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BIODEGRADABLE POLY(LACTIC ACID)/MULTIWALLED CARBON NANOTUBE NANOCOMPOSITE FABRICATION USING CASTING AND HOT PRESS TECHNIQUES

WYTWARZANIE BIODEGRADOWALNYCH NANOKOMPOZYTÓW TYPU POLI(KWAS MLEKOWY) /WIELOŚCIENNE NANORURKI WĘGLOWE TECHNIKAMI ODLEWANIA I PRASOWANIA NA GORĄCO

Biodegradable advanced polymer composites have recently received a large amount of attention. The present study aimed to design poly(lactic acid) multiwalled carbon nanotube nanocomposites (PLA/MWCNTs) using a simple fabrication technique. A PLA sheet was first dissolved in dichloromethane, and MWCNTs were subsequently added at various concentrations (0.5, 1.5 and 5%) while applying shear strain stirring to achieve dispersion of carbon nanotubes (CNTs). These solutions were then molded and a hot press was used to generate sheets free of voids with entrapped solvent. The prepared samples were characterized using field emission scanning electron microscopy (FE-SEM), x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). Our data showed composite samples free of defects and voids, indicating that the hot press is capable of generating sufficiently compact polymer matrices. Additionally, TGA and FTIR showed significant bonding interactions between the PLA matrix and the nano-fillers. Collectively, our results suggest that incorporation of CNTs as nano-fillers into biodegradable polymers may have multiple applications in many different sectors.

Keywords: CNTs, biodegradable polymer, advanced polymer matrix composites, hot press, mechanical properties

1. Introduction

Poly(lactic acid) (PLA) is extensively used in the production of surgical thread, implant materials, controlled drug delivery systems, and minimally invasive surgery due to its unique properties such as biodegradability, biocompatibility, and shape-memory qualities [1-6]. Poly-L(lactic acid) (PLLA), on the other hand, lacks sufficient mechanical properties for medical applications. Carbon nanotubes (CNTs) possess excellent mechanical, electrical, and thermal properties, and some polymer/CNT nanocomposites have been previously reported in the literature [7]. As a result, the combination of biodegradable polymers and various quantities of CNTs for second-phase reinforcement is of great interest for use in both academic and industrial settings. For high performance polymer/CNT nanocomposites, fine dispersion of CNTs in the polymer matrix is of great importance. To avoid the aggregation of CNTs in the polymer matrix, a fabrication sequential process may be considered. The preparation of polymer/CNTs nanocomposites via solution casting with sonication and subsequent hot pressing may improve the dispersion behavior of CNTs within the polymer matrix. If adequate dispersion is achieved, it has been hypothesized that the interaction between the nano-fillers and polymer molecules will increase, thereby improving the mechanical properties of the material. In this paper, we examined the influence of the fabrication process on molecular interactions and thermal properties of PLA/MWCNT composites using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The dispersion of CNTs in PLA was determined using field emission scanning electron microscopy (FESEM). For comparison, PLA as-received and PLA casted films were also characterized using the same methods.

2. Experimental

2.1. Materials and preparation of PLA/MWCNT nanocomposites

PLA is derived from an annually renewable resource and is specifically designed for use in food packing and biomedical applications (approved by the US Food and Drug Administration). The PLA used in this study was Ingeo Biopolymer 2003D, a NatureWorks, LLC (USA) product that was kindly supplied by Green Chemical Co., Ltd (Korea), and was received as a roll with a film thickness of 320 μm. This PLA type has a high molecular weight biopolymer grade. Dichloromethane (DCM) (Junsei Chemical Co., Japan) was

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used as a solvent. All of the chemicals used in the experiments were reagent grade. MWCNTs (purity >95%) with diameters of 30-50nm and lengths ranging from 10-20lm were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (Chengdu, China). The PLA/MWCNT nanocomposites containing 0.5, 1.5 and 3% MWCNTs were prepared by mixing CNTs with PLA-DCM solution using a magnetic stirring technique for more than 24 h. This mixture was subsequently shear strained at a rotor speed of 300 rpm for 10 min. The PLA/MWCNT nanocomposite solutions were then casted and vacusly dried. The casted films were finally introduced into a 5 ton hot press at 170°C.

PLA and PLA/MWCNT nanocomposites with 0.5, 1.5 and 3% CNTs are abbreviated as PLA, $CNTPLA_{0.5}$, $CNTPLA_{1.5}$, and $CNTPLA_3$, respectively.

2.2. Characterizations

A field emission scanning electron microscope (S-7400, Hitachi Co., Tokyo, Japan) was used to observe the morphology of the PLA/MWCNT nanocomposite surfaces fractured in liquid nitrogen. Each sample was coated with gold prior to examination. X-ray diffraction patterns were recorded using grazing angle x-ray diffraction (GA-XRD) with a Philips X'Pert, Holland X-ray diffractometer (Tokyo, Japan). The Cu Ka radiation source (k $^1/_4$ 0.15418nm) was operated at 40kV and 200mA. FT-IR (Jasco FT-IR-300 E) was used to analyze the phase, structure, and bonding between MWCNTs and PLA molecular chains. In the FT-IR experiment, the scanning range and resolution were 4000-400 and $4cm^{-1}$, respectively. TGA (SDT Instruments DSC Q600, Elmer Inc, USA) was used to determine the crystallinity and melting behavior of the fabricated samples which were ramped at 10°C/min under a nitrogen atmosphere.

3. Results and discussion

For polymer matrix nanocomposites, high power dispersion methods such as ultrasound and high-speed shearing are the simplest and most convenient way to improve the dispersion of nanosized fillers in a polymer matrix. In this study, these components were mixed using a stirring process followed by high-speed shearing. Figure 1 shows images
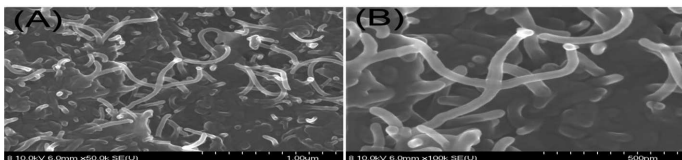

Fig. 1. FESEM images illustrating dispersion of CNTs in the polymer matrix

of the PLA/MWCNT nanocomposites after the solvent casting dispersion process, demonstrating that CNTs are efficiently entrapped within the polymeric net and homogeneously distributed on the surface. Aggregation and agglomeration of carbon nanotubes are a major obstacle for successful realization of their product potential [8]. Therefore, deagglomeration of CNTs is essential prior to incorporation into a polymeric

matrix. Furthermore, proper dispersion of CNTs likely directly reflects the bonding interactions between polymer molecules and CNT fillers. To support this hypothesis, FTIR spectra of the composite as well as solvent effects on bonding interactions were investigated, and their spectra are shown in Figure 2. There were slight changes in the spectrum of PLA before and after CNTs were incorporated. First, we observed that the peak at 1262 cm^{-1} increased in intensity with the fabrication process (solvent effects). This band had an asymmetric profile on its low frequency side, which shifted upward resulting in a symmetric profile with decreased intensity when the solvent was introduced. The bands in the 1350-1450 cm^{-1} range also shifted slightly higher and became sharper. Additionally, the band at 801 cm-1 disappeared after fabrication. This indicates that the shifts in bands correspond to the molecular interactions of CNTs with the polymer chains. These strong bonds could be due to the helical structure of PLA that tends to form a coil, thus forming polymer film that wraps around the CNTs.
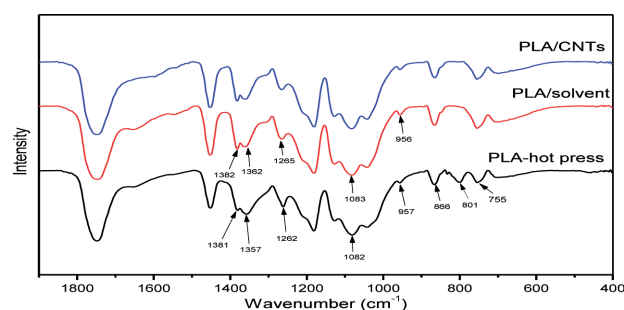

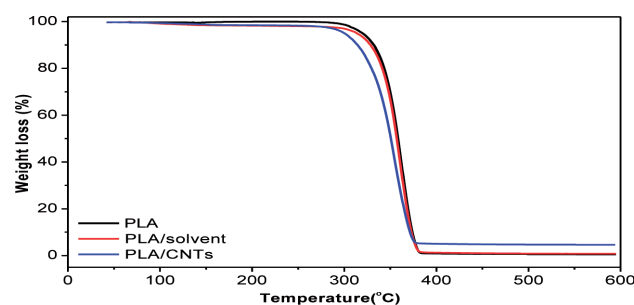Fig. 2. FTIR spectra of the fabricated samples

Fig. 3. TGA of the fabricated samples

TGA thermal behavior of PLA, PLA/DCM and PLA/MWCNT composites. Compared with neat PLA, the glass transition temperature (T_g) and the melting temperature (T_m) appear to decrease slightly in PLA/DCM and PLA/MWCNT composites (data not shown). The PLA/DCM and PLA/MWCNT composites, showed a decreased crystallization rate, likely due to the effects of DCM solvent which hindered the formation of new crystallite. The absolute mechanisms of decreasing T_m and crystallinity, however, remain unclear. The TGA curves shown support our results. CNTs loaded into the polymer matrix composite are clearly seen on the right side.

XRD patterns of PLA and its nanocomposites. PLA and nanocomposites containing different CNT concentrations exhibited nearly the same diffraction peaks at slightly different locations. This indicates that incorporation of the MWCNTs did not change the crystal structure of PLA. The slight shift-

ing of the composite 2-theta angles implies that the bonding interactions between PLA and CNTs may be solvent induced.
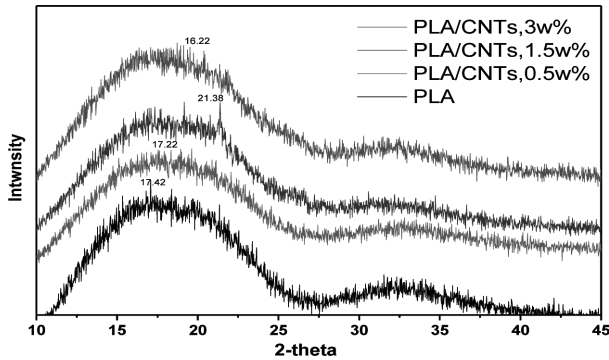

Fig. 4. XRD pattern of PLA and PLA/MWCNT nanocomposites with different CNT concentrations

4. Conclusion

Fabrication of PLA/MWCNT nanocomposites was successfully conducted using a solvent casting process and subsequent hot pressing. Our results indicate that CNTs inside of the matrix achieved adequate dispersion due to solvent effects. This dispersion allowed for bonding interactions between the nano-fillers and PLA chain molecules which were verified using FTIR and TGA. The fabrication process did not negatively affect the structure of PLA.

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