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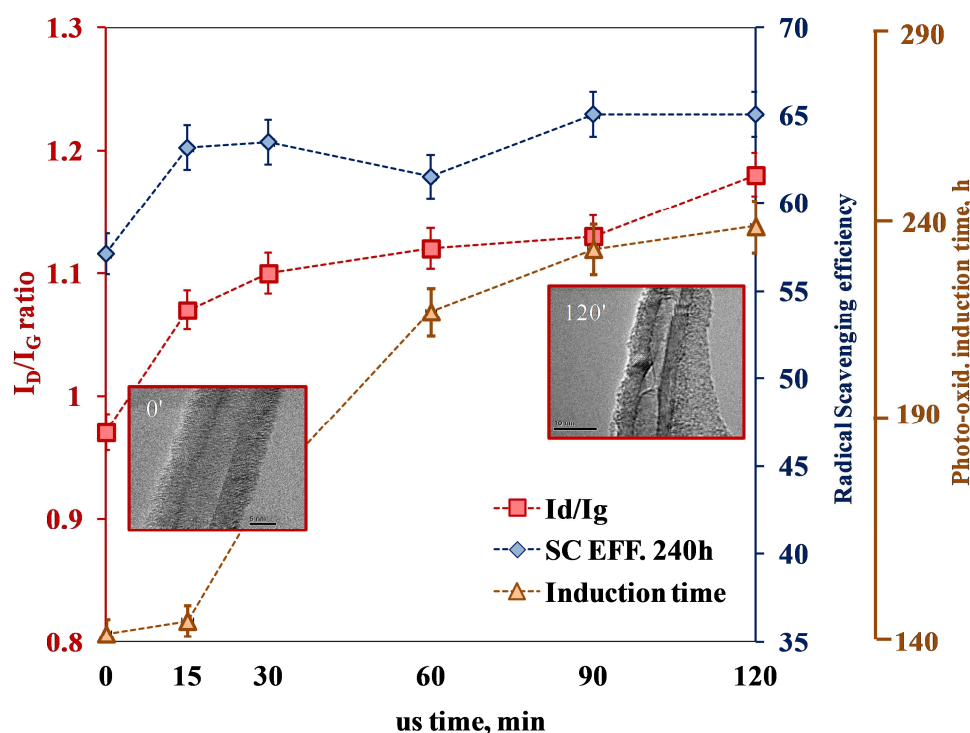
Tunable Radical Scavenging Activity of Carbon Nanotubes through Sonication

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Abstract

Carbon nanotubes (CNTs) having controlled radical scavenging activity have been achieved tuning the content of their lattice defects induced by an ultra-sound (us) treatment. The reactivity of CNTs, subjected to ultra-sonication for different time intervals, toward 1,1-diphenyl-2-picryl (DPPH) and hydroxyl ($\bullet\text{OH}$) radicals has been estimated and related to defect concentration, evaluated through Raman spectrometry. The radical scavenging efficiency of ultra-sound treated CNTs (us-CNTs) increases with increasing the content of the structural defects, suggesting that the defect resulting from us treatment can be capitalized to obtain an amplified and controlled radical scavenging activity. The us-CNTs have been incorporated in ultra high molecular weight polyethylene (UHMWPE) matrix by hot compaction with the aim to exploit their anti-oxidant activity against photo- and thermo- oxidative degradation. The us-CNTs containing nanocomposites show progressively improved photo- and thermo- oxidative resistance with increasing the us time, highlighting that the stability of the nanocomposites can be profitably modulated by controlling the amount of CNT structural defects.

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1. Introduction

In the last decade, carbon nanotubes (CNTs) have received a great attention due to their excellent electronic, mechanical and thermo-mechanical properties [1]. Besides, recent researches have probed that the CNTs exhibit peculiar radical scavenging activity, opening new avenues toward their use in some biomedical applications [2] and in the protection of polymeric matrices against the oxidative degradation [3]. Also theoretical studies based on Density Functional Theory predicted that CNTs can act as free-radical traps. Particularly, the reactions between CNTs and radicals have been modeled through two different mechanisms: electron-transfer and adduct formation, also considering the influence of length, diameter, chirality and possible functionalization on the CNT reactivity [4]. An interesting approach to enhance the CNT radical scavenging activity involves the immobilization of moieties carrying specific anti-oxidant functionalities. In particular, Lucente-Schultz et al. [5] grafted butylated hydroxytoluene (BHT) onto CNTs showing that, when the functionalization occurs through existing functionalities, the radical scavenging activity is increased. In our previous studies, the anti-oxidant action of CNTs against thermo- and photo-oxidation of polyolefin matrix has been increased through the chemical linkage of stabilizers molecules [6]. The improved anti-oxidant activity of CNTs has been attributed to the gathering of the anti-oxidant functionalities at the polymer-nanofiller interface, that represents a critical area for the degradation of the polymer-based nanocomposites.

The exceptional radical scavenging activity of CNTs is related to their electron donor and acceptor capability, coming from their peculiar electronic structure. In fact, the CNT extended graphitic lattice, involving several conjugated double bonds, provides CNTs with high electronic affinity, similarly to fullerenes, which are known to be efficient against free radicals [7]. Watt et al. [8] for the first time, reported that the acceptor-like electronic properties of CNTs are mainly responsible for their radical scavenging activity. Particularly, due to the presence of lattice defects, CNTs have acceptor-like localized states, accountable for the interruption of chain propagation during polymer degradation. Based on these findings, we amplified the CNT anti-oxidant activity through the increase of the structural defects onto CNTs. Specifically, the last has been achieved exploiting the strong interactions established between immobilized molecules, such as Vitamin E and Quercetin, and CNTs, that induce change of the hybridisation of some carbon atoms onto outer surface from sp^2 to sp^3 , thus increasing the concentration of the lattice defects [9-10].

To sum up, considering that the radical scavenging properties of CNTs are strictly dependent from the defects present on their surface, the CNT anti-oxidant ability can be profitably modified through the variation of the defect concentration. With this in mind, in this work we propose an innovative

approach to amplify and control the radical scavenging ability of CNTs through ultra-sound-assisted defects formation. Ultra-sonication is one of the most used method to disperse CNTs in solutions, as the CNTs aggregates, formed due to the intrinsic van der Waals attraction among nanotubes, can be broken by the forces rising from cavitation effects [11]. Furthermore, recently it has been shown that ultra-sonication can be profitably used to functionalize CNTs [12-13] and to formulate CNTs containing polymer nanocomposites by in-situ polymerization [14]. However, the ultra-sonication treatment, due to strong shear forces coming from cavitation phenomena, causes the formation of lattice defects in CNTs. Therefore, the main goal of this research is the capitalization of CNT structural defects, caused by ultra-sound treatment, to obtain nanofillers with tunable radical scavenging activity. The ability to trap radicals of CNTs subjected to ultra-sonication for different time intervals has been accurately investigated and the CNT anti-oxidant activity against thermo- and photo-oxidation of UHMWPE-based nanocomposites has been evaluated and discussed.

2. Experimental part

2.1 Materials

Ultra High Molecular Weight Polyethylene, 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 $T=136^\circ\text{C}$ (Vicat, ASTM D 1525B), melting point $T_m=138^\circ\text{C}$, degree of crystallinity about 48.1 % (estimated through DSC measurement considering a heat of fusion for perfectly crystalline polyethylene $\Delta H_f = 288.84$ J/g), and density $\rho=0.94$ g/mL at 25°C . The average molecular weight was detected by means of intrinsic viscosity ($[\eta]$) measurements according to ASTM D4020-05 using a Lauda Pro-line PV15 viscometer. The UHMWPE was dissolved in decahydronaphthalene (reagent grade Sigma-Aldrich) at 150°C and maintained under magnetic stirring for one hour. The viscosimetric average molecular weight, estimated from three independent measures of $[\eta]$ using the Margolies equation, $M_v=5.37*10^4[\eta]^{1.37}$, was $M_v\cong 4.9*10^6$ g/mol.

Multiwalled Carbon Nanotubes, CNTs, were prepared by the typical Chemical Vapor Deposition (CVD) protocol, using ethylene as carbon source [15] and a catalyst based on Fe supported on alumina (typically 10% w/w of Fe). The process is conducted in a fluidized bed reactor. The catalyst is loaded and heated at a temperature between 600 and 800°C under N_2 flow, then treated with a mixture of $\text{H}_2\text{-N}_2$ 30%-70%. The reacting mixture, composed by ethylene, H_2 and N_2 in 20%-30%-30% v/v proportion is fluxed through the catalyst. The reaction is monitored by in-line GC. At the end of the process the CNTs purity is between 70 and 85% w/w. The impurities are mostly residual catalysts and there are evaluated by ICP and TGA analyses, see Figure 1.

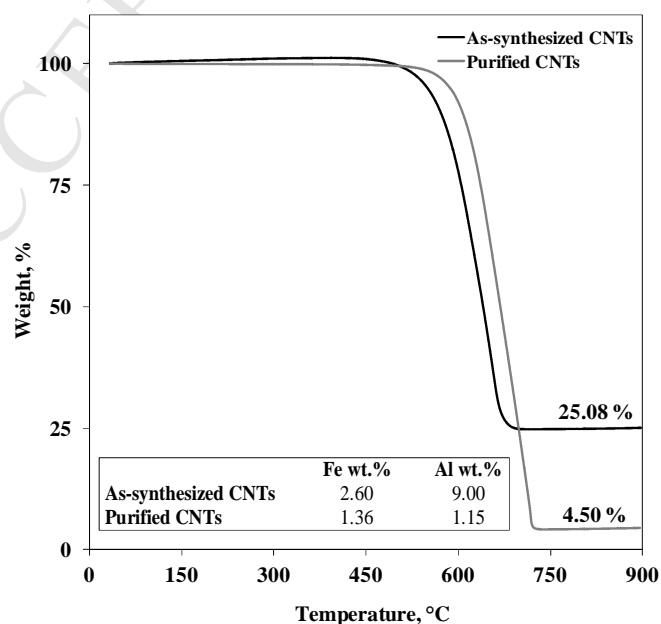


Figure 1. TGA analysis for as-synthesized and purified CNTs (ICP analysis in the inset)

The purification was performed with 50% aqueous sulfuric acid, obtaining carbon nanotubes with outer diameters ranging between 14 and 20 nm, inner diameters in the range of 2 to 5 nm, length $1\pm 10\ \mu\text{m}$, and purity $> 96\ \text{wt.}\%$. The last has been evaluated by ICP and TGA analysis (Figure 1). Moreover, after the purification process the content of carboxylic groups was estimated to be about 0.5% by means of XPS analysis and acid/base titration.

All chemicals and reagents were used as received, without further purification.

2.2 CNT sonication

Six identical samples of 0.2 g of CNTs were placed in 50 mL one-neck round bottom flasks, then 20 mL of distilled water were added in each one. The flasks were placed in an ultrasonic bath (water volume 2.5 L, power 260 W) taking care to have the water level higher than the level of the suspension. The six reaction mixtures were sonicated at room temperature for different time intervals, particularly, 15', 30', 60', 90' and 120'. The us treated CNTs are labeled as usX-CNTs, where X is the us treatment time.

2.3 Nanocomposite preparation

The UHMWPE powder and 1 wt.% of untreated CNTs and us-CNTs were manually mixed at room temperature and the resulting powder has been homogenized by thorough grinding in a porcelain mortar to the visually homogeneous state. Afterwards, the composite powder has kept under magnetic stirring for about 12 hours, until the achievement of a homogeneous black powder.

The blends were then hot compacted at 210°C for 5 min and under a pressure of 1500 psi to get thin films (thickness less than $100\ \mu\text{m}$) for the subsequent analyses.

The neat UHMWPE was subjected to the same procedure for comparison.

2.4 Characterization

Thermo-Gravimetric Analysis (TGA) was performed on a PerkinElmer STA 6000 thermal analyser; the samples were heated from $35\ ^\circ\text{C}$ to 900°C ($10\ ^\circ\text{C}/\text{min}$) in both air and nitrogen atmosphere in order to evaluate catalyst residual and organic content in CNTs, respectively.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP/OES) was performed on a PerkinElmer Optima 8300 ICP-OES Spectrometer; the samples were previously mineralized by acid treatment and the resulting solutions (properly diluted) analysed.

Micro-Raman spectroscopy has been performed at room temperature through a Renishaw Invia Raman Microscope equipped with a 532 nm Nd:YAG laser excitation and 100 mW power. Non-

confocal measurements were carried out in the range 3200–100 cm^{-1} with a spectral resolution between 0.5 and 1 cm^{-1} .

Transmission Electron Microscopy (TEM) analyses were performed on a homogeneous dispersion of the CNTs in 2% aqueous sodium dodecyl sulfate (SDS, supplied by Sigma-Aldrich) using a Philips CM 200 field emission gun microscope operating at an accelerating voltage of 200 kV. A Gatan US 1000 CCD camera was used and 2048x2048 pixels images with 256 grey levels were recorded. For the specimen preparation few drops of the water solutions were deposited on 200 mesh lacey carbon-coated copper grid and air-dried for several hours before analysis.

The 1,1-diphenyl-2-picryl (DPPH, supplied by Sigma-Aldrich) free radical scavenging assay was carried out according to published procedures [16-17]. Samples for a typical measurement were prepared by placing in a screw-capped vial 2 mg of functionalized carbon nanotube, to which 2 ml of a methanol solution of DPPH (10^{-4} M) were added. All samples were thermostated at 25 °C for the time required by the measurement. Then the supernatant liquid was removed and the UV-vis spectrum recorded in a Beckmann DU-800 spectrometer. Spectra were recorded on a spectrophotometer equipped with a Peltier temperature controller. Scavenging activities were determined from the drop in absorbance at 517 nm of each sample compared with that of the DPPH solution in the absence of contact with the material. Scavenging efficiency values were calculated by equation (1) [16]

$$\text{Radical Scavenging Efficiency (\%)} = \frac{A-B}{A-0.10} \times 100 \quad (1)$$

where A is the absorbance of the DPPH solution and B that of the DPPH solution after contact with the materials.

Electron spin resonance (ESR) spectrometer (Bruker ESR-300) was used to monitor the $\bullet\text{OH}$ radicals in presence of CNTs. Hydroxyl radicals were generated using the Fenton reaction [18], and captured by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to form DMPO/ $\bullet\text{OH}$ complex. The radical scavenging activity of us-CNTs was evaluated in homogeneous suspension of 1 mg of each CNTs in 50 μm of 5 wt.% SDS solution.

The photo-oxidative resistance of the samples was estimated using a Q-UV-Solar Eye weatherometer (from Q-LAB, USA) equipped with UVB lamps (313 nm), at $T= 55$ °C. The thermo-oxidative treatment has been performed in an air oven at 80 °C. The tests were carried out on the hot-compacted films with thickness less than 100 μm .

The progress of the photo- and thermo-oxidative degradation was followed by analysing the evolution in time of FTIR spectra on polymer films carried out by using a Perkin Elmer FT-IR

spectrometer (mod. Spectrum Two). FTIR spectra collected on three different films of each sample were obtained by performing 16 scans between 4000 and 500 cm^{-1} . The photo- and thermo-oxidation evolution was quantified by referring to the carbonyl index (CI) as a function of degradation 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 2019 cm^{-1} , which account for the sample thickness variation.

3. Results and Discussion

3.1. Assessment of CNT radical scavenging activity

To assess the effectiveness of ultra-sonication treatment in the formation of CNT structural defects, Raman analysis of CNTs subjected at sonication for various time intervals has been carried out; in Figure 2(a), the Raman spectra are reported. Two different peaks are visible: the defect induced disorder mode (D-band), centered at 1340 cm^{-1} , and the tangential mode (G-band), centered at 1580 cm^{-1} [19]. Each spectrum was normalized such that the G-band intensity was the base line. It can be noticed that intensity of D-band increases with increasing the ultra-sonication time, highlighting the growing of defects concentration due to the damage of CNTs. The high values of D-band for untreated CNTs could be understand considering that the purification treatment caused the CNT functionalization with oxygen containing groups, as reported in the experimental section. Moreover, the shift of G-band from 1573 cm^{-1} for untreated CNTs to 1581 cm^{-1} for us120-CNTs suggests a de-bundling of CNT aggregates upon us treatment [20]. To qualitatively evaluate the defects concentration, the ratio I_D/I_G , between the intensities of two Raman bands, which growing account for the increase of defect sites content, has been calculated and reported in Figure 2(b) as a function of the us time. The I_D/I_G ratio passes from 0.97 for untreated CNTs to 1.12 and 1.18 for us60-CNTs and us120-CNTs, respectively, indicating that the sonication progressively damages the CNT graphitic structure, causing the formation of non-graphitic hybrid structures.

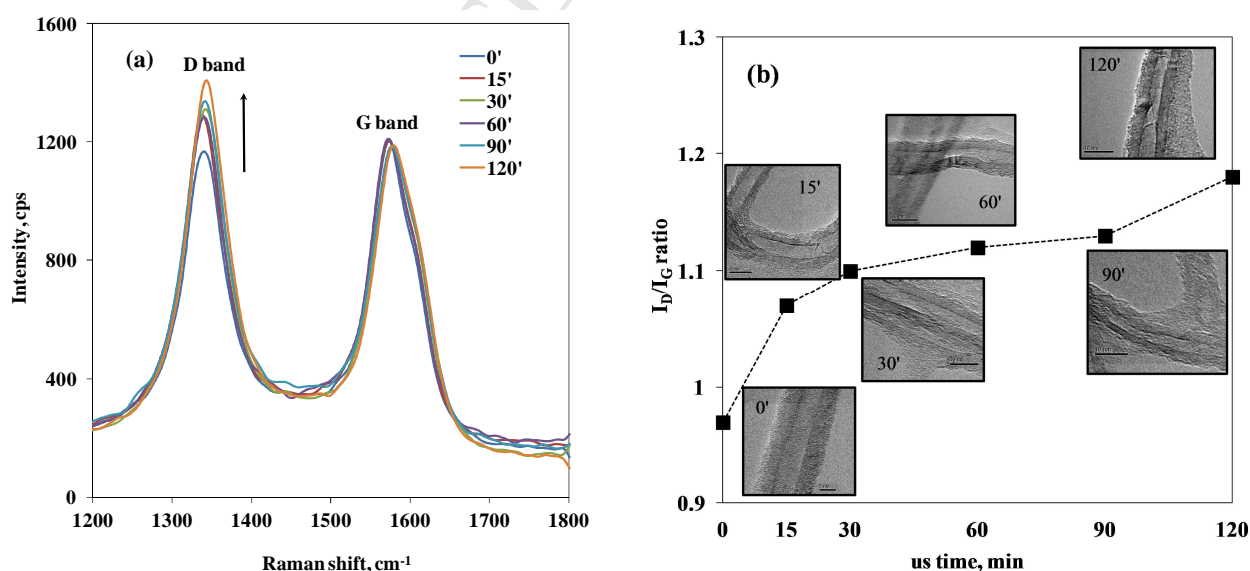


Figure 2. (a) Raman spectra and (b) I_D/I_G ratio and TEM observations for CNTs at different sonication times

The visual inspections of CNTs, through TEM, has been used to detect the morphological changes associated with the defects formation. As visible in the micrographs in Figure 2(b), untreated CNTs show well-ordered graphitic walls, while alterations of the CNT structural integrity, such as defective sites, waviness and presence of amorphous carbon on the nanoparticles surface can be noticed for us-CNTs. The above observations are in full agreement with the Raman results, demonstrating that the defects concentration increases with increasing of us time.

To investigate the correlation between the defects content and the radical scavenging activity, the trapping ability of CNTs toward DPPH and $\bullet\text{OH}$ radicals has been evaluated. Firstly, DPPH tests have been carried out, considering different reaction times.

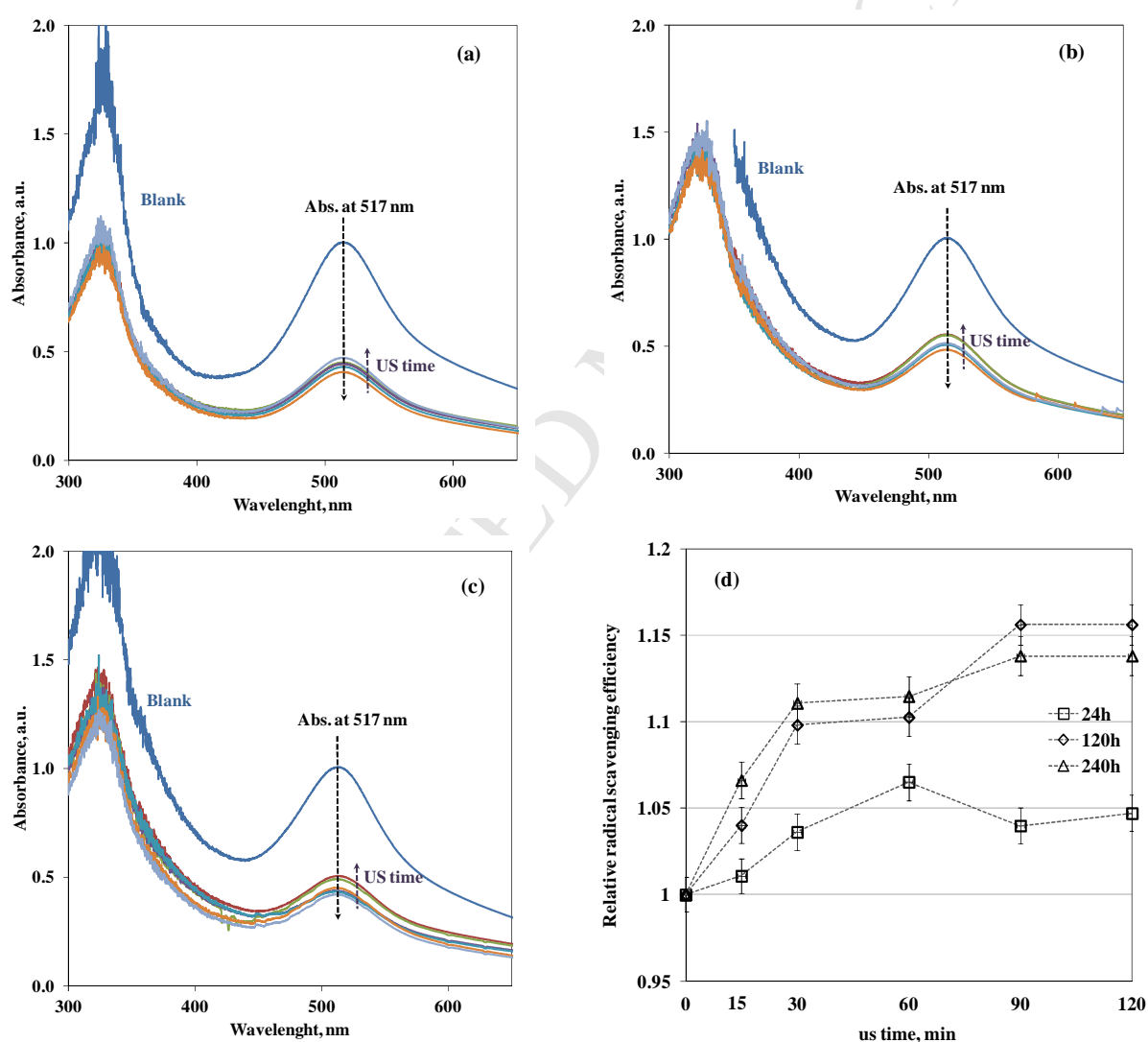


Figure 3. UV-VIS spectra of DPPH/MeOH solutions containing CNTs after (a) 24h, (b) 120h and (c) 240h and (d) DPPH radical scavenging efficiencies of CNTs at different sonication times

Methanol solutions of us-CNTs/DPPH have been prepared and analyzed via UV/Vis spectrometry and the results have been compared with those obtained for untreated CNTs. The UV/Vis spectra of untreated CNTs/DPPH and us-CNTs/DPPH solutions collected after 24h, 120h and 240h are reported in Figure 3(a-c). In the UV/Vis spectrum of DPPH/MeOH solution, the typical DPPH absorption band at 517 nm is clearly detectable [17]. The intensity of this band significantly decreases in presence of untreated CNTs, indicating that CNTs present an inherent radicals scavenging activity towards DPPH radicals. The last is amplified by us treatment, as noticeable looking at the progressively decrease of the band at 517 nm in the spectra of us-CNTs/DPPH/MeOH. To quantify the influence of us time on CNT trapping activity, the radical scavenging efficiencies have been calculated and plotted as a function of us time in Figure 3(d). Irrespective of the reaction time, i.e. 24h, 120h and 240h, the radical scavenging efficiency for us-CNTs is higher than that of the untreated CNTs and shows a progressive increase as a function of the treatment time.

In order to understand the mechanism of reaction between DPPH radicals and CNTs, further analyses on CNTs after the reaction have been carried out. As reported in theoretical studies, CNTs can react with free radicals through two different mechanisms: electron transfer process [21] and adduct formation [4, 22]. Concerning the first mechanism, in order to scavenge free radicals, CNTs can either donate or accept electrons; for this reason, two possible directions must be taken into account: from CNTs to free radicals and vice versa. The adduct formation mechanism involves the CNTs wall functionalization and it was shown that once the first radical is attached on CNTs, further addition are increasingly feasible; in other words, the CNTs act as free radicals sponges. To discriminate between these two phenomena, and to identify the mechanism which really happens between us-CNTs and DPPH radicals, Raman analysis has been performed after 240h of reaction time. After the reaction CNTs have been deeply washed with methanol (2 ml) and then vacuum dried at 60 °C for 1h. In Figure 4(a) and (b), the collected spectra and calculated I_D/I_G ratio are reported. The values of I_D/I_G ratio after the reaction between CNTs and DPPH radicals, are higher than those of unreacted CNTs; the last clearly suggests the grafting of DPPH on CNT sidewall. Indeed, as well known, the CNT wall functionalization leads to an increase of the defect content, recognizable in the grow of I_D/I_G ratio values [7]. It is worth nothing that I_D/I_G ratio values progressively increase with us time, as the reactivity of CNTs against DPPH radicals increases with increasing of structural defect content. Additional proof about the DPPH grafting on CNT sidewall comes from the TGA analysis, performed before and after reaction with DPPH radicals, see Figure 4(c). Both untreated CNTs and us120-CNTs samples after the reaction with DPPH decompose at temperature lower than the unreacted CNTs, probably because of the volatilization of DPPH grafted

on the CNT surface. The residuals at the end of the analysis were 97.1 wt.% and 96.2 wt.% for the untreated CNTs/DPPH and us120-CNTs/DPPH samples, respectively, whereas residuals of 99.2 and 99.0 wt.% were found for the unreacted CNTs due to a partial decomposition of the bulk material. Results coming from TGA analysis, therefore, indicate that about 2.1 and 2.8 wt.% of DPPH is grafted on untreated CNTs and us120-CNTs, respectively, at the end of reaction. The analyses performed on untreated and us CNTs after the reaction with DPPH radicals clearly suggest that CNTs scavenge DPPH through adduct formation, with grafting of DPPH on CNT surface. Furthermore, the results highlight that the CNT reactivity toward DPPH radicals is enhanced in presence of a large amount of structural defects.

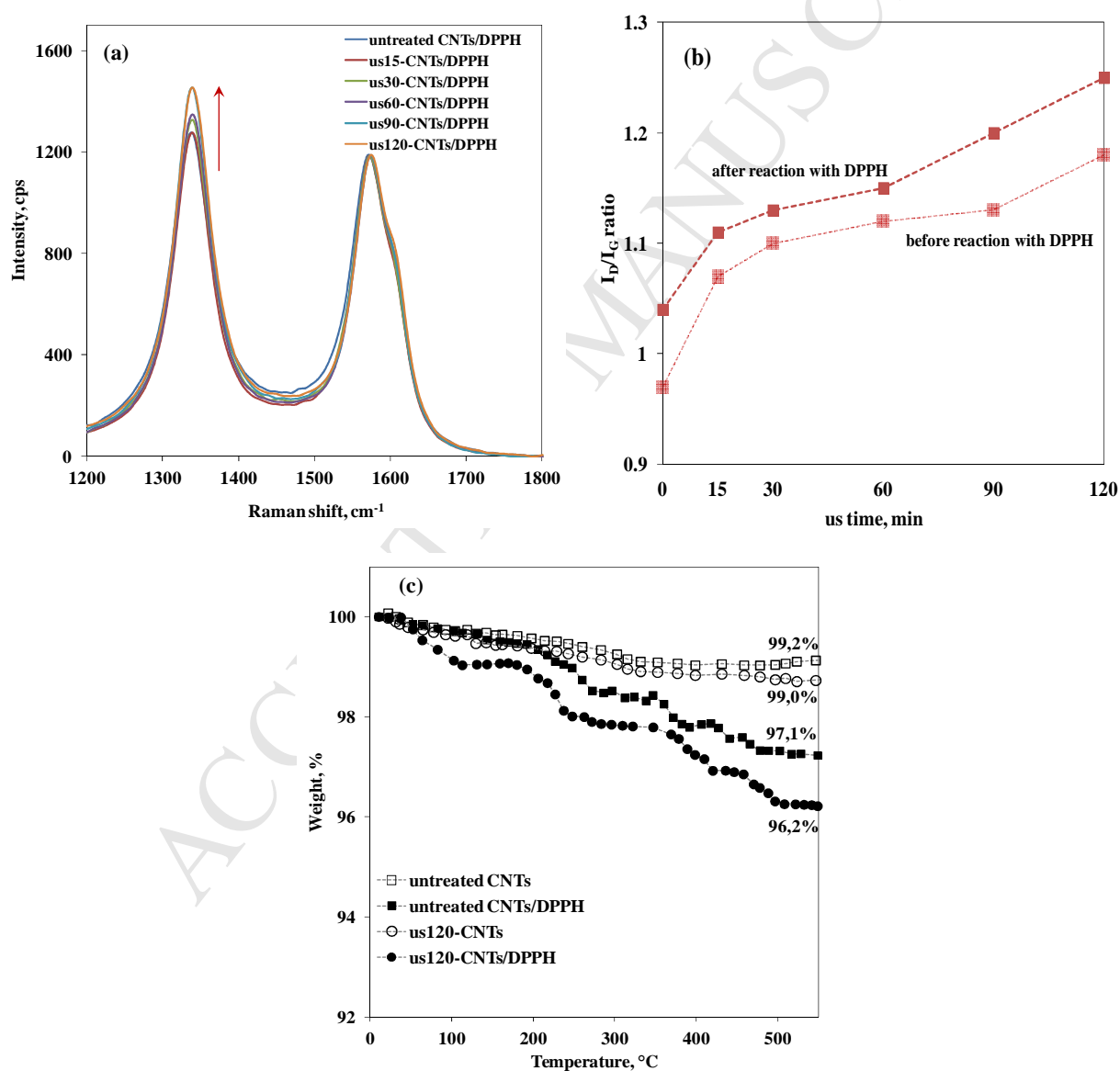


Figure 4. (a) Raman spectra, (b) I_D/I_G ratio and (c) TGA analysis of untreated and us CNTs before and after the reaction with DPPH radicals

Regarding the reactivity of CNTs toward free radicals, the radical scavenging activity of us-CNTs against $\bullet\text{OH}$ radicals has been evaluated through ESR measurements. The $\bullet\text{OH}/\text{DMPO}$ complex exhibit a 1:2:2:1 signal, which intensity is proportional to the amount of $\bullet\text{OH}$ radicals in solution. The lower is the peak intensity, the higher is the amount of scavenged radicals, until disappearance of the peak that indicates a complete quench of $\bullet\text{OH}$ radicals. In Figure 5, the ERS spectra, recorded in presence of untreated CNTs and us-CNTs are plotted. The peak intensity of $\bullet\text{OH}/\text{DMPO}$ complex in presence of us15-CNTs is almost unchanged to the respect of that of untreated CNTs, while us60-CNTs and us120-CNTs lead to a remarkable lowering of the signal intensity. This feature suggest that the $\bullet\text{OH}$ radicals in solution have been trapped more efficiently by us-CNTs.

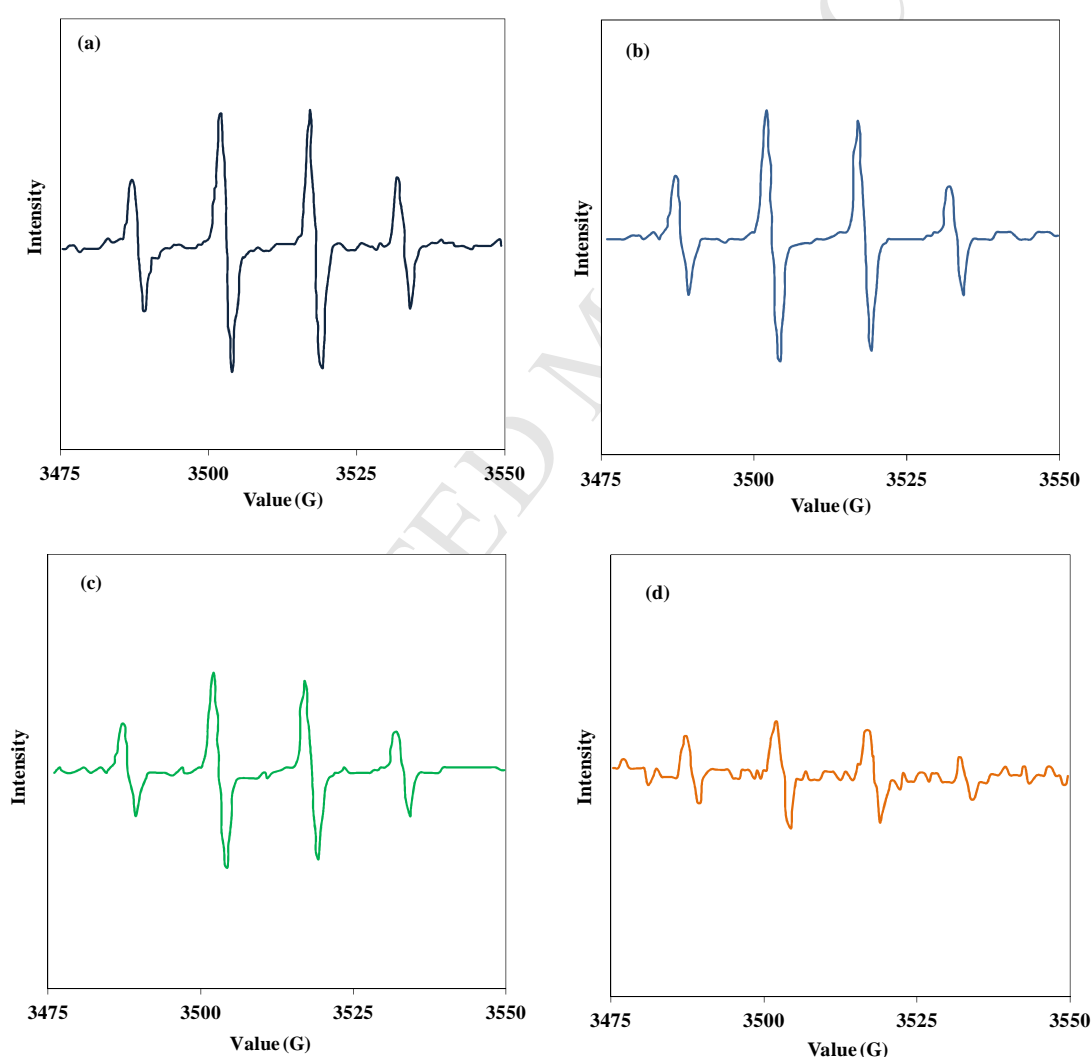


Figure 5. ESR spectra of solutions containing CNTs sonicated at (a) 0, (b) 15, (c) 60 and (d) 120 minutes

To sum up, all obtained results highlight that us treatment, being an efficient method to induce the formation of defect sites on CNTs, can be profitably used to control the content of structural defects

by tuning the us time. Given that the content of CNT defects regulates their radical scavenging activity, the controlled us treatment allows to obtain advanced nanofillers with tailored radical scavenging efficiency.

3.2. Anti-oxidant activity of us-CNTs in UHMWPE-based nanocomposites

The radical scavenging activity of CNTs, induced by us treatment, has been exploited to enhance the photo- and thermo-oxidative resistance of UHMWPE-based nanocomposites. Nanocomposites thin films have been subjected to UVB exposure and thermo-oxidation treatment and the progress of the degradation phenomena has been monitored through the analysis of the evolution time of the FT-IR spectra, see Figures 6(a) and 7(a).

As known, the photo- and thermo-oxidation of neat UHMWPE leads to the formation of carboxylic acids, ketones, esters and lactones, which accumulation reflects in the growth of a complex peak in the range $1850\text{-}1600\text{ cm}^{-1}$ [23]. The presence of carbon nanotubes does not affect the photo- and thermo-oxidation mechanism of UHMWPE, bringing about the formation of same oxidized species [9]. Taking the bending vibration peak of the $-\text{CH}_3$ at 2019 cm^{-1} as internal standard, we calculated the Carbonyl Index (CI) for neat UHMWPE and all investigated UHMWPE-based nanocomposites as a function of exposure time, as shown in Figures 6(b) and 7(b) for photo- and thermo-oxidation, respectively. As far as photo-oxidation behaviour is concerned, neat UHMWPE shows a suddenly increase of carbonyl formation, indicating that the degradation begins in the early stage of the UVB exposure. It is worth noting that such chemical alterations are coupled with a drastic embrittlement of neat UHMWPE and after 216h of exposure, the analysis cannot be performed. The presence of untreated CNTs slows down the oxidized species formation due to their reactivity towards macroradicals coming from polymer degradation. The anti-oxidant feature of CNTs against photo-oxidation is significantly enhanced by us treatment and their stabilizing action progressively increase with us time. In particular, untreated CNTs and even more us-CNTs, have a dual beneficial effect: a significant increase of the induction time for the photo-oxidative degradation and a remarkable reduction of the rate of oxidized species formation can be noticed. The induction time t_i can be conventionally defined as the time needed for CI reaches the value of 5; the estimated t_i values as a function of the us time are plotted in Figure 6(b), see inset. The induction time passes from 140h for UHMWPE/untreated CNTs to 230h for UHMWPE/us120-CNTs, indicating a significant increase of the time needed for the beginning of the oxidation process. Besides, a progressive decrease of the slope of carbonyl index trends is observed as a function of the us treatment time, suggesting that us-CNTs are able to slow down the photo-oxidation kinetic after the induction period.

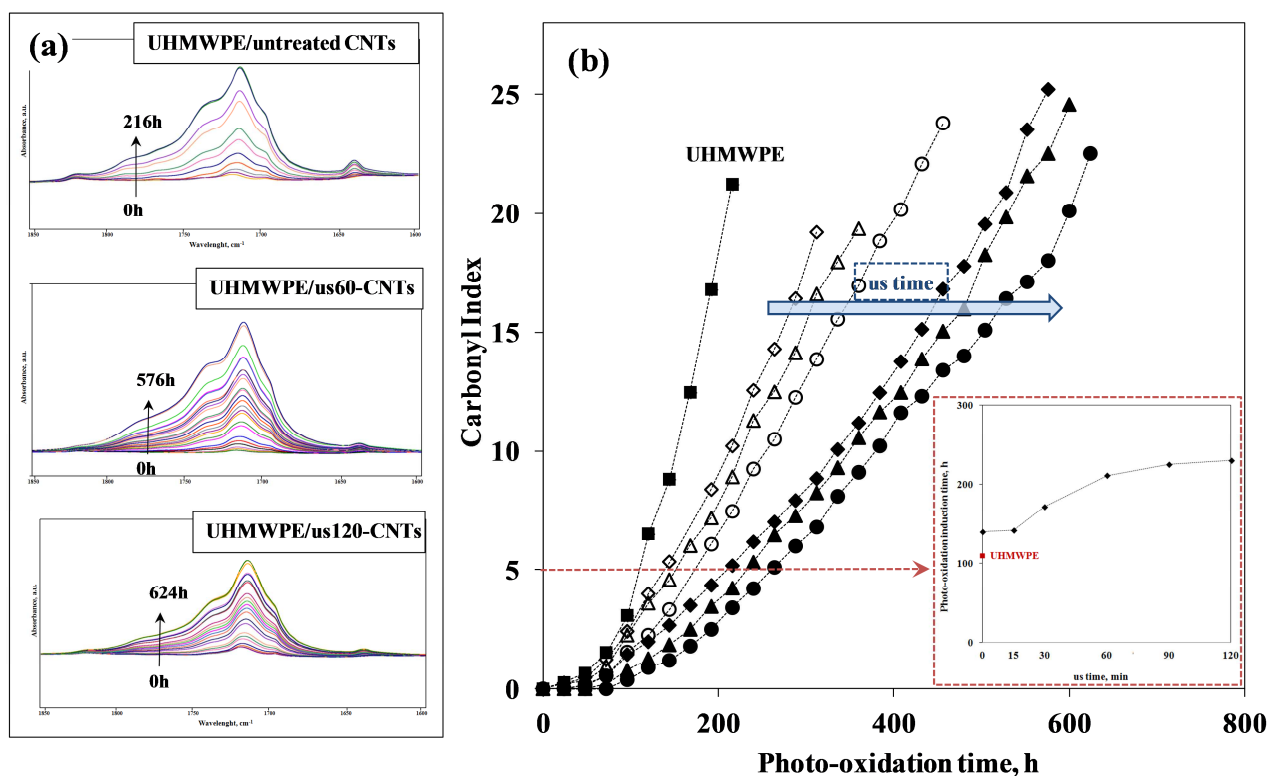


Figure 6. (a) Representative FTIR spectra in the carbonyl region ($1600\text{-}1850\text{ cm}^{-1}$) and (b) calculated Carbonyl Index (Photo-oxidation induction time in the inset) of neat UHMWPE and UHMWPE/CNTs nanocomposites subjected to UVB exposure

Concerning the thermo-oxidation behaviour, with increasing the aging time, the UHMWPE/us-CNTs nanocomposites exhibit a weakest increase of the relative carbonyl peak intensity (see Figure 7(a)) than the nanocomposite containing untreated CNTs. This issue can be understood considering that the degradation rate is remarkably decreased due to the amplified radical scavenging activity of us-CNTs induced by us treatment. The last reflects in the trend of carbonyl index build-up curves, highlighting that the amplified radical scavenging activity of us-CNTs results in an enhanced antioxidant activity against UHMWPE thermo-oxidative degradation phenomena. The calculated values of the induction time (from 785h for UHMWPE/untreated CNTs to >1000h for UHMWPE/us120-CNTs) are in full agreement with the results about the photo-oxidation behaviour, since higher is the time of us treatment on CNTs, higher is the time required to trigger the degradation process.

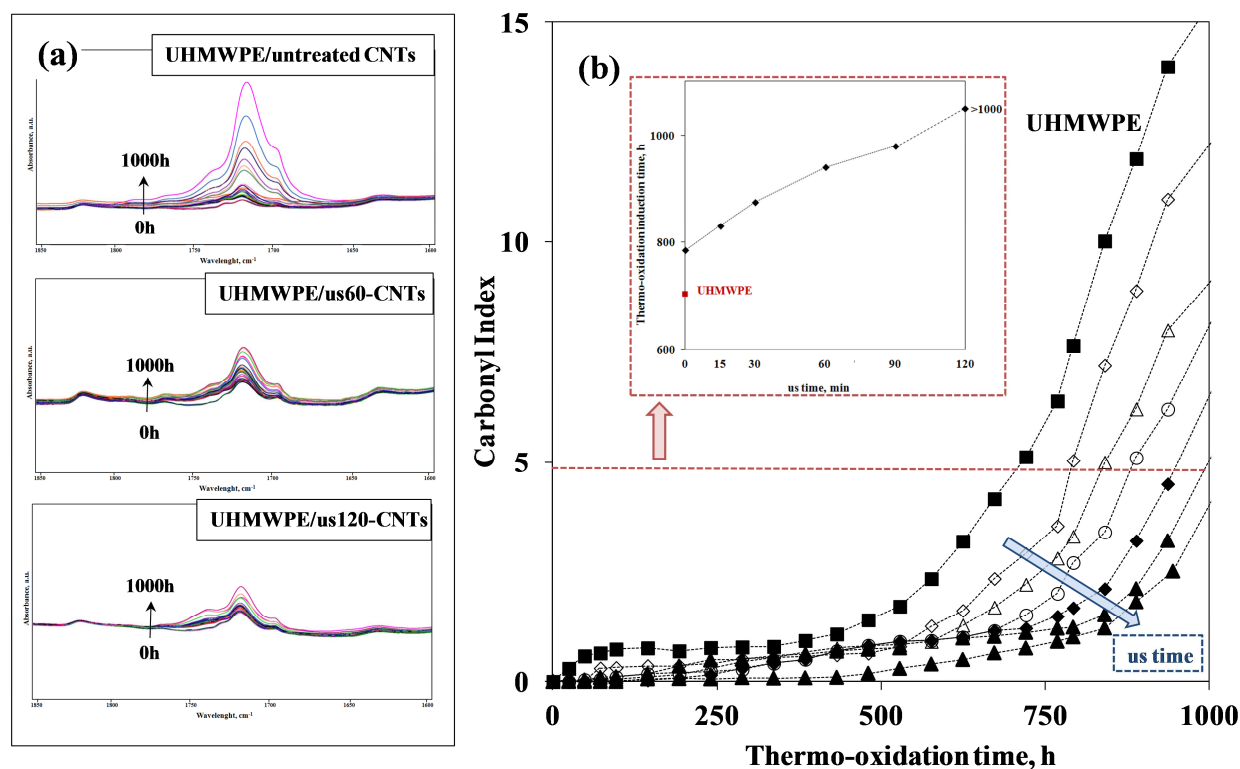


Figure 7. (a) Representative FTIR spectra in the carbonyl region ($1600\text{-}1850\text{ cm}^{-1}$) and (b) calculated Carbonyl Index (Thermo-oxidation induction time in the inset) of neat UHMWPE and UHMWPE/CNTs nanocomposites subjected to thermo-oxidative treatment

Summarizing, our results demonstrate that the lattice defects onto the CNTs surface, can represent the key factor to modify in a controlled way the radical scavenging activity of CNTs and their anti-oxidant action against polymer degradation phenomena. In particular, polymer-based nanocomposites with controlled photo- and thermo-oxidative stability can be obtained tuning the scavenging ability of CNTs through a simple method, such as us treatment, that allows a controlled defects formation.

4. Conclusions

CNTs have been subjected to us treatment with the aim to capitalize the structural defects induced by sonication, to obtain nanofillers with controlled radical scavenging activity. The assessment of us-CNTs reactivity toward DPPH and $\bullet\text{OH}$ radicals has been performed through UV/Vis and ESR spectrometry and the obtained results show that the CNT radical scavenging efficiency is strictly dependent on the content of structural defects. Nanocomposites containing us-CNTs show a photo-

and thermo-oxidative resistance significantly improved with respect to that of UHMWPE/untreated CNTs, indicating that our treatment is effective in enhancing the reactivity of CNTs toward macroradicals coming from the polymer degradation reactions.

In all, polymer-based nanocomposites with modulated photo- and thermo-oxidative resistance can be achieved, tuning the CNT radical scavenging properties, which can be rationally controlled by the ultra-sound assisted defects formation.

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