STRUCTURES AND PHYSICAL PROPERTIES OF CELLULOSE DRIVATIVE/EXFOLIATED GRAPHITE NANOCOMPOISTES PREPARED BY MELT-SHEAR MIXING

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1 Introduction

Cellulose, the most naturally abundant polymeric material on earth, is produced 100~150 billion tons each year. Owing to the renewability, low cost, and biodegradability of cellulose, it has been widely used as clothes, medical, industrial material for a long time. However, cellulose is not melt-processible due to the presence of strong inter- and intra-molecular interactions between hydroxyl groups of cellulose main chains [1]. Therefore, toxic polar solvents should be used to dissolve the cellulose, which solution process is harmful to human and environment. On the other hand, cellulose derivatives such as cellulose esters and cellulose ethers are melt-processible since the alkyl ester or ether groups interrupt the interaction between cellulose backbones. Recently, exfoliated graphite (EG) with high aspect ratio, exceptional mechanical and electrical properties has been envisaged as viable and inexpensive nanofiller for multifunctional composite materials [2]. In this study, we have prepared cellulose derivative/EG nanocomposites by melt-shear mixing and investigated systematically their structures, thermal stability, mechanical and electrical properties by using SEM, XRD, TGA, DMA, and electrical resistivity measurement.

2 Experimental

2.1 Materials

Cellulose acetate propionate (CAP, number average molecular weight of 75,000 g/mol, acetyl content of 2.5 wt%, propionyl content of 46 wt%) was used as a cellulose derivative matrix. Natural graphite flake with the average diameter of ~500 μm was purchased from Sigma-Aldrich, Inc. H_2SO_4, HNO_3, and $KClO_3$ were of analytical grade and used as received.

2.2 Preparation of Exfoliated Graphite

To prepare exfoliated graphite (EG), graphite oxide or acid-treated graphite (AG) was firstly obtained from the pristine natural graphite (NG) by the Staudenmaier method. NG of 20 g was added in sulfuric acid (320 mL) and nitric acid (180 mL) mixture at less than 20 °C. $KClO_3$ of 220 g was then slowly added into $NG/H_2SO_4/HNO_3$ mixture, because the reaction results in the formation of chlorine dioxide gas, which is explosive at high concentration. Oxidation (acid-treatment) of NG was carried out for 120 hrs. Subsequently, the suspension was washed with an aqueous hydrochloric acid solution (10 vol%) to remove the sulfate ions and then washed repeatedly with distilled water until neutral pH was attained. The AG slurry was dried at room temperature for 24 hrs and finally put into a furnace at 1050 °C for 30 seconds to obtain the EG.

2.3 Preparation of Nanocomposites

A series of CAP/EG nanocomposites were manufactured via melt-shear mixing method. Firstly, various contents of EG (0.1~10.0 wt%) and CAP powder were mixed in solid state and then melt-extruded at 225 °C with an aid of twin-screw extruder (BauTech Com., BAUTEK-11). CAP/EG nanocomposite films were prepared by using hot-press at 225 °C for 3 min, quenched in ice water bath, and then dried in vacuum oven at 80 °C for 24 hrs. For comparison, neat CAP film was also prepared at same procedure. Fig. 1 shows the digital images of CAP/EG nanocomposite films prepared in this study.

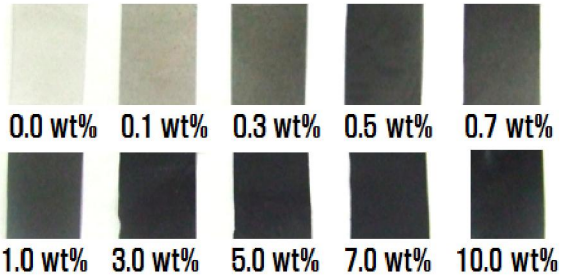

Fig. 1. Digital images of the neat CAP and CAP/EG nanocomposite films.

2.4 Characterization of Nanocomposites

To characterize the structural order and morphological features of CAP/EG nanocomposites, X-ray diffraction of CAP/EG nanocomposite films, X-ray diffractometer (XRD, Rigaku Inc., 2000-PC) and scanning electron microscope (FE-SEM, JEOL/JSM-6500F) were used, respectively. Thermal stability and mechanical property were characterized by using thermogravimetric analyzer (TGA, TA Instruments/Auto-TGA Q500) in oxygen atmosphere and dynamic mechanical analyzer (DMA, TA Instruments/DMA Q800), respectively. Electrical resistivity of CAP/EG nanocomposite films were measured with an electrometer/high resistance meter (Keithley/6517A).

3 Results and Discussion

3.1 Structures and Morphology

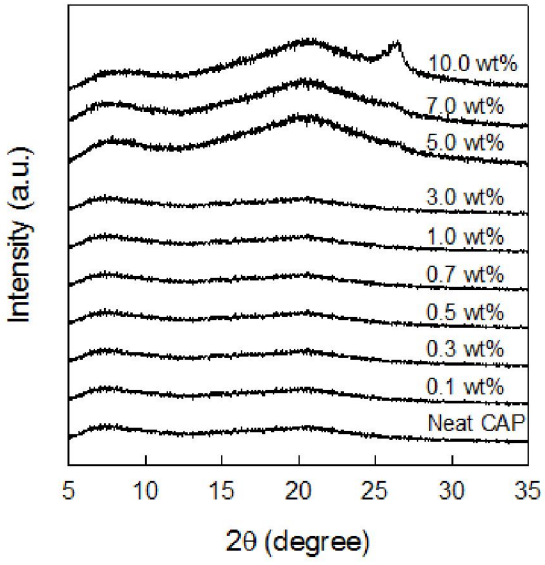

Fig. 2. X-ray diffraction patterns of the neat CAP and nanocomposites with various EG contents.

Fig. 2 shows X-ray diffraction patterns of the neat CAP and CAP/EG nanocomposites. Except for the nanocomposite with 10.0 wt% EG, there is no any diffraction peaks associated with the ordered structures in the neat CAP and CAP/EG nanocomposites. It indicates that CAP matrix are purely amorphous in the nanocomposites and the graphene sheets of EG are well distributed in the CAP matrix without forming any crystalline graphite aggregates. In case of the nanocomposite with the high EG content of 10.0 wt%, a broad diffraction peak appears at 2θ =25~30°, which stems from the presence of partially ordered EG aggregates in the CAP matrix.

Fig. 3 shows typical FE-SEM images of the neat CAP and CAP/EG nanocomposites. Fracture surfaces of neat CAP and nanocomposites with the low EG content were smooth and clean. However, SEM image of the nanocomposite with the high EG content of 10.0 wt% shows EG aggregates in the CAP matrix. This FE-SEM image is well consistent with the X-ray diffraction result.

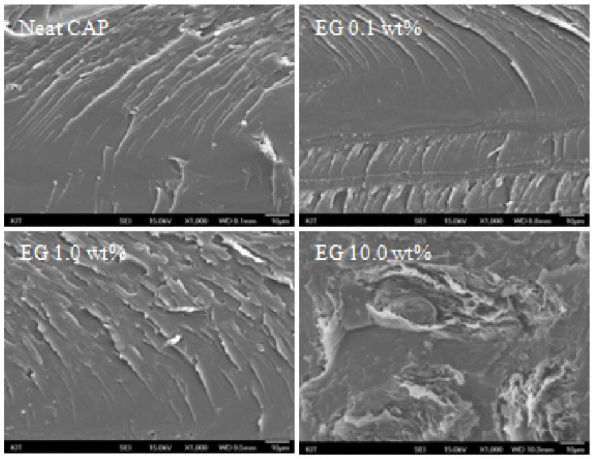

Fig. 3. FE-SEM images of fracture surfaces of neat CAP and CAP/EG nanocomposite films.

3.2 Thermal Stability

Fig. 4 shows TGA curves of the neat CAP and CAP/EG nanocomposites experimented under the oxygen gas atmosphere. It was found that, compared to the neat CAP, thermal stability of the nanocomposites was substantially improved with increasing the EG content. Furthermore, typical thermo-oxidative degradation temperatures for 5% and 50% weight loss ($T_{5\%}$ and $T_{50\%}$) of CAP/EG nanocomposites were far higher than those of neat CAP by 18 and 30 °C, respectively. $T_{5\%}$ and $T_{50\%}$

values of the neat CAP and CAP/EG nanocomposites were summarized in Table 1. Therefore, it is valid to content that CAP/EG nanocomposites have better thermal stability, compared to the neat CAP. This may be due to the good dispersion of graphene sheets of EG in the CAP matrix [3].

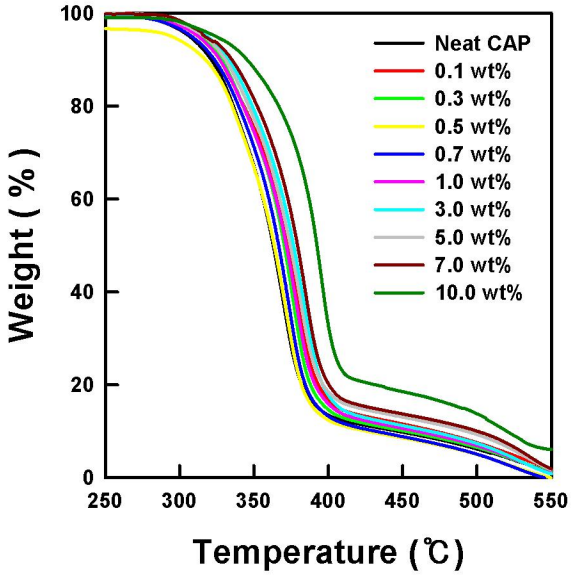

Fig. 4. TGA curves of the neat CAP and CAP/EG nanocomposites with various EG contents.

Tab. 1. Thermo-oxidative degradation temperatures for 5% and 50% weight loss ($T_{5\%}$ and $T_{50\%}$) of the neat CAP and CAP/EG nanocomposites

EG content (wt%)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
0.0	306.6	363.0
0.1	315.5	373.0
0.3	314.3	370.4
0.5	294.5	363.7
0.7	308.1	366.6
1.0	312.4	371.8
3.0	318.5	376.7
5.0	316.4	37435
7.0	317.0	379.2
10.0	324.1	392.4

3.3 Mechanical Properties

Thermo-dynamic mechanical properties of the neat CAP and CAP/EG nanocomposites films were measured by DMA instrument in the temperature range of 25~250 °C at 5 °C/min and 1 Hz. Fig. 5 shows the temperature-dependent dynamic storage modulus of the neat CAP and CAP/EG nanocomposites. When compared between storage modulus at room temperature, the moduli of the nanocomposites were somewhat higher than that of neat CAP. On the other hand, the storage moduli at high temperatures were much higher for CAP/EG nanocomposites with higher EG contents.

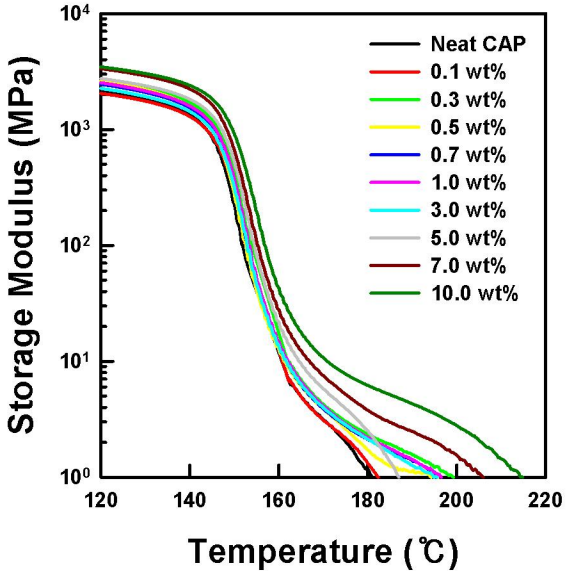

Fig. 5. Mechanical properties of the neat CAP and CAP/EG nanocomposites with various EG contents.

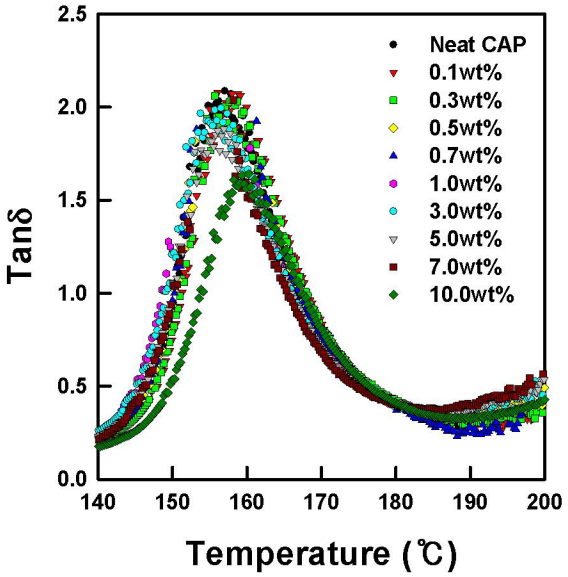

Fig. 6. Tan δ values of the neat CAP and CAP/EG nanocomposites.

Fig. 6 shows tan δ vs. temperature curves of the neat CAP and CAP/EG nanocomposite films. The tan δ peak, which is corresponding to the glass transition temperature, of the neat CAP was appeared at 152 °C. On the other hand, tan δ peak temperatures of CAP/EG nanocomposites were somewhat higher than that of the neat CAP. Overall, the enhanced storage modulus and tan δ peak temperatures are due to the effective mechanical reinforcement of graphene sheets of EG dispersed in the CAP matrix [3,4].

3.4 Electrical Properties

Fig. 7 shows electrical volume resistivities of the nanocomposites with various EG contents. The electrical volume resistivities of CAP/EG nanocomposites were varied appreciably from ~10^{15} Ω·cm to ~10^{6} Ω·cm at a certain EG content between 3.0 and 7.0 wt%, indicating that the electrical percolation threshold of the CAP/EG composites was formed at ~5.0 wt% EG.

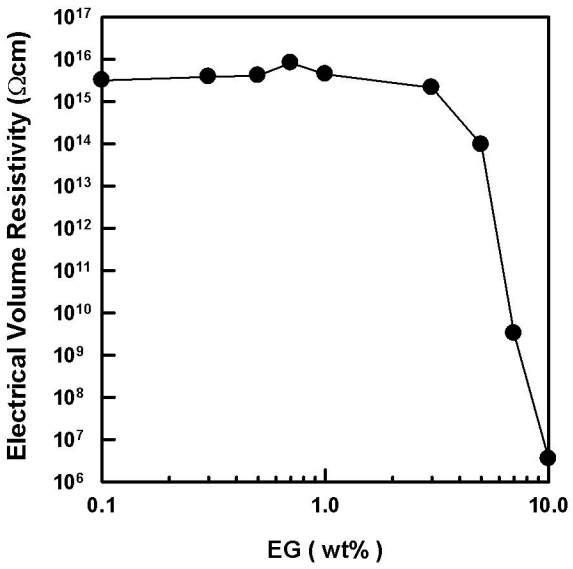

Fig.7. Electrical volume resistivities of CAP/EG nanocomposites as a function of EG content.

4 Conclusions

CAP-based nanocomposite films with a variety of EG contents were prepared via melt-shear mixing method and melt-compression. X-ray diffraction results exhibited that all the nanocomposite films are totally amorphous, regardless of the EG contents. Only a weak and broad peak at around 2θ= 25°~30° was detected for the nanocomposite film with higher EG content, which was associated with the parallel stacking of graphene sheets of EG. FE-SEM images of the nanocomposite films showed that EG was well dispersed in CAP but EG remained aggregated in the nanocomposite with high EG content. It was found that, in comparison with the neat CAP, thermal stability, dynamic mechanical property, and electrical conductivity of CAP/EG nanocomposites could be substantially improved by the good dispersion of graphene sheets of EG in the CAP matrix.

References

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