

VARIOUS TECHNOLOGICAL  
PROCESSES

# Influence of Curing Conditions and Dibutyl Phthalate Concentration on the Properties of Cured Epoxy Resin

A. E. Tarasov, G. V. Malkov, M. L. Bubnova, Ya. I. Estrin, and E. R. Badamshina

*Institute of Problems of Chemical Physics, Russian Academy of Sciences,  
pr. Akademika Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia  
e-mail: atarasov@icp.ac.ru*

Received November 16, 2015

**Abstract**—The influence of the curing conditions and dibutyl phthalate additions on the physicomechanical properties of cured polyepoxides based on ED-20 resin and 4,4'-diaminodiphenylmethane curing agent was examined. An increase in the curing temperature over 150°C does not noticeably influence the physicomechanical properties of the cured resin, and keeping of the reaction mixture at 180°C for 12 h leads to a considerable decrease in the glass transition temperature of the polymer. Addition of dibutyl phthalate in concentrations of up to 10 wt % decreases the glass transition temperature of the polymer by 44°C, but with increasing concentration of dibutyl phthalate the elastic modulus increases and the breaking strain slightly decreases. The dependence of the ultimate strength on the dibutyl phthalate concentration passes through a maximum at 3 wt % dibutyl phthalate.

DOI: 10.1134/S10704272150120174

Considerable attention has been given recently to the effect of carbon nanotubes (CNTs), including functionalized CNTs, on the physicomechanical properties of cured epoxy resins and of composite materials based on them [1–4]. To reach the maximum uniform CNT distribution in a polymer matrix, nanotubes are used in many cases as dispersions in various organic media, prepared by ultrasonic treatment. As shown by Wang et al. [5], CNTs owing to  $\pi$ - $\pi$  donor-acceptor interaction well adsorb on their surface dialkyl esters of phthalates, especially dibutyl phthalate (DBP), which allows preparation of stable CNT dispersions in DBP and their use for modification of epoxy binders. However, to reliably distinguish the effect exerted on the physicomechanical properties of a cured epoxy resin specifically by CNTs, it is necessary to study and take into account the effect of “classical” factors (solvent additions, curing conditions, etc.) on the physicomechanical characteristics of an epoxy compound to which CNTs will be added.

For example, it is well known that the temperature history of curing significantly influences the glass transition temperature and physicomechanical characteristics of cured epoxy resin [6–8]. The influence of the cur-

ing conditions on the storage modulus and glass transition temperature, measured using dynamic mechanical analysis, was described in the literature for DER 332 resin (analog of ED-20) produced by Dow Chemical and cured with 4,4'-diaminodiphenylmethane (DDM) as example [9]. The variation of the monitored properties was found to correlate with the conversion of epoxy groups. However, because the curing history can significantly influence the physicomechanical and physicochemical parameters of cured epoxy resins [10], it is necessary to check always whether the chosen curing conditions are optimum for the given system of the resin and curing agent.

As noted in [11], plasticization of epoxy resins with dibutyl phthalate leads to a monotonic decrease in the strength, elastic modulus, hardness, volume resistivity, and glass transition temperature of the cured compounds. Thus, DBP additions exert a plasticizing effect owing to the presence of flexible and nonpolar aliphatic groups in the DBP molecule. It should be noted that the effect of DBP additions was mainly examined in the concentration interval ~5–30%. Detailed studies of the effect of small DBP additions (up to 5%) on the properties of cured epoxy resins are lacking.

This study deals with the influence of the curing conditions and of small dibutyl phthalate additions on the physicomechanical properties of cured epoxy resins based on ED-20 and 4,4'-diaminodiphenylmethane curing agent.

## EXPERIMENTAL

ED-20 epoxy-4,4'-isopropylidenediphenol resin [GOST (State Standard) 10587-84] was used without preliminary purification. The epoxide equivalent weight determined by  $^1\text{H}$  NMR spectroscopy [12] was 191.

4,4'-Diaminodiphenylmethane (Fluka, main substance content 97%) was used in a series of experiments on studying the influence of the curing conditions on the properties of the cured epoxy-amine compound based on ED-20/DDM. DDM was used without preliminary purification, amine equivalent 50.4 g g-equiv $^{-1}$ .

Technical-grade 4,4'-diaminodiphenylmethane (Tonox) was used in a series of experiments on studying the effect of small dibutyl phthalate additions on the properties of the cured epoxy-amine compound based on ED-20/DDM. The weight fraction of the amine (counting on main substance) was 99%, and the crystallization temperature was 87.5°C. The product was used without preliminary purification, amine equivalent 53.7 g g-equiv $^{-1}$ .

Dibutyl phthalate (DBP) corresponded to the supreme grade according to GOST 8728-88 and was used without preliminary purification.

A reactor equipped with a power-driven stirrer and a temperature-control jacket was charged with the epoxy resin and DBP in experiments in which its effect on the properties of the cured resin was studied. The epoxy resin or its mixture with DBP was thermostated at 90°C with continuous stirring and evacuation for 30 min. Then, a calculated amount of DDM was added, and the reaction mixture was stirred again until the DDM dissolved completely and was thermostated (90°C) for 5 min with evacuation to a residual pressure of 0.5–1 mmHg. After that, the ready reaction mixture was cast into preheated to 100°C silicone molds in the form of blades meeting the requirements of ASTM D638-02 Type V. The molds were placed in an oven in which the epoxy resin underwent curing at different temperatures.

The physicomechanical tests of the cured polymers were performed on a Zwick Z010 TC-FR010TH tensile-testing machine at a strain velocity of 1 mm min $^{-1}$ .

The dynamic mechanical analysis of cured epoxy resins was performed with a DMA 242 C device (Netzsch-Gerätebau GmbH, Germany) in the three-point bending mode ( $l = 20$  mm) with continuous temperature scanning from 20 to 200°C at a rate of 2 deg min $^{-1}$  in air. A sinusoidal oscillating force allowing the development of 30  $\mu\text{m}$  strain amplitude at a fixed frequency of 1 Hz was applied to the samples. The glass transition temperature of the samples was determined from the ordinate of the peak maximum in the  $\alpha$ -relaxation region in the temperature dependence of the mechanical loss tangent.

The molecular mass between cross-links  $M_c$  (amu) of the cured epoxy resin was determined from the empirical equation suggested by Nielsen [11, 13]:

$$\log_{10} E' = 7.0 + \frac{293\rho}{M_c},$$

where  $E'$  is the storage modulus at a temperature exceeding the glass transition temperature by 30°C (dyne cm $^{-3}$ ), and  $\rho$  is the polymer density (g cm $^{-3}$ ).

The density of the cured samples of the epoxy resins was determined with a pycnometer in silicone oil.

## RESULTS AND DISCUSSION

*Influence of curing conditions on the properties of the cured epoxy-amine compound based on ED-20/DDM.* In experiments on studying the influence of the curing conditions on the physicomechanical properties of the cured epoxy resin, we used the reaction mixture with the component ratio ensuring the stoichiometric ratio of the epoxy and amino groups. The cured epoxy resin with such ratio of reactive groups exhibits the maximal glass transition temperature. The reaction mixture was divided into seven portions, which were cured under different temperature conditions. This was done to exclude the influence of the component ratio and mixing conditions on the properties of the cured resin. We tested three series of curing conditions (Table 1): one-step (mode nos. 1–3), two-step (nos. 4, 5), and three-step (nos. 6, 7).

The results of testing the samples cured under different conditions are given in Table 1.

As can be seen, the physicomechanical characteristics vary insignificantly depending on the curing conditions: The elastic modulus varies in the  $\pm 4\%$  interval; the ultimate strength, in the  $\pm 3\%$  interval; and the rela-

**Table 1.** Influence of curing conditions on physicochemical parameters<sup>a</sup> of the cured compound based on ED-20/DDM 80°C, 72 h

Mode no.	Curing conditions	$E_{\text{mod}}$ , GPa	$\sigma_m$ , MPa	$\epsilon_m$ , %	$T_g$ , °C	$\rho$ , g cm <sup>-3</sup>	$E'$ , MPa	$M_c$ , amu
1	80°C, 72 h	2.66 ± 0.03	86.5 ± 0.6	5.7 ± 0.2	No data <sup>b</sup>	1.171	No data <sup>b</sup>	No data <sup>b</sup>
2	160°C, 6 h	2.41 ± 0.03	80.9 ± 1.0	7.1 ± 0.2	160	1.182	48	205
3	180°C, 6 h	2.35 ± 0.05	82.2 ± 0.7	7.6 ± 0.5	165	1.171	49	203
4	100°C, 3 h; 160°C, 2 h	2.34 ± 0.04	81.1 ± 1.5	7.0 ± 0.5	168	1.168	48	203
5	100°C, 3 h, 160°C, 6 h	2.26 ± 0.02	80.8 ± 2.3	7.0 ± 0.8	162	1.168	40	215
6	100°C, 3 h; 160°C, 2 h; 180°C, 2 h	2.34 ± 0.03	82.5 ± 1.0	8.08 ± 0.06	163	1.172	51	201
7	100°C, 3 h; 160°C, 6 h; 180°C, 12 h	2.40 ± 0.01	84.6 ± 0.6	7.5 ± 0.4	161	1.183	42	214

<sup>a</sup> ( $E_{\text{mod}}$ ) Elastic modulus, ( $\sigma_m$ ) ultimate strength, ( $\epsilon_m$ ) relative elongation at ultimate strength, and ( $T_g$ ) glass transition temperature.

<sup>b</sup> The glass transition temperature, storage modulus, and molecular mass between cross-links could not be determined because of the sample after polymerization in the course of the analysis.

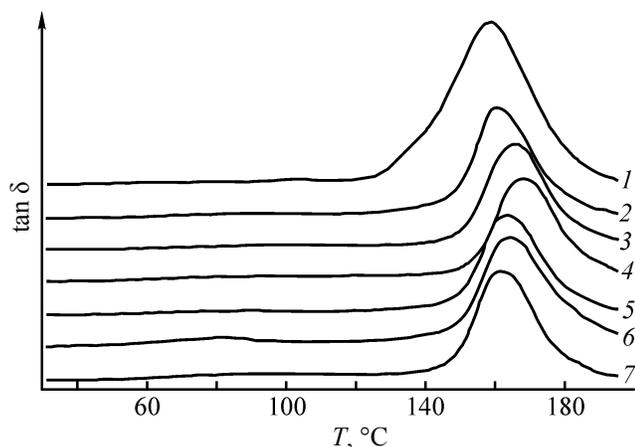
tive elongation, in the ±9% interval (without taking into account the sample cured in mode no. 1, because its curing was apparently incomplete). The influence exerted by variation of the curing conditions on the molecular mass between cross-links (±4%) and, correspondingly, on the glass transition temperature (±4°C) of the cured samples is also insignificant. It can be noted that only curing at a temperature higher than  $T_g$  of the final cured compound allows reaching the maximal network thickness (Table 1, mode no. 6).

In the one-step curing mode, the deformation and  $T_g$  increase with increasing curing temperature. The elastic modulus and  $M_c$  slightly decrease in this case, and the ultimate strength varies in the nonlinear fashion by no more than 10%. Going to multistep curing conditions is due to the fact that curing in the one-step mode can be accompanied by significant local overheating of the reaction mixture, especially when forming items of large volume, because the reaction of the epoxy ring opening is exothermic. Therefore, curing at a lower temperature, followed by aftercuring at the temperature higher than the glass transition temperature of the polymer, is justified. It should be noted, however, that in this study we prepared specimens 3 mm thick, and in this case we observed no significant differences between one- and

multistep curing. Curing in the multistep modes does not lead to significant changes in the physicochemical properties of the cured epoxy resin compared to one-step modes. However, the sample cured for 17 h, including 12 h at 180°C, is characterized by somewhat lower glass transition temperature, lower high-temperature storage modulus  $E'$ , and higher  $M_c$ . It should also be noted that the samples cured under these conditions are considerably darker than the samples cured under other conditions. This change in the sample color and a decrease in the glass transition temperature may be due to the onset of degradation when keeping the reaction mixture at 180°C for 12 h. In this connection, we believe that the after polymerization of the samples at 200°C, similarly to the conditions given in [4], is not appropriate, because in curing of ED-20 epoxy resin (analog of DER 332) under the action of DDM we failed to obtain a polymer with the glass transition temperature higher than 170°C as demonstrated in [4].

The results of dynamic mechanical analysis of samples cured under the examined conditions are compared in Fig. 1.

As can be seen, the peak in the  $\alpha$ -relaxation region in the temperature dependence of the mechanical loss tangent ( $\tan \delta$ ) for the sample cured in mode no. 1 is



**Fig. 1.** Mechanical loss tangent  $\tan \delta$  of samples of the compound based on ED-20/DDM, cured under different conditions, as a function of temperature  $T$ . (1–7) Mode nos. in Table 1.

considerably broader than the corresponding peaks for the other samples. This abnormal peak broadening is associated with the resumption of cross-linking reactions between epoxy and amino groups with increasing temperature in the course of the analysis [13]. These reactions stopped because of the fact that the glass transition temperature of the polymer exceeded the curing temperature, which led to a drastic decrease in the mobility of the reactive groups. As the temperature in the course of analysis became higher than the current glass transition temperature of the sample, the formation of the three-dimensional structure recommenced and continued until the sample temperature reached the maximum attainable glass transition temperature. For the other samples, the peak width is approximately equal, and only the positions of the peak maxima, corresponding to the glass transition temperature of the polymer, differ. In repeated analysis of the sample cured in mode no. 1, the width of the peak in the  $\alpha$ -relaxation region in the temperature dependence of the mechanical loss tangent decreased, and the peak maximum shifted toward higher temperatures to 163°C.

Close values of the glass transition temperature and storage modulus after curing under different conditions, except mode no. 1, suggest close cross-linking density and approximately equal extent of heterogeneity of the polymer network. Samples cured in mode nos. 5 and 7, according to the data of dynamic mechanical analysis, have lower cross-linking density and higher molecular mass between cross-links, compared to the other samples.

For further studies, we chose the sixth mode of curing because of the fact that it ensures, compared to the other modes, the maximal storage modulus and the minimal mass between cross-links at relatively short curing time. Such parameters suggest the maximal cross-linking density of the epoxy resin cured in this mode. On the other hand, the physicochemical parameters of this sample are comparable with those of the samples obtained under other curing conditions.

*Influence of small dibutyl phthalate additions on the properties of the cured epoxy–amine compound based on ED-20/DDM.* DBP is a widely used plasticizer for epoxy resins. It is known that, with increasing plasticizer concentration, the plasticizing effect can change to the antiplasticizing effect [5]. The manifestation of these effects is individual for each polymer–plasticizer pair. The antiplasticizing effect is manifested in a simultaneous increase in the elastic modulus and strength of the composite with the addition of filler exhibiting antiplasticizing effect. On the other hand, the glass transition temperature in this case decreases, as on adding a plasticizer.

In this study, we varied the DBP concentration from 0 to 10 wt % at a constant ratio of reactive groups,  $\text{NH}/\text{epoxide} = 1$ . Curing was performed in mode no. 6. The dependences of the physicochemical characteristics on the DBP concentration are given in Table 2.

When studying the influence of DBP additions on the properties of the cured epoxy resin, we used technical-grade DDM in which the fraction of functional amino groups in the p-position of the benzene ring was about 80%, in contrast to the DDM produced by Fluka and used in the first part of this study, in which the fraction of the functional amino groups in the p-position of the benzene ring was 97%. Technical-grade DDM is widely used as aromatic curing agent for epoxy resins, and it is considerably cheaper than its pure analog. Therefore, it is particularly interesting to compare the results of curing of the same epoxy resin with curing agents characterized by different content of the 2,2'- and 2,4'-isomers. Comparison of the results presented in Tables 1 (row 6) and 2 (row 1) shows that replacement of the curing agent exerts no appreciable influence on the properties of the cured epoxy resin, provided that the equivalent ratio of the amino and epoxy groups is kept. Variation of these characteristics on changing the curing agent grade does not exceed the uncertainty of their determination.

**Table 2.** Influence of DBP additions on the physicochemical parameters of the cured compound based on ED-20/DDM

DBP concentration, wt %	$E_{\text{mod}}$ , GPa	$\sigma_m$ , MPa	$\varepsilon_m$ , %	$T_g$ , °C	$\rho$ , g cm <sup>-3</sup>	$E'$ , MPa	$M_c$ , amu
0.0	2.39 ± 0.01	82 ± 1	7.5 ± 0.9	160	1.191	48	207
1.0	2.55 ± 0.05	84 ± 1	7.2 ± 0.4	150	1.190	48	207
2.0	2.50 ± 0.06	85.0 ± 0.8	6.8 ± 0.3	147	1.187	46	209
3.0	2.51 ± 0.05	85.5 ± 0.4	6.8 ± 0.2	142	1.192	45	212
5.0	2.59 ± 0.02	85.0 ± 0.4	6.6 ± 0.2	117	1.191	36	224
10.0	2.70 ± 0.02	81.9 ± 0.5	6.2 ± 0.1	116	1.187	38	220

Analysis of the influence of DBP additions on the properties of the cured epoxy resin shows that, up to a concentration of 3 wt %, DBP acts as antiplasticizer, because “abnormal” enhancement of the mechanical properties of the polymer in the glassy state is observed. Traditionally the antiplasticizing effect is characterized by a simultaneous increase in the strength and elastic modulus of the glassy polymer with a monotonic decrease in  $T_g$ . It should be noted that this effect has not been described previously for systems consisting of DBP, epoxy resin, and aromatic amine as high-temperature curing agent. This is caused by the fact that, in the studies of the influence of DBP additions on the properties of cross-linked systems, DBP was taken in appreciably larger amounts, 5–30% [9].

It is also seen from Table 2 that, as the DBP concentration is increased further, the strength of the cured system decreases, although the elastic modulus continues to increase up to a DBP concentration of 10 wt %. With increasing DBP concentration from 0 to 10 wt %, the glass transition temperature and breaking strain decrease, whereas the molecular mass of inter-cross-link chain segments increases.

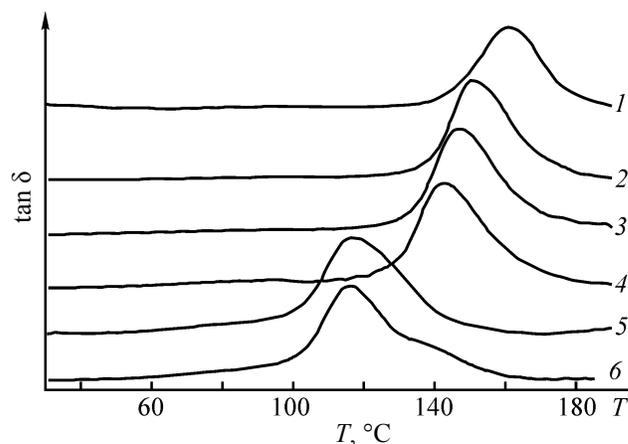
Thus, despite the fact that DBP is characterized in [9] as reference plasticizer exhibiting no antiplasticizing properties, the results of our study show that DBP is an antiplasticizer at low concentrations, as in the case of its small additions to the Epikote 828–ethylenediamine system [14].

The results of studying samples with different DBP content by dynamic mechanical analysis are shown in Fig. 2. As can be seen, the  $\alpha$ -relaxation region at DBP concentrations of 5 and 10 wt % is broader than for the other samples, and a second maximum appears. Such a pattern is usually attributed either to the presence of heterogeneities in the polymer matrix or to resumption

of curing, as in the case of curve 1 in Fig. 1. In this case, most probably, there are domains with different density of cross-linking of polymer chains in the matrix. The formation of such domains may be due to phase segregation, and with increasing DBP concentration the relative content of domains with increased plasticizer content changes.

## CONCLUSIONS

Variation of conditions in curing of the epoxy–amine compound based on ED-20/4,4'-diaminodiphenylmethane does not lead to significant changes in the physicochemical parameters of the cured samples. Variation of the isomeric composition of the curing agent leads only to a slight change in the glass transition temperature of the cured compound and does not noticeably influence its physicochemical characteristics. Dibutyl phthalate, when added to a concentration of 3–5 wt %, exerts



**Fig. 2.** Mechanical loss tangent  $\tan \delta$  of samples of the cured epoxy–amine compound based on ED-20/DDM as a function of temperature  $T$ . DBP concentration, wt %: (1) 0, (2) 1, (3) 2, (4) 3, (5) 5, and (6) 10.

antiplasticizing effect, which should be taken into account when studying the effect of small concentrations of nanotubes added into the compound in the form of a suspension in dibutyl phthalate.

#### ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 13-03-12164 ofi\_m).

#### REFERENCES

1. Badamshina, E.R., Gafurova, M.P., and Estrin, Y.I., *Russ. Chem. Rev.*, 2010, vol. 79, no. 11, pp. 945–979.
2. Spitalsky, Z., Tasis, D., Papagelis, K., and Galiotis, C., *Prog. Polym. Sci.*, 2010, vol. 35, no. 3, pp. 357–401.
3. Tasis, D., Tagmatarchis, N., Bianco, A., and Plato, M., *Chem. Rev.*, 2006, vol. 106, no. 3, pp. 1105–1136.
4. Valenkov, A.M., Gofman, I.V., Nosov, K.S., et al., *Russ. J. Appl. Chem.*, 2011, vol. 84, no. 5, pp. 735–750.
5. Wang, F., Yao, J., Sun, K., and Xing, B., *Environ. Sci. Technol.*, 2010, vol. 44, no. 18, pp. 6985–6991.
6. Chang, S.-S., *Polymer*, 1992, vol. 33, no. 22, pp. 4768–4778.
7. Wisanrakkit, G., Gillham, J.K., and Enns, J.B., *J. Appl. Polym. Sci.*, 1990, vol. 41, nos. 7–8, pp. 1895–1912.
8. Montserrat, S., *J. Therm. Anal.*, 1991, vol. 37, pp. 1751–1758.
9. Sanz, G., Garmendia, J., Andres, M.A., and Mondragon, I., *J. Appl. Polym. Sci.*, 1995, vol. 55, no. 1, pp. 75–87.
10. Chang, S.-S., in *37th Int. SAMPE Symp. and Exhibition "Mater. Work. for You 21st Century,"* Anaheim, California, March 9–12, 1992, Covina, California, 1992, pp. 358–368.
11. Khozin, V.G., *Usilenie epoksidnykh polimerov* (Reinforcement of Epoxy Polymers), Kazan: Dom Pechati, 2004.
12. Garcia, F. and Soares, B., *Polym. Test.*, 2003, vol. 22, no. 1, pp. 51–56.
13. Kenyon, A.S. and Nielsen, L.E., *J. Macromol. Sci., Part A: Chemistry*, 1969, vol. 3, no. 2, pp. 275–295.
14. Hata, N., Yamauchi, R., and Kumanotani, J., *J. Appl. Polym. Sci.*, 1973, vol. 17, no. 7, pp. 2173–2181.