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Time-Stability Dispersion of Carbon Nanotubes in Chloroform

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Abstract

A uniform distribution of carbon nanotubes in a polymer matrix is required for the fabrication of composite materials. Since carbon nanotubes for introduction into polymers are preliminarily dissolved in water or organic solvents, it is necessary to create uniform stable dispersion of carbon nanotubes in solvents.

It has been shown in this work that the concentration of nanotubes is a critical parameter determining the stability and composition of a solution. The kinetics of agglomeration of multiwalled carbon nanotubes dispersed in chloroform by means of sonication has been studied by the methods of optical spectroscopy and dynamic light scattering. It has been shown that such solutions can be stable for a long time at concentrations of nanotubes below 0.01 wt %.

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1. Introduction

Multi-wall carbon nanotubes (MWCNT), which are cylindrical particles with a large aspect ratio, are actively studied for the use in the creation of composite materials. In addition to the traditional problems such as the improvement of the strength and electric conductivity of polymers [1], numerous current studies are devoted to the

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development of new mixed matrix membranes with MWCNTs [2,3]. The introduction of MWCNTs not only strengthens polymer membranes, but also improves the selective transport of fluids and gases [4,5].

The methods of the creation of polymer composite materials with MWCNTs are permanently improved; in particular, the conditions for the improvement of dispersion and the creation of a uniform distribution of nanotubes in a polymer are studied. Sonication is used to destroy agglomerates of nanotubes in the main stages of the preparation of a composite. The initial degree of dispersion of MWCNTs in the solvent can be controlled by varying the power and duration of sonication [6, 7].

The kinetics of dispersion of carbon nanotubes in solvents, as well as the sizes of agglomerates of MWCNTs, was studied with the addition of surfactants and after the modification of MWCNTs. The addition of surfactants to the solvent or the treatment of the surface of MWCNTs by, e.g., acids reduces the formation energy of the MWCNT/solvent interface. This improves the wettability of MWCNTs by the solvent and «screens» the interaction between MWCNTs [8, 9]. An increase in the viscosity of the solution of MWCNTs upon the addition of polymers also reduces the mobility of MWCNTs and increases the agglomeration time and stability of solutions. At the same time, the concentration of MWCNTs in the solvent certainly determines the distance and intensity of the interaction between MWCNTs and, as a result, the agglomeration rate. In this work, we analyze the kinetics of solutions with various concentrations of MWCNTs in chloroform.

2. Experiment

In this work, we used multi-wall carbon nanotubes (MWCNTs) produced by the method of chemical vapor deposition (CVD) of hydrocarbons (CxHy) with Ni/Mg catalyst at normal pressure and temperature 580–650 °C (MWCNT «Taunito»™, «NanoTC», Tambov, Russia). According to the data of the producer, the «Taunito» carbon nanomaterial with an apparent density of 0.4–0.6 g/cm³ consists of one-dimensional polycrystalline graphite filaments with a length up to 2 μm, an outer diameter of 20 to 70 nm, and a specific surface area of 120–130 m²/g [10]. The samples of MWCNTs were treated by a nitric acid solution for the removal of a catalyst and for the deposition of functional groups on the surface of MWCNTs [11]. The characteristics of MWCNTs were determined by the methods of helium pycnometry (Micro-Ultrapyc 1200e Quantachrome) and low-temperature adsorption of nitrogen (Nova 1200e, Quantachrome). The specific area was calculated by the method of multipoint BET. The diameter of the inner channels in MWCNTs after treatment in nitride acid is \(d_{\text{inn}} = 3–6\) nm according to the calculations within the BJH method [12]. The outer diameter of MWCNTs can be calculated within the model of cylindrical channels is \(d_{\text{out}} = 20–70\) nm. After acid treatment nanotubes density is \(2.26±0.01\) g/cm³ outer diameter of 20 to 70 nm, and a specific surface area of 150±3 m²/g.

For the dissolution of CNTs was used chloroform with a density of 1.48 g/cm³ (purity 99%, LLC “Chimmed”, Moscow, Russia). In order to disperse MWCNTs in chloroform, we used sonication processes for 15 min with ultrasonic bath “Sapfir” (35 KHz, output power 100 W). After sonication processes, we determined the absorption spectrum and sizes of agglomerates in the solution. The concentration of MWCNTs in chloroform solutions was controlled using absorption spectra in the wavelength range of 400–1000 nm (Hach 500 DR) [15].

3. Results and discussion

The sizes of MWCNTs in chloroform were determined by the dynamic light scattering method with 780-nm laser radiation (Nanotrac 252, Microtrac Inc.) [13]. Fig. 1 shows the average size of particles in the solution is a nonlinear function of the concentration of MWCNTs. The average size is (250±15) nm at concentrations below 0.01 wt % and increases to (275±15) nm at concentrations from 0.01 to 0.03 wt % and to 450 nm at concentrations above 0.03 wt %.
As can be seen, the calculated average size of particles in solutions is inconsistent with the sizes of MWCNTs used because of the algorithm of the reconstruction of the sizes of nanoparticles from DLS measurements [14]. Correlations of the intensity of reflected radiation in the DLS method are attributed to the Brownian motion of particles in the solution and the hydrodynamic radius of a spherical particle is calculated for the resulting diffusion coefficient by the Stokes–Einstein formula. The calculations of the diffusion of cylindrical particles with the parameters of MWCNTs under study show that individual MWCNTs correspond to spherical particles smaller than 300 nm. Consequently, the average sizes obtained indicate that individual nanotubes are dispersed in solutions with a concentration below 0.01%. At a concentration above 0.03%, most nanotubes are agglomerated in the measurement time (180 s).

Agglomeration and sedimentation of nanotubes change the sizes and concentration of particles in solutions. To determine the stability, the sizes and concentration of particles in solutions with concentrations of MWCNTs 0.005, 0.01 and 0.05% were monitored for 480 h (Figs. 2, 3).

Fig. 1. Size of agglomerates of MWCNTs in chloroform versus the concentration of nanotubes.

Fig. 2. Average size of MWCNTs in chloroform according to the DLS method.
The size of agglomerates in the 0.005% solution after sonication was (240±15) nm and did not change for 480 h (Fig. 2). The absorbance of the solution varied insignificantly from 0.868 to 0.680 (Fig. 3); i.e., the concentration of particles in the solution decreased to (0.004 ± 0.0003) wt %, which can be attributed to the formation of a small amount of agglomerates. The average size of agglomerates in the 0.01% solution increases in 480 h by more than 70%, from 280 nm to (453 ± 15) nm, and the absorbance decreases from 1.729 to 0.697, which corresponds to a decrease in the concentration of particles from 0.01 to (0.004 ± 0.0003) wt %. This decrease in the absorbance can be caused by both sedimentation and a decrease in the total volume of particles in the solution upon agglomeration. The average size of particles in the 0.05 % solution in the first 48 h increased from 451 to (795 ± 15) nm. After that, the average size of particles decreased in 240 h to (546 ± 15) nm and then did not change. The absorbance in the first 48 h exceeded the measurement limit of the instrument (abs=3.85) and was not determined. Then, after 480 h, the absorbance decreased from 3.848 to 0.697 (Fig. 3), which corresponds to a decrease in the concentration of particles to (0.004 ± 0.0003) wt %. These changes can be explained by intense agglomeration of MWCNTs in the first hours after sonication, which reduces their mobility and moderates subsequent agglomeration. An increase in the sizes of agglomerates is accompanied both by the acceleration of sedimentation and by a decrease in the concentration.

Thus, the composition and stability of the solution is determined by the concentration of MWCNTs. Already at a concentration of ~ 0.01 wt %, the size of agglomerates increases significantly in three days and the concentration of nanotubes in chloroform decreases. Nanotubes are not dispersed in solutions with a concentration above 0.03 wt % after sonication.

Conclusions

The combination of UV–vis. spectroscopy and dynamic light scattering (DLS) allows simultaneously controlling in-situ concentration and sizes of nanotubes upon agglomeration and sedimentation of solutions. The investigation of chloroform solutions with the concentration of MWCNTs from 0.005 to 0.05 wt % shows that dispersion into individual nanotubes under room conditions is impossible above the critical concentration of MWCNTs equal to 0.03 wt %. In this case, individual MWCNTs remain stable for a long time or are agglomerated slowly at concentrations below 0.01 wt %. Thus, it is shown that the concentration of MWCNTs in the solvent is an important parameter determining the stability and uniformity of dispersion. In solutions with the concentration above the critical value, it is impossible to create a uniform distribution of single MWCNTs and, correspondingly, the effect of the introduction of MWCNTs into the composite material becomes less predictable and controllable.
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