РАДІАЦІЙНА ФІЗИКА

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SMALL-ANGLE NEUTRON SCATTERING OF MULTIWALLED CARBON NANOTUBES IN AQUEOUS SUSPENSIONS IN PRESENCE OF LAPONITE PLATELETS OR CETYLTRIMETHYLAMMONIUM BROMIDE

The results of small angle neutron scattering (SANS) study of semidiluted 0.1 and 0.3 % wt aqueous suspensions of multiwalled carbon nanotubes (MWCNTs) are reported. The additives of Laponite platelets or cationic surfactant cetyltrimethylammonium bromide (CTAB) were used for enhancing the dispersion ability of MWCNTs. At high values of wave vector q, (1 nm^{-1} < q < 3.5 nm^{-1}) all samples exhibited behavior characteristic for rigid rods (i.e., q^{-1} variation of neutron scattering intensity was observed). At low values of q (0.1 nm^{-1} < q < 0.5 nm^{-1}), the neutron scattering intensity followed the power law $q^{-\alpha}$ with exponent the α in the range of 1.2 - 2, depending on concentration of the Laponite platelets or CTAB. Addition of Laponite platelets or CTAB allowed improvement of dispersion ability of MWCNTs. The effects were optimal at the certain value of Laponite/MWCNTs ratio $X \approx 0.5$ or CTAB concentration (≈ 0.2 %wt). SANS also revealed existence of a mesh structure in MWCNT aggregates with characteristic mesh size of ≈ 7.4 nm and ≈ 6.3 nm in suspensions with concentration of 0.1 and 0.3 % wt of MWCNTs, respectively.

Keywords: SANS, elastic neutron scattering, nanotubes, Laponite platelets, CTAB.

Introduction

Nowadays different composites with carbon nanotubes (NTs) as an additive attract great attention [1, 2]. These materials manifest useful mechanical, electrical, magnetic and other properties and can find interesting industrial applications [3 - 5]. Highly dispersed and well stabilized NTs are required for production of such materials.

Usually, NTs dispersed in water connect producing bundles and form big aggregates owing to the strong hydrophobic and van der Waals inter-actions. To enhance dispersion ability of NTs, several physical methods, such as ultrasonication [6], high pressure homogenization [7] or high voltage discharges [8], are usually applied. But physical treatments have only a temporary effect and can result in significant damage of NTs. In order to obtain more stable NT suspensions, the chemical methods of oxidation, functionalization, or intro-duction of different polymers and surfactants were also used. However, the chemical methods also have many disadvantages and can result in deterioration of initial properties of NTs [9] Recently, introduction of supplementary nanoparticles was shown to have a positive effect on dispersion ability of NTs in water [10, 11]. E.g., it was shown that highly charged platelets of montmorillonite or Laponite can significantly improve dispersability of multiwalled carbon nanotubes (MWCNTs).

This work is devoted to the study of the effects of platelets of Laponite or cationic surfactant cetyltrimethylammonium ammonium bromide (CTAB) on dispersion ability of MWCNTs in an aqueous suspension. The aqueous suspensions of MWCNTs were taken in concentrations of C_n = 0.1 % wt and 0.3 % wt, which corresponded to the semi-dilute regime of partially overlapped NTs. The concentration of Laponite was varied in the range of (0.005 ÷ 0.3) % wt, which corresponded to Laponite/MWCNTs weight ratio X within 0.05 - 1. The concentration of CTAB, C_s, was varied in the range of (0.025 ÷ 0.5) % wt.

The small-angle neutron scattering (SANS) technique was used as a method for investigation. This method allowed determination of the structure features of MWCNT suspensions and estimation of the quality of MWCNT dispersion in the presence of Laponite and CTAB. Note that SANS allows using of the contrast variation method and thus minimizing the neutron scattering input of additives to the total scattering profile. This is an advantage as compare with small angle X-ray scattering technique that was traditionally applied for studying suspensions of nanoparticles [12, 13].

Materials and methods

MWCNTs were prepared from ethylene using the chemical vapor deposition method (TMSpetsmash_Ltd., Ukraine) with Fe-Al-Mo catalyst. The nanotubes had the outer diameter

$d \approx 20$ - 40 nm, while their length, l, was varying in the range of 5 to 10 microns. The average solid density of MWCNTs was 2.2 g/cm³, which is close to that of graphene. According to our calculations, the neutron scattering length density of MWCNTs was $7 \cdot 10^{10}$–cm⁻¹.

Laponite (Rockwood Additives Ltd., UK) was used as received. It has the empirical formula $Na_{0.7}[(Si_8Mg_{5.5}Li_0.4)\ O_{20}(OH)_4]_{0.7}$ [14] and its solid density is 2.53 g/cm³ [15]. Laponite consists of charged platelets with diameter $(25 \div 30)$ nm and radius 1 nm [16]. These particles bear both basal negative and rim positive charges [17]. Their scattering length density for neutrons is $3.76 \cdot 10^{10}$–cm⁻¹.

Cetyl trimethyl ammonium bromide (Fluka, Germany) is commonly used as a surfactant for organo-modification of Laponite. Its chemical formula is $C_{16}H_{33}N(CH_3)_3Br$ and its molar mass is 364.45 g/mol. The scattering length density of cetyl trimethyl ammonium bromide is $0.45 \cdot 10^{10}$–cm⁻¹, which is close to that of water, H_2O.

The hybrid suspensions of MWCNTs-Laponite and MWCNTs-CTAB were prepared by mixing the stock solutions/suspensions with water and consequent sonication of the samples during 10 min using an ultrasonic disperser UZDN-20/40 (UkrRosprylad, Sumy, Ukraine) at the frequency of 44 kHz and the output power of 150 W.

All the experiments were carried out at SANS facilities of Joint Institute for Nuclear Research (Dubna, Russia). The flux of thermal neutrons was high enough $(\sim 10^7\,\text{n/s} \cdot \text{cm}^{-2})$ to provide good resolution of the scattering pattern. The q-range of $0.1 \div 3.5$ nm⁻¹ was used. It corresponds to the real-space length range of $(1.7 \div 63)$ nm. The constant temperature of 298 K was maintained. The neutron scattering patterns of the studied samples were divided into three parts: power-law scattering of MWCNTs (I_p), coherent scattering of Laponite or CTAB (I_a) and background incoherent scattering (I_i):

$$I = I_p + I_a + I_i. \tag{1}$$

The contrast variation method was used for matching the scattering length density (SLD) and for reducing the neutron scattering intensity of additives.

Results and discussions

MWCNT-Laponite aqueous suspensions

To match the neutron scattering length intensity of Laponite, the mixture of H_2O and D_2O was used as a solvent in this series of samples. Fig. 1 presents the neutron scattering intensity I versus the wave

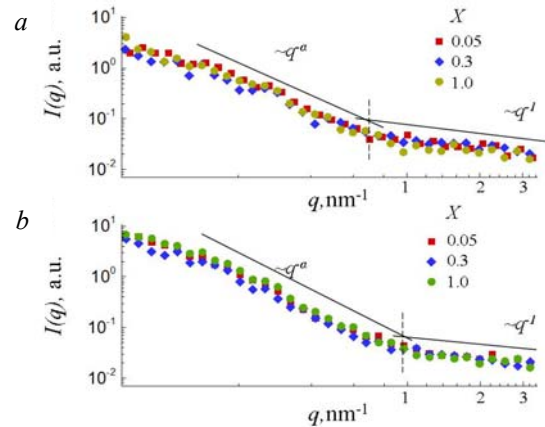vector q for samples with $C_n = 0.1$ % wt (a) and $C_n = 0.1$ % wt (b) at different Laponite/MWCNT weight ratio X.

Fig. 1. Neutron scattering intensity I versus wave vector q for samples with $C_n = 0.1$ % wt (a) and $C_n = 0.3$ % wt (b) at different Laponite/MWCNT ratio X.

The scattering patterns show the power dependencies $I(q) \propto q^{-\alpha}$ with different exponents at large $(1\ \text{nm}^{-1} < q < 3.5\ \text{nm}^{-1})$ and small $(0.1\ \text{nm}^{-1} < q < 0.5\ \text{nm}^{-1})$ values of wave vector q.

The constant value of $\alpha \approx 1$ was observed at high values of q. Such behavior is characteristic for the rigid rods and it is typical for MWCNTs [18]. From the other side, the exponent α value was higher $(= 1.2 - 2)$ at small values of q. The value α can be used for characterization of the dispersing ability of MWNTs in an aqueous suspension: better degree of dispersion of the MWNTs corresponds to smaller values of α [19].

Dependencies of the power exponent α versus Laponite/MWCNTs ratio X are presented in Fig. 2 for samples with different concentrations of MWCNTs: 0.1 and 0.3 % wt.
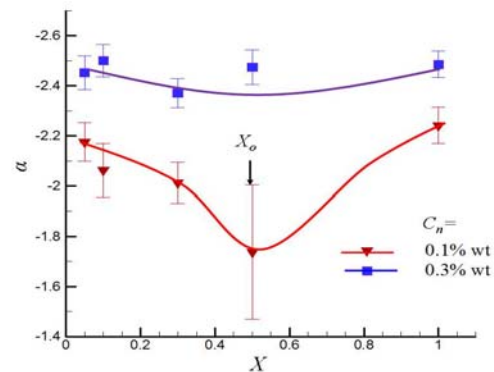

Fig. 2. Power exponent α versus Laponite/MWCNTs ratio X for two values of nanotube concentrations $C_n = 0.1$ % wt and $C_n = 0.3$ % wt.

With increase of Laponite/MWCNT ratio X, the power exponent α was passing through the minimum at certain optimal level of $X_o \approx 0.5$. Ability

of Laponite to stabilize the aqueous suspensions of MWCNTs was previously explained by adsorption of Laponite particles and formation of a hydrophilic charged shell on the surface of nanotubes [10]. The degree of MWCNT surface coverage by the platelets of Laponite can be estimated as

$$S_l/S_n \approx 6.06\ X \qquad (2)$$

and is equal to ≈ 3 at $X \approx 0.5$.

However, further increase of X value was accompanied by reduction of dispersing ability of MWCNTs, which can be explained by cross-linking of different MWCNTs via the Laponite platelets.

Note that transition from q-α to q-1 was observed at some crossover value of qc, which can be used for estimation of the scale of meshes in MWCNT networks, $\xi = 2\pi/q_c$ (Fig. 3). The similar behavior was observed earlier in SANS experiments with surfactant-stabilized single-wall carbon nanotubes in water [18]. The value of ξ was 7.4 nm and 6.3 nm for samples with MWCNT concentration $C_n = 0.1$ % wt and $C_n = 0.3$ % wt respectively. It reflected compacting of the aggregate structure with increase of C_n.
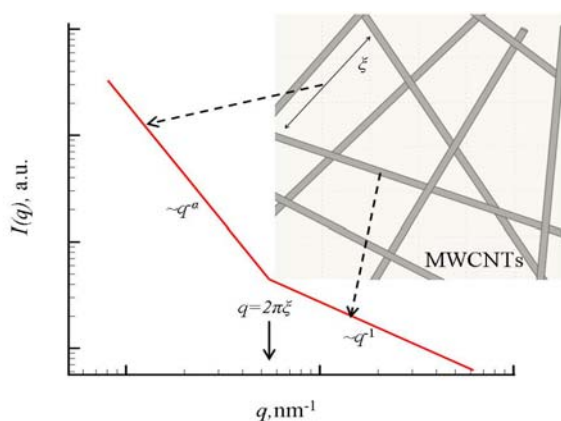

Fig. 3. Transition from $q^{-\alpha}$ to q^{-1} behaviour and mesh scale in MWCNT aggregates, $\xi = 2\pi/q_c$ [18].

MWCNT-CTAB aqueous suspensions

The scattering length density (SLD) of CTAB was approximately the same as for water H_2O, that's why H_2O was used as a solvent in this series of experiments. The scattering patterns of these samples also show the typical power dependencies $I(q)^\alpha\ q^{-\alpha}$ with different exponents at large (1 nm^{-1} < < q < 3.5 nm^{-1}) and small (0.1 nm^{-1} < q < 0.5 nm^{-1}) values of wave vector q (Fig. 4).

Dependences of the power exponent α versus concentration of CTAB, C_s, at different concentrations of MWCNTs, 0.1 % wt and 0.3 % wt, are presented in Fig. 5. Addition of surfactant also resulted in enhancing of the dispersing ability of MWCNTs. The optimum concentration of CTAB was

≈ 0.2 % wt for both 0.1 % wt and 0.3 % wt MWCNTs suspensions. At $C_s > 0.2$ % wt, the partial reduction of the dispersing ability was observed. These concentrations noticeably exceed the critical micelle concentration of CTAB, which is ≈ 0.036 % (1 mM), and formation of large CTAB micelles sized 6 nm is expected at such concentrations[20, 21].
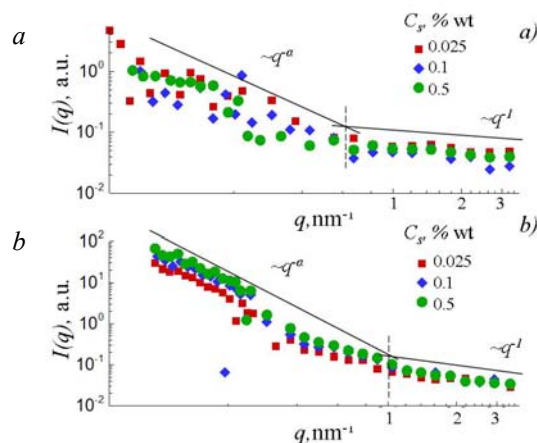

Fig. 4 Dependences of neutron scattering intensity versus q for samples with $C_n = 0.1$ % wt (*a*) and $C_n = 0.3$ % wt (*b*) at different CTAB concentrations C_s.
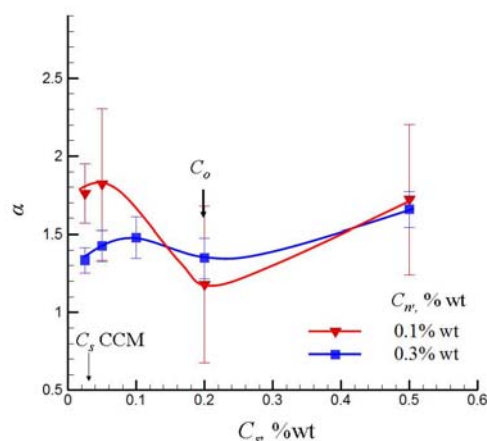

Fig. 5. Power exponent α versus CTAB concentration C_s for two values of MWCNT concentrations: 0.1 % wt and 0.3 % wt.

These micelles can cause rearrangement of MWCNTs at large concentrations of CTAB. The average mesh sizes of aggregates were 7.4 and 6.3 nm for MWCNT concentrations 0.1 and 0.3 % wt, respectively, i.e. they were practically the same as in MWCNT-Laponite aqueous suspensions.

Conclusions

The small-angle neutron scattering (SANS) is an appropriate experimental technique for investigation of the aqueous suspensions of MWCNTs stabilized by Laponite platelets or surfactant additive. This method enables to explore structures within (1 ÷ 50) nm and allows using of contrast variation technique.

Addition of charged Laponite platelets allowed improvement of the dispersing ability of MWCNTs in an aqueous suspension. The effect was optimal at the certain value of Laponite/MWCNTs ratio $X \approx 0.48$, which corresponded to the degree of MWCNT surface coverage by the platelets of Laponite ≈ 3. SANS also revealed existence of a mesh structure in MWCNT aggregates with characteristic mesh size of ≈ 7.4 and ≈ 6.3 nm in suspensions with concentration of 0.1 and 0.3 % wt of MWCNTs, respectively. The similar effects of CTAB addition on stabilization of aqueous MWCNT suspensions were also observed. The optimal surfactant concentration was ≈ 0.2 % wt. The partial reduction of dispersing ability above this level can be explained by formation of the large micelles of CTAB.

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МАЛОКУТОВЕ РОЗСІЯННЯ НЕЙТРОНІВ БАГАТОШАРОВИМИ ВУГЛЕЦЕВИМИ НАНОТРУБКАМИ У ВОДНИХ СУСПЕНЗІЯХ У ПРИСУТНОСТІ ЛАПОНІТУ АБО ЦЕТИЛТРИМЕТИЛ АМОНІЙ БРОМІДУ

Представлено результати дослідження структури напіврозведених 0,1 і 0,3 % вагових водних суспензій багатошарових вуглецевих нанотрубок (MWCNTs) методом малокутового розсіяння нейтронів (МКРН). Для підвищення ступеня дисперсності MWCNTs було використано домішки нанодисків лапоніту або катіонної поверхнево-активної речовини цетилтриметиламоній броміду (ЦТАВ). При високих значеннях хвильового вектора q (1 нм$^{-1}$ < q < 3,5 нм$^{-1}$) усі зразки проявляли поведінку характерну для жорстких стрижнів (тобто інтенсивність розсіяння нейтронів спадала як q^{-1}). При малих значеннях q (0,1 нм$^{-1}$ < q < 0,5) інтенсивність розсіяння нейтронів спадала як $q^{-\alpha}$ з показником α в діапазоні 1,2 - 2 залежно від концентрації нанодисків лапоніту або ЦТАВ. Домішки нанопластинок лапоніту або поверхнево-активної речовини ЦТАВ дозволяли поліпшити диспергування MWCNTs. Найбільш оптимальний ефект спостерігався при певному співвідношенні лапоніт/MWCNTs, $X \approx 0,5$ або концентрації ЦТАВ ($\approx$ 0,2 % вагових). Установлено також існування сіткової структури агрегатів MWCNT з характеристичною довжиною $\approx$ 7,4 і $\approx$ 6,3 нм у суспензіях концентраціями 0,1 і 0,3 % вагових MWCNTs відповідно.

Ключові слова: МКРН, пружне розсіяння нейтронів, нанотрубки, диски лапоніту, ЦТАБ.

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МАЛОУГЛОВОЕ РАССЕЯНИЕ НЕЙТРОНОВ МНОГОСЛОЙНЫМИ УГЛЕРОДНЫМИ НАНОТРУБКАМИ В ВОДНЫХ СУСПЕНЗИЯХ В ПРИСУТСТВИИ ЛАПОНИТА ИЛИ ЦЕТИЛТРИМЕТИЛАМОНИЙ БРОМИДА

Представлены результаты исследования структуры полуразбавленных 0,1 и 0,3 % весовых водных суспензий многослойных углеродных нанотрубок (MWCNTs) методом малоуглового рассеяния нейтронов (МУРН) . Для повышения степени дисперсности MWCNTs были использованы примеси нанодисков лапонита или катионного поверхностно-активного вещества цетилтриметиламмоний бромида (ЦТАВ). При высоких значениях волнового вектора q (1 нм$^{-1}$ < q < 3,5 нм$^{-1}$) все образцы проявляли поведение, характерное для жестких стержней (т.е. интенсивность рассеяния нейтронов спадала как q^{-1}). При малых значениях q (0,1 нм$^{-1}$ < q < 0,5) интенсивность рассеяния нейтронов спадала как $q^{-\alpha}$ с показателем α в диапазоне 1,2 - 2, в зависимости от концентрации нанодисков лапонита или ЦТАВ. Добавки нанопластинок лапонита или поверхностно-активного вещества ЦТАВ позволяли улучшить диспергирование MWCNTs. Наиболее оптимальный эффект наблюдался при определенном соотношении лапонит/MWCNTs, $X \approx 0,5$ или концентрации ЦТАВ ($\approx$ 0,2 % весовых). Установлено также существование сеточной структуры агрегатов MWCNT с характеристической длиной $\approx$ 7,4 и $\approx$ 6,3 нм в суспензиях концентрациями 0,1 и 0,3 % весовых MWCNTs соответственно.

Ключевые слова: МУРН, упругое рассеяние нейтронов, нанотрубки, диски лапонита, ЦТАБ.