HYPERBRANCHED ARAMID-GRAFTED CARBON NANOTUBES FOR HIGH PERFORMANCE NANOCOMPOSITES

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1 Introduction

Carbon nanotubes have received much attention due to their excellent, mechanical, electrical and magnetic properties [1, 2]. Due to these excellent properties carbon nanotubes are considered as an ideal reinforcing agent for high strength polymer composites. Despite significant research progress in polymer nanocomposites the dispersion of nanotubes in the polymer matrix is challenging one. Since carbon nanotubes forms stabilized bundles due to their van der Waals forces. Thus, to achieve high performance carbon nanotubes polymer composites it is necessary to find appropriate method to improve the dispersion of carbon nanotubes in polymer matrix. There have been significant research was done based on preparation of carbon nanotubes-polymer composites by solvent casting, melt compounding [3], and in-situ polymerization of monomers in the presence of carbon nanotubes [4]. Different types of polymer matrix are used for carbon nanotubes composites which including thermoplastics, thermosetting resins, conjugated polymers and etc.

Using hyperbranched polymers to improve the dispersion of carbon nanotubes into polymer matrix may be an alternative and attractive method to prepare high performance polymer nanocomposites. Hyperbranched polymers played an important role in interface and surface sciences due to their special chemical and physical properties. In addition, as compared with their linear analogues hyperbranched polymers have good solubility; lower melt viscosity, and extremely high density of functional groups at the surface [5]. Due to these properties hyperbranched polymers should increase the dispersion of carbon nanotubes in the polymer matrix. Recently, Cho et al. reported a fast and simple method for achieving high performance carbon nanotubes composites using hyperbranched polymer as a matrix [6]. Moreover, the hyperbranched polymers can be readily synthesized by using AB_n-type monomers. They are usually composed of terminal, linear and dendritic units as shown in Fig. 1.

On the other hand, aromatic polyamides are well known for its excellent thermal, mechanical and chemical properties [7]. However, the solubility of aromatic polyamides is limited to highly polar solvents such as concentrated sulfuric acid only. We anticipated good solubility of hyperbranched aromatic polyamide (HBA) as compared to their linear one. So far up to our knowledge, there is no work is reported on hyperbranched aramid based carbon nanotubes composites. In this study, hyperbranched aromatic polyamide (aramid) grafted multi-walled nanotubes were prepared by in-situ polymerization. The dispersion of HBA-grafted MWNTs was investigated.

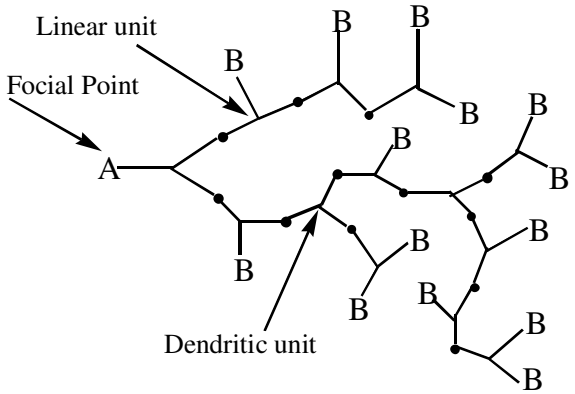


Fig. 1. Structure of hyperbranched polymer synthesized from AB_2 monomer.

2 Experimental Sections

2.1 Materials

MWNTs with diameter in a range of 10-15 nm were purchased from Hanwha Nanotech Co., Korea. 3, 5-Diaminobenzoic acid and triethylamine (TEA) were purchased from Sigma Aldrich. 2,3-Dihydro-2-thioxo-3-benzoxazolyl phosphonic acid diphenyl ester (DBOP) was received from Tokyo Chemical Industry Co. The composition of HBA-grated MWNTs was shown in Table 1.

Table 1. Composition of HBA-grafted MWNTs

Sample code	3,5-diamino benzoic acid (g)	NMP (ml)	TEA (ml)	MWNT -COOH (g)
HBA-MWNT 5 Wt%	0.210	1	0.07	0.010
HBA-MWNT 10 Wt%	0.210	1	0.07	0.020

2.2 Acid treatment of MWNTs.

In a 500 ml flask, 2.0 g of pristine MWNTs, 20 ml of nitric acid, and 60 ml of sulfuric acid were added with vigorous stirring. The mixture was then stirred for 90 min under reflux at 100 ℃. After cooling to room temperature, the reaction mixture was diluted with distilled water and then vacuum filtered through a filter paper with micro-pores of 1.0 µm. The washing steps continued until the pH of the filtered reached 7. Finally, the filtered solid was dried under vacuum for three days to obtain acid treated MWNTs

2.3 Synthesis of HBA-grafted MWNTs.

Acid treated MWNTs, 3, 5-diaminobenzoic acid, n-methyl pyrrolidone, TEA, and DBOP were added in a 100 ml three-necked flask equipped with a magnetic stirrer and nitrogen inlet. The solution was stirred at room temperature at 24 h. The reaction mixture was then poured into methanol. The crude product was filtered, dried under vacuum, and further characterized [8].

2.4 Characterization

Synthesis of HBA-grafted MWNTs was confirmed by Fourier transform infrared (FT-IR) spectroscopy and ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The morphology of the pristine and HBA-grafted MWNTs was compared using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements. Thermogravimetric measurements were also obtained to understand the thermal stability of the nanocomposites.

3 Results and Discussion

3.1 FT-IR analysis

Figure 2 shows the FT-IR spectra of pristine, acid treated and HBA-grafted MWNTs. The spectra of HBA-grafted MWNTs (Figs. 2c and 2d) exhibit a carbonyl absorption peak corresponding to amide bonds at 1644 cm^{-1} which clearly indicates the amide bond formation between acid treated and 3,5-diaminobenzoic acid.

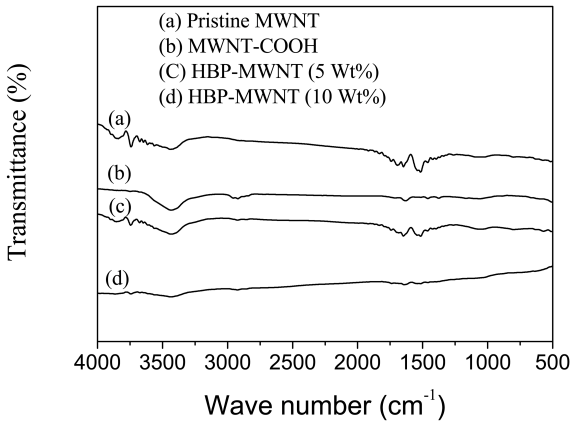
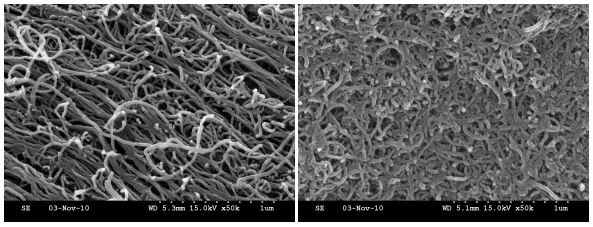


Fig. 2 FT-IR spectra of pristine MWNTs, acid treated MWNTs, and HBA-grafted MWNTs.

3.3 SEM Analysis

The SEM images of pristine and HBA-grafted MWNTs are shown in Fig. 3. Tubular structural morphology was observed for pristine MWNTs (Fig. 3a), whereas well dispersed polymer coated morphology was observed for HBA-grafted MWNTs (Fig. 3b). SEM results support the functionalization of MWNTs with HBA.

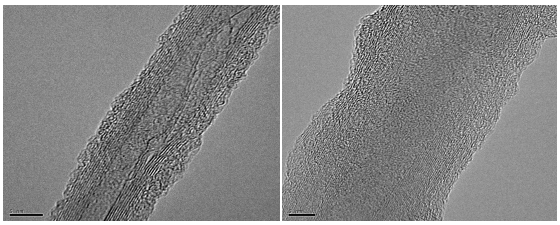


(a) (b)

Fig. 3. SEM images of (a) pristine MWNTs and HBA-grafted MWNTs.

3.4 TEM Analysis

The TEM images of pristine and HBA-grafted MWNTs are comparatively displayed in Figs. 4a and 4b, respectively. The pristine MWNTs show almost smooth surface as there is no such functional groups on the surface. After grafting with HBA the surface of the MWNTs becomes rough and the diameter has been also increased. The TEM results support the grafting of HBA on the MWNTs.



(a) (b)

Fig. 4 TEM images of (a) pristine MWNTs and (b) HBA-grafted MWNTs.

3.2 Thermogravimetric Analysis

Fig 5 shows the TGA curves for pristine, acid treated and HBA-grafted MWNTs respectively. The pristine MWNTs showed no weight loss up to 700 ºC, whereas HBA-grafted MWNTs showed significant weight loss at 250- 450 ºC. The difference in weight loss between pristine MWNTs and HBA-grafted MWNTs further supports the synthesis of HBA-grafted MWNTs.

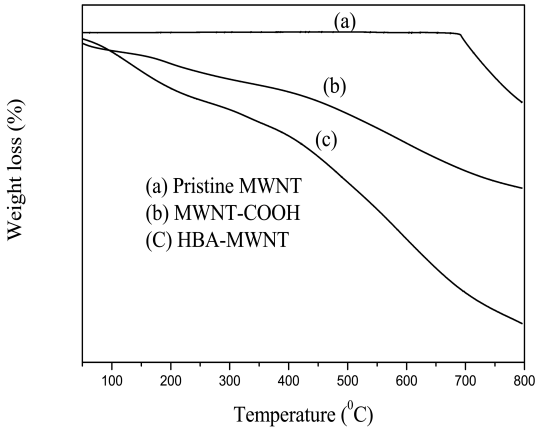


Fig. 5. TGA thermograms of pristine MWNTs, acid treated MWNTs, and HBA-grafted MWNTs.

4. Conclusions

The hyperbranched aramid-grafted MWNTs were successfully synthesized by insitu polymerization. Spectroscopic and TEM measurements supported their functionalization. Pristine MWNTs showed tubular morphology, however, in-situ polymerized HBA-grafted MWNTs showed well dispersed MWNTs. Due to their excellent properties of both hyperbranched aramid and carbon nanotubes the synthesized material was anticipated to have high performance.

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5. References

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