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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Synthesis and Properties of Polymeric Materials Prepared by Polymerization of Epoxy Oligomers with *N,N*'-Carbonyldiimidazole Transformation Products

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Abstract—The reaction of *N,N*'-carbonyldiimidazole with ethanol and epoxy oligomers of diphenylolpropane diglycidyl ether and 4,4'-bis(glycidylamino)-3,3'-dichlorodiphenylmethane was studied by gas chromatography–mass spectrometry and differential scanning calorimetry. From these oligomers and *N,N*'-carbonyldiimidazole transformation products, epoxy polymers were synthesized, and their physicomechanical and adhesion properties were determined.

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Imidazoles are promising ionic curing agents for epoxy oligomers, imparting to the resulting polymers high adhesion, resistance to heat and water, and good electrical and physicomechanical properties [1, 2].

The polymerization rate of the oligomers is determined by the rate of adduct formation with imidazoles, i.e., by the nucleophilic power of the imidazoles. Latent curing agents came into use, such as adducts of imidazoles with isocyanates, lactones, anhydrides, or tetrabutylammonium bromide and products of reactions of imidazole with acrylic acid and 1-(2-aminoethyl)piperazine [1, 3–5]. With these latent imidazole curing agents and also with complexes of BF_3 with Lewis bases, single-pack epoxy formulations were developed, which allowed considerable prolongation of the spreadable life and control over temperature and time conditions of curing [6]. However, not all the latent curing agents ensure the required service reliability of polymeric materials. For example, epoxy polymers prepared in the presence of boron trifluoride amine complexes have low heat resistance, which restricts their wide use [7].

In thermal dissociation of latent imidazole curing agents, the released products can negatively affect the properties of the polymeric materials obtained, as it takes place with boron trifluoride complexes. Therefore, it is appropriate to develop latent curing agents of purely imidazole type for single-pack epoxy formulations containing no foreign substances in the reaction system.

Here we report on polymerization of epoxy oligomers of various structures under the action of *N,N*'-carbonyldiimidazole transformation products and on physicochemical and adhesion characteristics of the polymeric compounds obtained.

EXPERIMENTAL

The following chemicals were used: *N,N*'-carbonyldiimidazole (CDI; Alfa Aesar, the United Kingdom); ED-20 epoxy–4,4'-isopropylidenediphenol resin [GOST (State Standard) 10587–84; weight fraction of epoxy groups 21.4% and of hydroxy groups 1.5%; dynamic viscosity at 25°C 14 Pa s); ethanol (analytically pure grade); 4,4'-bis(glycidylamino)-3,3'-dichlorodiphenylmethane oligomer (ESOD oligomer) synthesized by the reaction of epichlorohydrin with 4,4'-diamino-3,3'-dichlorodiphenylmethane, followed by dehydrochlorination with NaOH (weight fraction of epoxy groups 19.70%, dynamic viscosity at 50°C 4.35 Pa s; weight fraction of NH groups

7.1%) [8]. Polymerization of epoxy oligomers with CDI transformation products was studied by DSC with a DSC 822^e calorimeter (Mettler–Toledo, Switzerland) in the dynamic mode at a heating rate of 0.08 deg s^{-1} in the temperature interval 25–300°C. From the thermograms, we determined the reaction onset temperature T_{on}, peak temperature T_p, and thermal effect of the reaction Q. The effective activation energy E was calculated by Kissinger's method [9]:

$$d[\ln(\beta/T_p^2)]/d(1/T_p) = -ER,$$

where β is the heating rate (deg min^{-1}); T_p, peak temperature; and R, universal gas constant.

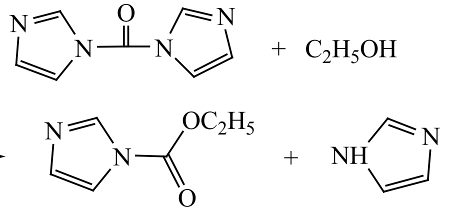
The glass transition point was also determined by DSC.

The deformation and strength characteristics and adhesion of the polymers and adhesive joints were determined at 25 ± 2 and 150 ± 2°C with an Instron 3565 tensile-testing machine (the United Kingdom). As adhesion substrates we used carbon-reinforced plastic (ENFB binder, LuP-0.1 tape, perpendicular reinforcement pattern) and D16AT grade aluminum. Prior to gluing, the specimens were cleaned with emery paper, degreased with acetone, and dried for 20 min. The compounds applied as a thin layer were kept at 60°C for 2 h and glued in molds, following the curing schedule for adhesive binders.

The rheological properties and spreadable life of epoxy compounds after mixing were evaluated from changes in the viscosity, monitored with a Rheotest-2 rotary viscometer (Germany) with a cone–plate working unit at a constant shear rate of 180 s^{-1} and a temperature of 25 ± 0.5°C.

Chemical transformations of *N,N'*-carbonyldiimidazole in the reaction with ethanol were studied with an Agilent Technologies 6890N/5975B gas chromatograph–mass spectrometer; HP-5ms column, 30 m × 0.25 mm, 0.025 μm, carrier gas He, electron impact ionization (70 eV).

The chromatogram of an ethanol solution of *N,N'*-carbonyldiimidazole at room temperature contains only peaks of its transformation products, imidazole and *N*-ethoxycarbonylimidazole, which were identified using NIST08 library (Fig. 1). The imidazole amount found corresponds to the CDI concentration in the solution. Both products are readily soluble in ethanol:



The kinetic data on polymerization of the epoxy oligomers with *N,N'*-carbonyldiimidazole, obtained by DSC, are well consistent with the data of gas chromatography–mass spectrometry (GC–MS). The DSC patterns of the kinetics of ED-20 curing with pure imidazole and with imidazole released in the reaction of *N,N'*-carbonyldiimidazole with ethanol coincide in shape (Fig. 2). Two peaks in the DSC curve characterize the known mechanism of formation of imidazole adducts with epoxy resin and of subsequent polymerization of the resin with the adducts [2]. The limiting step of the process is the adduct formation. The kinetic parameters of the polymerization of the epoxy oligomers are given in Table 1. The polymerization onset temperature for the epoxy oligomers is 94–112°C, and the maximal thermal effect is observed at 105–135°C. In polymerization of ED-20 oligomer with imidazole and CDI, it was 453 and 466 J g^{-1}, respectively. ESOD oligomer is polymerized by the above imidazoles at higher temperatures but with a smaller thermal effect: 301 and 294 J g^{-1}, respectively. The difference is associated with differences in the molecular structure of the oligomers. In this case, the lower thermal effect of the polymerization is a positive factor for reducing thermal stresses and enhancing the crack resistance in fabrication of massive articles from polymeric composite materials.

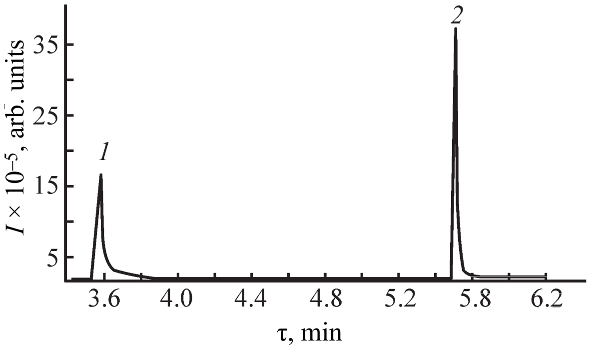


Fig. 1. Chromatogram of a solution of *N,N'*-carbonyldiimidazole in ethanol. (*I*) Intensity and (τ) retention time. (*1*) Imidazole and (*2*) *N*-ethoxycarbonylimidazole.

Table 1. Kinetic parameters of anionic polymerization of epoxy oligomers with imidazoles

Reaction system	T_{on}	T_p	Q, J g^{-1}	E, kJ mol^{-1}
	°C			
ED-20–imidazole	94	105	453	89
ED-20-CDI	97	110	466	102
ESOD oligomer–imidazole	110	120	301	95
ESOD oligomer–CDI	112	135	294	105

The data we obtained allow certain conclusions on specific features of the polymerization of the epoxy oligomers with *N,N'*-carbonyldiimidazole. In the first step, the adduct formation of the released imidazole and *N*-ethoxycarbonylimidazole with ED-20 resin occurs at a lower rate compared to the adduct formation of pure imidazole, taken separately, with the epoxy resin. This feature positively affects the process of preparing adhesive epoxy compounds; in particular, the spreadable life of the reaction mixtures increases by a factor of 3 compared to amine curing agents such as isophoronediamine and by a factor of 1.5 compared to the most active imidazole curing agent, 2-ethyl-4-methylimidazole (Fig. 3). The second step of the polymerization and formation of the structure and properties of the polymers occurs at 80–120–150°C within 4 h. The results obtained in studying the polymerization kinetics and rheological properties of the epoxy compounds allow these compounds to be classed with single-pack polymer formulations with latent curing systems.

The polymeric materials prepared by polymerization of widely used ED-20 epoxy resin (90 wt %) with *N,N'*-carbonyldiimidazole transformation products (10 wt %) exhibit fairly high physicomechanical characteristics: cohesion tensile strength at 25°C 70 MPa, relative elongation 10%. The glass transition point is 115°C.

In practice, it is frequently necessary to glue polymeric composite materials in units and parts of various structures operating at high temperatures. As a rule, high-softening-point adhesives are used for this purpose. Gluing of aluminum and its alloys, glass textolites, ceramics, and heat-insulation materials with high-softening-point epoxy adhesives K-153, K-300, and K-400 has been reported. The shear strength of the adhesive joint is 9–10 MPa at 20°C and 0.2–1.5 MPa at 200°C.

Tests of the epoxy compounds under consideration in adhesive joints showed (Table 2) that the shear strength in gluing aluminum and carbon-reinforced plastic with the new adhesive based on commercial ED-20 epoxy resin and *N,N'*-carbonyldiimidazole transformation products is 20–25 MPa at 20°C and 4.5–12 MPa at 150°C. High shear strength of the adhesive joints was also attained with the ESOD–*N,N'*-carbonyldiimidazole system. Enhancement of the adhesion strength is ensured by the imidazole curing agent, which is incorporated in the polymeric matrix

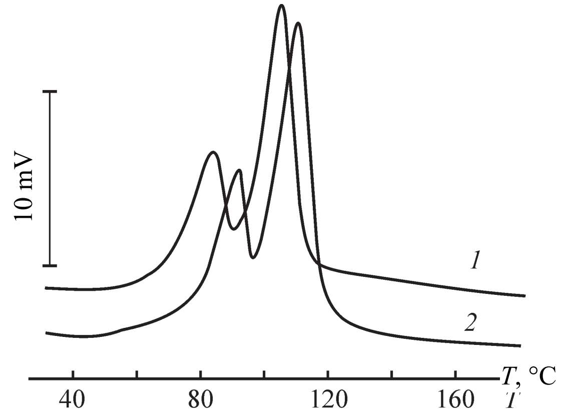


Fig. 2. DSC curves of curing of ED-20 epoxy–4,4'-isopropylidenediphenol resin with (*1*) imidazole and (*2*) *N,N'*-carbonyldiimidazole transformation products. (*T*) Temperature.

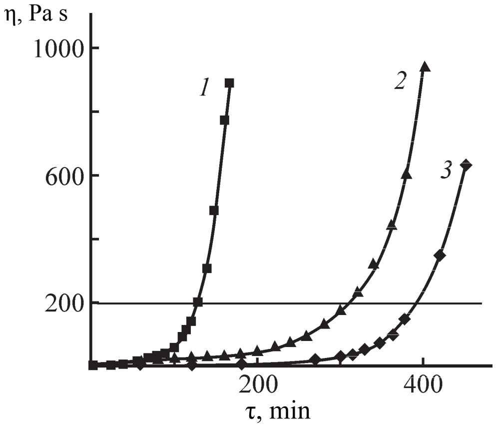


Fig. 3. Dynamic viscosity η of ED-20 epoxy–4,4'-isopropylidenediphenol resin at 25°C with various curing agents as a function of time τ. Curing agent: (*1*) isophoronediamine, (*2*) 2-ethyl-4-methylimidazole, and (*3*) *N,N'*-carbonyldiimidazole transformation products.

Table 2. Shear strength of adhesive joints

Testing temperature, °C	Adhesive joint strength, MPa		
	ED-20–CDI	ESOD–CDI	VK-9
	Carbon-reinforced plastic–adhesive–carbon-reinforced plastic		
25	21 Mixed break	20 Break within adhesive layer	–
150	6 Mixed break	14 Break within adhesive layer	–
	Aluminum–adhesive–aluminum		
25	26 Break within adhesive layer	12 Peeling of adhesive	14
150	16 Break within adhesive layer	12 Peeling of adhesive	4.5

in the course of polymerization and forms a polymer with strong intermolecular interactions. The strength of adhesive joints with VK-8 epoxy adhesive is given for comparison.

To sum up the data on the adhesion properties of compounds based on epoxy oligomers and *N,N*'-carbonyldiimidazole transformation products, we should note their advantages over commercial adhesives. Adhesive joints based on ED-20 epoxy resin and CDI are characterized by higher shear strength at both room and elevated temperatures. The ESOD–CDI epoxy adhesive compound, which can be classed with single-pack compounds with latent polymerization system, has high softening point on curing and preserves high strength at elevated temperature.

CONCLUSIONS

(1) *N,N*'-Carbonyldiimidazole reacts with ethanol to form imidazole and *N*-ethoxycarbonylimidazole.

(2) The kinetic parameters of the polymerization of various epoxy oligomers with *N,N*'-carbonyldiimidazole transformation products and the thermal characteristics of the system were determined.

(3) Epoxy polymers were synthesized from ED-20 and ESOD epoxy oligomers and *N,N*'-carbonyldiimidazole transformation products. The rheological, physicomechanical, and adhesion properties of the polymers were determined. The reaction mixtures show increased spreadable life, and the glue joints with aluminum and carbon-reinforced plastic exhibit enhanced adhesion strength.

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