Structural and mechanical properties of cellulose acetate/graphene hybrid nanofibers: Spectroscopic investigations

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Abstract. Cellulose acetate/graphene (CA/graphene) and cellulose acetate/graphene-COOH (CA/graphene-COOH) hybrid nanofibers were fabricated via electrospinning technique, and their morphologies, crystallinity and mechanical properties were investigated. The added amounts of graphene and graphene-COOH were varied from 0.5 to 5.0 wt%. The crystal structures and morphologies of the resultant hybrid nanofibers were investigated by wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Graphene-COOH incorporated CA nanofiber mats showed higher Young's modulus of about 910 MPa among than those of CA/graphene nanofibers, which is due to molecular interactions between –COOH groups in acid-treated graphene and C=O groups in CA via hydrogen bonding. This specific interaction was demonstrated by spectroscopic studies (Raman and Fourier transform infrared (FT-IR) spectroscopies).

Keywords: mechanical properties, nanofiber, graphene, molecular interactions, polymer composites

1. Introduction

In order to avoid the environmental pollutions by synthetic polymeric materials, in the recent few decades, the number of reports of the biodegradable polymers or green composites has been rapidly growing [1–5]. Certainly, electrospinning is a simple and very effective technique for the fabrication of nanofibers and nanocomposite fibers [6]. In particular, the fabrication of nanofibers using cellulose and its derivatives has played important role due to their excellent properties [7], especially due to their biodegradability in nature [8–11]. Moreover, due to potential compatibility, excellent optical and mechanical properties, cellulose acetate (CA) has been used for the applications in diverse areas such as

fibers, films, laminates, adhesives, coatings, plastic products, etc. [12–16]. In fact, the significant amounts and varieties of synthetic plastics, especially polyolefins, polystyrene (PS), etc. are currently produced from fossil fuels, consumed and discarded into the environment, ending up as nondegradable wastes. Their disposal by burning produces a considerable increase in carbon dioxide (CO₂) and, in some cases, toxic gases, which contribute to global pollution or green house effects. As a result, there is considerable interest in biodegradable polymers, which can be used as alternatives to traditional plastics, thus reducing the amount of wastes. Hence in order to control environmental pollution, researchers have been paid attention to green composites/fibers.

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Incorporation of electrically conductive nano-additives, such as carbon nanotubes (CNTs) and High Purity Graphene (HPG) [17], into these fibers can both improve mechanical properties and enable the multi-functionality needed for electrical energy storage [18], sensing [19], and actuation [20]. Many of the possible applications would greatly benefit from increased fiber toughness, which is the ability to absorb mechanical energy before rupture. Most importantly, the dispersion of carbon nanomaterials into the polymer matrices has been the subject of intensive research during the last decade [21–27]. The wonderful prospective of graphene nanoplatelets inside the polymer matrices has generated much interest among researchers. Because of their unique mechanical and electrical properties [29–30], the carbon materials incorporated hybrid nanofibers give much more interests to study their morphologies and to improve the mechanical and electrical properties.

In this work, we report the morphologies, crystal structures and mechanical properties of CA/graphene and CA/graphene-COOH hybrid nanofibers measured by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively. FT-IR and Raman spectroscopy were carried out for the resultant hybrid nanofibers to confirm the interactions between polymer matrix and graphene or graphene-COOH nano-additives.

2. Experimental section

2.1. Materials

Cellulose acetate (CA, 39.8% acetyl content, average $M_w = 30$ kDa) were obtained from Aldrich Chemical Company. Graphene with an average particle size of 800×300 nm, thickness of 5 nm, surface area of $150 \text{ m}^2/\text{g}$, and a purity of $>99\%$ (Graphene-150) were kindly supplied from Quantum Materials Co., India. DMF and acetone were purchased from Wako pure chemicals, Japan, and used directly without further purification.

2.2. Electrospinning

A high-voltage power supply (Har-100*12, Matsusada Co., Tokyo, Japan), capable of generating voltages up to 80 kV, was used as the source of the electric field. The CA solutions were made from CA 2.345 g, acetone 6.0 g, and DMF 4.0 g. The concentration of CA solutions was 19 wt%. In order to

improve the solubility of the CA polymer in acetone/DMF mixture, the CA solutions were heated to about 60°C for 2 hours and then this CA solutions were supplied through a plastic syringe attached to a capillary tip with an inner diameter of 0.6 mm. The copper wire connected to a positive electrode (anode) was inserted into the CA polymer solution, and negative electrode (cathode) was connected to a metallic collector. The voltage was fixed at 12 kV and the distance between the capillary tip and the collector was 15 cm.

2.3. Preparation of CA/graphene and CA/graphene-COOH hybrid nanofibers

In order to prepare the CA/graphene hybrid nanofibers, the dispersion of graphene was prepared in acetone/DMF (6:4 by weight) mixture (2.0 g) under sonication for 30 min, and CA (2.345 g) was dissolved in acetone/DMF (6:4 by weight) mixture (8.0 g) by stirring at 60°C , respectively. For the fabrication of graphene incorporated CA hybrid nanofibers, CA solution (8.0 g) was mixed with graphene solution (2.0 g) described above and stirred for 10 min after sonicating for 30 min. This process was repeated three times. The CA/graphene-COOH hybrid nanofibers were also obtained using the same strategy. The concentrations of graphene and graphene-COOH were 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 wt%, respectively. All solutions were electrospun onto a rotating metallic collector at room temperature under identical conditions.

2.4. Characterization

The morphologies of hybrid nanofiber mats were observed by scanning electron microscopy (SEM S-3000N, HITACHI, Japan). Transmission electron microscopy (TEM) (JEM-2100 JEOL Japan, accelerating voltage 120 kV) was used to investigate the dispersion and alignment of the graphene and graphene-COOH in the resulting CA/graphene and CA/graphene-COOH hybrid nanofibers. At least more than 100 fiber measurements from SEM images were used in order to ensure reproducible statistics when measuring fiber size distributions. Fiber diameters were measured by image processing software (Image J, NIST). The Raman spectra were recorded with a Raman spectrometer (Hololab 5000, Kaiser Optical Systems Inc., USA), and argon laser at 532 nm, with a Kaiser holographic edge filter. The wide-angle X-ray diffraction (WAXD) experiments

were performed at room temperature with hybrid nanofiber samples using a Rotaflex RTP300 (Rigaku Co., Japan) X-ray diffractometer operating at 50 kV and 200 mA. Nickel-filtered Cu K α radiation was used for the measurements, along with an angular range of $5 < 2\theta < 30^\circ$. The FT-IR spectra were measured at room temperature with hybrid nanofiber samples using a NEXUS670 FTIR spectrophotometer (Thermo Nicolet Co., USA). The spectra were recorded from 750 to 4000 cm $^{-1}$ at a resolution of 4 cm $^{-1}$. The mechanical behavior of resultant hybrid nanofibers mats was determined by a universal testing machine (TENSILON RTC1250A, A&D Company, Ltd, Japan) under a crosshead speed 5.0 mm/min at room temperature. In accordance with ASTM D-638, the specimens were prepared in the form of a dumbbell-shape by compression molding from fiber mats and then at least five specimens were tested for tensile behavior and the average values were reported. Two parameters were

determined from each stress-strain curve: Young's modulus and tensile strength. Then the values of Young's modulus for resultant hybrid nanofibers were calculated from the initial slope of stress-strain curves.

3. Results and discussion

3.1. Morphologies of CA/graphene and CA/graphene-COOH nanofibers

SEM images (Figure 1) and average fiber diameters (Figure 2) for pure CA and graphene or graphene-COOH incorporated CA nanofibers were taken in order to study the changes of average fiber diameters on different loading of graphene or graphene-COOH into the CA nanofibers. It was observed that the diameters of CA hybrid nanofibers largely decreased as increasing the graphene or graphene-COOH contents, typically ranging from 580 ± 200 nm for pure CA nanofibers to about 290 ± 75 nm for both 4.0 wt% graphene/CA or 4.0 wt% graphene-COOH/CA nano-

Figure 1. SEM micrographs of pure CA (a), CA/graphene – (b) 1.0 wt%, (c) 3.0 wt%, (d) 4.0 wt%, (e) 5.0 wt%, and CA/graphene-COOH – (f) 1.0 wt%, (g) 3.0 wt%, (h) 4.0 wt%, (i) 5.0 wt% nanofibers

Figure 2. Distribution of fiber diameters for pure CA, CA/graphene, and CA/graphene-COOH nanofibers prepared from different weight ratios of graphene or graphene-COOH

fibers, respectively. The diameter of nanofiber was given as the average of more than 50 measurements. This can be attributed to an increased conductivity of the CA solutions blended with graphene or graphene-COOH, which resulted in the formation of thinner fibers (Figure 2) [31]. This result also well coincided with those obtained in our previous works [32]. That is, the fiber diameter of graphene incorporated CA nanofibers gradually decreased until

graphene concentration increased up to 5.0 wt%. The fiber diameter of CA/graphene nanofibers at graphene content = 5.0 wt% was about 270 ± 80 nm. On the other hand, the CA/graphene-COOH nanofibers exhibited the smallest fiber diameter ($\sim 290 \pm 75$ nm) at graphene-COOH contents = 4.0 wt%. When the graphene contents further increased to 5.0 wt%, the average diameter increased to 440 ± 70 nm consequently. Such hybrid nanofibers formed under this condition were not uniform due to the formation of few droplets and beads via severe graphene aggregations (Figure 1i). As a result, it confirmed that at higher graphene or graphene-COOH contents the formation of continuous hybrid nanofibers was forbidden due to incapability to preserve the stable flow of the polymeric solution at the tip of the needle [32]. The formation of beads may suggest that the graphene-COOH and graphene at such higher concentration are not evenly dispersed in the CA solution.

In order to investigate the dispersions of graphene and graphene-COOH into the nanofibers, TEM images were taken for CA/graphene and CA/graphene-COOH nanofibers. As seen in Figures 3a and 3b, the morphologies showed that the graphene or graphene-COOH (content ~ 4.0 wt%) were well

Figure 3. TEM micrographs of graphene – (a) 4.0 wt%, (c) 5.0 wt%, and graphene-COOH – (b) 4.0 wt%, (d) 5.0 wt% incorporated CA hybrid nanofibers. The scale bar is 500 nm.

embedded in the hybrid nanofibers during electrospinning process. This could be due to higher electrostatic fields during electrospinning process and are expected to result in a good incorporation of the graphene or graphene-COOH into the nanofibers [32]. On the other hand, as seen in Figures 3c and 3d, the CA nanofibers with graphene or graphene-COOH contents of 5.0 wt% exhibited severe aggregation of graphene or graphene-COOH, aggregates are formed on their surfaces as well as inside of the fibers.

3.2. FT-IR spectral studies

In order to investigate the specific interactions of graphene or graphene-COOH with CA matrix, FT-IR spectral studies were carried out for pure CA and graphene or graphene-COOH incorporated CA hybrid nanofibers (Figure 4). FT-IR spectrum of pure CA shows characteristic peaks at 1738, 1369 and 1225 cm^{-1} due to the $\nu_{\text{C=O}}$, $\nu_{\text{C-CH}_3}$ and $\nu_{\text{C-O-C}}$ stretching, respectively. In Figure 4b, FT-IR spectra

of the graphene-COOH incorporated CA hybrid nanofibers revealed the presence of functional groups whose absorption frequencies correspond to C=O (slightly shifted from 1738 to 1734 cm^{-1}). The absorption band broadening of carboxyl groups for CA/graphene-COOH samples was also observed, which indicates hydrogen bonding interactions between CA matrix and graphene-COOH. The shift in the absorption band of the hybrid nanofibers strongly suggests strong interactions between -COOH groups of graphene-COOH and C=O groups of CA via hydrogen bonding. However, the IR spectra of pure graphene incorporated CA hybrid nanofibers (Figure 4a) showed no significant shift in the peaks, suggesting no interaction between graphene and CA molecules [33].

3.3. Raman spectral studies

Raman spectroscopy was recorded, in order to study the interfacial interactions between CA molecular chains and graphene or graphene-COOH nano-

Figure 4. FT-IR spectra of graphene (a) and graphene-COOH (b) incorporated CA hybrid nanofibers

Figure 5. Raman spectra of graphene (a) and graphene-COOH (b) incorporated CA hybrid nanofibers

additives in the resultant hybrid CA nanofibers (Figure 5). In Figure 5, Raman spectra of the pure CA nanofibers showed two characteristic bands at 1376 and 1748 cm^{-1} due to $-\text{CH}_3$ (anti-symmetric deformation vibrations of the methyl groups) and $-\text{C}=\text{O}$ vibrations, respectively. Similarly, Raman spectra of the both CA/graphene and CA/graphene-COOH hybrid resultant nanofibers also showed the same characteristic bands at 1376 and 1748 cm^{-1} . Furthermore, a new band at 1572 cm^{-1} (corresponding to G band of graphene) was observed except for pure CA nanofiber, suggesting that the graphene or graphene-COOH were well incorporated into the CA fibers during electrospinning [34]. Such G band of graphene or graphene-COOH is red-shifted by about 6 cm^{-1} compared with those of pure graphene and graphene-COOH. There may be several reasons for this which include 1) an enhanced specific surface area of graphene and graphene-COOH [35], 2) the rough/wrinkled surface texture [36] of graphene and graphene-COOH which can lead to a mechanical interlocking, and 3) the abundance of defects [37] in graphene and graphene-COOH which may provide chemical handles for good adhesion with CA polymer chains. The shift in the peak at 1572 cm^{-1} also confirms that there is a good adhesion and stress transfer between the CA polymer chains and the graphene or graphene-COOH nano-additives, suggesting the hydrogen bonding interactions between the $\text{C}=\text{O}$ functional groups of CA and $-\text{COOH}$ groups of graphene-COOH, which also well coincided with the previous FT-IR data. It is therefore expected that the graphene or graphene-COOH incorporated CA nanofibers show good

Young's modulus when compared with that of pure CA nanofibers.

3.4. Wide angle X-ray diffraction

In order to explain the interfacial interaction and the dispersion/incorporation of carbon nanomaterials into the CA matrix, WAXD was taken for pure CA and graphene or graphene-COOH incorporated CA hybrid nanofibers (Figure 6). The pure CA exhibited typical crystalline peaks at 8.7 and 17.2°, corresponding to the (110) and (200) reflections, as seen in Figure 6. It could be also seen from Figure 6, as increasing the graphene or graphene-COOH contents, the peak intensity at 8.7° decreased first and then increased again. That is, in case of the CA/graphene-COOH hybrid nanofibers the peak intensity at 8.7° started to increase above graphene-COOH = 2.0 wt%, while the CA/graphene hybrid nanofibers increased above graphene = 3.0 wt%. Such increased peak intensity revealed enhanced crystallinity of CA polymer chains, suggesting that the incorporated graphene and graphene-COOH might act as a heterogeneous nucleation points, and thus the crystallinity of the CA was improved [38]. Besides, it might be attributed to enhanced alignment of the CA crystals, which was induced by increased solution conductivity of the CA/graphene and CA/graphene-COOH solutions during the electrospinning process [39]. However, at higher loading (5.0 wt%), the graphene or graphene-COOH tend to aggregate and therefore the CA and the graphene or graphene-COOH are to be separated from each other, which results in an increased peak intensity at 26.5°, corresponding to the (002) reflec-

Figure 6. WAXD patterns of graphene (a) and graphene-COOH (b) incorporated CA hybrid nanofibers

tion of the incorporated graphene and graphene-COOH, in both CA/graphene and CA/graphene-COOH hybrid nanofibers, as seen in Figures 6a(h) and 6b(h). As expected, the peak intensity at 26.5° became evident gradually as the graphene or graphene-COOH contents increased. In addition, such peak intensity at lower loading of graphene or graphene-COOH disappeared (at loading contents ranging from 0.5 to 1.0 wt%), suggesting the disorder and loss of structure regularity of the graphene and graphene-COOH. Thus, the graphene and graphene-COOH are considered to be well-dispersed at the molecular level into the CA matrix [38]. Moreover, Figure 6 showed the shift in the peak at 26.5° for graphene-COOH incorporated CA nanofibers (approximately from 26.5 to 27.1°) when compared to that of graphene incorporated CA hybrid nanofibers (very little shift). It may be due to the fact that $-\text{COOH}$ group of graphene effectively acted as nucleation center, which therefore resulted in higher Young's modulus of CA/graphene-COOH hybrid nanofibers [39]. Furthermore, slight shift in the peak at 8.7° (from 8.7 to 8.3°) also strongly revealed that CA matrix was effectively disturbed by graphene and graphene-COOH [38].

3.5. Mechanical properties

Figure 7 shows Young's modulus of pure CA nanofiber, CA/graphene nanofibers and CA/graphene-COOH nanofibers as a function of graphene or graphene-COOH contents at room temperature. Young's modulus of graphene-COOH incorporated CA hybrid nanofibers increased gradually as increas-

Figure 7. Young's modulus of CA/graphene nanofibers and CA/graphene-COOH nanofibers as a function of graphene or graphene-COOH contents at room temperature

ing the graphene-COOH contents. In particular, the CA/graphene-COOH hybrid nanofiber mat with 4.0 wt% graphene-COOH showed the highest Young's modulus, which was approximately 3.7 times higher than that of pure CA nanofiber mat (~ 245.5 MPa, see Table 1), suggesting that mechanical properties of such hybrid nanofibers [40] were increased with increasing the amounts of graphene-COOH nano-additives. A similar tendency was also observed for CA/graphene hybrid nanofibers. Young's modulus of CA hybrid nanofiber mat with 4 wt% graphene was found to be 739.8 MPa, which was about 3 times higher than that of pure CA nanofiber mat (Table 1). However, at 5 wt% graphene or graphene-COOH contents, Young's modulus of the hybrid CA nanofibers started to decrease again. This

Table 1. Young's modulus of CA/graphene and CA/ graphene-COOH nanofibers

Weight percentages of graphene/graphene-COOH	Young's modulus of graphene/CA [MPa]	Young's modulus of graphene-COOH/CA [MPa]
0	247±102	
0.5	351.1±130	389.5±140
1.0	370.5±160	420.6±210
2.0	413.7±200	676.9±310
3.0	420.6±280	806.0±380
4.0	739.8±350	910.6±460
5.0	703.7±330	805.7±380

may be due to the beads formed on fiber's surface and hence a poorer mechanical performance of the nanofiber mats. Although the added amounts of graphene or graphene-COOH were the same, graphene-COOH showed higher Young's modulus values (Figure 7). It certainly demonstrated that the hydrogen-bonding between-COOH groups in the graphene-COOH and -C=O groups in the CA molecules was formed at the interfaces in the CA hybrid nanofibers, and thereby resulted in the higher Young's modulus of CA/graphene-COOH nanofiber membranes [41], which is also well correlated with the results of FT-IR, WAXD and Raman analysis.

4. Conclusions

We have prepared the pure CA, CA/graphene and CA/graphene-COOH nanofibers by electrospinning process, and studied the effects of graphene or graphene-COOH contents on the morphologies, microstructures and mechanical properties of the resultant CA hybrid nanofibers. SEM analysis demonstrated that the diameters of CA hybrid nanofibers were dramatically decreased as graphene or graphene-COOH contents increased, typically ranging from 580±200 nm for pure CA nanofibers to about 290±75 nm for both 4.0 wt% graphene/CA or 4.0 wt% graphene-COOH/CA nanofibers, respectively. This can be attributed to the increased conductivity which resulted in the formation of thinner fibers. Moreover, the hybrid nanofibers electrospun from the CA solution with 4 wt% graphene or graphene-COOH contents exhibited the smallest fiber diameter, and the fiber diameter distributions were also narrower, suggesting good distribution of the graphene or graphene-COOH onto the CA nanofiber matrix, which was also confirmed by TEM analysis. Specific interactions between -COOH groups in acid-treated graphene and C=O groups in CA via hydrogen bonding were demonstrated by

FT-IR and Raman spectroscopic analysis. The broadening and slight shifting from 1738 to 1734 cm⁻¹ of C=O absorption band in the CA/graphene-COOH samples clearly indicated strong interactions between -COOH groups of graphene-COOH and C=O groups of CA via hydrogen bonding. WAXD results also confirmed the good incorporation of graphene or graphene-COOH and good interfacial interaction between CA matrix and graphene or graphene-COOH nano-nano-additives. In addition, it was found that the CA hybrid nanofiber mat with 4.0 wt% graphene-COOH showed the highest Young's modulus, which was approximately 3.7 times higher than that of pure CA nanofiber mat (~245.5 MPa). It suggested that the brittleness of such hybrid nanofibers increased with increasing the amounts of graphene-COOH additives.

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