A BEHAVIOR OF CARBON NANOTUBES IN OXIDIZING MEDIUMS (REVIEW)

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The review briefs about the status of worldwide studies into impact of carbon nanotubes (CNTs) on the oxidation environments of polymeric composites and biological objects. CNTs reveal the higher antioxidant capacity preferably operating as a thermo-stabilizer in polymers and radical scavengers in vivo. In this respect, CNTs may be compared with strong commercial and natural well-known antioxidant moieties.

Keywords: carbon nanotubes, polymeric composites, thermal degradation, fullerenes, oxidation, radical scavenging

Introduction

Carbon nanotubes (CNTs) have electron affinities similar to those of fullerenes, and may therefore be hypothetically predicted to behave themselves as radical traps in chain reactions such as oxidation, polymerization or thermal degradation [1-3].

Radical scavenging efficiency of various and differently modified fullerenes of multi-walled CNT, including ball-milled, benzoyl peroxide-treated, acid-treated, and microwave-treated and other functionalized CNT patterns, have been analyzed in the research [4-9]. Raman spectrometry, X-ray photoelectron spectroscopy, scanning electron microscopy, and energy dispersive spectrometry were used to characterize the modified patterns. Electron paramagnetic resonance (EPR) and ultraviolet/visible spectrophotometer (UV/Vis) were used to measure radical scavenging efficiency of the modified CNT for hydroxyl (OH) radical and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical, respectively. EPR, UV/Vis, and Raman spectra revealed that the radical scavenging efficiency for both radicals rose together with growth in the content of defect sites on the modified CNT. The DPPH radical scavenging efficiency of the modified CNT proved to be relatively low as compared to the OH radical scavenging efficiency; the rankings in the scavenging efficiency, however, were similar for both radicals. The research work went to show that the modified CNT were effective radical scavengers suggested that identical carbon nanostructures have potential applications as antioxidants [5-12].

Polymer systems

Given their potential radical accepting capacity, CNTs can be expected to interrupt chain propagation, leading to antioxidant and stabilizing action in polymers [3,13]. Actually, the polymer-nanotube composites are able to stand high current densities which undoubtedly will afford Joule heating of the polymer. Authors of Ref. [3] observed the high heating effect (above 200°C) of the polymer on the passage of direct current through composites. It is therefore important to study how CNTs affect the stability of polymers at elevated temperatures. According to TGA and CL profiles, it revealed that CNTs acted as antioxidants during thermo-oxidative degradation of composites of polystyrene, polyethylene, polypropylene and poly-vinylidene fluoride. An increase in the CNTs content beyond 5% leads to insignificant rise in antioxidant efficiency. As for the poly-vinylidene fluoride case, it seems that the
nanotubes can act both as antioxidants and halogen absorbers [3].

Sterilization of implants and other clinical accessories is an integral part of any medical application. Although many materials are used as implants, polyethylene stands unique owing to its versatility. Carbon nanotubes are being used as a filler material to enhance the properties of polyethylene. However, the role of multi-walled carbon nanotubes (MWCNTs) as an effective antioxidant and radical scavenger in resisting the deteriorating effects of sterilization is yet to be studied thoroughly. The work [11] aimed to investigate mechanical properties and oxidation stability of irradiated high density polyethylene (HDPE) reinforced by MWCNTs with various concentrations such as 0.25%, 0.50%, 0.75% and 1.00 wt.%. The composites were exposed to $^{60}$Co source in air and irradiated at different dosage levels starting from 25 to 100 kGy and next came the shelf aged for a period of 120 days prior to investigation. The loss in toughness, Young’s modulus and ultimate strength at 100 kGy for 1 wt.% MWCNTs composite proved to be 21.5%, 20.3% and 19.2% respectively as compared to that of unirradiated composite. FTIR and ESR studies reaffirmed antioxidant and radical scavenging potentialities of MWCNTs together with increased concentration and irradiation dosage. It found that adding 1 wt.% MWCNTs to virgin HDPE made the oxidation index of the composite at 100 kGy drop by 56.2%. It may be concluded that the addition of MWCNTs into polyethylene not only restricts the loss of mechanical properties but also improves its post irradiation oxidative stability [11].

Carbon nanotubes are extensively incorporated as reinforcement into polymeric materials due to their extraordinary properties. The antioxidant ability of CNTs in HDPE was examined in [12]. Note that single-walled carbon nanotubes (SWCNTs), MWCNTs and hydroxylated multi-walled carbon nanotubes (MWCNTs-OH) were involved to investigate the influence of wall number and surface functionalization of CNTs on their antioxidant behavior in HDPE. Proceeding from measurements of the oxidation induction temperature and oxidation induction time of CNTs/HDPE composites, one can infer that the antioxidant ability of three kinds of CNTs is in the succession as follows: MWCNTs-OH > MWCNTs > SWCNTs. The antioxidant ability and mechanism of CNTs have further been examined by electron spin resonance spectra and Raman spectra. It revealed that the antioxidant behavior of CNTs is subject to a free radical scavenging mechanism. The order of the radical scavenging efficiency and the defect concentration for CNTs are in keeping with their antioxidant ability in HDPE. With more walls and surface hydroxyl groups, the CNTs have more structural defects and exhibit higher antioxidant ability. The study puts forward the probability that CNTs can improve both antioxidant and mechanical properties of polymer matrix [12].

The influence of carbon nanotubes on the photodegradation of ethylene-vinyl acetate (EVA)/carbon nanotube nanocomposites was analyzed by means of irradiation under photooxidative conditions (at $\lambda > 300$ nm, at 60 °C and in the presence of oxygen) [14]. The influence of the nanotubes on both photo-oxidation mechanism of EVA and rates of oxidation of the matrix was characterized on the basis of infrared analysis. On the one hand, it found that the CNTs act as inner filters and antioxidants, which contribute to the reduction of photo-oxidation rates of the polymeric matrix. On the other hand, it revealed that the light absorption could provoke an increase in the local temperature and then induce the photo-oxidation of the polymer. The confrontation between three effects determines global rates of photo-oxidation of the polymeric matrix. Several factors are involved in the process, including the concentration of the CNTs, the morphology of the nanotubes and the functionalization of the nanotube surface [14].

MWCNTs/linear low density polyethylene (LLDPE) nanocomposites were examined to reason out the stabilization mechanism for their thermal and oxidative degradation [15]. Thermogravimetry coupled with infrared evolved gas analysis and pyrolysis gas chromatography–mass spectrometry demonstrates that MWCNTs
presence slightly delays thermal volatilization (on 15–20 °C) without modification of thermal degradation mechanism. Whereas thermal oxidative degradation in air is delayed by about 100°C irrespective of MWCNTs concentration ranging between 0.5–3.0 wt.%. The stabilization is due to formation of a thin protective film of MWCNTs/carbon char composite on the surface of nanocomposites. It manifests itself in SEM and ATR FTIR degradation residues [15].

The paper [16] presents results of preliminary research into the effect of incorporating CNTs into polyamide-6 (PA6) with due regard for mechanical and thermal properties, as well as fire performance of woven glass reinforced with CNTs/PA6 nanocomposite laminates. The samples were characterized by tensile and flexural tests, thermal gravimetric analysis (TGA), heat distortion temperature (HDT) measurements, and thermal conductivity, as well as cone calorimeter tests. Incorporation of up to 2 wt% CNTs into CNTs/PA6/GF laminates contributed to raising the flexural stress of laminates up to 36%; the thermal conductivity by approximately 42% while the ignition time and peak HRR time was delayed by approximately 31% and 118%, respectively [16].

High energy ball milling (HEBM) was utilized as innovative process to incorporate CNTs into a polyethylene (PE) matrix and thus avoid high temperatures, solvents, ultrasonication and chemical modification of CNTs. Note that composites with 1, 2, 3, 5, and 10 wt % of CNTs were prepared. Films were obtained by melting powders on a hot press. Morphology and physical properties (thermal, mechanical and electrical) were evaluated [17]. Processing conditions made it possible to attain a satisfactory level of dispersion of CNTs into the PE matrix with a consequent improvement of physical properties of the samples. The thermal degradation essentially slowed with wt. 1–2% of CNTs, and mechanical properties appreciably improved for low filler content (up to 3 wt.%). Electrical measurements showed a percolation threshold in the range 1–3 wt. % of CNTs [17].

MWCNTs were incorporated into ultrahigh molecular weight polyethylene (UHMWPE), a polymer used for industrial and orthopedic purposes. Also, composites were prepared through the use of ball milling and thermo-compression processes at concentrations up to 3 wt.%, and subsequently gamma irradiated at 90 kGy. Electrical conductivity measurements showed a low percolation threshold of 0.5 wt.%. Electron spin resonance detection of the radiation-induced radicals proved to be radical scavenger behavior of MWCNTs: when the nanotube concentration rose, the number of radicals generated by the gamma irradiation process decreased. Allylic radicals seem to be radicals most affected by the presence of nanotubes in this polymeric matrix. Fourier-transformed infrared spectroscopy measurements and an accelerated ageing protocol were carried out to ascertain the influence of irradiation on the oxidation index. The results obtained were indicative of positive contribution of the MWCNTs to raising the oxidative stability of the composite as compared to pure UHMWPE. Cross-linking density induced by gamma irradiation was obtained by means of swelling measurements. The findings showed that despite the radical scavenger performance, MWCNTs proved to be capable of maintaining the efficiency of the cross-linking density, unlike other antioxidants which inhibit radiation cross-linking [18].

Polymer nanocomposites with CNTs as fillers turned out more attractive than other nanomaterials. An extensive development of these materials requires an in-depth comprehension of the way they behave in the current situation. In the work [19], the resistance to accelerated photooxidation of syndiotactic polypropylene/MWCNTs films was compared to the photooxidation behaviour of unfilled polypropylene films with the same structural organization. The chemical and structural modifications resulting from photo-oxidation were followed by infrared spectroscopy and diffractometric analysis. It
found that a good dispersion degree of the nanofiller evaluated by atomic force microscopy, contributes to the fall of rates of photooxidation and rise in the oxidative thermal stability of the polymeric matrix. Different concomitant effects are believed to explain these results, among which morphology and structure of the nanocomposites together with the MWCNTs capacity interacts with oxygen molecules which make them unavailable in the first stages of photo-oxidation [19].

Hindered Amine Light Stabilizer (HAS) molecules were covalently linked on the outer surface of multi-walled carbon nanotubes (CNTs), and thus obtained multi-functional fillers (HAS-f-CNTs) were compounded with Ultra High Molecular Weight Polyethylene (UHMWPE) to get composite films [20]. The success of the grafting reaction of the HAS molecules was scored through spectroscopic and thermo-gravimetric analyses. Morphological analyses reveal a segregated microstructure where CNT-rich channels surround the polymer domains. This morphology results in improved mechanical properties and appreciable electrical conductive features. More importantly, the addition of just 1 wt.% of HAS-f-CNTs brings about a significant improvement of the photo-oxidation resistance which HAS or CNTs can provide if used separately. The origin of this synergic effect is discussed. As a whole, our results demonstrate the possibility of using properly functionalized CNTs as multifunctional fillers to get high-performance polymer composites [20].

Another work of the said authors describes MWCNTs functionalizing with hindered phenol moieties which are dispersed in UHMWPE [21], and the stabilizing effect of the antioxidant (AO) functionalized CNTs (AO-f-CNTs) is examined through a combination of rheological and spectroscopic (FT-IR) analyses. The effectiveness of the two alternative compounding methods, namely hot compaction (HC) and melt mixing (MM), is compared. The combination of high temperature and mechanical stress experienced during MM brings about a noticeable degradation phenomena of the matrix already in the course of the compounding step. Differently, the milder conditions of the HC process contribute to the preservation of stability of the polymer, making this method preferable when dealing with highly viscous matrices. In addition, HC guarantees a better CNT dispersion, allowing for maximization of the stabilizing action of the AO grafted on nanotubes. As a result, the HC samples exhibit improved thermo-oxidative resistance despite the very low amount of AO grafted onto the CNTs. In addition to the effectiveness of our AO-f-CNTs as stabilizers for polymer matrices, our results prove that CNTs can serve as support on which grafting specific functional molecules may be dispersed in a host polymer matrix [21].

**Biological objects**

MWCNTs were synthesized at a low temperature on silicon substrates on a thermal chemical vapor reactor from ghee, clarified butter from cow's milk as the carbon source without using any catalyst. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses revealed bundles of micrometer long MWCNTs with an interlayer separation of 0.33 nm consisting of 25 concentric graphene sheets with outer and inner diameters of 27.45 and 13.68 nm, respectively. The powder X-ray diffraction (XRD) pattern showed a hexagonal structure of graphitic carbon with average crystallite size of 4.6 nm. The MWCNTs exhibited apparent antioxidant activity [22].

The authors report on synthesis of carbon nanodots (CNDs) which may be related to a new group of ultra-small nano structures (average 4-6 nm). The synthesis of CNDs was carried from date molasses by microwave irradiation similar to pH 11 [23]. The synthesized CNDs were characterized using UV-Vis spectroscopy, fluorescence spectroscopy, TEM, XRD analysis, FTIR study and Zeta potential measurement.
Average size of dots was found to be 5-7 nm. A clear band emission was visible around 480 nm while an excitation beam of 415 nm was incidental. For biological applicability, MTT assay and hemocompatibility studies were performed. The results exhibited the material to be highly cytocompatible within the application limit. Upon immediate exposure to CNDs, no significant changes to cellular surface morphology were observed via AFM imaging. Significant hemolysis or blood cell aggregation was not observed after incubation of CNDs with blood. After labeling with CNDs, MG-63 cells were found to be unbleached up to several hours even on exposure to light. Free radical scavenging property of CNDs in ex vivo and in vitro models was reported for the first time in the research [23]. Antioxidant activity was measured ex vivo via potassium permanganate assay and DPPH assay. In vitro superoxide inhibition activity was measured both by spectroscopy and under microscope by NBT reduction assay. Hydroxyl free radical inhibition activity was measured via DCFH-DA assay. The results were comparable to the scavenging activity of standard antioxidant molecules (BHT and L-ascorbic acid). A novel assay for quantitative analysis of cellular oxidative stress was also proposed. Therefore, this material could be useful for long-term live cell imaging and cell tracking in a scaffold with minimal cytotoxicity and oxidative stress [23].

The use of natural antioxidants is an attractive way to formulate nanocomposites with extended durability and with potential applications in bio-medical field. Vitamin E (VE) in the form of alpha-tocopherol and Quercetin (Q) are physically immobilized on the outer surface of multi-walled CNTs. Afterward, the CNTs-VE and CNTs-Q are used to formulate thermally stable ultra-high molecular weight polyethylene based nanocomposites. The latter is used for making catheters. The obtained results in the study of the thermo-oxidation behavior suggest a beneficial effect of the natural antioxidant-CNTs systems [24]. The unexpected excellent thermo-resistance of the nanocomposites seems to be due to a synergistic effect of the natural antioxidant and CNT, i.e. strong interaction between CNT surface and antioxidant molecules. Particularly, these interactions cause the formation of structural defects onto outer CNT surfaces which, in turn, increase the CNT radical scavenging activity [24].

MWCNTs were functionalized with a series of amino acids (lysine, arginine, cysteine, histidine, and aspartic acid) by means of sonication. Surface functional groups of the treated MWCNTs were investigated by infrared spectroscopy, Raman spectroscopy and thermo-gravimetric analysis. The results obtained are illustrative of the formation of various amino acid functionalities on the MWCNT surface, as well as the improved dispersion of MWCNTs in water [25]. After functionalization, the antioxidant activity of all treated samples was analyzed using 2,2-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), 1,1-diphenyl-2-picrylhydrazyl (DPPH), and hydroxyl radical scavenging, metal ion chelating, and reducing power assays. The antioxidant activity of the functionalized MWCNTs was up 2-2.5 times from the reduced glutathione (GSH) in ABTS radical scavenging, up 1.5-5 times from GSH in reducing power, up 1.3-1.8 times from butylated hydroxyanisole (BHA) in DPPH scavenging, and up 3-10 times from GSH in hydroxyl radical scavenging. Accordingly, the amino acid-functionalized MWCNTs turned out more potent than BHA and GSH synthetic antioxidants and thus considered as excellent antioxidants to scavenge free radicals [25].

**Conclusion**

Carbon nanotubes (CNTs) are intended to effectively prevent oxidation of hydrocarbons and thermo-photo- oxidative disruption of polymers from the trapping of...
formed radicals [26]. The stabilization of polymeric materials may also take place when a thin protective film of CNTs is generated on a surface of nanocomposites. The free radical scavenging property of CNTs in the vivo models has been unequivocally proved. The kinetic data obtained specify the level of antioxidative activity of the CNTs and the scope of their rational use in different systems.

REFERENCES


İcmalda karbon nanoborularının (KNB) polimer kompozisiyaları və bioloji obyektlərin oksidləşmə mühitinə təsirinə aspektində aparılan dünya miqyaslı tədqiqatlar barədə qısa məlumat verilmişdir. KNB əsas etibarı ilə polimerlərdə terməstabilizator və bioloji substratların tərkibində isə radikal akseptoru kimi təsir göstərməklə yüksək antioksidləşdirici xassə nümayiş etdirirlər. Oksidləşmə proseslərində inhibitor təsirinə gora KNB güclü sənaye və təbii mənşəli antioksidantlarla müqayisə oluna bilər.

Acar sözlər: karbon nanoboruları, polimer kompozitləri, termal destruksiya, füllerenlər, oksidləşmə, radikal akseptoru

**ПОВЕДЕНИЕ УГЛЕРОДНЫХ НАНОТРУБОК В ОКИСЛИТЕЛЬНЫХ СРЕДАХ**

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В обзоре приводятся сведения об исследованиях по изучению влияния углеродных нанотрубок (УНТ) на окислительные среды в полимерных композитах и биологических объектах. УНТ показывают высокую антиоксидантную способность, и предпочтительно действуют как термостабилизаторы в полимерах и акцепторы радикалов в биологических объектах. В этом отношении УНТ можно сравнить с сильными коммерческими и природными известными антиоксидантными остатками.

**Ключевые слова:** углеродные нанотрубки, полимерные композиты, термическая деградация, фуллерены, окисление, очистка радикалов.

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