



Multi-functional hindered amine light stabilizers-functionalized carbon nanotubes for advanced ultra-high molecular weight Polyethylene-based nanocomposites

N.Tz. Dintcheva^{a,*}, R. Arrigo^a, E. Morici^a, C. Gambarotti^b, S. Carroccio^c, F. Cicogna^d, G. Filippone^e

^a Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

^b Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milano, Italy

^c CNR-IPCB-Section of Catania, Via P. Gaufami, 18, 95126 Catania, Italy

^d Istituto di Chimica dei Composti Organo Metallici (ICCOM), Consiglio Nazionale delle Ricerche, UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy

^e Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale V. Teichio, 80, 80125 Napoli, Italy

ARTICLE INFO

Article history:

Received 30 January 2015

Received in revised form

11 May 2015

Accepted 30 July 2015

Available online 6 August 2015

Keywords:

A. Polymer-matrix composites (PMCs)

A. Nano-structures

B. Rheological properties

B. Mechanical properties

Photo-oxidative resistance

ABSTRACT

Hindered Amine Light Stabilizer (HAS) molecules have been covalently linked on the outer surface of multi-walled carbon nanotubes (CNTs), and the so-obtained multi-functional fillers (HAS-*f*-CNTs) have been compounded with Ultra High Molecular Weight Polyethylene (UHMWPE) to get composite films. The success of the grafting reaction of the HAS molecules has been confirmed through spectroscopic and thermo-gravimetric analyses. Morphological analyses reveal a segregated microstructure, in which CNT-rich channels surround the polymer domains. This morphology results in improved mechanical properties and appreciable electrical conductive features. More importantly, the addition of only 1 wt.% of HAS-*f*-CNTs brings about a significant improvement of the photo-oxidation resistance, which neither HAS nor CNTs can provide if used separately. The origin of this synergic effect is discussed. Overall, our results demonstrate the possibility of using properly functionalized CNTs as multi-functional fillers to get high-performance polymer composites.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The development of innovative multi-functional hybrid carbon-based nanoparticles and their polymer nanocomposites have gained a great interest among researchers in the last two decades [1–3]. One of the most promising candidates for the design of novel multi-functional nanoparticles are carbon nanotubes [4,5] whose high aspect ratio and carbonaceous nature provide them with unique properties, such as high electrical and thermal conductivity, electro-optical behaviour, chemical reactivity, and excellent mechanical stiffness. The superior properties of CNTs make them attractive for the formulation of advanced and high performance polymer-based composites, suitable for applications in such different areas ranging from biomedical engineering, optical

electronics, ultra filtration, energy storage, and photovoltaic cells [6,7]. Nevertheless, the performance of CNTs/polymer nanocomposites depends on the dispersion of CNTs in the host matrix and on the established interfacial interactions. Therefore, significant efforts have been directed towards developing methods to modify surface properties of CNTs and to improve their compatibility with host polymer matrices. The chemical functionalization of CNTs, that can be achieved through different methods, such as covalent linkage [6], non-covalent supramolecular absorption [7], defect functionalization [8] or modification through click chemistry [9]. Besides improving their dispersibility inside polymer matrices [10–12], such chemical modifications provides the CNTs with new functionalities, thus enlarging their possible fields of application [13,14]. In particular, CNTs can be profitably used as nano-carriers bearing specific functionalities to be dispersed in a polymer matrices. This strategy, which combines all the structural advantages of this 1D nanofiller with the specific properties of the functional groups, allows to obtain innovative multi-functional

* Corresponding author. Tel.: +39 091 23863704; fax: +39 091 23860841.

E-mail address: nadka.dintcheva@unipa.it (N.Tz. Dintcheva).

nanoparticles with several potential applications. In our previous works, CNTs bearing natural natural stabilizing molecules, such as vitamin E and quercetin, revealed to be able to greatly enhance the thermo-oxidative resistance of a host polymer [15–17]. The results have been explained considering that the natural anti-oxidant molecules boost up the intrinsic radical scavenging activity of CNTs [18,19]. The latter can be further increased through the insertion of specific anti-oxidant functionalities [20] or UV-stabilizers [21] on the outer surface of CNTs. Indeed, a recent study by Lonkar et al. [21] evidenced that MWCNTs modified with Hindered Amine Light Stabilizer (HAS) dispersed in polypropylene (PP) matrix are able both to increase the induction period of PP photo-oxidation and to improve the mechanical properties of the nanocomposites. HAS molecules are well-known to provide polyolefins with long-term stability through a well-documented mechanism that involves the formation of nitroxyl (NO) radicals. The latter are able to scavenge alkyl radicals formed during polymers oxidation. The HAS efficiency is due to the fact that, in the course of these reactions, NO radicals are regenerated according to the “Denisov cycle” [22].

In the specific case of Ultra High Molecular Weight Polyethylene (UHMWPE), and particularly in the radiation cross-linked material used in the design of artificial joints, HAS molecules have been suggested as possible stabilizers in place of the currently used Vitamin E (VE) [23]. HAS were proved to have better performances than VE due to the different stabilization mechanisms of the two classes of stabilizers. In particular, a fraction of VE can react with alkyl radicals already during the step of radiation cross-linking of UHMWPE. On the one hand, this leads to a reduction of radiation efficiency or cross-link density; on the other hand, part of VE becomes no longer available for the protection of the cross-linked polymer during their useful lifetime. In contrast, being added in a non radical form, HAS do not interfere with the cross-linking mechanism. Only after irradiation and in the presence of oxygenated species HAS are activated, giving rise to nitroxides able to react with radical species so as to stabilize the host polymer.

Currently UHMWPE components are limited in their thickness due to concerns about elevated stresses and the potential for fracture. Therefore, there is increased interest in UHMWPE composites to improve the strength of the material, without sacrificing its excellent performance such as bio-compatibility and wear resistance [24–26].

In this work, HAS molecules have been anchored on the outer surface of CNTs, and the obtained multi-functional fillers (HAS-*f*-CNTs) have been used for the formulation of advanced Ultra High Molecular Weight Polyethylene (UHMWPE) nanocomposites. The UHMWPE/HAS-*f*-CNTs nanocomposite exhibits segregated morphology consisting of conductive nanoparticles paths spanning the host matrix. More importantly, the HAS-*f*-CNTs provide high photo-oxidative stability due to a synergic effect of HAS and CNTs, which are not as effective if used separately.

2. Experimental part

2.1. Materials

The UHMWPE is a commercial grade purchased by Sigma–Aldrich in the form of a white powder. Its main properties are: average molecular weight $M_w = 3 \div 6$ MDa, softening point $T = 136$ °C (Vicat, ASTM D 1525B), melting point $T_m = 138$ °C and density $\rho = 0.94$ g/mL at 25 °C.

CNTs bearing hindered amine light stabilizer molecules (HAS) grafted on the outer surface (HAS-*f*-CNTs) were produced starting from multiwalled CNTs containing ~1 wt.% of covalently linked –COOH groups (CNTs-COOH) purchased by Cheap Tubes, U.S.A.

Their main features are: outer diameter $OD = 120 \div 180$ nm, inner diameter $ID = 10 \div 20$ nm, length $L = 10 \div 20$ μ m, purity >95 wt.%, ash <1.5 wt.%, specific surface area $SSA > 60$ m²/g and electrical conductivity $EC > 10^{-2}$ S/cm. Bare multiwalled CNTs were used to produce reference samples. They have $OD = 120 \div 180$ nm, $ID = 10 \div 20$ nm, $L = 10 \div 20$ μ m, purity >95 wt.%, ash <1.5 wt.%, $SSA > 40$ m²/g and $EC > 10^{-2}$ S/cm.

N,N'-dicyclohexylcarbodiimide (DCC) and 2,2,6,6-tetramethyl-4-piperidinol (light stabilizer molecules, HAS) were purchased from Sigma–Aldrich and utilized without further purifications.

4-piperidol, 2,2,6,6-tetramethyl-RPW stearin, a commercial light stabilizer with trade name Cyasorb[®] UV-3853 (UV-3853), was supplied by Cytec.

2.2. Side-wall functionalized CNTs-COOH

The covalent linkage between the side-wall carboxylic function of the CNTs (1) and the piperidinol (3) was obtained by esterification in the presence of DCC (see Fig. 1). Due to steric hindrances, the endocyclic amino function of 2,2,6,6-tetramethyl-4-piperidinol is rather inert in the reaction conditions, and only the hydroxyl group is involved in the esterification.

0.2 g of CNTs (1) were dispersed in a solution of 2,2,6,6-tetramethyl-4-piperidinol (3) (0.64 mmol, 0.10 g) and DCC (0.19 mmol, 0.040 g) in 30 mL of dry THF. The resulting mixture was sonicated in an ultrasound bath (240 W, 2.5 Lt) for 1 min then stirred at ambient temperature under nitrogen atmosphere for 96 h. After that time, the suspension was filtered using a sintered glass filter. Afterward, the CNTs were washed with hot N,N'-dimethylformamide and methanol under vigorous stirring, repeating the procedure up to 10 times before drying at 90 °C overnight.

2.3. Nanocomposite preparation

UHMWPE-based nanocomposites containing 1 wt.% of bare CNTs, CNTs-COOH or HAS-*f*-CNTs were prepared by hot compaction (HC) using a hydraulic Carver press. Polymer and CNTs were manually mixed at room temperature to obtain a homogeneous black powder, which was loaded between the plates of the press and compressed at a pressure $P = 1500$ psi for 5 min at temperature $T = 210$ °C. The resulting thin films (thickness ~80 μ m) were used for the subsequent analyses. HC films based on pure UHMWPE and UHMWPE/UV-3853 containing 0.5 wt.% of free stabilizer were used as reference samples.

2.4. Characterization

Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) analysis of CNTs-COOH and HAS-*f*-CNTs was performed using a Spectrum Two FTIR spectrometer (Perkin Elmer) equipped with a diamond crystal for surface analysis. ATR-FTIR spectra collected on three different batches of each sample (milligram level) were obtained by accumulation of 32 scans between 4000 and 1000 cm^{-1} , with a resolution of 4 cm^{-1} .

Thermogravimetric analyses (TGA) were carried out on the bare and functionalized CNTs by using an Exstar TG/DTA Seiko 7200 instrument. The tests were performed at a heating rate of 10 °C/min from 30 to 750 °C under nitrogen flow. The reported results are the average of three independent measurements on batches of ~5 mg. The standard deviation was $\pm 0.3\%$ for each investigated sample.

Micro-Raman spectroscopy has been performed at room temperature through a Bruker-Senterra micro-Raman equipped with a 532 nm diode laser excitation and 20 mW power. Non-confocal

Download English Version:

<https://daneshyari.com/en/article/817222>

Download Persian Version:

<https://daneshyari.com/article/817222>

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