)	14.8	160	80

*) HPR-204: Novolac-quinone diazide photoresist (Philip A. Hunt Chemical Co.)



$$\mathrm{-(CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C}})-}$$

PMMA



$$\mathrm{-(CH_2-\overset{CH_3}{\underset{CO_2CH_2SiMe_3}{C}})-}$$

P (SiMA)

Conclusion

Cyanoacrylate adhesives have a number of ideal properties, such as their one-part solvent-free formulations and room-temperature curing, but the physical performance of these adhesives can hardly be considered satisfactory. This is because cyanoacrylates are extremely reactive monomers; as a result, modifications are difficult and potential modifying agents are limited.

Even faced with these technical difficulties and limitations, numerous researchers have succeeded in cyanoacrylate modification, leading to the diverse line of cyanoacrylate adhesives available today. By developing cyanoacrylate products with enhanced performance that satisfy the demands of structural adhesive applications, and through the addition of useful new properties, we will continue our pursuit of new applications for cyanoacrylate adhesives.

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Instant adhesives-ThreeBond 1700 (TB 1700) series

Subdivisions of TB 1700 series

Types	Purpose	TB Grade	Viscosity (cP)	Remarks
ThreeBond 1700 series	Multi-purpose type	1701	3	Methyl cyanoacrylate For bonding metals, rubber, and plastics
		1702	35	
		1703	100	
		1741	2	Ethyl cyanoacrylate For bonding metals, rubber, and plastics
		1743	100	
		1745	500	
		1747	2,000	
		1713	100	Slow-curing type
	Heat-resistant type	1751	3	High heat-resistant type
		1753	80	
	Impact-resistant type	1781	3	High peeling strength, impact-resistant type
		1782	80	
		1783	1,000	
	Woodwork type	1785B	3	For bonding porous substrate materials such as wood and balsa
		1786	150	
		1787	1,100	
	Low-odor low blooming type	1721	10	Low-odor, low-blooming type
	Gel type	1739	Gel form	In gel form to permit use on ceilings and vertical surfaces
	Peeler	1795	1	For cleaning blooming and excess adhesive
	Curing accelerators	1796	1	For curing thick coats of adhesives such as in hardfacing
	Adhesive primers for hard-to-bond surfaces	1797	1	Allows bonding of PE and PP when used together with instant adhesives

* In addition to the standard products listed above, specialized products are available in a variety of different viscosities, colors, etc.

ThreeBond TECHNICAL NEWS

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