

EFFECT OF CARBON NANOTUBE FUNCTIONALIZATION ON THE STRUCTURE AND PROPERTIES OF POLY(3-HYDROXYBUTYRATE)/MWCNT BIOCOSITES

M. Jung,¹ M. Huh,^{1,2} Y. Park,^{1,2} S. Kang¹
R. Russell,³ P. Holden,³ S. Yun^{1*}

¹ Jeonju Institute of Machinery and Carbon composites, Jeonju 561-844, Republic of Korea

² Department of Polymer-nano Science and Technology, Chonbuk National University, Jeonju, Republic of Korea

³ Australian Nuclear Science & Technology Organisation, Locked Bag 2001, Kirrawee, N.S.W., 2232, Australia

* Corresponding author(ysi@jmc.re.kr)

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1 Introduction

Poly(3-hydroxybutyrate) (PHB) is a natural, linear, thermoplastic polyester synthesized by microorganisms as intracellular carbon reserves and ion sinks in response to limited nutrient availability and imposed stress conditions. The PHB has become one of the most interesting biomaterials for application in tissue engineering due to its excellent biodegradability and biocompatibility. Nanocomposites of biopolymers with carbon nanotubes (CNTs) offer significant potential for their increased utilization, as a result of the improvements in electric conductivity, mechanical and thermal properties. In regards to the fabrication of polymer/CNT composites, the most critical issue remains the development of methods to homogeneously disperse the CNTs throughout the polymer matrices. Dispersion of CNTs is an important first step toward many potential applications that harness the unique electronic, thermal, optical, and mechanical properties of the individual tube. Furthermore, conventional applications such as the use of single wall carbon nanotubes (SWNTs) as conductive fillers in composites will benefit from a well-dispersed system that will exhibit the same conductivity with a smaller percentage of filler. Although high power ultra-sonication can make metastable solutions of nanotubes, it is found invariably that the nanotubes tend to aggregate when slow solvent evaporation is employed, leading to an inhomogeneous distribution of nanotubes throughout the polymer matrix. One of most frequently used techniques to improve the CNT

solubility is to covalently functionalize CNT surface. Covalent functionalization can be accomplished by either modification of surface-bound carboxylic acid groups on the nanotubes or by direct reagents to the side walls of nanotubes. The amidation or esterification of oxidized CNTs has become one of the most popular ways of producing soluble materials in organic solvents or in polymers. Although nanocomposites of PHB/CNT have been studied by several groups, Attempt to utilize the covalently functionalized CNTs to obtain the better dispersion of CNTs within PHB matrix has not been made. The fundamental materials property, the electric conductivity of PHB/CNT nanocomposites has not also been reported, to our knowledge. In this paper we synthesized multiwall carbon nanotubes (MWNTs) and covalently functionalized MWNTs with alkyl group. The PHB and MWNTs functionalized with alkyl group were mixed in chloroform and the nanocomposite film was casted from the solutions. It was found that PHB composites of CNTs functionalized with alkyl groups showed a better solubility in PHB/chloroform solutions and casted films, which resulted in higher electric conductivity and higher mechanical properties compared to acid treated CNT.

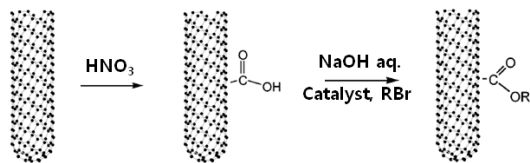
2 Experimental

2.1 Materials

Poly(3-hydroxybutyrate)(PHB) was purchased from Aldrich. MWNTs with a diameter 4-6 nm were produced via the chemical vapor deposition(CVD) method and purified according to commonly used

method in literature. All reagents were purchased from TCI, JUNSEI and Aldrich.

2.2 Sample preparation



Scheme 1. Functionalization of carbon nanotubes

Formation of MWNT-COOH was based on a conventional process. To make alkylated MWNTs, the MWNT-COOH was sonicated in NaOH aqueous solution and converted into the sodium salt form. Catalyst and alkyl bromide (RBr) were added in and the mixture was heated under vigorous stirring. The precipitation was collected and dried. Neat polymer and composite films were prepared by solvent casting method.

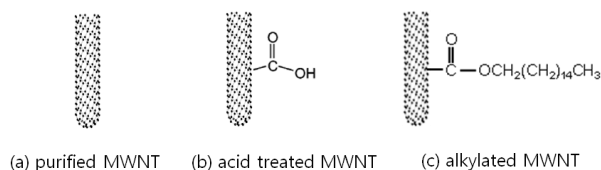


Figure 1. Structure of MWNTs used in the experiment.

2.3 Characterization

Transmission electron microscope (TEM) photographs of MWNTs powder and ultrathin sections of nanocomposite films were obtained by the JEM-2200FS (JEOL KOREA LTD.) using an acceleration voltage of 200kV. For the electrical resistivity measurement, ring probe method (3-electrode method), Hiresta UP (MITSUBISHI CHEMICAL ANALYTECH CO., LTD), was used to measure the surface resistivity of the samples. The thermal behaviors of samples were investigated by the SHIMADZU TA Instruments differential scanning calorimeter (DSC, model TA-60WS) and a thermogravimetric analyzer (TGA, model TGA-50) at a heating rate of 20 under N_2 atmosphere. Dynamic mechanical analysis of nanocomposite films was performed using the TA Instruments Q800 with the tensile mode at the fixed frequency of 1Hz over the temperature range from -20 to 120 °C.

3 Results and Discussion

3.1 Synthesis and Functionalization of MWNTs

MWNTs were produced via the chemical vapor deposition method. Figure 2 shows the TEM image of the purified MWNTs used in our experiments. It can be clearly seen that there are almost no amorphous carbon and metal parties after the purification procedure. The diameter (D) range of MWNTs was 4-6nm which generate relatively high aspect ratio compared to other commercial MWNTs (D=10-20nm).

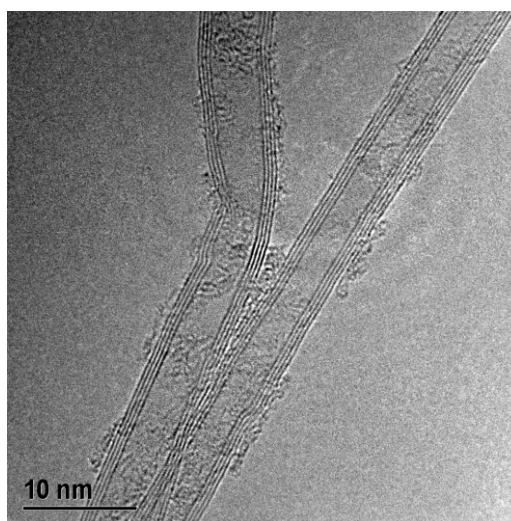


Figure 2. TEM images of the purified MWNTs

The TGA measures the decrease in sample mass as a function of annealing temperature. Because CNTs generally have higher decomposition temperatures than absorbed molecules and amorphous carbon, TGA data can be used to estimate CNT purity and the presence and concentration of organic molecules attached to CNT sidewalls. Figure 3 shows the TGA thermograms of purified MWNTs, acid treated MWNTs and alkylated MWNTs. For the purified MWNTs, almost no noticeable weight loss was detected over the temperature range of 30-600 °C and the residue amount at 600 °C was estimated to be 99.5 wt%. Similarly, acid treated MWNTs were scarcely decomposed due to their high thermal stability with the residue of 90 wt% at 600 °C. The TGA profile of alkylated MWNTs demonstrates the considerable weight

loss in the temperature range 200-500 °C which corresponds to the thermal disruption of the alkyl attachments. The results indicate the high degree of MWNT functionalization with the nearly 22 wt% of long alkyl chains.

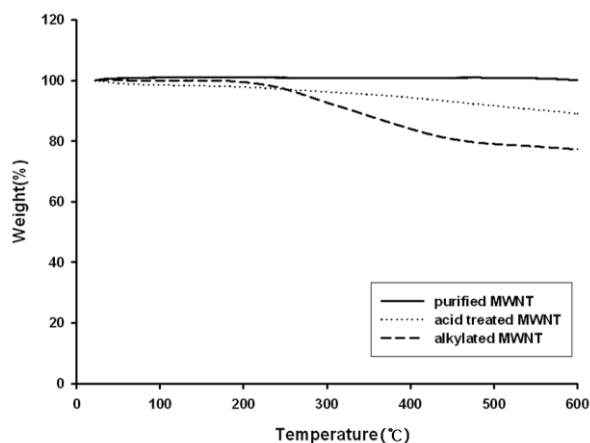


Figure 3. TGA curves of purified MWNT, acid treated MWNT and alkylated MWNT.

3.2 Dispersion of MWNTs

Commercial PHB polymer dissolved in chloroform at 100 °C and cooled down to the room temperature prior to casting of neat PHB films. The MWNTs in chloroform were sonicated for 5 minutes and PHB powders were placed into the MWNT solutions, then the composite solutions in chloroform were heated to 100°C and cooled down to room temperature. The composite solutions were cast onto glass plates to produce composite films. It was found that alkylated MWNTs showed a better solubility in the solvent, PHB solutions and casted films than the raw(=purified) and acid treated MWNTs as shown in Figure 4 and 5. However acid treated MWNTs did not improve the solubility in chloroform and PHB/chloroform, in fact the acid treated MWNTs displayed slightly decreased solubility in polymer solutions and casted films compared to the raw(=purified) MWNTs as shown in Figure 5.

To study the homogeneity of the films, the TEM was employed to investigate the ultrathin sections of composite films containing surface modified MWNTs 1%. As shown in Figure 6, alkylated MWNTs were better dispersed in PHB matrix than acid treated MWNTs.

3.3 Electric conductivity

CNTs have high aspect ratio and excellent electrical conductivity which in turn facilitate the formation of conducting networks and thus transform the insulating polymer to a conducting composite at a low CNT content.

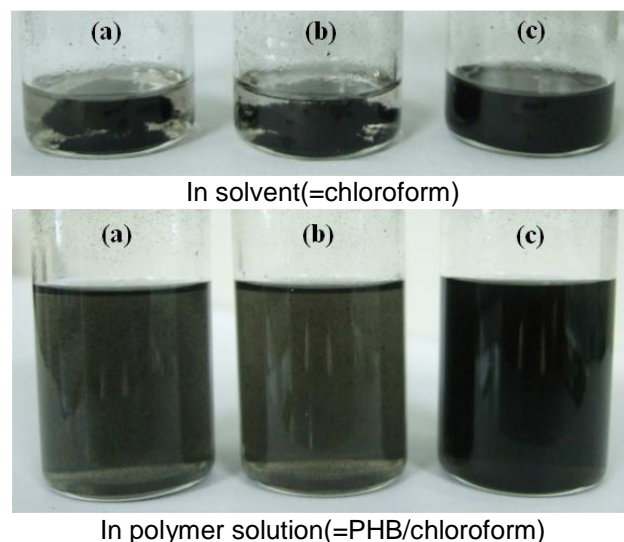


Figure 4. Photographs of MWNTs for solvent and polymer solution after the sonications: (a) purified MWNTs, (b) acid treated MWNTs and (c) alkylated MWNTs

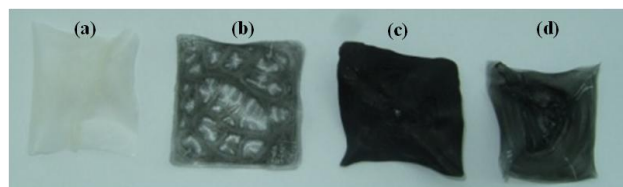


Figure 5. Photographs of MWNT dispersion in composite films: (a) Neat PHB, (b) acid treated MWNT, (c) alkylated MWNT and (d) purified MWNT.

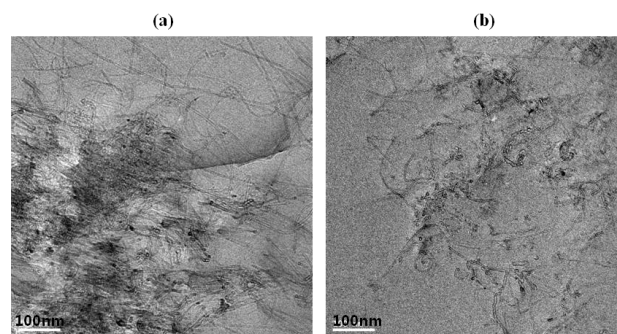


Figure 6. TEM images of PHB Nanocomposite Films containing (a) acid treated MWNT 1% and (b) alkylated MWNT 1%.

Table I lists the electrical conductivities of the films at room temperature using a ring probe(3-electrode) method. The surface resistivity of neat PHB films was measured to be $2.43 \times 10^{13} \Omega/\text{sq}$. The addition of purified CNTs significantly increases the electric conductivity of PHB with the surface resistivity of $1.66 \times 10^6 \Omega/\text{sq}$ for PHB/purified MWNT. However, the surface resistivity of PHB/acid treated MWNT was measured to be $1.12 \times 10^{13} \Omega/\text{sq}$, which is the result of CNT agglomerates. Even the well-dispersed alkylated MWNTs improve the electric conductivity of PHB less effectively (surface resistivity = $4.80 \times 10^7 \Omega/\text{sq}$) than non-modified CNTs. These results were explained by the fact that long alkyl chains which shielded the surface of MWNTs deteriorate electrical conduction throughout the MWNTs.

Table I . Electrical Property of PHB/functionalized MWNT nanocomposite films

Type	Surface Resistivity(Ω/sq)
PHB	2.43×10^{13}
PHB/purified MWNT 1.0%	1.66×10^6
PHB/acid treated MWNT 1.0%	1.12×10^{13}
PHB/alkylated MWNT 1.0%	4.80×10^7

3.4 Thermal properties

The addition of MWNTs greatly influences the crystallization rate of polymer. The DSC thermograms are shown in Figure 7 and a few important parameters obtained from the DSC are given in Table II . From Figure 7, it was found that the crystallization peaks of nanocomposites shifted to a higher temperature with the incorporation of MWNTs compared with neat PHB. In addition, purified MWNT appeared to be more effective as nucleating agents than functionalized MWNTs as shown by the higher T_c of composites with the same MWNT contents. Interestingly the ΔH_m value was found to be smaller for the alkylated MWNT composites than purified and acid treated MWNT composites. This is because bulky pendent group may disturb polymer chains to attain a high degree of crystallizations resulting in smaller ΔH_m . Annealing may eliminate this perturbing effect by inducing crystallization of PHB. Annealing of the samples at 100°C for a day, increased the ΔH_m

value, especially most dramatically for the alkylated MWNT /PHB composite. The result confirms that long alkyl chains on the CNT surfaces significantly decrease the crystallization of polymer matrix compared to raw CNTs (non-modified).

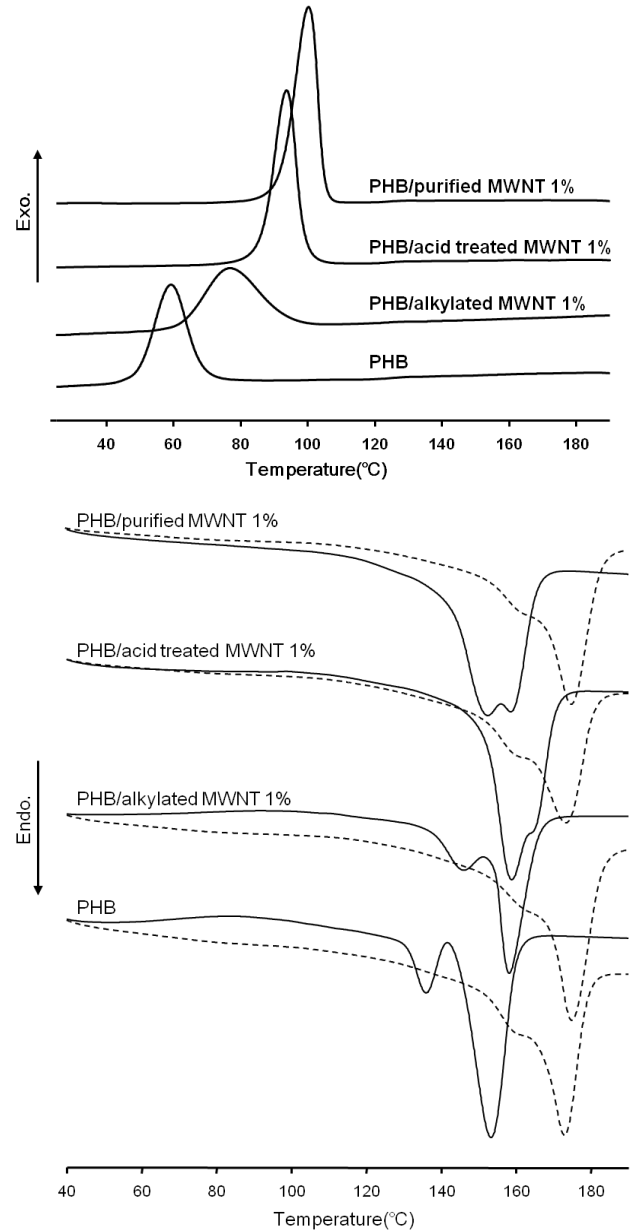


Figure 7. DSC thermograms of PHB/functionalized MWNTs composites before (solid) and after (dot) thermal annealing.

3.5 Dynamic mechanical properties

Figure 8 shows the temperature dependence of the storage modulus(E') of PHB/MWNT composites

with the different functional group of MWNT surface. The storage modulus of all samples decreases slowly and progressively with increasing temperature. The mechanical properties of the prepared PHB/MWNTs composites increase significantly with the addition of only small amount of MWNTs into the PHB matrix. The mechanical reinforcement was found to be relatively weak for alkylated MWNTs compared to non-modified MWNTs due to the lower degree of crystallization. Annealing of the samples considerably increased the storage modulus of alkylated MWNTs/PHB composites agreeing with the result of ΔH_m . The improved mechanical strength for PHB/alkylated MWNT composites is attributed to homogeneous dispersion of MWNTs in matrix as well as the strong interfacial interaction between MWNTs and polymer matrix due to the covalent functionalization of CNTs.

Table II. Thermal properties of PHB/functionalized MWNTs composites before and after thermal annealing.

Before annealing (—)		
Type	ΔH_m (J/g)	T_m (°C)
PHB	60.34	136, 153
PHB/purified MWNT 1%	64.17	152, 159
PHB/acid treated MWNT 1%	63.28	159
PHB/alkylated MWNT 1%	46.86	146, 158
After annealing (- - -)		
Type	ΔH_m (J/g)	T_m (°C)
PHB	61.42	173
PHB/purified MWNT 1%	61.10	175
PHB/acid treated MWNT 1%	59.01	173
PHB/alkylated MWNT 1%	66.22	175

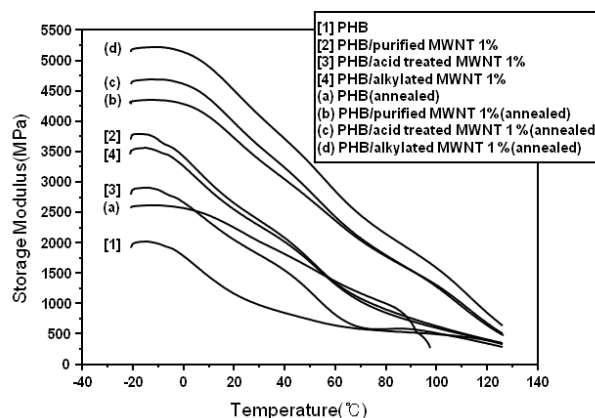


Figure 8. Typical plot of storage modulus against temperature for PHB/functionalized MWNTs composites: solvent casting films(1-4), thermal annealing for 1day of solvent casting films(a-d)

4 Conclusions

The covalent functionalization of CNTs with alkyl groups significantly improved the solubility of MWNTs in PHB matrix which resulted in increased mechanical properties of PHB composites.

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