



## Innovative transparent non-scattering TiO<sub>2</sub> bactericide thin films inducing increased *E. coli* cell wall fluidity



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### ABSTRACT

This study presents the first account for transparent, non-scattering TiO<sub>2</sub> films on radio-frequency (RF) plasma and ultraviolet light in the C-spectral region (UVC) pretreated polyethylene (PE). These pretreatments allow the PE to bind higher amounts of TiO<sub>2</sub> necessary to induce *E. coli* inactivation in the minute range under simulated sunlight irradiation. The uniform TiO<sub>2</sub> film was sputtered by direct current magnetron sputtering (DC). These higher TiO<sub>2</sub> loadings were necessary to obtain faster bacterial inactivation kinetics on the PE films. The peak shifts in the stretching of the symmetric and asymmetric vibrational infrared spectra of the C–H groups were followed during the time of bacterial inactivation (60 min). This time was concomitant with the time required for the hydrophobic to hydrophilic transition on PE-TiO<sub>2</sub>. The production of malondialdehyde (MDA) was observed during *E. coli* loss of viability. PE pretreatment led to a significant increase in the TiO<sub>2</sub> loadings on the PE surface as shown by X-ray fluorescence (XRF), X-ray-diffraction (XRD) by X-ray photoelectron spectroscopy (XPS).

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### 1. Introduction

TiO<sub>2</sub> film preparation on glass, iron plates, textile fabrics and polymer films is a subject of timely research related to self-cleaning and antibacterial films [1–4]. Sol-gel commercial methods are used to prepare TiO<sub>2</sub> thin films on heat resistant substrates [5]. But the thickness of the TiO<sub>2</sub> films is not reproducible, they are not mechanically stable, and they exhibit low adhesion since they can be wiped off by a cloth or thumb [6–10]. Colloid deposition on substrates requires a temperature of a few hundred °C for an adequate adherence to the selected substrate.

RF-plasma or UVC pretreatments were reported to induce an increase in the surface sites able to bind TiO<sub>2</sub> nanoparticles [9–12]. RF-plasma pretreatment increases the polarity, roughness and hydrophilicity (C–OH) of polymeric films improving its bondability and interfacial adhesion [15,16]. The largest increase in surface polarity has been reported for the surfaces presenting the highest O/C atomic ratio [13–18]. The RF-plasma pretreatment induces negatively charged functional groups, e.g., carboxylic, percarboxylic, epoxide and peroxide groups by the atomic O, excited O, anionic and cationic O generated in the RF-plasma chamber. The functionalized negative sites bind the

slightly positive sputtered Ti<sup>4+</sup> / (TiO<sub>2</sub>) through electrostatic attraction involving chelation/complexation [9,13].

Kelly and Sarakinos have reported sputtering of TiO<sub>2</sub> films on substrates [19,20] and recently, Mills [21], Parkin [22], Foster [23], Dunlop [24] and Yates [25] have deposited antibacterial TiO<sub>2</sub> films on glass and polymers by chemical vapor deposition (CVD). The disadvantage (CVD) is the high temperature required for the deposition, the high investment costs and the large amounts of heat used requiring costly cooling systems. Radetic and Kostic [26,27] have reported polymer surfaces with antibacterial properties.

Polyethylene (PE) is a low cost and widely available material. It is chemically inert, mechanically stable and flexible, UV-resistant and does not oxidize in air under sunlight. For this reason PE has been selected as the support for the TiO<sub>2</sub> film reported in this study. The PE-TiO<sub>2</sub> films are designed to increase the quantum yield for light induced processes due to the transparency [3–5,28,29]. This study focuses on the preparation of TiO<sub>2</sub> transparent, uniform, non-scattering films on PE (thermally stable up to 90 °C). The low temperature preparation of TiO<sub>2</sub> on polymers at temperatures below the PE flowing point is investigated in this study.

The present study addresses: a) design, preparation, evaluation and characterization of innovative pretreated PE-TiO<sub>2</sub> films inactivating *Escherichia coli*, b) the bacterial inactivation kinetics under solar simulated light concomitant with the time of the PE-TiO<sub>2</sub> hydrophilic–hydrophobic conversion, c) the surface characterization addressing:

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the film thickness, optical absorption roughness, nanoparticle size, Ti-loading and surface atomic concentration and d) the ATR-FTIR spectroscopy description of the vibrational-rotational peak shifts due to the increase of the –CH inter-bond distance leading to cell wall lysis causing bacterial death.

## 2. Experimental section

### 2.1. Pretreatment by RF-plasma and UVC; XRF determination of TiO<sub>2</sub>

The low density polyethylene (LDPE) consists of highly branched low crystalline semi-transparent film with the formula H(CH<sub>2</sub>–CH<sub>2</sub>)<sub>n</sub>H. The (LDPE) 0.1 mm thick was obtained from Goodfellow (ET311201), had a density of 0.92 g/cm<sup>3</sup>, an upper working temperature of 90 °C and a flowing point of 185 °C. The single bond in PE makes it stable towards chemical/corrosive agents favoring its wide use as insulator.

The polyethylene fabrics were pretreated in the cavity of the RF-plasma unit (Harrick Corp. 13.56 MHz, 100 W) at a pressure of 1 Torr. Oxygen RF-plasma reacts with the PE surface inducing functional PE-surface groups by: a) etching of the PE surface by the O-gas species, b) formation of surface O-hydrophilic surface groups and c) scission of intermolecular PE-bonds due to localized heat segmenting of the fibers [30].

The PE was also functionalized by UVC irradiation using the 185/254 nm low-pressure mercury lamp obtained from Ebara Corp., Tokyo, Japan. The UVC lamp presented emission lines at 254 nm and 185 nm in a ratio 4:1 with a total power of 25 W. The pretreatments were carried out at atmospheric pressure and at 1 Torr. The UVC activation, having a lower energy than the RF-plasma, does not lead to cationic or anionic oxygen species but only to atomic (O) and excited oxygen (O\*). The radiant energy at 185 nm provides energies above 241 nm equivalent to 495 kJ/mol or 5.12 eV, the energy required for slitting O<sub>2</sub> → 2O\*.

The Ti-content on the polyethylene was evaluated after the Ti sputtering in reactive O<sub>2</sub> gas by X-ray fluorescence (XRF) in a PANalytical PW2400 spectrometer.

### 2.2. Sputtering details of TiO<sub>2</sub> on PE and X-ray diffraction (XRD)

The TiO<sub>2</sub> was sputtered by direct current magnetron sputtering (DC) on PE as reported previously out of our laboratory [31]. Before sputtering the films, the residual pressure  $P_r$  in the sputtering chamber was set to  $P_r \leq 10^{-4}$  Pa. The substrate to target distance was set at 10 cm. The TiO<sub>2</sub> thin films were deposited by reactive DC-magnetron sputtering (DC) in an O<sub>2</sub> gas flow from a 5 cm diameter Ti-target 99.99% pure (Kurt J. Lesker, East Sussex, UK). The current on the Ti target was set at 280 mA, at a power of 128 W. The thickness of the sputtered layers was determined by means of a profilometer (Alphastep500, Tencor) by depositing TiO<sub>2</sub> films onto silica wafers.

The crystalline structure of the PE-TiO<sub>2</sub> film was investigated by X-ray diffraction (XRD) and recorded on an X'Pert MPD PRO from PANalytical equipped with a secondary graphite (002) monochromator and an X'Celerator detector operated in Bragg–Brentano geometry. A step size of 0.0081 was chosen and an acquisition time of 2 min per degree.

### 2.3. Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy was carried out a Perkin Elmer Lambda 900 UV–Vis–NIR spectrometer provided for with a PELA-1000 accessory within the wavelength range of 200–800 nm and a resolution of one nm. The absorption of the samples was plotted in the Kubelka–Munk (KM) units vs wavelength.

### 2.4. Atomic force microscopy (AFM) and contact angle

The AFM images were acquired in contact mode using a PSIA Xe-100 AFM. Silicon nitride cantilevers were used with feedback set points around 1.0 nN. The images originate from the Z-scanner and are not influenced by the non-linearity and the hysteresis of the z-scanner. The roughness values involve an experimental error below 10%. The mean surface roughness ( $R_a$ ) was calculated for the scanned area by applying Eq. (1)

$$R_a = \sqrt{\frac{\sum_{x,y}^N (Z_{x,y} - Z_{\text{average}})^2}{N^2}} \quad (1)$$

where:  $R_a$  is the normalized standard deviation calculated from the local heights ( $Z_{x,y}$ ) and the average height ( $Z_{\text{average}}$ ) determined over the  $x,y$  coordinates ( $N$ ) measured in the AFM image.

The hydrophilicity of the PE-TiO<sub>2</sub> films was determined by the water droplet contact angle by the sessile drop method on a DataPhysics OCA 35 unit.

### 2.5. Evaluation of *E. coli* inactivation on PE-TiO<sub>2</sub> and light sources

The samples of *E. coli* (*E. coli* K12) were obtained from the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ) ATCC23716, Braunschweig, Germany, to test the antibacterial activity of the PE-TiO<sub>2</sub> samples. The 2 cm by 2 cm samples were placed into a glass Petri dish to be inoculated with bacteria and irradiated in the cavity reactor. A 100- $\mu$ L of *E. coli* solution was contacted with the PE-TiO<sub>2</sub> uniform films. The 100  $\mu$ L culture aliquots with an initial concentration of  $\sim 10^6$  colony forming units per milliliter (CFU mL<sup>-1</sup>) in NaCl/KCl (pH 7) were placed on coated and uncoated (control) PE fabrics. After preselected irradiation times, the fabric was transferred into a sterile 2 mL Eppendorf tube containing 1 mL autoclaved NaCl/KCl saline solution. This solution was subsequently mixed thoroughly using a Vortex for 3 min. Serial dilutions were made in NaCl/KCl solution. A 100- $\mu$ L sample of each dilution was pipetted onto a nutrient agar plate and then spread over the surface of the plate using standard plate method. Agar plates were incubated lid down, at 37 °C for 24 h before colonies were counted. Three independent assays were done for each sputtered sample.

The 100- $\mu$ L of the *E. coli* solution was contacted with the PE-TiO<sub>2</sub> films. The PE samples were kept in a sterile oven at 60 °C to avoid contamination prior to the photo-activated bacterial tests. The 100- $\mu$ L bacteria samples were well distributed on the uniform PE-TiO<sub>2</sub> samples. The exposition of the PE-TiO<sub>2</sub> samples to the Suntest light was carried out on Petri dishes provided with a lid to prevent evaporation in the Suntest cavity. The agar was purchased from Merck GmbH, Microbiology division KGaA under the cat No. 1.05463.0500.

Three independent assays were carried for each PE-TiO<sub>2</sub> sample inactivating bacteria. The CFU statistical analysis was performed in calculating the standard deviation values. The average values were compared by one-way analysis of variance and with the value of statistical significance. The one-way analysis of variance (one-way ANOVA) was used to compare the mean of the samples using the Fisher distribution. The response variable was approximated for the sample data obtained from the photocatalytic bacterial inactivation on tested samples presenting the same distribution within the same sputtering time.

PE-TiO<sub>2</sub> samples were irradiated with the Xe-400 W light in the Suntest solar simulator CPS (Atlas GmbH, Hanau, Germany). The integral light dose in the range of 310 to 800 nm was 52 mW/cm<sup>2</sup>. The power density of 52 mW/cm<sup>2</sup> is equivalent to 52% of the AM1 sun full emission observed perpendicular in the Equator at 12 AM in a clear day. A cut-off filter was added in the Suntest cavity to block the light between 290 and 310 nm amounting to about 3% of the total irradiation.

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