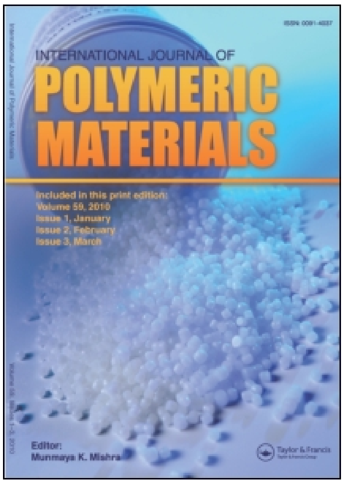

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Optical Materials the Based on Low Flammable Epoxy Resins

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The glycidylic ethers of phosphorus acids are offered as effective modifiers of optical, hardness, heat-physical, and technologic properties, as far as chemical active antipyrenes for epoxy resins. Materials properties at various forming steps were studied using a wide set of spectral, thermal, physico-mechanical methods. Peculiarities of olygomeric mixtures phase state and regularities of its change as a function of modifiers concentration and chemical structure are brought out. A large amount of quantitative information concerning glycidylic ethers content and structure, and materials forming regims influence on their maintanance and optical properties is presented. Compositions and manufacturing regims of optical materials are optimized on the bases of derived results. The developed materials are offered as an optical adhesives and glasses with regulated optical properties such as deflection index, optical density at different wavelength *etc.* Addition of phosphporus modifiers to epoxy oligomers led to increase of destruction temperature and coke yield, to decrease of mass loss and to smoke suppression. All produced materials are characterized by low inflammability and enhanced thermal stability.

Keywords: Epoxy oligomers; phosphorus; modifiers; flammability; optical properties

INTRODUCTION

Epoxy materials are widely used for agglutination of optical components in microelectronics, perfect mechanics, in motor and another

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fields of industry [1]. Thereat they are put in high requisitions on optical, strengthening, heat-physical and other properties, their simultaneous satisfying being impossible if using industrially manufactured olygomers.

Modification of epoxy resins (ER) by various glycidyl ethers seems to be a mostly perspective way of regulating optical (or example deflection index, transmittance) and some other resins properties [2, 3]. However, known optical adhesives obtained such a way do not possess an adequate high thermal, heat and fire stability as well as mechanical and adhesive properties. The glycidyl ethers of phosphorus acids (GEPA), proposed by us as a universal epoxy resins modifiers, combine a functions of glycidyl diluents and phosphorus-containing combustion inhibitors. Materials of various applications (including optical) have been developed using GEPA and epoxy dianic resins (ED-22, ED-20, ED-16, ED-14) [4–6]. Properties of all gained materials are determined both by their chemical composition and by formation regims at all steps. In this paper the main regularities of chemical structure and modifier concentration influence towards properties of the compositions as well as the ways of materials with designed properties producing are reported.

EXPERIMENTAL SECTION

A series of commercially available and specially synthesized samples of epoxy olygomers (EO), hardening agents and *P*-containing modifiers were investigated, their main characteristics being presented in Tables I and II. Among the used hardening agents were the next:

- 4,4′-di(amino) diphenylmethane (DADPM), stoichiometric coefficient $K = 1.15$.
- UP-0633M, (monocyanoethyl) diethylenetriamine, $K = 0.92$.
- UP-0638, modified aromatic amine (mixture of DADPM and *m*-phenylenediamine) $K = 0.92$.
- *iso*-methyltetrahydrophtalic acid anhydride (MTGPA), $K = 3.92$.

Density of liquid epoxy compositions was measured using specific gravity bottle. The cured samples density was determined by

TABLE I Some characteristics of studied epoxydianic olygomers

Epoxy resins name	*Molecular weight, M_n*	*Epoxy groups content (E.G.C.), %*	*Density d, kg/m^3*
ED-14	540-620	13.9-15.9	1155(at $t = 50°C$)
ED-16	480-540	16-18	1155(at $t = 50°C$)
ED-20	390-430	20-22.5	1166(at $t = 25°C$)
ED-22	390	22.1-23.6	1165(at $t = 25°C$)
DGEBA*	340	24	–

*Monomer – Diglycidylic Ether of Bishenol A.

comparing masses of equal volumes of compound under investigation and distilled water (hydrostatic weighing method).

A capillar viscousemeter VPG-1 (capillar diameter ranging from 0.54 to 5.1 mm) was used for viscosity measurements. Viscosity change during curing process was studied applying Heppler's viscousemeter (Fe-Ni pellet of 15.6 mm diameter).

Components incompatibility in EO-GEPA systems was studied using interference micromethod, by methods of turbidity spectra and light scattering. An SF-26 spectrophotometer (λ 350 – 1000 nm, couvetts of 0.1 – 10 mm thickness) was employed for turbidity measurements. Light scattering was investigated using "Sophica" (France) photogoniodiffusometer at λ 546 nm and scattering angles ranging from 30 to 150°. Deflection index was corrected using calculation of scattering intensity compared to benzene, quartz standart being used for calibration. Interference micromethod is based on multy-ray interference by two slab surfaces. The last form a small angle $\theta \leq 2°$, their inner surfaces being covered by semi-transparent metal layer with high reflection index. Forming interference picture gives concentration profile of liquids interdiffusion zone. For this purpose an original self-made interferometer-automatic optical diffusometer ODA-2 was used.

Deflection index values of olygomer mixture and cured films were determined by common way at IRF-22 apparatus. Molten specimen were used in 60° -prism manufacturing, the measurements being made at G-5 goniometer.

Investigation of thermal effects at heating and cooling (DTA method) along with mass loss at heating (TGA method) were carried out at Q-1500D model Pauilik-Paulik-Erdey derivatograph.

TABLE II Formula and some properties of glycidylic ethers of phosphorus acids (GEPA) under investigation

Name	*Abbreviation*	*Formula*	M_n	d_4^{20}	n_D^{20}	*E.G.C.*,%	*P*, %
Triglycidylphosphate	TGP*	$P(O)(CH_2—CH—CH_2)_3O$	266	1.3673	1.4602	48	11.65
Diglycidyl-di(oxymethyl)phosphate	DGOP**	$CH_3OP(O)(OCH_2—CH—CH_2)_2O$	224	1.3140	1.4499	38	13.84
Monoglycidylphosphate	MGP**	$(CH_3O)_2P(O)OCH_2—CH—CH_2O$	182	1.1795	1.4242	24	17.03
Diglycidyl-(methyl)phosphonate	DGMP*	$CH_3P(O)(OCH_2—CH—CH_2)_2O$	208	1.2789	1.4636	41	14.9
Methyl-di(oxymethyl)phosphate	MDMP**	$CH_3P(O)(OCH_3)_2$	124	1.1684	1.4146	–	25

*Commercially available compounds.

**Samples synthesized in A. E. Arbuzov Institute of Organic and Physical Chemistry (Kazan).

Glass transition temperatures of cured epoxy resins were determined thermo-mechanically with three-channel apparatus PTB-1 at various static load of samples.

Adhesion was studied by steady breakaway of agglutinated sapphier samples using disruptive machine.

The oxygen index (OI) was determined as a minimal volume concentration of oxygen in O_2—N_2 mixture flow necessary for inflammation and support of stable candle-like burning.

The rate of flame spread after ignition source removal was used for evaluation of inflammability.

Original filtration method was applied for smoke level determination (smoke number, SN). Method is based on photometrical determination of optical density of smut appeared at the filter paper after passing of given gas volume.

RESULTS AND DISCUSSION

Investigation of epoxy oligomer – GEPA binary compositions presents the first stage of our research. The compatibility of ER and GEPA have been studied refractometrically, using interference micromethod, by methods of turbidity spectra and light scattering. The phase diagrams of ER-GEPA systems had been derived using interferograms obtained at different temperatures. Their analysis showed full compatibility of both phosphonates (diglycidyl-(methyl) phosphonate, DGMP, and methyl-di(oxymethyl)phosphonate, MDMP) with all used sorts of epoxy oligomers, including DGEBA, whereas all glycidyl phosphates revealed limited compatibility with epoxy resins. In between, formation of light scattering long-life stable compositions in all investigated systems at modifiers content from 0 up to 30 – 70 mass % had been found using turbidity spectra and light scattering methods.

Phase diagrams of ED-20 – TGP system obtained using both turbidity spectra and light scattering methods (curve 1) and interference micromethod (curve 2), are presented as an example at Figure 1. Analysis of such a diagrams, obtained using various methods, permits one to mark out three ranges of concentrations for ER-glycidyl phosphate systems and two – for phosphonates. Both type systems contain regions of spontaneously forming colloid solutions of glycidyl

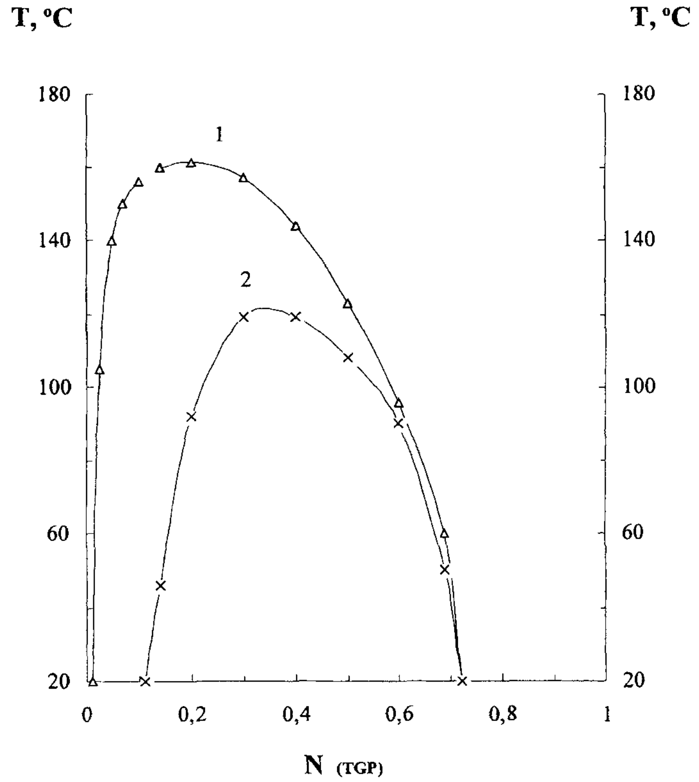

FIGURE 1 Phase diagrams of ED-20–TGP system derived from turbidity spectra (1) and interference micromethod (2) data.

ethers in epoxy oligomers and simple solutions of EO in GEPA. Moreover, there are regions of incompatibility in EO-glycidyl phosphate systems. Transparent compositions through all concentration range of both phosphates and phosphonates have been obtained by means of heating cloudy samples up to the temperatures of turbidity disappearence with subsequent fast cooling.

In order to identify the systems structural organization the densimetric and viscosimetric measurements had been carried out [7–9]. As an example some of the concentration dependences of viscosity and density in ED-20–TGP system are illustrated by Figure 2. Analysis of obtained results brings out formation of colloid particles in the GEPA concentration region of 0–10 molar parts.

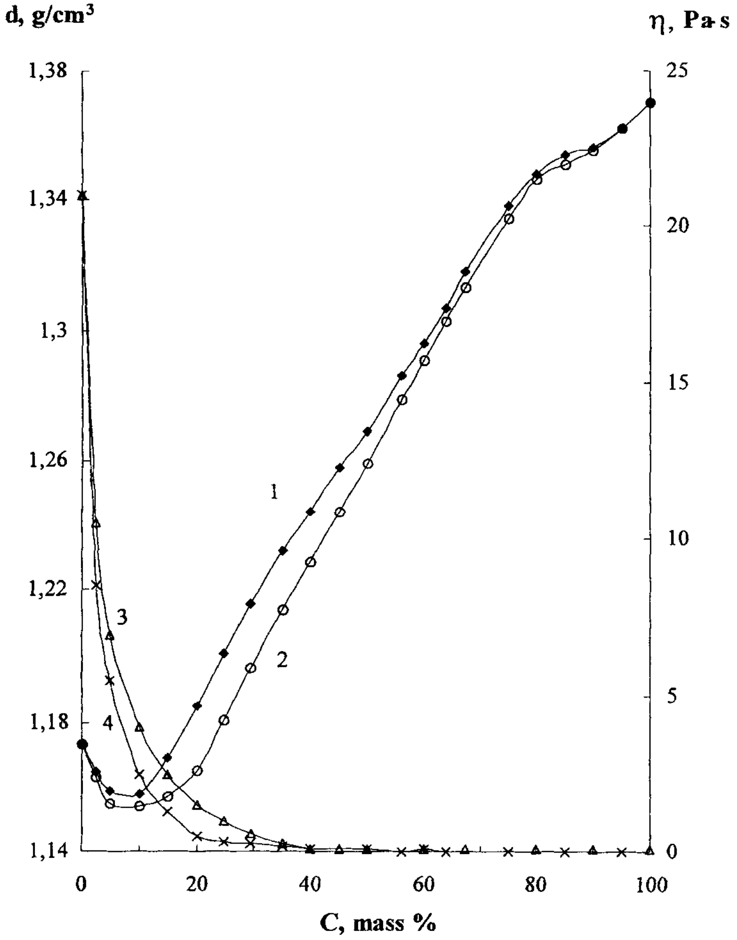

FIGURE 2 Concentration dependences of density (1, 2) and viscosity (3, 4) in ED-2–TGP systems before (1, 3) and after (2, 4) thermal treatment.

Quantity of such particles depends on both GEPA concentration, and DGEBA content in epoxy resin.

A set of experiments on surface tension measurements of EO-GEPA mixtures of various composition had been carried out in order to find out the structure of EO-glycidyl phosphate system in incompatibility region (Tab. III). Analysis of presented data shows similarity of surface tension values for EO, saturated by glycidyl phosphate, and

TABLE III Values of surface tension, $\gamma_{l/g}$, and interphase tension change, $\Delta\gamma_{l/g}$, for EO-GEPA/aluminium surface system

Modifiers content mass %	*Modifier*								
	TGP			*DGOP*			*DGMP*		
	$\gamma_{l/g}$, *mN/m*	θ	$\Delta\gamma_{l/g}$, *mN/m*	$\gamma_{l/g}$, *mN/m*	θ	$\Delta\gamma_{l/g}$, *mN/m*	$\gamma_{l/g}$, *mN/m*	θ	$\Delta\gamma_{l/g}$, *mN/m*
0	49	61	–	49	61	–	49	61	–
3	49	46	10	49	47	9	49	50	7
5	49	32	17	49	36	15	49	42	12
10	49	30	18	49	32	17	49	40	13
15	49	29	19	49	31	18	49	40	13
20	49	28	19	49	30	18	49	39	14
30	49	28	19	49	30	18	49	38	14
40	49	28	19	49	30	18	49	37	15
50	49	28	19	49	30	18	49	36	15
60	49	27	19	49	29	19	49	35	16
70	49	27	19	49	28	19	48	32	16
75	48	26	18	47	26	18	47	30	16
80	42	22	15	41	24	13	46	27	18
85	39	19	13	39	22	12	44	26	15
90	39	19	13	39	22	12	42	24	14
95	39	19	13	38	21	11	41	23	13
100	39	19	13	38	21	11	41	23	13

for glycidyl phosphate, saturated by epoxy oligomer. This may be a reason of emulsification of one substance in another. Increase of temperature and mixing intensity seems to accelerate emulsification pending non-scattering microemulsions.

Wetting ability is an important characteristic of olygomeric systems on using them as an adhesives. Presented in Table III data points to sharp enhancement of solid surfaces wetting by olygomeric compositions at low GEPA content (~5 mass %) in mixtures. Figure 3 illustrates concentration dependences of deflection index values for EO-GEPA mixtures, previously thermally treated. The last are transparent and thus useful as optical adhesives. Presented at Figure 3 data permits the GEPA use in order to obtain samples with deflection index values ranging from 1.57 to 1.44.

Considerable accelerating effect of GEPA has been found for processes of epoxy oligomers curing with amine hardening agents. Dependences of relative gel formation times for modified (τ_m) and non-modified (τ_{nm}) samples are presented at Figure 4. The most accelerating effect seems to be induced by glycidyl phosphates. This is

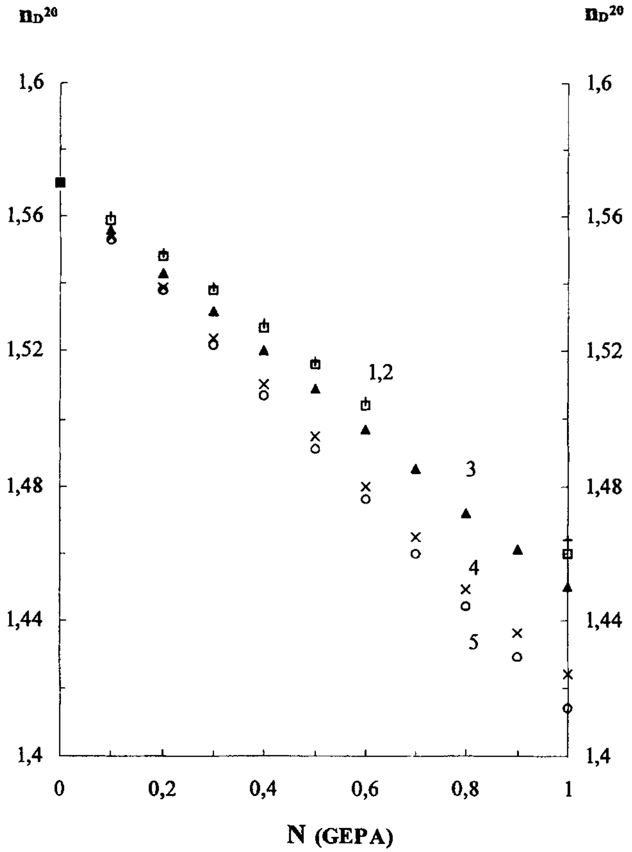

FIGURE 3 Deflection index, n_D^{20}, values dependences of ED-20–GEPA mixtures. GEPA: DGMP (1), TGP (2), DGOP (3), MGP (4), MDMP (5).

smaller in the case of glycidyl phosphonates, whereas butyl glycidylic ether and diglycidylic ether of butandiol exhibited practically no influence on epoxy oligomer curing process.

DTA and TGA methods were also used in studying the processes of epoxy resins curing in presence of GEPA. For the DTA curves in ED-20–DADPM systems with or without added 15% DGMP (or DGOP) the endo effect maximum seems to shift towards lower temperatures: from 160°C without additives to 145°C for glycidyl phosphonate and up to 130°C for glycidyl phosphate.

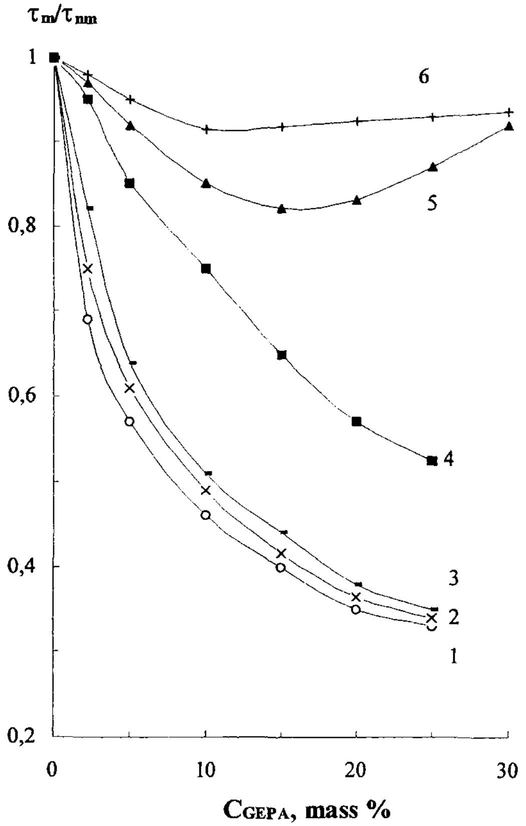

FIGURE 4 Gel formation relative time variation with concentration of *P*-containing modifiers in ED-20–DADPM–GEPA systems ($t = 80°C$). GEPA:TGP (1), DGOP (2), MGP (3), DGMP (4), BGE (5), DEB (6).

The modifiers under investigation has been established both to reduce temperature and to accelerate gel formation, the limiting degree of coversion remaining constant. The data obtained allowed us to find the best regims of hardening and to study structure and properties of such materials. The glass transition temperature (T_g) and seaming hardness ($1/M_c$) of GEPA-modified compositions, determined using thermomechanical method, had been found to depend both on additives chemical structure and its content (Tab. IV). Considerable growth of T_g observed at low concentrations (10–15 %) of di- and triglycidylphosphates may be explained by more favourable location

TABLE IV The glass transition temperature (T_g) and seaming hardness $(M_c)^{-1}$ values of GEPA-modified epoxy compositions

C_{GEPA},	*TGP*		*DGOP*		*DGMP*		*DEB*	
mass %	T_g,°C	$(10^3M_c)^{-1}$	T_g,°C	$(10^3M_c)^{-1}$	T_g,°C	$(10^3M_c)^{-1}$	T_g,°C	$(10^3M_c)^{-1}$
0	150	3.00	150	3.00	150	3.00	150	3.00
5	162	3.86	158	3.14	153	3.06	150	3.00
10	170	4.20	164	3.25	154	3.08	150	3.00
15	170	4.20	165	3.25	155	3.09	150	3.00
20	169	4.18	164	3.23	155	3.09	150	2.98
25	164	3.85	157	3.14	156	3.10	149	2.90
30	155	3.17	152	3.06	155	3.09	148	2.90
35	155	3.17	150	3.00	154	3.08	147	2.87
40	154	3.14	150	3.00	154	3.08	146	2.85
45	154	3.14	150	3.00	153	3.02	146	2.85
50	155	3.17	151	3.00	153	3.02	145	2.84
55	158	3.20	152	3.06	152	2.98	144	2.84
60	161	3.85	153	3.08	150	2.98	143	2.82
65	166	3.90	154	3.08	150	2.98	142	2.81
70	170	4.20	156	3.11	148	2.90	141	2.80
75	175	4.29	158	3.14	147	2.87	140	2.80
80	184	4.53	159	3.15	146	2.86	140	2.80
85	193	4.60	160	3.20	145	2.85	139	2.77
90	200	4.69	163	3.23	144	2.85	137	2.73
95	215	4.80	165	3.25	143	2.84	135	2.70
100	230	5.10	165	3.25	140	2.80	132	2.65

of functional groups as a result of structurization, passing in liquid systems. This reflects also at kinetic characteristics of curing processes. Di-(glycidyl)-methylphosphonate influences this parameter only slightly.

Some decrease of T_g values, observed in the glycidyl phosphate concentration range from 10 to 60% is probably caused by ED-20 and GEPA phase incompatibility and by irregular distribution of hardening agent in GEPA phase. The density concentration dependences for liquid and cured systems are similar. At the same time, thermal treatment of parent olygomeric compositions reflects at their density also both for liquid and cured conditions.

A correlation between the data for surface and interphase tension concentration dependences in EO-GEPA systems (Tab. IV) and obtained surface free energy values for cured compositions at the air/aluminium border presented in Table V, gives rise to a conclusion on boundary layers structure maintenance during liquid systems hardening. The gums adhesive stability may be explained using data concerning GEPA adsorption on solid surface. Herewith, glycidyl phosphates are characterised by more pronounced surface activity and by higher adhesive properties.

TABLE V Free surface energy of compositions formed on the border with air and aluminium

GEPA concentration, mass %	*Free surface energy, mN/m*					
	on air border			*on aluminium border*		
	TGP	*DGOP*	*DGMP*	*TGP*	*DGOP*	*DGMP*
0	46	46	46	51	51	51
3	46	46	46	57	57	54
5	46	46	46	65	63	59
10	46	46	46	66	64	60
20	46	46	46	66	65	60
30	46	47	46	67	66	61
40	46	46	46	67	66	61
50	46	46	46	67	66	62
60	46	46	46	67	66	63
70	46	46	45	66	66	63
75	45	45	44	65	65	63
80	40	41	43	61	61	63
85	37	39	41	59	59	62
90	37	39	41	59	58	61
95	37	38	40	59	58	60
100	37	38	40	59	58	60

The phosphorus-containing modifiers are known to increase thermal stability and refractoriness of adhesive polymers. Then the DTA and TGA methods had been used in studying thermal stability of modified compositions. The thermooxidative destruction curves for ED-20 - DADPM and ED-20 - DADPM - GEPA systems are adduced at Figure 5. The phosphonates appear to enhance the compositions

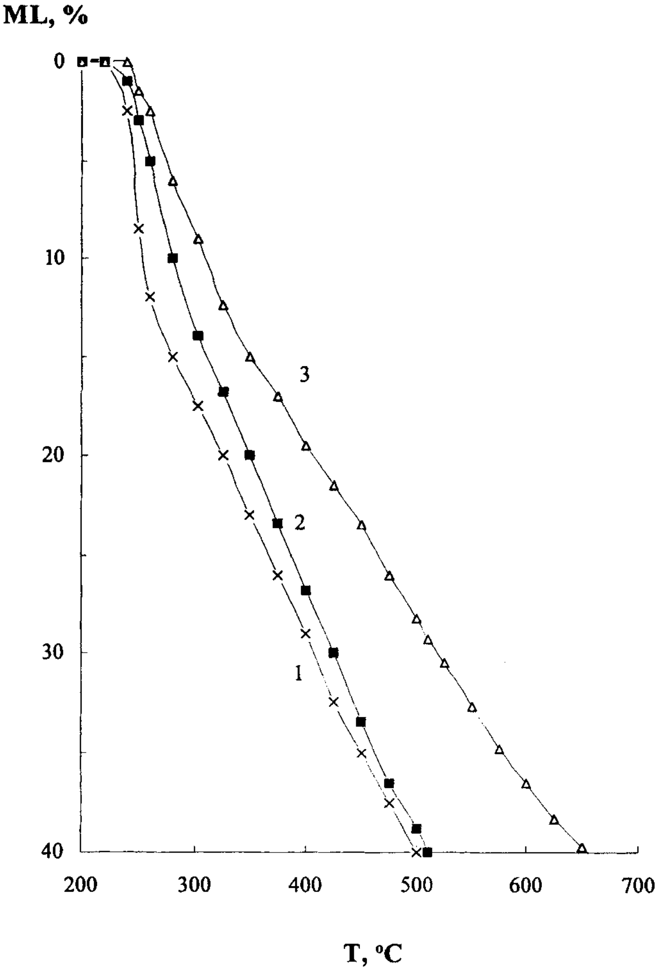

FIGURE 5 Mass loss, ML, curves obtained during air heating of DADPM-cured epoxy resins: ED-20 (1), ED-20 - 15% DGOP (2), ED-20 - 15% DGMP (3).

thermal stability to a greater extent than the phosphate do. Such a result is well within the data, known from literature [10]. A slight influence of compositions seaming hardness on thermal stability has also been established. The rate of burning, oxygen index values, the coke yield and burning mass loss were used to characterize the materials refractoriness (Figs. 6, 7).

The dependences of smoke number on modifiers phosphorus content for EO-GEPA compositions are inserted in Figure 8. The

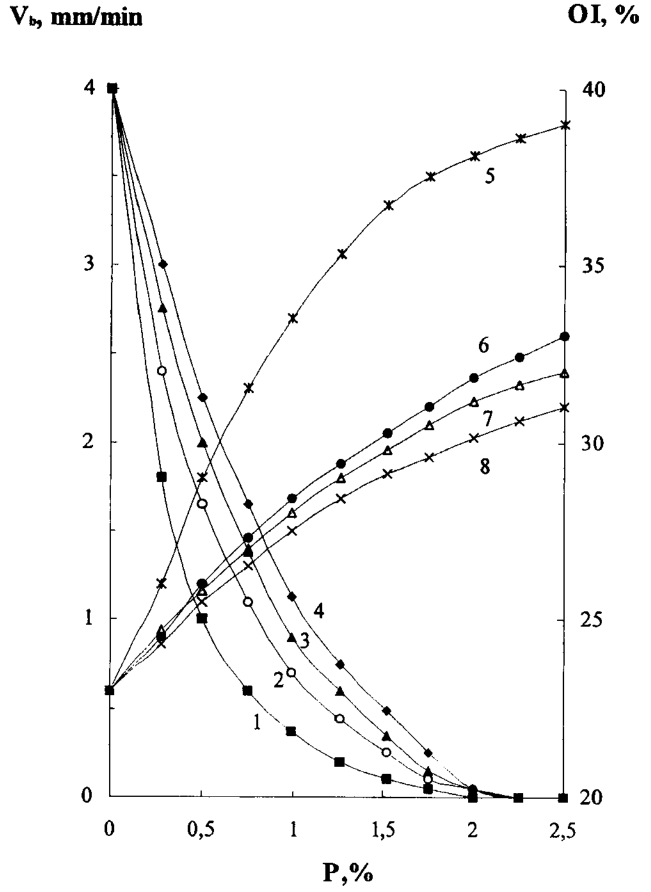

FIGURE 6 Influence of phosphorus content in GEPA on burning rate, V_b, (1 – 4) and oxygen index, OI, (5 – 8) of DADPM-cured epoxy compositions. GEPA: DGMP (1, 5), DGOP (2, 6), TGP (3, 7), MGP (4, 8).

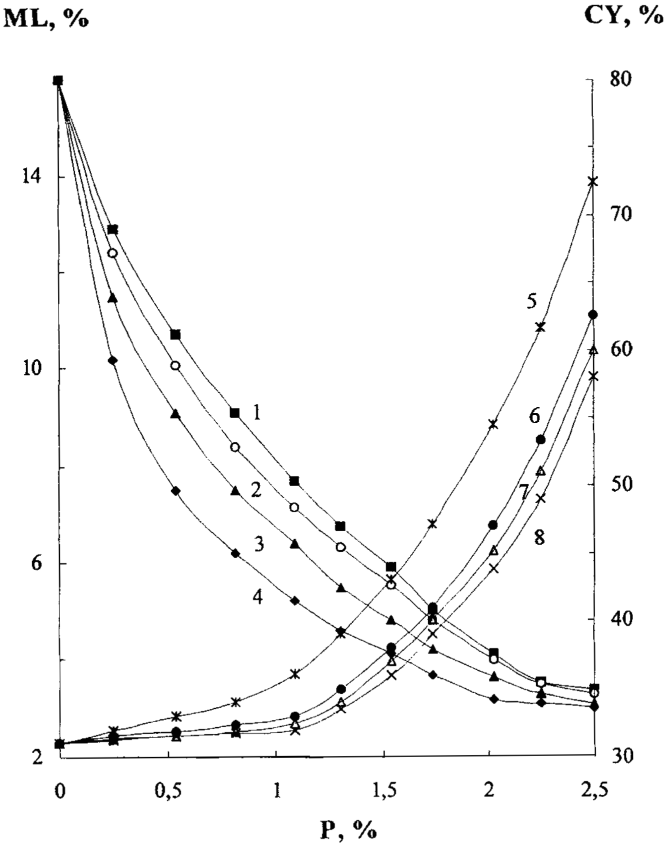

FIGURE 7 DADPM-cured epoxy compositions combustion mass loss, ML, (1–4) and coke yield, CY, (5–8) dependence on GEPA phosphorus content. GEPA: DGMP (1, 5), TGP (2, 6), DGOP (3, 7), MGP (4, 8).

effectiveness of smoke suppression enhances apparently through next row: MGP < DGOP < TGP < DGMP.

In summary it may be mentioned that the glycidylic ethers of phosphorus acids under study seems to be efficient and universal modifiers of epoxy resins. At olygomeric stage they reduce viscosity and elevate the wetting ability. Besides, on using amine hardening agents, they enhance rate and decrease temperature of curing. Cured compositions are marked by higher adhesive properties, thermal and

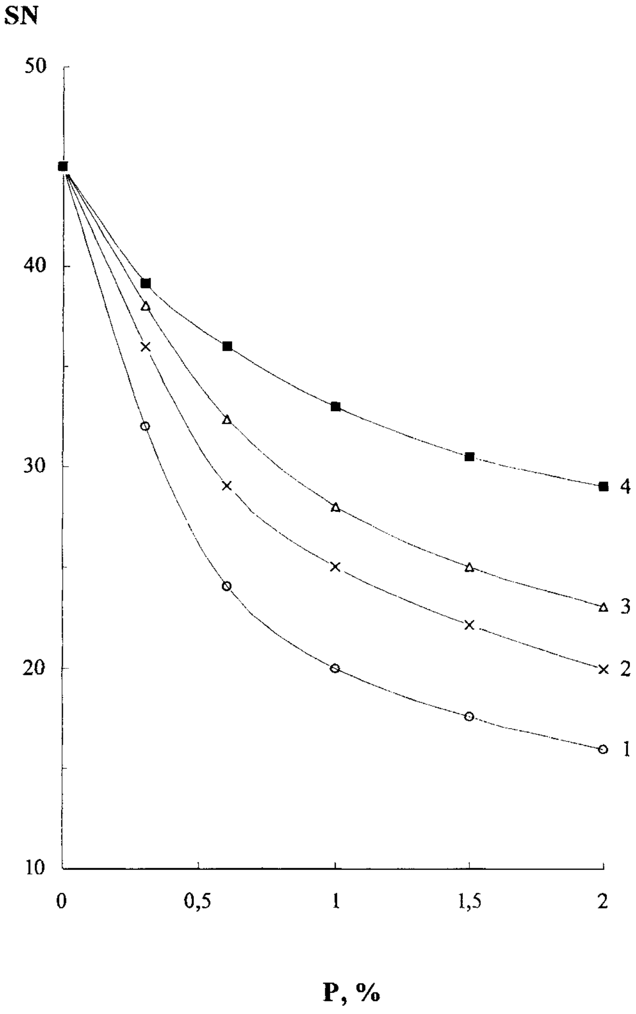

FIGURE 8 Influence of GEPA phosphorus content on smoke number, SN, of DADPM-cured epoxy resins. GEPA: DGMP (1), TGP (2), DGOP (3), MGP (4).

heat stability, refractoriness. The main characteristics of adhesives prepared on the basis of GEPA-modified ED-20 are presented in Table VI. The proposed optical adhesives appears to show a wide range of deflection index values, high adhesive properties, transmittance coefficient values.

TABLE VI Characteristics of optical adhesives on the basis of ED-20–GEPA–UP-0633M compositions

No.	*ED-20*	*GEPA, mass %*			n_D^{20}	*A**	*B***
		DGMP	*DGOP*	*TGP*			
1	100	5	–	–	1.572	98	20
2	100	10	–	–	1.570	99	24
3	100	50	–	–	1.551	99	21
4	100	100	–	–	1.535	99	20
5	50	100	–	–	1.517	99	18
6	10	100	–	–	1.509	99	17
7	0	100	–	–	1.499	99	17
8	100	–	5	–	1.570	98	21
9	100	–	10	–	1.567	99	25
10	100	–	50	–	1.549	99	22
11	100	–	100	–	1.530	99	21
12	50	–	100	–	1.513	99	20
13	10	–	100	–	1.501	99	18
14	0	–	100	–	1.491	99	18
15	100	–	–	5	1.571	98	23
16	100	–	–	10	1.569	99	29
17	100	–	–	50	1.552	99	31
18	100	–	–	100	1.533	99	32
19	50	–	–	100	1.515	99	33
20	10	–	–	100	1.506	99	34
21	0	–	–	100	1.497	99	34
22	100	–	–	–	1.544	97	18

* A – transmittance spectral coefficient of adhesive layer at $\lambda = 400-1000$ nm.

** B – adhesive strength at sapphier/sapphier breakaway, MPa.

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