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INFLUENCE OF THERMOPLASTIC MODIFIERS ON THE PROPERTIES AND THE PROCESS OF CURING OF EPOXY POLYMERS

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The basic features of the rheokinetic behavior of an epoxy oligomer cured by 4,4′-diaminodiphenylsulfone have been determined. It has been established that the process of curing obeys the phenomenological equation of first order with self-acceleration. Different modifiers based on linear thermally resistant polymers have been employed to improve the physicochemical properties of the compositions. Making such additions enabled us to increase the thermal resistance of materials and the resistance to impact loads.

In recent years, wide acceptance has been gained by thermoplastic modifiers of epoxy polymers whose addition enables one to substantially improve the strength characteristics of cured compositions without decreasing the elastic modulus and the vitrification (glass-transition) temperature. One can use reactive and nonreactive polysulfones, polyimides [1–3], polyetherimides, copolyethers, polyethylene terephthalate [4, 5], polymethyl methacrylate, and polycarbonates [6, 7] as additions. The optimum content of the thermoplastic varies with the chemical composition of the systems under study, but it usually does not exceed 20%.

In the present work, consideration has been given to the influence of heat-resistant thermoplastics on the properties of epoxy binders based on the epoxydian oligomer ED-20. Investigation of the mechanism of modification of the epoxy oligomer by thermally resistant polymers enables one to produce compositions with improved impact characteristics and an increased temperature interval of operation.

Experimental. We investigated a system based on the epoxy oligomer ED-20 and the curing agent 4,4′-diaminodiphenylsulfone (DADPhS). We employed thermally resistant thermoplastic polymers — Ultem 1000 polyetherimide (PEI) (manufactured by General Electric), Noryl, Ultrason S2010, polysulfone (PSF) (manufactured by BASF), and polyarylene etherketone (PAEK) as modifiers. The modifiers were combined with the epoxy oligomer at a temperature of 150^{o}C without using solvents.

On a torsion pendulum, we investigated the change in the mechanical properties by the technique of freely damped oscillations at a nominal frequency of 1 Hz: we measured the mechanical loss tangent tan δ and the dynamic elastic modulus G and found the vitrification point of the cured material from the maximum of tan δ. The thermal effects of the reaction were determined on a DuPont TA 2000 thermograph by the calorimetric method, while the physicomechanical properties were determined according to the standard procedures.

Discussion of the Results. In the present work, we have investigated the influence of heat-resistant thermoplastics on the properties of ED-20-based epoxy binders. We employed 4,4′-diaminodiphenylsulfone as a curing agent.

The addition of thermoplastics to epoxy resins substantially increases the viscosity of the polymer composition and hence leads to a decrease in the system's mobility, which in turn causes a retardation of the curing reaction. For a content of polysulfone of 0, 5, 10, and 20% the viscosity is equal to 9.38, 28.12, 64.8, and 353.5 Pa·sec, respectively.

Study of the processes of curing is of prime importance in producing materials with prescribed properties. The distinctive features of the process of structurization determine the technology of production of binders, the degree of cure (i.e., constancy of the properties in the course of operation), and the final operating characteristics. Therefore, investigations of the process of curing of compositions based on reactive oligomers and their mathematical description are important problems.

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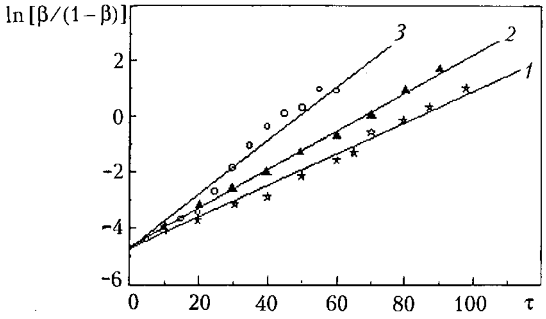

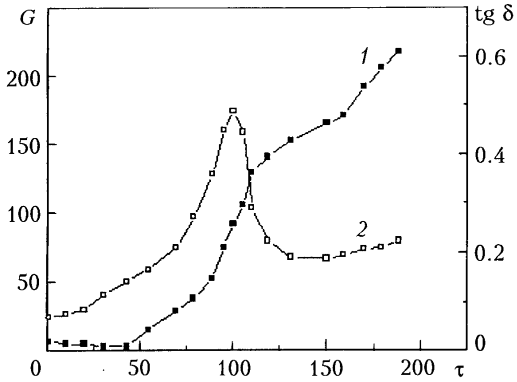

Fig. 1. Fractional conversion determined by the method of differential scanning calorimetry vs. curing time: 1) T_c = 160, 2) 170, and 3) 180°C. τ, min.

Fig. 2. Elastic modulus (1) and mechanical loss tangent (2) vs. curing time. ED-20-DADPhS, T_c = 160°C. G, MPA; τ, min.

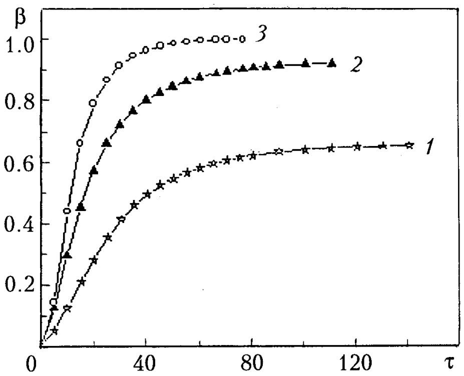

Fig. 3. Fractional conversion determined by the method of dynamic mechanical analysis vs. curing time in the coordinates of the equation which takes into account the self-acceleration effect: 1) T_c = 160, 2) 170, and 3) 180°C. τ, min.

The process of curing of the ED-20 composition was investigated by the methods of differential scanning calorimetry and dynamic mechanical analysis. The fractional conversions determined by the calorimetric methods as functions of the curing time are presented in Fig. 1.

By the method of dynamic mechanical analysis we obtained G and tan δ as functions of the time at different temperatures (Fig. 2). It is common knowledge that in the model of an ideal network which is found in the region of the high-elasticity state, the elastic modulus is in direct proportion to the density of the cross links in the network polymer. Then, in investigating the rheokinetics of the process of formation of a network polymer, its value characterizes the intensity of the curing reaction. But in most actual cases curing is carried out not only in the region of the high-elasticity state. At the same time, tracking a change in the elastic modulus remains a sensitive method of tracking a change in the structure (properties) of the material in curing.

In the general case, the fractional conversion is determined by the method of dynamic mechanical analysis from the formula

$$\beta_G = (G - G_0)/(G_\infty - G_0) . \quad (1)$$

However, in the situations investigated in the present work the material is vitrified in the process of curing. Then the final elastic modulus G_∞ turns out to be much larger than the modulus of high elasticity and the dependence of tan δ on the time passes through a maximum, which indicates a relaxation transition (vitrification) in the system.

Amine curing of epoxy resins is described, as a rule, by an equation of first order taking into account the self-acceleration effect:

TABLE 1. Rate Constant of the Process of Curing ($k \cdot 10^3$, min^{-1}) in (2) and (3) as a Function of the Content of Polysulfone at Different Curing Temperatures (ÉD-20-DADPhS)

T_c, °C	C_{PSF}, %			
	0	5	10	20
150	3.81	2.86	1.32	0.86
160	9.08	2.51	0.90	0.33
170	12.75	1.03	0.67	0.07

TABLE 2. Vitrification Time as a Function of the Curing Temperature for Different Contents of Polysulfone

C_{PSF}, %	T_c, °C	τ_v, min
0	150	140
	160	100
	170	70
5	150	120
	160	90
	170	80
10	150	120
	160	110
	170	100
20	150	140
	160	130
	170	100

$$d\beta / d\tau = k\,(1 - \beta)\,(1 + C\beta)\,. \tag{2}$$

In integral form, it is

$$\ln\,(1 - \beta) = \frac{1 + C\beta}{(1 + C)\,k\tau}\,. \tag{3}$$

In the coordinates of this equation $\beta/(1 - \beta) = f(\tau)$ (on condition $C_{\beta} >> 1$), we obtained linear dependences for the systems under study (Fig. 3) and determined the constants C and k (Table 1). As is clear from the table, the addition of polysulfone to the composition ÉD-20-DADPhS leads to a significant decrease in the rate of the curing process. Probably, this is due to a substantial increase in the viscosity and hence a decrease in the mobility of the compositions upon addition of thermoplastics.

The temperature dependence of the constant k is described by the Arrhenius equation; using it we have calculated the values of the activation energy of the curing process: upon addition of PSF it increases from 29 to 60 kJ for a content of the modifier of 20%.

The systems under study are vitrified in the process of curing. On the dependences of tan δ (Fig. 2), we observe a maximum corresponding to vitrification. Table 2 gives the values of the vitrification time at different curing temperatures of the compositions. In producing compositions based on epoxy polymers and thermoplastics, one first dissolves the latter in epoxy resin. However it is common knowledge that the compatibility in the system decreases in the process of curing and the polymer is separated as an individual phase at a certain stage.

It is common knowledge that the use of DADPhS enables one to produce binders with a heat resistance of ≈185°C. By the method of dynamic mechanical analysis we have obtained the temperature dependences of the elastic modulus and the mechanical loss tangent of ÉD-20- and DADPhS-based compositions containing 10 and 20% of thermoplastics cured at a temperature of 180°C. The values of the vitrification temperatures given in Table 3 were determined from the tan δ maximum. It is clear from the table that the increase in the curing temperature leads to an increase in the vitrification temperature of an unmodified polymer and hence in its degree of cure. The addition of

TABLE 3. Vitrification Temperatures of the Epoxy Matrix and the Modifier Polysulfone at Different Curing Temperatures

C_{PSF}, %	T_c, ^oC	T_v	
		epoxy matrix	polysulfone
0	160	186	–
	170	192	–
5	160	184	172
	170	178	172
10	160	182	168
	170	176	168

TABLE 4. Vitrification Temperature of the ÉD-20-DADPhS Composition as a Function of the Content of the Modifier (curing temperature 180^oC)

Modifier	C_m, %		
	10^*	20^*	100
PSF	165; 177	176; 195	194
PEI	179; 216	176; 211	222
Noryl	171; 216	–	218
PAEK	170; 230	183; 225	237

Note: *The first number (vitrification temperature) corresponds to the T_v of the matrix, while the second number corresponds to that of the modifier.

modifiers causes a decrease in the vitrification temperature of the system under study; an increase in the curing temperature can also decrease the vitrification temperature of the epoxy matrix. It is common knowledge that the influence of modifiers on the T_v change of the matrix is considerably determined by the process of separation of a modifier as an individual phase. The temperature regime of curing determines the type of phase separation and hence the size of the particles of the dispersed phase. The type of phase separation exerts an influence on the impact strength of the compositions formed. The maximum heat resistance is attained depending on the value of T_v of the modifier. If the vitrification temperature of the modifier is lower than in the polymer matrix, it is desirable to achieve a maximum phase separation in the process of curing. If the modifier is more heat-resistant that the epoxy polymer, it can turn out to be optimum to obtain a single-phase system (although this is not universally attainable).

By the method of dynamic mechanical analysis, we have also determined the influence of PSF, PEI, Noryl, and PAEK on the vitrification temperature of the system under study. As is clear from Table 4, addition of the thermoplastics leads to a decrease in the heat resistance of the composition.

We employed different regimes of curing of the PSF-containing composition; the content of the modifier was increased to 40%. On the step increase in the curing temperature from 120 to 180^oC, T_v turned out to be 185^oC for ÉD-20-DADPhS and 190^oC for the same composition containing 10% PSF. The change in the temperature regime of curing leads to a certain change in the vitrification temperature and to its increase in particular cases.

One of the most important characteristics of polymers is thermal resistance. We have determined the samples' mass at 300^oC and the temperature of loss of 5% of the mass by the samples for the compositions under study.

As is clear from Table 5, the addition of the modifiers leads to an increase in the thermal resistance of the samples; the increase is the largest when Noryl, polyetherimide, and polyarylene etherketone are added.

To evaluate the efficiency of PSF we have obtained the dependences of the impact strength A and the bending strength σ_b on the content of the modifier. As is clear from Table 6, these characteristics monotonically increase with the curing temperature and the content of the modifier. The obtained values of the physicomechanical characteristics of the compositions corresponds to those at the level of the grades of foreign companies (σ_b = 28–50 MPa and A = 11–54 kJ/m^2).

The addition of the thermoplastic modifiers leads to an improvement of approximately 20–50% in the polymer–fiber adhesion strength.

TABLE 5. Influence of Modifiers on the Thermal Resistance of ÉD-20-DADPhS-Based Compositions

Modifier	Mass at 300°C, %	Temperature of a 5% Loss, °C
Absent	93.7	295
PSF, 20%	94.7	298
PEI, 20%	95.8	304
PAEK, 20%	95.7	302
Noryl, 10%	97.4	313

TABLE 6. Values of the Bending Strength and the Impact Strength of a Polysulfone-Modified ÉD-20-DADPhS

T_c, °C	C_{PSF}, %	σ_b, MPA	A, kJ/m^2
150	0	16	2
	5	17	6
	10	22	15
	20	34	17
160	0	23	8
	5	31	14
	10	33	20
	20	42	30
170	0	25	14
	5	33	17
	10	42	23
	20	50	33

From our view, the results of the work done point to the efficiency of polysulfone and polyarylene etherketone as modifiers of binders for epoxy-oligomer-based plastics. It is probable that the action of thermoplastic modifiers on epoxy polymers is determined by the phase structure of a composition which is formed in the process of curing.

NOTATION

β, fractional conversion; $f(\tau)$, function of time; β_G, fractional conversion determined by the method of dynamic mechanical analysis; G, time-dependent elastic modulus, MPa; G_0, initial elastic modulus, MPa; G_∞, final elastic modulus of the completely cured sample which presumably remains in the high-elasticity state, MPa; k, rate constant of the process of curing, min^{-1}; C, constant reflecting the self-acceleration effect; σ_b, bending strength; A, impact strength, kJ/m^2; tan δ, mechanical loss tangent; T, temperature, °C; C_{PSF}, content of polysulfone, %; C_{m}, content of the modifier, %; τ, curing time; τ_{v}, vitrification time. Subscripts: 0, initial; ∞, final; b, bending; v, vitrification; imp, impact; c, curing; m, modifier; PSF, polysulfone.

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