ISSN 1811-2382, Polymer Science, Ser. C, 2007, Vol. 49, No. 3, pp. 235–239. © Pleiades Publishing, Ltd., 2007.
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Cyanoacrylate-Based Adhesives

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Received January 15, 2004

Abstract—The effect the curing conditions on the properties of adhesive joints formed using cyanoacrylate-based adhesives is investigated. The temperature dependences of relative rigidity and mechanical loss tangent are studied by torque analysis for poly(ethyl-, allyl-, allyloxyethyl-, allyloxyisopropyl-, propargyloxyethyl-, and propargyl-) cyanoacrylates after their thermal treatment in the temperature range of 20–250°C. The glass transition parameters of polycyanoacrylates and the dependence of the curing intensity on the structure of initial monomers and polymers are determined. It is established that the elastic modulus decreases with the lengthening of alkyl radicals in side chains. A list is experimentally determined of monomers used to obtain adhesive compositions with stable physicomechanical properties and heat resistances of up to 250°C.

DOI: 10.1134/S181123820703006X

2-Cyanoacrylates are employed as the bases for fast-polymerizing adhesives. Due to the presence of cyano and carboxyl groups, esters of 2-cyanoacrylic acid demonstrate a marked affinity for electrons and are highly reactive monomers with respect to basic reagents. The mechanism of adhesive bonding with cyanoacrylates involves the anionic polymerization of a 2-cyanoacrylic acid ester [1]. In this case, moisture on the surface of bonded materials acts as initiator. Metal ions present in a bonded material coordinate with cyano and carbonyl groups, thus additionally enhancing the reactivity of double bonds. Therefore, the rate of the anionic polymerization of 2-cyanoacrylates is extremely high. This process yields a linear polymer of regular structure with the dominant addition of units by head-to-tail type [2].

It is known [3] that methyl, ethyl, butyl, and allyl 2-cyanoacrylates are commonly used as bases for commercial cyanoacrylate adhesives.

The influence of the curing conditions and test temperature on the properties of adhesive joints formed with cyanoacrylate adhesives was investigated using a torsion-type device for determining their viscoelastic properties by free damping after torque [4]. The tests were performed with specimens of aluminum foil bonded with the commercial adhesive Cyanobond 5000.

During the storage of bonded specimens at room temperature, the shear modulus of the adhesive between foil layers gradually increased and, after reaching a maximum, remained almost constant. Upon heating to 35°C, the shear modulus does not decrease significantly; however, it drastically decreases to virtually zero with further heating to 120°C.

In order to study the effect of temperature on the elastic modulus and mechanical loss tangent of films prepared from poly(methyl, ethyl, butyl, and allyl cyanoacrylates), their physicomechanical properties were tested in the temperature range of 23–230°C [5]. It was established that the elastic modulus decreases with the lengthening of alkyl radicals in side chains. The influence of temperature on the elastic modulus is identical for poly(methyl, ethyl, and butyl cyanoacrylates). That is, above 100°C, the elastic modulus drops abruptly. It was shown that the thermal treatment of poly(allyl cyanoacrylate) above its glass transition temperature causes the polymer crosslinking.

A rise in the heat resistance of cyanoacrylate adhesives is one of the main problems in the development of fast-polymerizing adhesives and the expansion of their application fields. One of the possible ways to increase the heat resistance and thermal stability of cyanoacrylate adhesives is the crosslinking of adhesive layers, which increases the glass transition temperature of polymers and reduces their susceptibility to thermal degradation [6]. It is known that allyl and allyloxyethyl cyanoacrylates are used as basic materials of heat-resistant adhesives [7]. The high heat resistance of these adhesives is explained by the ability of allyl double bonds to polymerize at elevated temperatures, which leads to the crosslinking of macromolecules and the formation of a structured polymer.

Data on physicomechanical properties of poly(allyloxyalkyl cyanoacrylates) were not previously published.

It was of interest to investigate the structurization of polycyanoacrylates and the influence of temperature on the mechanical properties of polycyanoacrylates containing multiple bonds in side chains by filament tor-

Table 1. Physicomechanical parameters of 2-cyanoacrylates $CH_2=C(CN)COOR$

Monomer	Radical *R*	T_b at 133 Pa, °C	n_D^{20}	n_4^{20}	Shear strength, MPa			
					1	2	3	4
I	C_2H_5	56	1.4391	1.04	13.0	0	0	0
II	$CH_2CH=CH_2$	78	1.461	1.092	11.0	13.0	5.0	5.0
III	$CH_2CH_2OCH_2CH=CH_2$	107	1.462	1.075	8.0	10.0	4.0	4.0
IV	$CH_2CHOCH_2CH=CH_2CH_3$	101	1.457	1.072	6.0	7.0	5.0	5.0
V	$CH_2CH_2OCH_2C=CH$	115	1.473	1.088	7.0	9.5	7.0	7.0
VI	$CH_2C=CH$	T_m 34	–	–	12.0	3.5	3.5	3.5

Note: (1) 24 h after bonding at 20°C and after heating for 8h at (2) 150, (3) 200, and (4) 250°C.

sion analysis when the initial monomer is gradually transformed into a solid nonmelting polymer. Stock-produced polymers were used as testing specimens in [4, 5].

EXPERIMENTAL

Ethyl 2-cyanoacrylate (I), allyl 2-cyanoacrylate (II), allyloxyethyl 2-cyanoacrylate (III), allyloxyisopropyl 2-cyanoacrylate (IV), propargyloxyethyl 2-cyanoacrylate (V), and propargyl 2-cyanoacrylate (VI) were used as initial monomers. The 2-cyanoacrylates were synthesized from corresponding esters of cyanoacetic acid and paraform in the presence of catalyst with the subsequent pyrolysis of obtained product in vacuum by a known procedure [8]. Characteristics of the monomers thus obtained are listed in Table 1.

Test specimens were prepared as follows. Pretreated bundles of ten filaments of thermostable SVM fibers were fastened in the clamps of a working cell of an inverse torsion pendulum maintaining the length of the free part constant (60 mm). A cyanoacrylate monomer (0.1 g) was applied onto the fastened bundle of filaments from a polyethylene ampule. The specimens were cured in an oven at temperatures ranging from 25 to 240°C. Mechanical characteristics of the SVM fiber remain virtually unchanged throughout this temperature range.

Variations in the properties of the materials under examination were judged by the basic parameters of the filament torsion analysis: relative rigidity ρ, which is qualitatively similar to the dynamic shear modulus and determined as a reciprocal value of the squared period of freely damped torsion oscillations, and mechanical loss tangent $\tan\delta$ determined by dividing the logarithmic decrement of damping Δ by constant π [9].

The temperature dependence of the mechanical properties of the system was measured for all specimens during continuous transformation of an initial monomer into a solid polymer. After the cured specimens were cooled to 20°C, the temperature dependences of the mechanical properties of thermally treated specimens were measured again.

For comparison, analogous testing was performed with ethyl 2-cyanoacrylate.

The completeness of the structurization was controlled by determining the presence of multiple bonds in monomers and polymers in the Raman spectra, which were recorded with a Ramanor-HG-2S instrument equipped with an Ar^+ laser (5145 Å, 100 mW).

The Raman spectra of all monomers comprise a band at 1620 cm^{-1} attributed to the stretching vibrations of acrylate double bonds. The Raman spectra of monomers II–IV demonstrate a band at 1651 cm^{-1} assigned to the stretching vibrations of allyl double bonds. The spectra of monomers V and VI show a band at 2304 cm^{-1} attributed to the stretching vibrations of triple bond.

RESULTS AND DISCUSSION

Filament torsion analysis is a very sensitive method for characterizing the mechanical properties of polymers. It enables us to reveal the processes of polymerization, glass transition, curing, and the formation of a rigid crosslinked structure. The nature of the side chains of a polymer is also reflected in the pattern of the temperature dependences of relative rigidity and mechanical loss tangent measured by this method (Figs. 1–3).

Figures 1 and 2 show that at 25–30°C, the relative rigidity of all polymers, except for polymer II, clearly rises due to the process of anionic polymerization. It may be concluded that the nature of the ester group affects the reactivity of cyanoacrylate monomers. At room temperature, monomer II polymerizes most actively. Other monomers polymerize noticeably slower at room temperature and heating to 30°C is required for their complete polymerization.

Glass transition temperatures of polymers before and after thermal treatment and the temperature ranges of structurization of each polymer were determined

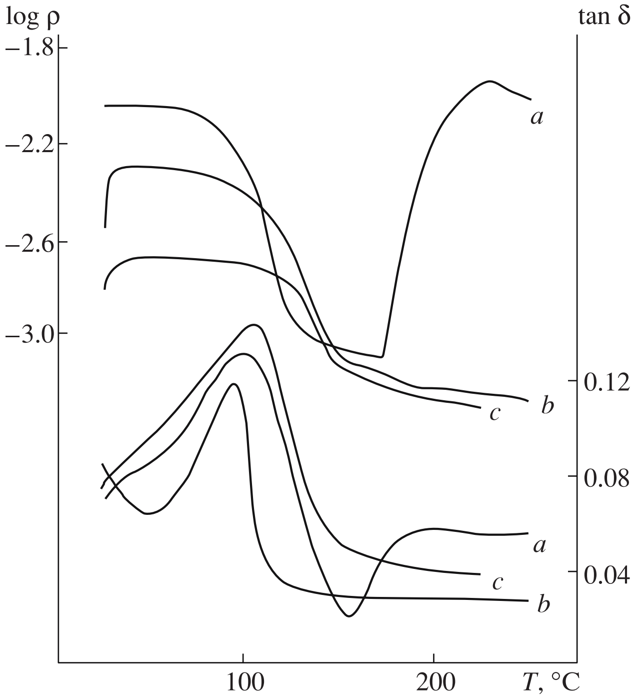

Fig. 1. Temperature dependences of the logarithm of the relative rigidity and the mechanical loss tangent for polymers (*a*) II, (*b*) I, and (*c*) VI

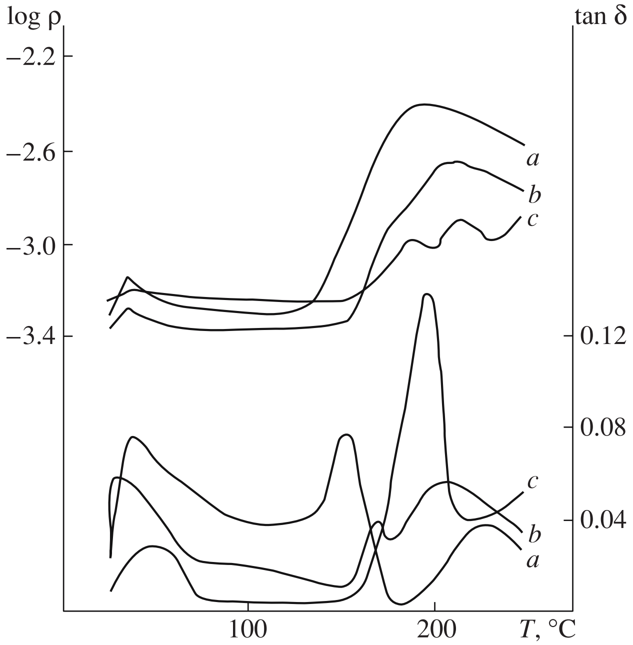

Fig. 2. Temperature dependences of the logarithm of the relative rigidity and the mechanical loss tangent for polymers (*a*) III, (*b*) IV, and (*c*) V

from the obtained dependences. The increment of the relative rigidity of polymers in the course and after the structurization was calculated to compare with initial linear polymers. The most important results of these calculations are listed in Table 2.

It may be concluded from Table 2 that polymer II is structured most strongly. For example, the increments of the relative rigidity resultant from the structurization indicate that, by the intensity of this process, polymers can be arranged in the following sequence: II > III > IV > V > VI.

From the data on the increments of the relative rigidity of polymers after the completion of structurization, in comparison with the initial linear polymers resulting from the polymerization at acrylate bonds, polymers are arranged by a decrease in the relative rigidity increment as follows: V > IV > III > VI > II.

This polymer behavior may be explained by the nature of their side chains. Polymer I, which does not

Table 2. The properties of polycyanoacrylates synthesized from monomers I–VI

Polymer	Temperature, °C			Relative rigidity increment	
	glass transition		curing	upon curing	after the curing is completed
	before the thermal treatment	after the thermal treatment			
I	106				
II	90	206	168…224	1.1	0.39
III	30	143	124…189	0.9	1.3
IV	31	153	154…200	0.7	1.38
V	48	65	158…240	0.4	1.78
VI*	114	260	280…300	0.214	0.41

* Thermal treatment was performed to 300°C.

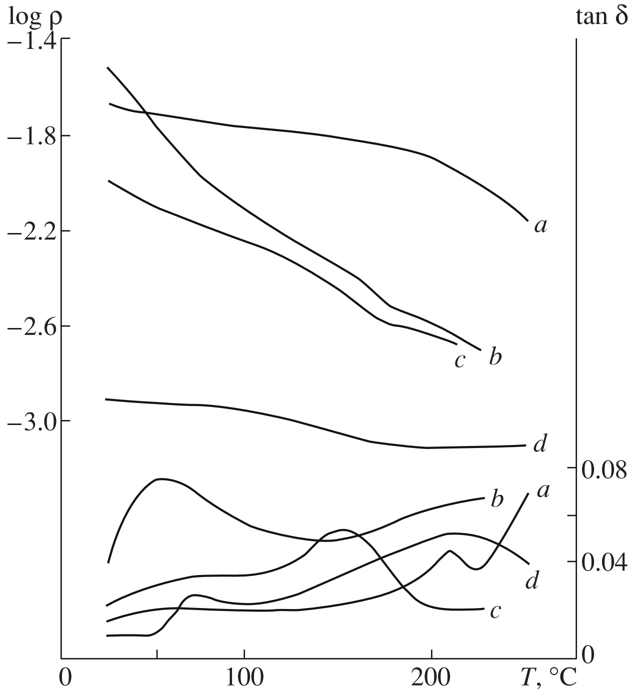

Fig. 3. Temperature dependences of the logarithm of the relative rigidity and the mechanical loss tangent for thermally treated polymers (*a*) II, (*b*) V, (*c*) IV, and (*d*) VI.

have additional multiple bonds, is not structured; during thermal treatment at 200°C, it undergoes complete degradation (Fig. 1*b*). During thermal treatment at temperatures below 200°C, the triple bonds in side chains of polymer VI are not opened and the polymer is not structured (Fig. 1*c*). Therefore, this polymer was subjected to the thermal treatment at 300°C and it was proven that the crosslinked structure is formed at 280–300°C.

The most interesting situation is observed for polymer II. This polymer has quite a high initial relative rigidity. In the vicinity of 90°C (Fig. 1*a*), the relative rigidity markedly decreases, which is accompanied by a distinct maximum of mechanical loss. These changes are explained by the devitrification of the polymer.

A rise in the relative rigidity due to structurization begins at 168°C and proceeds at a constant rate to 185°C. A further increase in the temperature leads to a gradual reduction in the intensity of structurization and, beginning with 224°C, the relative rigidity starts to decrease because of polymer degradation.

Another situation takes place for linear polymers III, IV, and V (see Fig. 2), which have low glass transition temperatures and low relative rigidity. The pronounced elastic properties of these polymers are explained by the nature of side chains containing multiple bonds connected to the backbones via $–OCH_2–CH_2–$ bridges, the circumstance that decreases the possibility of the close packing of polymer chains.

The thermal treatment causes the crosslinking of polymers III and IV to yield rigid materials with high glass transition temperatures.

The analysis of the temperature dependence of the relative rigidity of cured polymers (Fig. 3) testifies to the formation of highly crosslinked systems because their relative rigidity is higher than that of linear polymers. Evidence of large-scale segmental mobility, that is, a reduction in the relative rigidity and a corresponding increase in the mechanical loss, is observed at higher temperatures as compared to linear polymers. For polymers III and IV, the temperature dependences of the relative rigidity are similar. However, even in the cured state, polymers III and IV have a lower rigidity than polymer II.

The processes proceeding in the polymers during thermal treatment substantially influence the strength parameters of adhesive joints formed with monomers II–VI. It is obvious that monomer I cannot be employed for the preparation of heat-resistant adhesives. After thermal treatment at 150°C, adhesive joints based on monomers II–V have higher strength parameters (Table 1) than untreated joints. In the Raman spectra of polymers subjected to thermal treatment at 150°C, the band at 1629 cm^{-1} is absent. Apparently, polymers with high degrees of polymerization are formed under these conditions, thus ensuring the high strength of adhesive joints. The polymers are virtually not structured under these conditions. The bands at 1651 cm^{-1} for polymers II–IV and at 2304 cm^{-1} for polymers V and VI remain preserved in the Raman spectra.

However, it may be assumed that due to the insolubility of polymers after thermal treatment at 150°C, some crosslinks have already been formed, but their number is too small. As a result, the crosslinking does not lead to a noticeable rise in the rigidity of adhesive layers and does not reduce the adhesive strength.

The service of adhesive joints at 200–250°C, does not decrease their strength parameters. Presumably, this is caused by the fact that the thermal treatment at 200–250°C gives rise to the formation of a rigid crosslinked structure, thus reducing the strength of adhesive joints. The bands at 1651 and 2304 cm^{-1} are absent in the Raman spectra of polymers II–V thermally treated at 250°C, which testifies to the completion of structurization.

In order to obtain adhesive joints with stable physicomechanical properties in the temperature range of 20–250°C, monomers II–V should be used and bonded specimens should be subjected to thermal treatment at 150–180°C for a sufficient amount of the time for the completion of the structurization process.

On the basis of the described monomers and obtained experimental data, new cyanoacrylate-based adhesives with a set of unique properties were developed [10].

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