Manufacture and characterization of nanocomposite materials obtained from incorporation of d-glucose functionalized MWCNTs into the recycled poly(ethylene terephthalate)

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ABSTRACT
Plastics make considerable amount of solid waste in the worldwide corresponding to their use in many fields of our lives like construction, packaging, building, and so on. The manufacture of fuel-derived plastics is often dangerous to the environment; so, available waste administration systems including energy recovery operations and/or recycling are essential to solve this huge pollution. In this study, poly(ethylene terephthalate) (PET) bottle waste as considerable part of the total plastic waste bulk was recycled and white and fine-recycled PET powders (R-PET) were formed. The obtained R-PET showed semi-crystalline structure according to X-ray diffraction analysis. Then, the effect of functionalized multi-walled CNTs with D-glucose was investigated on R-PET properties. Transmission electron microscopy exhibited good dispersion of MWCNTs-Gl in the R-PET matrix. MWCNT-Gl as a nucleating agent increased the crystallization degree of R-PET.

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1. Introduction
Plastics have been extensively used due to their benefits such as durability, cheapness, lightness, and also their usage in many areas like packaging, construction, electronic, and automotive applications. Since they have high degradation temperature, high resistance to UV radiation, and are commonly not biodegradable, they can stay on both sea and land for years generating significant amount of solid waste and environmental pollution in the world.\cite{1,2} At present, polymer recycling contributes in environmental protection as well as in petroleum resources preservation.\cite{3} Packaging is the main post-consumer waste for plastics and poly(ethylene terephthalate) (PET) bottles create considerable part of this region. PET is a low-cost, high-performance, semi-crystalline thermoplastic polymer that is used in the automobile and electronic industries and also has a variety of applications such as textiles, films, industrial fibers, bottle containers, and food packaging.\cite{4,5} However, inadequate thermal stability and mechanical properties of PET have hindered its valuable application in a wide range of industry.\cite{6}

Carbon nanotubes (CNTs) are ideal candidates as reinforcements for thermoplastic polymer composites that can improve the electrical, mechanical, and thermal properties of the polymers.\cite{7} One of the main subjects on polymer/CNT composites is how to improve the dispersion of CNTs in a polymer matrix. In fact, poor interfacial adhesion between the polymer and CNT restrict the improvement of properties in CNT-based composites.\cite{8} So as to disperse the CNTs in the polymer homogeneously, surface functionalization of CNTs is essential. Surface tension of the nanotubes decreases by the surfactant treatment, therefore, it improves the wettability of CNTs by polymer with the aid of functional groups.\cite{9–12}

The main purpose of this study is to examine the influence of CNT surface functionality on the morphology, crystallinity, and thermal properties of the nanocomposites (NCs) based on the recycled PET (R-PET) matrix using d-glucose-treated multi-walled CNTs (MWCNT-Gl). First, recyclable PET bottles were changed to white and fine powder through ultrasonic irradiation-assisted solution route. Then, MWCNT-Gl (1, 2, and 4 wt.% of polymer) was incorporated into the R-PET matrix under sonication conditions. All CNT samples were characterized by means of Fourier transform infrared (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), thermal
2. Experimental details

2.1. Materials

The PET used in this study was obtained from Poroshat waste bottles (1500 mL) and it was used without any further processing. d-glucose, N,N-carbonyldiimidazole (CDI), N,N-dimethylacetamide (DMAc) as solvents were provided by Merck Chemical Co. (Darmstadt, Germany). Dimethylsulfoxide (DMSO) was obtained from DAEJUNG (Korea). The carboxyl-modified MWCNTs (MWCNT-COOH) with outer diameter of 8–15 nm, length of about 30 μm, carboxyl content 2.00 wt.%, and purity of >95 wt.% were purchased from Neutrino Co. (Tehran, Iran) and used without further purification.

2.2. Characterization

TGA, DTG, and DTA data of the composite materials were evaluated by STA503 TA instrument. All samples were dried at 120 °C for 12 h prior to the measurement. Weight loss was monitored from 25 to 800 °C at a heating rate of 20 °C/min in argon atmosphere. FT-IR spectra were recorded using a Jasco-680 (Tokyo, Japan) spectrometer at the wavenumber range of 400–4000 cm⁻¹ [taken in potassium bromide (KBr)]. The morphology and state of MWCNTs dispersion within the polymer were observed by FE-SEM and TEM. FE-SEM and TEM micrographs were obtained using a HITACHI S-4160 instrument (Tokyo, Japan) and Philips CM 120 microscope (Netherlands) with an accelerating voltage of 150 kV. XRD analysis was performed on the PET and their NCs using Philips X’Pert MPD X-ray diffractometer with CuKa radiation of λ = 0.154 nm in the range of 10–80°. The composites were prepared using a mechanical probe sonicator (TOPSONICS, Tehran, Iran) operating at power 400 W.

2.3. Preparation of PET powder

Recycled mineral water bottles were collected and chopped into small pieces of size 5 × 3 mm². Uniformly chopped pieces of PET waste (3 g) were mixed with DMSO (12 mL). The mixture was heated at 180 °C with continuous stirring until the solution was completely clear and homogeneous (10–20 min). Then, the obtained solution was cast on a Petri dish and was rapidly cooled with distilled water. Finally, it was washed with hot distilled water several times to remove DMSO and was dried in oven at 100 °C for at least 24 h to minimize the effect of moisture and obtain white and fine R-PET powder. All stages for the preparation of PET powder have been represented in Scheme 1.

2.4. Surface functionalization of MWCNT with d-glucose

Surface functionalization of MWCNTs with glucose (MWCNT-Gl) was performed as previously reported.[13] Schematic illustration of MWCNT functionalization is shown in Scheme 2.

2.5. Preparation of R-PET/MWCNT-Gl NCs

Composites containing 1, 2, and 4 wt.% of MWCNT-Gl were prepared through sonication in solution:

Scheme 1. Schematic representation of PET recycling.
first, DMAc (16 mL) was added to a vessel containing 0.1 g of R-PET. It was sonicated for 15 min to be partially dissolved. Then, MWCNTs-Gl was added to the mixture and it was sonicated for 1 h. The resulting dispersion mixture was centrifuged for 10 min at 6000 rpm. Finally, it was further dried at 120 °C for 24 h to remove the residue solvent and a black solid was formed.

3. Results and discussion

3.1 Functionalization of MWCNTs

MWCNTs usually tend to bundle together due to high aspect ratio and large surface area in combination with the van der Waals attractions between the individual nanotubes. It causes difficult dispersion of MWCNTs in the

Scheme 2. Functionalization of MWCNTs-COOH with D-glucose.

Scheme 3. Possible interactions between R-PET and MWCNTs-Gl.
polymer matrix.[14] In this study, the chemical modification was accomplished to achieve uniform dispersion and good interfacial adhesion between MWCNTs and R-PET matrix. As it was shown in Scheme 2, MWCNT-COOH was functionalized with glucose as a biomolecule under an esterification reaction, catalyzed by CDI. Reaction was run in water solvent system as green media. Scheme 2 also shows the stability of dispersions of MWCNTs-COOH and MWCNTs-Gl in DI water after 30 min of sonication. MWCNTs-Gl indicated highly dispersed and stable dark solution after 2 months of storage at room temperature, whereas the MWCNTs-COOH settled in water after three weeks.

### 3.2 Composite preparation

Recently, increased usage of synthetic polymers has caused the production of a significant amount of wastes based on polymer. They generally transfer hazard to the environment.[15,16] One of the most successful examples of polymer recycling is PET recycling. This compound is fully recyclable and may be applied for manufacturing new produces in various industrial fields.[17] Formation of an NC is an approach to further improve the properties of this polymer which can be reached by the addition of CNTs or other nanomaterials.[18,19] In order to employ MWCNT-Gl as an effective reinforcement in PET composites, proper interfacial adhesion between the CNTs and polymer matrix is essential. In the first step, MWCNTs were functionalized with glucose to increase functional groups on the surface of nanotubes. Actually, MWCNTs-Gl stabilized their dispersion in the PET NCs through hydrogen bonding creation between hydroxyl groups on their surfaces and C=O groups in the R-PET. Also, there are aromatic rings in the R-PET backbone and these structures have strong interactions with CNT surfaces through π–π interactions. In addition to the mentioned interactions, there are dipole–dipole attractions too as illustrated in Scheme 3.

### 3.3 FT-IR spectroscopy

FT-IR spectrum of R-PET powder is presented in Figure 1(a). The presence of C = O bond stretching in conjugation with aromatic ring was appeared at 1724 cm⁻¹. The absorption bands at 2906 and 2964 cm⁻¹ were ascribed to C–H bond stretching (methylene groups). Hydroxyl end groups were observed at 3543 cm⁻¹ and a peak at 3431 cm⁻¹ was corresponding to the carbonyl overtone. The splitting of O–C–C asymmetric stretching was seen at 1119 and 1097 cm⁻¹. [20–23] Figures 1(b) and 1(c) show the spectra of R-PET/MWCNT-Gl NCs of 2 and 4 wt.%, respectively. R-PET displayed a semi-crystalline XRD pattern with well-defined reflection peaks at 2θ = 16.8°, 2θ = 22.9°, and 2θ = 26.3° corresponds to the (0 1 0), (1 1 0), and (1 0 0) planes which relates to a triclinic unit cell.[25] The XRD patterns of the NC samples demonstrated narrow crystalline peaks, which are typical of R-PET.
in Figure 3. FE-SEM micrographs show that the original shape of R-PET was kept after undergoing ultrasonication in ethanol (Figure 3(b)). R-PET with spherical shapes was obtained when DMAc served as the dispersion medium (Figure 3(c)). Actually, the ultrasonication in DMAc caused the size of R-PET be closed to nanometer with a uniform morphology which sureties a strong interaction between nanofillers and the polymer. So, it was selected as a media for the NCs preparation.

The dispersion of nanotubes into the R-PET matrix was assessed by FE-SEM and TEM micrographs too. Bright spots in the FE-SEM micrographs showed MWCNTs-Gl which have been surrounded by the polymer matrix revealing a good dispersion of nanotubes in the R-PET (Figure 4(a)–(c)). TEM images of the R-PET/MWCNT-Gl NC 4 wt.% at various magnifications are shown in Figure 5. This figure gives a view of the dispersed nanotubes. It also confirmed the presence of MWCNTs-Gl in the polymer matrix.

3.6. Thermal stability

Figure 6 shows TGA thermograms of the R-PET and R-PET/MWCNT-Gl NCs of 1, 2, and 4 wt.%. The char residue of in Figure 3. FE-SEM micrographs show that the original shape of R-PET was kept after undergoing ultrasonication in ethanol (Figure 3(b)). R-PET with spherical shapes was obtained when DMAc served as the dispersion medium (Figure 3(c)). Actually, the ultrasonication in DMAc caused the size of R-PET be closed to nanometer with a uniform morphology which sureties a strong interaction between nanofillers and the polymer. So, it was selected as a media for the NCs preparation.

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are substantially shifted. The introduction of MWCNTs decreased the melting point of the composites. It seems that the interaction of nanotubes with this polar polymer matrix could weaken intermolecular interactions between the polymer chains.

4. Conclusions

PET bottle waste was recycled and changed to white and fine-recycled PET powder. Then, novel R-PET/MWCNT NCs with 1, 2, and 4 wt.% MWCNT content were prepared through ultrasonic irradiation-assisted solution method. To improve the compatibility between the R-PET polymer and nanotubes, MWCNT-COOH was functionalized with d-glucose carbohydrate as biomolecule. When, DMAc served as the dispersion medium, spherical shapes of R-PET with smaller size were gained. FT-IR spectra showed shift in the position of hydroxyl-stretching modes to a lower wave-number due to the creation of intermolecular hydrogen bonding between the nanotubes and the polymer. TEM micrographs represented well-dispersed nanotubes in the polymer matrix. The addition of MWCNT-Gl could weaken intermolecular interactions between the R-PET chains and decreased the melting points of the composites.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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