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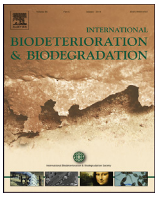

Enhanced photodegradation of titania loaded polyethylene films in a humid environment

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ABSTRACT

Common plastic goods, in general, and plastic shopping bags, that are generally made from polyethylene (PE), in particular, are a cause of considerable environmental nuisance. Development of a material that would degrade due to sunlight, in the open environment is, therefore, of considerable interest. In this study, for the first time ever, photocatalytic degradation of polyethylene, using titania nanoparticles, up to the maximum holding capacity of PE matrix (20% w/w), has been investigated under UV and visible light. The effect of water and air on the degradation of PE films was also studied. Materials were characterized using SEM, XRD, EDS, FTIR, TGA, Tensile Strength and Profilometry. Surface morphology of the exposed films was observed using light microscopy and Scanning Electron Microscopy (SEM). Formation of intermediate carbonyl species was investigated using the FTIR technique. It is conclusively demonstrated that the photocatalytic reaction rate constant was linearly dependent on the concentration of titania contained in the polymer matrix, with the degradation in the visible light about one-third slower than that under UV light. PE films containing 20% TNPs showed a maximum of 33% and 60% weight loss after 90 days exposed to visible light and UV light respectively. It was observed that highest weight loss of 21% was achieved when both air and water was available in the system. Presence of oxygen is very important for the initiation of degradation process however, the process cannot be sustained in the absence of moisture. The results of the study could be used to develop polyethylene films of the desired half-life, by changing the titania concentration.

1. Introduction

Polyethylene (PE), an important polymer that finds application, among other things, in the production of shopping bags and packaging films, represents 64% of synthetic plastic (Byuntae et al., 1991). These shopping bags and various forms of PE films, soon after their useful life, are discarded to the open environment. Significant amount of PE waste is, thus, introduced to the marine environment which poses a serious threat to the marine life as such waste causes death of sea fish, birds and mammals by blocking their digestive system (Teuten et al., 2009). Hence, common plastic goods in general, and plastic shopping bags, in particular, are a cause of considerable environmental nuisance (Kim et al., 2006; Tharanathan, 2003).

In order to deal with the problem a variety of techniques have been proposed for the disposal of plastic waste. These include plasma technology treatment, catalytic and thermal conversion of PE waste into fuel oils. While, recycling of PE is not an economically viable option (Zhao et al., 2008), because of their non-biodegradable nature and chemical inertness, waste PE materials are mainly being disposed off using incineration which, however, results in toxic by-products (Li et al., 2010).

In the photocatalytic degradation of solid, aqueous and gaseous phase contaminants Titanium Dioxide (TiO_2), commonly known as “titnia” is preferred over other photocatalysts due to its low cost, availability, non toxicity, high photocatalytic activity, favorable redox potential, chemical stability and its ability to completely mineralize the organic pollutants to CO_2 and water (Zhua et al., 2009). The possibility of PE degradation involving photocatalysis using titania is an alternative option (Mehmood et al., 2015).

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In this context a number of studies have been conducted on solid phase photocatalytic degradation of PE using titania (Cho and Choi, 2001; Zhao et al., 2007; Fa et al., 2010; Pablos et al., 2010; Thomas et al., 2013). Weight reduction of up to 42%, after 300 h of light exposure, of polyethylene films embedded with titania, has been reported (Zhao et al., 2007). Similarly, metal doping of TNPs with Molybdenum, and embedding these particles into PE also showed very encouraging results (Kemp and Robin, 2006). Whereas, good degradation has been reported for PE films containing polyacrylamide grafted TiO_2 (Liang et al., 2013) co-doping of TNPs, with metals (Fe, Ag, and Fe/Ag mix) has also been reported with very good degradation under visible light (Asghar et al., 2011). Photodegradation of polyethylene-TiO_2 nanocomposite film with oxidized polyethylene wax, using up to of 3% TNPs under UV and visible light resulted in high weight reduction, whereas 94% reduction in molecular weight was also observed (Fa et al., 2010). Photodegradation of PE films in the presence of CuPc modified TiO_2 photocatalyst was found to result in more than 90% of the total weight loss in the form of CO_2 (Zhao et al., 2008), while in a recent study, very high degradation results have also been reported (Thomas and Sandhyarani, 2013).

The application of titania for the degradation of PE has been conclusively demonstrated over the last decade; the controlled degradation of PE films having desired half-life, using titania, has, however, received little attention. This is important because the PE films have very diverse use under highly variable conditions. Control over the PE degradation rate is very crucial and also important in deciding the application of PE film and thus we propose a simple, yet effective, method to control the PE degradation rate by altering the titania content in the polymer matrix.

Photocatalysis using TNPs normally starts with the absorption of a high energy photon ($h\nu$), having energy equal to, or greater than, the band gap of TiO_2 resulting in the generation of an electron–hole pair. The electron–hole pairs can be trapped by the surface adsorbed water molecules and enhance the photocatalytic activity. The effect of humidity and oxygen thus plays a major role in the process. In the current study, we have investigated the photocatalytic behavior of laboratory prepared polyethylene films embedded with titania nanoparticles upto 20% (w/w) under a humid environment. Maximum capacity of PE films to hold the TNPs, beyond this limit the films became too brittle, even at the preparation stage, and was not amenable for further study, was evaluated. The effect of TNPs on properties of Titania-PE films and their photodegradation under UV and visible light are reported in this paper.

2. Materials and methods

2.1. Reagents

Commercial grade Low Density Polyethylene (LDPE), having a melting point of 115 °C and a density of 0.93 g/cm^3, was purchased from the local market. Cyclohexane (Merck) was used as a solvent to dissolve PE and TiO_2 (Merck) was used as a precursor material to synthesize titania nanoparticles. All the glassware (Pyrex, Germany) was used after washing carefully.

2.2. Preparation of titania nanoparticles

General purpose titania was added to 100 mL distilled water in a 500 mL Pyrex beaker. The slurry was stirred well and allowed to rest for 24 h and then dried in an oven at 105 °C for 12 h to get rid of any remaining moisture. The solid material resulting from this step was calcined at 500 °C for 6 h in a muffle furnace (NEY-525 SRIES II). After calcination the material was allowed to cool down slowly at room temperature, the resulting solids being finally ground for further application.

2.3. Preparation of polyethylene films

Polymer stock solution was prepared by dissolving 1 g of PE in 100 mL of cyclohexane at 70 °C under vigorous stirring for 1 h. Pure PE films were prepared by pouring 10 mL of the polymer stock solution on a glass petriplate of 4 cm radius and kept for 24 h at room temperature (27 °C). Following this, PE films were separated from the petri plates by placing in a water bath at 50 °C for 1 min. Titania composite PE films (0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20%) were prepared by adding the required quantity of TNPs in the molten polymer and exposed to ultra sonication at 70 °C, for 1 h and poured on the petriplates. PE films were cut into 5 cm × 5 cm square pieces and washed with distilled water before exposing these to UV or visible light.

2.4. Experiment for PE photocatalysis

Photocatalytic degradation of PE-TiO_2 composite films was carried out under UV or visible light in lamp housing. For UV irradiation, 6 W hand held UV-A lamp was used having primary wavelength of 365 nm. UV light intensity was 1.4 mW/cm^2 measured with ABM Model 150 digital intensity meter whereas, 24 W fluorescent lamp (Philips) was used as a visible light source. Both, UV and visible lamps were mounted on adjustable racks and positioned at 5 cm above the PE films. A set of films was also kept under dark. All the experiments were performed with three replicates at ambient temperature, with the mean values of the results being used for further analysis. Once the degradation rate of TNP-PE films was recorded under the 24 W fluorescent lamp, in order to speed-up the experimental work, 5% TNP-PE composite films were exposed to 85 W fluorescent lamp to evaluate the effect of humidity and air on the degradation rate under different conditions in air tight glass cells. While the 85 W fluorescent lamp is more than 3 times stronger than the 24 W lamp so it is believed to have the much faster degradation rate. Higher power of lamp allows achieving the higher degree of PE degradation in relatively lesser time.

2.5. Characterization and analysis

Various analytical techniques were employed to characterize the prepared titania nanoparticles (TNPs) and PE films. The crystal structure of the titania nanoparticles was studied using X-ray diffraction (XRD) spectroscopy using JEOL JDX-II with Cu-Kα radiation (voltage: 40 kV; current 20 mA). The range of diffraction angles (2θ) was 20°–80° and the scanning rate was 0.05° 2θ/s.

Rutile content in the TNPs was calculated based on the intensities of rutile and anatase peaks in the XRD patterns using following formula,

$$X_R = \frac{(I_R/I_A)0.79}{1 + (I_R/I_A)0.79} \tag{1}$$

here X_R shows the fraction by weight of the rutile phase TNPs, and I_A and I_R are the integrated X-ray intensities of the reflection of anatase at $2\theta = 25.4°$ and the rutile at $2\theta = 27.5°$, respectively.

Scherrer's formula was applied to calculate the particle size (L) using XRD data,

$$L = \frac{0.89\lambda}{\beta \cos \theta} \tag{2}$$

where L is the particle size, λ is X-ray wavelength, β is the full width