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TECHNOLOGICAL PROPERTIES OF NANODISPERSIONS BASED ON DER-330 EPOXY RESIN AND BS-50 FUMED SILICA

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The influence of silica dioxide nanoparticles in the form of fumed silica BS-50 on the rheological properties, residual shrinkage and shrinkage stresses upon curing an epoxy resin is considered. It is shown that the introduction of BS-50 in the optimum concentration of nanoparticles into DER-330 epoxy resin results in agglomeration, which is accompanied by an abnormal behavior of the disperse system with a decrease in viscosity by ~ 25%, ultimate shrinkage by ~ 15% and the level of residual stresses by a factor of ~ 4–10. These properties are manifested when the concentration of fumed silica is 0.05 vol. % The introduction of fumed silica slows the rise of residual stresses and increases the induction period from 2 to 4 hours. Depending on the mode of curing the minimum residual stress is observed at different concentrations of BS-50. At temperatures of 30°C and 50°C concentration was 0.5 vol. %, and at 70°C – 0.05 vol. %. Curing at 30°C and 50°C result in a fall of residual stress by a factor of 12 and 4, respectively, at 70°C, by a factor of 4.

Keywords: *epoxy resin, nanoparticles, fumed silica, nanocomposite.*

Introducing nanofillers allows to regulate the physicomechanical characteristics of disperse filled nanocomposite materials (DFNCM), as well as their radio transparency, electrophysical, membrane and other special characteristics [1–4]. Various types of carbon nanotubes, fullerenes, graphenes, astralenes, technical carbon, as well as titanium and silicon dioxides, nanodiamonds etc are widely used as nanofillers [5, 6].

This work presents results of a study on the influence of carbon white BS-50 concentration on the rheological properties of an epoxy oligomer, its shrinkage and residual stress upon hardening.

Experimental

Low-viscous epoxydianic oligomer DER-330 produced by Dow Chemicals was chosen as a polymeric matrix. Its characteristics are as follows: viscosity 7–10 Pa·s; density 1.15–1.17 g/cm^3; mass fraction of epoxide groups 23.2–24.4%; three-fractional composition with the content of the first low-molecular fraction 92% and the content of associates no more than 5% vol.) This oligomer has practically no initial heterogeneity.

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Triethylenetetramine (TETA) produced by Dow Chemicals (viscosity 30 mPa·s, density 0.995 g/cm^3, equivalent mass of amino groups 24 g/eq) characterized by stable properties was used for the hardening of epoxy nanosystems. The quantity of the hardener for the hardening of DER-330 was calculated on the basis of the stoichiometric equality of epoxy and amino equivalents.

Carbon white (silicon dioxide) BS-50 (GOST 18307-78, BSK company, Russia) was chosen as a nanofiller. The diameter of its particles was ~ 45 nm; specific surface 50 m^2/g; bulk weight 0.23 g/cm^3; real density 2.3 g/cm^3; φ_{max} parameter (particles packing, the maximum fraction of the filler) ~ 0.2 parts by volume.

The distribution of BS-50 nanoparticles and their sizes in liquid epoxy oligomer DER-330 were judged by turbidity spectra and Heller's curve by means of a KFK-2 colorimeter [7–9].

The influence of BS-50 concentration on the rheological properties of the binding agent based on epoxy oligomer DER-330 was studied with the use of a rotation viscometer (Brookfield R/S rheometer).

Nanocomposites were hardened for 24 h at 20°C. Their shrinkage was determined by the dilatometric technique developed at the department of chemistry and technology for processing plastic and polymeric composites of the Moscow technological university (Institute of fine chemical technologies) [10].

The kinetics of residual stress increase was studied with the use of the console method (A.T. Sanzharovsky method) on a glass substrate at 30, 50 and 70°C [11].

Results and Discussion

One of problems of introducing nanoparticles into viscous polymeric binding agents is their agglomeration and non-uniform distribution in the bulk of the dispersion medium depending on concentration.

In order to ensure uniform distribution of the nanoparticles in the bulk of the epoxydianic oligomer (without hardener) the method of fractional introduction was used. For this purpose the following operations were sequentially performed. A 1% dispersion of the nanoparticles in the epoxy oligomer was prepared. Then the preset concentration of the nanoparticles was obtained by dilution. After this the composition was mixed in a mixer at 80°C for 20 min. Then the dispersion was cooled to 10°C, and mixing was carried out at this temperature for 30 min. The hardener was introduced into the system after distribution of the nanoparticles in the bulk of the liquid oligomer.

Figure 1 presents the dependence of the diameter of the light-scattering BS-50 particles in DER-330 on their content.

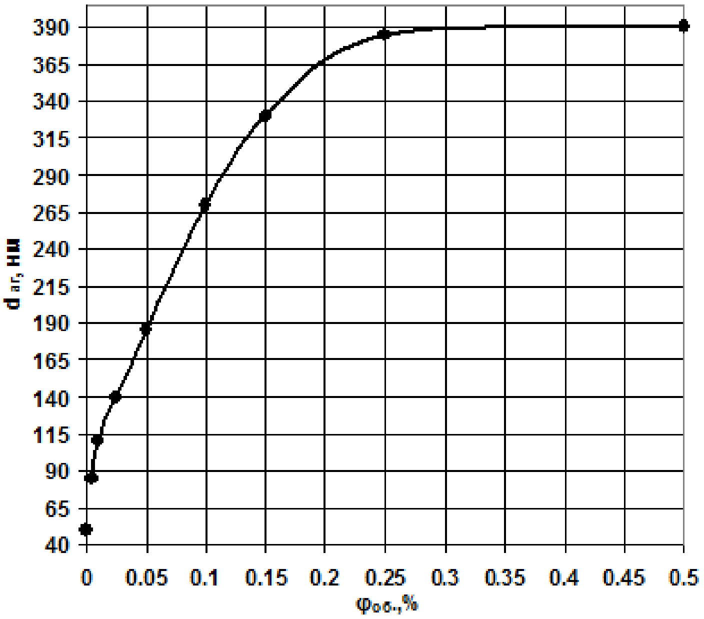


Figure 1. Dependence of the size of the light-scattering particles in DER-330 + BS-50 system on the nanofiller content

[нм means nm; об. means vol.; аг means ag (agglomeration)]

It was shown for all the studied dispersions that using the fractional method of mixing and obtaining nanodispersions in the epoxy oligomer makes it possible to distribute BS-50 nanoparticles up to the size 80–100 nm (that is, at the nanometer level) at concentrations no higher than 0.005–0.01% vol.

Introducing high-dispersion particles of nanofillers into epoxy oligomers, as a rule, increases viscosity and results in their densification. This should be considered when obtaining polymeric binding agents for impregnation of fibrous reinforcing fillers.

The rheological properties of dispersions of BS-50 nanoparticles in DER-330 epoxy oligomer with their different content were studied.

Figure 2 presents the dependence of the relative viscosity of DER-330 + BS-50 system on the nanoparticles concentration.

It was shown that introducing 0.01–0.15% vol. of carbon white decreases viscosity (approximately by 25%), and minimal viscosity is observed at concentration 0.05% vol. Such abnormal behavior of the nanosystem is due to structuring processes, the formation of a loose interfacial layer and nanoparticles agglomeration.

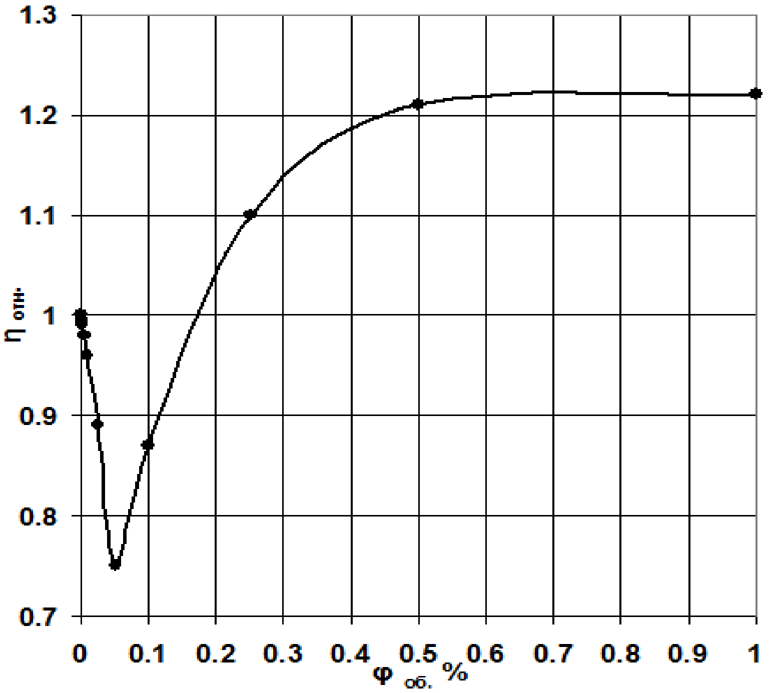


Figure 2. Dependence of the relative viscosity of DER-330 + BS-50 system on the nanofiller concentration.

[отн. means rel. (relative); об. means vol. (volume)]

The decrease in the viscosity of the disperse system based on DER-330 epoxy oligomer containing up to 0.15% vol. of BS-50 nanoparticles it due to the high specific surface of carbon white, adsorption and the formation of loose interfacial layers.

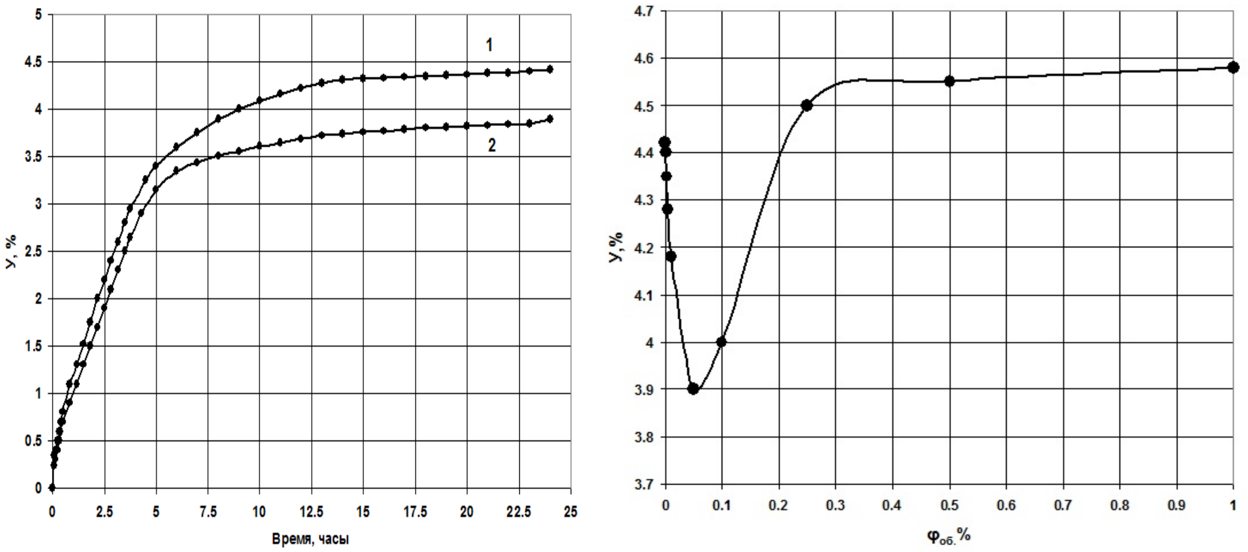
It was shown in works by Trostyanskaya E.B. et al that the adsorption of epoxy oligomers on silicon dioxide is followed by the structure loosening and formation of loose interfacial layers up to 300 nm thick [12, 13].

It follows from Heller's curve that increasing BS-50 nanoparticles concentration results in their agglomeration. The viscosity decrease in this case can be also due to “viscoelastic phase separation in soft environments” resulting from dynamic impact on a system consisting of two components, the relaxation rates of which considerably differ [14]. At small concentrations (up to 0.005% vol.) BS-50 nanoparticles are in dynamic equilibrium. There are a large number of nanoparticles that can be dissolved in an epoxy oligomer. When concentration is 0.005 – 0.05% vol., agglomeration of particles to a certain size occurs. It is followed by separation of the agglomerates into a separate “quasiphase”. In this case the agglomeration of BS-50 nanoparticles can be considered as phase separation with the formation of a new phase. In fact, this is a restructuring process leading to decrease in viscosity, by analogy with polymer blends [15].

The flow of such systems leads to the formation of a layered structure with layers sharply differing in viscosity. This results in layer-by-layer shear flow. The phenomenon of structuring and layer-by-layer shear flow emergence in dispersions containing nanoparticles are described in sufficient detail in [16].

The formation of the three-dimensional structure of the epoxy polymer upon oligomers hardening is followed by densification and shrinkage [10, 17, 18].

Results of the study on the processes of nanosystems shrinkage upon hardening are presented in Figure 3.



a b

Figure 3. Dependence of nanosystems shrinkage upon hardening:

a) on the epoxy nanocomposite hardening time: 1 – DER-330 + TETA;

2 – DER-330 + 0.05% vol. of BS-50 + TETA; b) on the nanofiller concentration:

DER-330 + BS-50 + TETA system.

[У means S; Время, часы means Time, h; об. means vol.]

It is shown in Figures 3a and 3b that introducing 0.005–0.2% vol. of BS-50 nanoparticles decreases the nanocomposite shrinkage, and the shrinkage minimum is observed at concentration 0.05% vol. (shrinkage decreases by ~ 15–20%). This is due to adsorption of the epoxy oligomer on the nanoparticles surface, the formation of a loose structure of interfacial layers and the influence of nanoparticles aggregation in the nanocomposite. Besides, BS-50 nanoparticles promote better dissipation of heat evolved in the course of the epoxy oligomer hardening. They also reduce overheating of the hardened system thereby slowing down the reaction, which has an impact on the shrinkage processes.

The chemical reaction of cross-linking upon the oligomer hardening is followed by shrinkage. This results in residual stress reducing the physico-mechanical characteristics of composite materials.

The slowing of shrinkage upon hardening of nanosystems based on DER-330 can lead to fuller relaxation and change of the kinetics of residual stresses increase (Figure 4), and also to their level (Figure 5).

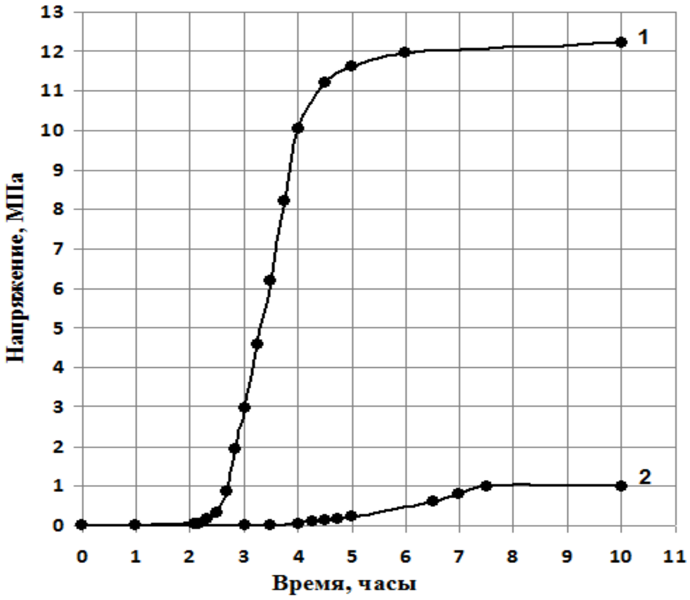


Figure 4. Kinetics of residual stresses increase at 30°C

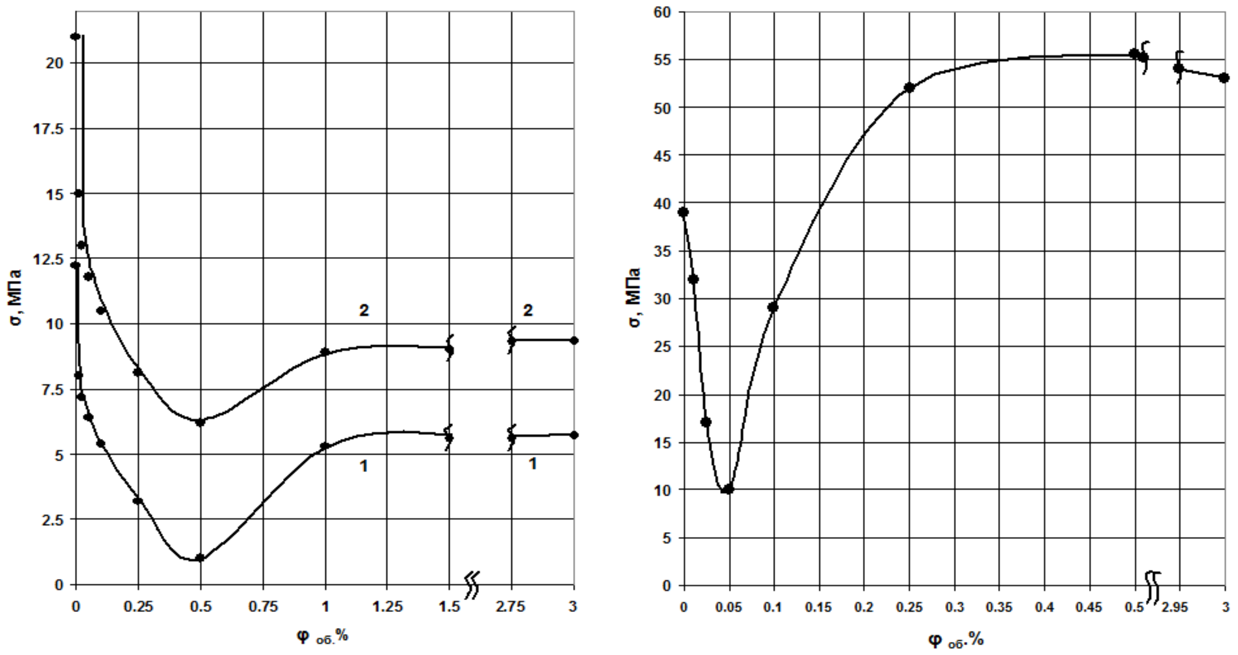
in DER-330 (1) and in DER-330 + 0.5% vol. of BS-50 (2) upon hardening.

[Напряжение, МПа means Stress, MGa; Время, часы means Time, h]

The kinetic curves of residual stresses increase (Figure 4) are S-shaped. Three characteristic areas can be found: area 1 – an induction period (up to 2 h), area 2 – the increase of residual stresses (from 2 to 6 h) and area 3 – a level of constant residual stresses (from 6 to 10 h).

The introduction of nanoparticles reduces the rate of increase and the level of residual stresses upon hardening of the epoxy oligomer (approximately 12-fold). At the same time the induction period increases from 2 to 4 h.

Figure 5 shows dependences of the nanosystems residual stress at different hardening temperatures on the nanoparticles concentration.



a b

Figure 5. Dependence of shrinkable residual stresses upon hardening of the nanocomposites based on DER-330 + BS-50 at 30°C (1a), 50°C (2a) and 70°C on the nanofiller content.

[МПа means MPa; об. means vol.]

In this case an abnormal behavior of the nanosystems and a sharp decrease of stress level (analogously to viscosity and shrinkage) in the range of small contents of the nanoparticles (up to 0.25–1.0% vol.) are also observed. It was shown that introducing 0.05–0.5% vol. of BS-50 nanoparticles into the DER-330 epoxy oligomer decreases residual stresses 3.5–12-fold, which significantly depends on hardening temperature. As hardening temperature increases (from 30 to 70°C), the level of residual stresses increases from 12 to 40 MPa, and the efficiency of the nanoparticles influence decreases. Thus, residual stresses decrease from 12.5 to 1 MPa (~ 12-fold) at hardening temperature 30°C, from 21 to 6.2 MPa (~ 3.5-fold) at 50°C and from 39 to 10 MPa (~ 4-fold) at 70°C.

Note that when temperature is 70°C, the minimum of residual stresses is attained even by introducing 0.05% vol. of BS-50 nanoparticles, and at 30°C and 50°C introduction of ~ 0.5% vol. is required.

This behavior of the nanosystems is, on one hand, due to the decrease of viscosity as temperature increases, and, on the other hand, due to the agglomeration of the nanoparticles in the variable viscosity medium as their content grows.

In general, the formation of loose interfacial layers and agglomeration of nanoparticles determine both the kinetics and the level of residual stresses in the nanosystem.

Conclusion

This work presents for the first time data on the abnormal behavior of nanosystems based on epoxy oligomers and BS-50 nanoparticles in the range of small (optimal) concentrations. A theoretical explanation of this fact is suggested. It is based on the formation of loose interfacial layers on the interphase boundary, agglomeration of particles and separation of aggregates from the nanoparticles solution in the oligomer similarly to the separation of polymer-polymer systems upon transition through the spinodal (spinodal decomposition).

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