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Communication

Liquid Crystallinity of *p*-Aramid/Multi-walled Carbon Nanotube Composites

Chae Bin Kim[1], Yong-Mun Choi[1], Hyun Ju Kim[1,2], Haena Lee[1,3], Nam-Ho You[1], Jae Kwan Lee[2], Bon-Cheol Ku[1], and Munju Goh[1]*

[1]*Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), Wanju 55324, Korea*
[2]*Department of Carbon Materials, Chosun University, Gwangju 61452, Korea*
[3]*Department of Organic Materials Engineering, Chungnam National University, Daejeon 34134, Korea*

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Abstract: A systematic study regarding the liquid crystallinity of *p*-Aramid and MWCNTs composite at various *p*-Aramid and MWCNTs concentrations in sulphuric acid was investigated and optimized by solution viscosity measurement and opalescence observation. We observed a merged liquid crystalline phase consisting of both *p*-Aramid and MWCNTs, and we believe this is the first study to report this combined liquid crystalline phase in one suspension. In addition to providing fundamental insights, we envision this study could be useful to those developing a strong, light, and high-performance polymeric composite fibers.

Keywords: Liquid crystal, Composite, Fiber, *p*-Aramid, Carbon nanotube

Introduction

Material scientists and engineers continuously attempt to develop stronger, high-performance materials with lighter weight. Those materials can be used in numerous industrial fields including aerospace [1], automotive [2], civil engineering [3], sports goods [4] as well as many other consumer and technical applications [5]. In order to meet these great industrial demands, high performance polymeric fibers have attracted a tremendous attention due to their high tensile strength-to-weight ratio and ability to withstand high impact [6].

Among such polymeric fibers, Kevlar is particularly known as a high-strength synthetic fiber. By the measure of tensile strength-to-weight ratio, Kevlar is 5 times stronger than steel, owing to many inter-chain interactions including hydrogen and aromatic stacking bonds [7]. Due to these inter-chain interactions, Kevlar's molecular structure consists of closely packed rod-like structures, resulting in Kevlar exhibiting liquid crystalline characteristics [7]. This means the orientation of rod-like Kevlar's molecular structures would significantly affect the mechanical properties of the Kevlar fiber. To maximize the mechanical properties by shear aligning the molecular orientation, therefore, Kevlar fibers have been produced via wet spinning from a lyotropic (liquid crystalline mesophase) suspension in sulphuric acid [7].

To further enhance the mechanical properties, reinforcement of the plastics by introducing fillers is the most commonly used strategy [8,9]. Carbon nanotubes (CNTs) have been extensively used as a filler due to its exceptional thermal, electrical, mechanical properties, and low density [10]. Compositing the CNTs with Kevlar, thus, would possibly yield stronger, high performance composites with even less weight than the neat Kevlar ascribing to the low density of CNTs [11]. In fact, Gun'ko and coworkers have demonstrated the incorporation of multi-walled CNTs into Kevlar significantly enhanced all mechanical parameters compared to the original Kevlar fibers [12]. In their experiment, compositing the CNTs into Kevlar was achieved by immersing Kevlar fibers into a suspension of CNTs in N-methylpyrrolidon (NMP) while ultra-sonicated. As a result of the CNTs incorporation, Young's modulus increased from 115 to 206 GPa, strength from 4.7 to 5.9 GPa, strain at break from 4.0 to 5.4 %, and toughness increased from 63 to 99 J/g.

By simply swelling the Kevlar in CNTs suspension, however, the orientation of the CNTs within the Kevlar could not be controlled. In a concept similar to that used for Kevlar, various studies have revealed that highly oriented CNTs exhibited significantly enhanced mechanical properties compared to randomly oriented CNTs either as itself [13] or as a filler in composites [14]. Since both Kevlar and CNTs can form a lyotropic suspension [13,15], we postulated liquid crystalline phase of Kevlar-CNTs composite can be formed in one suspension, and by extension the fibers can be produced by wet spinning from the suspension at a time. The resulting Kevlar-CNTs composite fibers would possess highly oriented CNTs in aligned Kevlar molecules along the same direction, thus it is anticipated to exhibit an even greater enhancement in mechanical properties compared to the Kevlar-CNTs composite fibers with randomly oriented CNTs.

To this end, we herein report a fundamental study regarding the liquid crystallinity of Kevlar-CNTs composite in suspension so that this study could be useful to those producing super-strong, high performance composite fibers with lighter weight. We systematically investigated and optimized the liquid crystallinity of Kevlar-CNTs composite

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*Corresponding author: goh@kist.re.kr

at various Kevlar and CNTs concentrations in sulphuric acid by both solution viscosity measurement and opalescence observation. In addition to providing fundamental insights, we envision this study could guide future material design in this area.

Experimental

Materials

A commercially available Kevlar, *p*-Aramid (HERACRON), was provided by Kolon Industries and used after washing with acetone thoroughly to remove sizing materials. Multi-walled CNTs (JENO Tube 9, 98 % purity, diameter 7-9 µm) was purchased from JEIO Co., Ltd. in Korea. All other chemicals used in this study were purchased from Fisher Scientific or Sigma Aldrich and used as received unless otherwise noted.

Synthesis of *p*-Aramid Nanofiber Functionalized Multi-walled CNTs

p-Aramid nanofiber functionalized MWCNTs was prepared to enhance the interaction between CNTs and *p*-Aramid by following the procedure described in elsewhere [16]. 0.3 g of *p*-Aramid fiber and 0.3 g of KOH were first added into 200 m*l* of dimethyl sulfoxide (DMSO) while stirring. Then, 0.1g of *p*-Aramid fiber was added each day until a total amount of p-Aramid fiber to be 1 g. In order to remove residual potassium ion from the solution, dialysis was performed using DMSO/water 2:1 (in volume) solution for 4 hrs. Subsequently, 0.5 g of multi-walled CNTs was added into the *p*-Aramid/DMSO solution and stirred using magnetic bar for 3 days. The resultant CNTs dispersed *p*-Aramid/DMSO was then filtered with PTFE membrane (pore size 0.2 µm). The obtained *p*-Aramid functionalized MWCNT was washed with water and ethanol several times followed by drying in vacuum oven at 80 °C overnight. By convention in this work, we use the MWCNTs to refer to *p*-Aramid functionalized MWCNT.

Solution Viscosity Measurement

Solution viscosity measurement was performed using Brookfield viscometer (LVDV II+ Pro) at ambient conditions. *p*-Aramid was dissolved in 98 % suphuric acid. Then, the prepared *p*-Aramid/MWCNT was added into the *p*-Aramid solution followed by sonication for 4 hrs.

Results and Discussion

Conventionally, *p*-Aramid fibers have been produced by wet spinning from a lyotropic suspension in sulphuric acid [7]. Liquid crystallinity of neat *p*-Aramid in sulphuric acid as a function of *p*-Aramid concentrations was first monitored by observing opalescence (Figure 1(a)). As evidenced by the presence of clear, uniform solution color (dark brown), at relatively low *p*-Aramid concentration (up to 12 wt% *p*-Aramid), the *p*-Aramid was homogeneously dissolved in the sulphuric acid. However, upon further increase in the *p*-Aramid concentration, the solution changed color to translucent white. This color change to translucent white is called opalescence, originated from light scattering through a suspension with highly dispersed crystalline *p*-Aramid. This confirms that the formation of liquid crystalline *p*-Aramid at concentration above 13 wt% in sulphuric acid.

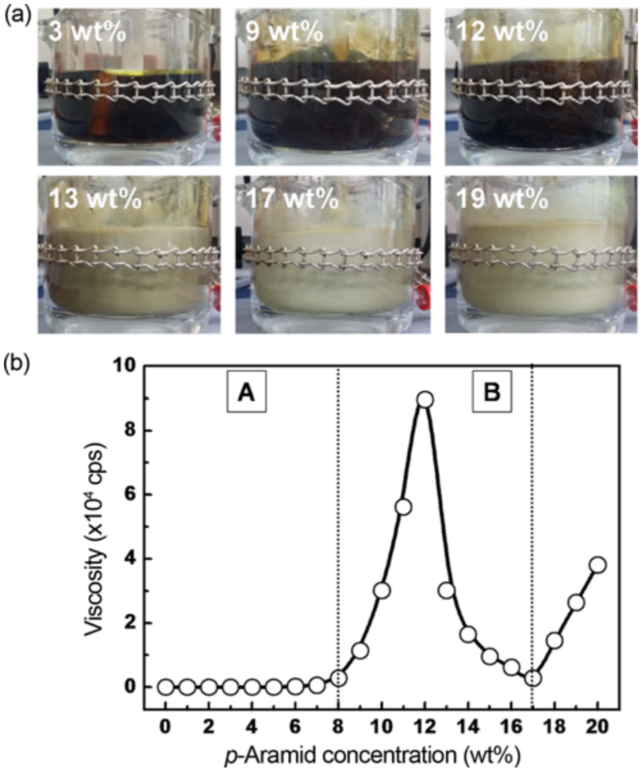

Figure 1. (a) Photographs of the *p*-Aramid in sulphuric acid at various *p*-Aramid concentrations and (b) viscosity of the *p*-Aramid in sulphuric acid as a function of the *p*-Aramid concentration.

In order to further investigate the liquid crystallinity of *p*-Aramid in sulphuric acid, solution viscosity was measured as a function of *p*-Aramid concentration at ambient conditions. Figure 1(b) shows that the solution viscosity increased with increasing *p*-Aramid concentration, reached a maximum, decreased to a minimum, and then finally increased again. This result well corresponds to the aforementioned opalescence observation shown in Figure 1(a). The initial increase in solution viscosity as increasing the *p*-Aramid concentration up to 12 wt% indicates the *p*-Aramid was homogeneously dissolved in sulphuric acid. A subsequent decrease in solution viscosity upon further increase in the *p*-Aramid concentration (from 12 to 17 wt%) is a consequence of liquid crystalline *p*-Aramid formation. As the crystalline *p*-Aramid formed in a liquid medium, the homogeneous solution turned into lyotropic suspension, reducing the

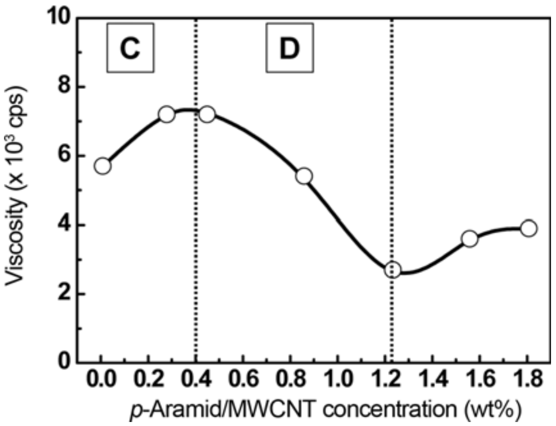

Figure 2. Viscosity of the *p*-Aramid and MWCNT in sulphuric acid as a function of the MWCNT concentration with respect to the total solution weight. For this measurement, 17 wt% of *p*-Aramid in sulphuric acid was used.

viscosity. Thus, the suspension with minimum viscosity corresponds to the maximum liquid crystallinity of the *p*-Aramid in sulphuric acid. Finally, further increase in *p*-Aramid concentration (above 17 wt%) yielded more concentrated suspension, increasing the viscosity again.

To study liquid crystallinity of *p*-Aramid-CNTs composite, the viscosity was characterized using the suspension composed of *p*-Aramid, MWCNT, and sulphuric acid as a function of MWCNT loadings (see Figure 2). Various amounts of MWCNT were added into the suspension of 17 wt% *p*-Aramid in sulphuric acid, corresponding to the suspension with the maximum liquid crystallinity of *p*-Aramid. Similar to the results shown in Figure 1(b), the viscosity increased with increasing MWCNT loadings, reached a maximum, decreased, and then finally increased again. As observed in neat *p*-Aramid in sulphuric acid, a reduction in viscosity at MWCNT concentration between 0.4 and 1.2 wt% was observed. It is noteworthy that Davis *et al.* have reported single-walled CNTs can be self-assembled into a polydomain nematic liquid crystalline phase at high concentration in sulphuric acid, thus reducing the solution viscosity upon increasing the CNTs loadings [15]. However, the viscosity reduction shown in Figure 2 is almost over twice the viscosity reduction reported using a suspension composed of only single-walled CNTs and sulphuric acid. Therefore, further reduction in viscosity here is an evidence for the formation of a merged liquid crystalline phase of *p*-Aramid and MWCNT.

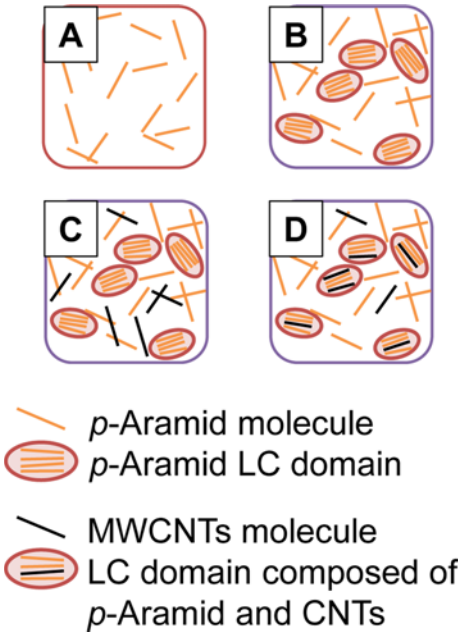

Figure 3. Schematic describing liquid crystallinity of *p*-Aramid and *p*-Aramid-CNTs composite in sulphuric acid. Each letter on the upper left side corresponds to regimes labeled with the same letters in Figures 1(b) and 2.

A schematic describing liquid crystallinity of both neat *p*-Aramid and *p*-Aramid-CNTs composite in sulphuric acid is given as Figure 3. As the *p*-Aramid contents increased in sulphuric acid, the solution viscosity first increased (region labeled as ‘A’ in Figures 1(b) and 3). A subsequent drop in the viscosity indicates the formation of liquid crystalline *p*-Aramid (region labeled as ‘B’ in Figures 1(b) and 3), reaching the minimum viscosity with the maximum liquid crystallinity (at 17 wt% in Figure 1(b)). At *p*-Aramid concentration with the maximum liquid crystallinity, MWCNT was then added. Initially, the viscosity increased as a function of the CNTs loadings (region labeled as ‘C’ in Figures 2 and 3), followed by a reduction in viscosity as *p*-Aramid-CNTs composite formed the liquid crystals (regions labeled as ‘D’ in Figures 2 and 3), reaching the minimum viscosity with the maximum liquid crystallinity of *p*-Aramid-CNTs composite (at 1.2 wt% in Figure 2).

Conclusion

In order to guide producing super-strong, light, high performance composite fibers, a systematic study regarding the liquid crystallinity of both *p*-Aramid and *p*-Aramid-CNTs composite in suspension was performed. We’ve observed that the maximum liquid crystallinity of neat *p*-Aramid was achieved at 17 wt% *p*-Aramid in sulphuric acid by both solution viscosity measurement and opalescence observation. Upon adding the MWCNTs in the *p*-Aramid suspensions, a merged liquid crystalline phase of *p*-Aramid and MWCNTs was observed at MWCNTs concentration between 0.4 and 1.2 wt%, and we believe this is the first study to report the liquid crystalline phase consisting of both *p*-Aramid and MWCNTs. We envision this study could be useful to those producing *p*-Aramid-CNTs composite fibers with both lighter weights and excellent mechanical properties.

Acknowledgements

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