

Modification of pristine multiwalled carbon nanotube by grafting with poly(methyl methacrylate) using benzoyl peroxide initiator

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ABSTRACT: Multiwalled carbon nanotube was successfully grafted with poly(methyl methacrylate) by free radical mechanism using benzoyl peroxide initiator. The reaction was carried out *in situ*, where the initiator and methyl methacrylate monomer generated the polymer-free radical that was subsequently grafted to the surface of the pristine multiwalled carbon nanotube. The multiwalled carbon nanotube grafted poly(methyl methacrylate) (MWCNT-g-PMMA) were characterized using Fourier transform infrared, differential scanning calorimetry, thermogravimetric analysis, ^{13}C -solid NMR spectroscopy, X-ray photoelectron spectroscopy, and scan electron microscopy. From the result of the characterizations, the grafting of poly(methyl methacrylate) on to multiwalled carbon nanotube was confirmed, and a percentage grafting of 41.51% weight was achieved under optimized conditions with respect to the temperature and the amount of the initiator. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43270.

KEYWORDS: carbon nanotubes; free radical polymerization; grafting; nanocomposites; poly(methyl methacrylate)

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INTRODUCTION

Carbon nanotubes (CNTs) were discovered by Sumio Iijima in 1991.¹ They have unique electronic, mechanical, thermal, and chemical properties that justify the increasing attention paid to them by researchers worldwide.^{2,3} However, the problem of processability, agglomeration, poor dispersion in polymer matrices, and poor solubility remains a severe limitation to the extensive use of CNTs.⁴ Therefore, the functionalization of the carbon nanotubes with polymers serves as a keystone to exploring more of their applications in the field of nanocomposite preparations.^{5,6}

The covalent attachment of polymers on the surface of carbon nanotubes (CNTs) was reported to be achieved using three major techniques: (i) the “grafting to” technique,^{7,8} (ii) the “grafting from” technique,^{5,9–13} and (iii) the “free radical addition” technique.^{14–16}

In the phenomenon of “free radical addition” technique used the polymer chain radicals which reacted with C=C bonds of the MWCNT were produced by three main approaches; *in situ* radical polymerization of the monomers in the presence of the MWCNT initiated by an initiator,^{3,4} γ -ray irradiation, and thermo-initiation.^{3,17} In previous research, MWCNT underwent pretreatment for functional group attachment such as —COOH, —OH, —NH₂, prior to covalent attachment of the polymer moieties.^{7,9,10,18–21} This was the case until Wu and Liu reported

a 15.6% weight grafted polystyrene on the surface of untreated MWCNT using the free radical addition process in the presence of a styrene monomer and 0.05g of 2,2'-azobisisobutyronitrile (AIBN) initiator.³

This is the first paper to report on the graft of polymer from acrylate family onto the surface of pristine MWCNT by simple *in situ* solution free radical polymerization using a methyl methacrylate (MMA) monomer and benzoyl peroxide (BPO) as the initiator that generated the polymer radical. To our knowledge, the percentage grafting of 41.51% weight obtained was the highest reported to date in the literature for untreated MWCNT grafting using the free radical mechanism. The MWCNT-g-PMMA may improve the dispersion of MWCNT in polymer matrices when used as a reinforcing filler.

EXPERIMENTAL

Pristine MWCNT with a diameter of 110–170 nm, a length of 5–9 μm , and a purity of 90% were obtained from Sigma Aldrich. MMA from Sigma-Aldrich was purified by vacuum distillation. Benzoyl peroxide (BPO) from Merck Schuchardt was recrystallized by dissolving it in chloroform and precipitated into methanol. Toluene, methanol, and all other solvents were used as received.

Synthesis of MWCNT-g-PMMA

MWCNT (0.1 g), 10 mL (9.4 g) of purified methyl methacrylate monomer, 10 mL of toluene, and 0.10 g of BPO were charged

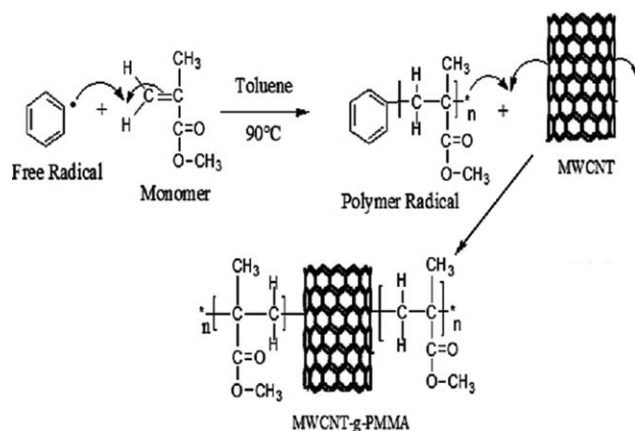


Figure 1. The mechanism for the synthesis of MWCNT-g-PMMA using *in situ* “grafting onto” technique.

into a three necked round bottom flask and fitted with a condenser at ambient temperature. The mixture was transferred into a preheated oil bath at 90°C for 11 h. After the reaction, the mixture was cooled to room temperature and precipitated in cold methanol, and then it was dried in a vacuum oven at an ambient temperature to obtain the crude MWCNT-g-PMMA. The MWCNT-g-PMMA was separated from the free homopolymer of PMMA by Soxhlet extraction with acetone as the solvent for 24 h. The extracted MWCNT-g-PMMA and the homopolymer were precipitated separately in cold methanol.³

Instruments and Characterizations

A Spectrum™ 400 Perkin Elmer infrared spectrometer was used for Fourier transform infrared (FT-IR) spectroscopy analysis of the MWCNT-g-PMMA. The differential scanning calorimetry (DSC) analysis was carried out using a Mettler Toledo instrument DSC822^e under nitrogen gas at a temperature range of 30–400°C with a heating rate of 10°C min⁻¹.¹ The TGA/SDTA851^e Mettler Toledo instrument was used for thermogravimetric analysis (TGA) at a temperature range of 50–700°C with a heating rate of 20°C min⁻¹ under the flow of nitrogen gas.

The solid ¹³C NMR spectroscopic analysis of MWCNT-g-PMMA was carried out at the ambient probe temperature on Bruker Avance III HD 400 MHz. A zirconium oxide rotor 4 mm in diameter was used to acquire the NMR spectrum at the spin frequency of 100.59 MHz. Finally, the ¹³C NMR spectrum was obtained with cross-polarization-Magic angle spinning (CP-MAS) and dipolar decoupling for high resolution spectrum.

The surface chemistry of the MWCNT-g-PMMA was analyzed using an X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD Shimadzu). The XPS spectrum was recorded in the hybrid mode with Al K α (1486.6 eV) as the X-ray source. A survey spectrum was recorded in the range of 0–1200 eV with a pass energy of 20 eV for a high resolution scan that generated the C1s and O1s peaks. The acquired data was converted to VAMAS format, analyzed, and deconvoluted using CasaXPS software. For the scanning electron microscopy (SEM) analysis, the Pristine MWCNTs and MWCNT-g-PMMA were coated with platinum. The morphology of the samples was examined using a JEOL JSM-6701 scanning electron microscope.

RESULTS AND DISCUSSION

Synthesis of MWCNT-g-PMMA

The simple *in situ* free radical addition mechanism used in grafting PMMA on the surface of MWCNT illustrated in Figure 1, was found to be facile and *in situ* “grafting on to” technique due to the possession of the C=C double bond by the MWCNT. The two benzoyloxy free radical species produced by the decomposition of BPO initiator in Figure 2, could further be decomposed to generate phenyl radicals. Toluene as a solvent was nonpolar and relative to benzene ring structure of MWCNT therefore, the charge separation due to nonpolarity predominate the chemical environment in which it favors the free radicals generated by the initiator interact with the methyl methacrylate monomer to produced more of the polymer radicals than been consumed by the conjugation structure of the carbon nanotubes.^{17,22–24}

The mechanism in Figure 1, shows clearly how the polymer free radicals produced use its terminal free radical electron and the π electron of the MWCNT to form a covalent bond between the polymer chain and the CNT. Therefore, this phenomenon could be used to describe the grafting process as one-pot polymerization because it involves the use of free radical to produce the PMMA polymer radicals *in situ* and subsequent grafting of the macro radicals to the surface of MWCNT by “grafting onto” technique.

Thermogravimetric analysis (TGA) was used to determine the relative amount of grafted PMMA from MWCNT through thermal decomposition that leads to weight lost because the PMMA has a lower decomposition temperature than MWCNT have.^{3,5,7,25,26}

Figure 3 shows the TGA results of the MWCNT-g-PMMA samples synthesized with different BPO added as the initiator as summarized in Table I. Slight weight losses were found on curve (g) (Pure PMMA) and curve (f) (0.10g BPO of MWCNT-g-PMMA) at temperatures of 150 and 170°C, respectively. This may be attributed to the release of moisture and decomposition of solvents absorbed, because actual decomposition of pure PMMA starts at a temperature >215°C. However, the grafted PMMA will expect to have much higher decomposition temperature than pure PMMA hence, the decomposition of the grafted PMMA starts at a temperature of almost 280°C as observed from the graph.^{3,27}

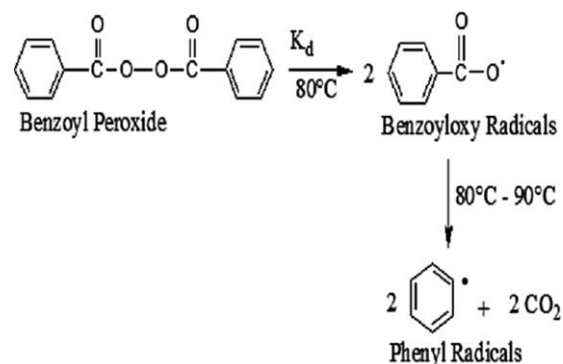


Figure 2. Thermal decomposition of benzoyl peroxide.

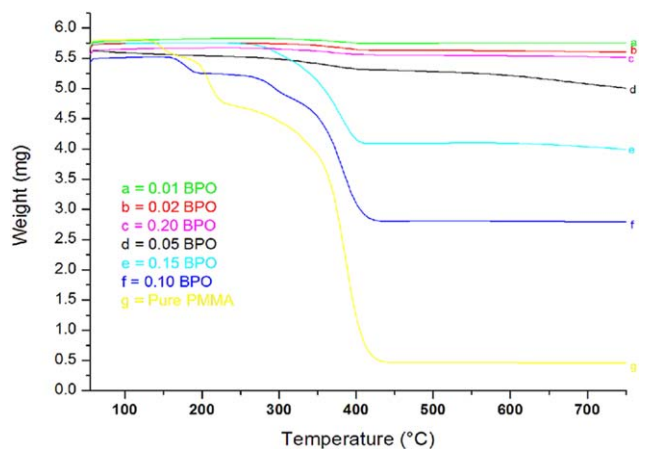


Figure 3. TGA curves of pure PMMA and MWCNT-g-PMMA with different amount of the initiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Weight loss was directly proportional to the amount of PMMA grafted; therefore, the percentage grafting was determined from the weight loss in each case.

However, the highest percentage grafting was achieved with 0.10 g BPO and the higher polymerization temperature was in favor of the PG %. In the case of *in situ* grafting polymerization, an increase in the amount of initiator at a higher temperature increases the addition of free radicals to the MWCNT, which results in an increase in the grafting rate. However, with much more initiator (>0.10 g) added, a coupling termination of the free radicals might be the dominant reaction.³ That was the reason for the low percentage grafting in curve c despite the higher amount (0.20 g) of BPO added.

The percentage grafting was determined from the TGA results of the analysis using the relationship below and the results were summarized in Table I³:

$$\%G = \frac{\text{Weight of Grafted PMMA Lost (mg)}}{\text{Total Mass Charged (mg)}} \times 100\%$$

The drastic increase in the percentage grafting at 90°C and 0.10 g of the initiator indicates the maximum amount of the initiator that favors the grafting.

Table I. Experimental Conditions and the Percentage Grafting

MWCNT-g-PMMA	BPO Added (g)	Temperature (°C)	% Grafting ^a
1	0.01	90	4.10
2	0.02	90	4.62
3	0.05	90	10.21
4	0.10	90	41.51
5	0.15	90	27.50
6	0.20	90	5.31

^a Determined by TGA.

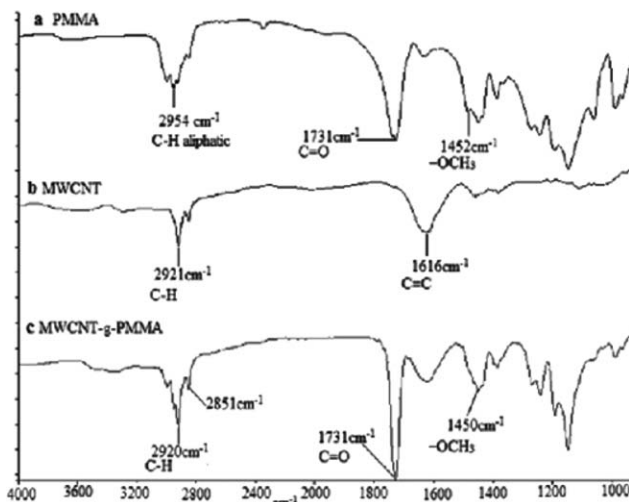


Figure 4. FT-IR spectra of (a) PMMA, (b) MWCNT, and (c) MWCNT-g-PMMA.

Characterization of MWCNT-g-PMMA

Figure 4 shows the FT-IR spectra of the pure PMMA (a), that of the pristine MWCNT (b), and compared with that MWCNT-g-PMMA (c). Signals of 2920 cm⁻¹ in spectrum c and 2921 cm⁻¹ in spectrum b was due to C—H stretching of aromatic ring from MWCNT. While band of 2954 cm⁻¹ in spectrum (a) was assigned to C—H stretching of aliphatic ester from PMMA. In the finger print region of spectrum c signal of 1731 cm⁻¹ was attributed to C=O of an ester, and band of 1450 cm⁻¹ was due to —OCH₃ bending peculiar to PMMA. Similar signals were observed in spectrum (a) which shows evidence of successful grafting.

In addition, signal of 1616 cm⁻¹ in spectrum b becomes broad in spectrum c with similar signal value. This indicates that modification has taken place on the surface of the MWCNT.

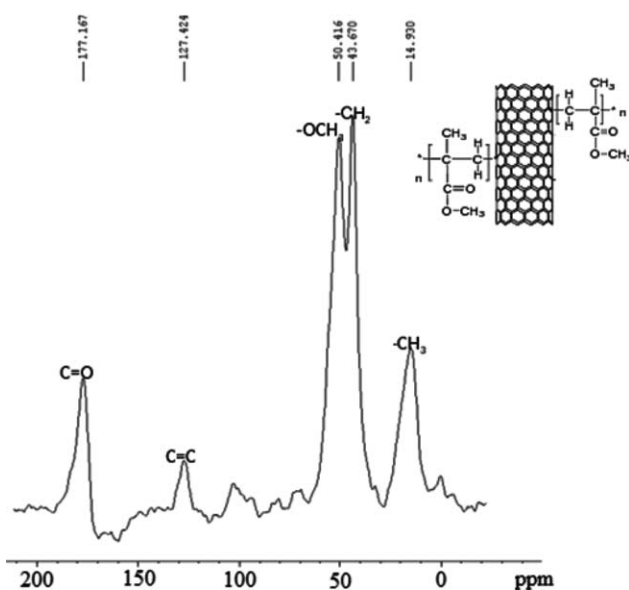


Figure 5. Solid-state ¹³C-NMR spectrum of MWCNT-g-PMMA.

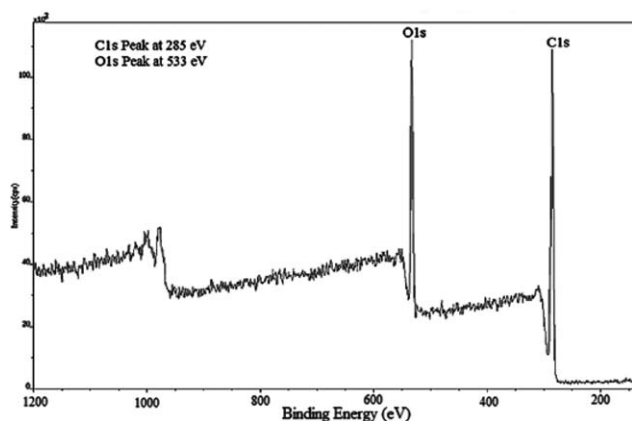


Figure 6. XPS survey spectrum of MWCNT-g-PMMA.

Similar peak values of Fourier transform infrared spectra were reported by Aldosari *et al.*, and De Falco *et al.*^{5,28}

Solid ^{13}C NMR was used for structural analysis of polymers with more concern to ^{13}C nucleus and any electronegative element than the ^1H proton. The MWCNT-g-PMMA was analyzed by solid ^{13}C NMR spectroscopy to confirm the grafting of the PMMA^{29–32} as shown in Figure 5. The peak at chemical shift of 14.93 ppm was attributed to $-\text{CH}_3$ carbon nucleus of methyl methacrylate repeat units of the PMMA. Peak at 43.67 was due to the carbon nucleus of $-\text{CH}_2-$ of the PMMA polymer which confirmed the presence of the polymer repeat unit, while signal at 50.42 ppm was for the $-\text{OCH}_3$ of the PMMA. The carbon nucleus of the carbonyl ($\text{C}=\text{O}$) of the PMMA was observed at chemical shift of 177.17 ppm.

In addition, the signal at 127.42 ppm was for the $\text{C}=\text{C}$ of the benzene ring from the MWCNT which is the backbone where the PMMA was grafted. From the results of the ^{13}C NMR analysis it was revealed, all the ^{13}C nucleons of the structural components of MWCNT-g-PMMA were observed; hence, a successful grafting of the PMMA onto the MWCNT.

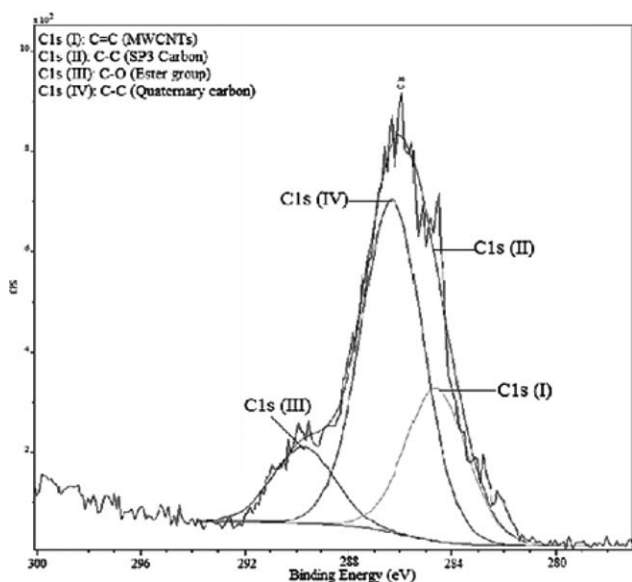


Figure 7. High-resolution XPS deconvoluted spectra of C1s.

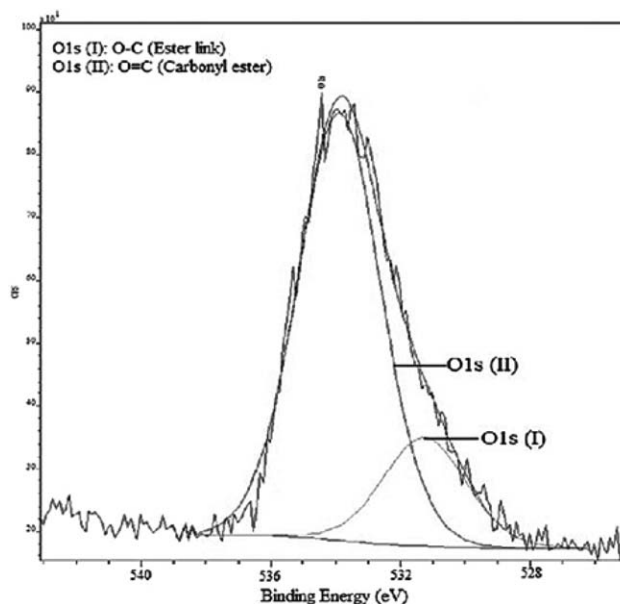


Figure 8. High-resolution XPS deconvoluted spectra of O1s.

X-ray photoelectron spectroscopy, with its high surface specificity and chemical state sensitivity, is an ideal tool for evaluating the surface chemistry of materials. The spectral data obtained from the XPS analysis could be used for both quantification and identification of chemical variation in materials.^{21,33–38}

The aim of the XPS analysis of MWCNT-g-PMMA is to determine its surface chemistry. The high resolution XPS survey spectrum (see Figure 6) shows peaks at 285 and 533 eV for C1s and O1s, respectively. Meanwhile, the high resolution C1s spectra in Figure 7 shows there are four fitted peaks in the main peak at 284.60, 286.30, 286.80, and 289.71 eV corresponding to carbon links of $\text{C}=\text{C}$ MWCNT, $\text{C}-\text{C}$ (sp^3), $\text{C}-\text{C}$ (PMMA quaternary carbon), and $\text{C}-\text{O}$ (ester group), respectively.

In addition, Figure 8 shows the higher energy shift in O1s deconvolution spectra of 531.26 and 533.8 eV that indicated the

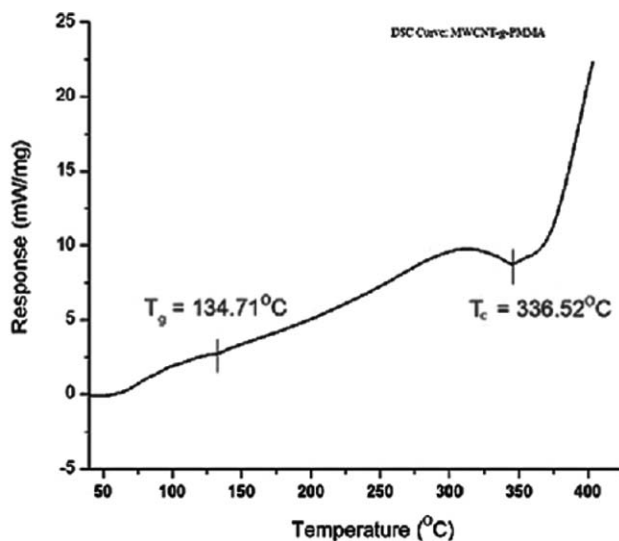


Figure 9. DSC curve of MWCNT-g-PMMA.

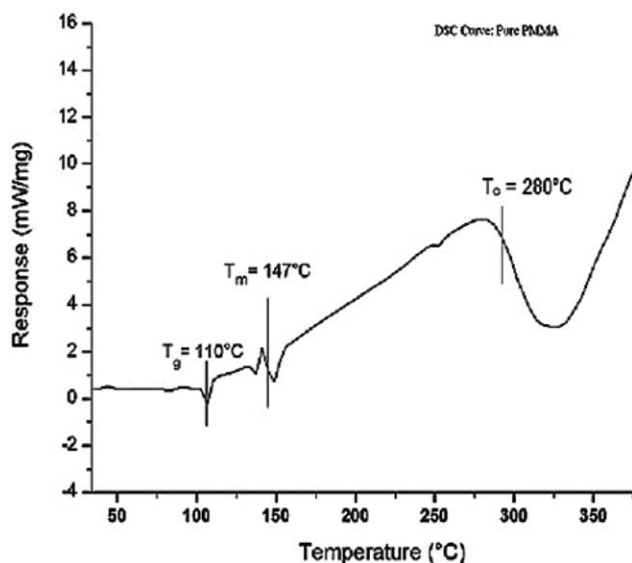


Figure 10. DSC curve of pure PMMA.

oxygen links in the ester group ($-\text{O}-\text{C}=\text{O}$) of the PMMA. The characteristic signals further confirm the existence of MWCNT and the grafted PMMA.

Thermal Analysis

Figure 9 illustrates the thermogram of differential scanning calorimetry (DSC) of the MWCNT-g-PMMA. From the results, the glass transition temperature (T_g) of 134°C was due to the grafted PMMA and found to increase significantly (by 24°C) compared to the actual T_g of 110°C for pure PMMA in Figure 10. The observed temperature (T_c) of 336°C may be regarded as the crystalline temperature of the grafted PMMA. Generally, in thermal analysis, polymers show a glass transition temperature (T_g) and a melting temperature (T_m). However, heating beyond the T_m the polymer tends to crystallize completely hence, lose their amorphous nature and turned opaque. Therefore, the observed temperature T_c of 280°C in Figure 10 was the crystalline temperature of the pure PMMA point at which PMMA becomes opaque (loss of optical property). Based on compari-

son of the two thermograms, the results indicate a successful grafting of PMMA onto the surface of the MWCNT.

Micrograph Analysis

Figure 11 shows the SEM images of pristine MWCNT before and after the grafting.^{10,20,39} Crucially, the image of the pristine MWCNT (A) before grafting has a smooth surface compared to the images of the MWCNT-g-PMMA (B) 0.05 g, (C) 0.10 g, (D) 0.15 g and (E) 0.20 g of BPO, respectively. In all the MWCNT-g-PMMA images were shown, a thick gray layers of PMMA on the surface of the MWCNT(s). The bulge or swollen surface circled in image (A) may be attributed to the end tips of the closed MWCNT. The thick gray layer exhibited in the image (C) 0.10 g BPO was an empirical evidence that proved grafting of the PMMA onto the MWCNT and confirmed to be the amount of BPO that yield the highest percentage grafting.

CONCLUSIONS

The vinyl monomer of methyl methacrylate (MMA) and benzoyl peroxide were successfully used in grafting PMMA onto the pristine MWCNT by simple *in situ* solution free radical polymerization. The amount of benzoyl peroxide added during the polymerization process significantly affected the percentage of the polymer grafted on the MWCNT. The method used was found to be a one-pot reaction, effective, and inexpensive. This provides to researchers a simple method of grafting vinyl polymers to the surface of pristine MWCNT and motivated them to explore more vinyl polymers hence, increases the applications of carbon nanotubes.

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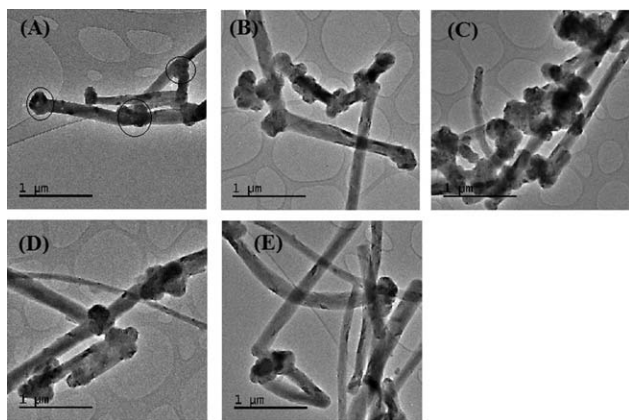


Figure 11. SEM images of MWCNT (A) and MWCNT-g-PMMA (B), (C), (D) and (E).

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