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Polymers and Composites Produced from Epoxy Resins Cured with 3,5-Diethyltoluenediamine: Synthesis and Properties

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Abstract—The kinetics of curing of epoxy resins characterized by different functionality with 3,5-diethyltoluenediamine was studied. The kinetic constants and temperature ranges of reactions were determined. Polymers and composites were synthesized according to the established regimes. The rheological properties of composites and physicomechanical, thermomechanical, and impact properties of polymers and high-strength organoplastics were determined. Polymers based on trifunctional epoxy-novolak resin UP-643 are characterized by the highest thermal stability.

Keywords: epoxy polymers and composites, amine curing, vitality, adhesion to fiber, thermal stability
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INTRODUCTION

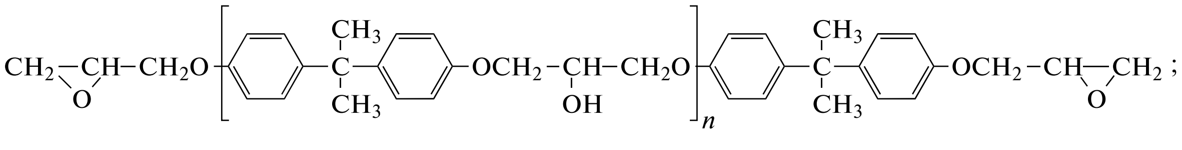
Polymers and composites based on epoxy resins and various curing agents are characterized by unique physicomechanical and adhesion properties. Such materials are irreplaceable in the radio and electronics industry and space and rocket engineering [1, 2]. Many diamines used for curing of epoxy resins (μ-phenylenediamine, 4,4'-diaminodiphenylmethane, 3,3'-dichloro-4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, 2,6-diaminopyridine) are solid. A number of technological difficulties emerge in the usage of these substances. These technological difficulties are related to the necessity of their preliminary melting, dissolution, and combination with epoxy resins at elevated temperature, causing the decrease in vitality of compositions and emergence of restrictions at the production of items for multiple purposes. It is known that epoxy binders are colloid disperse systems which exhibit phase separation upon mixing and in the course of time. In case of production of binders based on liquid epoxy resins and solid curing agents characterized by a low solubility threshold (as opposed to liquid curing agents), the observed phase separation does not terminate at the curing stage; it leads to the thermodynamic and aggregate instability of the polymer matrix, changing its microstructure. These processes can badly affect the change in properties of polymers, especially composites, during operation at elevated temperatures. Therefore, it is rational to use liquid curing agents for the production of polymer materials. Eutectic mixtures and modified curing agents are often used owing to the lack of liquid curing agents [3–5]. Modification of amine curing agents allows varying the technological properties of epoxy compositions (viscosity, vitality, temperature of curing). Usage of eutectic mixtures of aromatic diamines for curing of epoxy binders allows solving a number of technological problems and producing polymer composite materials characterized by improved properties. In [6–8], the curing of epoxy resins by Benzoam ABA, Benzenamine N, and Polyam BS-5 (products of condensation between aniline and formaldehyde) containing additional aromatic amines and catalytic additives characterized by different structure was studied. According to the data obtained, the authors classified such mixtures as effective curing agents making it possible to improve the physicomechanical, electric, and adhesion properties of epoxy compositions.

Epoxy polymer matrices for high-strength and thermally stable composites are introduced on the basis of different epoxy resins. 4,4'-Diaminodiphenylsulfone and its mixtures with 3,3'-diaminodiphenylsulforne and *p*-aminobenzenesulfonimide [9, 10] are frequently used as effective curing agents. In [11, 12], the obtainment of thermally stable polymer materials characterized by high physicomechanical and thermomechanical properties by curing epoxy resins with liquid curing agent 3,5-dimethyl thio-toluene diamine (mixture of 2,4- and 2,6-isomers) demonstrating latent properties was reported. Liquid curing agent 3,5-diethyltoluenediamine (E100) is also latent curing agent; as opposed to 3,5-dimethyl thio-toluene diamine (E300), it is more reactive, which allows performing curing of binders at lower temperatures.

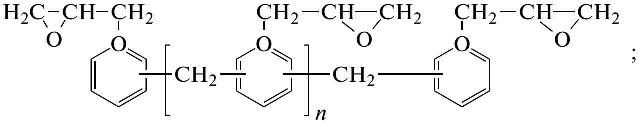
The goal of the present research is to the examine the general crucial properties of polymers and composites obtained by curing epoxy resins characterized by different functionality with 3,5-diethyltoluenediamine (E 100).

EXPERIMENTAL

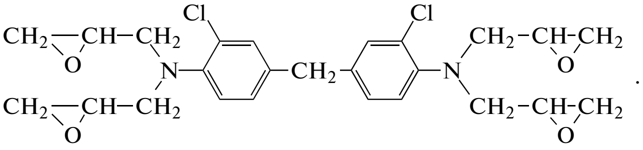
The following epoxy resins were used in the research: ED-22 bifunctional diane resin (GOST 105587-84, content of epoxy groups of 23%, dynamic viscosity at 25°C of 9.8 Pa s):



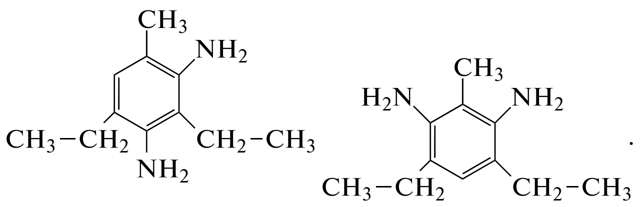
trifunctional epoxy resin UP-643 (TU 2225-605-11131395-03, content of epoxy groups of 23.4%, dynamic viscosity at 50°C of 55 Pa s):



tetrafunctional epoxy resin EKhD (TU 2225-607-11131395-03, content of epoxy groups of 28.3%, dynamic viscosity at 50°C of 15 Pa s):



3,5-Diethyltoluenediamine (E100, ETHACURE 100, Albemarle, USA, mixture of 2,4- (75–80%) and 2,6- (18–24%) isomers) was used as curing agent.



The kinetics of epoxy resins curing were studied using differential scanning calorimetry (DSC) on a DSC 822^e calorimeter (METTLER-TOLEDO, Switzerland) under isothermal and dynamic regimes; the heating rate was 5, 10 and 15 K/min; the experiments were performed within 25—300°C. The temperature range of reactions and power of heat emission Q depending on time were registered on thermograms.

The rheological properties of epoxy resins and their vitality t (the induction effect) were estimated according to the change in viscosity on a Rheotest-2 rotation viscometer (Germany) using a cone–slab knot under constant shear rate of 180 s^{-1}; the experiments were performed at the temperature of 25 ± 0.5°C.

Components of the composition were stoichiometrically mixed in a laboratory mixer for 15–20 min at 40–50°C under vacuum to prepare the polymers. The reaction mixture was poured into metal slit-type molds; it was thermostated up to complete curing under regimes determined by the study of kinetics of curing using DSC of corresponding reactions. Ring samples of organoplastics were prepared using a T635 impregnating machine by passing the cord of the set grade through the bath containing the binder heated to 60°C. Then the cord was wound onto a special arbor under tension. The composite on the arbor was also thermostated up to complete curing under the set regime. After curing, the samples of polymers and organoplastics were kept at room temperature for one day before the tests.

A well-known technique [13] was used to determine the adhesion to the fiber. A metal mesh characterized by small diameter of cells was used as the carrier of epoxy binder. A thin organic fiber was passed at a right angle through the cells of the mesh, the thickness of which determines the length of the junction. Adhesive compounds were placed into the thermostat and cured according to the set regimes. The samples were tested using the pulling method on a UTS 110 MK-1 tensile testing machine after storage for 24 h at room temperature; the deformation rate was 5 mm/min. The diameter of fiber and length of conjunction were determined using a Carl Zeiss Axiovert 200 MAT microscope. Ten samples were tested during each experiment.

The physicomechanical characteristics of cured polymers at tension: conditional strength σ (maximum stress divided by the area of the initial cross section of sample) and relative critical deformation were determined by testing trowel-shaped samples on an Instron 3565 tensile machine (UK) at the set temperature and tension rate of 100 mm/min according to GOST 11262-80.

The Charpy impact strength was determined using a KM-04 copra at 23°C according to GOST 4647-15; the impact rate was 2.9 m/s; cylindrical samples were used.

The polymer structure was examined by thermal mechanical analysis on a TMA/SDTA 841^e analyzer (METTLER-TOLEDO, Switzerland). Thermograms of cylindrical samples (diameter of 5 mm, length of

Table 1. Kinetics of curing of epoxy resins with 3,5-diethyltoluenediamine

Epoxy resin	Temperature, °C		Thermal effect Q, J g^{-1}	Activation energy E, kJ mol^{-1}
	T_{in}	T_{peak}		
ED-22	105	177	268	106
UP-643	105	174	224	105
EKhD	110	190	323	112

6 mm) were registered at the heating rate of 5 K/min. Modulus E_{he} within the region of the high-elasticity plateau was calculated on basis of the difference between linear deformation of sample without load (penetration regime) and under load of 1 N (dilatometric regime). The average statistical molecular weight M_c of the chain segment between the knots of chemical crosslinking and effective crosslinking density V_c were calculated according to the formulas

$$M_c = \frac{3\rho R T_{in} \Delta\varepsilon}{P h_0}; \quad V_c = \frac{2\rho N_A}{3M_c},$$

where ρ is the polymer density; R is the universal gas constant; T_{in} is the initial temperature of forced high elasticity; Δε is the quasiequilibrium hyperelastic deformation; h_0 is the initial height of the sample; and N_A is the Avogadro number.

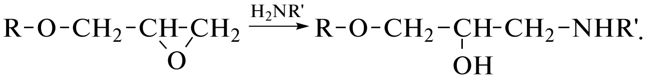
The concentration of chains of polymer network C was determined as the ratio between density ρ and M_c.

The study of thermomechanical properties of polymers was performed on a NETZSCH DMA 242C analyzer. It allows determining dynamic elastic modulus E and loss tangent tan E'/E, which is equal to the ratio between loss modulus E' and elastic modulus E and characterizes the viscoelastic properties and the thermal stability, which was estimated on the basis of the maximum of tanE'/E at set frequency (the value of the glass transition temperature). The experiment was performed at different frequencies within 30—280°C; the heating rate was 2 K/min. Beams with size of ~40 × 6 × 4 mm were used as samples. The accuracy of measurements of each sample size was 0.05 mm. The load was applied under three-point bending. The set displacement was loaded to the middle cross section of the beam. The bending amplitude of the beam was 50–60 μm. Such regime of external load caused the deformation rate of ~5×10^{-3} (1/s) in surface layers of the beam.

The study of thermal properties of polymers was performed using a Paulik–Paulik–Erdey Q-1500D derivatograph (MOM). The programmed heating of samples (100 mg) was performed at the rate of 10 K/min up to 1000°C in air atmosphere. Annealed aluminum oxide (specific surface of 3.4 m^2/g) was used as a standard.

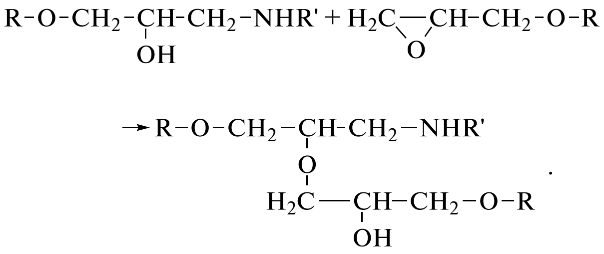
RESULTS AND DISCUSSION

It is known that the polymer properties and adhesion of the binder to the fiber are determined by the kinetics and degree of curing of the resin by the amine curing agent [14, 15]. The reaction of curing exhibits multiple stages. In the first stage, a linear polymer is formed during the interaction between the epoxy group and primary amine:



$$\mathrm{R{-}O{-}CH_2{-}\underbrace{CH{-}CH_2}_{O}} \xrightarrow{H_2NR'} \mathrm{R{-}O{-}CH_2{-}\underset{OH}{CH}{-}CH_2{-}NHR'}.$$

In the second (and the following) stages, the interaction between secondary amines and formed alcohol groups takes place; as a result, 3D crosslinked structures are formed, the structure and branching of the which determine the thermal stability and physicomechanical properties:



$$\mathrm{R{-}O{-}CH_2{-}\underset{OH}{CH}{-}CH_2{-}NHR'} + \mathrm{\underbrace{H_2C{-}CH}_{O}{-}CH_2{-}O{-}R}$$
$$\rightarrow \mathrm{R{-}O{-}CH_2{-}\underset{\underset{H_2C{-}\underset{OH}{CH}{-}CH_2{-}O{-}R}{|}}{\underset{O}{CH}}{-}CH_2{-}NHR'}.$$

The temperature ranges of reactions and thermal effects were determined using the DSC method during the study of kinetics of reactions of curing of epoxy resins by 3,5-diethyltoluenediamine (E100); the activation energies were calculated according to the Kissinger method (Table 1). Typical DSC curves of the reactions of curing of epoxy resins are given in Fig. 1. The beginning of curing reactions is shifted by 30–50°C for different resins compared to 3,5-dimethyl thio-toluene diamine (E300). The calculated activation energy of reactions with E100 is lower by 10–22 kJ/mol compared to E300 [12].

The process of curing of resins with E100 runs at elevated temperatures. In line with latent curing agent

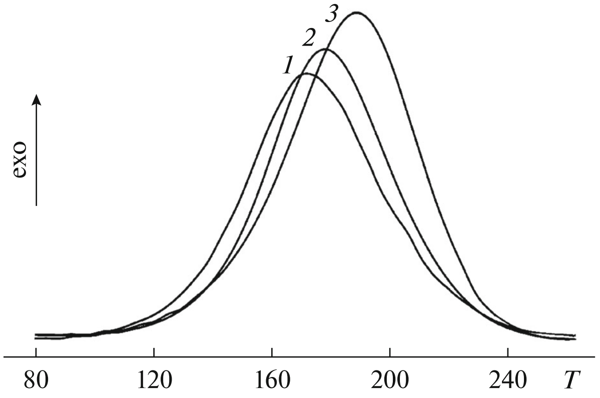


Fig. 1. Kinetics of epoxy resins curing with 3,5-diethyltoluenediamine (E100): (*1*) UP-643; (*2*) ED-22; (*3*) EKhD.

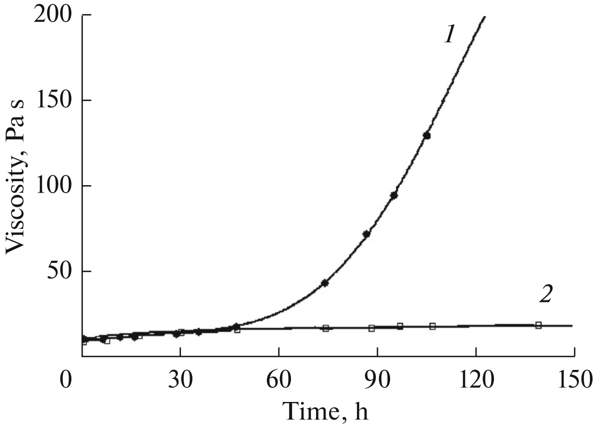


Fig. 2. Increase in dynamic viscosity in the course of time at 25°C for epoxy compositions based on ED-22 resin and curing agents: (*1*) E100; (*2*) E300.

E300 [12, 16, 17], it should demonstrate latent reaction activity at low temperatures. The change in dynamic viscosity at 25°C in the course of time is evidence of this fact (Fig. 2). The viscosity of the composition with E300 curing agent hardly changes in 150 h. However, its vitality (time of achieving viscosity of ~50 Pa s) is about 75 h. Compositions characterized by such vitality can be classified as one-pot ones; the curing agent can be classified as a latent one.

Crosslinked polymer networks were obtained by curing of epoxy resins of different functionality with E100; their structural characteristics are given in Table 2. The physicomechanical, thermomechanical, and thermal properties of polymers are given in Tables 3–5 and in Figs. 3–5. No direct relationship between individual structural characteristics of polymers and their properties was detected. The glass transition temperature, which characterizes the thermal stability, depends on the crosslinking density and functionality of the resin. The highest values were obtained for the polymers based on tri- and tetrafunctional resins.

Dynamic mechanical analysis showed that polymers obtained by curing with E100 are characterized by high values of glass transition temperature (180–206°C, Fig. 3, Table 3). A series of curves at different frequencies of applied load was obtained for the sample based on ED-22 resin (Fig. 4). The mechanical loss tangent is shifted to the region of higher temperatures as the frequency is increased. A straight line dependence of the logarithm of frequency on inverse temperature was established. The obtained temperature–frequency dependence of the dynamic mechanical spectrum characterizes the viscoelastic properties

Table 2. Influence of functionality of epoxy resin cured with E100 on structural characteristics of polymers

Epoxy resin	Resin functionality	T_g, °C	$V_c \times 10^{20}$, mol cm^{-3}	M_c, g mol^{-1}	C, mol dm^{-3}
ED-22	2	180	3.5	1250	0.87
UP-643	3	206	4.09	1062	1.02
EKhD	4	201	9.35	527	2.5

Table 3. Thermomechanical properties of polymers at frequency $f = 0.5$ Hz

Epoxy resin (mixture of resins)	Elastic modulus E, MPa at 30°C	Glass transition temperature, °C	T_{1000}, °C	Mechanical loss tangent at $E = 1000$ MPa
ED-22	2240	179	167	0.25
UP-643	2900	206	180	0.26
EKhD	3720	201	187	0.22
ED-22 + ED-610 (50/50)	2850	190	180	0.28
ED-22 + UP-643 (50/50)	2620	187	178	0.28
UP-2217 Regular binder	2750	160	150	0.19

Table 4. Physicomechanical properties of polymers and impact strength

Epoxy resin (mixture of resins)	Property under extension				K	Impact strength, J/cm^2
	25°C		150°C			
	σ, MPa	ε, %	σ, MPa	ε, %		
ED-22	46	12	42	18	0.91	1.82
UP-643	47	9	46	13	0.97	1.72
EKhD	26	3	23	8	0.88	1.23
ED-22 + ED-610 (50/50)	31	11	30	16	0.97	2.61
ED-22 + UP-643 (50/50)	42	10	39	12	0.93	1.77
UP-2217 Regular binder	45	10	40	11	0.88	1.24

Table 5. Thermal properties of polymers

Epoxy resin	Mass loss (%) at temperature (°C)			Residue weight (%) at 650°C
	5	10	50	
ED-22	350	368	397	1
UP-643	355	364	455	2
EKhD	306	318	423	1

of the studied epoxy polymers. This characteristic is known as time–temperature superposition [18].

The thermal stability of the obtained polymers determines the stability of strength characteristics at elevated temperature. Polymers based on E100 are characterized by high values of strength which exhibit insignificant changes at test temperature of 150°C: the coefficient of thermal stability K is 0.91–0.97 irrespective of functionality. The impact strength of these polymers is higher than that of other known polymer systems (Table 4).

Thermogravimetric analysis of the studied polymers shows that intense decomposition takes place at temperatures higher than 300°C. The polymer based on UP-643 resin demonstrates the highest thermal stability (Table 5).

The production of composite material was the logical conclusion of the present research. Two epoxy binders (based on ED-22 and UP-643 resins) were selected for the tests. The adhesion strength against shear of the novel binders to organic fiber was determined. It appeared to be fairly high; it is inferior no none of the known systems (Table 6). Organoplastic samples were made on basis of high-modulus Armos fiber and two novel epoxy resins according to the existing "wet spinning" technique. Data on tensile strength properties of organoplastics at different temperatures

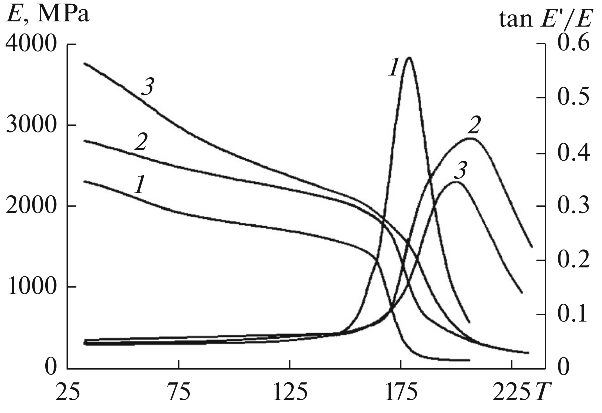


Fig. 3. Temperature dependence of dynamic elastic modulus (E) and mechanical loss tangent ($\tan E'/E$) for polymers cured with E100 based on (*1*) ED-22, (*2*) UP-643, and (*3*) EKhD.

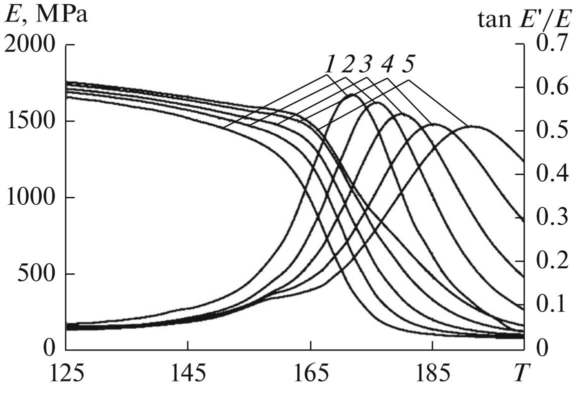


Fig. 4. Temperature dependence of dynamic elastic modulus and mechanical loss tangent for polymer obtained by ED-22 curing with E100 at frequencies of (*1*) 0.1 Hz, (*2*) 0.5 Hz, (*3*) 2 Hz, (*4*) 10 Hz, and (*5*) 50 Hz.

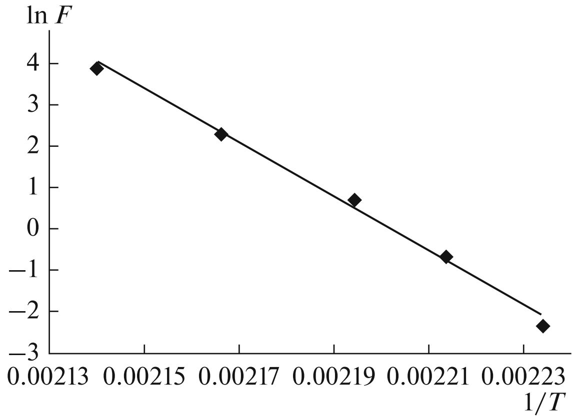


Fig. 5. Dependence of logarithm of frequency on inverse temperature for polymer based on ED-22 and E100.

are given in Table 6; the ring-shaped samples had a diameter of 150 mm and thickness of 2 mm; they were prepared using novel binders. Table 6 also contains comparative data obtained on basis of the known epoxy compositions. The main conclusion can be drawn on basis of tests: composition materials—organoplastics based on novel epoxy binders with E100 curing agent can be an alternative to the known materials owing to their thermomechanical, thermophysical, and physicomechanical properties. Their technological properties exceed the ones of known binders obtained by amine curing; this fact allows recommending them for the production of novel materials which satisfy modern requirements.

Table 6. Properties of organoplastics

Binder composition	Adhesion to fiber, MPa	Tensile strength (MPa) at test temperature (°C)		
		25	150	200
ED-22 + E100	59.0	2850	1640	1620
UP-643 + E100	53.8	2560	2350	1860
UP-2217 regular	48.4	2660	1770	1690

CONCLUSIONS

Liquid amine curing agent 3,5-diethyltoluenediamine (E100) was proposed for curing. The kinetics of curing of epoxy resins characterized by different functionality (ED-22, UP-643, EKhD) were studied using the DSC method. The curing agent E100 demonstrated fine reaction activity at high temperatures; it provided high vitality to the binder at room temperature. The complex of properties of polymers based on epoxy binders with E100 curing agent was determined. The influence of individual characteristics of polymers on the glass transition temperature and elasticity modulus was shown. The polymers based on three-functional resin UP-643 and E100 curing agent are characterized by the highest glass transition temperature. Organoplastic composite materials were produced and tested according to the existing technology. They can be alternative to the known materials of the same type owing to their thermomechanical, adhesive, and physicomechanical properties; several technological characteristics of the elaborated materials can exceed the ones of the known materials.

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