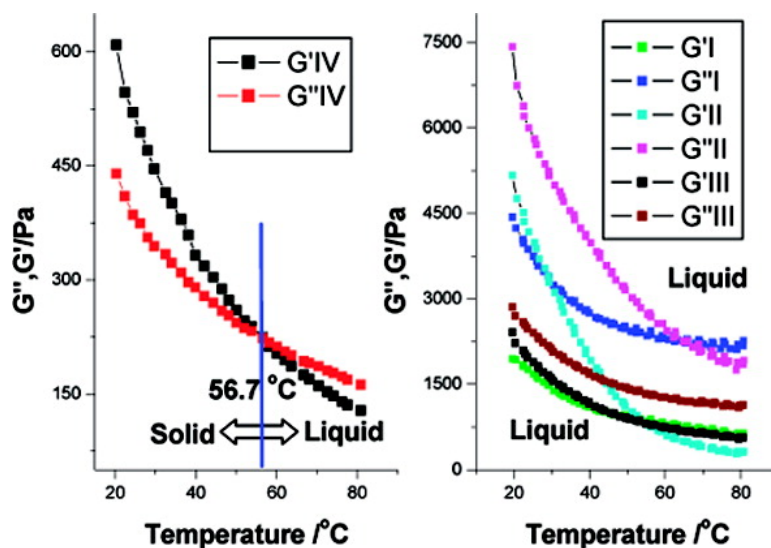


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## Controlled Viscoelastic Carbon Nanotube Fluids

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Inorganic nanoparticles coated with a soft organic shell possess a different rheological property<sup>1</sup> and novel functionalities compared with common solutions or colloids, and these may find important applications in smart sensors,<sup>2</sup> advanced composites,<sup>3</sup> and novel devices or systems.<sup>4–6</sup> These hybrid nanostructures include SiO<sub>2</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>7</sup> TiO<sub>2</sub>,<sup>8</sup> and carbon nanotubes (CNTs).<sup>9,10</sup> All the reported nanosystems exhibit a liquid-like behavior in the absence of solvents. However, our investigations show that the PEG-functionalized CNTs (PEG-CNTs) with higher functional density and smaller aspect ratio appear as low-viscous liquid but give an unexpected solid state and can even change from solid to liquid<sup>7,9</sup> with increasing temperature. Our finding suggests that novel controllable rheology nanofluids can be achieved through simply controlling the oxidation time of nanotubes.

Recent studies mainly focused on expanding the nanofluids and achieving specific functions by using different cored inorganic nanoparticles and organic moieties.<sup>7</sup> Nevertheless, the available qualitative descriptions about isolating modified nanosystems in liquid form are limited to most of the so-called 0D nanostructures, but they cannot predict our unexpected rheological behavior for quasi 1D carbon nanotube nanofluids. In this work, we modeled the rheological response governed by nanotubes' functional density, CNT contents and aspect ratio. Outstandingly, our finding can pave a way for realization of controlled viscoelastic nanofluids and novel functional nanodevices.

In a typical procedure,<sup>11</sup> multi-walled carbon nanotubes (MCNTs) are first oxidized with a HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture for 6, 10, 14, and 18 h and then react with PEG-substituted tertiary amine<sup>9</sup> [(C<sub>18</sub>H<sub>37</sub>)N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>H,  $n + m = 50$ ]. The resulting PEG-MCNTs, respectively, named I, II, III, and IV, usually contain an organic fraction of ~75% w/w (TG trace not given here). Figure 1 shows viscosity versus temperature in a range of 20–80 °C. The viscosity of all the samples normally decreases with increasing temperature. However, it is noted that the viscosity of sample IV is found to be 630–130 Pa·s, which is much lower than the data of others, namely, 12.5–5.3%. Direct observations are inconsistent with the above viscosity results: the first three samples are viscous, tar-like products at room temperature. In sharp contrast, the fluidity of sample IV is by far much higher under the same condition.

The corresponding moduli versus temperature (shown in Figure 2) of four samples are extremely interesting. For samples I, II, and III, the shear-loss moduli  $G''$  are, respectively, much higher than the storage modulus  $G'$  throughout the measured temperature range, suggesting a liquid-like behavior. For comparison, the viscoelastic response of sample IV is greatly different from the above samples. There is a critical temperature ( $T_c = 56.7$  °C) for solid–liquid transition in the temperature spectrum. When  $T < 56.7$  °C, the

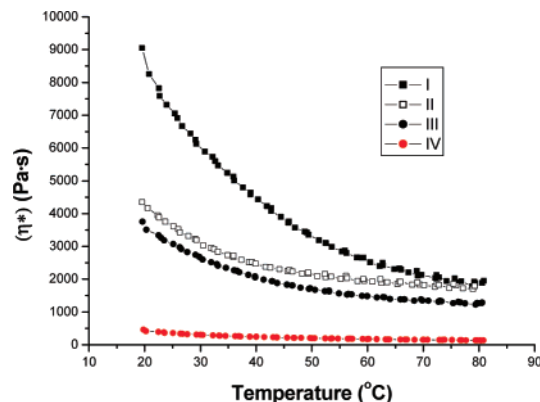


Figure 1. Viscosity–temperature traces of PEG-MCNT with different oxidation time: (I) 6 h, (II) 10 h, (III) 14 h, (IV) 18 h.

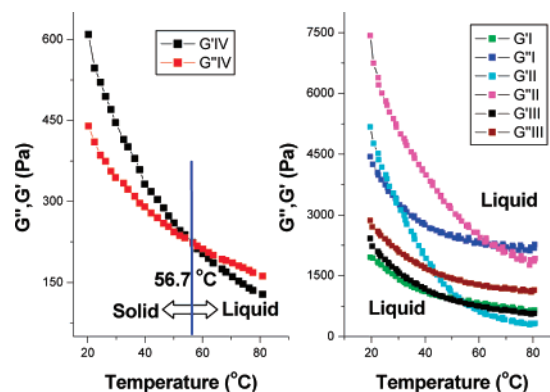


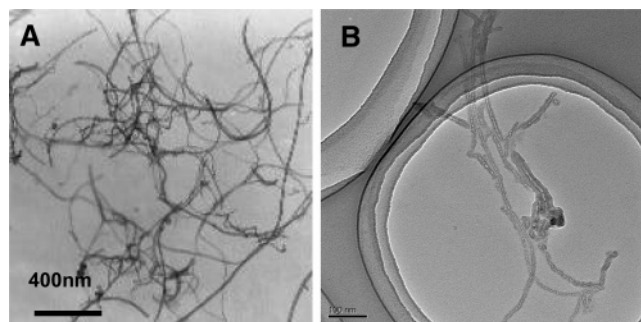
Figure 2. Moduli–temperature plots of PEG-MCNT with different oxidation time: (I) 6 h, (II) 10 h, (III) 14 h, (IV) 18 h.

system exhibits a solid-like behavior ( $G' > G''$ ). However, the behavior is liquid-like ( $G' < G''$ ) once the temperature is above  $T_c$ . The above inconsistency between viscosity results and rheology response is very interesting because all reported functional nanoparticles give a liquid behavior ( $G'' > G'$ ).<sup>6–9</sup>

To explore the reason for the unusual property, we investigated the functionalization and morphology of the oxidized MCNTs using X-ray photoelectronic spectra (XPS) and transmission electron microscopy (TEM). Figure 3 shows the morphological change of MCNTs with different oxidation time. Compared with the MCNTs with 6 h oxidation time (Figure 3A), the MCNTs at 18 h are sharply shortened from ~30 to ~0.5  $\mu$ m (Figure 3B). XPS results are in agreement with the TEM analysis: a longer oxidation time will produce a deeper functional and shorter MCNT pipes.<sup>11</sup> From the XPS investigations of four samples shown in Table 1 and TEM images for length changes of MCNTs, we can calculate the unit length oxygen content ( $J$ ) of the samples. The value increases significantly from 0.2385 (6 h) to 34.84 (18 h) with increasing oxidation time. The results suggest that more functional groups<sup>12</sup>

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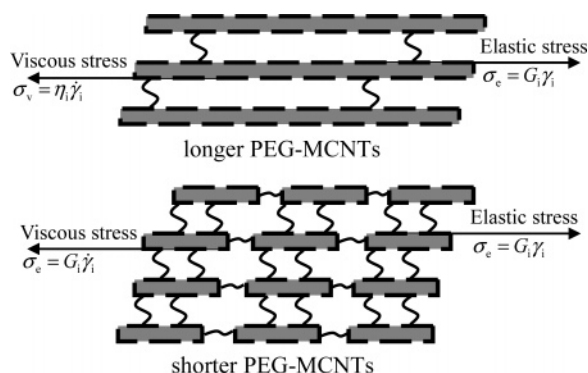


**Figure 3.** TEM images of MCNTs with different oxidation time: (A) 6 h, scale bar = 400 nm, and (B) 18 h, scale bar = 100 nm.

**Table 1.** XPS Results and TEM Length Analysis of Oxidized MCNTs with Different Oxidation Time

sample	oxygen content (%)	average length of MCNTs ( $\mu\text{m}$ )	unit length of oxygen content ( $J/\mu\text{m}^{-1}$ )
I	7.99	33.5	0.24
II	13.88	22.5	0.62
III	16.68	12.5	1.33
IV	17.42	0.5	34.84

**Chart 1.** Slipping and Fluidity Models of PEG-MCNT



(OH, COOH, C=O) were introduced into the unit length nanotubes with the elongation of oxidation time. In other words, sample IV has a higher functional density and smaller aspect ratio than the other samples.

The reported literature<sup>6–8</sup> disclosed many qualitative factors that can dominate the rheological properties of 0D nanofluids. However, the XPS results and TEM investigations suggest that the aspect ratio, CNT contents and functional density are key factors for the unique rheological behavior of quasi 1D PEG-MCNTs. We therefore apply a deformation and interaction mechanism<sup>13,14</sup> for the functional nanopipes' slipping and fluidity (shown in Chart 1). The central idea which we used to model the viscoelastic response of the nanofluids is that the deformation and fluidity are governed by the viscous interaction (both protonation and physisorption) of PEG-MCNT cells.

If we consider the start up of a steady shear, the equilibrium condition on the forces for each PEG-MCNT cell gives  $\sigma = \sigma_{\text{viscous}} - \sigma_{\text{elastic}} = 0$ . We analyzed the results in terms of three important parameters, one of which is  $a$ , the average length of each PEG-MCNT cell, the volume fraction of CNTs ( $x$ ), and the other is functional density ( $J$ ). Energetically, there are good reasons why

this unusual rheological behavior could occur. Using the Arrhenius equation, we calculated the slipping and fluidity active energy of each cell, namely,  $1/Jx = K \times \exp(-E_a/RT)$  (or  $a/x = K' \times \exp(-E_a/RT)$ ), where  $K$  is a coefficient,  $R$  is a constant, and  $T$  is the temperature. The above analysis suggests that the sample with a higher functional density (larger  $J$ ) or smaller aspect ratio (smaller  $A_f$ ) and smaller CNT contents will have a higher  $E_a$ . Therefore, our deformation and interaction mechanism explains why the longer PEG-MCNT system at the same temperature behaves as a fluid but shorter PEG-MCNTs appear as a solid (for details, see Supporting Information). Moreover, the quantitative relation between  $J$ ,  $x$ , and  $A_f$  and  $E_a$  paves the way for realization of controllable viscoelastic nanofluids.

In summary, we produced controlled viscoelastic quasi 1D MCNT nanofluids via a simple oxidation technique, which had a greater different rheological response from reported 0D nanostructures. Our investigations and calculation demonstrated that the functional density and aspect ratio of the nanopipes play a crucial act in the output properties of the addressed system. This gives us a quantitative understanding of the relationship between particle interaction, shape, and rheological property, which will be convenient for the development of viscoelasticity-specific devices. Moreover, facile control of the aspect ratio and functional density of nanostructures will give us a versatile route for fantasy functional nanofluids with different rheological response.

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**Supporting Information Available:** Experimental preparations, TEM images with different oxidation time, and calculation of slipping and fluidity model for PEG-MCNT cells. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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