



Photo-oxidative stabilization of carbon nanotubes on polylactic acid

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ABSTRACT

This paper aims to study the effect of multiwall carbon nanotubes (MWCNTs) on the photo-degradation behavior of polylactic acid (PLA) composites exposed to UV-light. The MWCNT dispersion state within the PLA matrix was analyzed by electrical conductivity measurements. From gel permeation chromatography it was verified that the rate of photo-degradation of PLA/MWCNT composites is lower than that of the unfilled PLA. The surface morphology modifications induced by UV have been analyzed by optical and scanning electron microscopy. Thermal analysis revealed an increase in the polymer crystallinity and a decrease in the degradation temperature during the UV treatment. The mechanical properties (Young's modulus and tensile strength at the yield point) were significantly increased by the addition of MWCNTs. However, the tensile strength and strain to failure slightly decreased with an increase in irradiation time. This complex behavior was attributed to a molecular reorganization in the first period of photo-aging followed by a severe macromolecular chain scission.

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1. Introduction

The ability of a polymer material to resist at a wide variety of chemical reactions and physical processes which occur when it is exposed for extended periods of time to aggressive environmental conditions is called “polymer durability” [1,2]. Extensive literature research has shown that for the great majority of polymers, the most important degradation mechanisms are associated with the combined action of ultraviolet (UV) light and oxygen absorption [3–5]. The overall light-initiated processes in the presence of oxygen generally are referred to as oxidative photo-degradation or photo-oxidation. Furthermore these reactions are influenced by molecular structure, polymer morphology (chains orientation and crystallinity), internal impurities, specimen thickness, temperature, irradiation intensity and other climatic conditions [5]. For that, the problem of stabilizing polymers against UV-light is not a simple task. It is generally done by addition of ultraviolet screens, absorbers, or deactivators to the polymer matrix [3]. In particular, the UV screens prevent the penetration of UV radiation beyond the surface thus restricting the total amount of degradation to a thin surface layer [4].

Carbon black is one of the most effective stabilizers for most polymers [6], and it is a relatively inexpensive commodity. The effectiveness of carbon black is dependent on its purity, the particle size and the degree of dispersion within the polymer matrix [7]. It is considerably more efficient than would be predicted on the basis of just its ability to screen the polymer from UV-light [8]. The increased efficiency of carbon black is usually ascribed to its ability to trap radicals produced during the photo-oxidative processes which lead to chain degradation. Heskins and Guillet [9] have suggested that carbon black may also stabilize polymers by its ability to quench the excited states induced in the polymer by the absorption of UV radiation. One of the more important drawbacks to the use of carbon black is that this stabilizer at high concentration affects negatively the mechanical properties of the resultant composites. For example, the stabilization of polyethylene increases with concentration of carbon black, but higher concentrations may result in the loss of mechanical properties such as elongation and impact strength [10].

The emerging availability of nanometer feature materials, such as fibers, plates, whiskers and carbonaceous fillers, opens the possibility of manipulating the morphology of these systems at nanoscale [11,12]. In particular, the very appealing physical and mechanical properties of carbon nanotubes, such as high elastic modulus, as well as remarkable thermal and electrical conductivity, have stimulated great interest due to the wide range of possible technological applications [13]. Among the huge literature on

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carbon nanotube based composites, only few papers deal with the polymer UV photo-degradation [14–16].

Polymers produced from renewable resources have attracted increasing interest as possible alternative to the exhaustion of petroleum resources [17]. However, the low resistance to atmospheric degradation is now becoming major limits to the use of these plastic materials in several outdoor applications. In fact, the effect of exposure to moisture and UV radiation may degrade rapidly the properties of these materials during the period of use. This effect is caused by the combination of scission of the main-chain, photo-induced crystallization and crosslinking [2,5]. Although the latter two processes can, initially, improve the properties of the polymer, if the action is allowed to go on for an extended period of time the ultimate result is usually deleterious [18].

Poly(lactic acid) (PLA) has one of the most important positions on the market of biodegradable polymers. As the interest devoted to this polymer grew, attention was increasingly given to durable PLA applications, especially with regard to thermal and light resistance [19]. In literature are reported different degradation mechanisms suggesting that the main-chain scission of PLA randomly occurred by UV irradiation following Norrish type I and/or Norrish type II reactions [5,19–21]. Ho and Pometto [22] and Copinet et al. [23] described separately action of UV, temperature and relative humidity on PLA. They observed a faster decrease of crystallinity, molecular weight and faster hydrolysis at the ester linkage by increasing humidity and temperature. However, among the huge literature on the degradation of PLA, only few papers deal with the possibility of use nanoparticles as UV stabilizers. These studies mainly concern composites with clay [24–26] and in all the cases it is shown that composites degrade faster than the pristine polymers.

In this paper the effect of carbon nanotubes on the photo-oxidation of composites composed of PLA and multiwall carbon nanotubes (MWCNTs) is investigated and compared to the behavior of the pristine PLA. Mechanical, thermal and electrical properties were evaluated on the composites and discussed as a function of photo-aging time.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) was supplied from Nature Works (NatureWorks® PLA Polymer 2002D) in pellet form. Multiwall carbon nanotubes were purchased by Aldrich (CAS Number 308068-56-6). They were synthesized by catalytic vapor deposition (CVD) process and have a content of carbon higher than 98%. Their diameter was between 6 and 13 nm and their length between 2.5 and 20 μm . The specific surface area determined with the BET method was 220 m^2/g .

2.2. Composite preparation

All the composites were prepared using a Minilab twin-screw mini-extruder equipped with co-rotating screws and a closed loop for re-circulation. Temperature of the mini-extruder was set at 180 °C. The PLA/MWCNT mixture was introduced in the mini-extruder for 5 min at 150 rpm screw speed. The extrudates were cooled in air at the exit of the die having a 1 mm diameter. Composites with three different concentrations of carbon nanotubes, namely 1.5, 3.0, 5.0 wt%, were prepared. For comparison, the neat PLA sample was also processed under similar conditions in order to ensure identical thermal history. The PLA based composites and unfilled PLA were molded in a hot press (Carver Inc.) at 180 °C forming 70 \pm 5 μm thick film films and cooled at ambient temperature.

2.3. UV-light irradiation

Composite samples in the form of films were exposed to UV irradiation (220–640 nm) in a climatic chamber (Angelantoni Challenge 250) at constant temperature (30 °C) and constant relative humidity (50%) for several days. The irradiation intensity was about 125 W/m^2 at an irradiated area of 50 \times 50 cm, and the films were exposed in a distance of 20 cm from the lamp. In order to irradiate both surfaces, the films were manually turned every 12 h.

It is important to point out that the UV wavelengths found in the sunlight penetrating the Earth's surface ranges from 295 to 380 nm. However, the majority of the polymeric materials absorb light in the range 200–300 nm. These wavelengths, normally used to sterilize workspaces, biology laboratory tools and medical facilities, cause a severe degradation of the polymer chains that does not occur under natural conditions. For that, the results obtained in this paper refer to an ample spectrum of conditions, generally not present in other studies that use normal terrestrial wavelengths. For major details, the spectral distribution of the used light source was reported in the [Supplementary data](#).

2.4. Methods of investigation

Gel permeation chromatography (GPC) were carried out on a system equipped with a Waters 1525 binary pump, a Waters 2414 RI detector and four Styragel columns (range 103–106 Å). The measurements were achieved at 25 °C, using THF as eluent (1.0 mL/min) and polystyrene standards as references. All samples before testing were previously dissolved in THF for 24 h under stirring. After dissolving samples in THF no gel formation was observed. In order to separate MWCNTs from PLA, solutions were centrifuged with a Thermo ALC centrifuge (Mod PK 110) at 4000 rpm for 1 h. Solutions of PLA in THF were then separated from the deposited MWCNTs and filtered three times using nanosieves Whatman.

Light microscope (LM) model Olympus BX41 equipped with a digital camera was used to characterize the microstructure of the samples.

Scanning electron microscopy (SEM) analysis was performed with a LEO 1525 microscope. Before the SEM analysis the sample was covered with a 250 Å thick gold film using a sputter coater (Agar mod. 108 A).

The electrical conductivity was measured at room temperature with a Keithley 6517A electrometer unit in a two-probe resistance measurement configuration. The source delay for each point of measurement was about 5 s. To enhance the electrical contact between the samples and the electrodes, metallization with Au was used. The electrical conductivity was measured in the voltage range –10–10 V whereas the results were averaged on three samples.

Thermogravimetric analysis (TGA) was carried out with a Mettler TC-10 thermobalance. Polymer composites samples were heated from 25 °C to 800 °C at 10 °C/min heating rate under air flow.

Differential scanning calorimetry (DSC) analysis was carried out on samples with a mass ranging between 5 and 7 mg. The tests were carried out by means of a DTA Mettler Toledo (DSC 30) under nitrogen atmosphere. The samples were heated from 25 °C to 200 °C at 5 °C/min. To ensure the reliability of the data obtained, heat flow and temperature were calibrated with standard materials, indium, and zinc.

The oxidation induction temperature (OIT) was evaluated according to the testing procedure of ISO 11357-6-2008. Samples of approximately 10 mg were heated in the DSC from 20 °C to 400 °C at a rate of 10 °C/min with an oxygen flow of 50 mL/min. OITs were determined by the onset of exothermic oxidation reaction of PLA shown in the calorimetric curves. Each experiment was repeated for three times, and the results indicated a good repeatability.

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