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A DSC study of effect of carbon nanotubes on crystallisation behaviour of poly(ethylene oxide)

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Abstract

Crystallisation behaviour of poly(ethylene oxide) (PEO)/multi-walled carbon nanotubes (MWCNT) and PEO/chemically modified MWCNT nanocomposites were investigated by means of differential scanning calorimetry. Non-isothermal crystallisation experiments showed that incorporation of MWCNT and chemically modified MWCNT reduced the crystallinity and restricted the spherical crystal growth of PEO. The nucleation sites decrease and spherical crystal size increased compared to the neat PEO. Change of crystal structure from spherical to disk-like was revealed by Avrami equation when MWCNT was added up to 1 wt.%.

Keywords: Poly(ethylene oxide); Carbon nanotube; Crystallisation; Nanocomposite; DSC

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1. Introduction

Since Ajayan et al. first reported a polymer/carbon nanotubes (CNTs) composite in 1994 [1], it has been considered an up-to-date frontier research topic in the field of material science. Extensive research and developments have been devoted to the use of CNTs as nano-fillers to produce a variety of high-performance polymer nanocomposites for targeted applications. These include poly(methyl methacrylate) [2,3], polystyrene [4–6], epoxy [7–10], polypropylene [11–13], nylon [14,15], polyurethane [16], etc. CNTs as reinforcing fibres for composites can improve the performance of a matrix or achieve new properties [17,18], because of their extraordinary mechanical strength, electrical and thermal conductivity, and thermal stability [19,20]. One of important factors for an effective enhancement of composite properties is that CNTs have large surface area that can induce a better adhesion with polymer matrix. Compared to conventional carbon fibre or glass fibre, carbon-nanotube filled polymer composites are easily processed due to its small diameter. Among the most versatile polymers, CNTs provide great opportunities for designing new multi-functional materials with broad industry applications.

However, numerous investigations demonstrate that the mechanical and thermal properties for some polymer/CNTs systems were only slightly improved. It is known that some inorganic fillers such as glass fibres, clay, carbon black, etc., which are incorporated into polymer matrix, usually act as nucleation agents to accelerate crystallisation [21,22]. Therefore, the crystallisation behaviour of a semi-crystalline polymer as function of processing conditions are important in preparing CNT nanocomposites, which should be strongly influenced by CNTs. Recently, the effects of CNTs on polymer crystallisation behaviour have been reported. Kim et al. showed that the incorporation of multi-walled carbon nanotubes (MWCNT) in poly(ethylene 2,6-naphalate) accelerates nucleation and spherical crystal growth, and this effect is more pronounced at lower MWCNT content [23]. The MWCNT in the poly(ethylene 2,6-naphalate) nanocomposites exhibits much higher nucleation activity than any nano-scaled reinforcement. Winey and co-workers demonstrate similar effects with single walled carbon nanotubes (SWCNT) in polyethylene [24]. The results interpreted that the nanotubes provide nucleation sites to polyethylene and accelerate the spherulite growth rate of the polyethylene while reducing the crystal dimensionality from spherulite to disk-shaped. Grady et al. studied polyvinyl alcohol (PVA)/SWCNT nanocomposites [25]. Their results demonstrate that the effect of nucleation crystallisation depended on the presence of weight fraction of SWCNT, and as SWCNT content was higher (1%)

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the crystallinity did not change. The crystallisation behaviour of polypropylene composites reinforced by SWCNTs was investigated by Kenny and co-workers [26]. The results illustrated that no significant change in the crystallinity of polypropylene was found. More recently, poly(ethylene oxide) (PEO)/MWCNT nanocomposites have been prepared in our research group. Our results show that crystallisation behaviour of PEO in PEO/MWCNT nanocomposites was quite different from that in other polymer/CNTs systems. The crystallisation process was influenced by MWCNT, which led to a decrease in the spherical crystal growth and increase in spherical crystal size. Our conclusion is that MWCNTs did not act as a nucleation agent for PEO.

PEO/MWCNT nanocomposites have been subjected as potential optical materials because they possess strong nonlinear optical properties [27]. Such materials have potential applications in the protection of optical sensors from high-intensity beams. However, crystallisation kinetics is significantly important for determining the optical-limiting properties of PEO/MWCNT composites. These motivated us to study the crystallisation behaviour of PEO in PEO/CNT nanocomposites and to understand why incorporation of MWCNT in semi-crystalline PEO lead to different crystallisation behaviour compared to other semi-crystalline polymers. In this paper three kinds of MWCNTs: pure MWCNT, chemically modified MWCNTs with carboxylic functional groups (MWCNT–COOH) and chemically modified MWCNTs with hydroxyl functional groups (MWCNT–OH), were chosen to produce PEO/CNTs nanocomposites.

2. Experimental

2.1. Materials and sample preparation

Poly(ethylene oxide) with a molecular weight, M_n, of 20,000 g/mole was purchase from BDH Laboratory Supplies. The carbon nanotubes used were multi-walled carbon nanotubes (MWCNTs), and chemical modified MWCNTs–COOH (∼3.5 wt.%) and MWCNT–OH (∼3.5 wt.%), which were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. The diameter of the nanotubes is at about 8–15 nm.

Prior to preparation of nanocomposites, PEO was dried in a vacuum oven for 24 h at 40 °C. First CNTs were dispersed in deionised water by utrasonication for 30 min using a sonic Dismembrator (Fisher Scientific, 20 kHz). Dispersions with 0.1, 0.5 and 1 mg/ml were prepared. Solubilized CNTs were then added to 5% PEO aqueous solutions. The PEO and MWCNT

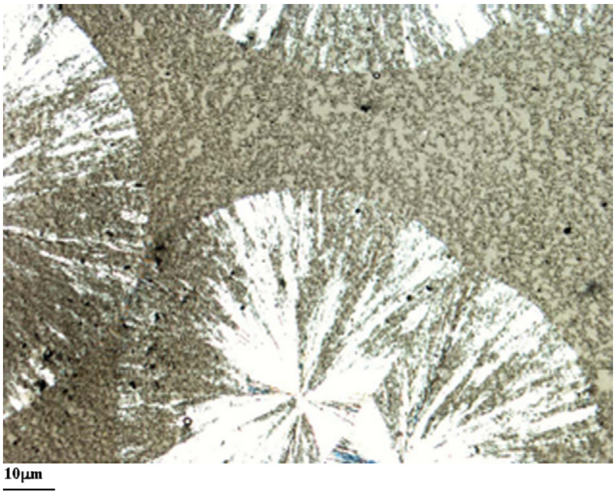

Fig. 1. An optical microscopy image of PEO/MWCNT (1 wt.%).

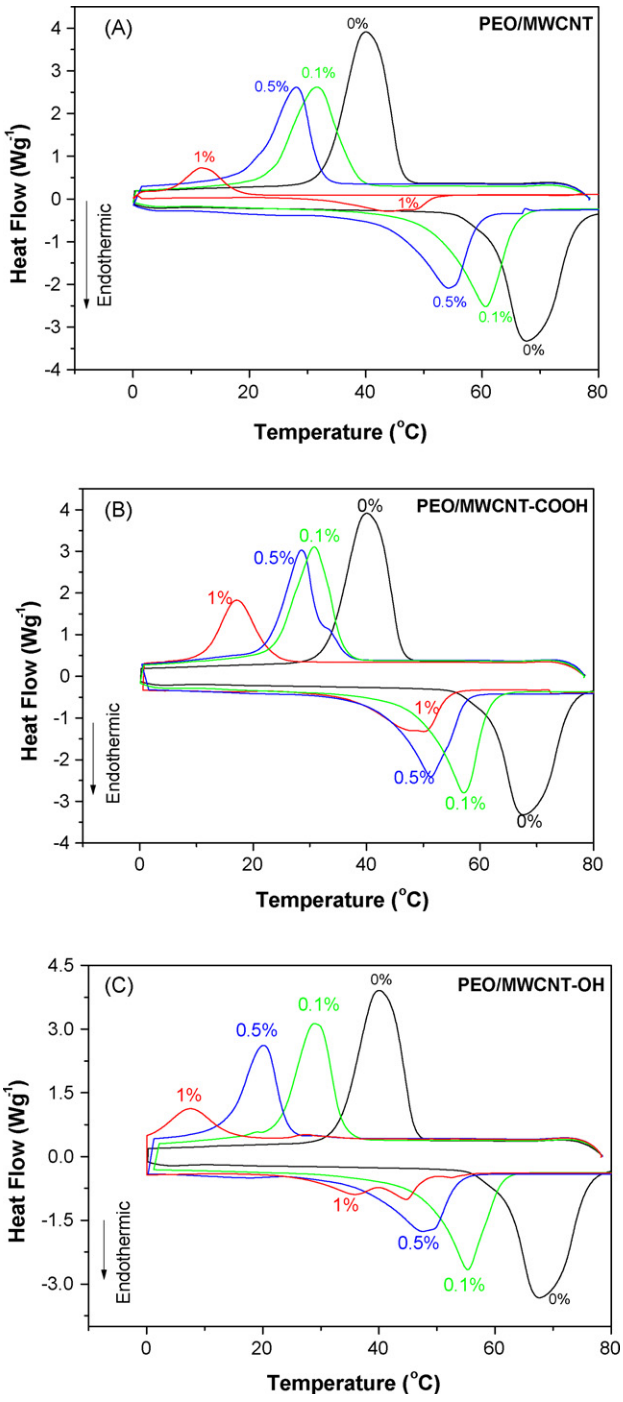

Fig. 2. DSC thermograms for (A) PEO/MWCNT, (B) PEO/MWCNT–COOH and (C) PEO/MWCNT–OH composites.

mixed solutions at different weight percentage ratios (99.9/0.1 by weight, 99.5/0.5 or 99/1) were stirred for 48 h at room temperature after utrasonication for 10 min. Well-mixed solutions were then cast onto a glass plate, evaporated in an oven at 40 °C and dried to constant weight.

2.2. *Characterisation*

Crystallisation analysis was performed using a TA Instrument DSC 2920 differential scanning calorimetry (DSC) under both non-isothermal and isothermal conditions. Heating rate was 10 °C/min for non-isothermal experiments, in which the sample was melt at 80 °C for 10 min. For isothermal experiment, the sample was melt at 80 °C for 10 min, and then quenched to that temperature for isothermal crystallisation. N_2 gas at 50 ml/min was used in the DSC experiment.

The crystalline morphology was observed using an optical polarizing microscope. Samples were melted and squeezed between a microscope cover glass at 60 °C for 10 min and then quenched to room temperature (20 °C). Fig. 1 shows an optical microscopy image of PEO/MWCNT (2 wt.%). This image shows that there are no big clusters of MWCNTs formed in PEO matrix.

Fourier Transform Infrared Spectroscopy (FT-IR) was employed to study molecular interactions between PEO and CNTs. The transmission spectra of the samples were recorded using a Mattson 3000 FT-IR spectrometer for 64 scans at a resolution of 4 cm^{-1}.

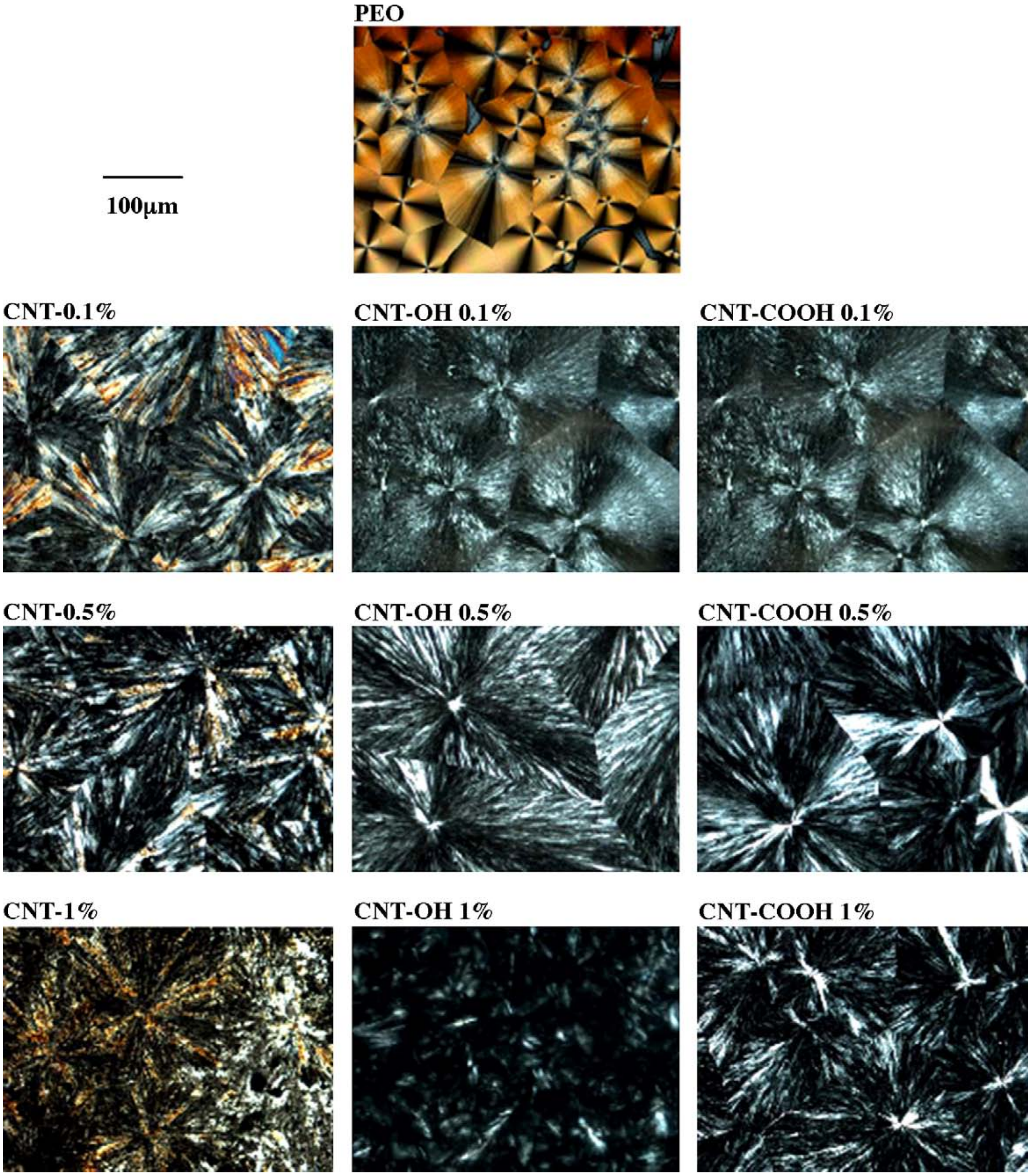

Fig. 3. Polarized optical microscopy images of PEO and its nanocomposites after isothermal crystallisation at 20 °C.

3. Results and discussion

DSC analysis is generally one of the most convenient methods for analyzing crystallisation and melting for semi-crystalline polymers. The three kinds of PEO/CNTs (MWCNT, MWCNT–COOH and MWCNT–OH) nanocomposite samples with varying concentration of CNTs were subjected to DSC analysis under non-isothermal conditions. The dynamic thermograms are shown in Fig. 2. It was clearly observed that incorporation of CNTs has a significant influence on crystallisation and melting behaviours for the three different systems. The crystallisation temperature (peak position), T_c, and melting temperature, T_m, and degree of crystallinity, x_c, as a function of CNTs concentration are listed in Table 1. As seen, incorporation of MWCNT (or MWCNT–COOH, or MWCNT–OH) results in the decrease in melting and crystallisation temperatures, and also reduces the crystallinity of PEO. With increasing CNTs concentration the effect became stronger. For example, the crystallisation temperature was down to 7 °C and crystallinity was only 28% of the pure PEO in PEO/MWCNT–OH system with 1% MWCNT–OH concentration.

In order to know what happened in these systems, a polarized optical microscope was used to observe the crystalline morphology, as presented in Fig. 3. It clearly shows that larger spherulites formed in PEO/CNTs blends and number of nucleation sites in the blends dramatically reduced as compared with the pure PEO. These suggest that the incorporation of MWCNT significantly disrupted the crystallisation process of PEO.

In order to better know crystallisation behaviour the crystallisation kinetics under non-isothermal condition were analysed from the DSC crystallisation curves. The relative degree of crystallisation can be measured by following equation.

$$x_c(t) = \frac{A(t)}{A(\text{total})}$$

where $A(t)$ is the partial area of the peak at time t and $A(\text{total})$ is the total peak area.

The relative degree of crystallisation as function of crystallisation time for three kinds of PEO/MWCNTs nanocomposite systems are shown in Fig. 4. It shows that incorporation of MWCNT caused a slow growth in crystals. When CNT concentration is higher the results were more effective. For the PEO/MWCNT–OH systems these effects were more obvious. This means that effect of MWCNTs has been attributed to the retardation of the rate of spherulite growth arising from the effect of the stiff nanotubes molecular chains on the overall mobility in the blend.

In order to thoroughly elucidate crystallisation kinetics, the isothermal crystallisation behaviour was also investigated by DSC. Avrami equation was used to describe isothermal crystallisation kinetics [28]

$$X_t(t) = 1 - \exp(-Kt^n)$$

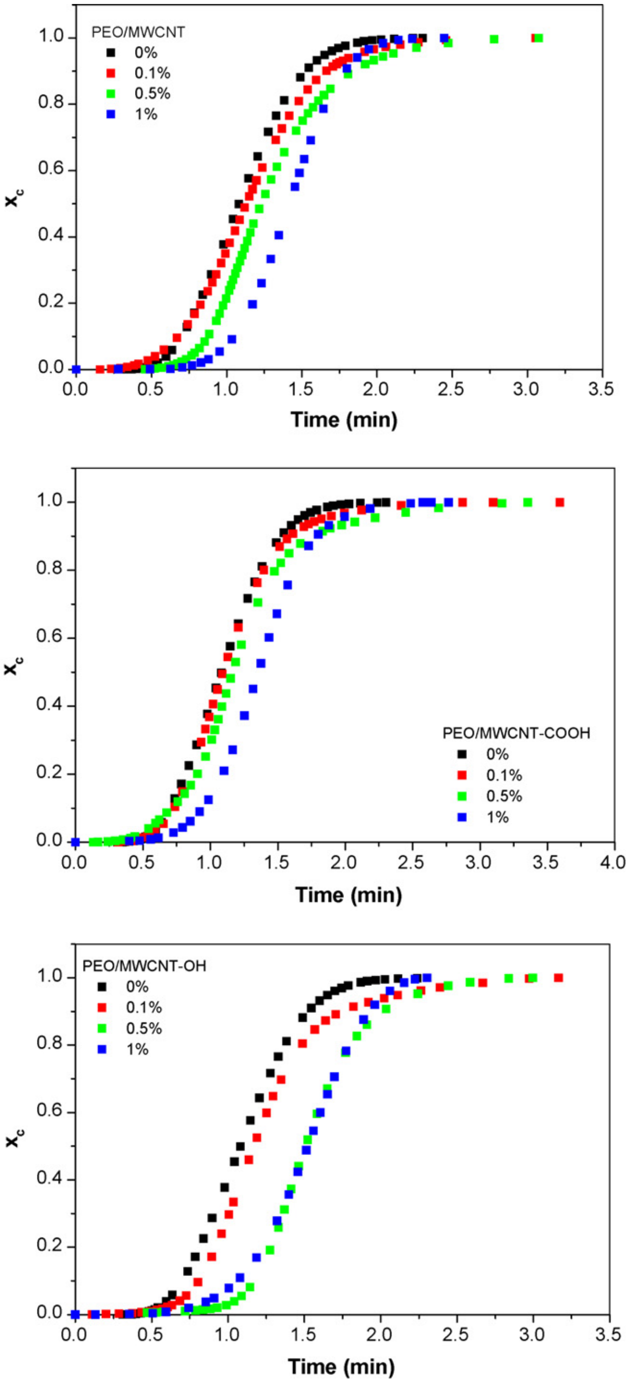

Fig. 4. Plots of relative crystallinity vs. crystallisation time for PEO and its nanocomposites.

Table 1
Crystallisation temperature (T_c), melting temperature (T_m) and crystallinity (χ_c) for PEO and its nanocomposites

Sample	T_c (°C)	T_m (°C)	χ_c (%)
PEO	40.1	67.6	86.7
PEO/CNT (0.1)	31.6	60.6	61.4
PEO/CNT (0.5)	28.1	54.2	47.8
PEO/CNT (1)	11.7	43.7	14.1
PEO/CNT–OH (0.1)	28.9	55.3	58.7
PEO/CNT–OH (0.5)	20.2	47.6	43.5
PEO/CNT–OH (1)	7.0	44.7	24.3
PEO/CNT–COOH (0.1)	30.8	57.1	60.1
PEO/CNT–COOH (0.5)	28.6	51.3	53.4
PEO/CNT–COOH (1)	11.7	50.1	35.4

where X_t is the relative crystallinity, t the crystallisation time, K the kinetic rate constant, which depends on the nucleation and growth mechanism of crystals and n is the Avrami exponent, which value can be used to assign to a specific crystalline dimension.

Fig. 5 shows the dependence of relative degree of crystallisation on crystallisation time for the PEO and its nanocomposites with 0.5%, or 1% different types of CNTs. Each isothermal curve presents the similar S-shape and was in good agreement with the Avrami theory.

For pure PEO the Avrami exponent, n, was found to be 2.2–2.5 at different crystallisation temperatures, reflecting spherical crystal growth [29]. When 0.1 or 0.5% MWCNT or modified MWCNTs introduced the Avrami exponent was slightly lower and still kept at above 2, indicating that although the crystallisation kinetics is influenced by incorporating CNTs, the spherical crystal morphology did not changed. However, n for the 1% CNT (including MWCNT–OH and MWCNT–COOH) nanocomposites was less than 2. An exponent between 1 and 2 in the nanocomposites corresponds to crystal dimensionality disk-shaped growth [30,31], which result is certainly suggestive of the change in growth morphology. This phenomenon was also found in polyethylene/SWCNT nanocomposites [24].

From above study it can be concluded that incorporation of MWCNT or chemical modified MWCNT into PEO leads to decrease in crystallinity, and also reduce spherulite growth rate and nucleation sites in the blends. When CNTs concentration was 1% the blend presented disk-shaped morphology. These results were very different from that in other polymer systems.

General speaking, the change of crystalline morphology in a binary blend by the other polymer component, which is amorphous, arise from two effects: the dilution effect and intermolecular interactions between two components. The dilution effect was revealed by depression of T_m. In our study MWCNT concentration is much lower and the change of the crystalline morphology is importantly considered by existence of intermolecular interactions between PEO and MWCNT. FT-IR is a powerful technique commonly used to investigate the molecular interactions between polymer chains. In this work, the presence of interactions between PEO and carbon nanotubes was evaluated using FT-IR spectroscopy.

FT-IR analysis basically provides information about the presence of attached functionalities. The FT-IR spectra of MWCNT and chemical modified MWNT (COOH or OH) are shown in Fig. 6. Because carbon nanotubes are electrically conducting, the baselines in the spectra are slanted due to plasma reflection [32]. It is very difficult to remove moisture of FT-IR sample completely because substrate (KBr) and amide derivative easily absorb vapour in atmosphere.

MWCNT–COOH appeared to contain hydroxyl and carboxylic group as evidenced by the presence of hydroxyl band at $3400\ \mathrm{cm}^{-1}$ and carbonyl peak at $1744\ \mathrm{cm}^{-1}$, respectively, in the FT-IR spectrum of MWCNT–COOH. Further, MWCNT–OH, also exhibit hydroxyl bands at $3400\ \mathrm{cm}^{-1}$, indicating it contains hydroxyl groups. When modified MWCNT is incorporated into

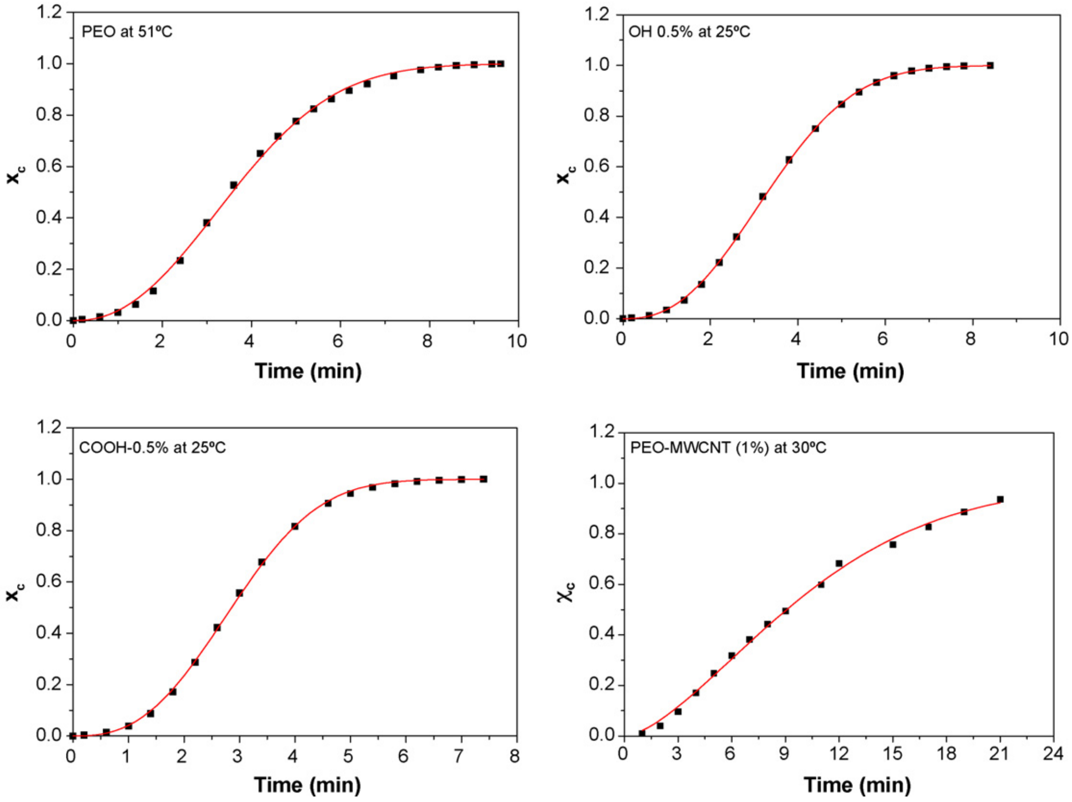

Fig. 5. Crystallisation vs. crystallisation time for calculation of Avrami exponent.

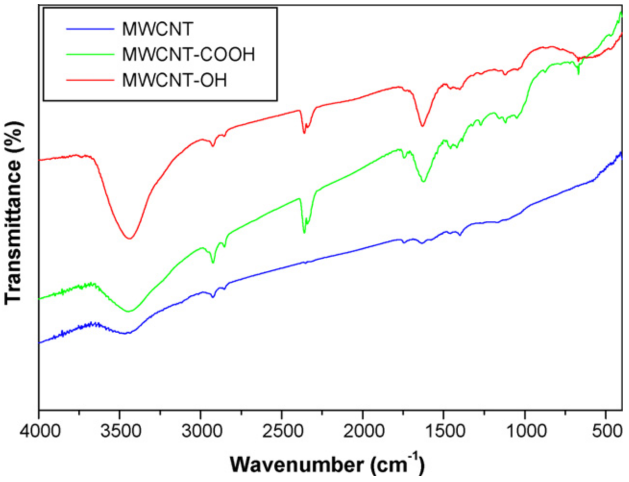

Fig. 6. FT-IR spectra of CNTs.

PEO to form nanocomposites, it could be anticipated that some interactions such as H-bonding, dipole–dipole interactions, can be formed between PEO and the functional groups present in modified MWCNT.

The FT-IR spectra of pure PEO and the nanocomposite samples with 0.5% CNT content are shown in Fig. 7. In the region of 1200–1000 cm^{-1} as shown in Fig. 7A, it was highlighted that the peak at 1109 cm^{-1} in PEO which is for asymmetric stretching vibration of the C–O groups [33], C–O stretching vibration of nanocomposites containing MWCNT–COOH and MWCNT–OH has shifted towards higher frequency of 1116 cm^{-1} compared to the pure PEO. It is also interested to note that a minute peak tends to immerge at 1060 cm^{-1}. They were very prominent in the nanocomposites containing modified CNTs and it may be evidence for presence of interactions.

As shown in Fig. 7B, C–H stretching of PEO is present as a broad peak spanning from 2750 to 3000 cm^{-1}. The same behaviour is observed at 2925 cm^{-1} in the FT-IR spectra of MWCNT–OH or MWCNT–COOH. C–H stretching vibration of the nanocomposites, having CNT–OH or CNT–COOH, apparently presented between these two peaks 2925 cm^{-1} (CNT) to 2875 cm^{-1} (PEO). Immerging of shoulder at 2765 cm^{-1} perhaps indicates the changes in the absorption due to some interference caused by some interactions.

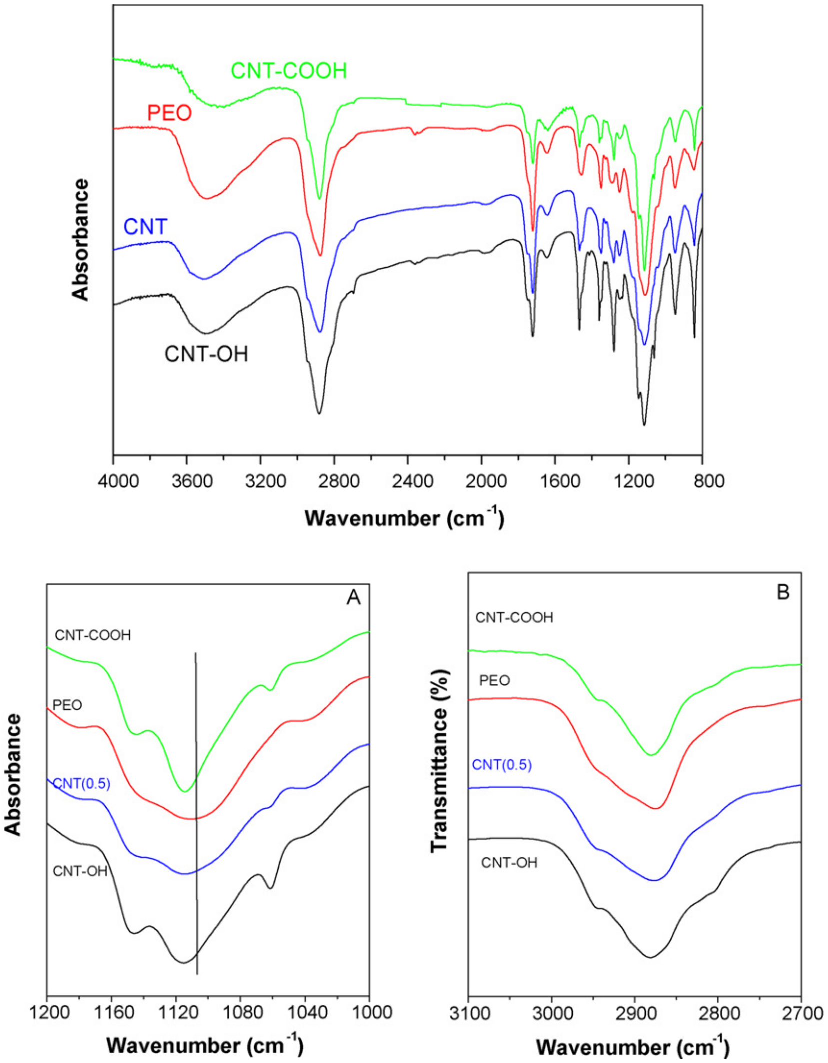

Fig. 7. Spectra of PEO and PEO/CNTs nanocomposites with 0.5% CNT.

Analysis of the spectra of PEO/CNTs blends indicates that MWCNTs show significant influences on the C–O and C–H stretching vibrations of PEO, which could lead the decrease in crystallinity and melting temperature of PEO in the blends. However, more detailed information on conformation change of the PEO can only be obtained from solid-state NMR experiments, which are being carried out.

4. Conclusion

Crystallisation behaviour of poly(ethylene oxide)/multi-walled carbon nanotubes is strongly affected by the incorporation of MWCNTs. Non-isothermal crystallisation experiments showed that incorporation of MWCNT and chemically modified MWCNT reduced the crystallinity and restricted the spherical crystal growth of PEO. The nucleation sites decrease and spherical crystal size increased compared to the neat PEO. Change of crystal structure from spherical to disk-like was evidenced revealed by Avrami equation when MWCNT was added up to 1 wt.%. FT-IR revealed that the incorporation of MWCNTs has a significant influence on the C–O and C–H stretching vibrations of PEO, which could lead the decrease in crystallinity and melting temperature of PEO in the blends.

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