Elsevier Editorial System(tm) for Composites Part B
Manuscript Draft

Manuscript Number:

Title: Multi-functional Hindered Amine Light Stabilizers functionalized Carbon Nanotubes for advanced Ultra-High Molecular Weight Polyethylene-based Nanocomposites

Article Type: Full Length Article

Keywords: A. Polymer-matrix composites (PMCs)
A. Nano-structures
B. Physical properties
B. Rheological properties
B. Mechanical properties

Corresponding Author: Prof. Nadka Tzankova Dintcheva,

Corresponding Author's Institution: Università di Palermo

First Author: Nadka Tzankova Dintcheva

Order of Authors: Nadka Tzankova Dintcheva; Rossella Arrigo; Elisabetta Morici; Cristian Gambarotti; Sabrina Carroccio; Francesca Cicogna; Giovanni Filippone

Abstract: Hindered Amine Light Stabilizer (HAS) molecules were covalently linked onto outer surface of multi-walled carbon nanotubes (CNTs) and the obtained multi-functional fillers (HAS-f-CNTs) were dispersed in Ultra High Molecular Weight Polyethylene (UHMWPE) aiming at obtaining advanced nanocomposites with enhanced photo-oxidative stability, electrical and mechanical properties. The effective grafting of HAS molecules is confirmed by spectroscopic, spectrometric and thermo-gravimetric analyses, and the influence of the multi-functional nanoparticles on the morphology, mechanical and electric behaviour and photo-oxidative stability of the nanocomposites are investigated. UHMWPE/HAS-f-CNTs nanocomposite shows improved electrical and mechanical properties compared with those of bare CNTs based nanocomposites and, due to the multi-functional nature of used nanoparticles, shows enhanced photo-oxidative stability caused by a synergic action between the immobilized HAS molecules and the radical scavenging activity of CNTs.

Suggested Reviewers: Pieter Gijsman
pieter.gijsman@dsm.com

Vincenzo Malatesta
malatesta_vincenzo@fastwebnet.it

Opposed Reviewers:

UNIVERSITÀ DEGLI STUDI DI PALERMO

DIPARTIMENTO DI INGEGNERIA CIVILE, AMBIENTALE, AEROSPAZIALE, DEI MATERIALI

DICAM

Palermo, 30/01/2015

To: Prof. L. Feo,
Editor for Europe

From: Prof. N.Tz. Dintcheva
University of Palermo

Dear Editor,

Enclosed please find the manuscript entitled "Multi-functional Hindered Amine Light Stabilizers-functionalized Carbon Nanotubes for advanced Ultra-High Molecular Weight Polyethylene-based Nanocomposites", to be considered for publication in Composites part B - Engineering.

We report about advanced Ultra-High Molecular Weight Polyethylene (UHMWPE)-based Nanocomposites with enhanced photo-oxidative stability, electrical and mechanical properties achieved through multi-functional fillers adding. In particular, Hindered Amine Light Stabilizer (HAS) molecules were covalently linked onto outer surface of multi-walled carbon nanotubes (CNTs) and the obtained multi-functional fillers (HAS-*f*-CNTs) were dispersed in the host polymeric matrix. To confirm the effective grafting of HAS molecules onto CNTs spectroscopic, spectrometric and thermo-gravimetric analyses has been accurately performed and discussed. Besides, the influence of the multi-functional nanoparticles on the morphology, mechanical and electric behaviour and photo-oxidative stability of the nanocomposites were investigated. UHMWPE/HAS-*f*-CNTs nanocomposite shows improved electrical and mechanical properties compared with those of bare CNTs based nanocomposites and, due to the multi-functional nature of used nanoparticles, shows enhanced photo-oxidative stability caused by a synergic action between the immobilized HAS molecules and the radical scavenging activity of CNTs.

Concluding, we believe that our results can be potentially extended to many other systems; the CNTs can be profitably used as a substrate on which grafting molecules carrying specific functionality. Furthermore, it is important to note that the approach is quite general, and the nature of both functional molecules and nanoparticles can be properly selected to design polymer materials for demanding applications.
We hence believe that our manuscript may be suitable for publication in Composites part B - Engineering, and we shall welcome any comments you or your Referees may have about our work.

Sincerely yours,

Nadya Tz. Dintcheva

Prof. N.Tz. Dintcheva

Viale delle Scienze, Edificio 8 – 90128 Palermo – C.F. 80023730825 – P. IVA 00605880822
Centralino: (091) 23896510 - Amministrazione: (091) 23896768/69/74/75/77 - Fax: (091) 6657749 – (091) 427121
e-mail: dipartimento.dicam@unipa.it - pec: unipa.pa.037@pa.postacertificata.gov.it

Multi-functional Hindered Amine Light Stabilizers-functionalized Carbon Nanotubes for advanced Ultra-High Molecular Weight Polyethylene-based Nanocomposites

N. Tz. Dintcheva[*1], R. Arrigo[1], E. Morici[1], C. Gambarotti[2], S. Carroccio[3], F. Cicogna[4], G. Filippone[5]

(1) Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

(2) Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Piazza Leonardo da Vinci, 32 - 20133 Milano, Italy

(3) CNR-IPCB-Section of Catania, Via P. Gaifami, 18 -95126 Catania, Italy

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

(5) Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale V. Tecchio, 80, 80125 Napoli, Italy

[*] Corresponding author. Tel: +39 091 23863704. Fax: +39 091 23860841. E-mail address: nadka.dintcheva@unipa.it (N.Tz. Dintcheva).

Abstract

Hindered Amine Light Stabilizer (HAS) molecules were covalently linked onto outer surface of multi-walled carbon nanotubes (CNTs) and the obtained multi-functional fillers (HAS-*f*-CNTs) were dispersed in Ultra High Molecular Weight Polyethylene (UHMWPE) aiming at obtaining advanced nanocomposites with enhanced photo-oxidative stability, electrical and mechanical properties. The effective grafting of HAS molecules is confirmed by spectroscopic, spectrometric and thermo-gravimetric analyses, and the influence of the multi-functional nanoparticles on the morphology, mechanical and electric behaviour and photo-oxidative stability of the nanocomposites are investigated. UHMWPE/HAS-*f*-CNTs nanocomposite shows improved electrical and mechanical properties compared with those of bare CNTs based nanocomposites and, due to the multi-functional nature of used nanoparticles, shows enhanced photo-oxidative stability caused by a synergic action between the immobilized HAS molecules and the radical scavenging activity of CNTs.

Keywords: A. Polymer-matrix composites (PMCs) A. Nano-structures B. Physical properties B. Rheological properties B. Mechanical properties

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 and novel high performance polymer-based composites are the carbon nanotubes [4-5]. Particularly, the carbon nanotubes can be used as nanoparticles able to improve the electrical, thermal, mechanical and optical properties of the host matrix [6-7]. The chemical functionalization of CNTs, that can be achieved through *i*) covalent linkage [6], (*ii*) non-covalent supramolecular absorption [7], (*iii*) defect functionalization [8], or (*iv*) modification through click chemistry [9], besides improving their dispersibility inside polymer matrices [10-12], provides them new functionalities enlarging their possible fields of application [13-14]. Thus CNTs can be used as substrate to graft functional groups having specific functionalities and they can be successfully considered as nano-carriers of the grafted moiety allowing, once dispersed in a polymer matrix, to combine all the structural advantages of this 1D nanofiller with the specific properties of the functional groups. In this work, hindered amine light stabilizers HAS molecules have been anchored onto 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. As well know, HAS are able to absorb the UV-light ensuring long-term stability of the host matrix [15]. A recent study by Lonkar [16] evidenced that MWCNTs modified with HALS dispersed in polypropylene matrix are able both to increase the induction period of PP photo-oxidation and to improve the mechanical properties of the nanocomposites. In the specific case of 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) [17]. HAS were proved to have better performances than VE due to the different stabilization mechanisms of the two classes of stabilizers. VE can react with alkyl radicals also during the radiation cross-linking of UHMWPE leading to a reduction of radiation efficiency or

cross-link density, this reaction caused also a lost of VE that was no more available during the use of the cross-linked material. HAS do not interfere with the cross-linking mechanism because they are added to the matrix in a non radical form, only after irradiation and in the presence of oxygen species HAS can be activated giving rise to a nitroxide able to react with radical species. Moreover, after the first step, the nitroxide can be regenerated according to the accepted radical scavenger mechanism of HAS [15]. As far as the preparation and use of CNTs/UHMWPE composites, they were reported in the literature also as possible alternative to, or as filler in, the radiation cross-linked material in the arthroplastic applications [18]. However, some concerns exist about the effective reinforcing ability of CNTs in the CNTs/UHMWPE composites because, due to the high viscosity of the matrix, the composites were generally prepared by solution or dry blending of CNTs with powdered UHMWPE followed by hot compaction. This procedure gives rise to composites having segregated structure instead of a random distribution and the segregated structure can introduce defects on the microstructure of UHMWPE that can negatively influence the mechanical properties of the material. To partially overcome this problem, chemical modification of CNTs with different functional groups was used to enhance the interactions between the filler and the polymer matrix giving good results both in terms of mechanical reinforcement of the matrix and by increasing also the stability of the composites because of the antioxidant effect of CNTs that limits the degradation of the material after long post-irradiation period. Indeed, according to the current literature, the CNTs exert a radical scavenging activity against oxidation of the polymer-based nanocomposites [19-20] and slightly UV-protective action during manufacture lifetime [21-22]. The radical scavenging activity of CNTs can be exacerbated through introduction of specific anti-oxidant functionalities [23] or UV-stabilizers [16] onto outer surface or immobilization of natural hindered phenols and/or polyphenols as experimentally demonstrated [24-25]. Meanwhile, the segregate structure of CNTs/UHMWPE composites has also the specific feature to allow the preparation of conductive material characterized by ultralow percolation threshold that probably can be further reduced by improving the dispersion of CNTs [26]. In this work, the preparation

and properties of UHMWPE/HAS-*f*-CNTs nanocomposites having enhanced photo-oxidative stability and durability were reported. Besides, due to the multi-functional nature of used nanofillers, the UHMWPE/nanocomposite show improved electrical and mechanical properties compared with those of bare CNTs based nanocomposites.

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÷6 MDa, softening point *T*=136°C (Vicat, ASTM D 1525B), melting point T_m=138°C and density ρ=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÷180 nm, inner diameter *ID*=10÷20 nm, length *L*=10÷20 μm, purity >95 wt.%, ash <1.5 wt.%, specific surface area *SSA*>60 m^2/g and electrical conductivity *EC*>10^{-2} S/cm. Bare multiwalled CNTs were used to produce reference samples. They have *OD*=120÷180 nm, *ID*=10÷20 nm, *L*=10÷20 μm, purity >95 wt.%, ash <1.5 wt.%, *SSA*>40 m^2/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.

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 Figure 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 hours. After that time, the suspension was filtered on a sintered glass filter, the CNTs were deeply washed many times with hot N,N'-dimethylformamide and methanol, and dried 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 μm) were used for the subsequent analyses. Pure UHMWPE and UHMWPE/HAS thin films prepared by HC were used as reference samples.

2.4 Characterization

ATR-FTIR analysis of CNTs-COOH and HAS-*f*-CNTs was performed using a Fourier Transform Infrared Spectrometer (FTIR) (Spectrum Two FTIR spectrometer, Perkin Elmer) equipped with a diamond crystal for surface analysis. 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}.

Fourier transform infrared spectroscopy (FT-IR) of polymer films was carried out by using a Perkin Elmer FT-IR spectrometer (mod. Spectrum Two). The spectra were collected by performing 16 scans between 4000 and 500 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 ±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 measurements were carried out in the range 4000–400 cm^{-1} with a spectral resolution between 9 and 15 cm^{-1}.

The Py-GCMS experiments were carried out on a Frontier Laboratories' Multi-Shot Pyrolyzer EGA/PY-3030D with direct connection to a Shimadzu GCMS-TQ8040 gas chromatography mass spectrometer (GC-MS) equipped with a 30 m × 0.25 mm inner diameter (5%-phenyl)-methylpolysiloxanenon-polar column (HP5MS). The pyrolyzer was set at 350°C to a final of experiment. The GC/MS conditions were the following: inlet temperature at 250°C, pressure 7.1 psi, split ratio 50:1. The oven temperature of the GC was held at 40°C for 1 min followed by continuous heating (6°C/min) to 280°C with 1 mL/min helium carrier gas. Then, the final temperature was held for 15 min to ensure that no heavy molecules remained in the column. The mass spectrometer conditions used were: transfer line temperature 150°C, ion source temperature 230°C, and electron impact ionization (EI) at 70 eV.

Rheological tests were performed using a strain-controlled rheometer (mod. ARES G2 by TA Instrument) in parallel plate geometry (plate diameter 25 mm). The complex viscosity (η^*) was measured performing frequency scans from $\omega=10^{-1}$ to 10^{2} rad/s at T=210°C. The strain amplitude was γ=2%, which preliminary strain sweep experiments proved to be low enough to be in the linear viscoelastic regime.

Optical microscopy was performed using a Leica Microscope in reflection mode at a magnification of 20x. Images were acquired on the surface of the nanocomposite films.

Electrical resistivity of each film was measured employing a commercial setup (ECOPIA HMS-3000, B=0.55 T) at room temperature.

Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Rheometrics DMTA V instrument, single cantilever bending method. The test has been carried out in the temperature swift mode, between 10 and 120°C at a heating rate of 2 °C/min. The frequency was set to 1 Hz and the maximum strain amplitude was 0.5%. The elastic modulus (E') as a function of the temperature was recorded.

Photo-oxidation of polymer films was carried out using a Q-UV weatherometer equipped with UVB lamps (313 nm). The progress of the photo-degradation was quantified by referring to the carbonyl (CI) and hydroxyl (HI) indices as a function of irradiation time. CI was calculated as the ratio between the integral of the carbonyl absorption region (1850-1600 cm^{-1}) and that of a reference peak at about 1370 cm^{-1}; HI refers to the hydroxyl absorption region (3570–3150 cm^{-1}), which integral was normalized by the peak at 1370 cm^{-1}.

3. Results and Discussion

3.1 Characterization of HAS-f-CNTs

Reactive hindered amine light stabilizer molecules were successfully grafted onto the outer surface of the CNTs-COOH (see Figure 1) and the surface functionalization was assessed through ATR-FTIR, Raman spectroscopy, TGA and mass spectrometry. In Figure 2, the ATR-FTIR spectra of CNTs-COOH and HAS-*f*-CNTs are shown. The spectra of HAS-*f*-CNTs displays a strong absorption band at 2966 cm^{-1} and a broad absorption band centred at around 2852 cm^{-1} due to the asymmetrical ($\nu_{as}CH_3$) and symmetrical ($\nu_{s}CH_3$) stretching of C-H bonds in methyl groups, respectively. Besides, a broad absorption band centred at around 3100 cm^{-1} possibly due to N-H stretching vibration of the grafted functional group, is also visible.

Additionally, the TGA analysis suggest that both the CNTs-COOH and HAS-*f*-CNTs decompose faster than the bare CNTs with increasing the temperature, because of the volatilization of carboxyl and HAS molecules on the nanotube surface. The gradual weight loss related to the thermal decomposition of the HAS groups takes place in the range 300÷400°C, i.e. well above the temperature at which the nanocomposite thin films were prepared and characterized. Probably, the weight loss up to 100 °C is due to a small amount of residual water in all the samples. The residues at the end of the analysis were 98.1% wt and 96.0% wt for CNTs-COOH and HAS-*f*-CNTs, respectively, whereas a residual of 99.1% wt was found for the bare CNTs due to a partial decomposition of the bulk material, see Figure 3. Moreover, TGA revealed an overall content of HAS around 2.0 wt.% (see Figure 3).

The surface functionalization of CNT with HAS already evidenced by ATR-FTIR and TGA analysis, was further confirmed by the GC-MS analysis of pyrolyzed HAS-f-CNT obtained. Particularly, in Figure 4, (a) an enlargement portion of GC signal assigned to 2,2,6,6-tetramethyl-4-piperidinol in Py-GC MS and (b) corresponding mass spectrum matched with (c) database mass spectrum of 2,2,6,6-tetramethyl-4-piperidinol are shown, respectively. Almost total matching between the MS spectra of our sample (see spectra b) and database mass spectra (see spectra c) can be observed suggesting the presence of 2,2,6,6-tetramethyl-4-piperidinol. Finally, according to our previous study [24], CNTs lattice defect due to the functionalization can be detected by the Raman spectroscopy by considering the ratio between the signal intensities of the disorder-induced D-band at ~1340 cm^{-1} (I_D) and tangential G-band at ~1570 cm^{-1} (I_G) [27-28]. The Raman spectra of bare CNTs, CNTs-COOH and HAS-*f*-CNTs sample are compared in Figure 5.

The I_D/I_G ratio of bare CNTs is about 0.47, while it increases significantly for both CNTs-COOH (I_D/I_G = 1.12) and HAS-*f*-CNTs (I_D/I_G = 1.40) samples, suggesting that the presence of carboxylic groups, and even more HAS, allows for the formation of a large amount of surface defects. Furthermore, a slight shift of tangential G-band for HAS-*f*-CNTs compared to the bare CNTs and intensification of the shoulder centred at around 1605 cm^{-1} are due to the

modification occurring in the structure of CNTs suggesting successful grafting of HAS, also according to the literature [28].

3.2 Characterization of UHMWPE-based nanocomposites

As well known, the molecular architecture changes in polymers and polymer-based nanocomposites may be gainfully investigated through rheology analysis. Additionally, the rheological analysis of nano-filled polymers provides valuable information in terms of the state of nanoparticles dispersion. The complex viscosity curves (η*) and elastic (G') and loss (G'') moduli of neat UHMWPE and investigated nanocomposites as a function of frequency are shown in Figure 6 (a-b). First we evaluate the effect of the HAS presence on the rheological behaviour of UHMWPE. The complex viscosity and both moduli of UHMWPE/HAS are slightly lower than those of neat UHMWPE because of a plasticizing effect exerted by HAS. Indeed these low molecular weight compounds can diffuse within the molten polymer causing the decrease of the matrix viscosity through an increase of the free volume, by increasing the space between macromolecules and sometimes facilitating their slipping. Concerning the effect of the nanotubes addition, the η* values of all nanocomposites are higher than those of neat UHMWPE in the whole investigated frequency range. The bare CNTs have an irrelevant effect, resulting in a mere vertical shift of the η* curve, without actually altering the relaxation spectrum of matrix macromolecules. This feature is typical of not uniformly dispersed fillers. Differently, CNTs-COOH and especially HAS-*f*-CNTs are able to generate noticeable rheological alterations; the disappearance of Newtonian plateau for HAS-*f*-CNTs containing nanocomposites suggests their arrangement in interconnected structures, resulting in the formation of a semi-3D network of nanoparticles into the host matrix. Consistent with the addition of solid particles into a polymer matrix, G' and G'' of UHMWPE-based nanocomposites increases at all frequencies with the nanoparticles adding, following the same trend observed for the viscosity. Nevertheless, alterations in the low frequency behaviour emerge, and the low frequency G' modulus of functionalized CNTs containing nanocomposites

tends to become almost independent of frequency, suggesting a pseudo solid-like behaviour. Once again, this issue is more pronounced for nanocomposite containing HAS-*f*-CNTs.

The visual inspections of the nanocomposite films agree with the indications emerged from the rheological analysis. Representative optical micrographs of the UHMWPE-based nanocomposites containing bare CNTs, CNTs-COOH and HAS-*f*-CNTs are shown in Figure 7. The CNTs appear as the dark phase. The optical observations show that a segregated structure, in which CNTs are mainly localized in the interfacial regions of UHMWPE particles, has been successfully achieved in all UHMWPE-based nanocomposites. In fact, when "hot-compaction" method is used for the nanocomposites preparation, the nanotubes cover the surface of the polymer particles in powdered UHMWPE/nanoparticles mixture, and after hot pressing the nanoparticles remain at boundaries between the polymer particles. As a result the formation of CNTs-rich channels around UHMWPE-rich islands can be achieved [18]. Comparison between the morphology of bare and functionalized-CNTs based nanocomposites indicates that in the former a broader segregated networks within host matrix has been obtained, probably due to some re-aggregation phenomena between CNTs that hinder their distribution in the interfacial regions. The presence of COOH and HAS functional groups in functionalized-CNTs based nanocomposites, avoid the CNTs agglomeration, allowing the formation of a well-ordered segregated structure.

These segregated networks are beneficial to form conductive nanoparticles paths through the host matrix. The electrical resistivity of neat UHMWPE and CNTs containing nanocomposites with segregated morphology has been measured at least three times for each sample and the average values were calculated and reported in Table 1. As expected the unfilled UHMWPE shows highest values of resistivity and the addition of bare CNTs causes a variation of the resistivity value by two orders of magnitude. Even more, by adding of CNTs-COOH and HAS-*f*-CNTs, the values of the resistivity change by three orders of magnitude suggesting a beneficial effect of the presence of both COOH and HAS functional groups in the nanotubes dispersion and formation of segregated morphology, as reported above. It is interesting to highlight that the

presence of HAS moiety onto CNTs outer surface does not affect negatively the formation of the conductive channels around UHMWPE-rich islands highlighting the possibility to use HAS-*f*-CNTs as multi-functional fillers for the formulation of advanced innovative polymer-based nanocomposites.

To investigate the mechanical behaviour of the nanocomposites, the elastic modulus (E') as a function of the temperatures for neat UHMWPE and all nanocomposites has been monitored and the trends are shown in Figure 8; the insert reports the values of the E' at two different temperatures. As expected the E' decreases with temperature increase for all investigated samples and this effect is more pronounced for the neat UHMWPE and UHMWPE/HAS samples. The presence of free HAS molecules causes a slight decrease of the elastic modulus value, confirming the plasticizing action of the HAS molecules noticed by rheological investigations.

The CNTs-containing samples show less pronounced temperature dependence and higher E' values than that of neat UHMWPE. All used CNTs exert reinforcement action for UHMWPE matrix and this effect is more pronounced for the functionalized CNTs. The obtained segregate morphology, discussed before, for CNTs-containing samples could be considered responsible for the mechanical behaviour.

3.3 Photo-oxidation behaviour of UHMWPE-based nanocomposites

To investigate the photo-oxidation behaviour of UHMWPE-based nanocomposites, thin films have been subjected to accelerate UVB exposure and the formation of carbonyl and hydroxyl species as a function of the exposure time has been monitored through FTIR analysis. In Figure 9 (a-b), the calculated carbonyl (CI) and hydroxyl (HI) indices of investigated neat UHMWPE, UHMWPE/HAS and UHMWPE-based nanocomposites are shown. The CI refers to the signals in the range 1850 to 1600 cm^{-1}, which are due to the formation of different amount of carbonyl species and reflect the formation of acid (1715 cm^{-1}), ketones (1718 cm^{-1}), esters (1738 cm^{-1}) and lactones (1786 cm^{-1}). The HI is related to the presence of linked and free -OH groups

deriving from the photo-oxidation process. Concerning the CNTs and CNTs-COOH based nanocomposites, the nanotubes are able to protect or slightly slow down, the photo-oxidation of UHMWPE [21]. Indeed CNTs are able to exert a radical scavenging activity because of the presence of surface defects that causes the formation of acceptor-like localized states and this future significantly improve the radical scavenging activity of the carbon nanotubes [19-20]. Moreover, CNTs can also act as inner filter, decreasing the rate at which the polymer matrix is oxidized [29]. Furthermore, the CNTs upon UV light are able to physisorbe the oxygen molecules which, being strongly bonded on the walls of carbon nanotubes, are not available for the oxidative phenomena [22]. All these features can explain the observed slight protection activity of CNTs and CNTs-COOH against UVB light in the UHMWPE/CNT composites which is more pronounced for CNTs-COOH characterized by a large amount of structural defects as confirmed by Raman analysis. The dispersed HAS molecules in UHMWPE are able to protect the UHMWPE against the UVB exposure for longer time with respect to pristine polymer or CNT/UHMWPE composites, however its low molecular weight could be considered responsible for volatilization during processing and subsequent reduced protection action. The protective activity of both CNTs or HAS is further increased by the presence of HAS molecules covalently linked onto their outer surface. In fact, UHMWPE/HAS-f-CNTs show best photo-oxidation resistance, in terms of delayed induction time (time at which the slop of the carbonyl and hydroxyl indices curves change suddenly) and of decreased rate of oxygen containing species formation. The very high photo-oxidative resistance of UHMWPE/HAS-f-CNTs film can be understood considering different features. First of all, immobilized HAS molecules are not subjected to volatilization and/or migration so they can exert their stabilisation effect for a longer time. Moreover, they are localized and available at the interfacial area between polymeric phase and the inert nanofillers that is the critical area for the beginning of photo degradation process. Moreover, the chemical functionalization (shown in Figure 1) induces the formation of sidewall defects, as confirmed by Raman analysis, which act as acceptor-like

localised states conferring an additional free-radical scavenging activity to the nanoparticles, as recently documented by experimental [19-20] and theoretical [30] studies.

4. Conclusions

Multi-functional filler based on CNTs bearing covalently linked HAS molecules has been successfully obtained and its characterization has been performed through advanced spectroscopic, spectrometric and thermo-gravimetric analysis. Besides, the HAS-*f*-CNTs has been incorporated into UHMWPE for the formulation of advanced nanocomposite, whose properties and performance have been compared with those of bare CNTs and CNTs-COOH based nanocomposites. The UHMWPE/HAS-*f*-CNTs nanocomposite shows enhanced photo-oxidative stability, electrical and mechanical properties due to the multi-functional nature of the successfully formulated nanofiller.

Acknowledgements: this work has been financially supported by Ministry of University and Research in Italy (MIUR), FIRB2010 – Futuro in Ricerca, Project title: "GREENER – Towards multifunctional, efficient, safe and stable “green” bio-plastics based nanocomposites of technological interest via the immobilization of functionalized nanoparticles and stabilizing molecules" (cod: RBFR10DCS7).

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Captions for Table and Figure

Table 1. Electrical resistivity values for neat UHMWPE and all investigated nanocomposites

Figure 1. Scheme of side-wall functionalization of CNTs by 2,2,6,6-tetramethyl-4-piperidinol

Figure 2. ATR-FTIR spectra of CNTs-COOH and HAS-*f*-CNTs

Figure 3. TGA curves of bare CNTs, CNTs-COOH and HAS-*f*-CNTs

Figure 4. (a) An enlargement portion of Py-GC signal assigned to 2,2,6,6-tetramethyl-4-piperidinol in Py-GC MS and (b) corresponding mass spectrum matched with (c) database mass spectrum of 2,2,6,6-tetramethyl-4-piperidinol

Figure 5. Raman spectra of bare CNTs, CNTs-COOH and HAS-*f*-CNTs

Figure 6. (a) Complex viscosity curves (η*) and (b) elastic (G') and loss (G'') moduli of neat UHMWPE and investigated nanocomposites

Figure 7. Optical micrographs of all investigated UIHMWPE-based nanocomposites

Figure 8. Elastic modulus E' as a function of temperature for all investigated systems

Figure 9. Carbonyl (a) and hydroxyl (b) indices as a function of the photo-oxidation time for all investigated systems

	ρ [Ω*m]
UHMWPE	$1.1*10^{8}$
UHMWPE/CNTs	$1.6*10^{6}$
UHMWPE/COOH-CNTs	$7.7*10^{5}$
UHMWPE/HAS-*f*-CNTs	$5.2*10^{5}$

Table 1. Electrical resistivity values for neat UHMWPE and all investigated nanocomposites

Figure

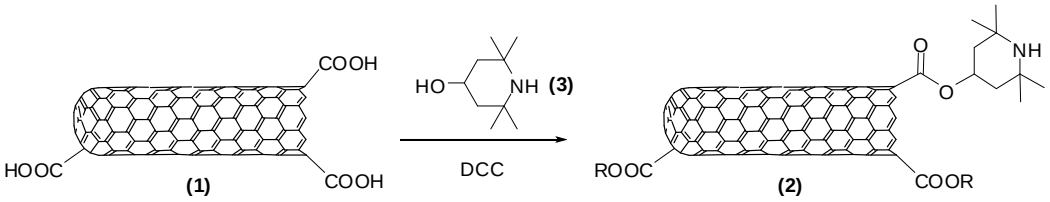


Figure 1. Scheme of side-wall functionalization of CNTs by 2,2,6,6-tetramethyl-4-piperidinol

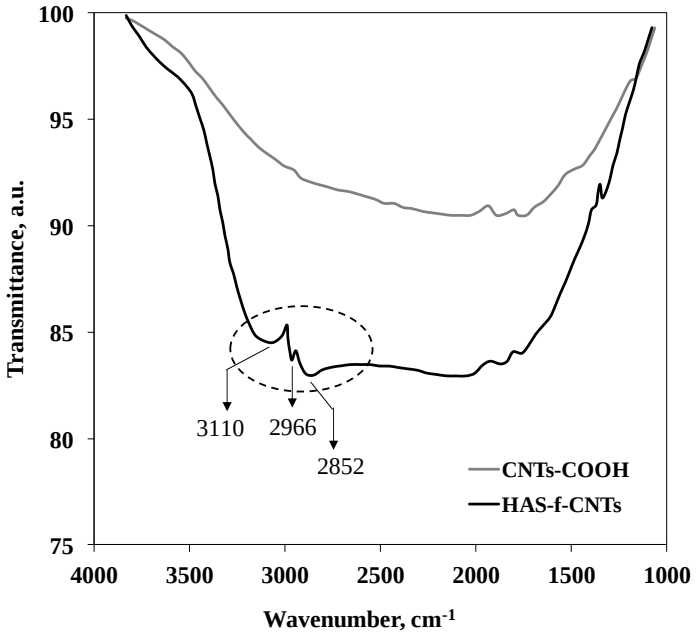


Figure 2. ATR-FTIR spectra of CNTs-COOH and HAS-*f*-CNTs

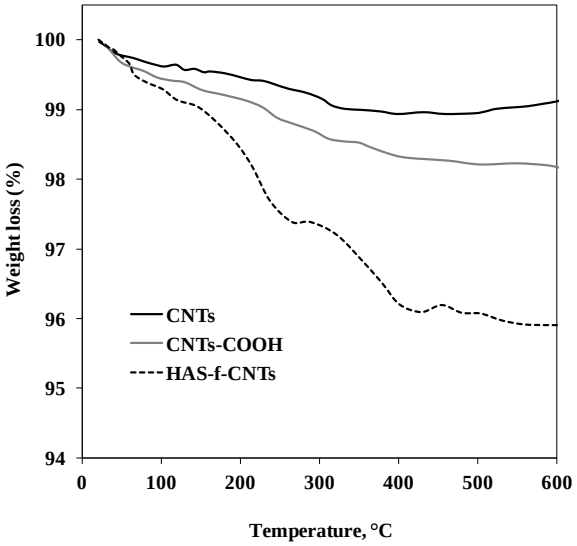
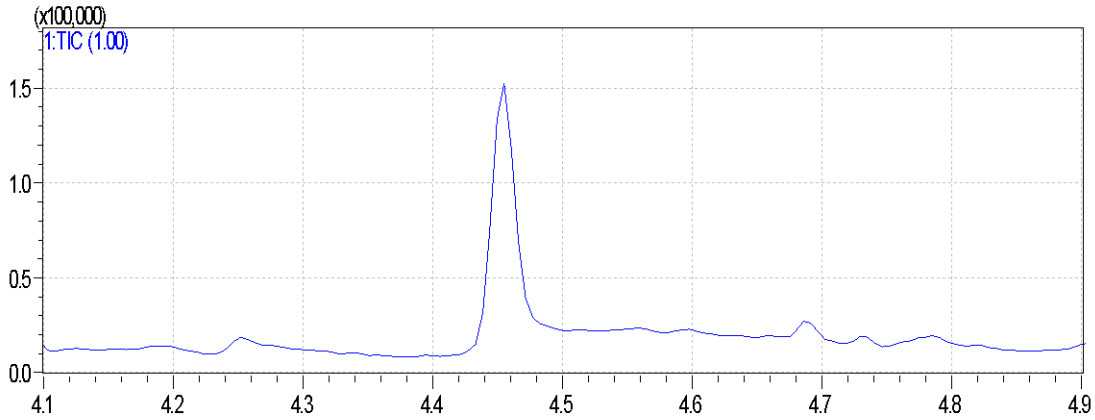
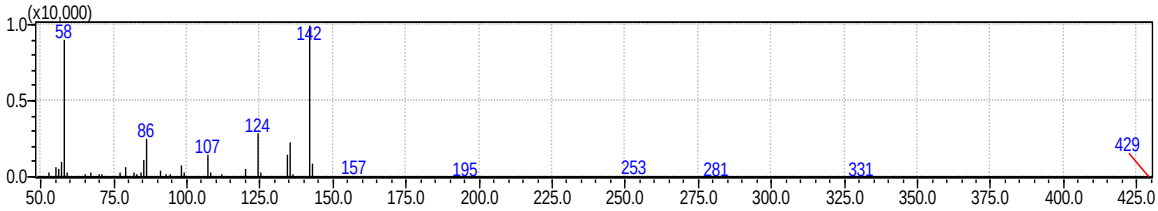


Figure 3. TGA curves of bare CNTs, CNTs-COOH and HAS-*f*-CNTs



(a)



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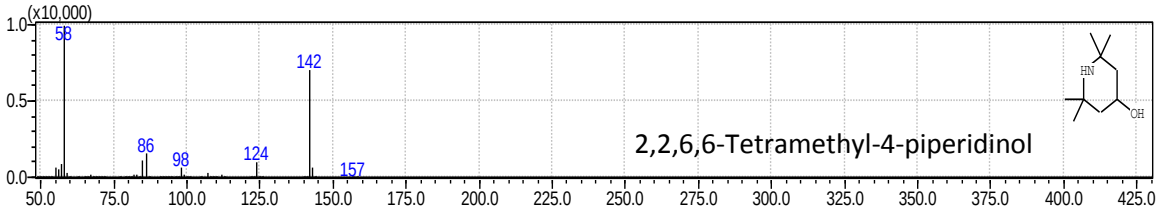
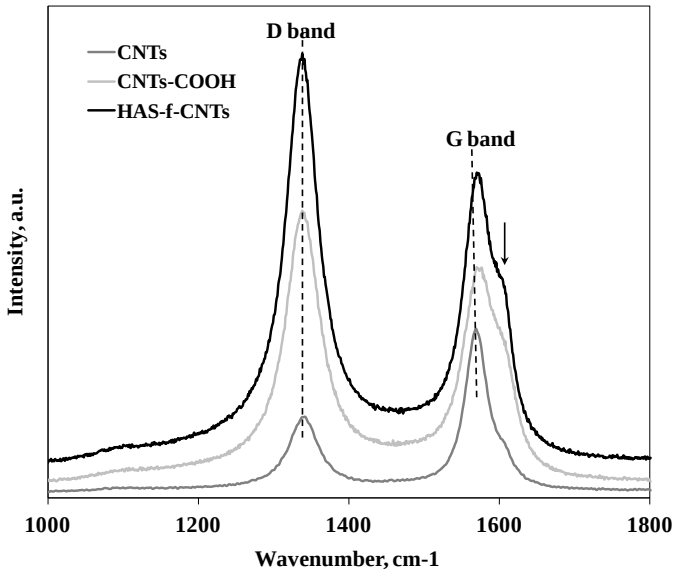


(c)

Figure 4. (a) An enlargement portion of Py-GC signal assigned to 2,2,6,6-tetramethyl-4-piperidinol in Py-GC MS and (b) corresponding mass spectrum matched with (c) database mass spectrum of 2,2,6,6-tetramethyl-4-piperidinol



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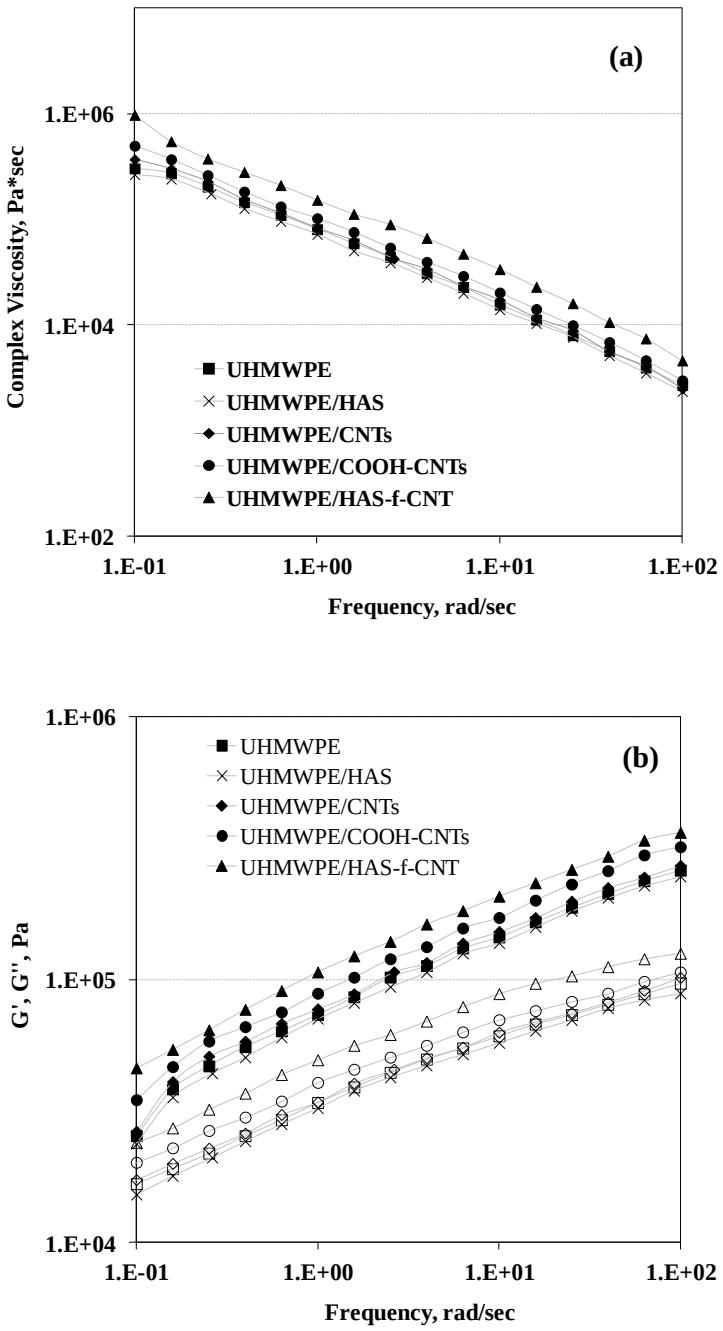

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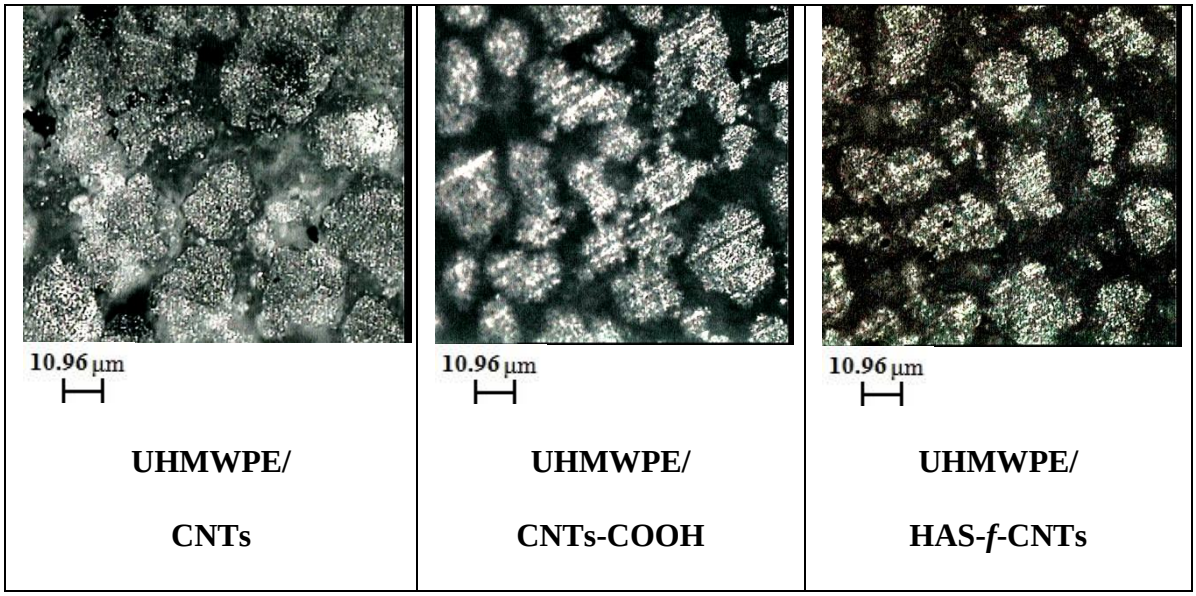
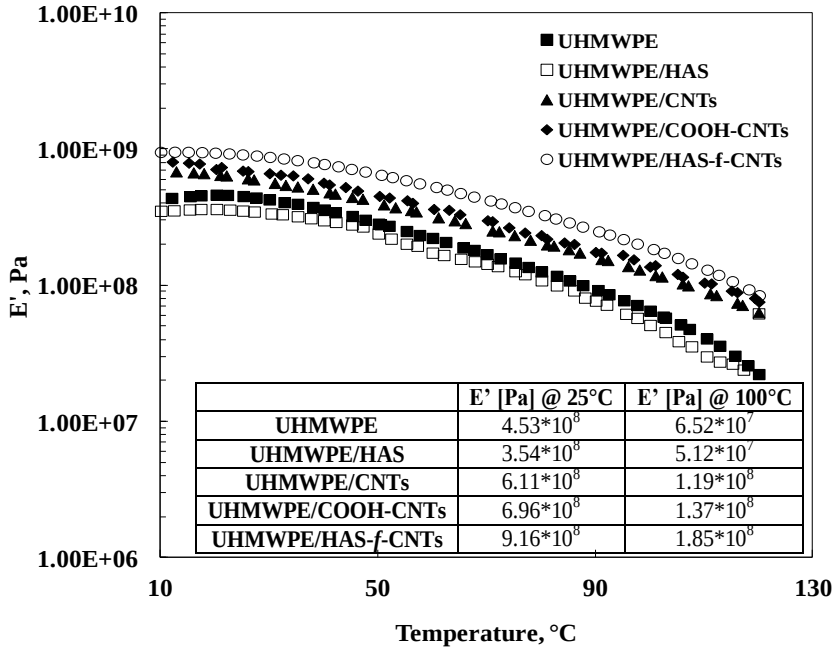


Figure 7. Optical micrographs of all investigated UHMWPE-based nanocomposites



	E' [Pa] @ 25°C	E' [Pa] @ 100°C
UHMWPE	$4.53*10^8$	$6.52*10^7$
UHMWPE/HAS	$3.54*10^8$	$5.12*10^7$
UHMWPE/CNTs	$6.11*10^8$	$1.19*10^8$
UHMWPE/COOH-CNTs	$6.96*10^8$	$1.37*10^8$
UHMWPE/HAS-*f*-CNTs	$9.16*10^8$	$1.85*10^8$

Figure 8. Elastic modulus E' as a function of temperature for all investigated systems

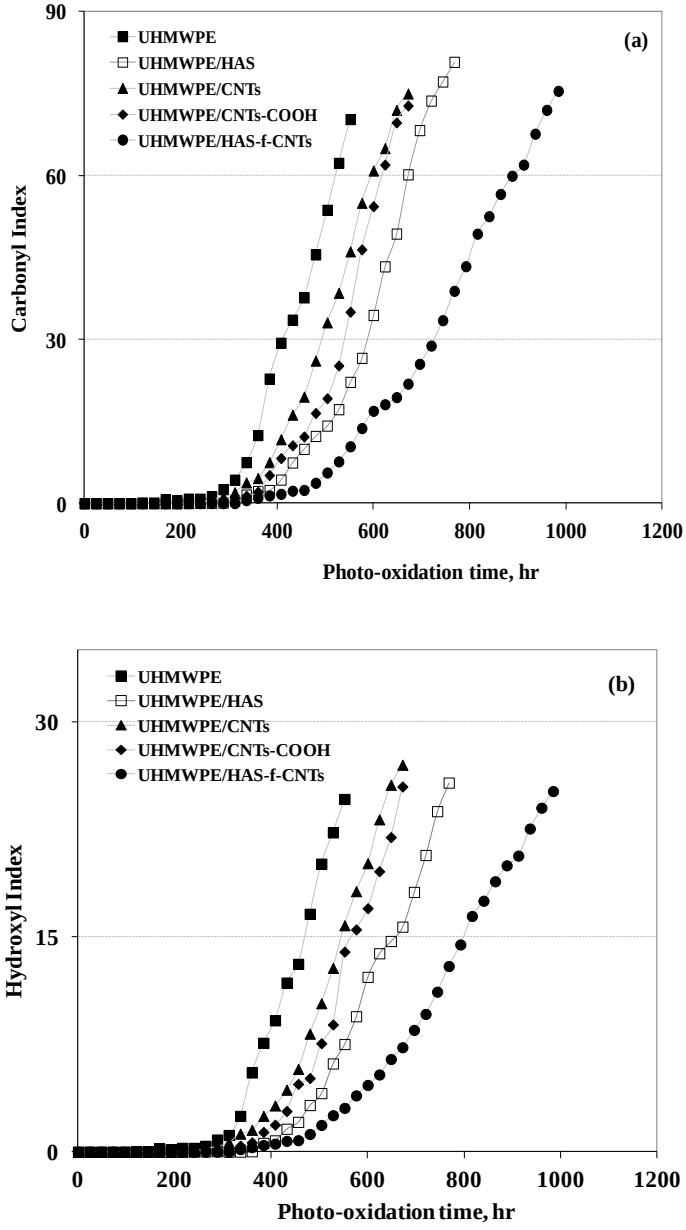


Figure 9. Carbonyl (a) and hydroxyl (b) indices as a function of the photo-oxidation time for all investigated systems