

Study of the Influence of Single-Wall Carbon Nanotube Dispersion Techniques upon the Properties of Epoxy Resin-Based Nanocomposites

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Abstract—A comparison of two techniques, ultrasonication and the controlled wave treatment, for the dispersion of ultra-small concentrations of carbon nanotubes in epoxy resin has been carried out with specially designed instruments. Studies with optical microscopy and physicomechanical and thermomechanical tests showed that both techniques provide almost equal degrees of nanotube dispersion in the matrix and dependences of the basic physicomechanical properties of cured epoxy polymers on the nanofiller concentrations. However, the difference between the two techniques has been shown at the study of the structural properties of the cured epoxy polymers (the molecular weight of the internode chains of the polymeric network, and the vitrification temperature), which are more stable in the case of the wave treatment. Thus, wave treatment is a promising dispersion technique, and it is applicable at the industrial scale because it is almost unlimited by the size and capacities of the equipment.

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The development of polymeric composite materials having improved properties is a current issue. A popular solution is the modification of polymers by nanoparticles, in particular, carbon ones, among which are carbon nanotubes (CNTs).

Earlier, it was shown that in some cases an essential change in the physicomechanical properties of polymers can be achieved by the introduction of ultrasmall concentrations of CNTs (less than 0.01 wt %), and concentration dependences of the properties have an extreme character [1–3].

To actualize the enhanced properties of nanotubes in polymers, it is necessary to provide as homogeneous distribution of the filler particles within the matrix as possible. However, due to their high surface energy and aspect ratio (length to diameter ratio), CNTs form stable aggregates, which impedes their stable dispersion in water and organic media, including polymers. Modification techniques involving CNTs are being widely studied [4–7]. It is shown that both covalent and noncovalent modification of CNTs surfaces lead to easier disaggregation (down to individual nanotubes) due to the decrease their surface energy and the intertube van der Waals interaction.

In case of noncrosslinked soluble polymers able to make the transition to a viscous state (thermoplastics or thermoplastic elastomers), fillers, including nanoparticles, can be introduced either

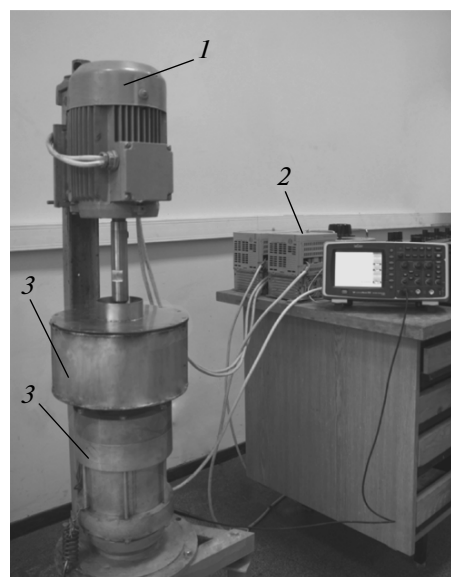


Fig. 1. VSM-2 laboratory instrument for wave treatment: (1) electric drive, (2) control panel and measuring apparatus, (3) wave reactor, (4) resonant electro-mechanical oscillator.

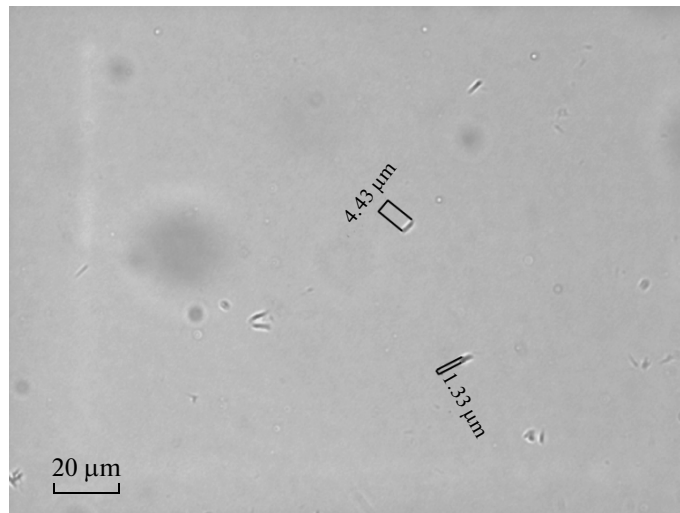


Fig. 2. Microphotographs of the probe 3 (table) of the cSWCN suspension (2×10^{-3} wt %) in epoxy resin.

into the starting mixture of monomers at the synthesis of polymers (in situ) or into the ready polymer in a solution and/or in a melt [3, 6, 7]. In case of crosslinked polymers, the only possible introduction technique is in situ, i.e., into a reaction mixture before curing. This refers both to crosslinked elastomers [1, 6, 7] and to hard plastics, particularly, epoxy resins [2, 6].

Irrespective of the technique of CNTs introduction into polymers (except the introduction into a melt), the reaction mixture or a polymer solution is treated by the ultrasonication (US) to provide the dispersion of CNTs aggregates and the maximum homogeneity of their distribution in the polymeric matrix. However, it is a laboratory technique inapplicable in industrial production. At the Research Center for Nonlinear Wave Mechanics and Technology of the Russian Academy of Sciences, new techniques are being developed for the dispersion of solid, liquid and gaseous fillers in liquid media, including highly viscous ones, using the controlled wave treatment (WT) with specially designed instruments providing homogeneous distribution of fillers in either discrete or continuous mode at industrial scale [8–11].

The aim of the present work is to compare the two techniques, US and WT, for the dispersion of the ultrasmall CNTs concentrations in epoxy resin regarding their efficiency and influence upon the main physicomechanical and structural properties of the cured resin.

EXPERIMENTAL

The components used in this study are ED-20 epoxy resin, ETAL-450 hardener, and carboxylated single-wall carbon nanotubes (cSWCN) as a filler.¹ Two techniques for the CNTs dispersion and introduction into epoxy resin were compared.

According to the first technique, the cSWCN suspension in dibutyl phthalate (DBP) with a concentration of 1 mg/mL was US treated with the IL10-0.63 ultrasonic generator at the maximum power (630 W, middle rod) over 60 min. The quantity of the dispersion necessary for the target CNTs concentration in the resin product was solved in DBP and then added into the epoxy resin. In all experiments, the DBP concentration was 6 pbw per 100 pbw of the resin–hardener mixture. The mixture was stirred in a high-speed stirrer at a simultaneous vacuumation for 1 h at a temperature of 60°C to eliminate volatile admixtures and solved gases. The estimated quantity of the hardener (27 g per 100 g of resin) was introduced into the degassed mass and stirred during 3 min at a simultaneous vacuumation.

According to the second technique, the estimated quantity of the cSWCN suspension in DBP, pre-treated by US for 10 min, was added to the epoxy resin, then the mixture was WT treated during 60 min in the VSM-2 wave stirrer (Fig. 1). Then the estimated quantity of the hardener was added at stirring and additionally treated by WT for 10 min.

¹ The cSWCN were synthesized at the Uglерod ChG small enterprise <http://www.carbonchg.ru>

The technique and parameters of the synthesis of nanomodified epoxy binder using WT

Operations	τ , min	Parameters of electric drive		Parameters of wave drive			T , deg
		n , rpm	W_t , W	f , Hz	W_w , W	A , mm	
Loading of resin into reactor, start	—	56	20	57.2	120	4.5	24
Taking probe 1	20	50	18	56.0	98	5	41
Taking probe 2	40	50	18	58.2	100	5	42
Taking probe 3, stop	60	50	15	58.2	80	5	42
Loading of hardener, start	70	65	20	54.9	130	5	44
Stop	—						45

n – the rotor rotational speed of the electric drive, W_t – active capacity of the electric drive, f – the wave treatment frequency, W_w – the active capacity of the wave drive, and A – the amplitude of the shift waves at the frontier.

The technique and parameters of the WT dispersion of CNTs in the epoxy resin was the same for each of the probes. In Table 1, the parameters of the experiment for the case of the nanofiller concentration of 2×10^{-3} wt % is presented.

The microphotographs of the CNT–epoxy resin mixture probes after the US and WT treatment are almost identical showing only insignificant number of CNTs agglomerates (individual nanotubes are invisible in the optical range), which indicates a rather high degree of dispersion. In Fig. 2, there are the microphotographs of the mixture probe after WT with the cSWCN concentration of 2×10^{-3} wt % (for the other concentrations of the modifier the microphotographs

In the both cases, detachable molds (for mechanical tests) were filled with the reaction mass and cured at 160°C for 6 h with annealing at 80°C (10–12 h). The procedure of preparation and treatment of the cured epoxy resin probes without CNTs was the same (with the same DBP concentration).

The mechanical properties of the cured polyepoxides (CPE) were tested on an Instron tensile testing machine at a tension speed of 5 mm/min. CPE thermomechanical behavior was studied on a UIP-70 thermal analyzer the (hemispherical quartz tube of the diameter of 2 mm, the load of 20 g, the temperature range of 0 to 260°C , cooling and heating rates of $5^\circ\text{C}/\text{min}$).² Based on these data, the vitrification temperature (T_g) and the average molecular weight of the internode chains of the polymeric network (M_c) were determined by the technique described in [12].

RESULTS AND DISCUSSION

The US treatment of epoxy resin, especially in large volumes, is difficult due to its high viscosity even at elevated temperature, which leads to insufficient circulation of the reaction mixture and subsequent local overheating at the ultrasound source. Thus, in this work the dispersion of nanotubes by US was conducted in less viscous DBP, often applied as a plasticizer of epoxy resins. The pretreatment of CNTs in DBP during 10 min used in the both techniques allowed us to obtain a stable homogeneous concentrated mixture, which was convenient to dose for preparing the suspension of CNTs in DBP of the target concentration. Earlier works show that for the addition of such suspension into epoxy resin without long-term US pretreatment does not give homogeneous CNTs distribution in the conditions of long-term mechanical stirring of the reaction mixture. Thus, the WT treatment of the mixture of resin and CNTs suspension in DBP substitutes a long-term US treatment of the suspension in the first technique for the CPE preparation.

Mechanical tests of the samples of CPE modified by cSWCN showed that both dispersion techniques in the range the data set give almost the same dependences of the tensile strength and deformation and the elastic modulus upon the nanotubes concentration (Figs. 3–5). It is noteworthy that, unlike polyurethanes showing the essential influence of ultrasmall cSWCN concentrations upon the physicomechanical properties of the nanocomposites, there is no such influence in case of CPE based on the ED-20 resin and the ETAL-450 hardener.

² CPE thermomechanical behavior was studied by Yu. A. Ol'khov.

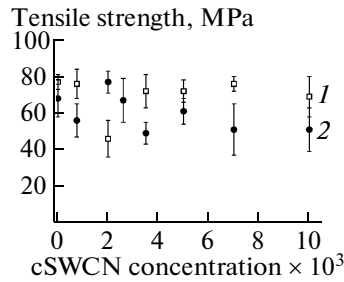


Fig. 3. The dependence of the tensile strength of the modified CPE synthesized using US (1) and WT (2) on the cSWCN concentration.

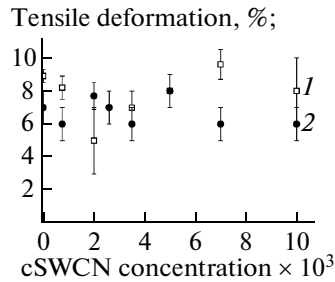


Fig. 4. The dependence of the tensile deformation of the modified CPE synthesized using US (1) and WT (2) on the cSWCN concentration.

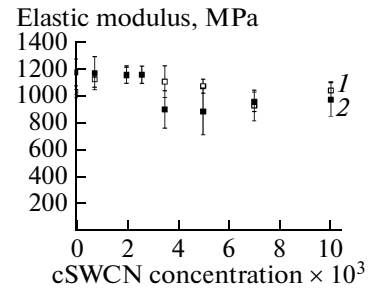


Fig. 5. The dependence of the elastic modulus of the modified CPE synthesized using US (1) and WT (2) on the cSWCN concentration.

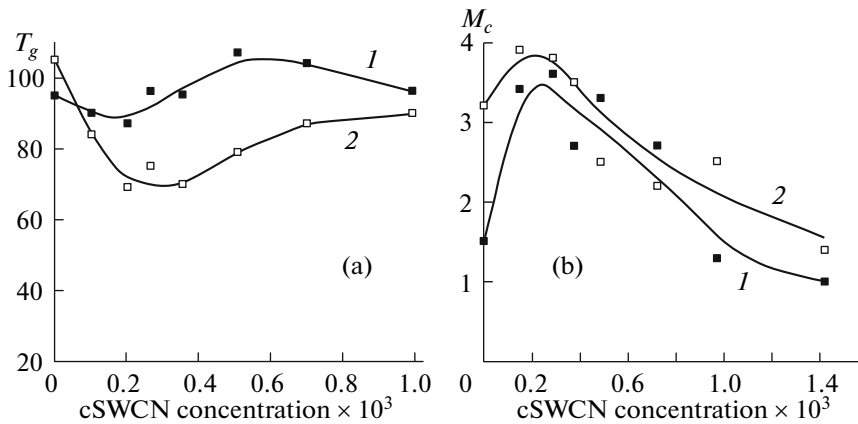


Fig. 6. (a) The dependence of the vitrification temperature of the modified CPE on the concentration of cSWCN introduced using WT immediately after the synthesis (1) and after the storage during 9 months (2). (b) The dependence of M_c of CPE on the cSWCN concentration introduced using WT immediately after the synthesis (1) and after the storage during 9 months (2).

More visible difference between the two dispersion techniques are demonstrated for the study of the CPE structural properties and their changes over time.

According to earlier works concerning both unmodified CPEs and ones modified using US, their structural properties essentially change at storage: the molecular weight of the internode chains of the polymeric network (M_c) increases several times, and the vitrification temperature (T_g) decreases 20–30°C, especially at relatively high (10^{-2} wt %) nanotubes concentration. It is shown in Fig. 6 that in case of the cSWCN addition at WT, the changes of these properties at storage are essentially decreased, especially at high concentrations of the modifier, and in their absence T_g of the polymer treated by WT, on the contrary, increases 10°C at storage.

Hence, the comparison of the two techniques, US and WT, for nanoparticle dispersion in a polymeric matrix demonstrated that the WT treatment is promising because it provides more stable properties of CPE and, unlike US, it can be applied in larger scales, including the industrial production, since it is not limited by the sizes and capacities of the equipment.

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