

Preparation and Characterization of Polymer/Multiwall Carbon Nanotube/Nanoparticle Nanocomposites and Preparation of Their Metal Complexes

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ABSTRACT: Carbon nanotube-polymer nanocomposites were synthesized and characterized successfully. In this work, multiwall carbon nanotubes (MWCNT) were opened using $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture and filled by metal nanoparticles such as silver nanoparticles through wet-chemistry method. The oxidized MWCNT were reacted subsequently with thionyl chloride, 1,6-diaminohexane, producing MWNT-amine functionalized. Then the MWCNT containing metal nanoparticles were used as a monomer with different weight percentages in melt polymerization with An and CNCl separately. Furthermore,

the polyamide and polytriazine modified MWCNT were used for the preparation of metal ion complexes such as Fe^{+2} and La^{+3} . The structures and properties of nanocomposites were evaluated by TEM, DSC, TGA, and FT-IR methods. The chelating behavior and sorption capacities of prepared nanocomposites were carried out by using some metal ions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 113–120, 2010

Key words: nanocomposites; carbon nanotube; nanoparticles; metal complex

INTRODUCTION

Recently, many studies are focused on the preparation of polymer/CNT composites because of their unique mechanical, thermal, and electrical properties. The first report of polymer nanocomposites using The multi-walled carbon nanotubes (MWCNT) were by Ajayan et al.¹ In the past decades, the inorganic clay minerals have been widely used for preparation of polymer nanocomposites because of their nanoscale size and intercalation/exfoliation properties.^{2,3} However, the unique structure and properties have also made CNTs' and their derivatives very attractive and potential candidates for nanocomposite materials and other applications such as nanoelectronics, nanolithography, sensors, optical actuators, biomolecular recognition, and biomedical applications including DNA-modification, drug delivery, and gene delivery.^{4–6} Therefore, a number of research groups have focused recently, on the functionalization of CNTs and the modified carbon nanotubes are used to replace clay for the preparation of the polymer/CNTs nanocomposites.^{7–9} Also covalent functionalized CNTs can also provide a

means for engineering nanotube/polymer interface for optimal composite properties. The possibility of modifying carbon nanostructure using various materials such as organic molecules like alcohols, amines,^{10–13} polymers,^{14–17} and metals^{18–20} has opened a wide field of researches. Particularly, the interest is in those nanotubes containing magnetic particles because of their potential applications in the areas, for instance, magnetic recording, nuclear medicine, and environmental protection. Metal nanocomposites and nanoparticles are few examples of nano-size materials, which are made by filling of CNTs (Kim et al.,²¹ Ajayan and Iijima,²² Satishkumar et al.,²³ Cao et al.,²⁴ Nian and Teng,²⁵ Gao et al.,²⁶ Lee et al.,²⁷ Yang et al.,²⁸ Murugesan et al.,²⁹ Adeli et al.³⁰). Clearly, combination of these materials can lead to the novel nanomaterials with new properties. For example, conjugation of polymers on the filled CNTs by metal nanoparticles will lead to novel nanocomposites containing metal nanoparticles/CNTs and polymers. Also, there are few reports about the metal complexes of polymers connected carbon nanotubes.^{31–33} Accordingly, in the present research, we report synthesis and characterization of carbon nanotube-polymer nanocomposites containing silver nanoparticles and investigation of their properties. The resulting polyamide-CNTs and polytriazine-CNTs nanocomposites were used to prepare novel metal ions complexes.

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EXPERIMENTAL

Materials

MWCNT thionyl chloride, sulfuric acid (96%), nitric acid (61%), AgNO₃, ethylenediaminetetraacetic acid (EDTA), 1,6-diaminohexan, cyanuric chloride, ethanolamine, Ni(NO₃)₂ · 6H₂O, Cu(NO₃)₂ · 6H₂O, Cr(NO₃)₂ · 6H₂O, and Co(NO₃)₂ · 6H₂O were purchased from Merck and purified by common methods.

Analytical measurements

FT-IR spectra were measured on a Shimadzu model FT-IR-8101M spectrometer. The thermogravimetric analysis (TGA) was performed using a Dupont 651US. The scan rate of TGA was 10°C/min in air atmosphere. Transmission electron microscopic (TEM) analyses were performed by an Philips 200 electron microscope. A differential scanning calorimeter STA 625 was used to determine phase-transition temperatures at the heating and cooling rates of 10°C/min. The metal absorption capacities of polymer nanocomposites were measured by atomic absorption spectrophotometer AA-3600A shimadzu and UV-Vis shimadzu-120 spectrophotometer at room temperatures in aqueous solution.

Opening of CNTs

The CNTs were opened according to the reported procedures in the literature (Tsang et al., 1994). Briefly, they were milled and dispersed in a 3 : 1 mixture of H₂SO₄ and HNO₃. The mixture was refluxed for 10 h. Then it was cooled, filtered, and washed by water adjusted at pH 5. The opened CNTs were dried at 120°C for 6 h.

Filling of CNTs

About 1 g of the opened CNTs was added to a solution of AgNO₃ in water/ethanol 10/2 v/v. The mixture was then sonicated at room temperature for 30 min, stirred at room temperature again for 72 h and filtered. The product was washed several times by water and dried by vacuum oven at 150°C.

Preparation of CNTs-NH₂

The carboxylic acid groups were converted into the corresponding acylchloride by reaction with SOCl₂ at 70°C for 24 h. Then, the excess SOCl₂ was removed by distillation. The CNTs-COCl was immediately reacted without further purification with 1,6-diaminohexane for 48 h at 120°C. Finally, amine-functionalized CNTs were obtained by repeated filtration and washing.

Preparation of EDTA dianhydride (1)

EDTA (5 g, 17 mmol), pyridine (8 mL) and acetic anhydride (10 mL) were placed in a 100 mL-flask equipped with a condenser and a magnetic stirrer. The reaction was carried out at 70°C for 12 h. The resulting anhydride was filtered off and washed thoroughly with acetic anhydride and dry diethyl ether. The white-cream powder was then dried under vacuum at 40°C (yield 90%).

Synthesis of polyamide (2)

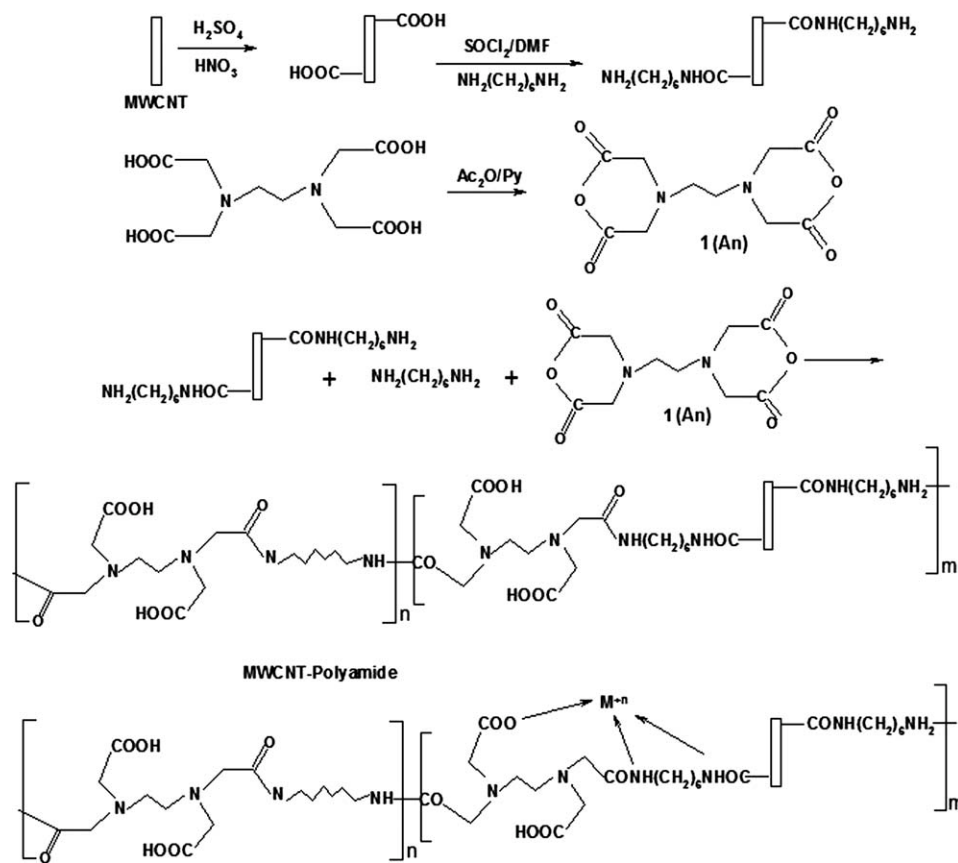
Polyamide was synthesized through the method given in the literature.³⁴ Briefly, 1,6-diaminohexane (0.332 g, 2 mmol) was melted under nitrogen atmosphere in an oil bath at 80°C. To the molten, dry 1 (0.256 g, 2 mmol) was slowly added and the obtained mixture was stirred for 5 h. The product was made in contact with toluene and cold acetone to purification (yield 80%).

Synthesis of polytriazine (3)

Polytriazine was synthesized through similar method was given by Li et al. in the literature.³⁵ Briefly, cyanuric chloride (0.2 mol) and acetone (150 mL) were fed into a 500-mL flask provided with a stirrer, a thermometer, reflux condenser, and a dropping funnel. Both solutions of ethanolamine in acetone and of NaOH in water were simultaneously added dropwise into the flask where and the reaction temperature was kept at 0–5°C. The mixed solution of both 1,6-diaminohexane (0.4 mol) and NaOH (0.8 mol) in water was added to the above reactive system containing Intermediate I. The reaction temperature rose to 40–50°C, and the time was kept at over 10 h. After cooling, the Intermediate II was filtered, washed, and dried. A white powder (yield: 98%) was obtained. The Intermediate II (0.5 mol) and a mixed solution of 1,6-diaminohexane (0.5 mol) and NaOH (0.1 mol) in 200 mL water were added to the reaction solution was kept under reflux for 10 h. After the reaction completion followed by filtration, washing, and drying, a white powder (yield: 87%) was obtained.

Preparation of MWCNT-polyamide nanocomposites containing silver nanoparticles

All kinds of metal complexes of MWCNTs/polymers were prepared in the same way, which was shown in the Schemes 1 and 2. Briefly, to synthesize the nanotube/polyamide and nanotube/polytriazine composites, different wt % of nanotubes (0.05, 0.1, 0.5, and 1 wt %) were carried out using the same procedure, as described for the polyamide and polytriazine synthesis.



Scheme 1 Synthetic route of MWCNT-polyamide nanocomposite.

Preparation of MWCNT-polyamide complex

Quantitative FeSO₄(a)/La(NO₃)(b) was added to a stirred DMF solution of products under an argon atmosphere for 24 h at 80°C. The products were collected by centrifugation, and then the precipitated complexes were washed successively with water and ethanol. The final polymeric complexes were dried under vacuum at 40°C for 24 h.

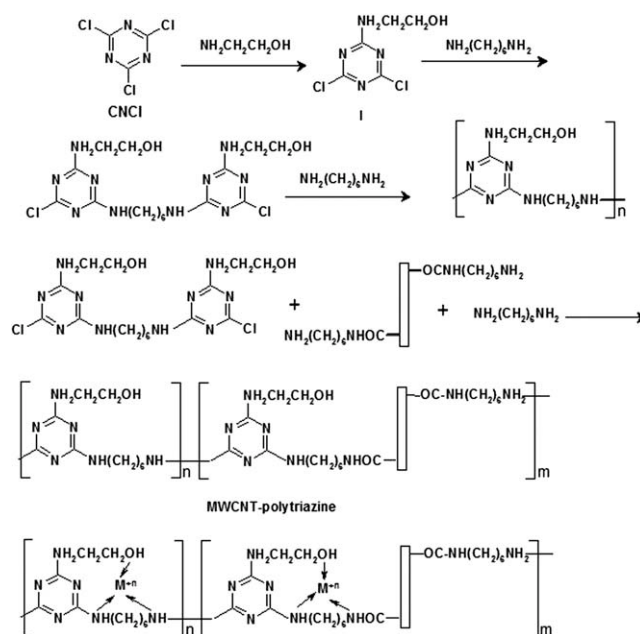
Metal sorption capacity

A solution of 2 mmol metal salt in 10 mL water was added to 200 mg of polymer nanocomposite. The pH of solution was adjusted at 3–5. The mixture was shaken at 30°C for 24 h. The residue concentrations of metal ions were measured by atomic absorption spectrometry.

RESULTS

We report, the synthesis of MWCNT-polymer nanocomposites based on polyamide and polytriazine. The synthetic route leading to MWCNT-polymer nanocomposites structures is outlined in Schemes 1 and 2. Polyamide was prepared from diamine and activated EDTA in the form of dia-

hydride in a one step polyaddition reaction. The dianhydride of EDTA was synthesized according to the method of Tuelue and Geckeler³⁶ at 65–70°C



Scheme 2 Synthetic route of MWCNT-polytriazine nanocomposite.

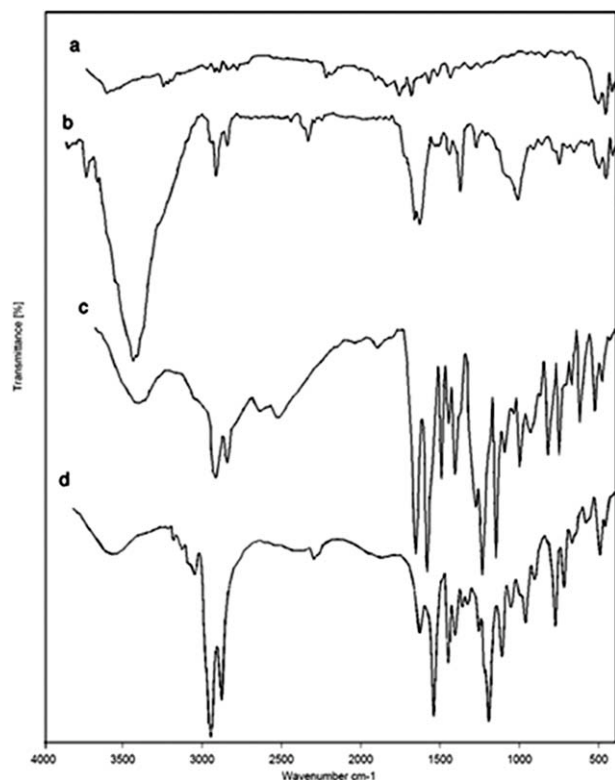


Figure 1 FT-IR spectra of (a) opened MWCNT, (b) functionalized MWCNT-NH₂, (c) MWCNT-polyamide nanocomposite, and (d) Fe-complex nanocomposite.

with about 85% yield (Scheme 1). The polyaddition reactions of dianhydride and hexamethylene diamine were performed in the melt condition (Scheme 1) by the similar method described in the literature.³⁴ Polyamide/MWCNT hybrids were prepared from diamine (1,6-diaminohexane and MWCNT-NH₂ in different weight ratios) and activated EDTA in the form of dianhydride in a one step polyaddition reaction. Polytriazine was synthesized using the similar route reported in the Ref. 35. The reactions of cyanuric chloride a step-wise and selective reaction of three symmetric chlorides in the triazine ring of the modified melamine resins.³⁷ The amine substitutions were carried out at different reaction temperatures and solvents for three individual chlorides in the triazine ring. The results indicated that the reaction temperature is an important parameter in controlling the amine substitution. Under the reaction temperatures of -55°C, the first chloride in the triazine ring was selectively substituted by 1 equivalent of amine to produce a Intermediate I. The substitution at the second equivalent amines on the second chloride occurred at about 25°C. Only at higher temperatures such as 130°C does the chloride in the triazine ring by reaction for the third equivalent of

amine. Polytriazine/MWCNT nanocomposites were prepared by similar manner used for the preparation of polyamide/MWCNT hybrids described in the Scheme 2. For preparation of polyamide/MWCNT/nanoparticle nanocomposites, the MWCNT were opened using sulfuric and nitric acid mixture, consequently converted into the corresponding acylchloride Intermediate, and followed by amidation with the 1,6-diaminohexane under mild conditions. Figure 1 shows the FT-IR spectra of the crude and opened CNTs similar to the findings of Adeli et al.³⁰

The IR spectra of the crude CNTs do not show a distinguishable absorbance band, but in the IR spectra of the opened CNTs the absorbance bands at 3600–3100, 1700, and 1620, 1500 cm⁻¹ are related to the O–H, C=O, and C=C bonds. The –COOH of MWCNT was transformed into acyl chloride functionalities by the reaction of thionyl chlorides (SOCl₂) and the distinctive stretching vibration of –COCl should have been observed. However, the detection of the stretching vibration of –COCl in the FT-IR spectrum (operated in air) is extremely difficult, because the high hydrolytic reactivity of –COCl in air tended to convert them back into carboxylate ions.¹⁴ To form the stronger chemical bonds of NH₂, the MWCNT-COCl reacted with 1,6-diaminohexane to produce MWCNTs-NH₂ and result of FT-IR analysis are shown in Figure 1. The polyaddition reactions of the compound 1, MWCNT-NH₂ and 1,6- diaminohexane in different amounts of MWCNT-NH₂ were performed in the melt system.³⁸

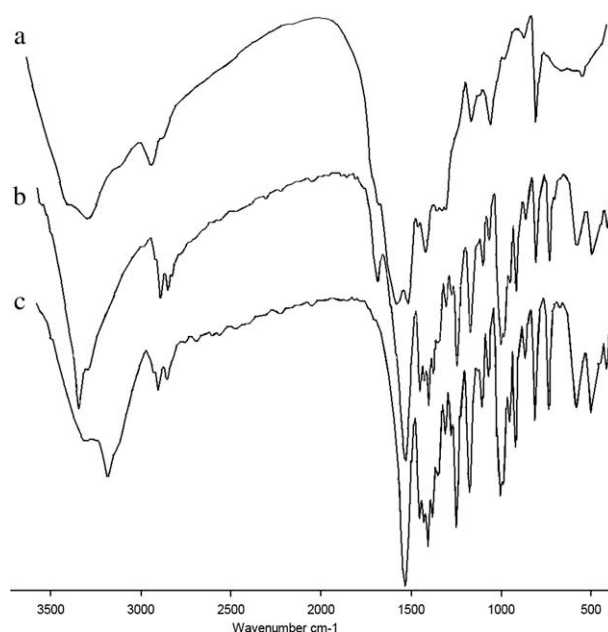


Figure 2 FT-IR spectra of (a) polytriazine, (b) MWCNT-polytriazine nanocomposite, and (c) Fe-complex nanocomposite.

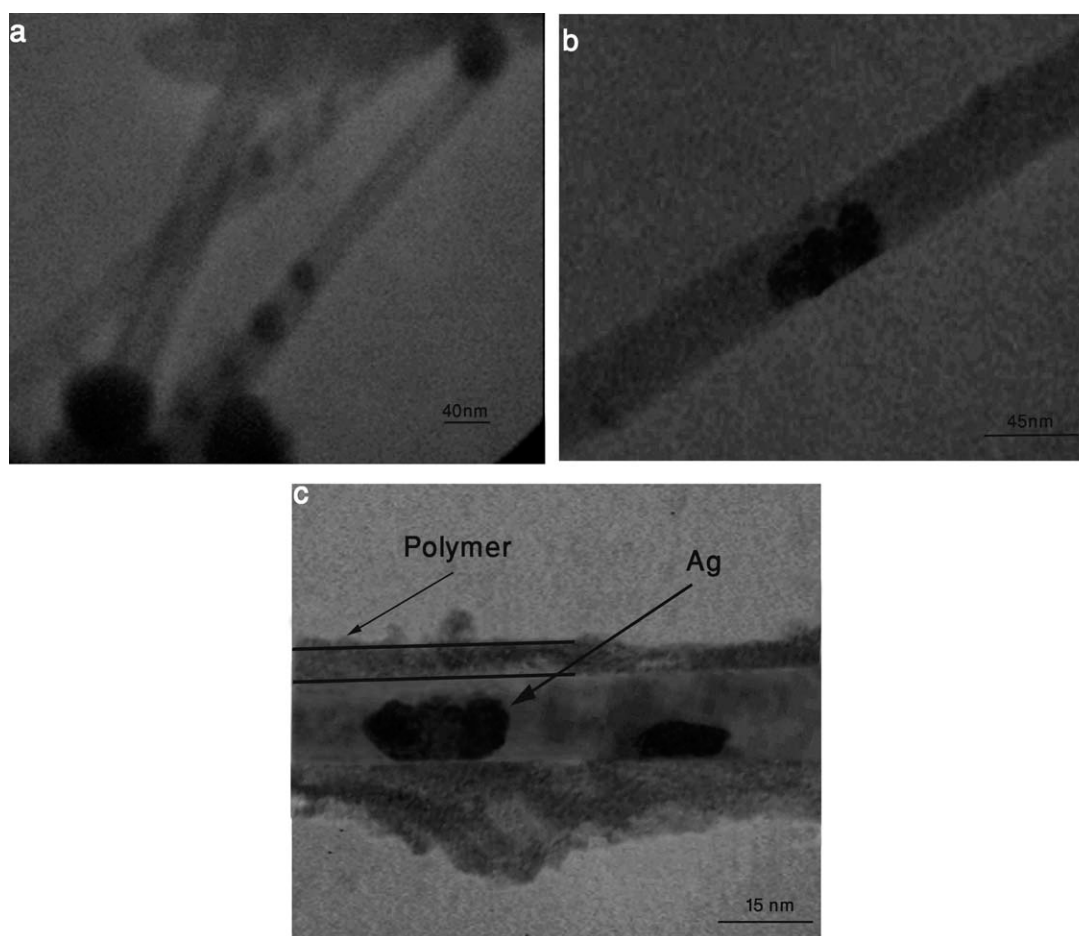


Figure 3 TEM image of (a,b) CNTs filled by silver nanoparticle and (c) MWCNT-polyamide nanocomposite prepared using with 0.05 wt % of CNT.

The formation of amide functionalities in MWCNT-polyamide was evidenced by the presence of 1678 cm^{-1} (C=O stretch of amide carbonyl), 1565 cm^{-1} (stretch of C–N and bend of N–H in the amide) as shown in Figure 1. The absorption band in 1678 cm^{-1} for polyamide nanocomposite corresponds to C=O bonding, after complex formation shift to 1663 and 1668 cm^{-1} for Fe^{+2} and La^{+3} , respectively with the sorption of metal on polymer nanocomposite and the intensity of peak at about 1680 cm^{-1} decreased. A shift was observed for C–N stretching bond from 1565 cm^{-1} in the parent polyamide nanocomposite to 1553 and 1558 in Fe^{+2} and La^{+3} complexes, respectively. Figure 2 shows the FT-IR spectra for the polytriazine/MWCNT nanocomposites and their complexes with the metal ions adsorbed on the surface. Although the overlapping of the N–H and O–H stretching vibrations usually forms a broad band region of about $2941\text{--}3404\text{ cm}^{-1}$ wavenumbers peak shifts from 3404 to 3391 and 3395 cm^{-1} , respectively, were observed when metal ions complexes were formed. The decrease of the wavenumber for the peak indicating the existence of

interactions between the Fe^{+2} and La^{+3} ions with the nitrogen and oxygen atoms in the NH and OH groups. The peaks at a wavenumber of 1597 cm^{-1} were, however, not changed with the complexation of the metal ions, suggesting that the C=N groups in the triazine rings were not involved in the complexation of the metal ions.

The cavity of CNTs in this nanocomposite is empty. It can be used to deliver different materials for different applications. For example, the cavity of CNTs can be filled by metal nanoparticles, which leads to the formation of new nanocomposites containing polymer, CNTs, and metal nanoparticles. For preparation of CNT/polymer containing silver nanoparticles, the CNTs were opened and filled by silver nanoparticles using wet-chemistry method.³⁰ Figure 3(a) shows the TEM image of the CNTs filled by silver nanoparticles. It clearly shows the encapsulated silver nanoparticles in the cavity of the CNTs. The TEM image of the CNTs-polyamide nanocomposite was prepared using 0.05 wt % of CNT is shown in Figure 3(b). Nanocomposites containing polyamide/CNT is of

TABLE I
Sorption Capacity and Sorption Molar Ratio of MWCNT-Polymer Nanocomposite

Polymer complex	Metal sorption capacity (mg/g)				pH	Metal sorption capacity (mmol/g)			
	Cu	Ni	Cr	Co		Cu	Ni	Cr	Co
Polyamide	213.2	117.5	140.1	181.6	5	3.4	2.0	2.7	3.1
	133.4	88.5	78.9	237.3	3	2.1	1.5	1.5	4.0
P-Am-0.01 CNT	214.6	117.3	141.1	243.1	5	3.4	2.0	2.7	4.1
P-Am-0.05 CNT	241.3	126.2	150.3	250.2	5	3.8	2.15	2.9	4.2
P-Am-0.1 CNT	252.3	140.6	164.4	258.3	5	3.9	2.4	3.2	4.4
Polytriazine	82.7	46.6	92.4	66.3	5	1.3	0.79	0.18	7.4
P-Tri-0.01 CNT	88.7	51.7	96.3	72.2	5	1.4	0.89	1.8	1.2
P-Tri-0.05 CNT	97.5	59.9	105.8	79.5	5	1.5	1.0	2.0	1.3
P-Tri-0.1 CNT	108.3	72.6	127.4	91.5	5	1.7	1.2	2.4	1.5

particular interest for the preparation of magnetic particle complexes.

The novel complexes of CNTs/polymer composites was reported by Weilin San.³¹ These complexes exhibit an interesting magnetic behavior. Further, complicated magnetic interaction existed in the system. In addition, the cavity of CNTs in the CNT/nanocomposite is empty, which can be used to deliver different materials. However, polyamides and polytriazine in these nanocomposites bearing EDTA and amine groups in the surface are stable complexes with heavy metal ions. They are useful in separation, recovery, and purification of a wide range of metal ions. The complexation capacity of functional polymer were determined by the relation to pH dependency for Cu^{+2} , Ni^{+2} , Cr^{+2} , and Co^{+2} using atomic absorption method. The findings are shown in Table I.

In all cases by increasing the pH values, the metal sorption capacities of the polymer nanocom-

posites increased. In higher pH values, the protonation of ligand on the polymer backbone (especially, in the amine and oxygen groups) decreased, leading to a higher metal absorption. The maximum metal sorption was observed for Ni, whereas the lowest metal content was observed for Cr. Furthermore, by increasing of the percent of CNTs in polymer nanocomposites, the metal sorption capacities increased.

Thermal properties

To obtain further information, the TGA was performed with $10^\circ\text{C}/\text{min}^{-1}$ in air. Figure 4 shows the TGA diagrams of CNTs-polyamide nanocomposites prepared using 0.01, 0.05, and 0.1 wt % CNTs. In this figure, the onset of decomposition is around 300°C . The rate of decomposition of the nanocomposites

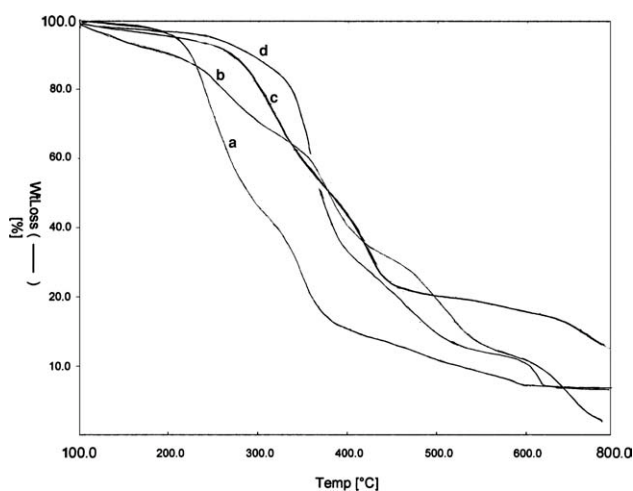


Figure 4 TGA diagrams of (a) polyamide, (b) MWCNT-polyamide nanocomposite prepared using with 0.05 wt % of CNT, (c) 0.1 wt % of CNT, and (d) Fe-complex nanocomposite containing 0.05 wt % of CNT.

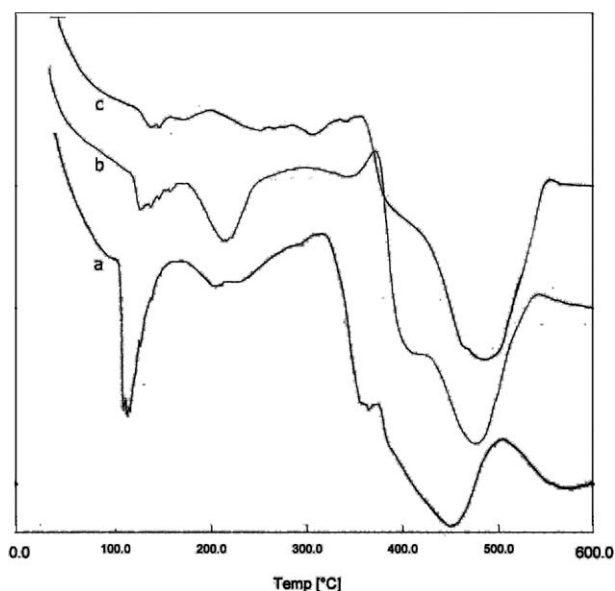


Figure 5 DSC thermograms of (a) linear polyamide (b) MWCNT-polyamide nanocomposite prepared using with 0.05 wt % of CNT, and (c) 0.1 wt % of CNT.

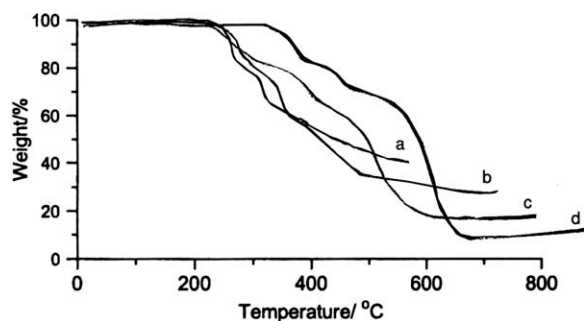


Figure 6 TGA diagrams of (a) polytriazine, (b) MWCNT-polyamide nanocomposite prepared using 0.05 wt % of CNT, and (c) 0.1wt % of CNT.

decreased when the amount of CNTs ratio in the nanocomposites increased.

Accordingly, the thermal stability of the nanocomposites depends on their CNTs percent so that with the increasing of CNT percent of the nanocomposites, their thermal stability rises. Figure 5 shows the DSC thermograms of the linear polyamide and CNT-nanocomposites prepared using 0.01, 0.05, and 0.1 ratios, where all samples show almost the same thermal behaviors.

The same thermal behaviors for the nanocomposites, which are also similar to the thermal behavior of the linear polyamides, show that the role of CNTs in the thermal behavior of nanocomposites is negligible, probably because of the low-weight percent of CNTs, so that their thermal behavior does not affect the nanocomposites thermal behavior. Figure 6 shows the TGA diagrams of the CNTs-polytriazine nanocomposites prepared using 0.01, 0.05, and 0.1 percentage weight of the CNTs and the corresponding thermogravimetric analytical data are given in Table II.

CONCLUSIONS

MWCNT-polymers nanocomposites were synthesized using polyaddition reaction under melt condition. CNTs were opened, functionalized, and filled by silver nanoparticles and the filled CNTs were used as a monomer. The TEM images clearly show the metals in the CNT segments. The synthetic

TABLE II
Thermal Degradation Data by TGA

Sample	T_{initial} (°C)	$T_{1 \text{ peak}}$ (°C)	$T_{2 \text{ peak}}$ (°C)
Polytriazine	275	335	437
P-Tri-0.01 CNT	299	346	473
P-Tri-0.1 CNT	336	374	482
P-Tri-0.05 CNT	346	395	533

MWCNT-polymer nanocomposites were applied to prepare the novel metal complexes. These products have been shown to be effective in metal removal from the diluted and concentrated solutions, allowing for metal recovery. The MWCNT-polymer nanocomposites are promising materials for preparation of nanodevices. For example, the MWCNT-polymer nanocomposite containing Fe nanoparticle, which is a magnetic nanocomposite can be prepared using this procedure.

References

- Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. *Science* 1994, 265, 1212.
- Vaia, R. A.; Ishii, H.; Giannelis, E. P. *Chem Mater* 1993, 5, 1694.
- Okamoto, M.; Morita, S.; Kotaka, T. *Polymer* 2001, 42, 2685.
- Shim, M.; Kam, N. W. S.; Chen, R. J.; Li, Y.; Dai, H. *Nano Lett* 2002, 2, 285.
- An, K. H.; Jeong, S. Y.; Hwang, H. R.; Lee, Y. H. *Adv Mater* 2004, 16, 1005.
- Roy, S.; Vedala, H.; Choi, W. *Nanotechnology* 2006, 17, S14.
- Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *Macromolecules* 2004, 37, 752.
- Fisher, F. T.; Bradshaw, R. D.; Brinson, L. C. *Appl Phys Lett* 2002, 80, 4647.
- Yao, Z.; Braid, N.; Botton, G. A.; Adronov, A. *J Am Chem Soc* 2003, 125, 16015.
- Stanislaus, S. W.; Jeselevich, E.; Wooley, A. T.; Cheung, C. L.; Lieber, C. M. *Nature* 1998, 392, 52.
- Stanislaus, S. W.; Jeselevich, E.; Wooley, A. T.; Lieber, C. M. *J Am Chem Soc* 1998, 120, 8557.
- Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J Am Chem Soc* 2002, 124, 760.
- Lin, Y.; Meziani, M. J.; Sun, Y. P. *J Mater Chem* 2007, 17, 1143.
- Wu, C. S.; Liao, H. T. *Polymer* 2007, 48, 4449.
- Adeli, M.; Bahari, A.; Hekmatara, H. *Nano: Brief Rep Rev* 2008, 3, 37.
- Chen, J.; Liu, H. Y.; Weimer, W. A.; Halls, M. D.; Waldeck, D. H.; Walker, G. C. *J Am Chem Soc* 2002, 124, 9034.
- Geng, H.; Rosen, R.; Zheng, B.; Shimoda, H.; Fleming, L.; Liu, J.; Zhou, O. *Adv Mater* 2002, 14, 1387.
- Lee, R. S.; Kim, H. J.; Fischer, J. E.; Thess, A.; Smalley, R. E. *Nature* 1997, 388, 255.
- Liu, S. W.; Zhu, J. J.; Mastai, Y.; Felner, I.; Gedanken, A. *Chem Mater* 2000, 12, 2205.
- Gao, C.; Vo, G. D.; Jin, Y. Z.; Li, W.; Armes, S. P. *Macromolecules* 2005, 38, 8634.
- Kim, B. M.; Qian, S.; Bau, H. H. *Nano Lett* 2005, 5, 873.
- Ajayan, P. M.; Iijima, S. *Nature* 1993, 361, 333.
- Satishkumar, B. C.; Vogl, E. M.; Govindaraj, A.; Rao, C. N. R. *J Phys D: Appl Phys* 1996, 28, 3173.
- Cao, L.; Chen, H. Z.; Li, H. Y.; Zhou, H. B.; Sun, J. Z.; Zhang, X. B.; Wang, M. *Chem Mater* 2003, 15, 3247.
- Nian, J. N.; Teng, H. *J Phys Chem B* 2006, 110, 4193.
- Gao, C.; Li, W.; Jin, Y. Z.; Kong, H. *Nanotechnology* 2006, 17, 2882.
- Lee, H.; Yoon, S. W.; Kim, E. J.; Park, J. *Nano Lett* 2007, 7, 778.
- Yang, Y.; Wang, X.; Liu, L.; Xie, X.; Yang, Z.; Li, R. K. Y.; Mai, Y. W. *J Phys Chem C* 2007, 111, 11231.

29. Murugesan, S.; Park, T. J.; Yang, H.; Mousa, S.; Linhardt, R. J. *Langmuir* 2006, 22, 3461.
30. Adeli, M.; Sepahvand, R.; Astinchap, B.; Kabiri, R. J. *Nanopart Res* 2008, 10, 1309.
31. He, B.; Sun, W.; Wang, M.; Liu, S.; Shen, Z.. *Mater Chem Phys* 2004, 84, 140.
32. Jiang, L. M.; Sun, W. L.; Weng, J.; Shen, Z.. Q. *Polymer* 2002, 43, 1563.
33. Jiang, L. M.; Sun, W. L.; Weng, J.; Shen, Z.. Q. *Macromol Rapid commun* 2000, 21, 1099.
34. Arsalani, N.; Mousavi, S. Z. *Iran Polym J* 2003, 12, 291.
35. Li, B.; Xu, M. *Polym Degrad Stab* 2006, 91, 1380.
36. Tuelue, M.; Geckeler, K. E. *Polym Int* 1999, 48, 909.
37. Mahler, J.; Rafler, G. *Opt Mater* 1999, 12, 363.
38. Moniruzzaman, M.; Chattopadhyay, J.; Billups, W. E.; Winey, K. I. *Nano Lett* 2007, 7, 1178.