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Improving post irradiation stability of high density polyethylene by multi walled carbon nanotubes

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ABSTRACT

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 in detail. The present work is aimed to investigate the 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 level starting from 25 to 100 kGy and then 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 were found to be 21.5%, 20.3% and 19.2%, respectively compared to that of unirradiated composite. FTIR and ESR studies confirmed the antioxidant and radical scavenging potentialities of MWCNTs with increased concentration and irradiation dosage. It was found that by the addition of 1 wt.% MWCNTs into virgin HDPE, the oxidation index of the composite at 100 kGy was decreased by 56.2%. It is concluded that the addition of MWCNTs into polyethylene not only limits the loss of mechanical properties but also improves its post irradiation oxidative stability.

1. Introduction

Materials have been continuously evolved over ages to fulfill the requirement of engineering and medical applications. Iijima's article in 1991 [1] has triggered thoughts of multifarious researchers to investigate the potential use of carbon nanotubes as a reinforcing element for polymer nanocomposites due to their remarkable properties such as extremely high Young's modulus and tensile strength, Treacy et al. [2]. Though MWCNTs are being considered in different applications, medical science is one of the fields where they are explored to restrict the consequence of the degradation of material properties. Various researchers have studied the properties of polyethylene as a function of filler materials [3–11] and gamma irradiation dosage [10–14]. Barus et al. [3] reported that the presence of MWCNTs (0.1–2 wt.%) in polyethylene delayed thermal volatilization of composites by 15–20 °C without modifying the thermal degradation mechanism. It was also reported that thermal oxidative degradation of HDPE in air was also delayed up to 100 °C depending on MWCNTs concentration and the degree of their dispersion. Bocchini et al. [4] reported that the addition of MWCNTs into LLDPE increased its thermal stability by 100 °C. It was confirmed that the stabilization was due to the formation of degradation residues of MWCNTs/carbon char on the surface of the polymer, which induced the fire retardant behavior, not by the concentration of MWCNTs [5]. Kodjie et al. [6] reported that addition of single wall carbon nanotubes (SWNTs) in HDPE increased the crystallization temperature and thermal stability by 115 °C. Kanagaraj et al. [7] observed an enhancement of Young's modulus and toughness of a 0.44% v/v of MWCNTs in HDPE by 22% and 32%, respectively. It was also observed that the onset temperature of the degradation of composites decreased due to carbonaceous impurities present in MWCNTs; however the melting point of the composites was same irrespective of MWCNTs concentration. Mehta et al. [8] reported that both Young's modulus and ultimate strength of MWCNTs/HDPE nanocomposites were increased by 36% for 1 wt.% of MWCNTs in HDPE. Zou et al. [9] studied the mechanical properties of MWCNTs/HDPE composites having 0.3, 0.5, 1.0, 2.0 and 3.0 wt.% of MWCNTs along with SiO_2 particles, where the optimum concentration of MWCNTs was found to be 1 wt.% for the enhancement of mechanical properties of composites.

Morlanes et al. [10] incorporated MWCNTs (1, 3 and 5 wt.%) in ultra high molecular weight polyethylene (UHMWPE) and irradiated at 90 kGy. It was reported that thermal stability of

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composites was significantly improved in addition to 71% increase of Young's modulus of irradiated nanocomposites compared to unfilled irradiated UHMWPE. Carmen et al. [11] prepared hydroxyapatite (HA)/HDPE composites, which were then gamma irradiated. Though Young's modulus of the composite was increased by HA addition, tensile strength of the composites was not shown significant variation at different dosage level. However, it was reported that elongation at break showed a drastic reduction with reinforcement of HA. Puig et al. [12] characterized the thermal behavior of gamma irradiated HDPE/LDPE blends and observed a good enhancement of the crystallinity of polyethylene with irradiation dose. Catano et al. [13] studied the influence of gamma irradiation (25 kGy and 100 kGy) on mechanical, thermal and rheological properties of HDPE filled with seaweed residues. Though Young's modulus of the composites was increased by 40% at 100 kGy dosage, the fracture strain was reduced by 8.4% at 40 wt.% of filler material. Rimnac et al. [14] reported an inhomogeneous degradation of the properties of gamma irradiated and shelf aged polyethylene. According to Watts et al. [15], MWCNTs have shown electron affinities and they might behave as strong radical traps in chain reactions, which interrupted chain propagation leading to antioxidant effects in polymeric materials. Anti-oxidative effect of MWCNTs and carbon nanofiber of platelet structure was studied by the method of initiated oxidation reaction, Zeynalov and Friedrich [16]. It was reported that kinetic measurements of the oxygen uptake showed reduced values of oxidation rates in the presence of MWCNTs. Post irradiative treatments were usually performed in polymers to mobilize the free radicals and help them to recombine with each other to enhance the oxidative stability of polyethylene, Kurtz [17].

Though MWCNTs have been used as a filler material to enhance the properties of a polymer, a detailed study on the role MWCNTs both as a filler material and an antioxidant has not been carried out to enhance the material properties and post irradiative oxidative stability. Thus, an attempt was made to study the influence of MWCNTs in resisting the post-irradiative oxidation and counter its deteriorating effects on mechanical properties of polyethylene. In the current study, typical mechanical properties of shelf aged gamma irradiated MWCNTs/HDPE composites were evaluated using small punch technique according to ASTM F2183-02 standard. The oxidation index (OI) of the composites was obtained from Fourier transform infrared (FTIR) spectroscopy and the results were analyzed to estimate the influence of MWCNTs as an antioxidant material in resisting the post irradiative oxidation. To support the above findings, electron spin resonance (ESR) studies were conducted to observe the radical concentration in composites at different MWCNTs concentration and irradiation dosage.

2. Materials and methods

2.1. MWCNTs/HDPE composites

The MWCNTs/HDPE composites with different concentration of MWCNTs viz 0.25%, 0.50%, 0.75% and 1.00% by weight required for the present investigation were supplied by Prof. Simoes, University of Aveiro, Portugal. The materials used, preparation and processing techniques followed in composite preparation were discussed in detail by Kanagaraj et al. [7]. However, a brief description is given here. The required sample of MWCNTs was suspended in the mixture of concentrated nitric acid (65%) and sulfuric acid (95–97%) by the volume ratio of 1:3 and boiled at 140 °C for 30 min. The chemically treated nanotubes were washed with deionized water until the supernatant attained a pH around 7, and the sample was dried in a hot air oven at 100 °C. The MWCNTs thus obtained were dispersed in water to prepare nanofluid and the pellets of HDPE were mixed in it and continuously stirred in a magnetic hot plate stirrer to ensure uniform coating of MWCNTs over HDPE, which were then used as a raw material in an injection molding machine to get the required test sample. Samples received from University of Aveiro, Portugal were in the form of hemispherical cups resembling liner for the acetabular cup used in total hip replacement.

2.2. Preparation of small punch test specimen

The required test specimen was cut from the composite using a shear punch, which was then polished down to a thickness of 0.50 mm using emery papers of different grades. All machining operations were done carefully in order to maintain the required dimension. The test specimen thus obtained was in accordance with ASTM F2183-02 standard [18] having the final dimension of 6.4 mm in diameter and 0.50 mm in thickness.

2.3. Gamma irradiation

The test specimen of all composites has been gamma irradiated in air by ^{60}Co source at a dosage rate of 2.5 kGy/h for 25, 50, 75 and 100 kGy dosages. As the mechanical properties and wear resistance of the polymer saturate at above 100 kGy irradiation, Muratoglu [19], the proposed study was carried out up to 100 kGy dosage level, which was performed at M/s Microtrol Sterilization Private Limited, Bangalore, India.

2.4. Small punch test assembly

The small punch test assembly consists of a hemispherical head punch, die and a guide, which were obtained in accordance with ASTM F2183-02 standard [18]. The test assembly was mounted in a digitally controlled closed loop Servo Hydraulic universal testing machine, INSTRON 8801. The tests were conducted at a cross head speed of 0.5 mm/min. in the temperature range of 20–24 °C. In order to ensure the repeatability of the results, the experiments were repeated six times with same working condition. The reported results were an average of data obtained from six specimens. The test samples were shelf aged for 120 days prior to their investigation.

2.5. Scanning electron microscope (SEM)

To understand the nature of failure of the test sample, the failure section of the fractured specimen was observed in SEM Leo 1430 VP.

2.6. Fourier transform infrared spectroscopy (FTIR)

The amount of oxidation of a test sample was quantified by FTIR spectroscopy by measuring the relative amount of carbonyl groups. The area under the peak was proportional to the concentration of carbonyls present in the test sample. In case of carbonyl and CH_2/CH_3 peaks, the tie-line was extended from 1690 to 1750 cm^{-1}, and 1330 to 1390 cm^{-1}, respectively. The OI was a relative quantification of the concentration of oxidation within the polyethylene and it was calculated by finding the ratio between the area of carbonyl peak to the area of CH_2/CH_3 peak [20]. The FTIR spectrum of the irradiated samples was obtained after shelf aging for a period of 120 days. As the thickness of the test sample was 0.50 mm, the OI was calculated on the surface of the specimen with an assumption that the surface oxidation was the same as that of bulk oxidation. The PerkinElmer, spectrum one FTIR spectrometer was used in this study.