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Structural Formation and Physicomechanical Characteristics of Epoxy Nanocomposites

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Abstract—The effect of nanofiller particles with various shapes and chemical nature on the physical and mechanical characteristics of the cured epoxy oligomer-based composites has been considered. As is established, the highest physical and mechanical characteristics of epoxy nanocomposites are enriched independently on the origin of the initial nanoparticles at the aggregate size of ~140–300 nm. Herewith, the strength increases by ~1.5 times, the elastic modulus is 2.5 times higher, and the shock viscosity (the crack resistance) of nanosystems in the optimum amount redoubles the shock viscosity.

Keywords: epoxy diane oligomers (EOs), nanofiller, nanocomposite, carbon nanotubes (CNTs), astralenes, carbon nanoporous microfibers (CNPMFs), white soot, bentonite

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INTRODUCTION

With the elaboration of polymer material science, the appearance of nanocomposites has expanded our abilities to manage their properties via introducing the nanoparticles into polymer nanosystems [1]. Due to their developed surface and nanoscale dimensions, nanoparticles exert a strong influence on the formation of the heterogeneous structure and the interaction at the interface [1, 2], which causes changes in many properties.

The composition and structural parameters of a dispersively filled nanocomposite (DFNC) determine the properties of the latter [3–7]. The nanocomposite structure is formed upon the technological process of the nanoparticle distribution in the bulk of the polymer matrix which depends on the mixing conditions and separation of components, for example, the mixing in the gas phase, in a low- or highly viscose liquid medium, in polymer melts, or stratified single-phase systems with the release of nanoparticles, as well as the formation of nanoparticles and their release in a polymer phase at different chemical reactions.

The numerous works published in scientific and technical literature, as a rule, do not provide correct data on nanoparticle distribution in highly viscose polymer matrices or the formation of agglomerates, the sizes of which are 100–1000 times higher than their initial dimensions [1, 8]. Our study [9] reveals that the displacement of polymer melts with nanoparticles on modern compounders ($L/D \geq 40$) even at low amounts (no more than 0.5 vol %) causes their agglomeration in a dispersively filled nanocomposite. Herewith, the degree of heterogeneity in a nanocomposite, as well as the generalized structural parameters and the properties of the material, changes [3–7].

In this connection, the experimental data on the technological and operation properties of DNNC are of importance, if only knowing the dimensions of nanoparticles and agglomerates.

The main achievements of many works on nanosystems are the presence of abnormal maxima in the curves showing the dependence of characteristics of nanoparticles at their very low concentrations (to 0.001–0.5 vol %) on their concentrations. As is reported in [3], the structural formation and percolation transitions in nanosystems occur at much lower nanoparticle contents, as the maximum packing parameter for nanoparticles is typically on the order of 15–20 vol %, unlike for coarse (above 1.0 μm) filler particles (from 35 to 64 vol %).

This work is dedicated to the creation of a heterogeneous structure and physicomechanical properties of epoxy nanocomposites with nanoparticles of various shapes, chemical natures, and concentrations. The distribution of nanoparticles and their agglomerates in the bulk of epoxy oligomer-based viscous polymer binders is a focus of particular attention.

DER-330 epoxy oligomer (EO) (Dow Chemical Corp.) served as a polymer binder with a viscosity of 7–10 Pa s, a density of 1.15–1.17 g/cm^3, and a weight concentration of epoxy groups of 23.2–24.4%, with a bifraction composition, where the content of the first

Table 1. Characteristics of nanofillers

Nanofiller	Diameter of nanoparticles, nm	S_{sp}, m^2/g	Density, g/cm^3		Particle shape, k_e	φ_{max}, vol %
			true	bulk		
B-type astralenes UFN A2 01a	50	200	2.0	0.80	Polyhedral, 2.5	0.18
Carbon nanotubes UFN A1 01t (CNT)	15—25	400	1.6	0.7	Cylindrical, 5.9	0.25
Carbon nanoporous microfibers (CNPMFs)	30—40	400	1.6	0.9	Plane lamellar, 5.0	0.2
We soot WS-50	45	50	2.3	0.23	Spherical, 2.5	0.2
Bentonite PBA (montmorillonite)	135	75	2.3	1.4	Lamellar, 5.0	0.3

low-molecular fraction is 92% and the molar weight is ≈346 g/mol with a lack of initial heterogeneity (the associate content is no more than 5 vol %).

Epoxy nanosystems were cured with tri-ethylene tetramine (TETA) from Dow Chemical (with a viscosity of 30 mPa s, a density of 0.995 g/cm^3, and an equivalent weight of amino groups of 24 g/eq.), which is characterized by stable properties. The amount of DER-330 curing agent was determined from the stoichiometric equality of epoxy and amine equivalents. Nanocomposites were cured with TETA at 20°C for 24 h and then at 80°C for 10 h.

Nanofillers with different chemical natures, surface states, surface energies and, particle sizes and shapes were used for this study. The main characteristics of nanofillers are listed in Table 1. Nanofillers were embedded in concentrations of from 0.005 to 1.0 vol %.

A homogeneous nanoparticle distribution in the bulk of epoxy diane oligomer (without the curing agent) was achieved via the successive dilution of the concentrated dispersion. As the desired nanoparticle concentration was obtained, the compound was stirred in a mixer at 80°C for 20 min, after which the dispersion was cooled to 10°C and stirred for 30 min at low temperature. The curing agent was introduced into the system after attaining the nanoparticle distribution in the bulk of epoxy oligomer.

The distribution of nanoparticles and their sizes in liquid epoxy oligomer were evaluated via the optical method from the turbidity spectra using a KFK-2 calorimeter and a Geller curve [9], as is done in colloidal chemistry for investigation of ultradisperse particles. The determination of particle sizes from the turbidity spectra is based on the experimental evaluation of the optical density at different wavelengths of the incident light. This allows the χ parameter (the exponent depending on radius r of a light-scattering particle) to be found with subsequent estimation of the particle radius by means of the special calibrating Geller curve $\chi(r)$. The χ magnitude is defined as the slope of a straight line related to the appropriate dependence of $\ln D$ on $-\ln\lambda$(where D is the optical density of dispersion and λ is the wavelength of the incident light).

As was experimentally established for all studied nanoparticles, the proposed fractional blending method and synthesis of nanodispersions in oligomer allows the nanoparticle distribution to sizes of ~80 nm in MWCNTs and WS-50, of ~90 nm in CNPMFs and B-type astralenes, and of ~135 nm in PBA at the nanoparticle concentrations below 0.005 vol %. It is worth mentioning that the particle distribution to their initial size was successful only for PBA bentonite.

If the concentration of nanoparticles in EO exceeds 0.005 vol %, they agglomerate and the light-scattering nanoparticles enlarge. As an example, Fig. 1 displays the sizes of light-scattering particles in DER-330 EO as a function of the concentration of UFN A1 01t (CNT) nanotubes and B-type astralenes UFN A2 01a.

An increase in the contents of CNTs and B-type astralene nanoparticles in EOs from 0.0025 to 0.5 vol % is accompanied by their agglomeration, and the diameter of diametraglomerate rises from 80 to 400 nm.

Similar curves were obtained for other nanofillers (CNPMFs, WS-50, and PBA), the agglomerate sizes of which also increase with the nanofiller content. The PAB bentonite particles were established to have rather large initial dimensions ($d \approx 135$ nm) without forming agglomerations during stirring and quite homogeneously distributing in the bulk of EO.

Thus, almost all nanofillers (CNTs, CNPMF, B-type astralenes, WS-50 and PBA) form agglomerates upon their embedding in EO, the sizes of which depend on their concentration.

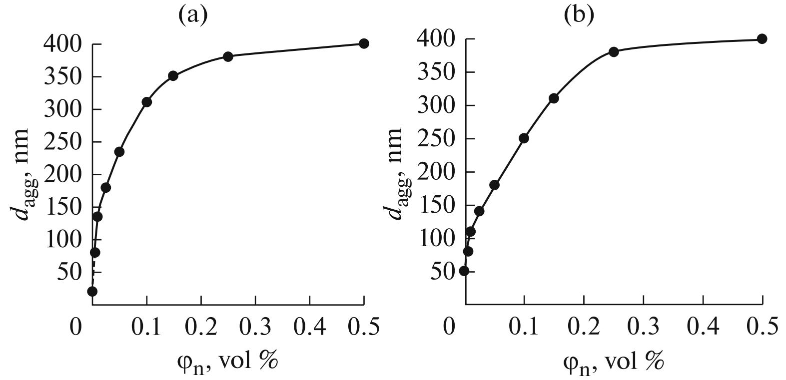

Fig. 1. The nanoparticle aggregate size (d_{agg}) in DER-330 as a function of nanofiller content φ_n: (a) CNTs in DER-330; (b) B-type astralene in DER-330.

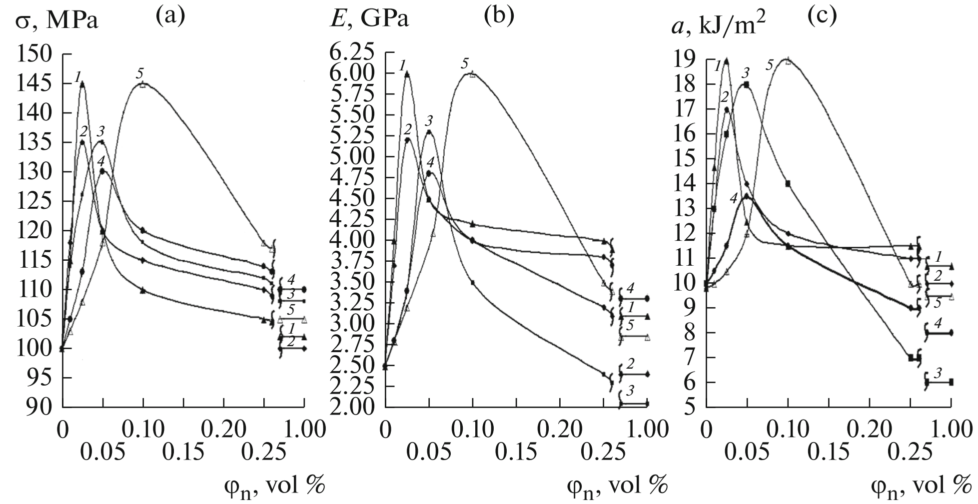

Fig. 2. (a) The compressive strength, (b) the elastic modulus, and (c) the shock viscosity of DER-330 epoxy oligomer-based nanocomposite as functions of the contents of nanocomposites: (*1*) PCNT, (*2*) CNT, (*3*) WS-50, (*4*) bentonite PBA, and (*5*) B-type astralene.

The physical and mechanical characteristics of nanocomposites depend on the structural formation and homogeneous particle distribution in the bulk of epoxy oligomer, as well as on the size, content, and agglomeration of nanoparticles in the polymer matrix and the generalized parameters of the dispersive structure [4, 7].

The complex of physical and mechanical properties of cured epoxy polymer containing nanoparticles of different natures, sizes, and surface states was established according to *GOST* (State Standard) *4561–82* (for the elastic modulus and compressive strength) and *GOST* (State Standard) *4647–80* (for the Sharpi shock viscosity without a notch at an angle of 94°). The relative error in the determination of the strength and elastic modulus upon compression did not exceed ±5%, while in the case of the shock viscosity it is ±7%. Figure 2 shows the compressive strength, elastic modulus, and shock viscosity of nanocomposites based on DER-330 epoxy polymer as functions of nanoparticle content.

For all studied nanocomposites, a maximum is observed in the property–composition dependences in the vicinity of from 0.005 to 1.0 vol % of the nanofiller content. Its position and height depend on the nanofiller nature, surface state, wetting, shape, initial size of nanoparticles and agglomerates, and thickness and structure of the boundary layer, as well as the generalized parameters of the dispersively filled structure [3, 5].

The physical and mechanical indices enrich their maxima under the introduction of various amounts of nanofiller, vol %: carbon nanotubes at ~0.025, bentonite and WS-50 white soot at ~0.05, and B-type astralenes at ~0.1. A further increase in the nanofiller

Table 2. The sizes of aggregates and nanoparticle concentrations in the aggregate at the highest physical and mechanical characteristics of epoxy nanocomposite

Nanofiller	φ_n, vol %	d_{np}, nm	d_{agg}, nm	Amount of nanoparticles in aggregate, un.
B-type astralenes UFN A2 01a	0.1	50	300	170
Carbon nanotubes UFN A1 01t (CNT)	0.025	20	160	140
Carbon nanoporous microfibers (CNPMFs)	0.025	35	140	30
White soot WS-50	0.05	45	190	40
Bentonite PBA (montmorillonite)	0.05	135	135	1

φ_n is the nanofiller content, d_{np} is the nanoparticle diameter, d_{agg} is the diameter of nanoparticle aggregates.

content (to 1.0 vol %) leads to a decrease in the physical and mechanical characteristics of DNPMFs.

Introducing the B-type astrolenes into carbon nanoporous microfibers DNPMFs causes an increase in the physical and mechanical characteristics of epoxy nanocomposites: the strength rises by ~1.5 times, the elastic modulus increases by ~2.5 times, and the shock viscosity (the crack resistance) of nanosystems with CNPMFs, B-type astralenes, WS-50, and CNTs in the optimum amounts almost doubles the shock viscosity.

As we have shown, the highest physical and mechanical characteristics of EO-based nanocomposites can be achieved only upon the formation of agglomerates with certain sizes of ~140–300 nm therein (the nanoparticle-agglomerate sizes are listed in Table 2).

For epoxy nanocomposites with agglomerate sizes close to those of the initial nanoparticles (80–90 nm), there is no increase in the strength and their physical and mechanical characteristics almost correspond to epoxy polymers. Therefore, the homogeneous nanoparticle distribution at a nanolevel in epoxy nanocomposite (to 100 nm) causes no improvement in its physical and mechanical characteristics.

The most sensitive parameter to the nanoparticle size in nanocomposites and crack sprouting is shock viscosity, which is determined by the interplay of the growing micro- and nanocracks with disperse particles.

It is worth mentioning that, in shock-resistant shockproof ABS plastics, the optimum particle size of the disperse phase is ~200–300 nm [10], which almost coincides with the nanoparticle-agglomerate dimensions in the studied nanocomposites (from ~140 to 300 nm).

Embedding nanoparticles in EO increases the elastic modulus and, simultaneously, the shock viscosity, which makes such compounds different from shock-resistant plastics with rubber particles, where the elastic modulus decreases with the introduction of disperse particles.

In analyzing the above dependences and the maxima, let us note that, from the technological point of view, the industrial synthesis of nanocomposites revealing a narrow nanoparticle concentration maximum (from 0.025 to 0.05 vol %) is a rather complicated technological task, because even a slight change in the nanofiller concentration can provoke a decrease in the physical and mechanical properties to the point of the initial values for an epoxy polymer.

For the presented nanofillers, the broadest peak is observed for nanocomposite with B-type astralene (from 0.06 to 0.25 vol %), which is technologically more convenient for applying this system in the industry. On the other hand, the B-type astralene content necessary to improve the physical and mechanical characteristics is somewhat higher (~0.1 vol %) than in carbon nanotubes (~0.025 vol %); however, their price is half that of CNTs and four times less than that of CNPMFs.

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