ISSN 1995-4212, Polymer Science, Series D, 2024, Vol. 17, No. 3, pp. 745–747. © Pleiades Publishing, Ltd., 2024.
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Properties of Epoxy Matrix Modified with Boron Nitride

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Received December 1, 2023; revised December 12, 2023; accepted December 25, 2023

Abstract—The viscoelastic properties of epoxy polymers modified with hexagonal boron nitride are studied in this work. The calculated elastic modulus is compared with its experimental value. It was found that boron nitride does not significantly influence the glass transition temperature of epoxy polymers.

Keywords: epoxy resin, boron nitride, Voigt equation, mechanical loss tangent, glass transition temperature

DOI: 10.1134/S1995421224701284

Epoxy resins are often used in domestic industry as the basis for composite materials, including dispersed–filled ones [1, 2]. The physical and mechanical properties of such materials (for example, an elastic modulus) are mainly defined by a filler and depend slightly on characteristics of a binder. On the other hand, the thermophysical properties (for example, glass transition temperature) are determined by those of a polymer matrix [3].

One of the promising fillers to create dispersed–filled composites is boron nitride, which can increase the adhesive strength of epoxy polymers by two to three times [4] and increase the thermal conductivity of adhesive epoxy resin joints [5]. In addition, boron nitride can also act as a modifier for tribological purposes, which will significantly expand the use of epoxy polymers in mechanical engineering [6, 7].

When epoxy resins are modified and filled, it is important to maintain the glass transition temperature at high level; this is not always possible when dispersed additives are used. It was shown that the incorporation of boron nitride allows one to maintain the thermophysical properties of epoxy polymers together with an improvement in physical and mechanical characteristics [8].

The aim of this work is to develop epoxy polymers filled with boron nitride.

ED-20 epoxy diane oligomer (GOST (State Standard) 10587–84) was used in this work, and 4,4'-diaminodiphenylsulfone (DADPS, TU 6-14-17–95) (30 pts wt of DADPS per 100 pts wt of ED-20) was used as a hardener. Hexagonal boron nitride (BN, TU 2112-003-49534204–2002) introduced into the epoxy resin in amounts of 20, 40, and 60 pts wt was used as a modifier for the epoxy resin. BN and hardener were mixed with epoxy oligomer on an overhead mixer to provide the uniform distribution of the components. Curing was performed in a heating oven at 180°C for 8 h.

The viscoelastic properties of the polymers were studied according to GOST (State Standard) 56753–2015 and a three-point loading scheme on a NETZSCH DMA Gabo Eplexor device with a heating rate of 2°C min^{-1} and a frequency of 1 Hz.

A relationship between storage modulus G' and the temperature was established during the dynamic mechanical analysis (DMA) process (Fig. 1). The storage modulus, which in its physical sense is an elastic modulus, increases approximately by two to four times with an increase in an amount of boron nitride from 20 to 60 wt pts in the epoxy polymer, which is due to the high elastic modulus of boron nitride, which is 34 GPa (Young's modulus). The shear modulus, how-

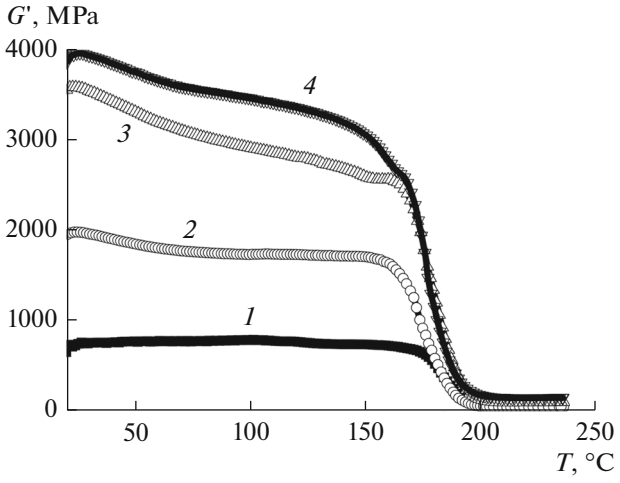

Fig. 1. Relationship between elastic modulus (G') and temperature of epoxy polymers: (*1*) ED-20 + DADPS, (*2*) ED-20 + BN (20 wt pts) + DADPS, (*3*) ED-20 + BN (40 wt pts) + DADPS, and (*4*) ED-20 + BN (60 wt pts) + DADPS.

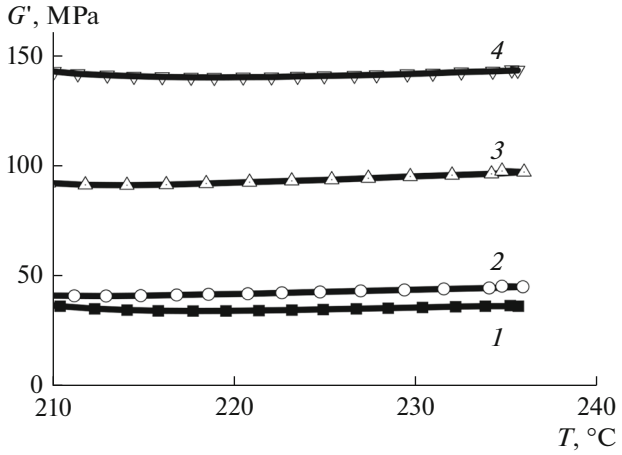

Fig. 2. Relationship between high-elasticity modulus (G') and temperature of epoxyamine binders: (*1*) ED-20 + DADPS, (*2*) ED-20 + BN (20 wt pts) + DADPS, (*3*) ED-20 + BN (40 wt pts) + DADPS, and (*4*) ED-20 + BN (60 wt pts) + DADPS.

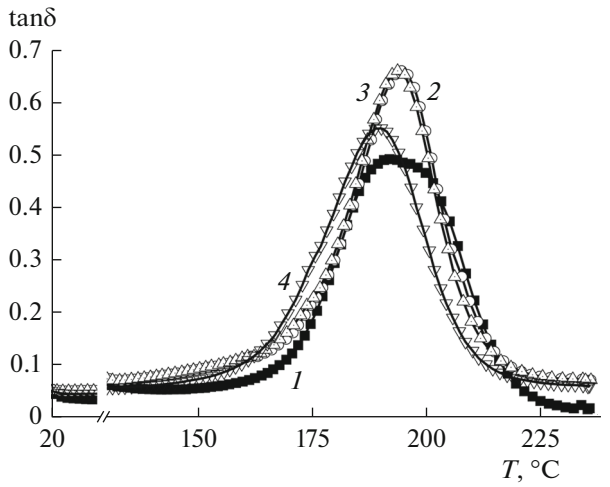

Fig. 3. Relationship between mechanical loss tangent (tanδ) and temperature of epoxyamine binders: (*1*) ED-20 + DADPS, (*2*) ED-20 + BN (20 wt pts) + DADPS, (*3*) ED-20 + BN (40 wt pts) + DADPS, and (*4*) ED-20 + BN (60 wt pts) + DADPS.

ever, was detected during DMA in this work, and it is necessary to recalculate the modulus for BN through its Poisson's ratio (0.21) according to Eq. (1):

$$G = E/2(1 + \mu), \quad (1)$$

where G is shear modulus (in GPa), E is Young's modulus (in GPa), and μ is Poisson's ratio. Then, the shear modulus for boron nitride appears to be 14 GPa.

It is possible to calculate the theoretical modulus of elasticity of a composite material according to Voigt (2) and Royce (3) if the densities of boron nitride (2.1 g cm^{-3}) and ED-20 + DADPS (1.2 g cm^{-3}) determined by hydrostatic weighing are known (Table 1).

$$G^* = G_f\varphi_f + G_m\varphi_m, \quad (2)$$

$$1/G^* = 1/G_f/\varphi_f + 1/G_m/\varphi_m, \quad (3)$$

where G^* is the modulus of a composite material (in GPa), G_f the modulus of a filler (in GPa), φ_f the volume fraction of a filler, G_m the modulus of a matrix (in GPa), and φ_m the volume fraction of the matrix [9].

The data indicate that the elastic modulus of the composite material consisting of ED-20 and boron nitride, calculated according to Voigt, coincides satisfactorily with the experimental elastic modulus at temperatures from 70 to 155°C (Fig. 1). This temperature range can be considered as the most probable during operation with such composite materials.

It is known that the modulus, being higher than the glass transition temperature, is the high-elasticity modulus (G'_∞), which is related to the cross-linking parameters by relationship (4). This indicates that, the higher the high-elasticity modulus, the higher the degree of curing in the thermoset.

$$G' = RT/M_0, \quad (4)$$

where G'_∞ is the high-elasticity modulus (MPa), ρ is the density (g cm^{-3}), R the universal gas constant (J K^{-1} mol^{-1}), T is the temperature (K), and M_0 is the molecular weight of a chain section between the cross links of the epoxy resin (g mol^{-1}).

Figure 2 shows a relationship between the modulus of high elasticity of composite materials and the temperature. The high-elasticity modulus also increases by approximately 50–100 MPa after the introduction of 40–60 wt pts of BN into ED-20. This observation, however, is not due to the cross-link density. This is seen, first of all, from the slight change in the glass transition temperature of epoxy polymers modified with BN, because an increase in the glass transition temperature would be expected with a significant increase in degree of curing. Second, boron nitride is a refractory material (its melting point is about 3000°C), so that it does not undergo any phase or

Table 1. Calculations of elastic modulus

Sample	Calculated Voigt modulus, GPa	Calculated Royce module, GPa
ED-20 + BN (20 wt pts) + DADPS	1.84	0.86
ED-20 + BN (40 wt pts) + DADPS	2.72	0.93
ED-20 + BN (60 wt pts) + DADPS	3.60	1.00

Table 2. Glass transition temperature of epoxy polymers

Sample	According to the elastic modulus, °C	According to the mechanical loss tangent, °C
ED-20 + DADPS	170	194
ED-20 + BN (20 wt pts) + DADPS	165	195
ED-20 + BN (40 wt pts) + DADPS	168	194
ED-20 + BN (60 wt pts) + DADPS	166	189

relaxation transitions in the temperature range studied by DMA (20–235°C). As a result, an increase in modulus higher than the glass transition temperature during the introduction of boron nitride can also be explained by the interaction between the filler and the epoxy polymer.

When dynamic mechanical analysis was performed, a relationship between the mechanical loss tangent (tan δ) and temperature was also established (Fig. 3, Table 2). The temperature at which the transition from the glassy to highly elastic state is completed was found from the maximum mechanical loss tangent, and the average glass transition temperature was determined from the elastic modulus.

Table 2 indicates that boron nitride slightly decreases the glass transition temperature of the epoxy polymer. This is probably due to the fact that the introduction of a dispersed modifier, on the one hand, leads apparently to the formation of a hard interphase layer at the polymer–filler interface, while, on the other hand, a decrease in mobility of the system probably leads to its undercuring, so that the glass transition temperature in the filled system does not increase. This is also clear from the high tanδ maximum value, which characterizes the mobility of the system in a highly elastic state.

CONCLUSIONS

It was found that the introduction of hexagonal boron nitride in an amount of 60 wt pts into the epoxy matrix allows one to increase the elastic modulus of the filled system up to 4000 MPa. The Voigt equation makes it possible to calculate the elastic modulus of a mixture of ED-20 and boron nitride, comparable with experimental data. It was shown that the glass transition temperature of epoxy polymer decreases by 2–5°C in the filled systems compared to unfilled ones. The resulting modified epoxy systems can be used in tribotechnical compositions that operate under high temperatures and loads.

FUNDING

This work was supported by ongoing institutional funding. No additional grants to carry out or direct this particular research were obtained.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. M. L. Kerber, *Polymer Composite Materials: Structure, Properties, Technology*, 5th ed., Ed. by A. A. Berlin (Professiya, St. Petersburg, 2019) [in Russian].
2. D. S. Tikhonova, A. Yu. Abramochkin, A. S. Borodulin, V. A. Nelyub, and G. V. Malysheva, "A neural network approach to processing photos of carbon-fiber-reinforced polymer microstructures for their further diagnostics," Polym. Sci., Ser. D **16**, 307–312 (2023).
3. I. D. Simonov-Emelyanov, A. A. Pykhtin, A. A. Glebova, and A. N. Kovaleva, "Injection molding of products from dispersed-filled polymer composite materials with different types of structures," Vse Mater. Entsikl. Sprav., No. 10, 2–8 (2023).
4. S. N. Gorbacheva, I. Yu. Gorbunova, M. L. Kerber, and S. V. Antonov, "Properties of composite polymer materials based on epoxy resin modified with boron nitride," Usp. Khim. Khim. Tekhnol. **31**, 35–36 (2017).
5. S. N. Gladkikh, I. V. Tkachenko, G. P. Shusherina, V. V. Mironovich, T. A. Islentyeva, and E. V. Vishnevskaya, RU Patent No. 2561201 (2015).
6. S. V. Gruby and V. V. Lapshin, "Study of the cutting properties of boron nitride cutters," Mashinostr. Kompyut. Tekhnol., No. 06, 5 (2012).
7. E. Yu. Vasinkina, E. V. Plakunova, Yu. A. Kadykova, and S. G. Kalganova, "Study of the influence of basalt and boron nitride on the properties of a plasticized epoxy binder," Polim. Mater. Tekhnol. **8**, 39–43 (2022). https://doi.org/10.32864/polymmattech-2022-8-2-39-43
8. A. S. Mostovoy and A. N. Ledenev, "Modification of epoxy polymers with hexagonal boron nitride," Vopr. Materialoved., No. 1, 147–154 (2017).
9. V. T. Erofeev, A. S. Tyuryakhin, and T. P. Tyuryakhina, "Multitudes of Voigt–Reuss forks and Voigt-Christensen-Reuss tridents," Struct. Mech. Eng. Const. Build. **16**, 323–333 (2020).

Translated by A. Tulyabaew