Nanofiller-Modified Epoxy Oligomers as Binders for Reinforced Plastics

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ABSTRACT

The methods of physico-chemical modification that allow to regulate stress-strain, technological and operational properties of epoxy binders are considered. It is shown that the acid-base characteristics of the surface of nanofillers affect the curing process of epoxy compositions.

KEYWORDS: Epoxy Oligomers, Nanofillers, Aluminum Oxide Nanotubes, Cnts, Organomodified Montmorillonite, Modification.

INTRODUCTION

The main objective of the study is to develop a modified curing system to produce a high-strength epoxy binder for reinforced plastics. Requirements for the binder: the average curing temperature is not higher than 95 °C and long working life of uncured binder. To regulate the physical, mechanical and operational properties of the binder, the latent hardener and several nanomodifiers were used.

Analysis of scientific literature has shown that there is a large number of works devoted to the study of epoxy oligomers modified by nanomodifiers, and that these studies have been conducted for a long time [1-6]. This method of modification of epoxy oligomers makes it possible to regulate strength, elastic-deformation and operational properties of epoxy binders and composites within a wide range.

A lot of difficulties and disadvantages arise when using epoxy oligomers: high exothermic effect of reactions leads to a spontaneous increase in temperature during curing and processing; many epoxy systems are characterized by a short working life and instability of technological properties; irregularity of curing in the presence of nanofillers is also a problem. Thus, formation of end structures with necessary properties is a complex physicochemical process. Regulation of structure and properties of epoxy oligomers during curing and creation of composites with a given set of properties is a serious matter. Here we describe the method for improving the properties of epoxy binders by introducing a nanofiller into a binder through a slurry.

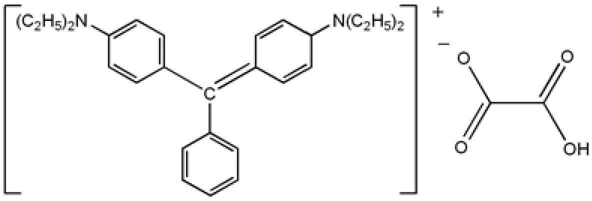
MATERIALS AND METHODS

The epoxy oligomer ED-20 (mass fraction of epoxy groups – 22,1 %, viscosity at 25 ºC – 9 Pa·s) and latent nitrogen-containing hardener (solid crystalline substance, pH = 8,7) were used as the main components of the binder.

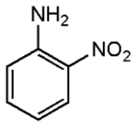
It is known that properties of reinforced plastics based on epoxy binders can be varied within a wide range. One of the ways to obtain some specific properties and to improve technological and operational properties of epoxy binders is modification. The influence of aluminum oxide nanotubes (ANT), carbon nanotubes (CNTs), and organomodified montmorillonite (OM) on the properties of epoxy binder was investigated. The nanofillers were dispersed in ED-20 by ultrasonic action to obtain a stable 20% suspension. Then, this suspension was added to epoxy binder in the required amount.

The acid-base properties of the surface of nanofillers were studied by the indicator method. This method is based on the fact that an indicator adsorbs on the surface of a solid phase and changes the color, which is a measure of the acidity (basicity) of the active centers on the surface [7]. The acid-base force of the surface of an adsorbent can be assessed by observing the change in the color of indicators in a certain range of pKa values. To determine the acid-base properties of nanomodifiers, the following indicators were used:

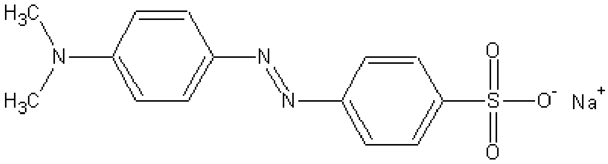
1. Brilliant green [tetraethyl-4,4-diaminotriphenylmethane oxalate]; conversion from green to yellow at pH = 0,1 - 2,6.



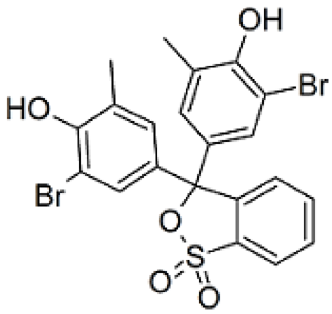
1. o-nitroaniline (1-amino-2-nitrobenzene); conversion from red-orange to light yellow at pH = 2,0 – 4,0



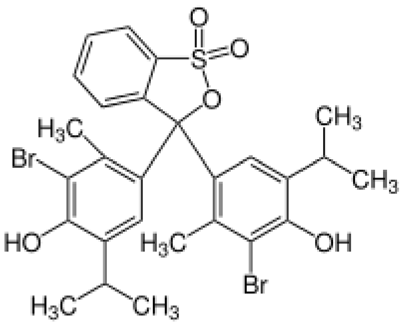
3. Sodium methyl orange [4-(4-dimethylaminophenylazo) benzenesulfonate]; conversion from red to orange-yellow at pH = 3,1 - 4,4.



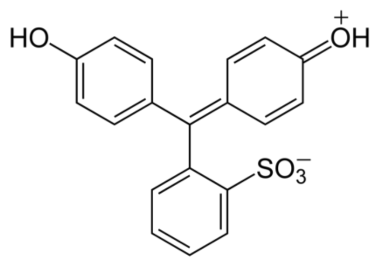
4. Bromocresol purple [dibromo-o-cresol sulfophthalein]; conversion from yellow to bright red at pH = 5,2 - 6,8.



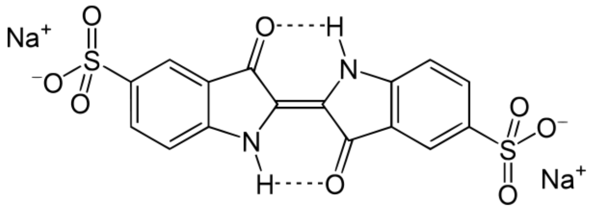
5. Bromothymol blue [3',3'-dibromothymolsulfophthalein]; conversion from yellow to blue at pH = 6,0 - 7,6.



6. Phenolic red [phenol sulfophthalein, phenolrot, sulfental]; conversion from yellow to bright red at pH = 6,5 - 8,0.



7. Indigocarmine [disodium salt of indigo-5,5'-disulfonic acid]; conversion from blue to yellow at pH = 11,6 - 14,0.



The content of active centers of a given acid strength, equivalent to the amount of the adsorbed indicator (q_{pKa}), is calculated by the formula 1:

$$q_{pKa} = \frac{C_{Ind} \cdot V_{Ind}}{D_0}\left(\frac{D_0 - D_1}{m} + \frac{D_0 - D_2}{m}\right) \quad (1)$$

where C_{Ind} – concentration of indicator solution, mg/ ml;
V_{Ind} – volume of indicator solution taken for analysis, ml;
D_0 – optical density of the "dummy" experiment;
D_1 – optical density of indicator solution before adsorption;
D_2 – optical density of the indicator solution after adsorption;
m – weight of indicator.

The magnitude of the residual stresses in the cured binder was determined by the cantilever beam method. The tested binder was applied to rectangular steel substrates with the thickness of 0.35 mm. These substrates were fixed in clamps parallel to a reference steel plate of 2 mm thickness. The initial distance between the steel substrate and the metal plate of each clamp was measured by an optical method. After that the clamps were placed in a heating chamber and held in accordance with the chosen time-temperature curing regime. Every hour, the distance between the steel substrate and the reference steel plate of the clamp was measured. The residual stresses (δ) that arose in the binder were calculated according to the formula 2:

$$\delta = \frac{hE\delta_1^3}{3l^2\,(\delta_1 + \delta_2)\delta_2 \cdot (1-\mu^2)} \quad (2)$$

where *E* – storage modulus of steel (200 GPa);
δ_1 – thickness of the steel substrate, cm;
δ_2 – thickness of the binder film, cm;
μ – Poisson's ratio;
l – length of the free end of the substrate, cm;
h – deviation of the free end of the substrate.

RESULTS AND DISCUSSION

Surface activity of the nanofillers, as well as the influence of their surface properties on the adhesion of epoxy binder, was investigated.
According to the proton theory of Brönsted, acid centers are proton donors, and base centers are proton acceptors. A distinctive feature of the electronic theory of Lewis is that acid centers interact with the basic ones to form a donor-acceptor bonds.

The surface of the nanofillers creates conditions for adsorption interaction with active acidic centers of Brönsted (pKa ≤ +1.5), the amount of which on the surface of ANT is much larger. Observing the change in the color of the indicators in a certain range of pKa values, it is possible to estimate the acid-base force of the solid surface (nanofiller). The results are shown in Table 1.

Table 1. Distribution of acid-base centers on the nanofiller surface

pKa	The number of active centers on the surface of ANT, q $*10^7$, mol/g	The number of active centers on the surface of OM, q $*10^7$, mol/g
-0,2	12,3	10,3
+1,8	125,6	10,4
+3,8	98,5	16,5
+6,0	38,5	12,4
+7,9	12,4	87,6
+8,0	6.0	90,5
+12,5	6.4	128,7

A significant increase of Brönsted basic centers (pKa = + 12.5) on the OM surface in comparison with ANT is associated with the hydrolysis of adsorbed octadecyl ammonium chloride molecules. This is also confirmed by an increase in the pH of the aqueous extract of OM (pH = 8.2).

The dependence of the residual stresses (σ) on the curing time (t) of the binders based on the epoxy oligomer is shown in Fig. 1.

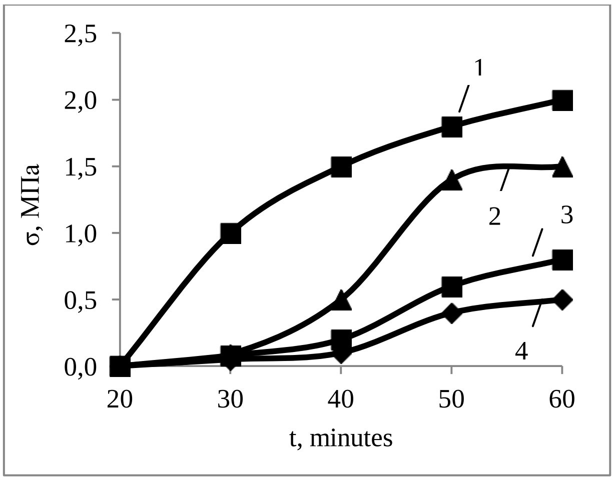


Fig. 1. Residual stresses of epoxy binders (σ) vs curing time (t) at T= 80 °C:
1 – without nanofiller; 2 – 0,5 wt. p. of CNTs; 3- 0,5 wt. p. of OM; 4 – 0,5 wt. p. of ANT

Curing process was carried out at a T = 80 ° C. Under these conditions, lattice structures are formed in the cured epoxy binder, the density of which increases with the time of exposure at elevated temperature. The residual stresses were increased during curing of ED-20. The introduction of nanofillers up to 0.5 weight parts (wt. p.) for 100 wt. p. of ED-20 leads to stress relaxation and increase of stress-strain properties of modified binder. Probably, the nanosized modifier is introduced into the free volume formed in the epoxy binder after curing, as well as into microcracks and defective areas of the cured material. As a result - decrease in the level of residual stresses.
The influence of nanofillers on the properties of epoxy binders has been studied (Table 2).

Table 2. Properties of cured materials based on modified epoxy binder

Показатели	Modifier			
	Without modifier	OM	ANT	CNTs
Working life, min	65	60	35	60
Glass temperature, ^{0}C	56	68	73	50
Flexural strength, MPa	30	33	48	30
Compressive strength, MPa	73	70	68	65
Impact strength, kJ/m^2	15	17	14	14
Adhesive strength, MPa	10	12	15	10
Water absorbtion, %	0,70	0,06	0,09	0,20
Open porosity, %	1,3	0,6	0,8	0,9

CONCLUSION

The use of nanosized modifiers leads to a change in the character of the structuring of the epoxy oligomer. The acid-base characteristics of the surface of nanofillers can influence the curing process of the epoxy oligomer. Acid centers on the surface of aluminum oxide nanotubes determine its catalytic properties. It has been established that nanomodified binders exhibit good operational properties and are characterized by a reduced level of residual stresses.

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