



## Fructose functionalized MWCNT as a filler for starch nanocomposites: Fabrication and characterizations



Shadpour Mallakpour<sup>a,b,c,\*</sup>, Leila khodadadzadeh<sup>c</sup>

<sup>a</sup> Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Islamic Republic of Iran

<sup>b</sup> Research Institute for Nanotechnology and Advanced Materials, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

<sup>c</sup> College of Pardis, Chemistry Section, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

### ARTICLE INFO

#### Keywords:

Multi-walled carbon nanotubes  
Fructose  
Biofunctionalization  
Plasticized starch  
Polymer bionanocomposite

### ABSTRACT

Plasticized starch is one of the outstanding matrices for the fabrication of polymer bionanocomposites (bioNCs). In this study, water-plasticized starch was used for the preparation of novel starch NC films while in many other reported works glycerol was used as plasticizer. Multi-walled carbon nanotubes (MWCNT)s functionalized with D-fructose (Fr) biomolecule (MWCNT-Fr) were used as nanofiller. However, in many previous works only carboxyl functionalized MWCNT were incorporated into starch. Here, the (MWCNT-Fr)s with weight percentages of 0.5, 1 and 2% (respect to polymer weight) were distributed into the plasticized starch with the aid of sonication and the films were prepared by casting the starch/MWCNT-Fr mixtures. The resulting bioNCs were characterized using Thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, Field emission scanning electron microscopy, and Transmission electron microscopy. Surface morphology results proved that functionalization of MWCNTs with carbohydrate led to a good compatibility between nanofiller and matrix which caused to a homogeneous distribution of nanotubes throughout the starch.

### 1. Introduction

The appearance of the polymer nanocomposites (NC)s may be ascribed to Hauser when he reduced the swelling of clay in water via surface modification of it [1]. Indeed, polymer NCs consist of incorporated nanofillers throughout the polymer matrix which nanofillers can be metal and metal oxide nanoparticles, carbon nanotubes (CNT)s and metal wires, clays and grapheme [2]. It's notable that even low loading of such nanofillers can be resulted to outstanding improvement in polymer properties [3].

Among various nanofillers for the preparation of polymer NCs, CNTs which are referred to Ijima [4], have great susceptibility due to their remarkable electrical [5,6], mechanical [7,8], and thermal properties [9,10]. Indeed, the sheets of carbon atoms can be rolled and produce single walled CNT (SWCNT) or multi walled CNT (MWCNT) while the latter is less expensive and plentiful compared to the former one [11]. The hydrophobic nature of CNTs leads to its incompatibility with hydrophilic polymers. Therefore, aggregation of CNTs can occur when the rough nanotubes add to polymer matrix which is caused by Van der Waals attraction between CNTs along with their high surface area and high aspect ratio [12]. This despite the fact that, proper distribution of

CNTs throughout the polymer matrix is the main factor needed to obtain the expected performance of polymer/CNT NCs. Surface functionalization of CNTs can help to overcome this drawback. One of most applied rout for modification of CNTs is oxidation by strong acids which can create –COOH groups on the surface of nanotubes (MWCNT–⊖COOH). It's noteworthy that further modification of CNT–COOH is possible. Mallakpour et al. reported the further functionalization of MWCNT–COOH via the reaction of –COOH group with some organic molecules especially with biomolecules such as vitamins, proteins, amino acids, carbohydrates, etc. [13–15].

As most of the petro-chemically based polymers are not biodegradable and biocompatible thus, researchers changed their center of attention to bio-based polymers. Among biopolymers, starch, is one of the most applied one due to its biocompatibility, biodegradability and right price. On the other hand, plasticized starch is a good candidate to replace with petrochemical based plastics. A plasticizer is a material that could be incorporated into plastic materials, and will increase the flexibility and applicability of them. Plasticizer molecules penetrate starch granules, and destroy the inner hydrogen bonds of starch at high temperature, pressure, and shearing. These molecules eliminate starch–starch interactions because they are replaced by

\* Corresponding author at: Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Islamic Republic of Iran.

E-mail addresses: [mallak@cc.iut.ac.ir](mailto:mallak@cc.iut.ac.ir), [mallak777@yahoo.com](mailto:mallak777@yahoo.com), [mallakpour84@alumni.ufl.edu](mailto:mallakpour84@alumni.ufl.edu) (S. Mallakpour).

<http://dx.doi.org/10.1016/j.porgcoat.2017.08.013>

Received 6 February 2017; Received in revised form 27 June 2017; Accepted 26 August 2017

0300-9440/© 2017 Elsevier B.V. All rights reserved.

starch–plasticizer interactions. Water is the most common solvent or plasticizer used in starch. Also, a wide variety of plasticizers, such as formamids, urea, acetamide, sugar, polyols, amino acids, lipid, and phosphate sorbates, have been used to increase the flexibility of plasticized starch [16]. Indeed plasticizers [17–19] reduce the melting temperature of starch (it's near to decomposition temperature) via destroying the crystalline structure of it [20].

Incorporation of CNTs into starch in the presence of the glycerol as a plasticizer has been studied several times [21–24]. Zhanjun et al. [21] studied the effect of MWCNT–COOH on the performance of the glycerol-plasticized corn starch NCs. Swain et al. [22] prepared the glycerol-plasticized starch NCs incorporated with the MWCNT–COOH as a gas barrier material. In this study, water was used as a plasticizer for the preparation of the starch NCs. A carbohydrate, D-fructose (Fr), was used for the surface modification of MWCNT–COOH. The Fr functionalized MWCNTs (MWCNT–Fr)s with weight percentages of 0.5, 1 and 2 wt.% were incorporated into starch to produce starch/MWCNT–Fr NCs. The effect of functionalization with Fr on the distribution state of MWCNTs in the starch has been assessed. The thermal stability of the starch/MWCNT–Fr NCs was studied as well. These NCs can be used for removal of dyes from water due to the ability of both carbohydrate functionalized MWCNTs [25] and starch [26].

## 2. Experimental procedure

### 2.1. Materials

A MWCNT–COOH with approximately 30  $\mu\text{m}$  length, 8–15 nm outer size and 3–5 nm inner size was obtained from Neutrino Co. Iran. Fr and *N,N'*-carbonyldiimidazole (CDI) were purchased from Merck Chemical Co. Germany. Corn starch (formula weight:  $(162.5)_n$ , formula:  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , density (g/ml): 1.45–1.6) was supplied by SK-Science Kit, Tonawanda NY 14150, USA with the product code of 81460–03.

### 2.2. Apparatus

#### 2.2.1. Ultrasonic device

In this work, sonication process was performed by a TOPSONIC homogenizer ultrasonic liquid processor (Tehran, I. R. Iran) with 25 kHz and power of 100 W.

#### 2.2.2. Fourier transform infrared (FT-IR)

The specimens were powdered and mixed with potassium bromide and then converted to proper sheets to perform FT-IR analysis with a Jasco-680 (Tokyo, Japan) apparatus.

#### 2.2.3. X-ray diffraction (XRD)

A Philips X'Pert MPD (Germany) with a copper (Cu) target ( $\text{Cu K}\alpha = 1.54 \text{ \AA}$ ) at 40 kV and 35 mA was utilized for XRD analysis. The scans were generated in the span of 10–80 °C with 0.05 ° per minute scan speed.

#### 2.2.4. Thermogravimetric analysis (TGA)

A STA503 thermogravimetric analyzer was employed to assess the thermal behavior of starch/MWCNT–Fr NCs. Mass loss was recorded in the range of 25–800 °C with 20 ° per minute heating speed in the existence of argon.

#### 2.2.5. Field emission scanning electron microscopy (FE-SEM)

Specimens were coated with gold and then their FE-SEM photographs were obtained by employing a Hitachi S-4160 electron microscope device (Tokyo, Japan).

### 2.2.6. Transmission electron microscopy (TEM)

A Philips CM 120 electron microscope (Germany) instrument with 150 kV accelerating voltage was utilized for TEM analyses.

## 2.3. Methods

### 2.3.1. Preparation of MWCNT–Fr

The MWCNTs were functionalized with the Fr using the same method has been addressed in our previous work [27]. Briefly, appropriate amount of MWCNT–COOH was distributed in purified water with the aid of sonication. Then CDI was added and the suspension was agitated for 2 h at room temperature (RT). Finally, Fr was added and stirred for 2 h, at RT and then sonicated for 1 h. After centrifuging the suspension, the black precipitate was collected, washed with water, and dried in an oven at 60 °C for 24 h to obtain the MWCNT–Fr.

### 2.3.2. Preparation of starch/MWCNT–Fr NCs

In order to generate starch/MWCNT–Fr NCs, 0.2 g of corn starch was dispersed in 10 mL of distilled cold water. Then 0.5, 1 and 2 wt% of MWCNT–Fr (respect to polymer weight) was added and stirred at first for 30 min at RT and then 30 min at 90–100 °C. The mixture was then sonicated for 20 min and casted onto a polystyrene Petri dish, with the length of 7.5 cm and the width of 1.5 cm. The mixture was dried at the top of the oven for 24 h. The films were further dried in vacuum for 8 h at 120 °C. The obtained films were brittle and had the thickness of 0.04 mm, which were kept in a plastic bag prior to all testing. The possible interactions in starch/MWCNT–Fr NCs are graphically presented in Fig. 1.

## 3. Results and discussion

### 3.1. FT-IR

During surface functionalization of MWCNT–COOH, CDI catalyzed the reaction between –OH groups of Fr and –COOH groups on the surface of nanotubes resulting to generation of ester functional groups. The creation of such ester groups were proved by observation the band at 1723  $\text{cm}^{-1}$  (C=O) in FT-IR spectrum of MWCNT–Fr (see Fig. 2a). To characterize the starch/MWCNT–Fr NCs, their spectra were compared with the pure starch. The spectrum of the pure starch is shown in Fig. 2b. As can be seen, starch has three characteristic bands deposited at 1156, 1081 and 1020  $\text{cm}^{-1}$ , which two formers are ascribed to the –C–O– bond stretching in –C–O–H groups and the latter is attributed to the –C–O– bond stretching in –C–O–C groups [22]. The spectra of all starch/MWCNT–Fr NCs revealed that these three special peaks are presented in NCs and no new band was observed compared to the pure starch which can proved that only physical attractions between the MWCNT–Fr and starch occurred. On the other hand, it was observed that the broad peak at 3100–3600  $\text{cm}^{-1}$  in the pure starch converted to the sharper peak in the starch/MWCNT–Fr NCs, indicating lower hydrogen bonding and higher free hydroxyl groups compared to the pure starch (see Fig. 2(c–e)). Actually, hot water demolished the crystalline regions in starch via breaking the hydrogen bonds in the starch chains and between them. This process created the amorphous phase in starch, which made the incorporation of the MWCNT–Fr possible.

### 3.2. FE-SEM

For evaluating the morphology of MWCNT–Fr and starch/MWCNT–Fr NCs, FE-SEM analysis was performed. Granules with spherical shape and smooth surface are crystalline regions in starch which are shown in Fig. 3b. As can be seen in Fig. 3(c–e), these granules disappeared in NCs

Download English Version:

<https://daneshyari.com/en/article/7106292>

Download Persian Version:

<https://daneshyari.com/article/7106292>

[Daneshyari.com](https://daneshyari.com)