Materials Letters 180 (2016) 7–10

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Nano-hybrids based on quercetin and carbon nanotubes with excellent anti-oxidant activity

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ARTICLE INFO

Article history:
Received 15 February 2016
Received in revised form
11 April 2016
Accepted 19 May 2016
Available online 20 May 2016

Keywords:
Carbon nanotubes
Quercetin
Radical scavenging activity
Nanocomposites
Oxidative degradation

ABSTRACT

Multi-functional nano-hybrids based on Quercetin (Q), a natural antioxidant, and functionalized Carbon Nanotubes (CNTs) have been formulated and used to prepare Ultra High Molecular Weight PolyEthylene (UHMWPE)-based nanocomposites. The study of the nanocomposites rheological behaviour shows that the immobilization of Q molecules onto CNTs outer surface leads to a beneficial effect on the state of the interface between polymer and nanoparticles. Additionally, the investigation of the thermo- and photo-oxidation processes reveals that the hybrids nanoparticles are able to exert a remarkable stabilizing action, due to strong physical interaction between Q and CNTs. In particular, the presence of Q molecules causes the formation of CNTs structural defects, remarkably amplifying the intrinsic CNTs radical scavenging activity.

1. Introduction

In the last years, significant attempts have been directed towards the formulation of polymer nanocomposites containing multi-functional nano-hybrids based on CNTs [1]. Indeed, due to their intriguing surface chemistry, CNTs can be profitably used as a substrate in which functional groups carrying specific functionalities can be anchored. Besides provide CNTs with new functionalities, the grafted active molecules are useful to obtain engineered CNTs/polymer interface, improving the nanocomposite properties [2]. Recent research have probed that CNTs are excellent free-radical scavengers, being able to enhance the thermo- and photo-oxidative stability of polymer matrices in which they are dispersed [3,4]. The outstanding radical scavenging activity of CNTs is related to their peculiar structure; indeed, due to their extended pattern of conjugated double bonds, CNTs show great electron donor and acceptor capability and, similarly to fullerenes, they are very reactive towards free radicals [3]. Although CNTs can either donate or accept electrons through an electron transfer mechanism, the anti-oxidant activity of CNTs is mainly due to their acceptor-like electronic properties. Specifically, CNTs show acceptor-like localized states, arising by the presence of lattice defects, which are responsible for the CNTs anti-oxidant activity [5]. In this work nano-hybrids consisting of functionalized CNTs and quercetin, a natural flavonoid with excellent anti-oxidant activity, have been formulated and used as nanofillers in UHMWPE-based nanocomposites, with the dual aim to improve the state of polymer/nanoparticles interface and to enhance the nanocomposites thermo- and photo-oxidative resistance. Obtained results demonstrate that the manipulation of the surface of CNTs at nanoscale level is an effective strategy to produce high-performance polymeric materials with engineered interface.

2. Material and methods

2.1. Materials

UHMWPE is a commercial grade (average MW = 3–6 MDa) purchased by Sigma-Aldrich®. CNTs (OD = 14–20 nm, ID = 2–5 nm, L = 1–10 μm, purity > 98 wt%) were prepared by typical CVD protocol. Quercetin and all chemical reagents have been purchased by Sigma-Aldrich® and used as received.

2.2. CNTs functionalization

CNTs were functionalized by in situ thermal degradation of glutaryl peroxide: 1 g of CNTs was dispersed in a solution of glutaryl peroxide (3.8 mmol) in 250 mL of H_2O. The mixture was sonicated in an ultrasound bath for 30′, then heated and stirred for 7 h at 90 °C. The obtained suspension was filtered and the

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http://dx.doi.org/10.1016/j.matlet.2016.05.096
0167-577X/

carboxypropyl-*f*-CNTs were washed 10 times with hot water under stirring and dried at 90 °C overnight. Afterwards, 0.200 g of functionalized CNTs were added to a solution of Q (0.33 mmol) in 15 mL of THF. The suspension was sonicated for 30 min and filtered. The obtained carboxypropyl-*f*-CNTs/Q nanohybrids was finally dried at 105 °C for 5 h.

2.3. Nanocomposite preparation

The UHMWPE powder and 1 wt% of nanoparticles were manually mixed at room temperature and the resulting powder has been homogenized by thorough grinding in a porcelain mortar. Afterwards, the composite powder has been kept under magnetic stirring for about 12 h, until the achievement of a homogeneous black powder. The blends were then hot compacted in a Carver laboratory press at 210 °C for 5 min, under a pressure of 1500 psi, to get thin films (thickness about 100 μm).

2.4. Characterizations

Micro-Raman spectroscopy has been performed through a Bruker-Senterra micro-Raman. Thermo-Gravimetric analysis was carried out using an Exstar TG/DTA Seiko 7200. ATR-FTIR and FTIR analysis was performed using a Spectrum Two spectrometer (Perkin Elmer) equipped with a diamond crystal. Thermo-oxidative treatment was carried out in an air oven at T = 120 °C. Photo-oxidative aging was performed in a Q-UV-Solar Eye weatherometer equipped with UVB lamps (313 nm). Rheological tests were performed using a ARES G2 rheometer in parallel plate geometry (plate diameter = 25 mm).

3. Results and discussion

In order to asses the occurred functionalization of CNTs and the immobilization of Q molecules, spectroscopic and thermo-gravimetric analyses have been carried out. In Fig. 1(a), Raman spectra of bare and functionalized CNTs are reported. It is known that the ratio I_D/I_G between the intensities of "defect induced disorder mode" D-band and "tangential mode" G-band, allows the qualitatively evaluation of the CNTs structural defects [6]. The calculated values of I_D/I_G for CNTs and carboxypropyl-*f*-CNTs are 0.588 and

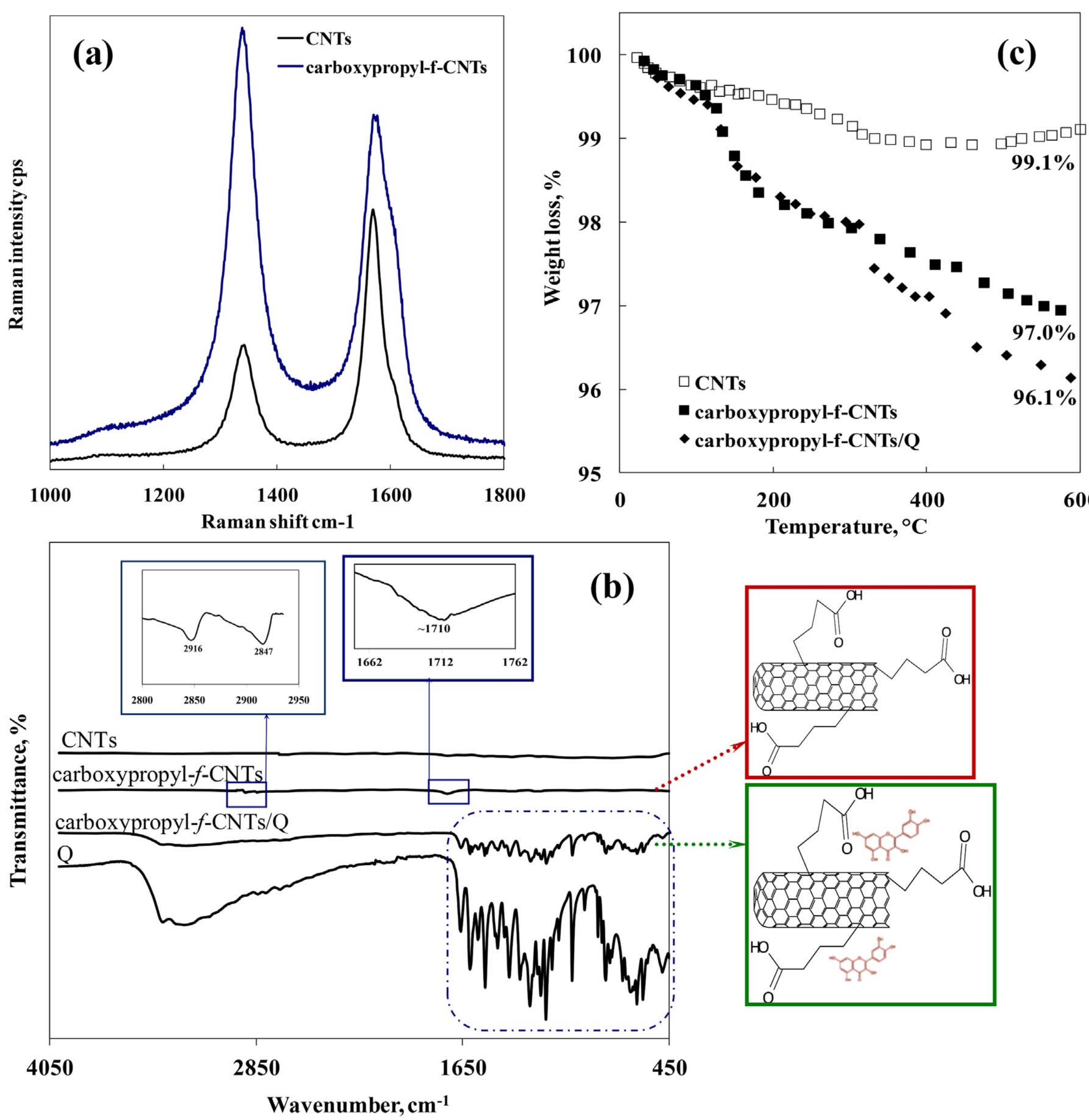

Fig. 1. Characterization of nano-hybrids: Raman spectra (a), ATR-FTIR spectra (b), TGA (c).