ISSN 1995-4212, Polymer Science, Series D. Glues and Sealing Materials, 2009, Vol. 2, No. 1, pp. 27–30. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.M. Vetrova, D.A. Aronovich, G.N. Chervyakova, A.P. Sineokov, 2007, published in Klei. Germetiki. Tekhnologii, 2007, No. 8, pp. 22–25.

Improvement of the Thermal Stability of Cyanoacrylate Adhesives

A. M. Vetrova, D. A. Aronovich, G. N. Chervyakova, and A. P. Sineokov
Federal State Unitary Enterprise Kargin Scientific Research Institue of Polymers (FGUP NIIP),
Dzerzhinsk, Nizhegorodskoi oblast, 60600 Russia
e-mail: niip@kis.ru

Received on 12 April 2007

Abstract—The results of studies of the effect of synthesized modifiers based on cyanosorbic acid on the thermal properties of cyanoacrylate adhesives have been presented.

DOI: 10.1134/S1995421209010055

At room temperature, cyanoacrylate monomers, which are widely used as binders for fast-setting adhesives in the polymerization on the anion mechanism, form linear thermoplastic polymers with low stability at high temperatures. The problem of improving the thermal stability of cyanoacrylate compositions is solved mainly in two ways, i.e., by the use of cyanoacrylate monomers with multiple bonds in alcohol radical and by structuring the polymer chain with various modifying additives [1–3].

One of the most efficient methods is the introduction into adhesive compositions [4-6] of various β-vinyl-α-cyanoacrylates that are easily copolymerized with α-cyanoacrylates in the process of gluing and form structured polymers with higher thermostability. At the same time, the synthesis of β-vinyl-α-cyanoacrylates, as a rule, takes place with low yield and involves the application of high-toxicity acrolein.

In light of this, derivatives of α-cyanosorbic (cyanopentadine, crotolidencyanacetic) acids, which are synthesized by the condensation of respective cyanoacetate with crotonic or cinnamic aldehyde in aqueous and alcohol solutions with a zinc chloride catalyst [7] are of particular interest. The compositions

Table 1. Strength of adhesive joints based on allyl-α-cyanoacrylate and modifiers

Composition no.	Base of adhesive composition	Modifier formula $[XCH=CH-CH=C(CN)-COO]_nR$			Tensile strength*, MPa, at the temperature, °C			
		X	*n*	R	20	150	200	250
1	Unmodified allyl-α-cyanoacrylate				26.2	7.2	1.7	1.8
2	Allylcyanosorbinate	CH_3	1	$-CH_2CH=CH_2$	29.0	11.0	7.0	7.6
3	Propargylcyanosorbinate	CH_3	1	$-CH_2C\equiv CH$	28.0	9.3	6.8	6.4
4	Etoxyethylcyanosorbinate	CH_3	1	$-C_2H_4OC_2H_5$	35.0	3.1	3.5	4.1
5	Diallyloxyisopropilcyanosorbinate	CH_3	1	$-CH(CH_2OCH_2CH=CH_2)_2$	26.0	10.0	3.5	6.8
6	Dicyanosorbinate of ethylene glycol	CH_3	2	$-CH_2CH_2-$	25.6	12.0	5.2	4.2
7	Tetracyansorbinate pentaerithrytol	CH_3	4	$=(CH_2)_2C(CH_2)_2=$	29.0	11.5	4.5	3.8
8	Allylcyanomilidencyanoacetate	C_6H_5	1	$-CH_2CH=CH_2$	21.0	9.8	1.1	2.4
9	Dicynnamilidencyanoacetate ethylene glycol	C_6H_5	2	$-CH_2CH_2-$	23.2	7.8	4.5	4.6
10	Tris-(cyanomilidencyanacetate) glycerin	C_6H_5	3	$-CH_2-\underset{\vert}{C}H-CH_2-$	26.5	9.2	5.0	4.0

* Adhesive compositions were subject to 24 h of storage at 20°C and 24 h of warming at testing temperature.

Table 2. Intensity change of valent fluctuations of double bonds C=C groups of ethyl-α-cyanoacrylate at different temperatures

Polymer compound	Optical desity (R)* at temperature, °C		
	20	150	190
Poly-ECA	0.125	0.095	0.291
Poly-ECA+ACS	0.162	0.160	0.167
Poly-ECA+PCS**	0.179	0.094	0.279

* $R = \frac{D_{1620}\ \text{cm}^{-1}}{D_{1480}\ \text{cm}^{-1}}$.

** Propil-α-cyanosorbinate.

synthesized and studied are presented in Table 1; they turned out to be rather stable during storage. The introduction of these compositions into ethyl (ECA), etoxyethyl (EECA) butyl, and allylic (ACA) ethers of α-cyanoacrylate acids had no influence on their stability, setting time, and initial strength. At the same time, we observed a substantial increase in the stability of adhesive compositions at high temperatures. So, the introduction of compositions 2, 6, 7 (Table 1) in quantities of 10 wt % into ECA resulted in improved strength at an even tensile strength of 8–25 MPa after adhesive joints were warmed at 150°C for two hours. The test results of steel samples glued together at 150–250°C by compositions based on ACA [8] that are more thermal stability than ECA, as well as synthesized modifiers, are given in Table 1.

Table 1 shows that the introduction of cyanosorbic acid is more preferable. Allyl-α-cyanosorbinate (ACS) has the best thermostabilizing properties.

To study the processes that take place in an adhesive composition based on cyanoacrylate, which contains ACS modifier, we have used the infrared spectroscopy method introduced previously [9]. This method enables us to continually monitor the structural modifications of the glue matrix during cianoacrylate polymerization. In this case, we use monocrystal KBr or NaCl as the glue substrate and control the hardening kinetics in the thin glue layer according to the changing intensity of specific absorption bands –CH=CH– ECA bonds (1620 cm^{-1}), $-CH_2=CH-CH=CH_2-$ conjugated ACS bond (1590 and 1640 cm^{-1}), $CH_2=CH-CH=CH_2-$ allylic ACS bond (1655 cm^{-1}). Optical densities R were measured by the basic line method, which takes the

Table 3. Impact of allyl-α-cyanosorbinate on radical polymerization of α-cyanoacrylates

Oligomer	Concentration ACS, wt %	Polymerization parameters		
		$W_n \times 10^2$, % s^{-1}	$W_m \times 10^2$, % s^{-1}	Time of reaching W_m, min
α-cyanoacrylate		2.9	1.9	40
α-cyanoacrylate–EECA modified α-cyanoacrylate C_2H_5–ECA	0.1	1.8	1.3	48
	0.5	1.0	0.7	77
	1.0	0.7	0.4	113
	5.0	0.4	0.2	300
α-cyanoacrylate		2.3	1.6	70
α-cyanoacrylate–EECA modified α-cyanoacrylate $C_2H_5OC_2H_4$–EECA	0.1	1.6	1.2	85
	0.5	1.3	0.8	115
	1.0	0.3	0.3	140
	5.0	0.2	0.2	340

Note: W_n is the initial speed and W_m is the maximum speed.

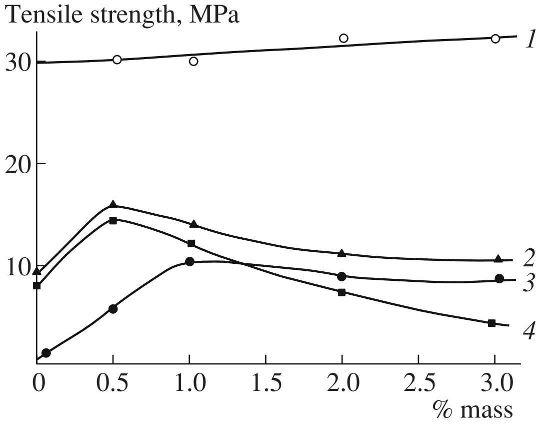

Fig. 1. Influence of tertiary butyl peroxide in allyl-α-cyanoacrylate composition with allylcianosorbinate (5% mass) onto the strength of adhesive joint. (*1*) warming at 150°C, testing at 20°C; (*2*) warming and testing at 150°C; (*3*) warming and testing at 200°C; (*4*) warming and testing at 250°C.

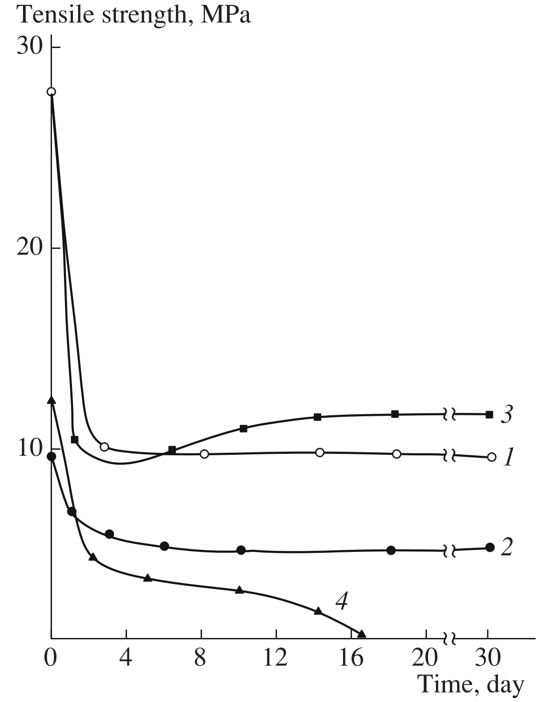

Fig. 2. Influence of thermal aging on adhesive joint strength. (*1*) warming at 150°C, testing at 20°C; (*2*) warming and testing at 150°C; (*3*) warming and testing at 200°C; (*4*) warming and testing at 250°C.

band at 1480 cm^{-1} as a standard that is typical for C–H deformation oscillations.

It was determined that ACSs glued at room temperature do not polymerize according to the anion mechanism. However, in compositions with ECA (5 wt %, for 1–1.5 h, the intensity of double-conjugated bonds decreases by 15–20% (ECA double bonds are exhausted by 80–85%), which serves as evidence of the copolymerization of monomers. The closeness of half-wave potential values for ECA ($E_{1/2}$ = 1.20) and ACS ($E_{1/2}$ = 1.26) determined polarographicly also proves the possibility of anion copolymerization [10]. Thus, by the moment that the composition is nearly set, the glue line turns into a copolymer of ECA and ACS (1.5–2%) containing unpolymerized ACS and small amount of

Table 4. Strength of various materials joints made by adhesive compositions based on allyl-α-cyanoacrylate*

Glued materials	Tensile strength, MPa			
	σ_{20}	σ_{150}	σ_{200}	σ_{205}
Steel 12Kh18X10T	31.2	20.0	11.2	8.8
Aluminum	23.4	9.5	8.6	6.5
Composition metal	28.0	8.2	9.2	3.5
Titanium	21.8	6.9	8.5	5.0

Note: Terms of testing are given in the note to Table 1.

* Composition contains 5 wt % ACA and 0.5 wt % peroxide of tert.-butyl.

Table 5. Influence of thermal cycles onto strength of joint made by adhesive compositions based on allyl-α-cyanoacrylate*

Tensile strength, MPa				Strength at displacement, MPa			
initial at 20°C	after thermal cycles**, °C			initial at 20°C	after thermal cycles**, °C		
	−60…+150	−60…+200	−60…+250		−60…+150	−60…+200	−60…+250
29.5	20.5	4.5	4.0	15.0	6.5	4.0	5.0

* Formula of adhesive composition is the same as in Table 4.

** Three thermal cycles were carried out with a 1-h time delay at each temperature and rigorous mode switch.

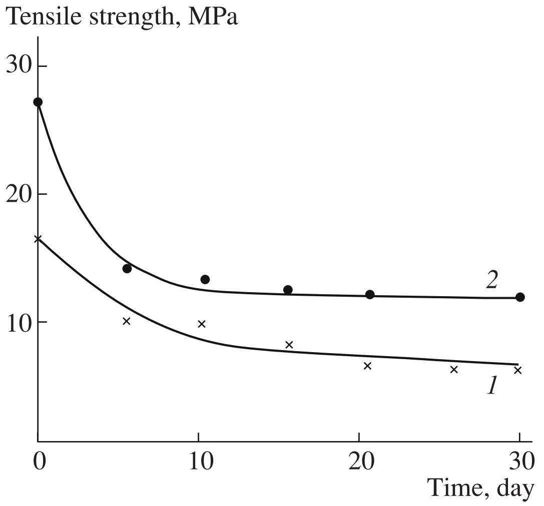

Fig. 3. Aging of adhesive materials at 40°C and 98% humidity. (*1*) strength at displacement; (*2*) strength at even detachment.

unpolymerized ECA. After additional heating at 150°C for 30–60 min, double-conjugated bonds of ACS disappear, which structures the polymer so as to cause an increase in thermostability. At a further increase in the warming temperature to 190°C, the content of the double bonds in pure ECA again grows as a result of poly-ECA depolymerization. In the presences of ACS, additional double bonds do not form, which is evidence of the stabilizing effect of ACS on poly-ECA thermodestruction (Table 2).

If we use propyl-α-cyanosorbinat (PCS) that is free of allyl bonds as a modifier, the IR spectrum of the polymer in adhesive composition has another character (Table 2); i.e., there is no thermostabilizing effect at 190°C, which proves the importance of the allylic group in stabilization. This group, as is known [11], may serve as a trap for radicals in the radical processes.

In connection with this, the influence of ACS on the radical polymerization of cyanoacrylate ECA and EECA at 60°C (Table 3) has been studied. Polymerization was initiated by dicyclohexylperoxidicarbonate (0.5 wt %). It is clear that even a minor addition of ACS substantially slows down radical polymerization.

Thus, the obtained data prove that increased thermal stability of cyanoacrylate adhesive compositions at the introduction of ACS can be explained as follows. Partial copolymerization and cross-linking during gluing take place first and, later, at increased temperatures, radical processes of the destruction of poly-α-cyanoacrylate slow down.

Since ACAs and ACSs contain nonsaturated double bonds, it would be interesting to examine an influence of peroxide additives on adhesive composition strength (Fig. 1). The introduction of tertiary butyl peroxide has no effect on the initial strength, but it does increase the strength at higher temperatures.

The influence of the nature of glued substrates and thermocycles on the strength of adhesive compositions based on ACA is presented in Tables 4 and 5. Thermal and humidity aging of adhesive compositions at 40°C and 98% humidity are demonstrated in Figs. 2 and 3.

The results of these studies support the recommendation of cyanoacrylate adhesive compositions modified by cyanosorbinates for use at higher temperatures.

REFERENCES

1. N.N. Trofimov, D.A. Aronovich, V.S. Etlis, N.M. Pivchuk, *Plastic masses*, 1976, No. 9, p. 55.
2. D.L. Kotzev, T.C. Ward, D.W. Wright. J. Appl. Polym. Sci., 1981, Vol. 26. No. 6, pp. 1941–1949.
3. V. Vijayalakshmi, J.N. Rupavani, N. Krushnamurti. *J. Appl. Polym. Sci*. vol. 49, 1394 (1993).
4. N.N. Trofimov, V.S. Etlis, D.A. Aronovich. Pat. 1415102, Great Britain, 1973.
5. D.A. Aronovich, A.M. Vetrova, *Glues. Sealing Materials. Technologies*, 2007, No. 4, pp. 10–14.
6. Z.Z. Denchev, V.S. Kabaivanov. J. Appl. Polym. Sci., vol. 47, N. 6, pp. 1019–1026 (1993).
7. A.M. Vetrova, N.M. Pinchuk, A.P. Sineokov et al. A. c. 1089927 USSR, B.I. 1980, N16.
8. A.M. Vetrova, N.M. Pinchuk, N.N. Trofimov et al. A. c. 730779 USSR, B.I. 1980, N16.
9. E.G. Pomerantseva, D.A. Aronovich, D.A. Meiman, A.P. Sineokov. Scientific and practical seminar materials “Glues, metal and plastic sealing”, Leningrad, LDNTP, 1979, pp. 89–91.
10. K. Höfelman, R. Sattelmayer, *Macromol. Chem.,* 1968, 112, pp. 300–302.
11. D. Oudian. Fundamentals of polymer chemistry. Ed. by acad. V. V. Korshak, Moscow, Mir, 1974, p. 212.