

Thermo-oxidative resistant nanocomposites containing novel hybrid-nanoparticles based on natural polyphenol and carbon nanotubes

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1. Introduction

Ultrahigh Molecular Weight PolyEthylene (UHMWPE) has many interesting properties including high strength and modulus, excellent toughness, good chemical and impact resistance, low moisture absorption, good wave transmission, and good electrical insulation [1–3]. However, oxidative degradation of UHMWPE is

one of the major drawbacks of this technical polymer, which might prevent its use in advanced applications. As an example, superior wear resistance, high fracture toughness and biocompatibility enable the use of UHMWPE in joint arthroplasty, but oxidative degradation has been often identified as a cause for implant failure [3]. In particular, free radicals generated by radiation sterilization or during crosslinking process (useful to improve the UHMWPE wear resistance) can react with oxygen through a cyclic process, leading to degradation of the polymer chains, with consequent loss of mechanical strength and wear resistance [4–6].

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Several strategies can be pursued to improve the oxidation resistance of UHMWPE. Post-irradiation thermal treatments can be conducted to bring down the radical content and improve the oxidation resistance of UHMWPE, but such a process may reduce the strength and the toughness of polymer [7]. Anti-oxidants and radical scavengers have been also used to reduce free radicals. However, the use of low molecular weight stabilizing systems is often restricted because of their possible physical loss by volatilization, migration, and water extraction [8,9]. One of the possible approaches is promoting an increase of the molecular weight of the anti-oxidant systems, for example through the introduction of long alkyl chains, which is the common industrial practice. On the other hand, if the molecular weight is too high, an inadequate dispersion of the antioxidant in the host matrix can eventually occur. The appropriate alkyl chain length is strictly dependent on the kind and intrinsic molecular weight of polymeric matrix, hence the formulation of universal stabilizing systems is not easy. Another possibility is the grafting of the stabilizing molecules directly onto the polymeric macromolecules [10]. However, such an approach envisages a multi-step chemical modification way, which is hard to control and, hence, unaffordable in industrial contexts. An innovative method to immobilize low molecular weight chemicals is their physical entrapment [11]. This approach allows to preserve the active functionalities in the structure of the molecules, that could be damaged through covalent linkage.

In recent years, the attention in the field of stabilizing agents has been focused on the use of compounds coming from natural sources because of their presumed safety and bio-compatibility [12–14]. In particular, natural vitamins [15,16] and polyphenols [17–19], easy available in nature, are widely studied and considered for several environmental applications. Among others, quercetin (Q) is a flavonoid with numerous biological activities, e.g. anti-cancer, antiviral and antioxidant [20–22], which has disclosed a great potential as stabilizing agent for polyolefins end biopolymers against both thermo-oxidation and UV radiation [23–25]. The immobilization of such a powerful molecule can be considered a promising way to overcome drawbacks arising from their easy volatilization at high temperatures during melt processing of polymer matrices, as well as migration issues during the manufacture life-time. In particular, the physical immobilization onto the outer surface of carbon nanotubes (CNTs) [26,27] allows to formulate multi-functional nanoparticles having in-build reinforcement and stabilizing actions.

In this work an innovative approach is proposed for the immobilization of Q molecules onto the outer surface of CNTs. The latter have been first functionalized with long alkyl chains. In a second distinct step, the anti-oxidant Q molecules have been entrapped between these long chains, aiming at preserving the integrity of active functionality of the stabilizing molecules. The so-obtained Q-functionalized CNTs have been compounded with UHMWPE to produce nanocomposite films, whose thermo-oxidation behaviour has been accurately investigated. The excellent thermo-oxidation resistance of the films has been explained by invoking a synergic effect stemming from the physical interaction between Q and CNTs, which causes a damage of the CNTs surface providing them with radical scavenging activity.

2. Experimental part

2.1. Materials

The UHMWPE is a commercial grade purchased by Sigma–Aldrich. It has weight-average molecular weight $3\div 6$ MDa, softening point $T = 136$ °C (Vicat, ASTM D 1525B), melting point $T_m = 138$ °C (determinate by DSC) and density 0.94 g/mL at 25 °C.

Commercial grade (Cheap Tubes, U.S.A.) multi-walled CNTs have been used. The main properties are: outer diameter $OD = 150\div 200$ 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 $SSA > 60$ m^2/g and electrical conductivity $EC > 10^{-2}$ S/cm.

Lauroyl peroxide, heptane, methanol, N,N-Dimethylformamide (DMF) and quercetin (Q), all supplied by Sigma–Aldrich, were used as received. The Q has molecular weight 302.24 g/mol.

2.2. CNT functionalization

2.2.1. Synthesis of lauroyl-f-CNTs

The CNTs have been subjected to chemical modification to obtain CNTs functionalised with long chain alkyl groups (lauroyl-f-CNTs) according to the chemical pathway represented in Fig. 1. First, 0.500 g of CNTs were added to the solution of lauroyl peroxide (1.0 g, 2.51 mmol) in 150 mL of heptane. The resulting suspension was then sonicated in a 2 L ultrasonic bath (power 260 W) for 15 min and left under vigorous stirring at 90 °C for 7 h. After that, the black suspension was filtered, the solid was washed 5 times with hot dimethylformamide (DMF) and 5 times with hot methanol, and it was finally dried at 80 °C overnight.

2.2.2. Immobilization/adsorption of Q molecules onto lauroyl-f-CNTs surface

The Q molecules have been immobilized onto the outer surface of the CNTs as follow: 0.200 g of lauroyl-f-CNTs were added to a solution of Q (0.100 g, 0.33 mmol) in 15 mL of THF. The resulting suspension was sonicated in a 2 L ultrasonic bath (power 260 W) for 30 min to allow for the entrapping of the anti-oxidant in between the alkyl chains linked to the CNTs. Then, the solute was filtered over a glass Buchner funnel and the black solid was dried at 105 °C for 5 h.

2.3. Nanocomposite preparation

The UHMWPE powder and 1 wt.% of CNTs were manually mixed at room temperature until a homogeneous black powder was obtained. Then the blends were hot compacted at 210 °C for 5 min and under a pressure of 1500 psi to get thin films (thickness less than 100 μ m) for the subsequent analyses. The pure UHMWPE film used as reference material was subjected to the same procedure.

2.4. Characterizations

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 $4000\text{--}400$ cm^{-1} with a spectral resolution between 9 and 15 cm^{-1} .

Thermo-Gravimetric analysis (TGA) was carried out using an Exstar TG/DTA Seiko 7200 instrument with a heating rate of 10 °C/min from 30 to 700 °C under nitrogen flow. The reported results are the average of three independent measurements on batches (around 5 mg) of CNTs and lauroyl-f-CNTs without and with immobilized Q molecules. The standard deviation was about 0.4% for each investigated sample.

ATR-FTIR analysis 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 (milligramme level) were obtained by accumulation of 32 scans between 4000 and 400 cm^{-1} , with a resolution of 4 cm^{-1} .

Rheological tests were performed using a strain-controlled rotational rheometer (ARES G2 by TA Instruments) in parallel

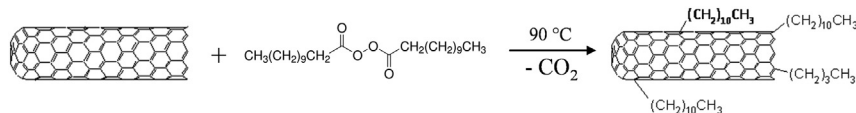


Fig. 1. Synthesis of lauroyl-f-CNTs.

plate geometry (plate diameter 25 mm). The complex viscosity (η^*) was measured performing frequency sweep tests at $T = 210^\circ\text{C}$ from 10^{-2} – 10^2 rad/s at a maximum strain of 2%. As proved by preliminary strain sweep experiments, such an amplitude is low enough to be in the linear viscoelastic regime. Besides, linear stress relaxation measurements were carried out submitting the samples to a single step strain $\gamma_0 = 1\%$, and the shear stress evolution during time $\sigma(t)$ was measured to obtain the relaxation modulus $G(t) = \sigma(t)/\gamma_0$.

Transmission Electron Microscopy (TEM) observations were performed at the Centro Grandi Apparecchiature – UninetLab, University of Palermo. The analyses were carried out on the ultrathin films with thickness of about 100 nm; they were prepared via cutting from the epoxy block with a Leica Ultramicrotome EMUC6. The ultrathin slides of the samples were mounted on lacey carbon films on 300 mesh copper grids and then observed using a Jeol JEM-2100 at 200 kV.

A Fourier Transform Infrared Spectrometer (FTIR) (Spectrum Two FTIR spectrometer, Perkin Elmer) was used to record the infrared spectra. FT-IR analyses were carried out to infer the advance of the degradation phenomena on nanocomposite films. Specifically, the samples were first treated in an air oven at $T = 120^\circ\text{C}$, which is a temperature lower than the T_m of the polymer but high enough to accelerate the degradation processes. Then, FT-IR spectra were collected performing 16 scans between 4000 and 500 cm^{-1} on samples subjected to thermo-oxidation for different exposure times. The carbonyl index (CI) was calculated as the ratio between the carbonyl absorption area (1850–1600 cm^{-1}) and the area of a reference peak at about 2019 cm^{-1} . The hydroxyl index (HI) was calculated as the ratio between the hydroxyl absorption area (3570–3150 cm^{-1}) and the area of the same reference peak. Since the previous indices are strictly related to the degradation phenomena, the progress of the latter was followed by monitoring the evolutions of CI and HI with the thermo-oxidation time.

3. Results and discussion

3.1. Assessment of CNTs covalent functionalization and physical immobilization of Q molecules

In order to assess the success of the covalent functionalization of CNTs with long chain alkyl groups, Raman spectra of the CNTs before and after chemical modification have been collected, see Fig. 2. Two prominent peaks are observed at about 1340 and 1570 cm^{-1} ; the first is identified as defect induced disorder mode (D band), which arises from sp^2 carbon samples containing structural defects. The peak at about 1580 cm^{-1} is the tangential mode (G band), which is caused by the in-plane vibrational motion of the carbon atoms [28,29]. Generally, the ratio of the Raman intensities of the D and G band (I_D/I_G) is used as a criterion for estimating the concentration of structural defects in CNTs: the higher the I_D/I_G ratio, the higher the concentration of defects [30]. The comparison shown in Fig. 2 clearly indicates that the chemical functionalization has remarkably damaged the CNT surface. Compared with bare CNTs, the intensity of D band of the lauroyl-f-CNTs is significantly increased, the I_D/I_G ratio passing from 0.478 to 1.147. In addition, the

shift of G band from 1567 cm^{-1} to 1560 cm^{-1} is a typical feature of chemical charge-transfer, and provides further direct evidence of the changes occurring in the graphite structures of the CNTs due to covalent functionalization [31].

The presence of Q molecules trapped in between the long alkyl chains covalently linked to the CNTs surface has been investigated through ATR-FTIR and TGA analyses. The ATR-FTIR spectra of pure Q and CNTs without and with immobilized antioxidant molecules are shown in Fig. 3. The ATR-FTIR spectrum of lauroyl-f-CNTs sample shows two peaks at 2916 and 2847 cm^{-1} attributed to stretching vibration of CH_2 e CH_3 groups, and a shoulder at 1362 cm^{-1} due to the symmetrical bending vibration of methyl groups. The ATR-FTIR spectrum of pure quercetin shows the characteristic bands corresponding to: (i) OH groups (broad peak centered at about 3200 cm^{-1}); (ii) C=O absorption (1662 cm^{-1}); (iii) bands of C–C stretching (1618 cm^{-1}); C–H bending (1456, 1383, and 866 cm^{-1}); a band attributed to the C–O stretching of the oxygen in the ring (1272 cm^{-1}); the region for C–O stretching (1070–1150 cm^{-1}) [32]. Such specific bands are clearly detectable in the spectrum of lauroyl-f-CNTs/Q, clearly revealing the presence of Q molecules in this sample.

Additional convincing proofs of the presence of Q molecules physically immobilized onto the lauroyl-f-CNTs surface come from the results of TGA analysis reported in Fig. 4. Apart from the weight loss around 100 $^\circ\text{C}$, which is probably due to the loss a small amounts of residual water in all the CNTs samples, the lauroyl-f-CNTs sample exhibits a gradual weight loss related to the decomposition of the alkyl chains grafted on the CNT surface. The residuals at the end of the analysis were 97.3 wt.% lauroyl-f-CNTs sample, whereas a residual of 99.1 wt.% was found for the bare CNTs due to a partial decomposition of the bulk material. The lauroyl-f-CNTs/Q exhibits an additional weight loss due to the volatilization of Q molecules, which begins at about 200 $^\circ\text{C}$. The residue at the

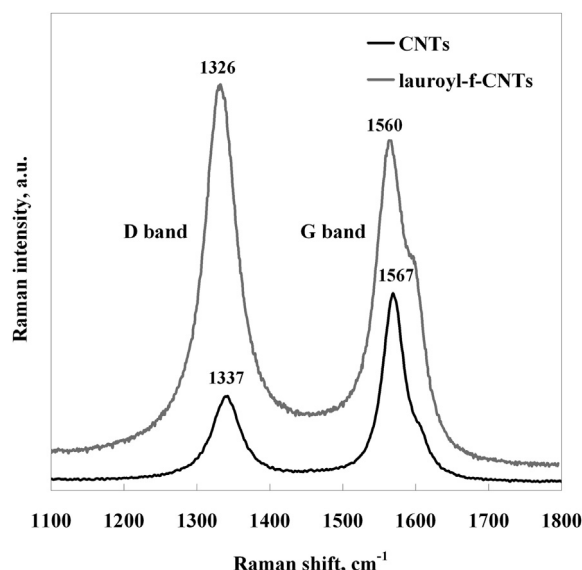


Fig. 2. Raman spectra of bare CNTs, and lauroyl-f-CNTs.

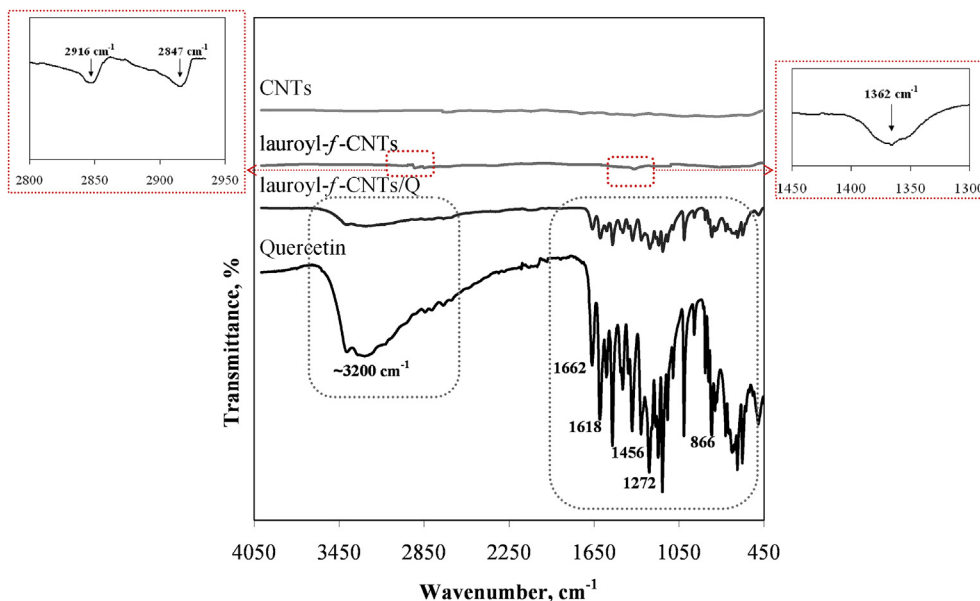


Fig. 3. ATR-FTIR spectra of bare CNTs, and lauroyl-*f*-CNTs without and with immobilized Q.

end of the analysis for lauroyl-*f*-CNTs/Q is about 96.0 wt.%, meaning that about 1 wt.% of Q is physically immobilized on the CNTs at the end of the functionalization procedure. This is in quantitative agreement with the amount of quercetin used during CNTs functionalization.

3.2. Rheological behaviour and morphology of nanocomposites

The rheological analysis of polymer nanocomposites provides useful information in terms of state of dispersion of the nanoparticles. Here, linear viscoelastic measurements are used to infer the state of dispersion of nanoparticles through the analysis of their impact on the relaxation spectrum.

The complex viscosity (η^*) curves and elastic moduli (G') of the neat UHMWPE and their nanocomposites are shown in Fig. 5 as a function of frequency. The neat polymer essentially exhibits power-law behaviour, showing signals of relaxation (plateauing of $\eta^*(\omega)$

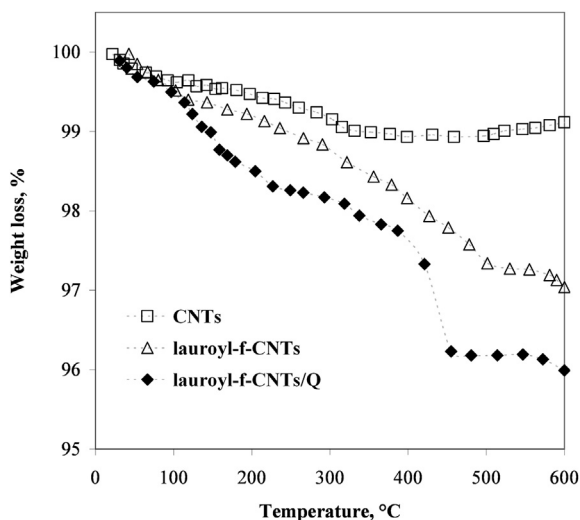
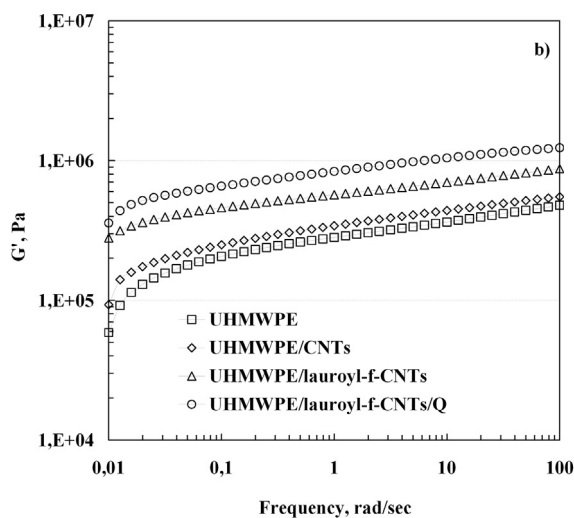
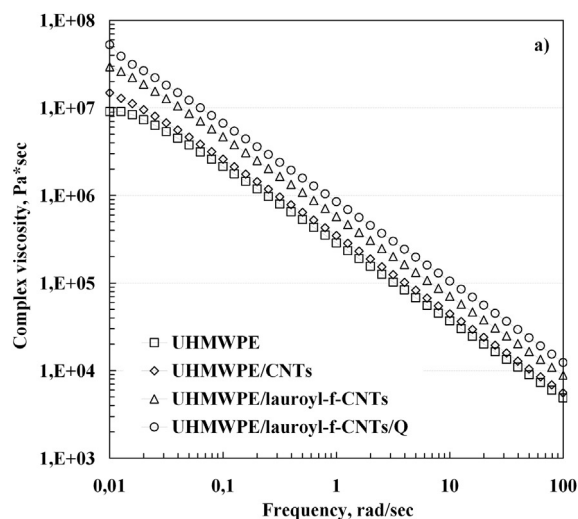


Fig. 4. TGA analysis of unmodified CNTs, and lauroyl-*f*-CNTs without and with immobilized Q.

Fig. 5. Complex viscosity (a) and G' modulus (b) of UHMWPE based nanocomposites. The complex viscosity of the neat polymer is reported for comparison.

and drop of $G'(\omega)$) only at the lowest investigated frequencies, i.e. over timescales of order of $2\pi/10^{-2} \sim 600$ s. Such a markedly non-Newtonian behaviour reflects the very high molecular weight of the polymer, whose chains are so entangled to require very long times to relax. The η^* values of all nanocomposites are generally higher than those of neat UHMWPE in the whole investigated frequency range. However, subtle and yet significant differences emerge when comparing the three samples. The bare CNTs have a negligible effect, causing a mere upward shift of the $\eta^*(\omega)$ curve. This means that the unmodified nanoparticles only have a hydrodynamic effect, which is typical of badly dispersed fillers. In contrast, functionalizing the CNTs with long alkyl chains enhances the affinity with the polyolefin matrix, and this is expected to improve their dispersability. This is consistent with the increased values of η^* and G' and, more importantly, with the disappearance of relaxation processes at low frequency noticed for both the nanocomposites containing lauroyl-*f*-CNTs and lauroyl-*f*-CNTs/Q.

The ability of better dispersed CNTs to hinder the polymer relaxation processes has been confirmed with stress relaxation measurements. The shear relaxation moduli, $G(t)$, of the neat UHMWPE and its nanocomposites are compared in Fig. 6. The pure polymer and the sample filled with bare CNTs relax in ~ 600 s, which is in quantitative agreement with the frequency sweep experiments. In contrast, $G(t)$ does not exhibit any sign of drop in the nanocomposites containing the lauroyl-*f*-CNTs, either with or without immobilized quercetin. Interestingly, the latter ensures higher moduli, which might indicate an even better filler dispersion. This is important for the purpose of oxidation resistance, as a good dispersion is expected to maximize the contact with the polymer, thus optimizing the stabilizing action of quercetin.

TEM micrographs of the investigated UHMWPE-based nanocomposites are shown in Fig. 7. The bare CNTs are not uniformly dispersed into the polymeric matrix as suggested by rheological analysis. The presence of long alkyl chains onto the CNTs surface significantly improves the distribution and this feature is exacerbated by the presence of physically immobilized Q molecules.

3.3. Thermo-oxidative behaviour of nanocomposites

The protective action of the Q molecules immobilized on CNTs against the thermo-oxidative degradation is investigated through

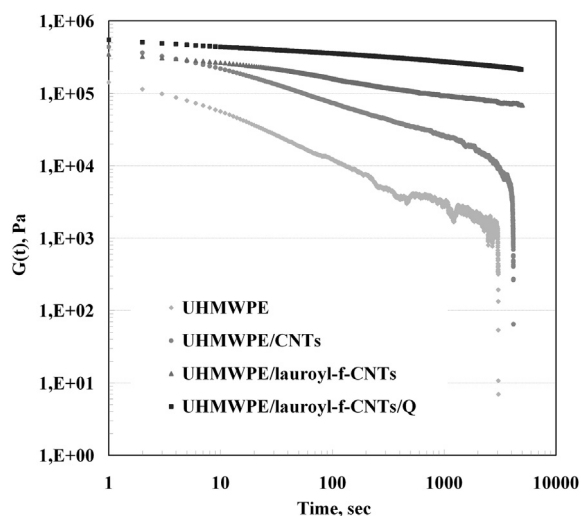


Fig. 6. Linear stress relaxation moduli for neat UHMWPE and all CNTs-based nanocomposites.

the analysis of the evolution time of the FT-IR spectra of the nanocomposites during a thermo-oxidation process performed in an air oven at 120 °C. In particular, the growth of carbonyl (CI) and hydroxyl (HI) indices is monitored in the course of thermo-oxidation. The CI assesses the intensity of the peaks in the range 1850–1600 cm^{-1} , thus reflecting the formation of carboxylic acids (1713 cm^{-1}), ketones (1718 cm^{-1}), esters (1738 cm^{-1}), and lactones (1786 cm^{-1}) in the course of degradation [33]. As far as the HI is concerned, it refers to the hydroxyl absorption area (3570–3150 cm^{-1}) and, hence, it is related to the formation of free and linked $-\text{OH}$ groups deriving from the thermo-oxidation process [33]. Regarding the frequency of analysis, in order to accurately monitor the evolution of the degradation process at the early stage of the thermo-oxidative treatment, FT-IR spectra were collected every 2 h for the first 30 h of thermo-oxidation, being shown in Fig. 8 (range 1840–1600 cm^{-1}) and Fig. 9 (range 3600–3100 cm^{-1}). After the first 30 h, one estimate per day was carried out for about one month.

The calculated carbonyl and hydroxyl indices are reported in Figs. 10 and 11, respectively. As shown in the enlarged zones, the amount of the carbonyl and hydroxyl species for the neat UHMWPE starts growing till the beginning of measurements, meaning that degradation begins in the early stage of the thermo-oxidation process. A kind of induction time t_i can be conventionally defined as the time needed for CI reaches the value of 5 and HI reaches 2: for times $t < t_i$ the indices grow very slowly, while around t_i a sudden switch of the kinetics takes place, and the growth becomes very fast reflecting the progress of degradation. It is important to highlight that the chemical modifications, which occur during such later stages, are coupled to a considerable embrittlement of the material. The estimated t_i values are summarized in Table 1. The quantitative agreement between the values computed from CI and HI indicates that both indices are suited for monitoring the degradation of UHMWPE. The nanocomposite containing lauroyl-*f*-CNTs shows slightly enhanced thermo-oxidative resistance. Such a result can be ascribed to the well-documented anti-oxidant effect of CNTs [34–36]. The adding of 0.1 wt.% of free quercetin results in a considerable improvement of the thermo-oxidation behaviour of UHMWPE. More precisely, the induction time almost triples upon simply addition of free quercetin. This is essentially in line with what reported in the literature [37,38]. In particular, Tátraaljai et al. ascribed the stabilizing action of quercetin to the presence of a large number of active $-\text{OH}$ groups, whose are able to scavenge both carbon and oxygen centered radicals present in polyethylene during degradation.

On the other hand, the drastic improvement of the thermo-oxidative resistance of the samples containing the lauroyl-*f*-CNT/Q is unexpected. A ten-fold increase of t_i is noticed with respect to neat UHMWPE. Furthermore, we also notice that the samples containing the lauroyl-*f*-CNT/Q exhibit a slower grow rate of both CI and HI after the induction period. Quercetin molecule is known to be efficient in the protection of the polymeric matrices against thermo-oxidation, but the excellent stabilizing action achieved in our samples is much higher than what one would expect considering the effect of adding Q and lauroyl-*f*-CNTs separately.

Similar remarkable results were recently obtained by our research group using CNTs bearing physically absorbed Vitamin E molecules [26]. In that case, taking into account theoretical studies that predict strong interaction between ascorbic acid (vitamin C) and nicotinamide (vitamin B3) and the carbon atoms of CNTs [39,40], the surprisingly high resistance to thermo-oxidation was ascribed to the establishing of specific chemical interactions between VE molecules and the CNTs. In more detail, these interactions induce the formation of CNT surface defects, which promote the formation of acceptor-like localised states eventually inducing a pronounced radical scavenging activity of the CNTs.

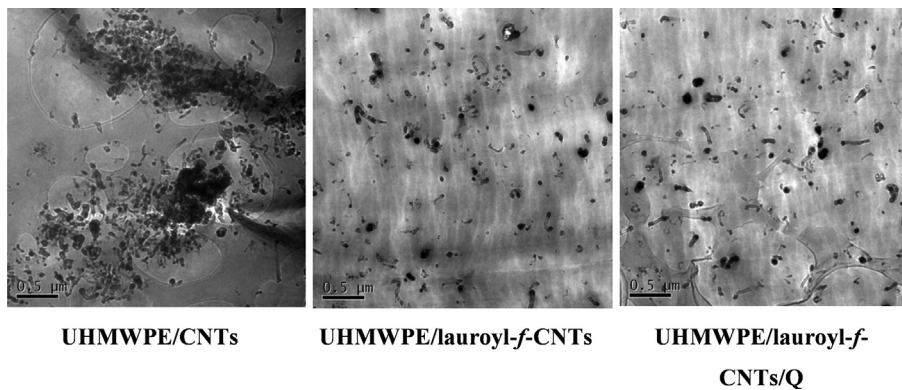


Fig. 7. TEM micrographs of investigated nanocomposites.

Similar conclusions can be drawn to explain the present results. Specifically, the radical intermediates coming from Q molecules can interact with the CNT surface, inducing a degeneracy of the electronic system of the CNTs that breaks their mirror symmetry. As a consequence, some carbon atoms of the CNTs outer surface change the hybridization from sp^2 to sp^3 , resulting in lattice defects onto the CNTs surface that induce radical scavenging activity. Increased free-radical scavenging activity as a consequence of presence of structural defects in the carbon lattice of CNTs is a documented

phenomenon [41], which has been also predicted by Galano et al. through theoretical studies [42].

To sum up, the unexpected excellent thermo-resistance of the lauroyl-*f*-CNTs/Q containing nanocomposites seems to be due to a synergic effect of the natural anti-oxidant and carbon nanotubes, i.e. strong interaction between the CNT surface and Q molecules. It is worth noting that the simply covalent functionalization of the CNTs with long alkyl chains, which also generate a damage of their outer surface (see Fig. 2), is not sufficient to induce noticeable

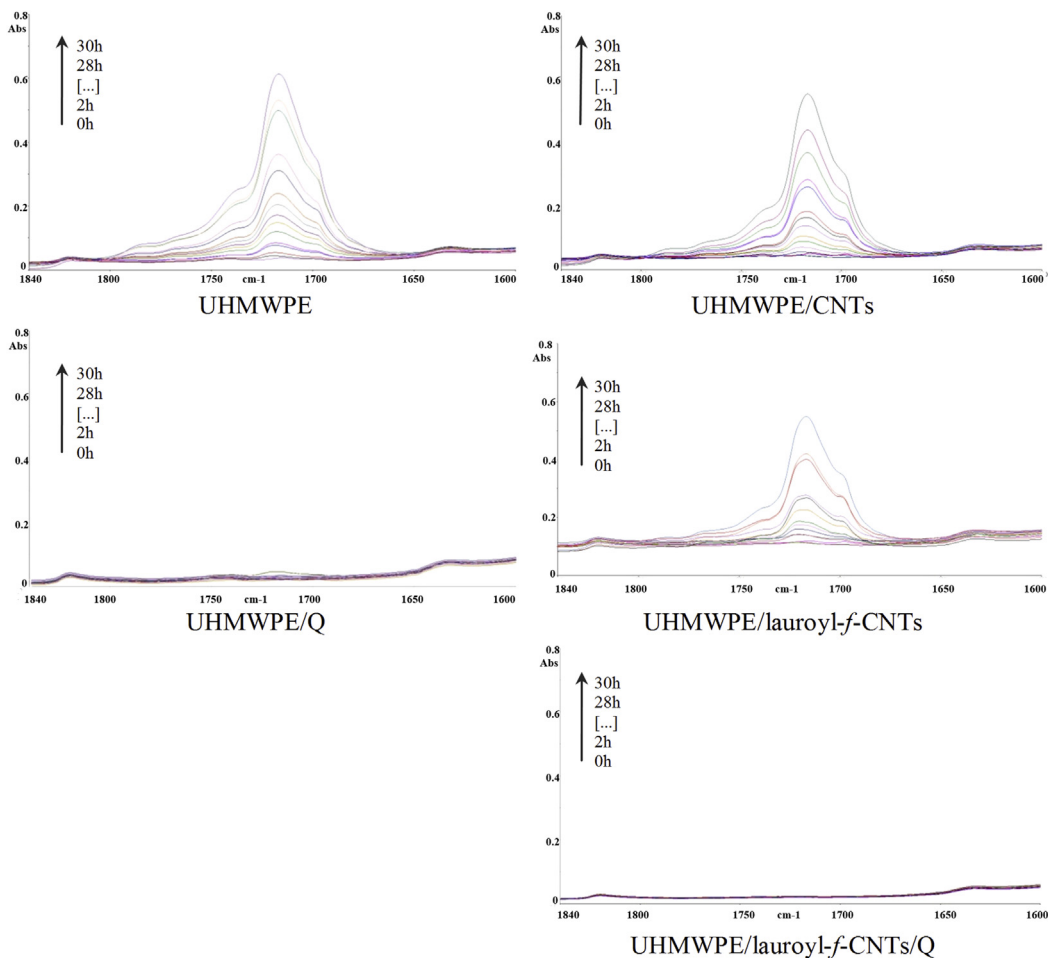


Fig. 8. FT-IR spectra (range 1840–1600 cm^{-1}) up to 30 h of thermo-oxidative treatment for all investigated samples.

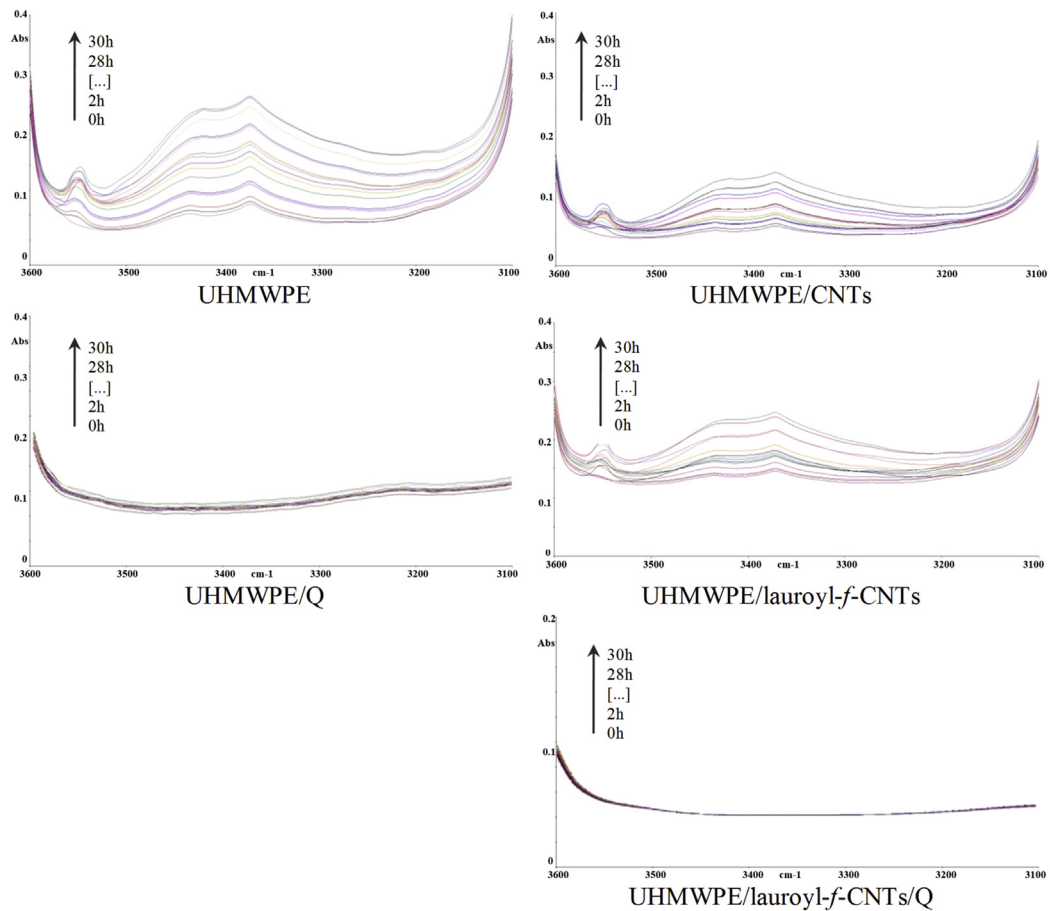


Fig. 9. FT-IR spectra (range 3600–3100 cm^{-1}) up to 30 h of thermo-oxidative treatment for all investigated samples.

stabilizing action. This means that the establishing of specific interactions between the Q molecules and the CNTs is strictly required to fully exploit the stabilizing potential of the systems of interest.

Moreover, it cannot be excluded that the proposed mechanism is combined with the regeneration of Q via interaction with the defected CNTs, similarly to the mechanism of synergism between vitamin E and vitamin C [43]. If Q is added alone to the polymer it is consumed linearly with time during the inhibition period and a fast

oxidation occurs when it is depleted. The conservation of Q for a longer time, that contributes to increase the UHMWPE stability, is likely ascribed to the reduction of Q radical by the defected CNTs. Q scavenges the polymer radicals to interrupt their propagation and the resulting Q radical is reduced by defected CNTs to regenerate Q (Fig. 12).

Finally, another factor that is also expected to play a role is the degree of dispersion of CNTs. Quercetin is known to have low solubility in polyethylene [37]. Immobilizing it onto CNTs and using

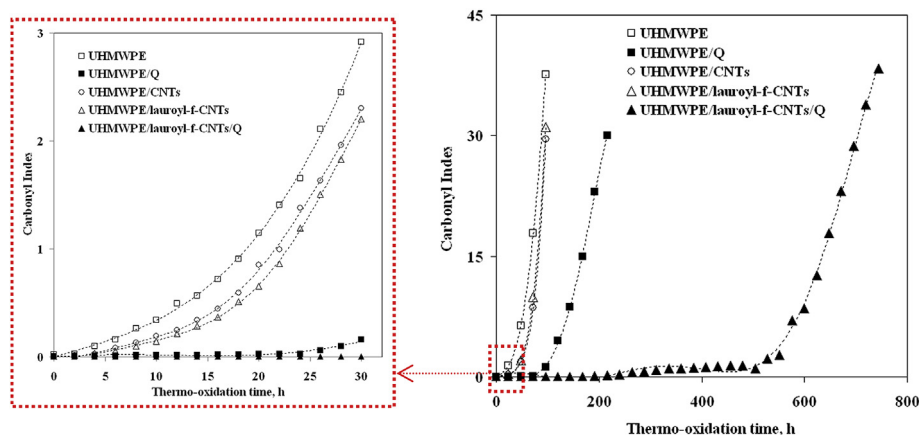


Fig. 10. Carbonyl index (CI) as a function of the thermo-oxidation time for all investigated systems. On the left is reported the evolution of CI at the early stage of thermo-oxidation process.

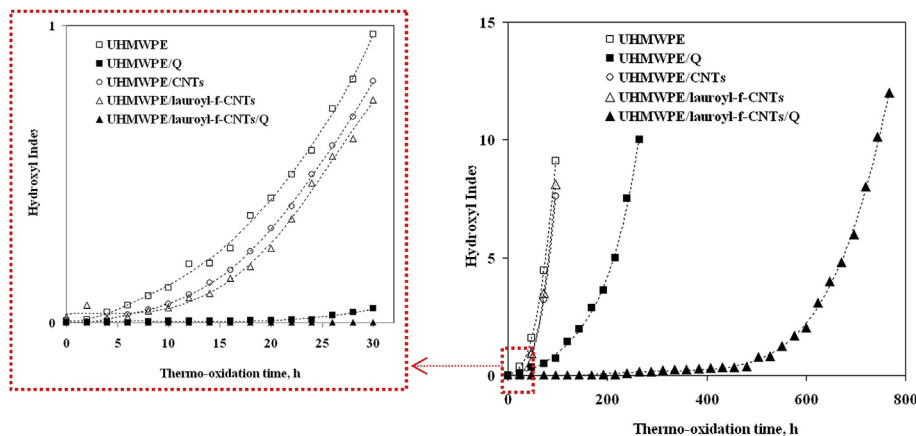


Fig. 11. Hydroxyl index (HI) as a function of the thermo-oxidation time for all investigated systems. On the left is reported the evolution of HI at the early stage of thermo-oxidation process.

Table 1
Values of the thermo-oxidation induction time.

Sample	t_i @ CI = 5 [h]	t_i @ HI = 2 [h]
UHMWPE	43	50
UHMWPE/Q	125	136
UHMWPE/CNTs	63	62
UHMWPE/lauroyl-f-CNTs	60	60
UHMWPE/lauroyl-f-CNTs/Q	565	577

the latter as nano-carriers could maximize the contact of the Q molecules with the host matrix, allowing for a better exploitation of their inherent anti-oxidant features.

4. Conclusions

Quercetin was physically immobilized on multi-walled carbon nanotubes covalently functionalized with long alkyl chains (C_{14}), and the so-obtained hybrid nanoparticles were used as multifunctional fillers to obtain thermo-oxidative stable UHMWPE nanocomposites. The success of CNT functionalization and physical immobilization of the Q molecules was demonstrated through micro-Raman, ATR-FTIR and TGA analyses. Rheological analyses carried out on nanocomposite polymer films and morphological analysis showed that the functionalized CNTs are better dispersed than their bare counterpart. The monitoring of the carbonyl and hydroxyl indices via FTIR analyses confirmed that quercetin is a good stabilizing agent for polyethylene. However, an exceptionally high thermo-oxidation resistance was found when the Q molecules are physically immobilized on the CNT outer surface. Such an unexpected finding confirms recent results obtained by our group with another natural anti-oxidant molecule such as α -tocopherol [28], demonstrating that synergic effects set up because of specific

chemical interactions between the natural anti-oxidant molecules and the CNT outer surface. As a result, a radical improvement of thermo-oxidation resistance is achieved owing to the formation of CNT surface defects, which confer marked radical scavenging features to the nanotubes. Besides, this mechanism could be combined with the regeneration of Q via interaction with the defected CNTs. Finally, CNTs seem acting as efficient nano-carriers for the quercetin molecules, improving the dispersion of the latter in the host matrix in spite of their poor solubility. Overall, our results demonstrate that physically immobilizing natural anti-oxidant molecules on nanoparticles, and using the latter as multifunctional filler for nanocomposites, is a viable route towards to produce high-performance polymeric materials.

Acknowledgements

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References

- [1] Lewis G. Properties of crosslinked ultra-high-molecular-weight polyethylene. *Biomaterials* 2001;22(4):371–401.
- [2] Ding H, Tian Y, Wang L, Liu BJ. Preparation of ultrahigh-molecular-weight polyethylene membranes via a thermally induced phase-separation method. *J Appl Polym Sci* 2007;105(6):3355–62.
- [3] Ogawa T, Mukai H, Osawa S. Effects of functional groups and surface roughness on interfacial shear strength in ultrahigh molecular weight polyethylene fiber/polyethylene system. *J Appl Polym Sci* 1999;71(2):243–9.
- [4] Kurtz SM, Muratoglu OK, Evans M, Edidin AA. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. *Biomaterials* 1999;20(18):1659–88.
- [5] Premnath V, Harris WH, Jasty M, Merrill EW. Gamma sterilization of UHMWPE articular implants: an analysis of the oxidation problem. *Biomaterials* 1996;17(18):1741–53.
- [6] McKellop H, Shen FW, Lu B, Campbell P, Salovey R. Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. *J Orthop Res* 1999;17(2):157–67.
- [7] Atwood S, Van Citters DW, Patten EW, Furmanski J, Ries MD, Pruitt LA. Tradeoffs amongst fatigue, wear, and oxidation resistance of cross-linked ultra-high molecular weight polyethylene. *J Mech Behav Biomed Mater* 2011;4(7):1033–45.
- [8] Lundbaeck M, Strandberg C, Albertsson A, Hedenqvist MS, Gedde UW. Loss of stability by migration and chemical reaction of Santonox R in branched polyethylene under anaerobic and aerobic conditions. *Polym Degrad Stab* 2006;91(5):1071–8.

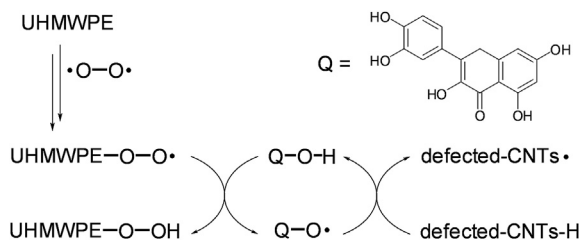


Fig. 12. Proposed mechanism of Q regeneration.

- [9] Billingham NC. Chapter 4-The physical chemistry of polymer oxidation and stabilization. In: Scott G, editor. Atmospheric oxidation and antioxidants atmospheric oxidation and antioxidants. Amsterdam: Elsevier; 1993. p. 219–77.
- [10] Al-Malaika S, editor. Reactive modifiers for polymers. London: Blackie, Academic and Professional, an imprint of Chapman and Hall; 1997. ISBN 0-7514 0265 6.
- [11] Chen RJ, Zhang Y, Wang D, Dai H. Noncovalent Sidewall functionalization of single-walled carbon nanotubes for protein immobilization. *J Am Chem Soc* 2001;123(16):3838–9.
- [12] Ambrogi V, Cerruti P, Carfagna C, Malinconico M, Marturano V, Perrotti M, et al. Natural antioxidants for polypropylene stabilization. *Polym Degr Stab* 2011;96(12):2152–8.
- [13] Tátraaljai D, Major L, Földes E, Pukánszky B. Study of the effect of natural antioxidants in polyethylene: performance of β -carotene. *Polym Degr Stab* 2014;102:33–40.
- [14] Tátraaljai D, Kirschweng B, Kovács J, Földes E, Pukánszky B. Processing stabilisation of PE with a natural antioxidant, curcumin. *Eur Polym J* 2013;49(6): 1196–203.
- [15] Al-Malaika S, Ashley H, Issenhuth S. The antioxidant role of α -tocopherol in polymers. I. The nature of transformation products of α -tocopherol formed during melt processing of LDPE. *J Polym Sci Part A Pol Chem* 1994;32(16): 3099–113.
- [16] Al-Malaika S, Goodwin C, Issenhuth S, Burdick D. The antioxidant role of α -tocopherol in polymers II. Melt stabilising effect in polypropylene. *Polym Degr Stab* 1999;64(1):145–6.
- [17] Fu J, Shen J, Gao G, Xu Y, Hou R, Cong Y, et al. Natural polyphenol-stabilised highly crosslinked UHMWPE with high mechanical properties and low wear for joint implants. *J Mater Chem B* 2013;1:4727–35.
- [18] Shen J, Costa L, Xu Y, Cong Y, Cheng Y, Liu X, et al. Stabilization of highly crosslinked ultra high molecular weight polyethylene with natural polyphenols. *Polym Degr Stab* 2014;105:197–205.
- [19] Shen J, Liu X, Fu J. Effect of squalene absorption on oxidative stability of highly crosslinked UHMWPE stabilized with natural polyphenols. *Polym Degr Stab* 2014;110:113–20.
- [20] Cao G, Sofic E, Prior RL. Antioxidant and prooxidant behavior of flavonoids: structure–activity relationships. *Free Radic Biol Med* 1997;22(5):749–60.
- [21] Osorio E, Pérez EG, Areche G, Ruiz LM, Cassels BK, Flórez E, et al. Why is quercetin a better antioxidant than taxifolin? Theoretical study of mechanisms involving activated forms. *J Mol Model* 2013;19(5):2165–72.
- [22] Cirillo G, Vittorio O, Hampel S, Iemma F, Parchi P, Cecchini M, et al. Quercetin nanocomposite as novel anticancer therapeutic: Improved efficiency and reduced toxicity. *Eur J Pharm Sci* 2013;49(3):359–65.
- [23] Samper MD, Fages E, Fenollar O, Boronat T, Balart R. The potential of flavonoids as natural antioxidants and UV light stabilizers for polypropylene. *J Appl Polym Sci* 2013;129(4):1707–16.
- [24] Dintcheva NT, La Mantia FP, Arrigo R. Natural compounds as light stabilizer for a starch-based biodegradable polymer. *J Polym Eng* 2014;34(5):441–9.
- [25] Morici E, Arrigo R, Dintcheva NT. Quercetin as natural stabilizing agent for bio-polymer. *AIP Conf Proceed* 2014;1599:314–7.
- [26] Dintcheva NT, Arrigo R, Gambarotti C, Carroccio S, Filippone G, Cicogna F, et al. α -Tocopherol-induced radical scavenging activity in carbon nanotubes for thermo-oxidation resistant ultra-high molecular weight polyethylene-based nanocomposites. *Carbon* 2014;74:14–21.
- [27] Nichita C, Stamatini I. The anti-oxidant activity of the biohybrides based on carboxylated/hydroxylated carbon nanotubes – flavonoid compounds. *Dig J Nanomat Biostruct* 2013;8(1):445–55.
- [28] Dewald JL, Talla J, Pietrass T, Curran SA. Defect analysis of carbon nanotubes. *Electron Prop Nov Nanostruct* 2005;786:215–9.
- [29] Borowiak-Palen E, Costa S, Kruszynska M, Bachmatiuk A, Kalenczuk RJ. Characterization of carbon nanotubes by Raman spectroscopy. *Mater Sci Pol* 2008;26:433–41.
- [30] Qian WZ, Liu T, Wei F, Yuan HY. Quantitative Raman characterization of the mixed samples of the single and multi-walled carbon nanotubes. *Carbon* 2003;41:1851–4.
- [31] Holzinger M, Abraham J, Whelan P, Graupner R, Ley L, Hennrich F, et al. Functionalization of single-walled carbon nanotubes with (R)-Oxycarbonyl nitrenes. *J Am Chem Soc* 2003;125(28):8566–80.
- [32] Pool H, Quintanar D, Figueroa J, Marinho Mano C, Bechara E, Godínez LA, et al. Antioxidant effects of quercetin and catechin encapsulated into PLGA nanoparticles. *J Nanomater* 2012;2012:12. Article ID 145380.
- [33] Costa L, Luda MP, Trossarelli L. Ultra high molecular weight polyethylene—II. Thermal- and photo-oxidation. *Polym Degr Stab* 1997;58(1–2):41–54.
- [34] Watts PCP, Fearon PK, Hsu WK, Billingham NC, Kroto HW, Walton DRM. Carbon nanotubes as polymer antioxidant. *J Mater Chem* 2003;13(3):491–5.
- [35] Martínez-Morlanes MJ, Castell P, Alonso PJ, Martínez MT, Puertolas JA. Multi-walled carbon nanotubes acting as free radical scavengers in gamma-irradiated ultrahigh molecular weight polyethylene composites. *Carbon* 2012;50(7):2442–52.
- [36] Dintcheva NT, La Mantia FP, Malatesta V. Photo-oxidation behaviour of polyethylene/multi-wall carbon nanotube composite films. *Polym Degr Stab* 2009;94(2):162–70.
- [37] Tátraaljai D, Földes E, Pukánszky B. Efficient melt stabilization of polyethylene with quercetin, a flavonoid type natural antioxidant. *Polym Degr Stab* 2014;102:41–8.
- [38] Koontz JL, Marcy JE, O'Keefe SF, Duncan SE, Long TE, Moffitt RD. Polymer processing and characterization of LLDPE films loaded with α -tocopherol, quercetin, and their cyclodextrin inclusion complexes. *J Appl Polym Sci* 2010;117(4):2299–309.
- [39] De Menezes VM, Fagan SB, Zanella I, Mota R. Carbon nanotubes interacting with vitamins: first principles calculations. *Microelectr J* 2009;40(4–5): 877–9.
- [40] Cadore AR, Zanella I, de Menezes VM, Rossato J, Mota R, Fagan SB. Metal-doped carbon nanotubes interacting with vitamin C. *Phys Chem Chem Phys* 2012;14(48):16737–44.
- [41] Shi X, Jiang B, Wang J, Yang Y. Influence of wall number and surface functionalization of carbon nanotubes on their antioxidant behaviour in high density polyethylene. *Carbon* 2012;50(3):1005–13.
- [42] Galano A, Francesco-Marquez Martínez A. Influence of point defects on the free-radical scavenging capability of single-walled carbon nanotubes. *J Phys Chem C* 2010;114(18):8302–8.
- [43] Niki E. Interaction of ascorbate and α -tocopherol. *Ann N. Y Acad Sci* 1987;498: 186–99.