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Filament Formation in Biological Carbon Nanotube Suspensions†

ABE Hiroya *, TAN Zhenquan *, KONDO Akira *, and NAITO Makio *

Abstract

In this study, aqueous carbon nanotube (CNT) suspensions were prepared using biological surfactant of sodium deoxycholate (NaDC). The influence of NaDC concentration on the NaDC self-association in water and the rheological responses of the NaDC-CNT-water system were investigated. It has been found that the yield stress of the suspension increased with NaDC concentration, which was strongly related to the NaDC self-association of lyotropic liquid crystals. Due to the enhanced viscoelastic properties at high NaDC concentration (30%), it allowed the shear-induced filament formation in which the CNTs were aligned along to the shear direction. This filament formation may be attractive for transferring aligned CNTs on substrates in a controlled manner.

KEY WORDS: (Filament-type printing technique), (Single wall carbon nanotube), (Sodium dodexycholate), (Ink rheology)

1. Introduction

Carbon nanotubes (CNTs) have drawn considerable attention in the last decade due to their nanoscale size, their unique quasi one dimensional structure and their electrical, mechanical, and thermal properties [1]. In order to utilize CNTs in a wide variety of applications such as microelectronic circuit, advanced sensors and structural composites, methods are needed to efficiently assemble CNTs into controlled nano- and micro-patterns over large scale area [2]. In view of the large mechanical, electrical and optical anisotropy of CNTs, it is often important to control the CNT orientation as well.

Recently, we have demonstrated that the biological aqueous CNT suspensions, which contain CNTs and sodium deoxycholate (NaDC) as dispersing phases, can be applicable to a direct writing technique [3]. NaDC is a bile salt that is an anionic biological surfactant, and has been recently proven to be extremely efficient at dispersing CNTs in aqueous solution [4]. The stabilization mechanism can be explained by the adsorption of NaDC molecules onto the surface of CNTs driven by the hydrophobic interaction. NaDC has a convex hydrophobic surface consisting of a steroid nucleus with two hydrophobic interactions. NaDC also exhibits a rich and complex phase behavior in aqueous solution because of its unique molecular structure. Based on the rich phase behavior in water, NaDC can form complex supramolecular nanostructure triggered by CNTs. CNTs were reported to form ordered nanowires in the template of NaDC nanotube self-assembly [5]. At very high surfactant concentration (ϕ_{NaDC} >> critical micelle concentration, where ϕ_{NaDC} is weight $_{NaDC}$/weight$_{water}$), the excess NaDC forms fibrous long aggregates (lyotropic liquid crystals) in aqueous solution. In our previous study, it was found that the NaDC-functionalized CNTs disperse well in a NaDC-hydrated matrix and form supramolecular hydrogels in such a matrix. The biological CNTs hydrogels were also used as a solid ink, and an artificially controlled micronozzle was used to directly write the filament patterns. In addition, the NaDC was successfully removed by EtOH rinse, resulting in nocovalently re-bundled CNTs with the filament pattern.

In this work, we have investigated the influence of the NaDC concentration on the formation of NaDC lyotropic liquid crystals and the rheological responses of the biological CNT suspensions. It has been found that the yield stress of the hydrogel increased with ϕ_{NaDC}, which was related to the microscopic self-association of the biological surfactant in water. In addition, the hydrogel could be extended to be long along the direction of additional stretching forces. This filament formation may be attractive for CNT fiber production or for transferring aligned CNTs on substrates in a controlled manner.

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2. Experimental

Hipco type of single-wall carbon nanotubes (SWCNTs, CNI/USA) was used in this work. The SWCNTs have a diameter of about 1nm and a length in the range of hundreds of nanometers. The suspensions were prepared by mixing SWCNTs and NaDC in a defined ratio in water and then applying ultrasonic treatment for several hours with the assistance of zirconia balls, as described elsewhere [6]. The ultrasonic-treated samples were black sol and were aged in an inert environment for 24 h. A series of samples was prepared with mass concentration of SWCNT(ϕ_{SWCNT}) of 3% and mass concentration of NaDC(ϕ_{NaDC}) of 10% and 30%. The rheological properties were evaluated using a HAAKE rheostress 600 system (Thermo Scientific/Germany). SEM and optical microscopy studies were performed using a Hitachi SU-70 field emission SEM (Hitachi/Japan) and ECLIPSE LV100POL (Nikon/Japan). The flexible filament pattern was directly drawn on a glass substrate from the biological SWCNT-NaDC hydrogel. The NaDC was removed in the subsequent EtOH washing, resulting in noncovalently re-bundled SWCNTs patterns.

3. Results and Discussion

Figure 1 shows the optical microscopic image observed for the NaDC-water system with ϕ_{NaDC} =30% at room temperature. As can be seen, many fibers were formed and had a length more than several hundreds of micrometers. From the inset magnified image, diameters of the fibers were of ~1μm or more. A polarizing microscopic study was also performed for the sample. By rotating a quarter-wave plate between the polarizers and monitoring, the color change of the fibers was clearly observed due to anisotropic optical texture, indicating that the NaDC formed the giant fibrous liquid crystalline. On the other hand, no specific structures and no anisotropic optical texture were observed for the NaDC-water system with ϕ_{NaDC} =10%, as shown in Fig.2.

It has been reported that the formation of liquid crystals by NaDC is a typical phenomenon and there is a common pattern of lyotropic phase behavior at room temperature [7]. The lyotropic liquid crystals are formed at concentrate region beyond the isotropic solution phase. In the present study, the 10% NaDC-water system can be indentified as the isotropic solution phase. The giant anisotropic liquid crystals were formed in 30% NaDC-water system.

NaDC-water system is a rheological material and the viscosity properties increase with the NaDC concentration. In the previous study, we found that SWCNT could great enhance the rheological properties of NaDC-SWCNT [3]. Here, we investigated the enhancement effect of SWCNT for the rheological properties of the NaDC-SWCNT-water system containing varying amount of NaDC. Figure 3 shows the

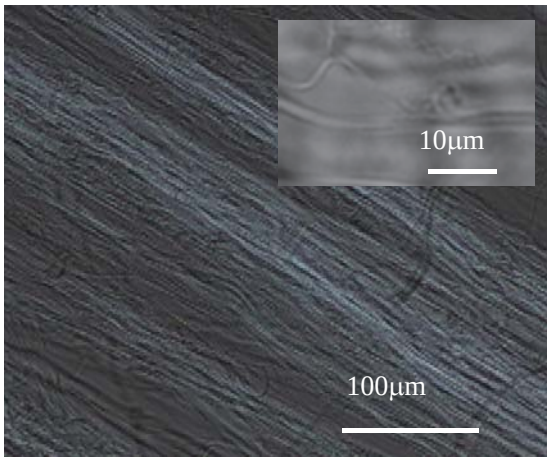

Fig.1 Optical microscopic observations for NaDC-water system at room temperature (ϕ_{NaDC} =30%).

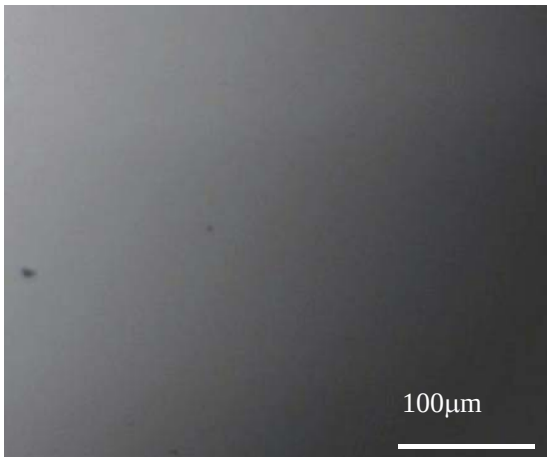

Fig.2 Optical microscopic observations for NaDC-water system at room temperature (ϕ_{NaDC} =10%).

shear stress of three kinds of NaDC-SWCNT hydrogels as a function of the shear rate. At low loading of the NaDC ($Ø_{SDC}$ = 10%), the NaDC-SWCNT hydrogel showed a small shear stress less than 70 Pa, and the shear stress increased with the shear rate during the measured range from 0.1 to 100 s^{-1}. On the other hand, the viscosuty of the hydrogel was smaller than 100 Pa·s, and decreased with the shear rate during the same measured range (Fig.4).

Actually, pure NaDC hydrogel in the same NaDC loading was too weak in viscosity and too unstable to measure the rheological properties in our study. Both of the shear stress and the viscosity increased with the loading amount of NaDC. The shear stress even increased 100-folds to above 2000 Pa by loading NaDC to $Ø_{SDC}$ = 30% (Fig.3). A similar increase degree was also observed in the viscosity (Fig.4). Pure NaDC hydrogel loading in $Ø_{SDC}$ = 30%, just had a shear stress less than 100 Pa during the same measured range of shear rate. It proved

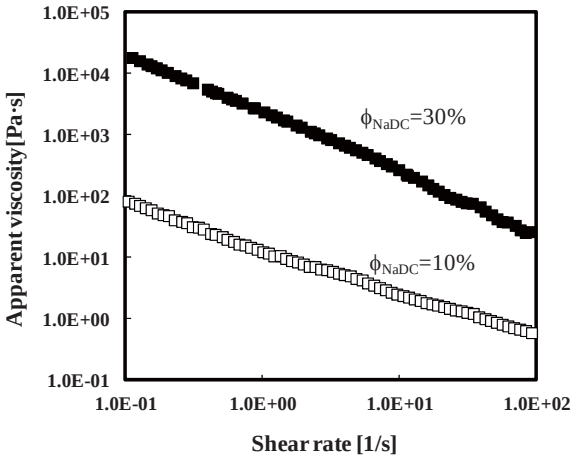

Fig.3 Shear stress of SWCNT-NaDC-water system as a function of shear rate at room temperature. (ϕ_{SWCNT} =3%, ϕ_{NaDC} =10% and 30%)

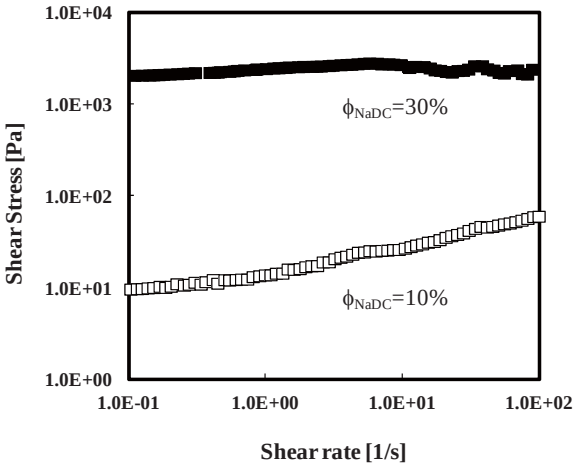

Fig.4 Apparent viscosity of SWCNT-NaDC-water system as a function of shear rate at room temperature. (ϕ_{SWCNT} =3%, ϕ_{NaDC} =10% and 30%)

that SWCNT indeed enhanced the shear stress and viscosity of the NaDC hydrogel. The enhancement of the rheological properties was considered as a result of the entanglement and framework effect of SWCNT [3]. As demonstrated in this study, the rheological properties of the NaDC-SWCNT-water system can be well enhanced with host phase containing biological lyotropic liquid crystals. Generally, the solid concentrations of CNTs suspensions are much lower than those of ceramic slurries, and it is quite difficult to enhance their viscoelastic response by tuning interparticle forces in such dilute system. The biological CNT suspension may be a potential candidate as printable CNT materials for direct-writing techniques.

Because SWCNTs have excellent electric conductivity and extremely high aspect ratio and ultra light quality, they are considered a sweet candidate for the flexible, stretchable electronics applications. Due to the excellent rheological properties of NaDC-SWCNT hydrogel, it may also have a potential in such electronic applications. NaDC-SWCNT hydrogel was used as a novel “solid ink” to fabricate micropartterns by an omnidirectional print method as described elsewhere [8]. When SWCNTs dispersed in NaDC matrix, the very low conductivity of NaDC reduced the conductivity of the supramolecular hydrogel of SWCNT-NaDC. However, NaDC could be removed by ethanol washing since it is much easily miscible in ethanol and SWCNT do not dissolve in ethanol. SWCNTs enriched and reassembled to noncovalent SWCNT patterns during a water-ethanol exchange process. As a result, the conductivity was greatly improved. We used a current pulse generator (HC-11, Hokuto Denko, Japan) to supply a stable current and an R6452A digital multimeter (Advantest, Japan) to record the voltage using a four terminal method. The cross sectional area of the SWCNT electrode was determined by HRSEM measurement. The conductivity was calculated. We found that such noncovalent SWCNT had an ohmic conductivity of about 55 $S \cdot cm^{-1}$, which is higher than the previously reported SWCNT based composite materials [9].

It was also found that the biological CNTs hydrogel displayed a strong tendency to form thin and very long filaments when subjected to shear, as shown in Fig.5. The filament was directly formed simply by dipping a spatula into a bulk sample of the biological CNTs hydrogel and then pulling it away. Similar observation has been also observed for the CNT-doped lyotropic liquid crystals of cationic surfactant of CTAB [10]. These observations are quite interesting from an applied point of view, since it opens a way of depositing CNTs on a substrate, resulting the uniaxial alignment of CNTs, and then washing away the lyotropic liquid crystals (surfactants).

We have extended the biological CNT suspension and directly deposited the NaDC-based biological CNT filament on a glass substrate. Then, it was washed using EtOH to remove NaDC from the filament. Figure 6 shows the SEM images of the resulting CNT pattern. As can be seen, the reconstructed SWCNT-bundles were preferentially oriented along the shear direction. This approach may be a useful for “top-down” CNT assembly for some specific applications.

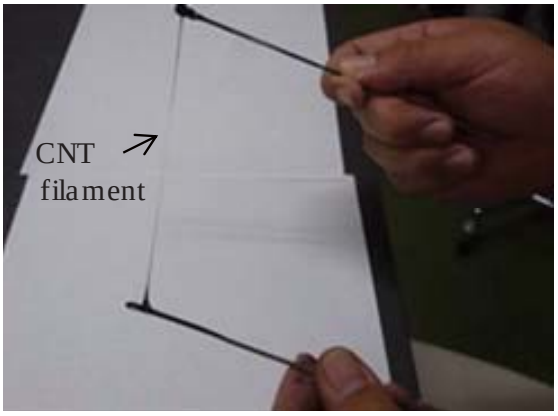

Fig.5 Thin filament drawn out of a biological CNT suspensions (ϕ_{SWCNT} =3%, ϕ_{NaDC} =10% and 30%).

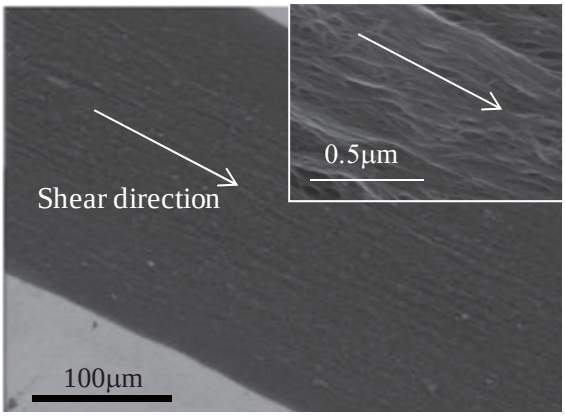

Fig.6 SEM images of the SWCNT-bundles patterned by the present method.

Acknowledgment

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