RESEARCH PAPER

Synthesis and Characterization of Phenylene Diamine and Poly (Methyl Methacrylate) Coupled with Multi-Walled Carbon Nanotubes by in Situ Oxidation Polymerization

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ABSTRACT

In this study, an effective approach for preparation of functionalized multi-wall carbon nanotubes (MWCNTs) through grafting with PDA (phenylene diamine) and PMMA (poly methyl methacrylate) by in situ oxidation polymerization method was demonstrated successfully. To this purpose, first the carboxylated MWNCTs (MWNCTs–COOH) after treatment with pristine MWCNTs were obtained with a compound of 3:1 (v/v) HNO_3 and H_2SO_4. Then, MCNTs-CO-NH-Ph by treated MWCNTs-COOH with aniline, DCC and DMAP were produced. Following that, ring of aniline was nitrated by means H_2SO_4 and HNO_3. In order to synthesize MCNTs-PDA, nitro group was reduced to amine group with HCl in ethanol. Finally, MWCNTs-PDA was functionalized by in situ oxidation polymerization with PMMA to afford MWCNTs-g-(PDA-g-PMMA). The resulting of functionalized MWCNTs (Oxidation, decrease and coupling) were demonstrated by FT-IR spectroscopy and morphology attachment of PDA and PMMA onto MWCNTs surfaces was confirmed by SEM, TEM and AFM. Thermal particularities of grafted polymers onto MWCNTs surfaces were studied using TGA and DSC analysis. The prepared MWCNTs-g-(PDA-g-PMMA) can be used as an improvement for polymeric (nano-) composites owing to excellent properties of MWCNTs in addition their adaptability with polymeric materials after functionalization processes.

INTRODUCTION

Carbon nanotubes (CNT) for the first time was reported by Iijima in 1991 [1]. This nanostructure has received more and more consideration as attractive material for polymer matrix in practical studies, due to their nanometer size, better electrical conductivity, high aspect ratios, negligible mass density, great chemical activity, thermal stability, good electro-active surface

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area and capability of excellent mechanical [2-5]. Also, CNTs have been introduced as an excellent filler for polymers based on nanocomposite. Researcher have exanimated benefits of their high aspect ratios and conductivity (usually ca. 300 – 1000) with weak influence, in order to provide conductive plastics [6]. In last years, using of CNTs in biomedical (relating to both biology and medicine) have received many considerations and for this reason it's have been employed as gene carriers, drug delivery systems or compound materials based on tissue scaffolding [2, 6]. Furthermore, owning to capacity of increasing electron transfer reactions, they may be utilized in discovery of low concentrated electron synthesized in complex analysis [7, 8]. Since, the first investigation of nanocomposites using MWCNTs in 1994 [9], many of scientists deal with the polymer based on preparation of composites [10-12]. Lately, the nanocomposites including polymer and MWCNTs have receiving considerable attention because of their especial and performances features [13–17]. On the other hands, CNTs typically are irresoluble and intensely condensed owning to Van der Waals absorption between the nanotubes, making a problem when homogeneous distribution is favorable. In order to dominate this drawback, different chemical and physical methods have been discovered including in situ polymerization in the presence of MCNTs, facile suspension of MCNTs in polymer solution by means sonication [18–21], and the chemical improvement of CNTs in order to increase solution.

In the last decades, CNTs have been employed to develop a wide-range of polymers consisting of, poly (methyl methacrylate) [22], polystyrene (PSt) [23], polyamide [24], polyethylene [25], polycarbonate [26], and poly (propylene) [27]. Poly (methyl methacrylate) (PMMA) is a shapeless plastic with a great surface smooth, good radiation, a refractive index of 1.49, a visible luminosity of 92% (inorganic bottle also has a luminosity of 92%). PMMA has low water absorption and capability of high mechanical that can be well dimensional resistance. Other feature includes a fine stiffness with weak elongation when disintegrate. PMMA has profitable processing features, well thermal, and can be improved with pigment, UV absorbing additives, flare retarder activity and scrape consisting coating [28, 29]. Many researches were accomplished on PMMA and its performance [30-33]. In this study, PMMA is utilized in a various

method, i.e., as an improver for CNTs comment to error viewpoint of bridging the CNTs with a natural polymer or solvent. Baskaran et al. [34]. On the other hands, in the case of the absorption approach, the CNTs are not existing on the inside of the nanoparticles, but only on their surface. In contrast, in the case of the in situ polymerization method, the CNTs can be existing both on the inside and on the surface of polymers. Also, between the different polymerization methods, the oxidation polymerization method is one of the most significant methods of synthesizing PDA and PMMA grafted MWCNTs. Covalent grafting of CNTs to PDA and PMMA will obtains more stable nanocomposite, prevent washing of materials during uses, developing hydrophobicity relating to the functionality presented and guarantee long-range term stability of CNTs in the mass media.

In this research, an effective and facile approach was demonstrated successfully for the preparation of well-defined polymer-grafted MWCNTs by in situ oxidation polymerization method. Also, for the first time, atomic transfer radical polymerization method was used for the controlled grafting of hydrophobic monomer (methyl methacrylate) on MWCNTs, through formation of intermediate MWCNTs-PDA and bonding of resulting monomer into the main chain of CNTs to obtain controlled molecular weight of MWCNTs-g-PDA-g-PMMA. First, acid functionalized MWCNTs by oxidized MWCNTs with aniline, DCC and DMAP to obtain MWCNTs-CO-NH-Ph. Following that, the nitro group (nitrated by HNO_3 and H_2SO_4) to amine group was decreased with HCl in ethanol, in order to synthesize of MWCNTs-PDA. Finally, MWCNTs-PDA was functionalized by in situ oxidation polymerization with PMMA to produce MWCNTs-PDA-PMMA.

MATERIALS AND METHODS
Materials

The specimens of MWCNTs (over 95 wt. %) were acquired from Times nano Inc., Chengdu, China by chemical steam deposition (CSD) with length and an average diameter of about 30 μm and 10–20 nm, respectively, and purified as explained in 2.1. section. The Analytical degree chemicals were prepared by means Shanghai Chemical Reagent Company (S.C.R.C) and were employed for preparation of MCNTs-PDA-PMMA: Tetrahydrofuran (THF) (Merck, Darmstadt, Germany) were dried by refluxing over sodium

and distilled under argon prior to use. Potassium persulfate ($K_2S_2O_8$), (Merk, Germany) was prepared by adding potassium bisulfate ($KHSO_4$) to a solution of the more soluble salt ammonium peroxydisulfate ($(NH_4)_2S_2O_8$). Originally, it can be prepared by chemical oxidation of potassium sulfate using fluorine. Dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) were obtained from Aldrich. Methyl methacrylate (MMA), monomer from Merck (Darmstadt,

Germany) was dried over calcium hydride, vacuum-distilled, and then kept at $-20\,°C$ before use. Sulfuric acid (H_2SO_4), nitric acid (HNO_3), sodium hydroxide (NaOH), dichloromethane (DCM), $SnCl_2.2H_2O$ and acetic acid were acquired from Merk or Sigma and utilized without purification [35].

Purification of MWCNTs

Over the past decade, various methods have been represented to purify CNTs without
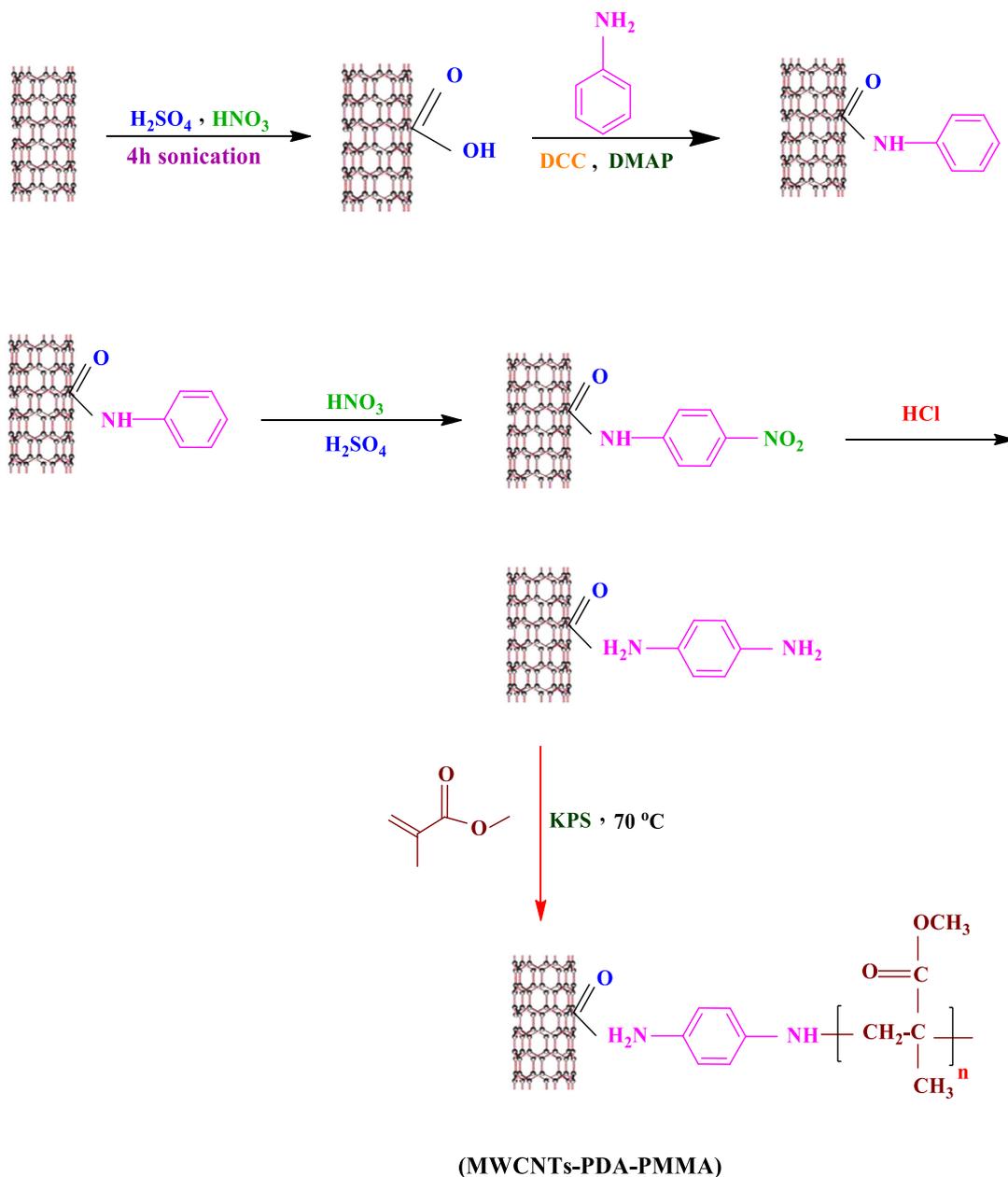

(MWCNTs-PDA-PMMA)

Fig. 1. Synthesis of MWCNTs-g-(PDA-g-PMMA)

considerably damaging the structure of nanotubes. The favorable conditions investigated in the literature. The obtained pristine MWCNTs was purified chemically and thermally in order to eliminate amount of impurities for example, catalyst particles and amorphous carbon. This impurity was eliminated using thermal oxidation of MWCNTs at 560 °C for 40 minutes under air flow. The chemical purification was successively accomplished with the solutions of HCl and HNO_3, under stirring for about 3 hours.

Synthesis of MWCNTs-COOH

A 100-mL glass flask fitted with a flux condenser and a magnetic stirrer was charged with purified MWCNTs in the previous step (0.90 g), and a mixture (3:1 v/v) of H_2SO_4 (20 mL, 96–98%) and HNO_3 (40 mL, 67%). The content of the flask was then sonicated and refluxed through ultrasonic bath at 100 °C for about 5 hr to open aggregation of nanotubes and represent functional carboxylic acid groups on the surface of MWCNTs. After the end of this time, several times dilution was then exerted to the reaction mixture, in order to terminate oxidation reaction. The obtained product was washed for several time with distilled water until the pH water becomes 7. Finally, the product was dried in vacuum oven at 60 °C for about 12 hrs. The obtained product was 0.5 gr and attributed as carboxylated MWCNTs (MWCNTs–COOH).

Synthesis of MCNTs-CO-NHPh (MCNTs-aniline)

The produced CNTs-COOH (0.5 g) in DCM (40 ml), then aniline (1.5 g), DCC (31.8 mmol, 6.61 g) and DMAP (3.18 mmol, 0.39 g) were added, respectively. The mixture was refluxed for 24 hrs at 100°C with intense mechanical stirring under N_2 protection. Following that, the material was washed with DCM and distilled water and then dried in a clean vacuum oven at 40° C overnight.

Nitration of CNTs-aniline

A 150-mL round-bottom glass flask was charged with, 1.5 gr of obtained MCNTs-aniline and 30 mL HNO_3 at temperature 0° C. At temperature 0° C, 45 mL H_2SO_4 was added drop-wise to the content flask. Afterwards, the reaction temperature was increased and was stirred at about 10 hours at 100 °C. After this time, the material was washed and dried in vacuum oven.

Reduce NO$_2$ group on the aniline to NH$_2$ (synthesis of MWCNTs-PDA)

In order to reduction of nitro group in the nitro-CNTs to amine group, a 150 mL two round-bottom flask was charged with $SnCl_2.2H_2O$ (3 g) and absolute ethanol (45 ml) along with nitro-nanotubed (1.1 g) and 40 ml of HCl (6 M). The mixture was allowed to reflux for 12 hours at 75° C. After terminate reaction time, the product is first was filtered and washed with 10% sodium hydroxide and lots of distilled water, then dried in vacuum oven.

Synthesis of MWCNTs-g-(PDA-g-PMMA)

MMA (2 gr) only with 0.5 gr of obtained material from the functionalization of MWCNTs-PDA and $K_2S_2O_8$ (0.05g) were weighed after that reacted for 24 hours at 70°C. The materials were washed with THF (Tetrahydrofuran) and with distilled water for several times, then was dried in vacuum oven at 160° C to produce the material in a powdered form. Schematically, the overall strategy for functionalized MWCNTs is displayed in (Fig. 1).

Characterization

FTIR (Fourier transform infrared) was run on a Shimadzu 8400 M FTIR (Shimadzu, Japan, Kyoto) in the wavenumber of 400–4000 cm^{-1} to demonstrate the near of functional groups derived from MMA and MWCNTs. Freeze-dried materials and dried KBr (potassium bromide) were employed, in order to provide pellets. The thermal particulary of MWCNTs-PDA-PMMA were carried out on a TGA-TOLEDO / METTLER 851e. The materials around 4 mg were heated from 40 to 760°C under N_2 protection at ratio of 10°C min^{-1}. About 10 mg of the sample was heated between 25 and 600 °C at a rate of 10 °C/min^{-1} under N_2 flowing. Differential scanning calorimetry (DSC) analysis were provided by means DSC-METTLER/TOLEDO 822^e. The specimen was first heated to 200 °C and then allowed to cool for 5 min to remove the thermal history. Afterword, the specimen was reheated to 200 °C at a rate of 10 °C/min. The entire test was carried out under nitrogen purging at a flow rate of 50 ml min. The morphologies and size of the synthesized samples were carried out by means transmission electron microscopy (TEM; PHILIPS EM 208 microscope) and scanning electron microscopy (SEM; Cam Scan MV 2300) with a 100 kV accelerator voltage. Atomic force microscopy (AFM; JPK apparatus AG, Germany, Berlin) images were collected in non-contact tapping method.

RESULT AND DISCUSSION

FT-IR spectroscopy study

FTIR spectrum of pristine MWCNTs and derived from MWCNTs were as demonstrated by the connection of PMMA onto PDA and MWCNTs-PDA, are shows in Figs. 2 and 3. The results for the purification and functionalization of the MWCNTs can be seen clearly in the FTIR spectrum. In pristine MWCNTs, rather strong band at ~1637 cm^{-1} is related to the C=C stretching method associated with MWCNTs sidewall defects. The FTIR spectra of the oxidized MWCNTs shows three new peaks in comparison with produced nanotubes. The absorption band at 1706 cm^{-1} is visibly belonged to the C=O stretch vibration of – COOH in nitric acid treated with MWCNTs. The peak at ~3536 cm^{-1} is related to the stretch vibration of O-H while the peak in the wavenumber of 1380-1430 cm^{-1}

might be owning to bending vibrations of nitro groups or O-H groups [36]. in the spectrum of MWCNTs–COOH closer examination disclosed two particular peaks, one be reveal around 1706 cm^{-1}, obtained from the stretch vibration of the carboxyl group and another at 1166 cm^{-1}, obtained from the stretch vibration of the C-O group, that both due to existence of –COOH group have changed when treatment with acid. These results are a sign for presentation of a carboxylic acid group on the nanotubes. However, the peak seen at around 2900 cm^{-1} is not visibly unrealized.

The FT-IR spectrum of MWCNTs-CO-NHPh, MWCNTs-CONHPh-NO$_2$, MWCNTs-PDA and MWCNTs-g-(PDA-g-PMMA) are shows in Fig. 3. As seen in the spectra of MWCNTs-CO-NHPh [Fig. 3 a], the addition of PDA was proved successfully by the near of bands at 2995 cm^{-1} aromatic C-H.
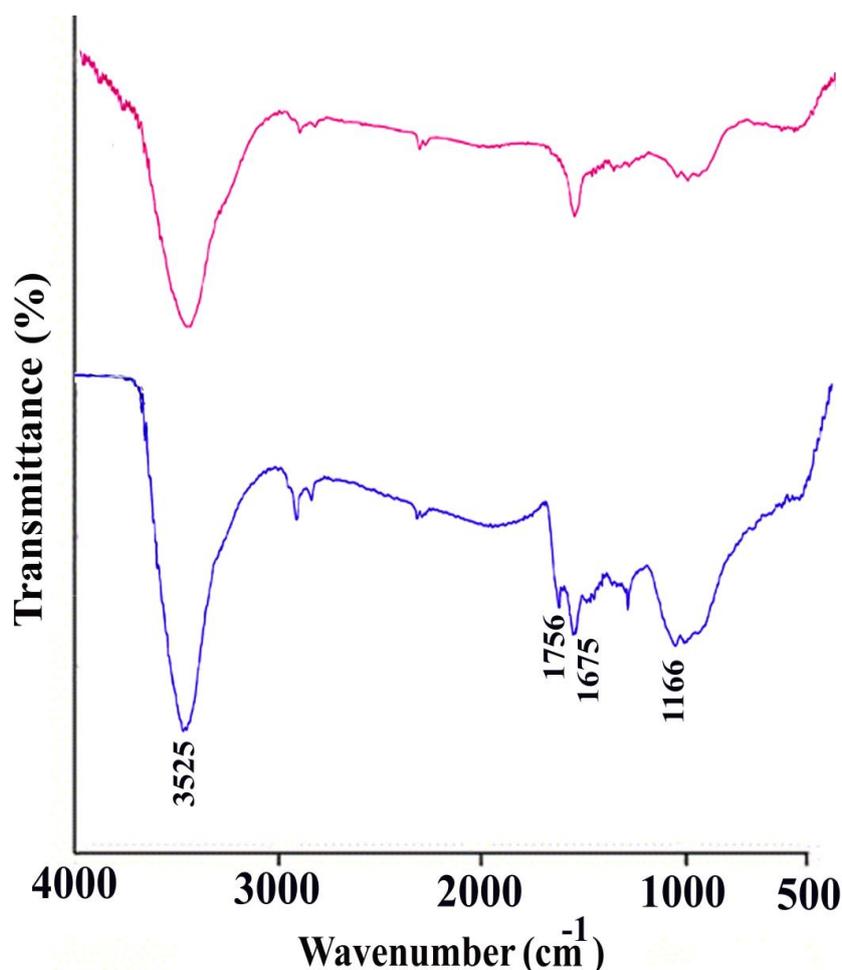

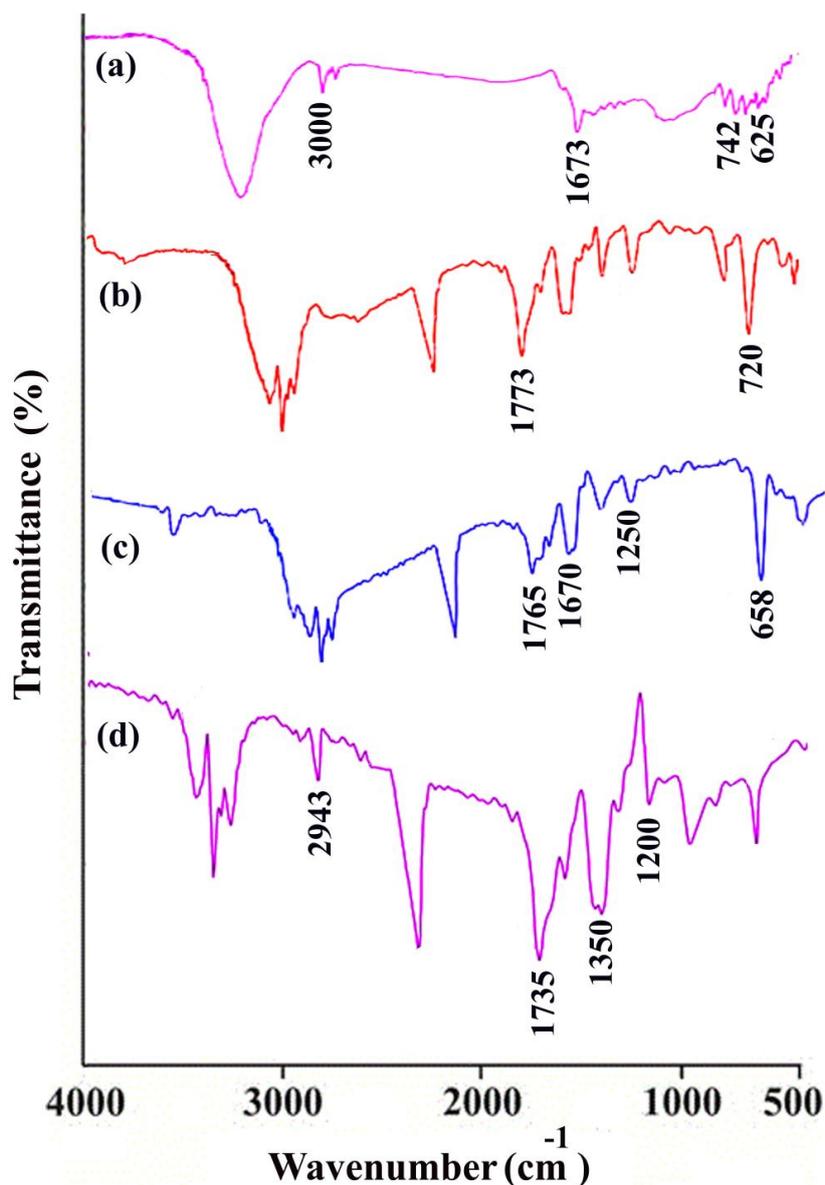Fig. 2. FT-IR spectra of (a) pure MWCNTs and MWCNTs-COOH (b)

Fig. 3. FT-IR spectrum of (a) MWCNTs-CO-NHPh, (b) MWCNTs-CONHPh-NO$_2$,

The absorption band at 1556 cm^{-1} can be related to bending vibration in the amide kind II. The first adsorbent vibration of one-substituted ring observed at 687 cm^{-1} and the second strong peak observed at 745 cm^{-1} that was demonstrated successful attachment of aniline onto MWCNTs. in the spectrum of MWCNTs-CONHPh-NO$_2$ [Fig. 3 b], As can be seen the band severity at 1633 cm^{-1} was decreased and a novel band manifests at 1739 cm^{-1} that is might be due to near of NO$_2$ on the ring. Probably because of NO$_2$ the resonance consequence is decreased. The FT-IR spectrum of

MWCNTs-PDA shows in [Fig. 3c]. Because of the reduction of nitro group in the nitro-MWCNTs to amine group, couple peak severity of nitro group was decreased and these peaks become clear for NH$_2$ at 1371 and 1544 cm^{-1}. The stretching vibration of C-N appears at 1213 cm^{-1}. The peak at 671 cm^{-1} might be is corresponds to N-H. The strong peak that is observed at close 3440 cm^{-1} in entire spectrum, display hydroxyl group in the functionalization of MWCNTs and could be containing N-H stretching in MWCNTs–PDA. According to [(Fig. 3 d], the PDA was reacted
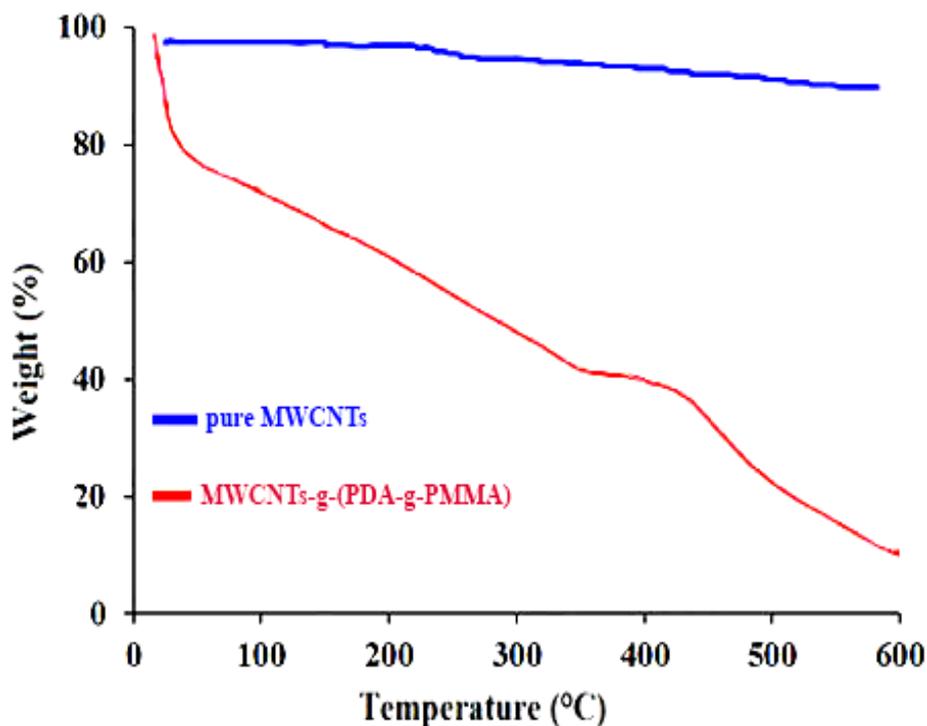
Fig. 4. TGA trace of the pure MWCNTs and MWCNTs-g-(PDA-g-PMMA).

with MMA to obtain MWCNTs–PDA–PMMA in which the near of bands at 1633 cm^{-1} and a twofold between 1230 and 1320 cm^{-1} displayed near of the carboxyl (C=O) attached with amide as well as, N-H bending and C-N stretch vibration of the amide. The spectra of MWCNTs-PDA (not observed) displayed that PMMA was attached onto MWCNTs-PDA derivative as demonstrated by peaks about 1739 cm^{-1} associated with the near of PMMA, respectively.

Thermal properties study

Fig. 4, shows the good thermal particularity of pristine MWCNTs until 400 °C. The connection of functional groups to MWCNTs appears an intense decrease in the thermal particularity as illustrated by the weight loss indicated in TGA curves. From the TGA curve for MWCNTs-g-(PDA-g-PMMA), first weight loss was seen at 100-350 °C which degradation close of 100 °C is due to vaporization of humidity absorbed on the surface of MWCNTs. Weight loss at 160-350 °C can be related to starting of the degradation of head to head well-defined structure of PMMA. Furthermore, this curve shows that PMMA backbone probably degrading nearby 350 °C. Also weight loss nearby

400 °C is in conformation with the degradation of PDA [37, 38]. As can be seen, after the grafting polymerization reactions, the thermal stability of the resulted polymer is reduced.

DSC investigation of the neat MWCNTs and MWCNTs-g-(PDA-g-PMMA) were performed as appeared in Fig. 5. The glass transition is clearly obvious in both specimens. The (T_g) for MWCNTs (140 °C) is higher than the Tg of MWCNTs-g-(PDA-g-PMMA). It was possibly because of the grafted branches, which disordered the order of the chain structures in MWCNTs-g-(PDA-g-PMMA) and increased the spacing between the chains; as a result, the percent crystallization reduced. Therefore, DSC results show that functionalization reduces Tg and thermal properties (Fig. 5).

Morphology analysis

Using AFM and SEM image, investigate the dispersion of samples and also by comparing AFM image before and after graft polymer, the presence of polymer on carbon nanotube can be confirmed. The surface morphologies of the pristine MWCNTs and polymers based on CNTs were seen by means of SEM and AFM as shown in figure 5 and 6, AFM image for pristine MWCNTs [(Fig. 6 a], shows that
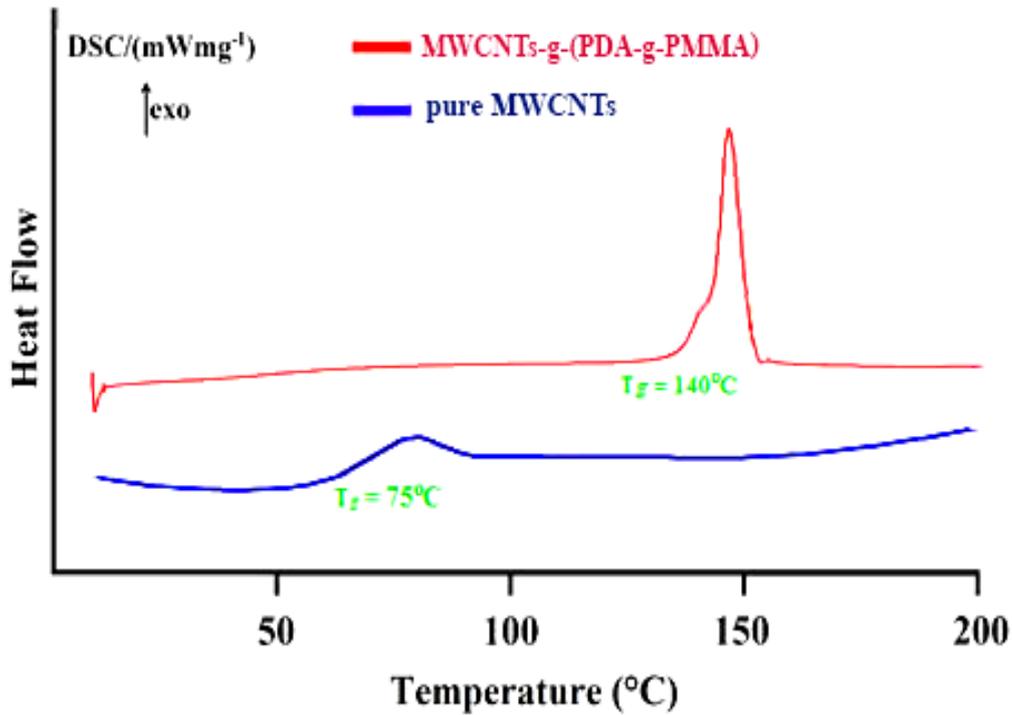
Fig. 5. DSC trace of the pure MWCNTs and MWCNTs-g-(PDA-g-PMMA).

the group of particles with the large amount of particles being small-scale and orbicular. Also, this may have been shortening MWCNTs. AFM image of MWCNTs-g-(PDA-g-PMMA) on bundled up CNTs [(Figs. 6 b and c] shows particles attached to MWCNTs could be PMMA particles (are placed in the form of batches) that successfully was attached into MWCNTs. Some of these particles are band-like, which might be related to the presence of CNTs. This images indicates amount of particles crystalized in the form of spiral that demonstrate particles of PMMA. After PMMA polymerization

on MCNTs, the morphology the surface changed. It is clear from AFM images that the MCNTs surface was covered with PMMA.

The amine derivatives, PDA was grafted onto MWCNTs before grafting of PMMA onto the surface of MWCNTs. It was believed that these amines synthesized would aid in the alignment of MWCNTs. The surface morphologies of pristine MWCNTs and MWCNTs-PDA-PMMA are appeared in Fig. 7, respectively. Size index below the images indicates nano dimensions of synthesized composite. In addition, SEM was applied in order
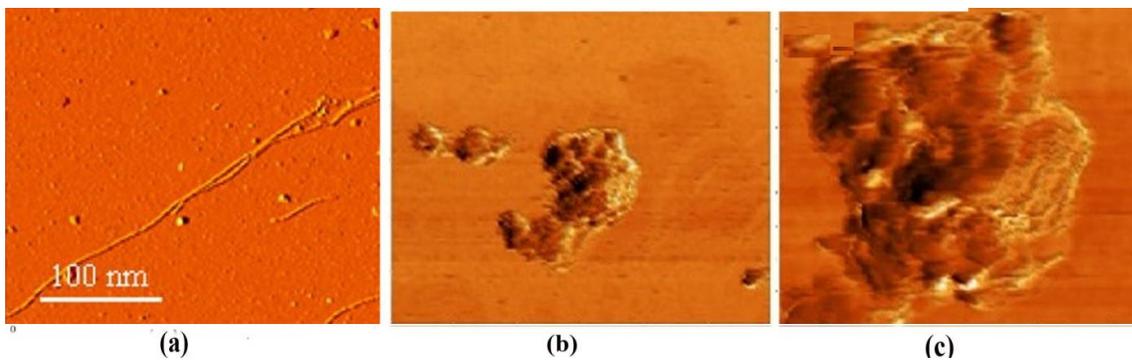

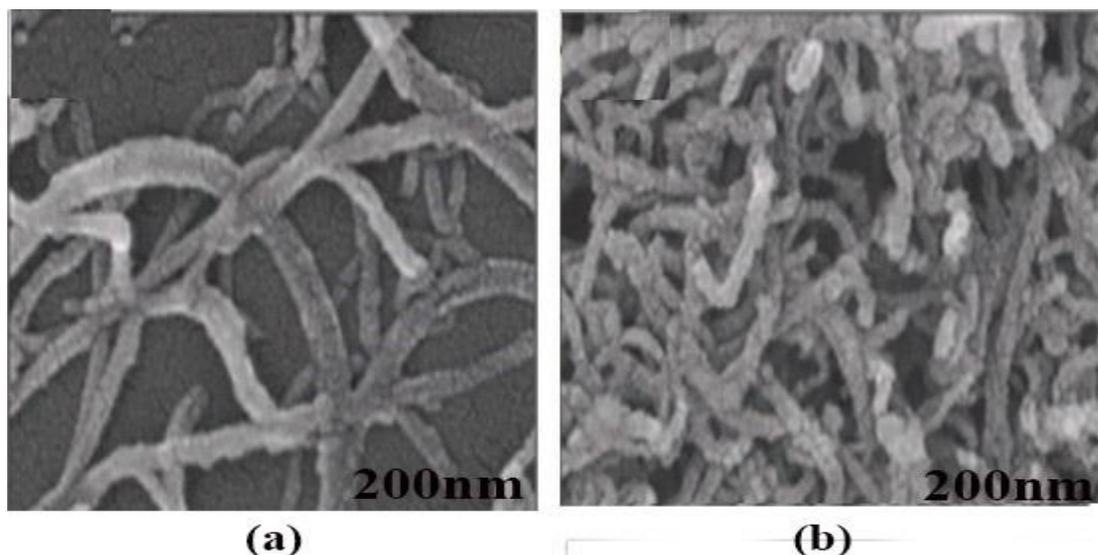Fig. 6. AFM image of (a) pure MWCNTs and (b) MWCNTs-g-(PDA-g-PMMA)

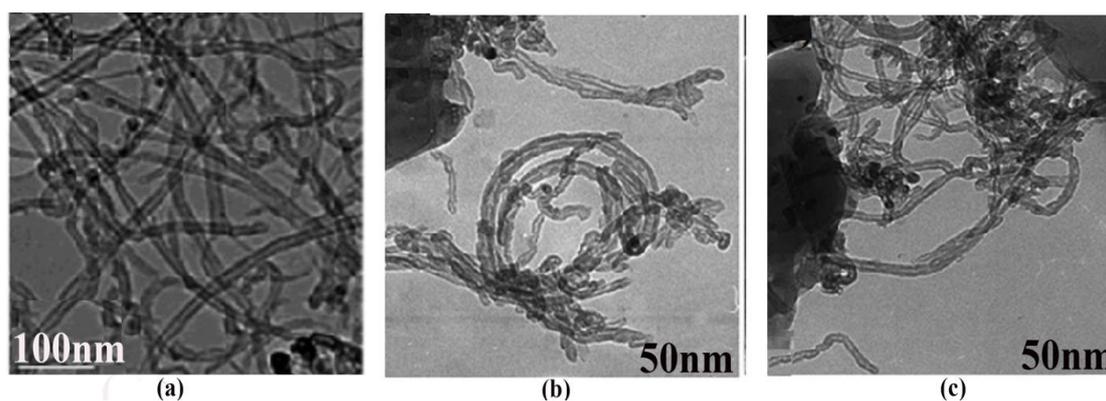Fig. 7. SEM image of (a) pure MWCNTs and (b) MWCNTs-g-(PDA-g-PMMA)

Fig. 8. TEM image of (a) pure MWCNTs and (b) MWCNTs-g-(PDA-g-PMMA)

to evaluate of the structure and morphology of synthesized MWCNTs derivative. SEM image of MWCNTs-g-(PDA-g-PMMA) indicate the high lines bundled on MWCNTs that display attachment of PMMA onto MWCNTs.

TEM characterization of pristine MWCNTs and MWCNTs–PDA–PMMA

It is quite accepted that TEM represents an objective image of the surface morphology of the MWCNTs and polymers based on MWCNTs by oxidation polymerization method. Fig. 8, displays the TEM image of pristine MWCNTs (a) and MWCNTs-g-(PDA-g-PMMA) (b and c), respectively and disclose that the tubes are coated and bundled. The black bumps on the smooth surface of nanotubes indicates that the polymer layer has grown on the nanotubes during the oxidation polymerization process. In so many of areas in each specimen, several CNTs be revealed coated and de-bundled. In the de-bundled areas, MWCNTs-g-(PDA-g-PMMA) derivatives probably have more covering than CNTs–PDA and this was related to the near of PMMA on the CNTs.

CONCLUSION

In conclusion, Synthesis and characterization of MWCNTs-PDA grafted to PMMA was performed successfully. The MWCNTs were functionalized by grafting of PDA and PMMA. The grafted polymers were investigated using FTIR, SEM, AFM and TEM technique. The TGA and FTIR investigations proved

that PDA and PMMA are completely grafted onto MWCNTs. The nanocomposite was higher than pure PMMA in thermal particularity. Synthesize of MWCNTs-g-(PDA-g-PMMA) represented here was fast, facile and cheap. The simplifying and chemical functionalization of method may be an alternative way for carbon nanotubes. However, more investigations requirement to be accomplished in finding the most appropriate functional group and reaction circumstances that will develop dispersion. In addition, the Synthesized MWCNTs-g-(PDA-g-PMMA) has potential as a reinforcement for polymeric (nano-) composites owing to great physicochemical and mechanical features of MWCNTs as well as their compatibility with polymeric materials after functionalization processes.

ACKNOWLEDGMENT

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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