Dispersions of carbon nanotubes in nematic liquid crystals: effects of nanotube geometry

L.N.Lisetski, A.M.Chepikov, S.S.Minenko,
N.I.Lebovka[*], M.S.Soskin[**]

Institute for Scintillation Materials STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine
[*]F.Ovcharenko Institute of Biocolloidal Chemistry, National Academy of Sciences of Ukraine, 42 Vernadsky Pr., 03142 Kyiv, Ukraine [**]Institute of Physics, National Academy of Sciences of Ukraine, 46 Pr. Nauky, 03039 Kyiv, Ukraine

Comparative studies were carried out of aggregate formation by carbon nanotubes (CNT) of different geometry dispersed in nematic liquid crystal 5CB. The picture of aggregation was found to be essentially similar for multi-walled and single-walled nanotubes (MWCNTs and SWCNTs), apparently not affected by the difference in aspect ratios, while for "short" nanotubes (s-MWCNT) the aggregation threshold was several times higher. A model is proposed describing the eventual effects of CNT bending in the liquid crystalline media, with effective values of the nanotube length and aspect ratio controlling the process of aggregate formation. The results obtained present a consistent picture interrelating geometrical parameters of CNTs, their concentration in the nematic dispersion, orientational order parameter, temperature-dependent optical transmission of the dispersion, and the rate of aggregate formation determining time stability of the obtained composite materials.

Проведены сравнительные исследования образования агрегатов углеродными нанотрубками различной геометрии, диспергированными в нематическом жидком кристалле 5СВ. Картина агрегации оказывается сходной для многостеночных и одностеночных нанотрубок, без существенного влияния аспектного отношения. В то же время для "коротких" многостеночных нанотрубок концентрационный порог агрегации в несколько раз выше по сравнению с "длинными". Предложена модель, описывающая возможные эффекты изгиба нанотрубок, ориентированных жидкокристаллической средой; при этом процесс агрегации контролируется эффективными значениями длины нанотрубки и ее аспектного отношения. Полученные результаты дают согласованную картину, связывающую геометрические параметры нанотрубок, их концентрацию в нематической дисперсии, параметр ориентационного порядка, зависящее от температуры оптическое пропускание дисперсии и скорость образования агрегатов, что определяет временную стабильность получаемых композитных материалов.

1. Introduction

Dispersions of carbon nanotubes (CNT) and other types of anisometric micro- and nanoparticles in liquid crystalline (LC) media have rapidly developed into a new class of composite materials with broad prospects of their practical application [1–3]. However, an important drawback of LC+CNT composites is that nanotubes dispersed in orientationally ordered LC medium show a tendency to their gradual aggregation, which leads to structural inhomogeneity of the samples and time instability of their characteristics. The pre-
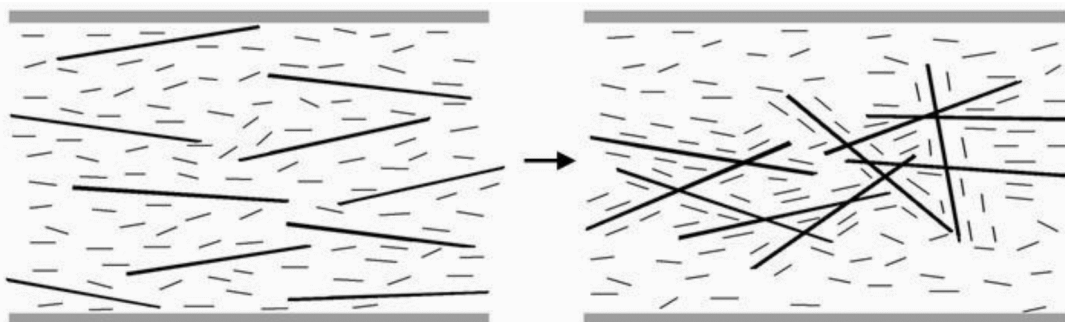
Fig. 1. A model picture of CNT aggregation in nematic liquid crystal medium.

sent-day situation with this problem is largely summarized in two recent papers by J.Lagerwall and co-workers [4,5], as well as in our previous publication [6].

To achieve suppression or slowdown of the aggregation process without resorting to chemical modification of the nanotube surface or introduction of additional components into a LC+CNT dispersion, one should first clear up the physical picture of how the aggregates of nanotubes are formed in the anisotropic medium. The first step was made when a simple experimental method was proposed [7] that allowed monitoring of CNT aggregation on the real time scale by measuring the optical transmission through a LC cell with dispersed nanotubes in the vicinity of the nematic to isotropic transition temperature. Further experimental data were obtained using differential scanning calorimetry, measurements of electrical conductivity, and other methods [6, 8–10]. To summarize, a tentative physical picture can be described in the following way. The initial CNT bundles are rather efficiently destroyed by ultrasonication, and the resulting dispersion consists of individual nanotubes, which are more or less homogeneously dispersed in the nematic matrix and aligned by the nematic director (Fig. 1, left). After sonication, the nanotubes gradually assemble into fractal aggregates, incorporating some molecules of the nematic matrix into the "micropores" of the aggregate "skeleton" (Fig. 1, right). The presence of such aggregates was first noted in experiments using optical methods [11], with fractal boundaries observed as a certain visible "coat". To distinguish this type of aggregates from initial CNT bundles, percolation networks and other structures that can emerge in dispersions of nanotubes, the term "S-aggregates" has been coined [6]. After several hours or days of incubation such S-aggregates behave like micron-sized small particles of flattened shape occupying up to 20–40 % of the bulk nematic volume. This can be described by a heuristic relationship [9]

$$C_{aggr} = cAr^{d_f}, \qquad (1)$$

where C_{aggr} is the volume concentration of S-aggregates, c is the CNT volume concentration in the dispersion, A is a phenomenological parameter accounting for the details of the geometry, r is the aspect ratio of the nanotubes (nanotube length l divided by its diameter d), and d_f is the experimentally determined (see, e.g., [7]) fractal dimensionality of the aggregate.

The aim of this work was comparison of aggregation behavior of CNTs of different types in a nematic liquid crystal 5CB.

2. Theoretical considerations

To give a quantitative estimate of the conditions required for the S-aggregate formation, one can assume a simplified picture of CNTs dispersed in a nematic medium as shown in Fig. 2. Let us consider two nanotubes of length l and diameter d (i.e., aspect ratio $r = l/d$) in a nematic medium that imposes orientational ordering on the nanotubes, which is described by the orientational order parameter S ($S = \langle 3\cos^2\theta - 1 \rangle/2$, where θ is the angle between the nanotube long axis and the nematic director, and the brackets $\langle\ \rangle$ denote statistical averaging). As a next step, we assume that the system is time stable ("vitrificated") with its parameters determined by the statistically averaged values. The minimum average distance between the nanotubes in Fig. 2 (or, generally speaking, between adjacent nanotubes in the imagined quasi-lamellar layer) that allows their mutual contact (eventually leading to aggregation) may be estimated as $m = l\sin\theta/2$.

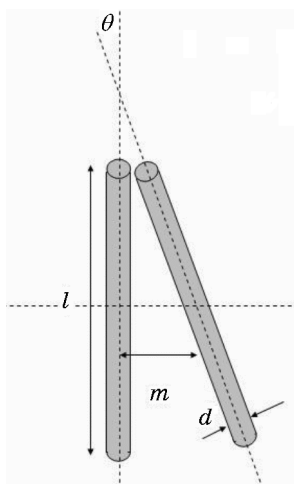From another viewpoint, if the volume concentration of nanotubes is c (which is

Fig. 2. A simplified picture of mutual orientation of two neighboring nanotubes in the orientationally ordered medium.

also their concentration in the quasi-lamellar layer), then CNT concentration in the planar projection ("linear concentration") is $\sqrt{c}$. At "linear concentration" $\sqrt{c}$, the average distance between the nanotubes in the quasi-lamellar layer is $m = d/\sqrt{c}$. Thus, we may write down the equation

$$\sin\theta = 2d/(l\sqrt{c}) = 2(r\sqrt{c})^{-1}, \qquad (2)$$

which determines the critical CNT concentration (i.e., the minimum concentration of nanotubes of a specified aspect ratio r that allows the CNT aggregation at a given value of S). The value of $r\sqrt{c}$ can thus be considered as a certain "similarity criterion" describing the aggregation behavior of nanotubes in quasi-homogeneous LC+CNT dispersions.

If the order parameter S substantially decreases, the aggregation threshold should also decrease. Recent experimental data [12] show that CNT dispersions in the nematic E7 (liquid crystal mixture on the basis of cyanobiphenyls) are more stable than in 5CB (4-pentyl-4′-cyanobiphenyl). This can be easily explained accounting for much higher nematic-isotropic transition temperature of E7 as compared with 5CB — under the same conditions (i.e. at the room temperature) the value of S is higher in E7 than in 5CB. Experimental data [13], as well as our own data, show that aggregation is much more intensive in the isotropic than in the nematic phase.

3. Experimental results

To check up the validity of the above-described theoretical considerations, one should obtain experimental data on aggregate formation in LC+CNT dispersions using nanotubes of different geometrical characteristics, with all other experimental conditions being the same.

In our experiments, we used several different types of carbon nanotubes. Single-walled carbon nanotubes (SWCNTs, $d = 1$-2 nm, $l \sim 20$ μm), as well as "short" multi-walled carbon nanotubes (s-MWCNTs, $d = 5$-10 nm, $l \sim 0.5$-2 μm) were obtained from Arry International GmbH, Germany and used without further treatment. Multi-walled carbon nanotubes (MWCNTs, $d = \sim 10$ nm, $l \sim 10$-20 μm) used for comparison (TMSpetsmash Ltd., Kyiv, Ukraine) were the same as used in our previous works [6–10], as well as the nematic matrix-4-pentyl-4′-cyanobiphenyl — a typical LC substance with dielectric anisotropy $\Delta\varepsilon > 0$ and nematic range 22-35°C (Chemical Reagents Plant, Kharkiv, Ukraine). The dispersions were prepared using an UZDN-2T ultrasonic mixer as described previously [7]. Optical transmission of the obtained dispersions in the vicinity of the nematic to isotropic transition was measured using a Hitachi 330 spectrophotometer in a 50 μm thick layer of planar texture placed in a temperature-controlled cell. All optical transmission values were measured at 700 nm. This wavelength was chosen as optimal because it was well above the absorption region and selective reflection bands of the 5CB.

Fig. 3 present optical transmittance "jump" in the vicinity of nematic-isotropic transition for 5CB + SWCNTs (a) and 5CB + s-MWCNTs composites (b) with different thermal pre-history.

The essential features of the results obtained can be summarized as follows.

1. The behavior of 5CB + SWCNT composites (Fig. 3a) is strikingly similar to 5CB + MWCNT systems studied previously [7, 8]. The optical transmission jump at the nematic-isotropic transition and its evolution during incubation show the same features (after incubation, the transmission jump becomes smaller, and a slight overall increase in transmission is observed; at CNT concentration of 0.1 %, even the absolute measured values are similar within several percent). The microscopic images of the aggregates were rather similar for initial (Fig. 4a) and incubated suspensions (Fig. 4b), however, a
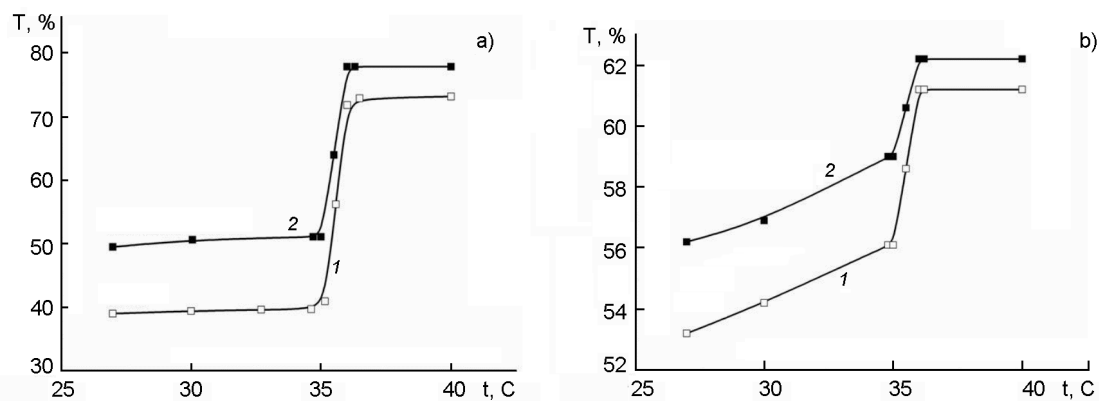
Fig. 3. Optical transmittance "jump" in the vicinity of isotropic-nematic transition for composites with different thermal pre-history: 5CB + SWCNTs, 0.1 % (a) and 5CB + s-MWCNTs, 0.4 % (b). *1*– correspond to non-incubated samples, and *2* – correspond to the samples incubated at 323 K for 24 h.
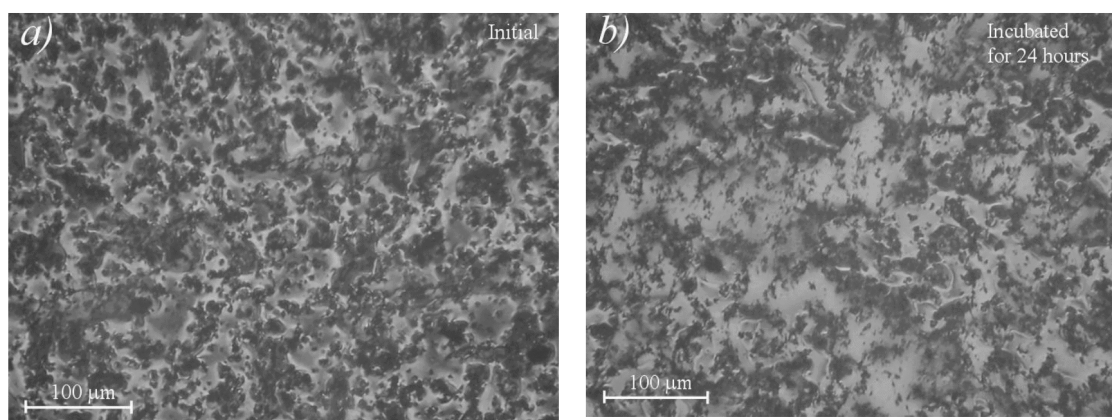

Fig. 4. Microscopic images of 5CB + SWCNT (0.1 %) composites in the nematic phase at $T = 295$ K. Images were taken immediately after sonication (a) and after incubation for 24 h. (b).

long-term (24 h.) incubation evidently resulted in spatial distribution changes, and increase of the size of cavities between clusters.

More detailed data obtained for other CNT concentrations indicate that probably the aggregate formation threshold is slightly higher (which is not consistent with the criterion of Eq.(2) suggesting much lower critical concentrations for SWCNTs having much higher aspect ratio.

2. On the contrary, the 5CB+s-MWCNT composites (Fig. 3b) appear to be noticeably different. At 0.1 % or 0.2 %, no signs of aggregation progress during incubation were noted, and optical transmission showed even larger jumps. At 0.4 %, the behavior became largely similar to the "standard" picture, while at 0.8 % clear signs of CNT sedimentation could be noted. This could be easily understood in terms of the Eq.(2) criterion — CNTs of shorter length and the

same diameter required noticeably higher concentrations for the start of S-aggregate formation. The narrow concentration range of "standard" behavior is limited from above by eventual onset of sedimentation processes. The microscopic images evidenced that incubation for 5CB+s-MWCNT composites was clearly expressed and resulted in formation of larger clusters (Fig. 5).

Thus, certain modifications of the above-described theoretical picture should be made to consistently describe all the set of experimental data.

4. Discussion

A fundamental assumption in the proposed picture of the nanotube ordering in the nematic medium is that the CNTs are to be considered not as rigid rods of fixed length and diameter, but as semi-flexible rods that can be easily bent by certain angles in several places.
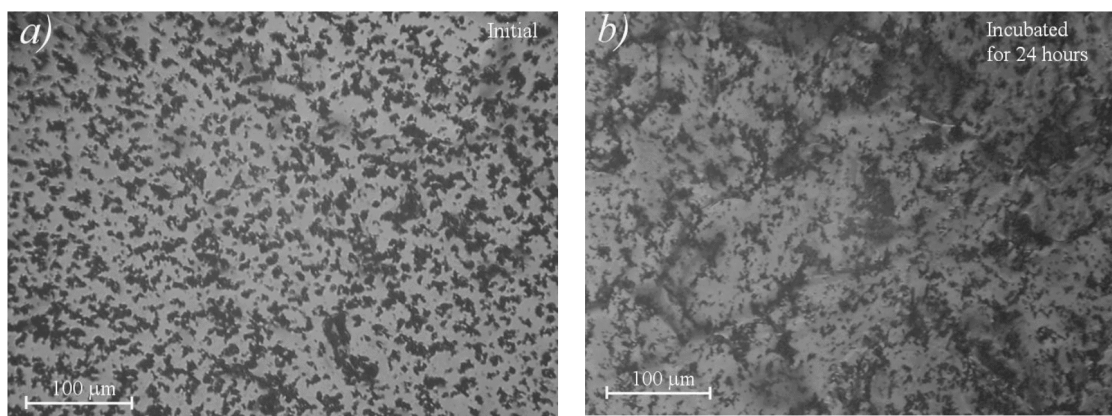
Fig. 5. Microscopic images of 5CB + s-MWCNT (0.4 %) composites in the nematic phase at $T = 295$ K. Images were taken immediately after sonication (a) and after incubation for 24 h. (b).

Such a model for CNTs in an isotropic medium was considered in [14], where the "contour length" and "end-to-end distance" were introduced to characterize the actual form of a nanotube. Analyzing images of individual CNTs obtained by scanning electron microscopy and experimental viscosity data for CNT dispersions in dimethylformamide, it was shown that these parameters can differ by at least 2–4 times, making the effective shape of the nanotube substantially different from that suggested by the formal aspect ratio value.

As for many other cases in the physics of liquids, the problem can be greatly simplified due to orientational ordering of the dispersion medium. It is generally accepted that the orientational ordering of the nematic liquid crystal imposes orientational ordering of the dispersed nanotubes [15, 16], thus restricting their freedom of movement (in particular, rotation of CNTs as anisometric particles about their short axes is strongly hindered, as well as lateral displacement of CNTs; the latter can be described in terms of highly anisotropic viscosity). One could assume that the nematic orientational ordering would also restrict internal degrees of freedom of the dispersed anisotropic particles (CNTs). When large organic molecules that can exist in the form of two (or more) conformations with different anisometry are dissolved in the LC medium, the equilibrium between conformations is shifted towards the conformation with higher anisometry (recent examples can be found, e.g., in [17, 18]).

Treating CNTs as very large "molecules" that can assume different conformational states — from the fully stretched to rolled up into a coil — one can assume that bend-ing of a nanotube in the orientationally ordered medium will be less strong, and the CNT segments will tend to be aligned along a certain direction (which can be called, in analogy to the standard LC term, an "internal director" of the nanotube). Then the model of the "multiply bent" CNTs used in [14] can be substantially simplified.

Assuming, as a first approximation, that the segments are of the same length and the bending angles are equal, we consider a model of CNT in the orientationally ordered medium as shown in Fig. 6. Using this model, the "effective CNT length" L_{eff} and "effective CNT diameter" D_{eff} may be calculated as

$$L_{eff} = aN\sin\frac{\varphi}{2} = aN\cos\varphi, \qquad (3)$$

$$D_{eff} = a\cos\frac{\varphi}{2} + d, \qquad (4)$$

where N is the number of segments.

When $\varphi = 180°$ (i.e. no bending), $L_{eff} = aN = l$ (the CNT contour length), and $D_{eff} = d$. When $a\cos\varphi/2 > d$ (i.e., when the segment length is much larger than the nanotube diameter, and the bending is sufficiently strong), the effective aspect ratio is $r_{eff} = L_{eff}/D_{eff} = N\text{tg}(\varphi/2)$, i.e., it is not dependent upon the CNT diameter. This can explain that MWCNT and SWCNT of similar length unexpectedly showed quite similar behavior in their aggregation, while the picture observed with "short" MWCNT was strikingly different.

A more detailed analysis can naturally take into account the difference in bending stiffness for nanotubes of different diame-
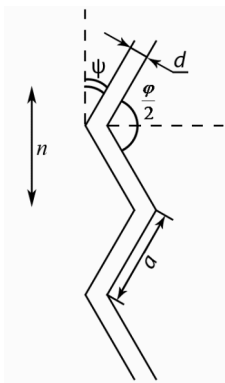
Fig. 6. A model picture of "flexible" CNT in the orientationally ordered medium. Here a is the length of one segment, d is the CNT diameter, φ is the angle between the neighboring segments, and ψ is the angle between a segment and the "internal director" (effective long axis) of the nanotubes. When the orientational order parameter S is close to 1, CNT is assumed to be aligned along the director of the nematic host.

ter, scatter in the values of a and φ along the nanotube, etc.

These considerations can also explain a certain contradiction that is implicitly present in many papers describing LC+CNT dispersions. Schematic drawings illustrating essential structural features of such systems (see, e.g., [2, 19–21]) show nanotubes as anisotropic particles that are much larger than anisometric LC molecules, but still of qualitatively comparable dimensions. This clearly contradicts the data on physical parameters of pure CNTs with aspect ratios of several hundred and more and lengths of several microns (i.e., close to thickness of standard LC cells). The observed properties, as well as theoretical descriptions, in fact, correspond to much smaller lengths and aspect ratios of the dispersed particles. So, the "effective" parameters L_{eff}, D_{eff} and reff can probably be considered as real physically meaningful parameters determining many properties of LC+CNT systems.

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Дисперсії вуглецевих нанотрубок у нематичних рідких кристалах: ефекти геометрії нанотрубок

Л.М.Лисецький, А.М.Чепіков, С.С.Міненко, М.І.Лебовка, М.С.Соскін

Проведено порівняльні дослідження утворення агрегатів вуглецевими нанотрубками різної геометрії, диспергованими у нематичному рідкому кристалі 5СВ. Картина агрегації виявилася подібною для багатостінкових та одностінкових нанотрубок, без істотного впливу аспектного відношення. В той же час для "коротких" багатостінкових нанотрубок концентраційний поріг агрегації був у кілька разів вищим у порівнянні з "довгими". Запропоновано модель, яка описує можливі ефекти вигинання нанотрубок, що орієнтуються рідкокристалічним середовищем, причому процес агрегації контролюється ефективними значеннями довжини нанотрубки та її аспектного відношення. Отримані результати дають узгоджену картину, яка пов'язує геометричні параметри нанотрубок, їх концентрацію у нематичній дисперсії, параметр орієнтаційного порядку, залежне від температури оптичне пропускання дисперсії та швидкість утворення агрегатів, що визначає часову стабільність композитних матеріалів, що отримують.