Effect of Electron Beam Irradiation on Thermal and Mechanical Properties of Polyamide Copolymer/Multiwall Carbon Nanotube Composites

CUI Chengwen (崔成文), *CHEN Yuting* (陈禹廷), *ZHANG Yong** (张　勇)

(School of Chemistry and Chemical Engineering; State Key Laboratory of Metal Matrix Composites,
Shanghai Jiao Tong University, Shanghai 200240, China)

Abstract: Ternary polyamide (tPA) copolymer is susceptible to degradation when it is irradiated by electron beam (e-beam), and effective methods to avoid degradation and increase gel content are highly desirable for crosslinking. Carboxylated multiwall carbon nanotube (MWCNT) is modified by hydroxyethyl acrylate (HEA) in this paper and used as a co-agent for the e-beam irradiation crosslinking of tPA copolymer. HEA modified MWCNT can function as an effective co-agent for the e-beam irradiation crosslinking of tPA copolymer to increase the gel content and improve the mechanical properties of tPA copolymer. Under an irradiation of 160 kGy, addition of 2 parts per hundred (phr) HEA modified MWCNT into tPA copolymer can increase the gel content of tPA copolymer from about 20% to 40% (mass ratio) and increase the tensile strength from 45 to 59 MPa. The irradiation also affects the glass transition temperature of tPA copolymer by increasing the gel content. The results show that HEA modified MWCNT can act as a nucleating agent to increase the crystallization temperature, melting temperature and crystallinity of tPA copolymer.

Key words: electron beam (e-beam) irradiation, ternary polyamide (tPA) copolymer, multiwall carbon nanotube (MWCNT), mechanical properties, thermal properties

CLC number: TQ 327.9　　**Document code:** A

0　Introduction

Compared with traditional methods for modification, electron beam (e-beam) irradiation has the advantages of high efficiency and environmental protection, and it can be used for polyamide modification[1-2]. The irradiation of e-beam leads to the crosslinking, degradation, and changed crystallinity of polyamide[3-4]. Among all the members of polyamide family, polyamide 66 was first crosslinked by high energy irradiation[5-6]. Since then, there are many studies on the e-beam irradiation of polyamide, including all kinds of polyamide materials such as fiber, membrane and engineering plastics[7-10]. The irradiation can create free radicals that lead to crosslinking reactions and network structure, but it can also lead to the degradation of polyamide chains. The crystallinity, mechanical properties and thermal properties are significantly affected by the crosslinking and degradation reactions. The modification efficiency of e-beam irradiation also depends on irradiation tempera-

ture and atmosphere[11-13]. An increase in the crosslinking degree of polyamide by e-beam irradiation can improve their mechanical properties and broaden the application, and some chemicals can be used as crosslinking co-agents to promote the irradiation crosslinking of polyamide[14-16].

Carbon nanotube (CNT) has attracted a great attention due to the unique physical, structural, mechanical and electrical properties since its discovery in 1991[17]. CNT can be classified into three groups: single walled carbon nanotube (SWCNT), double walled carbon nanotube (DWCNT) and multiwall carbon nanotube (MWCNT). Research has shown that MWCNT can improve the mechanical, thermal and electrical properties of polyamide[18-19]. The compatibility of CNT can be improved by functionalization[20-22]. The chemically-modified CNT owning good compatibility with polyamide has obvious effects on the mechanical, thermal and electrical properties of polyamide[23-28].

Ternary polyamide (tPA) copolymer can be used as a reinforcing material in thermoplastic elastomers for its excellent mechanical properties, relatively low processing temperature, high modulus, and excellent chemical resistance. Most of the studies on tPA

copolymer focus on improving its thermal and mechanical properties[29-31]. But there are few reports on the modification of tPA copolymer containing CNTs by e-beam irradiation so far. Imam et al.[32-33] investigated the effect of e-beam irradiation on polyamide 6/diamond coated CNT composite fiber. The tensile strength of polyamide 6 has been significantly improved with the addition of diamond coated CNT, but e-beam irradiation has little effect on the improvement of thermal properties of polyamide 6/diamond coated CNT composite fiber.

CNT affects the properties of polyamide, and e-beam irradiation also affects the properties. So a combination of tPA copolymer and CNT would be expected to improve the thermal and mechanical properties of tPA copolymer. Therefore, we prepare 2-hydroxyethyl acrylate (HEA) modified multiwall carbon nanotube (hereinafter referred to as HEA-f-MWCNT), and use it as a crosslinking co-agent for the e-beam irradiation of tPA copolymer. HEA-f-MWCNT has a positive effect on the mechanical and thermal properties of tPA copolymer modified by e-beam irradiation. This study offers a novel approach to the modification of tPA copolymer. With the combination of HEA-f-MWCNT and e-beam irradiation, the gel content of tPA copolymer is increased by an efficient and environmentally friendly approach.

1 Experiment

1.1 Materials and Method

Carboxylated MWCNT is purchased from Nanjing XFNANO Materials Tech Co., Ltd (purity, i.e., mass fraction: above 95%; outside diameter: below 8 nm; inside diameter: 2—5 nm; length: 10—30 μm; carboxyl group mass fraction: 3.86%). A copolymer of polyamide 6, 66 and 1010 (mass fractions, 30%, 30% and 40%, respectively), i.e., tPA copolymer, is produced by Suzhou Kai Lai Chemical Co., Ltd. with a melt flow index of 3.5 g/min (13.5 g/°C) and a melting point of 156 °C. Anhydrous tetrahydrofuran (THF) is obtained from JK Chemical Ltd. Thionyl chloride (SOCl$_2$), triethylamine, HEA, chloroform and anhydrous ethanol are purchased from Aladdin Industrial Corporation. HEA and SOCl$_2$ are distilled before use. The antioxidants of tPA are used as received.

1.2 Synthesis of HEA-f-MWCNT

About 500 mg of carboxylated MWCNT is stirred for 24 h at 70 °C with an excess amount of SOCl$_2$. The suspension is centrifuged at 6 000 r/min, washed with chloroform and subsequently dried under vacuum at 40 °C for 1 h to get modified MWCNT (MWCNT-COCl). MWCNT-COCl is added to 30 mL of THF and ultrasonically dispersed for 10 min. The mixture is added drop by drop to a three-neck flask equipped with 2 mL HEA and 1 mL triethylamine. The three-neck flask is placed in an ice-water bath. Triethylamine is used as acid scavenger. This mixture is stirred for 24 h at 60 °C under nitrogen atmosphere. Then, the resultant mixture is centrifuged at 6 000 r/min, washed with distilled water and dried in vacuum oven at 40 °C for 12 h.

1.3 Fabrication of tPA/HEA-f-MWCNT Nanocomposites

The particles of tPA copolymer are dried at 60 °C in vacuum oven for 8 h, and then mixed with HEA-f-MWCNT and antioxidant at 170 °C for 6 min with a rotor speed of 65 r/min in a rheometer to obtain tPA/HEA-f-MWCNT compounds with different HEA-f-MWCNT contents. The blends through compression molding at 190 °C under 10 MPa for 10 min are fabricated into a sheet with a thickness of 0.2 mm. The sheet is irradiated in one pass by an e-beam accelerator under nitrogen atmosphere. Different doses of e-beam irradiation are chosen to investigate the effects on the properties of tPA/HEA-f-MWCNT.

1.4 Characterization

Thermal stability of modified MWCNT is characterized by thermogravimetry analysis (TGA) under nitrogen atmosphere. The heating process is carried out from room temperature to 900 °C at a rate of 20 °C/min.

The gel content is measured with the method suggested by Sengupta et al[34]. About 0.5 g of each sample, denoted as m_1, is immersed in 85% (volume fraction) formic acid for 72 h at room temperature. After evaporating the solvent, the mass of the undissolved portion, denoted as m_2, is weighed. Therefore, the gel content r_{gel}, i.e., the ratio of m_2 to m_1, can be calculated. Charlesby-Pinner equation is used to calculate the chemical radiation yield of crosslinking and chain scissions[35]:

$$w_{sol} + w_{sol}^{1/2} = q_{s0}/q_{l0} + 1/(q_{l0}UD),$$

where w_{sol} is the sol mass fraction, q_{s0} is the chain scission density per unit dose (kGy^{-1}), q_{l0} is the crosslinking density per unit dose (kGy^{-1}), U is the number-average degree of polymerization of the polymer before irradiation, and D is the radiation dose (kGy). The value of q_{s0}/q_{l0} is the intercept for the experimental curve of $w_{sol} + w_{sol}^{1/2}$ versus $1/D$[35]. Here, G_s is the number of polymer chain scissions per 100 eV energy absorbed, and G_x is the number of polymer crosslink sites per 100 eV energy absorbed, so the relation of G_s/G_x and q_{s0}/q_{l0} can be expressed as[34,36-38]

$$G_s/G_x = 2q_{s0}/q_{l0}.$$

The value of G_s/G_x indicates the crosslinking degree of the polymer. The greater the value of G_s/G_x is, the smaller the crosslinking degree is, and the more severe the degradation of the material is.

Scanning electron microscope (SEM) is used to characterize the change in the cross-section morphology of irradiated tPA/HEA-f-MWCNT composites. Tensile tests of tPA/HEA-f-MWCNT samples are carried out by the ASTM D638M standard with a universal test machine at a crosshead speed of 100 mm/min. The average results of five samples are the final data. Differential scanning calorimetry (DSC) measurements are conducted with a modulated differential scanning calorimeter. All the samples are dried under vacuum, and then about 10 mg is prepared respectively. The samples are heated from −20 to 200 °C, held at 200 °C for 2 min, then cooled down to −20 °C and subsequently reheated to 200 °C. Both the rates of heating and cooling cycles are 10 °C/min. Thermograms are used to investigate the change of thermal properties of irradiated tPA/HEA-f-MWCNT composites.

2　Results and Discussion

2.1　Thermal Stability of MWCNT

Thermal stability of HEA-f-MWCNT is investigated by TGA. As shown in Fig. 1, carboxylated MWCNT has higher stability and lower decomposition below 450 °C than HEA-f-MWCNT. There is a mass loss of nearly 10% at 450—800 °C for carboxylated MWCNT, due to the pyrolysis of carboxyl groups. The decomposition temperature of HEA-f-MWCNT is much lower than that of carboxylated MWCNT. Mass loss observed in HEA-f-MWCNT (about 16%) is higher than that in carboxylated MWCNT (about 10%) at 450—800 °C.
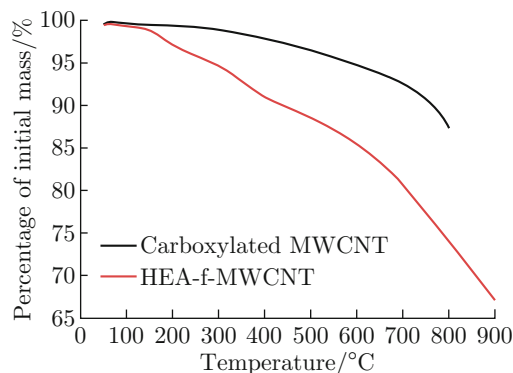

Fig. 1　TGA curves

2.2　Gel Content of tPA/HEA-f-MWCNT Composites

The change in gel content can represent the variation in the crosslinking degree of tPA copolymer and its composites[24]. Here, addition of 2 parts per hundred (phr) HEA-f-MWCNT into tPA copolymer is referred to as tPA/HEA-f-MWCNT(100/2) composite. The relationship between the gel content of tPA/HEA-f-MWCNT composites and the e-beam irradiation dose is shown in Fig. 2. The gel content of
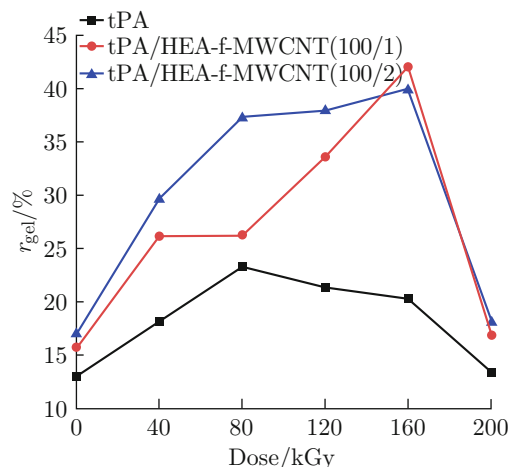

Fig. 2　Gel content as a result of different irradiation doses of tPA copolymer and its composites

tPA copolymer before e-beam irradiation is 13%. It changes slightly with the increase of the irradiation dose, and reaches a maximum of 23% at 80 kGy. After that, the gel content gradually decreases with the increase of the irradiation dose. This phenomenon indicates that e-beam irradiation cannot efficiently initiate crosslinking reaction in the molecular chains of pristine tPA copolymer. However, the gel contents of tPA/HEA-f-MWCNT(100/1, 100/2) composites are higher than that of tPA copolymer. With the increase of the irradiation dose from 80 to 160 kGy, the gel content of tPA/HEA-f-MWCNT(100/2) composite increases gradually, reaches a maximum value of 40% at 160 kGy, and subsequently drops to 16% at 200 kGy. The gel content of tPA/HEA-f-MWCNT (100/1) composite increases sharply to about 43% at 160 kGy, and subsequently, it is similar to that of tPA/HEA-f-MWCNT(100/2) composite. Compared with tPA/HEA-f-MWCNT(100/1) composite, tPA/ HEA-f-MWCNT(100/2) composite gets a higher gel content at a low irradiation dose. Besides, it can be seen from Table 1 that the value of G_s/G_x for tPA copolymer is 3.44, while this value turns to 2.36 for tPA/HEA-f-MWCNT(100/1) composite, and 2.02 for tPA/HEA-f-MWCNT(100/2) composite. As an effective crosslinking co-agent, HEA-f-MWCNT has played a very important role in accelerating the process of crosslinking through the generation of free radicals during irradiation by e-beam. Free radicals can not only promote the crosslinking reactions between the molecular chains, but also cause the degradation of a polymer. The degradation degree is small at a low irradiation dose, and the change of gel content is mainly affected by the crosslinking degree. However, the degradation degree is gradually increased with further increasing the irradiation dose, and thus the gel content is reduced. The effect of HEA-f-MWCNT on the gel content has been removed.

Table 1 Crosslinking degree for tPA copolymer and tPA/HEA-f-MWCNT composites

Material	q_{s0}/q_{10}	G_s/G_x
tPA	1.72	3.44
tPA/HEA-f-MWCNT(100/1)	1.18	2.36
tPA/HEA-f-MWCNT(100/2)	1.01	2.02

2.3 Mechanical Properties of tPA/HEA-f-MWCNT Composites

The results of tensile strength with varying doses of irradiation for tPA copolymer and tPA/HEA-f-MWCNT composites are presented in Fig. 3. It can be clearly observed that the tensile strength of tPA copolymer and its composites exhibits a similar pattern of rise with the increase of the irradiation dose from 0 to 160 kGy, and then decreases until 200 kGy. The change of tensile strength of tPA copolymer is smaller than those of tPA/HEA-f-MWCNT composites. The tensile strength of tPA/HEA-f-MWCNT(100/2) composite irradiated at 160 kGy reaches the maximum which is 59 MPa, while that of tPA copolymer is 45 MPa. It is evident from the results that e-beam irradiation can be used to affect modification in the tensile strength of tPA copolymer. Incorporation of HEA-f-MWCNT leads to further maneuvering of the tensile strength of tPA copolymer[13-14].
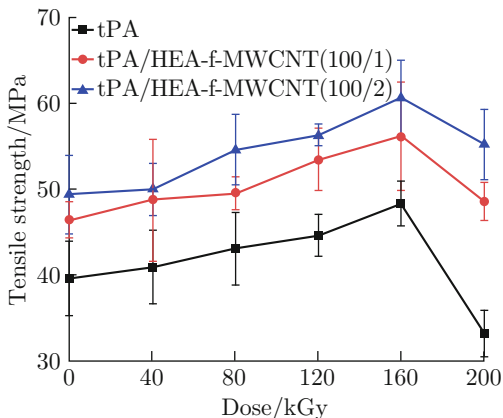

Fig. 3 Tensile strength at different irradiation doses

Elongations at break are shown in Fig. 4. The irradiation dose has a slight effect on the elongation. The elongations of tPA/HEA-f-MWCNT composites are lower than that of tPA copolymer, and they are independent of the irradiation doses.
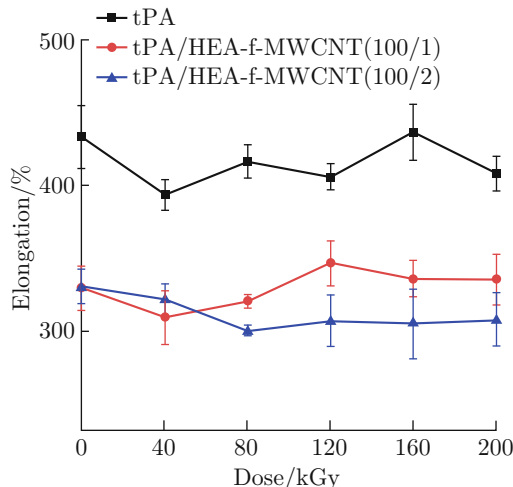

Fig. 4 Elongations at break at different irradiation doses

2.4 Morphology of tPA/HEA-f-MWCNT (100/2) Composite

SEM images for tPA/HEA-f-MWCNT(100/2) composite and tPA copolymer irradiated at 0 and 160 kGy are shown in Figs. 5 and 6. It can be noted that the cross-section morphology of the composite irradiated at 160 kGy (Fig. 5(b)) shows more compact structure than that of non-irradiated tPA/HEA-f-MWCNT composite (Fig. 5(a)). Besides, the lines of the cross-section in Fig. 5(b) are more obvious than those in Fig. 5(a). This difference indicates that the composite irradiated at a proper dose is harder to break than the non-irradiated one. However, the difference of the cross-section morphology between non-irradiated tPA copolymer and tPA copolymer irradiated at 160 kGy is not obvious (Figs. 6(a) and 6(b)). This fact indicates that HEA-f-MWCNT has an effect on the crosslinking of tPA copolymer with e-beam irradiation.
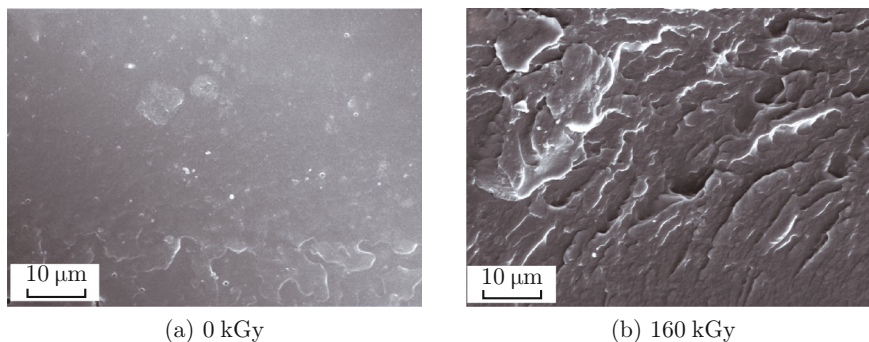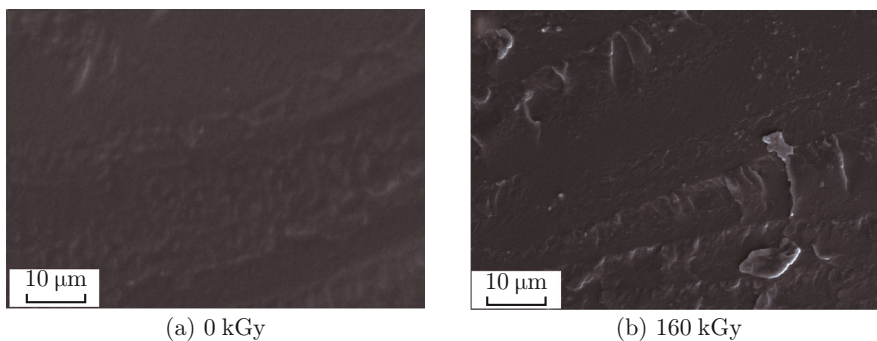

(a) 0 kGy

(b) 160 kGy

Fig. 5 Cross-section morphology of tPA/HEA-f-MWCNT(100/2) composite

(a) 0 kGy

(b) 160 kGy

Fig. 6   Cross-section morphology of tPA copolymer

2.5 Thermal Properties of tPA/HEA-f-MWCNT Composites

The DSC heating and cooling scans are conducted to find out the glass transition temperature (θ_g) and the melting temperature (θ_m) for tPA copolymer and its composites as a function of irradiation dose (Figs. 7 and 8). Figure 7 shows the values of θ_g for tPA copolymer and tPA/HEA-f-MWCNT composites. With the increase of the irradiation dose, θ_g of tPA copolymer changes slightly, but θ_g of the composites changes significantly. With the increase of the irradiation dose from 0 to 160 kGy, θ_g of tPA/HEA-f-MWCNT(100/1) composite increases from 16 to 36 °C, and drops to 32 °C at 200 kGy. The decrease of θ_g can be explained by the formation of degradation. Similarly, θ_g of tPA/HEA-f-MWCNT(100/2) composite reaches the maximum at 160 kGy and decreases with further increasing the irradiation dose. It has been known from Fig. 2 that the gel content of tPA/HEA-f-MWCNT composites increases significantly with the increase of the irradiation dose from 0 to 160 kGy. With e-beam irradiation, the free radicals are formed on the polyamide molecule chain, the olefinic bonds of vinyl groups and other covalent bonds in HEA-f-MWCNT are also broken to form free radicals, and then coupling reaction occurs between the active chains to form network structure. With the formation of the crosslinked structure, the motion of polymer chain segments is impeded, so θ_g shifts to higher temperature.

Figure 8 shows the values of θ_m for tPA copolymer and tPA/HEA-f-MWCNT composites. Compared with the change of θ_g induced by irradiation, e-beam irradiation has a limited effect on θ_m. With the increase of the irradiation dose, θ_m of tPA copolymer decreases. However, θ_m of tPA/HEA-f-MWCNT composites is improved slightly as compared with tPA copolymer, and it is almost unchanged with the increase of the irradiation dose.

The effect of HEA-f-MWCNT on the crystallization behavior of tPA copolymer is investigated. In Fig. 9, tPA/HEA-f-MWCNT composites have higher crystallization peaks than tPA copolymer, i.e., addition of HEA-f-MWCNT results in a rise of crys-
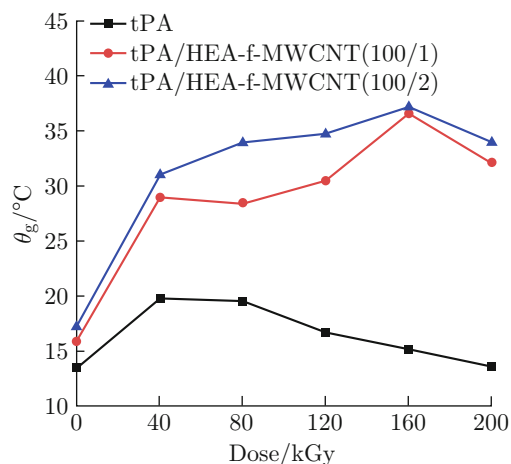

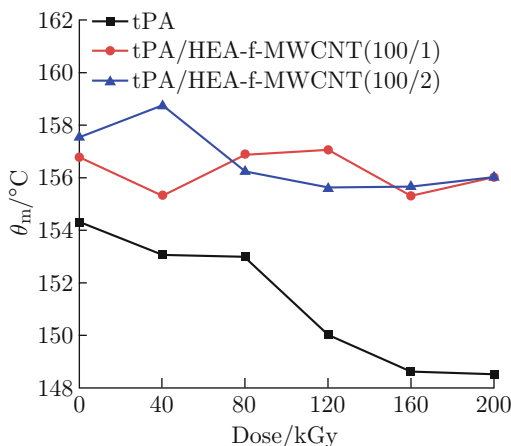Fig. 7   Glass transition temperatures of tPA copolymer and its composites

Fig. 8   Melting temperatures of tPA copolymer and its composites

tallization temperature (θ_c) of tPA copolymer, indicating that HEA-f-MWCNT is an effective heterogeneous nucleating agent for tPA copolymer[25]. Besides, tPA/HEA-f-MWCNT(100/2) composite has higher θ_c than tPA/HEA-f-MWCNT(100/1) composite. The crystallization peak of tPA copolymer is sharper than the crystallization peaks of the composites,

indicating that HEA-f-MWCNT influences the perfection of crystallization[25]. It can be seen from Fig. 10 that θ_c of tPA/HEA-f-MWCNT(100/2) composite decreases with the increase of the irradiation dose. The crystalline region may become slightly impaired due to branching and crosslinking at the interface, which might be a reason for the diminished crystallinity of the composite[7].
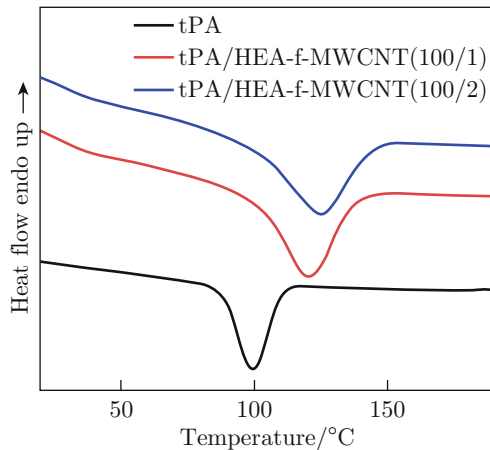

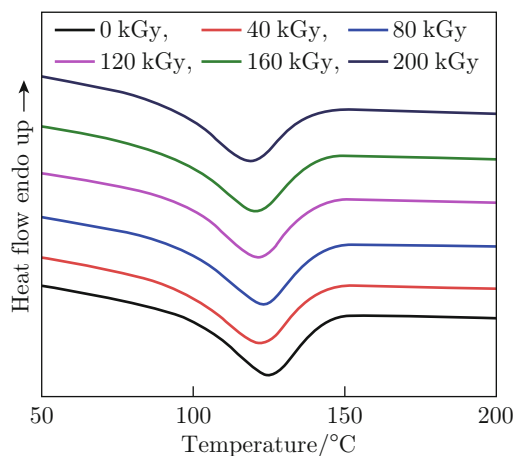Fig. 9   DSC curves of crystallization without e-beam irradiation

Fig. 10   DSC curves of crystallization of tPA/HEA-f-MWCNT(100/2) composite at different irradiation doses

3   Conclusion

Carboxylated MWCNT is successfully modified by HEA and used as an effective crosslinking co-agent for the irradiation crosslinking of tPA copolymer. The irradiation can promote the crosslinking degree of tPA/HEA-f-MWCNT composites. The composites have higher gel contents and better mechanical properties than tPA with e-beam irradiation. The composite of tPA/HEA-f-MWCNT(100/2) has high tensile strength

at 120 and 160 kGy, corresponding to high glass transition temperature. Crystallization behavior analyses reveal that a small amount of HEA-f-MWNT can act as a nucleating agent for tPA copolymer, leading to high crystallization temperature for tPA copolymer. With the help of e-beam irradiation and using HEA-f-MWCNT as a crosslinking co-agent, tPA copolymer is expected to be modified so as to broaden its application.

References

[1] CHMIELEWSKI A G, HAJI-SAEID M. Radiation technologies: Past, present and future [J]. *Radiation Physics and Chemistry*, 2004, **71**(1/2): 17-21.

[2] PRAMANIK N K, HALDAR R S, BHARDWAJ Y K, et al. Radiation processing of nylon 6 by e-beam for improved properties and performance [J]. *Radiation Physics and Chemistry*, 2009, **78**(3): 199-205.

[3] VALENTINE L. Interaction of polyamides with solvents. I. A preliminary survey of the swelling of crosslinked nylon 66 in various types of solvents [J]. *Journal of Polymer Science, Part A*, 1957, **23**(103): 297-314.

[4] LUGÃO A B, HUTZLER B, OJEDA T, et al. Reaction mechanism and rheological properties of polypropylene irradiated under various atmospheres [J]. *Radiation Physics and Chemistry*, 2000, **57**(3/4/5/6): 389-392.

[5] CHARLESBY A. Effect of high-energy radiation on long-chain polymers [J]. *Nature*, 1953, **171**(4343): 167.

[6] LAWTON E J, BUECHE A M, BALWIT J S. Irradiation of polymers by high-energy electrons [J]. *Nature*, 1953, **172**(4367): 76-77.

[7] DADBIN S, FROUNCHI M, GOUDARZI D. Electron beam induced crosslinking of nylon 6 with and without the presence of TAC [J]. *Polymer Degradation and Stability*, 2005, **89**(3): 436-441.

[8] SHIN B Y, KIM J H. Rheological and mechanical properties of polyamide 6 modified by electron-beam initiated mediation process [J]. *Radiation Physics and Chemistry*, 2015, **112**: 88-96.

[9] LEO C P, LINGGAWATI A, MOHAMMAD A W, et al. Effects of γ-aminopropyltriethoxylsilane on morphological characteristics of hybrid nylon-66-based membranes before electron beam irradiation [J]. *Journal of Applied Polymer Science*, 2011, **122**(5): 3339-3350.

[10] HUANG H, ZHANG X Y, LU H B. The chain segment motion and traps in γ-irradiation crystalline nylon 1010 [J]. *Journal of Macromolecular Science, Part B*, 2007, **46**(6): 1105-1114.

[11] BURILLO G, ADEM E, MUÑOZ E, et al. Electron beam irradiated polyamide-6 at different temperatures [J]. *Radiation Physics and Chemistry*, 2013, **84**(3): 140-144.

[12] ADEM E, BURILLO G, CASTILLO L F D, et al. Polyamide-6: The effects on mechanical and physicochemical properties by electron beam irradiation

at different temperatures [J]. *Radiation Physics and Chemistry*, 2014, **97**(2): 165-171.

[13] BERNSTEIN B S, ODIAN G, ORBAN G, et al. Radiation crosslinking of nylon 66 and poly(vinyl alcohol) [J]. *Journal of Polymer Science, Part A*, 1965, **3**(10): 3405-3412.

[14] PRAMANIK N K, HALDAR R, NIYOGI U K, et al. Effect of electron beam irradiation on the kinetics of non-isothermal crystallization of nylon 66 [J]. *Journal of Macromolecular Science, Part A*, 2014, **51**(4): 296-307.

[15] PRAMANIK N K, HALDAR R S, BHARDWAJ Y K, et al. Radiation processing of nylon 6 by e-beam for improved properties and performance [J]. *Radiation Physics and Chemistry*, 2009, **78**(3): 199-205.

[16] PRAMANIK N K, HALDAR R S, BHARDWAJ Y K, et al. Modification of nylon 66 by electron beam irradiation for improved properties and superior performances [J]. *Journal of Applied Polymer Science*, 2011, **122**(1): 193-202.

[17] IIJIMA S. Helical microtubules of graphitic carbon [J]. *Nature*, 1991, **354**(6348): 56-58.

[18] SHEN Z Q, BATEMAN S, WU D Y, et al. The effects of carbon nanotubes on mechanical and thermal properties of woven glass fibre reinforced polyamide-6 nanocomposites [J]. *Composites Science and Technology*, 2009, **69**(2): 239-244.

[19] CHIU F C, KAO G F. Polyamide 46/multi-walled carbon nanotube nanocomposites with enhanced thermal, electrical, and mechanical properties [J]. *Composites, Part A*, 2012, **43**(1): 208-218.

[20] LIU J, RINZLER A G, DAI H J, et al. Fullerene pipes [J]. *Science*, 1998, **280**(5367): 1253-1256.

[21] AJAYAN P M. Nanotubes from carbon. [J]. *Chemical Reviews*, 1999, **99**(7): 1787-1800.

[22] BIANCO A, PRATO M. Can carbon nanotubes be considered useful tools for biological applications? [J]. *Advanced Materials*, 2003, **15**(20): 1765-1768.

[23] ZHANG W D, SHEN L, PHANG I Y, et al. Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding [J]. *Macromolecules*, 2004, **37**(2): 256-259.

[24] ZHAO C G, HU G J, JUSTICE R, et al. Synthesis and characterization of multi-walled carbon nanotubes reinforced polyamide 6 via in situ polymerization [J]. *Polymer*, 2005, **46**(14): 5125-5132.

[25] MENG H, SUI G X, FANG P F, et al. Effects of acid- and diamine-modified MWNTs on the mechanical properties and crystallization behavior of polyamide 6 [J]. *Polymer*, 2008, **49**(2): 610-620.

[26] LIU H M, WANG X, FANG P F, et al. Functionalization of multi-walled carbon nanotubes grafted with self-generated functional groups and their polyamide 6 composites [J]. *Carbon*, 2010, **48**(3): 721-729.

[27] GHARIB-ZAHEDI M R, TAFAZZOLI M, BÖHM M C, et al. Interfacial thermal transport and structural preferences in carbon nanotube-polyamide-6, 6

nanocomposites: How important are chemical functionalization effects? [J]. *Physical Chemistry Chemical Physics*, 2015, **17**(22): 14502-14512.

[28] KAYNAK C, SANKAL S. Effects of oxidative functionalization and aminosilanization of carbon nanotubes on the mechanical and thermal properties of polyamide 6 nanocomposites [J]. *Journal of Thermoplastic Composite Materials*, 2015, **28**(9): 1321-1333.

[29] NASEF M M, SAIDI H, DAHLAN K Z M. Preparation of composite polymer electrolytes by electron beam-induced grafting: Proton- and lithium ion-conducting membranes [J]. *Nuclear Instruments and Methods in Physics Research B*, 2007, **265**(1): 168-172.

[30] LIU F, DU C H, ZHU B K, et al. Surface immobilization of polymer brushes onto porous poly(vinylidene fluoride) membrane by electron beam to improve the hydrophilicity and fouling resistance [J]. *Polymer*, 2007, **48**(10): 2910-2918.

[31] KIM H, ABDALA A A, MACOSKO C W. Graphene/polymer nanocomposites [J]. *Macromolecules*, 2010, **43**(16): 6515-6530.

[32] IMAM M A, GOMES M G, MOURA E A B, et al. Effect of electron-beam irradiation on nylon- 6/diamond coated CNTs composite fiber [C]//*Proceedings of SAMPE Tech 2013 Conference and Exhibition*. Wichita, USA: Society for the Advancement of Material and Process Engineering, 2013: 1-10.

[33] IMAM M A, JEELANI S, RANGARI V K, et al. Electron-beam irradiation effect on thermal and mechanical properties of nylon-6 nanocomposite fibers infused with diamond and diamond coated carbon nanotubes [J]. *International Journal of Nanoscience*, 2016, **15**(1/2): 1650004.

[34] SENGUPTA R, SABHARWAL S, TIKKU V K, et al. Effect of ambient-temperature and high-temperature electron-beam radiation on the structural, thermal, mechanical, and dynamic mechanical properties of injection-molded polyamide-6, 6 [J]. *Journal of Applied Polymer Science*, 2006, **99**(4): 1633-1644.

[35] CHARLESBY A, PINNER S H. Analysis of the solubility behaviour of irradiated polyethylene and other polymers [J]. *Proceedings of the Royal Society A*, 1959, **249**(1258): 367-386.

[36] SENGUPTA R, TIKKU V K, SOMANI A K, et al. Electron beam irradiated polyamide-6, 6 films. I. Characterization by wide angle X-ray scattering and infrared spectroscopy [J]. *Radiation Physics and Chemistry*, 2005, **72**(5): 625-633.

[37] KUMAR N A, GANAPATHY H S, KIM J S, et al. Preparation of poly 2-hydroxyethyl methacrylate functionalized carbon nanotubes as novel biomaterial nanocomposites [J]. *European Polymer Journal*, 2008, **44**(3): 579-586.

[38] SREENIVASAN K. An aqueous process to graft 2-hydroxyl ethyl methacrylate onto polyvinyl chloride through its functional group [J]. *Journal of Applied Polymer Science*, 2015, **74**(1): 113-118.