The Rheology and Processing of Carbon Nanotubes for Polymer Composite Applications

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ABSTRACT

This presentation first highlights experimental observations on the rheology of: (1) non-functionalized CNTs that aggregate and (2) functionalized CNTs that do not aggregate in flow. The shear and extensional flow behavior of these two types of CNTs are compared and contrasted. Extensional flow is of particular relevance to fiber spinning and inkjet printing of CNT-containing "fluids". In the second part of the presentation, two different rheological models are presented and discussed. These models connect the viscosity data with the orientation and the aggregation state of CNTs, offering insights into controlling CNT dispersion, alignment, and the final properties of CNT polymer composites.

Keywords: rheology, processing, carbon nanotube, fiber spinning, inkjet printing

1 MOTIVATION

Carbon nanotubes (CNTs) have a diameter on the nanometer scale and a reported length on the micrometer or even centimeter scale [1]. The aspect ratio is defined as the length to diameter ratio, and the high-aspect-ratio of CNTs offers a unique competitive advantage for using CNTs as conductive fillers for polymers. Only a small CNT loading (typically < 0.1 wt.%) is needed to achieve conductive pathways and impart sufficient electrical conductivity for electrostatic dissipation applications [2]. However, the high-aspect-ratio of CNTs also results in significant viscosity enhancements, posing a processing challenge. To this end, understanding the rheology, or the complex flow behavior, of CNTs dispersed within a polymer matrix is critical to processing CNTs into functional materials in a scalable and controllable manner.

2 RESULTS AND DISCUSSIONS

2.1 Flow-induced Optical Microstructures

Both chemically functionalized and non-functionalized CNTs were first dispersed in epoxy and acrylic resins with relatively simple base rheology. Flow-induced microstructures of CNT were subsequently studied using a shear stage mounted on an optical microscope [3]. Non-functionalized CNT suspensions showed a richer optical texture compared to functionalized CNT suspensions, where specially designed functional groups were covalently attached to the CNTs to prevent aggregation [4, 5]. Low shear was found to induce aggregation whereas high shear was capable of breaking up the aggregates and creating a more uniform dispersion. As simple shear was applied to non-functionalized CNTs suspended within a low viscosity solvent, an unusual type of flow-induced structures was observed and identified as "helical bands" [3]. "Helical bands" (HBs) are highly anisotropic structures that aligned perpendicular to both the shear and the velocity gradient directions. The way in which these structures were formed is intriguing and has great resemblance to the process of hand spinning cotton into short fibers.

2.2 Steady-Shear and Extensional Rheology

Incorporation of CNTs into a Newtonian medium increased the base viscosity of the whole system but this viscosity enhancement effect decreased as a function of increasing shear rates. Such behavior is known as "shear-thinning". Although shear-thinning behavior has been reported for other types of suspensions [6], non-functionalized CNT suspensions showed a much stronger shear-thinning effect compared with traditional glass or carbon fiber suspensions at a similar concentration level. In one experiment, addition of 0.1 wt.% non-functionalized CNTs resulted in two decades of increase in the low shear viscosity [7].

Understanding the extensional rheology of CNT suspensions is relevant to processes such as fiber spinning [8], curtain coating, and inkjet printing [9]. The extensional rheology of functionalized and non-functionalized CNT suspensions was characterized using a capillary thinning technique [10]. It was observed that liquid filaments formed by functionalized and non-functionalized CNT suspensions behaved differently when subjected to uniaxial elongation. Functionalized CNTs increased the apparent extensional viscosity and prolonged the liquid filament thinning process, whilst non-functionalized CNTs created instability to the filament formed, consequently resulting in non-uniform curvature along the liquid filament axis and early filament breakup. Irregularity of the non-functionalized

CNT filaments was consistent with optical images, where spatial variation in CNT concentration was observed. In the case of functionalized CNT suspensions, the enhanced extensional viscosity was modeled in terms of the alignment of CNTs in the stretching direction, and the degree of alignment was subsequently estimated using an orientation model.

2.3 Rheological Modeling

Steady shear rheology of both functionalized and non-functionalized CNT suspensions was modeled. For the functionalized CNT suspension showing no shear-induced aggregation, its shear-thinning effect was successfully modeled by a Fokker-Planck (FP) based orientation model [4]. The model assumes that the shear flow aligns CNT in the flow direction, but there are also events such as Brownian motion and tube–tube interactions that randomize CNT orientation. These randomizing events were modeled with an appropriate rotary diffusion coefficient and the relatively mild shear-thinning behavior was explained in terms of progressive alignment of CNTs toward the shear direction. In the case of the non-functionalized CNT suspensions, CNT orientation alone was proved to be inadequate in explaining the more pronounced shear thinning behavior. It is necessary to develop a more advanced model taking into account both elements of CNT orientation and aggregation. Inspired by earlier modeling work on associative polymers, a new Fokker-Planck based aggregation/orientation (AO) model was formulated [7]. This model considered a hierarchy of states between CNTs that are free from entanglement and a complete CNT network, thereby enabling different microstructure populations to exist for different shear conditions. Using one additional parameter that describes the aggregation/disaggregation kinetics, the experimental data was fitted with reasonable precision.

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