

Study of Thermal Properties of Cyanoacrylate Adhesives Modified with Unsaturated Compounds

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Abstract—The effect of allyl derivatives of muconic, malonic, and isocyanuric acids, as well as some other unsaturated compounds on the properties of adhesives based on ethyl- and allyl- α -cyanoacrylates, is studied.

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Cyanoacrylate adhesives with enhanced thermal stability are of interest for bonding in various fields of technology. An analysis of the published data [1–5] demonstrates that the basis for such adhesives is bifunctional cyanoacrylate monomers containing multiple bonds in the alcohol radical, e.g., allyl-, propargyl-, and allyloxyethyl cyanoacrylates. Such monomers attract attention based on the fact that they are first cured by the anionic mechanism using cyanoacrylate functionality; then, upon heating, multiple bonds of alcohol radical are revealed.

Moreover, thermal properties of adhesives can be improved by the addition of thermally curing agents, such as bi- and polyfunctional compounds containing, e.g., (met)acrylate and allyl groups (dimethacrylate glycols, diallylisophthalate, tri- and tetraallylpyromellitate, allyl and propargyl esters of dibasic acids, etc.). As has been shown by us previously [6–8], composi-

tions containing derivatives of β -vinyl- α -cyanoacrylic and cyanosorbic acids as modifiers of cyanoacrylate adhesives are characterized by enhanced thermal properties.

In order to further study the heat resistance and thermal stability of cyanoacrylate adhesives, we tested, compounds containing unsaturated groups as structuring agents, such as diallyl muconate $[\text{CH}_2=\text{CHCH}_2\text{O}(\text{O})\text{CCH}=\text{CH}-]_2$ (I), crotonideneallyl malonate $\text{CH}_3\text{CH}=\text{CHCH}=\text{C}[\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2]_2$ (II), and cinnamylidene malononitrile $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{C}(\text{CN})_2$ (III) (Tables 1 and 2). Structurization was performed in both the presence and absence of tert-butyl peroxide, which can initiate crosslinking at elevated temperatures.

As can be seen from Tables 1 and 2, the addition of modifiers to the composition leads to some increase in the initial strength of adhesive joints probably due to

Table 1. Properties of adhesive compositions based on ethyl- α -cyanoacrylate modified with unsaturated compounds

Compound	Content of additive, wt %	Amount of peroxide, wt %	Tensile strength*, MPa, after exposure to temperature, °C		
			20	150	170
			during, h		
			24	2	2
I	no additive	0.1	23.8	6.1	3.1
	0.5		26.2	10.0	4.0
	0.5		26.7	10.5	18.2
	1.0		28.4	15.4	18.8
II	10	1	24.7	12.0	5.3
	10		25.6	17.5	12.4
III	5	0.5	28.0	9.0	6.8
	5		29.0	13.4	10.2

* Tests were performed at 20°C using sample made of steel 40.

Table 2. Properties of adhesive compositions based on allyl- α -cyanoacrylate modified with unsaturated compounds

Com- pound	Content of additive, wt %	Amount of peroxide, wt %	Tensile strength*, MPa, after exposure to temperature, °C							
			20	150		170		200		
			during, h							
			24	2	6	2	6	1	6	
I	no additive		23.0	24.0	9.2	8.4	7.7	4.0	3.2	
		0.5	23.5	27.4	14.8	12.6	10.0	4.8	3.7	
	1	0.5	25.4	20.8	12.8	13.0	9.0	9.5	5.0	
	10	1.0	29.6	16.6	18.8	10.5	14.0	3.0	4.1	
II	5	1	30.0	28.0				11.6	5.0	
III	5		30.7	26.0	20.0		16.0	9.2	3.2**	
	5	0.5	30.2	28.2	22.1		17.5	10.4	4.6	

Notes: * At 20°C.

** Samples were tested at the temperature of heating.

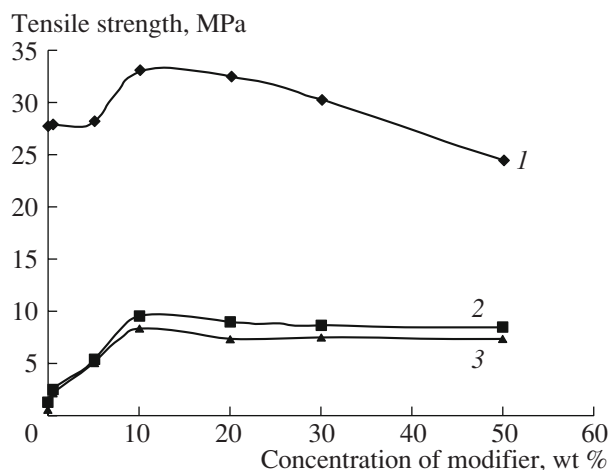
the plasticization of polymer and the enhancement of the thermal properties of both alkyl and allyl esters of poly- α -cyanoacrylate. It was of interest to test unsaturated derivatives of isocyanuric acid, which can be copolymerized with allyl groups of poly- α -cyanoacrylate at elevated temperatures, as modifiers (Table 3).

In order to synthesize isocyanuric derivatives of β -vinyl- α -cyanoacrylic and cyanosorbic acids, we conducted the esterification of tris(hydroxyethyl) isocyanurate with cyanoacetic acid to form tris(cyanoacetoxylethyl) isocyanurate, which then was condensed with acrolein or crotonic aldehyde [9]. Tris(allyloxycarboxylethyl) isocyanurate (IV) was synthesized by the interaction between allylchloroformiate with tris(hydroxyethyl) isocyanurate. Prepared compounds of tris(allyloxycarboxylethyl) (IV), tris(β -vinyl- α -cyanoacryloxyethyl) (V), and tris(cyanosorbiniloxyethyl) (VI) isocyanurates are solid substances with melting points of 63, 127, and 149°C for compounds IV, V, and VI, respectively, and are well soluble in monomeric cyanoacrylates. Their structures were confirmed by elemental analysis, the determination of molecular mass, and the IR spectroscopy.

Note that the addition of compounds VII, VIII, IX, XI, and XII, in which allyl group is directly bound to nitrogen of triazene cycle, resulted in the spontaneous polymerization of cyanoacrylates during storage; therefore, such compounds can be used as activators upon their deposition onto substrates in the form of solutions in organic solvents directly prior to bonding.

As can be seen from Table 3, compounds V and VI increase the initial strength of adhesive joints, which is probably due to copolymerization during bonding, as

was shown in [5–7]. In addition, such compounds increase the stability of adhesive joints to thermal cyclic treatment at temperatures ranged from –60 to +200°C. The best strength properties at elevated temperatures are demonstrated by the composition containing compound IV as modifier. The addition of 0.5% tert-butyl peroxide to such composition increases the strength of adhesive joints to 12 MPa after heating at



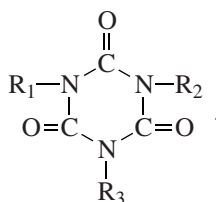
The effect of the amount of tris(allyloxycarboxylethyl) isocyanurate (compound IV) in adhesive compositions based on allyl- α -cyanoacrylate on the strength properties of adhesive joints after exposure for 24 h at (1) 20, (2) 250, and (3) 300°C.

Table 3. Strength properties of adhesive compositions based on allyl- α -cyanoacrylate containing derivatives of isocyanuric acid

Com- pound	Modifier			Tensile strength at 20°C, MPa, after exposure to temperature, °C		
	R ₁	R ₂	R ₃	20	250	300
				during, h		
				24	24*	3
	no modifier			22.7	1.4	0
IV	CH ₂ =CHCH ₂ OC- -(O)OCH ₂ CH ₂ -	CH ₂ =CHCH ₂ OC- -(O)OCH ₂ CH ₂ -	CH ₂ =CHCH ₂ OC- -(O)OCH ₂ CH ₂ -	27.1	9.6	8.4
V	CH ₂ =CHCH=C(CN)- -COOCH ₂ CH ₂ -	CH ₂ =CHCH ₂ =C(CN)- -COOCH ₂ CH ₂ -	CH ₂ =CHCH=C(CN)- -COOCH ₂ CH ₂ -	33.2	7.3	5.0
VI	CH ₃ CH=CHCH= =C(CN)-COOCH ₂ CH ₂ -	CH ₃ CH=CHCH= =C(CN)-COOCH ₂ CH ₂ -	CH ₃ CH=CHCH= =C(CN)-COOCH ₂ CH ₂ -	30.8	8.6	5.3
VII	CH ₂ =CH-CH ₂ -	CH ₂ =CH-CH ₂ -	CH ₂ =CH-CH ₂ -	24.8	3.6	2.5
VIII	CH ₂ =CH-CH ₂ -	CH ₂ =CH-CH ₂ -	CNCH ₂ CH ₂ -	24.4	7.4	5.7
IX	CH ₂ =CH-CH ₂ -	CH ₂ =CH-CH ₂ -	CH ₂ = =CHCH ₂ OCOCH ₂ CH ₂ -	24.3	5.6	3.5
X	CH ₂ =CHCH ₂ OCOCH= =CH-COOCH ₂ CH ₂ -	CH ₂ =CHCH ₂ OCOCH= =CH-COOCH ₂ CH ₂ -	CH ₂ =CHCH ₂ OCOCH= =CH-COOCH ₂ CH ₂ -	28.4	4.7	4.0
XI	CH ₂ =CH-CH ₂ -	CH ₂ =CH-CH ₂ -	C ₇ H ₁₅ OCOCH ₂ CH ₂ -	28.2	6.9	4.1
XII	CH ₂ =CH-CH ₂ -	C ₇ H ₁₅ OCOCH ₂ CH ₂ -	C ₇ H ₁₅ OCOCH ₂ CH ₂ -	28.5	4.5	2.1

* Tested at 250°C.

Note: 1. General formula of isocyanuric acid derivatives is



2. The amount of modifier is 10 wt %

300°C, which supports the radical mechanism of crosslinking.

We studied the effect of the content of modifier IV in the adhesive composition based on allyl- β -cyanoacrylate on strength properties of adhesive joints at different temperatures (see figure). The composition containing 10 wt % modifier turned out to be stable to prolonged thermal aging within a temperature range of 150–250°C. Residual strength after aging at these temperatures for 500 h was equal to 9–12 MPa.

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