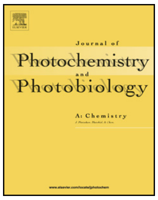
Journal of Photochemistry and Photobiology A: Chemistry 299 (2015) 159–165

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Antibacterial titania-based photocatalytic extruded plastic films

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ARTICLE INFO

Article history:
Received 7 August 2014
Received in revised form 13 November 2014
Accepted 15 November 2014
Available online 18 November 2014

Keywords:
TiO_2
LDPE
Photocatalytic
Antibacterial
Methylene blue
E. coli

ABSTRACT

Photocatalytic antibacterial low density polyethylene (LDPE)–TiO_2 films are produced by an extrusion method and tested for photocatalytic oxidation activity, via the degradation of methylene blue (MB) and photocatalytic antibacterial activity, via the destruction of *Escherichia coli*. The MB test showed that extruded LDPE films with a TiO_2 loading 30 wt.% were of optimum activity with no obvious decrease in film strength, although the activity was less than that exhibited by the commercial self-cleaning glass, Activ®. UVC pre-treatment (9.4 mW cm^{-2}) of the latter film improved its activity, with the level of surface sites available for MB adsorption increasing linearly with UVC dose. Although the MB test revealed an optimum exposure time of ca. 60 min photocatalytic oxidation activity, only 30 min was used in the photocatalytic antibacterial tests in order to combine minimal reduction in film integrity with maximum film photocatalytic activity. The photocatalytic antibacterial activity of the latter film was over 10 times that of a non-UVC treated 30 wt.% TiO_2 film, which, in turn was over 100 times more active than Activ®.

1. Introduction

Irradiation of titanium dioxide with the light of energy equal or greater than its band gap value results in the creation of electron–hole pairs, which, in turn, can lead to the photocatalytic process, in which the photoinduced holes oxidise donor molecules on the surface of the photocatalyst, such as adsorbed water, and the photoinduced electrons reduce acceptor molecules, usually ambient oxygen. The oxidation of adsorbed water generates adsorbed $OH^•$ radicals which can oxidise a wide variety of materials, including organic and inorganic pollutants [1–3]. The reduction of ambient oxygen can produce other reactive oxygen species (ROS), such as superoxide and hydrogen peroxide, which can also oxidise pollutants and act as a further source of $OH^•$ radicals. Titanium dioxide is the most used photocatalytic material both in research and in commercial photocatalytic products [1,4,5], and has been shown to be highly effective in the photocatalytic destruction of a wide range of organic and inorganic pollutants [3].

Photocatalysis has also been used extensively to destroy microbial species. The mechanism of photocatalytic bacteria inactivation was first proposed by Matsunaga et al. [6], and has been well-reviewed subsequently by others [7,8]. The antimicrobial effect of TiO_2 is attributed to the $OH^•$ radicals and oxygen reactive species (ROS) generated as part of the photocatalytic process in which the bacterial cell membrane is the primary ROS attack site, leading to lipid peroxidation, cell membrane damage and eventually cell lysis and death [9,10]. The photocatalytic antibacterial properties of titanium dioxide, along with its otherwise non-toxic and inexpensive nature, have attracted a great deal of attention and are now the basis for a number of commercial antibacterial products [11–13].

Many of polymeric materials find a wide range of applications in everyday life due to their chemical inertness, low cost, durability, flexibility and good mechanical properties. Not surprisingly, there is an increasing interest in polymer-supported photocatalytic materials, although in most cases the TiO_2 photocatalyst is used in the form of a coating on the polymer, rather than being embedded in the polymer [14–17]. In the case of hydrophobic polymers (such as polyethylene), the low surface energy of the polymers leads to low adhesion of such coatings [18] which, as a result, tend to delaminate, i.e. flake off.

One of the reasons for the interest in combining photocatalysis and hydrophobic polymers, is that the hydrophobic nature of the polymeric materials leads to low bacterial adhesion [19] and so are good materials to use in environments where the levels of pathogenic microbes should, in particular, be kept as low as possible, such as found in the health care industry. The use of such polymers in this environment is extensive and extends to their use in: aprons, sheets, curtains, etc. The combination of a highly hydrophobic polymer with an antimicrobial agent is obviously

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http://dx.doi.org/10.1016/j.jphotochem.2014.11.014
1010-6030/

very attractive and many antibacterial polymer films have been reported, usually involving the addition of an antibacterial agent, such as silver or copper [20,21], but also, more recently, by adding photocatalysts, such as TiO_2 and ZnO, usually in the form of surface coatings or surface embedded particles [22,23] although they are not usually that robust [24].

Although the preparation of TiO_2-loaded polymers has been reported previously [25,26], most have not used extrusion to produce thin, flexible films of the usual hydrophobic polyolefins used in the healthcare industry. A notable exception is the work of Bodaghi et al. who prepared LDPE films loaded with TiO_2, with glycerol and PE-MA as additives to aid particle dispersion [27]. The 30 μm extruded LDPE–TiO_2 films were tested as a possible antimicrobial food packaging material, with *Pseudomonas* spp. and *Rhothia mucilaginosa*. The use of glycerol as an additive in these films may inhibit their antimicrobial activity since glycerol is a very effective sacrificial electron donor [28] and so will compete with microbial species for oxidation.

In this paper, no such additives were used and we describe the incorporation of the highly effective photocatalyst, Evonik P25 TiO_2, into a highly hydrophobic polymer, low density polyethylene (LDPE), via extrusion and the subsequent testing of the polymer film sheets for both photocatalytic activity (using a modified methylene blue test) and antibacterial activity (based on the destruction of *Escherichia* coli) with and without UVC pre-treatment. The results reveal the plastic films to be antibacterial, with an activity that is enhanced significantly through the use of UVC pre-conditioning.

2. Experimental

2.1. Film preparation

Photocatalyst-embedded LDPE films were prepared by the extrusion of LDPE–TiO_2 masterbatch pellets, with pigment loadings ranging from 0 to 30 wt.%, using a Rondol Microlab 10 mm twin screw extruder. P25 TiO_2 (supplied by Evonik Industries), with a primary size of 25 nm and a mixture of 75% anatase and 25% rutile, and low density polyethylene (LDPE) powder, with a melt-flow index (MFI) of 20 (supplied by PW Hall, UK), were used to prepare a range of differently formulated masterbatches of TiO_2-pigmented pellets. For each masterbatch, the TiO_2 was dispersed through the LDPE powder prior to extrusion by stirring rigorously the two together. The pigmented pellets were then produced using a processing temperature that increased gradually from 90 °C (feed zone) to 140 °C (die) with the feed hopper rate set at 41 rpm, extruder screw speed 85 rpm and pelletiser speed 0.5 m min^{-1}. The pigmented masterbatch pellets so produced, each batch with a different TiO_2 loading, were then extruded in turn to produce photocatalyst-embedded LDPE films with the same loading of TiO_2 as the masterbatch pellets used. In making the titania-loaded films, the same temperatures and conditions were used as described above; with the take-off rollers speed set at 1 m min^{-1}. The average central thickness of all the TiO_2-loaded films produced, as measured using a micrometer, was 90 μm. Pure LDPE films (with no TiO_2), of identical thickness, were also prepared as blank samples, under otherwise the same conditions.

2.2. Methylene blue (MB) photocatalytic activity test

The photocatalytic activity of each of the extruded films prepared as above was assessed by measuring the ability of the film under test to photodegrade the dye, methylene blue (MB). The photocatalytic degradation of MB is commonly used to assess the activity of new materials and is the basis of an international standard for assessing photocatalytic activity, i.e. ISO 10678:2010 [29]. The photocatalytic mineralisation of MB, mediated by a TiO_2 photosensitiser, can be summarised as follows:

$$C_{16}H_{18}N_3SCl + 25.5O_2 \xrightarrow[h\nu>3.2\,eV]{TiO_2} HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \qquad (1)$$

Thus, in this work, the photocatalyst-bearing polymer film/sheet, plus supporting silicone rubber mattress layer, were clamped to a 1 cm spectrophotometric cell in place of a removed side; a schematic representation of the test cell is shown in Fig. 1.

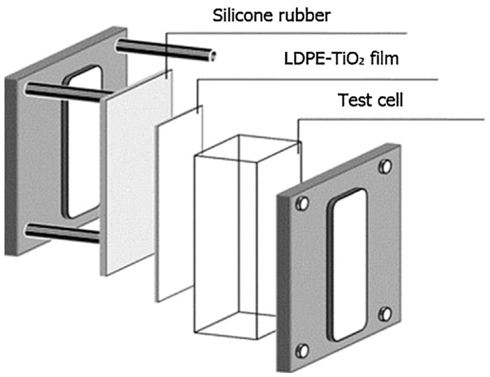

Fig. 1. Scheme of the test cell for assessing photocatalytic activity using the MB test. UVA irradiation was through the right hand side face of the test cell with the LDPE–TiO_2 film filling the place of the removed left-hand side face and held in place by the silicone rubber film and metal back and front clamps.

This arrangement allowed the absorption spectra of the MB solution placed in the cell (3.5 cm^3, 5×10^{-5} M) to be monitored spectrophotometrically at 30 min intervals with constant magnetic stirring until the MB was fully bleached by the photocatalytic film under test, or an irradiation time of 700 min was exceeded. Note that the photocatalysed bleaching of MB was monitored and used as a guide to photocatalytic activity, and that bleaching is unlikely to signify complete dye mineralisation as described by Reaction (1). Using this set up, the LDPE–TiO_2 film (or Activ® self-cleaning glass) under test was irradiated from the side, opposite to the test piece with UVA light from two 4 W black light blue (BLB) lamps generating a UVA irradiance of 1.6 mW cm^{-2}. A measure of the photocatalytic activity of the film under test was then taken as the value of the initial gradient of the plot of the measured absorbance of the MB solution at 665 nm vs irradiation time decay data.

2.3. MB adsorption

TiO_2 has a surface of OH groups, ≡Ti—OH, which can be protonated or deprotonated, depending on the ambient pH, i.e.

$$\equiv Ti{-}OH_2{}^{+} \Leftrightarrow \equiv Ti{-}OH + H^{+} \Leftrightarrow \equiv Ti{-}O^{-} + H^{+} \qquad (2)$$

Since TiO_2 has a pzc (point of zero charge) of ca. pH 6.6 [30]. Previous work [31] has established that it is possible to gain a measure of the available surface area of TiO_2 powers (for adsorption) by rendering the surface anionic (by adjusting the solution pH to 11) and adding a cationic dye, such as MB, which will ion-pair onto the surface of the TiO_2. In this paper, we shall refer to this combination of a high MB concentration (100 mg dm^{-3}) in a 10^{-3} M NaOH (pH 11) aqueous solution as the staining solution. The ≡Ti—O^-–MB ion-pair is very stable and so the adsorbed MB cannot be removed readily by just rinsing the stained titania film