

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

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ABSTRACT: Biodegradable advanced polymer nanocomposites 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 free entrapped solvent. The results showed that a very good dispersion of MWCNTs in a PLA matrix could be observed. Further, the composite samples illustrated free of defects and voids, indicating that the hot press is capable of generating sufficiently compact polymer matrices. The investigation of the (fracture-) mechanical properties resulted in an increase of strength and Young's modulus at a nanotube content of both 0.5 and 1.5 wt%. 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.

I. 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]. PLA, on the other hand, lacks sufficient mechanical properties for medical applications. The development of nano-fillers reinforced polymer composites is presently seen as one of the most promising approaches in the field of future engineering applications. The unique properties of at least some of these nanofillers (e.g., carbon nanotubes, CNTs, nanofibers, NFs) and the possibility of reinforcement of these fillers into the PLA matrix, has led to an intense in the field of nanocomposites. Especially, CNTs filler posses excellent mechanical, electrical, and thermal properties, and some polymer/CNT nanocomposites have been previously reported in the literature [7, 8]. 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. Gojny and et.al have reported that two main issues have to be solved to effectively improve the material properties of polymers by adding carbon nanotubes as filler. These issues are the interfacial bonding and especially the proper dispersion of the individual CNTs in the polymeric matrix. 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 behaviour 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 mechanical properties, molecular interactions and thermal properties of PLA/MWCNT composites using, tensile test machine, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The dispersion of CNTs in

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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.

II. EXPERIMENTAL

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 μ m. This PLA type has a high molecular weight biopolymer grade. Dichloromethane (DCM) (Junsei Chemical Co., Japan) was 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 10–20 μ m 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 24h. This mixture was subsequently shear strained at a rotor speed of 300rpm for 10min. The PLA/MWCNT nanocomposite solutions were then casted and vacuosity dried. The casted films were finally introduced into a 5 ton hot press at 170 $^{\circ}$ C. PLA and PLA/MWCNT nanocomposites with 0.5, 1.5 and 3% CNTs are abbreviated as PLA, CNTPLA0.5, CNTPLA1.5, and CNTPLA3, respectively.

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 K α radiation source (λ 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 4 cm^{-1} , respectively. TGA (SDT Instruments DSC Q600, Elmer Inc, USA) was used to determine the crystallinity and melting behaviour of the fabricated samples which were ramped at 10 $^{\circ}$ C/min under a nitrogen atmosphere.

Tensile Test of Composite Samples: The tensile properties for the plain and composites PLA samples were conducted by an Instron Universal Testing Instrument model 4206 using a cross-head speed of 5 mm/min. The tensile test behaviour of PLA/CNTs composites samples was carried out according to the ASTM D3039-00 [9] test method. Each polymer sample included at least five specimens. Due to the scattering in readings, we take the average value was taken for the most three adjacent readings in each sample for each characteristic. The temperature and relative humidity for all experiments were about 25 \pm 2 $^{\circ}$ C and 55 \pm 5%, respectively.

III. RESULTS AND DISCUSSION

An efficient exploitation of the CNT properties in polymers is therefore related to their homogeneous dispersion in the matrix. The technique employed for CNT dispersion can influence, to a large extent, on the mechanical properties of CNT/polymer nanocomposites. 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 technique. Figs. 1A-C show FESEM fracture structure images of the PLA/MWCNT nanocomposites after the solvent casting dispersion process at 0.5 and 3 MWCNTs wt%, demonstrating that CNTs are efficiently entrapped within the polymeric net and homogeneously distributed on the surface particularly at the lower concentration (Figs. A,B). Only small agglomeration can be observed at 3 wt% CNTs loading. A possible advantage of this dispersion method is the homogeneous introduction of shear strain forces over the whole volume of the composite, while the sonication process only introduces the energy locally. However, in this small agglomerate that is completely impregnated by the PLA matrix, which opens up the question whether this form of distribution (combination of dispersed and exfoliated CNTs) is favourable especially for improved mechanical properties or if a more homogeneous dispersion is required. The achieved dispersion reveals the applicability of a high speed shearing technique also to efficiently disperse various nanofillers in polymer matrix and probably also in other liquid polymers and polymer solutions [10].

Aggregation and agglomeration of carbon nanotubes are a major obstacle for successful realization of their product potential [11]. 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 $1350\text{-}1450\text{ cm}^{-1}$ 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.

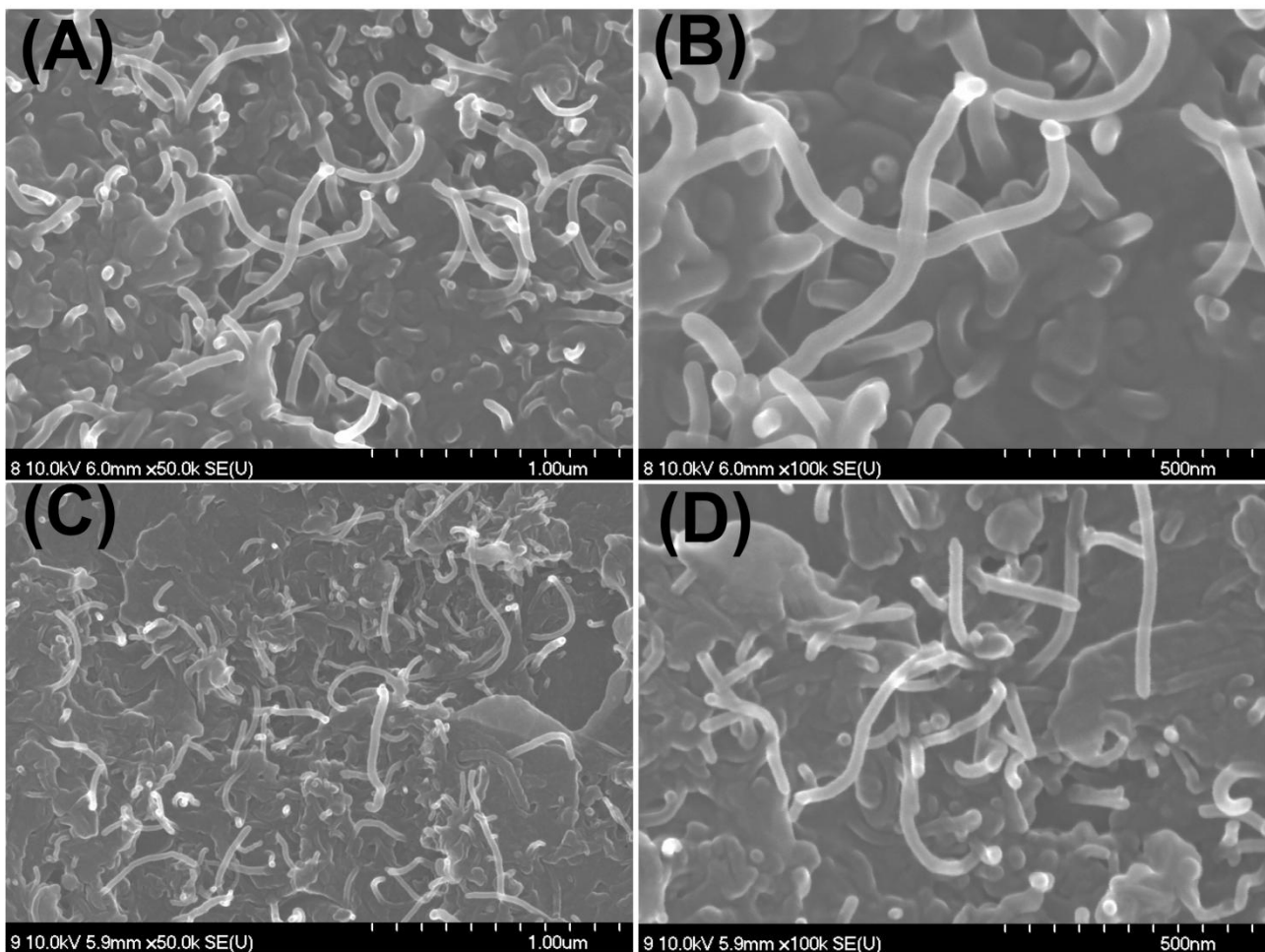


Figure 1. FESEM images illustrating dispersion of CNTs in the polymer matrix at 0.5 (A,B) and 3(C,D) MWCNTs wt%

TGA thermal behavior of PLA, PLA/DCM and PLA/MWCNT composites are shown in Fig .3. The weight-loss patterns for the samples are not the same the start of weight-arise, which due to the presence of MWCNTs loading. CNTs loaded into the polymer matrix composite are clearly seen on the right side. 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. Apparently, the onset of decomposition of nanocomposites take places earlier than in any other sample. This difference in onset temperature could be explained by the following hypothesize which was reported elsewhere [12]. The high thermal conductivity of nanotubes may create localized high temperature in MWCNTs lumps as

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compared to PLA matrix with and without chemical dispersion solvent for which the PLA molecules at the periphery of the lumps may start to degrade earlier.

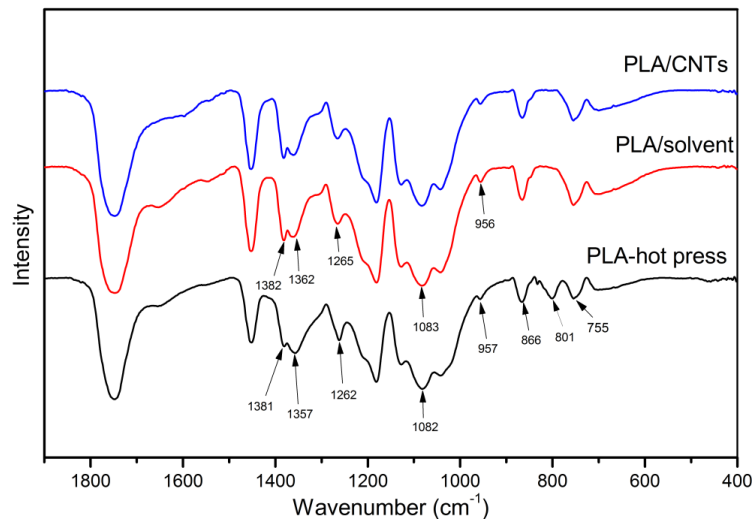


Figure 2. FTIR spectra of the fabricated samples

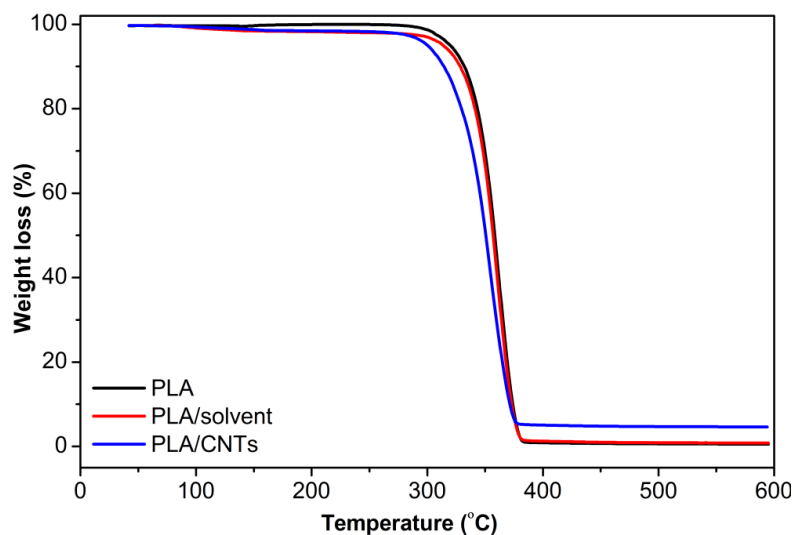


Figure 3. TGA of the fabricated samples

XRD patterns of PLA and its nanocomposites are displayed in Fig. 4. The important crystalline peak is diffused, appearing on a broad scattering, which is originated from the amorphous phase region of PLA structure. The broadly diffused peak suggests that PLA chains are poorly ordered with a low degree of crystallinity might be due to the cooling condition of the prepared samples.

The peak position angle for PLA, and PLA/MCNTs with 3 wt% of MWCNTs is observed close to $2\theta=17.42^\circ$, and 16.22° a lower angle compared to the previous one. To analyze these results, we introduce the reported crystalline structures of PLA (please see the supporting data), which shows the α -phase with pseudo-orthorhombic unit cell and the β -phase with orthorhombic cell where the former one is more stable than the latter [13]. Further, 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

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crystal structure of PLA. The slight shifting of the composite 2-theta angles implies that the bonding interactions between PLA and CNTs may be solvent induced.

The utility of nanotubes as the strongest or stiffest elements in nanoscale devices or composite materials remains a powerful motivation for the research in this area. Many studies have addressed that CNTs exhibit excellent mechanical properties with Young's modulus as high as 1.2 TPa and tensile strength of 50-200 GPa. The combination of these exceptional mechanical properties along with the low density, high aspect ratio and high surface area make CNTs an ideal candidate for reinforcement in composite materials. The mechanical properties of the as-prepared samples were measured and summarized in Table. 1. Our results showed that the mechanical properties of PLA/CNTs at the two low loading CNTs were improved in comparison with the pure PLA. The tensile strength of the plain PLA and PLA/CNTs nanocomposites at 0.5 and 1.5 wt% measured during the experiment were about 50.52±3.4, 65.75±6.1 and 57.23±4.5 MPa. It has been found that the Young's modulus is directly related to the cohesion of the solid and therefore to the chemical bonding of the constituent atoms. Two different values for nanocomposites were found. Comparing the Young's modulus values of net polymer and nanocomposites, addition of CNT increases the stiffness: it rises by ca. 40% for the material containing 0.5wt% of MWNTs, and by 53.4% for the one containing a weight fraction equal to 1.5wt%. Indeed, dispersion is the foremost important issue in producing polymer/ CNT nanocomposites. A good dispersion not only makes more filler surface area available for bonding with polymer matrix, but also prevents the aggregated filler from acting as stress concentrator, which are detrimental to mechanical performance of composites. This uniform dispersion of MWNTs in the PLA matrix is achieved via formation of covalent bond between the -OH group of PLA and -COCl group of MWNTs, as confirmed from FTIR study [14].

Table. 1 Mechanical properties of PLA/CNTs nanocomposite samples

MWCNTs weight fraction	Tensile strength (MPa)	Young's modulus
0% (Pure PLA)	50.52±3.4	1.72±0.25
0.5%	65.75±6.1	2.38±0.47
1.5%	57.23±4.5	2.64±0.34

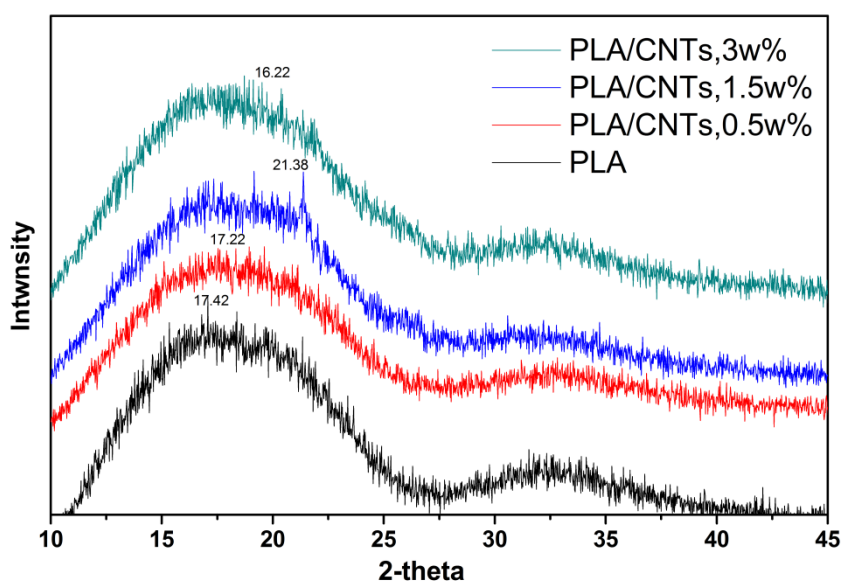


Fig.4. XRD pattern of PLA and PLA/MWCNT nanocomposites with different CNT concentrations

IV. CONCLUSION

PLA/MWCNT nanocomposites were successfully prepared by using a solvent casting process and subsequent hot pressing. The adhesion and dispersion properties of CNTs in polymer matrix were the most important function of polymer matrix reinforced with CNTs as nanofillers. The formation of nanotubes with free agglomeration during

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mixing process with polymer has been a major feature of the development of CNT-based polymeric nanocomposites. 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. Mechanical properties studied were Young's modulus and tensile strength. It was important to observe that these properties increase, compared to those of pure PLA matrix.

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