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Synthesis and characterization of fluoro-modified polypropylene films for inhibition of biofilm formation

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ABSTRACT

Surface hydroperoxide-conjugated polypropylene (PP) films were prepared by optimal ozonolysis processing of the films. These hydroperoxide-conjugated groups were then used as initiators at room temperature for redox graft polymerization of the fluoro vinylic monomer 1H,1H-heptaflourobutyl methacrylate (HFBM). The ozonolysis process allows, on one hand, for the formation of the desired hydroperoxide-conjugated groups while, on the other hand, leads to an undesired degradation of the PP. The ozone treatment time was therefore optimized to obtain sufficient hydroperoxide groups for graft polymerization, while maintaining the mechanical strength of the films, which was barely affected. The resulting PP-PolyHFBM (PP-PHFBM) films were characterized by methods such as AFM, ATR, TGA, contact angle goniometry and XPS. The antibiofilm properties of the PP-PHFBM films were evaluated, using two bacterial strains. An 86% inhibition was observed for the Gram-negative *Escherichia coli*, and a 37% inhibition was observed for the Gram-positive *Listeria*.

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1. Introduction

There has been growing concern in recent years about increased bacterial resistance to common antibiotics. One of the ways by which bacteria exert this recalcitrant behaviour is through biofilm development [1]. Biofilms are structured communities of bacteria held together by an extracellular matrix consisting of proteins and exopolysaccharides. These biofilms are ubiquitous in nature, protect the individual bacterial cells from environmental insults and are resistant to antibiotic treatment. In addition to increased resistance, biofilms are able to efficiently evade the host defense system, thus hindering treatment [1,2]. Biofilm development takes place through a series of well-regulated steps: (i) bacterial attachment to a surface; (ii) cell growth and aggregation into microcolonies; (iii) extracellular matrix production and maturation; (iv) dissemination of progeny cells to form new colonies [3,4]. Biofilm infections share clinical properties because they tend to form on inert surfaces, on both dead and live tissues, and occur commonly on medical devices [4–8]. Over 60% of bacterial infections currently under treatment in hospitals are caused by biofilms [5,8]. These biofilm infections may be caused by a single species or by a mixture of several bacterial species. Furthermore, multiple bacterial strains are capable of growing on plastics and fabric surfaces for days and even months [4,6–8]. Therefore, there is a growing demand for reliable antibacterial surfaces to combat this commonly occurring contamination.

Plastics are usually sterilized by means of either dry/wet heat or ionizing radiation [9]. On exposure to the atmosphere, however, these polymers are contaminated by bacteria. It is apparent that, in principle, the ideal solution to this problem is to develop approaches to render biomaterials resistant to microbial colonization. Antimicrobial polymers can provide a highly opportune way to achieve this goal. Antimicrobial polymers can be achieved by adding an organic or inorganic biocide to the polymers during the processing of the material [9–11]. Another method involves endowing the polymer with a biocidal function after processing [11–13]. This can be achieved by surface functionalization of the polymer substrate by high-energy radiation (e.g., gamma, glow discharge, corona discharge, or photo-irradiation) [14] or ozonolysis [15–17], thus effectively controlling the adhesion of biocides onto the substrate surfaces. A different approach for the preparation of polymer bearing groups with antimicrobial activity involves the preparation of polymerizable monomer-containing biocide moieties and then the subsequent polymerization or copolymerization with another monomer [13,18–21].

The present article describes a simple and efficient method for surface modification of polypropylene (PP) films by ozonolysis

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followed by graft polymerization of a vinylic fluoro-containing monomer for the inhibition of bacterial adsorption. This method should also enable surface modification of polymers other than PP, e.g., polyethylene, polystyrene, polyethyleneterphthalate. The oxidation of PP films was obtained by exposing the films to ozone gas for different time intervals. The generated conjugated-hydroperoxides were then decomposed by redox reaction to initiate, at room temperature, graft redox polymerization of the monomer 1H,1H-heptaflourobutyl methacrylate (HFBM). The HFBM monomer was chosen for its high fluoro-type hydrophobicity. Fluoro-type surfaces have been shown to inhibit bacterial growth because of the low surface energy and minimal contact with the surface for bacterial adhesion [22,23]. The formed biofilms of *Escherichia coli* and *Listeria* sp., representing Gram-negative and Gram-positive bacteria, respectively, were quantified on the modified PP films versus unmodified ones.

2. Experimental

2.1. Materials

The following analytical-grade chemicals were purchased from Aldrich (Israel) and were used without further purification: potassium iodide (KI), sodium iodide (NaI), acetic acid (AcOH), acetone, ethanol, isopropanol (ISP), sodium metabisulfite ($Na_2S_2O_5$), benzoyl peroxide (BP), crystal-violet (CV), the fluorosurfactant zonyl FSE and the vinylic monomer 1H,1H-heptaflourobutyl methacrylate (HFBM). This monomer was passed through an activated alumina (ICN) to remove the inhibitor before use. PP films of 1 cm^2 and 95 ± 15 μm thickness were purchased from Plazit Industries Plastic Solution, Israel. These films were washed by dipping in ethanol, water and acetone; they were then dried and kept in a closed vial under N_2 atmosphere. Water was purified by passing deionized water through an Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK). Ozone was produced by passing a current of oxygen through a corona discharge (Ozomax, Canada) at voltages from 4.5 to 9 kV.

2.2. Preparation of the oxidized PP films

A stream of O_3/O_2 containing an ozone output of 4 g/h was bubbled through water containing the PP films for different time periods (2, 20, 40 and 60 min) at room temperature at a flow rate of 1.0 L/min. The oxidized films were then washed with water to remove excess ozone until the presence of free ozone was no longer detected, as measured spectrophotometrically with KI [24]. The oxidized films were dried with nitrogen gas. Films containing different conjugated hydroperoxide concentrations were prepared by controlling the ozonolysis time period.

2.3. Redox graft polymerization of HFBM onto the oxidized PP films

In a typical experiment, the oxidized films were placed in a 10 mL deaerated aqueous solution containing zonyl 1% (w/v) and 1% (w/v) of the monomer HFBM. Graft polymerization of HFBM was initiated at room temperature at [$NaHSO_3$]/[HFBM] mole ratio of 10 by the addition of sodium metabisulfite to the former mixture shaken at room temperature for 33 h. The formed PP-PHFBM films were washed of excess reagents with ethanol and water and then dried with nitrogen gas. The influence of various polymerization parameters, e.g., monomer concentration, conjugated hydroperoxide concentration and the mole ratio [$NaHSO_3$]/[HFBM] on the graft polymerization was also elucidated.

2.4. Synthesis of pure PHFBM

PHFBM was formed by free surfactant dispersion polymerization. In a typical experiment, pure PHFBM was prepared by introducing 1 g HFBM and 20 mg of the initiator BP into a reaction flask containing 10 mL 2-methoxy ethanol. Nitrogen was bubbled through the solution for about 15 min to exclude air, after which the solution was heated to 73 °C. The polymerization reaction continued for 24 h, and was then stopped by cooling to room temperature. The formed polymer was washed by extensive centrifugation cycles with ethanol and water, and then dried by lyophilization.

2.5. Characterization of the modified and unmodified PP films

The conjugated hydroperoxide concentration was determined according to Carlsson and Wiles' method [25]. Briefly, 20 mL of a NaI/ISP (14 g/100 mL) solution and 70 mL of an AcOH–ISP (1:10, v/v) solution were introduced into a 250 mL round bottomed flask containing the oxidized film. After a 30 min reflux, the suspension was cooled to room temperature, and 10 mL of distilled water was added. The film was then separated from the supernatant. The I^{3-} concentration in the supernatant (formed due to the decomposition of the conjugated hydroperoxides by I^-) was determined by a Cary-1E UV-visible spectrometer at 360 nm, using a calibration curve. All reported values are an average of at least ten measurements taken for different oxidized PP films.

The thermal behaviour of the films was measured with a TC15 system equipped with TGA (Thermal Gravimetric Analysis), model TG-50, and DSC (Differential Scanning Calorimetry), model DSC-30, Mettler Toledo.

The % mass (m) increase (MI) of the PHFBM on the PP films was measured and calculated according to the following equation:

$$\%\mathrm{MI} = \frac{m \text{ of PP-PHFEM} - m \text{ of PP}}{m \text{ of pp}} \times 100\%$$

All reported values are an average of at least ten measurements taken for different PP-PHFBM films.

Wettability studies of the unmodified and modified PP films were determined with a Goniometer, System OCA, model OCA20, USA. All measurements were performed at 25 °C and at 60% relative humidity by the sessile drop technique. Double distilled water was used as the wetting liquid. The films were placed on a Goniometer, 5 μL of double distilled water was placed upon it, and then advancing angles were measured. All reported values are the average of at least six measurements taken at different locations on the film surface with a maximum error of ±5%.

Atomic force microscopy (AFM, NanoScope 8.10) images were recorded in air on unmodified and modified PP films, operated in torsional resonance (TR) mode. The cantilevers used were RFESP Model MPP-2110-10 with a resonant frequency of 69–93 kHz. The area of 2000 nm × 2000 nm was scanned. The roughness measurements were obtained in root mean square (Rq) values. The reported values are an average of at least 3 different points of four PP-PHFBM different films.

The diameter and size distribution of the PHFBM nanoparticles grafted on the PP films were determined using AFM images. The reported values for each measurement are obtained by averaging over at least 200 nanoparticles.

ATR analysis was performed on a Bruker Alpha spectrometer (US) using a diamond ATR crystal as the internal reflection element, and the incident angle was fixed at 45°. The films were scanned over 50 times at 4 cm^{-1} resolution.

Surface elemental analysis was obtained by X-ray photoelectron spectroscopy (XPS), model AXIS-HS, Kratos Analytical, England, using Al-Kα lines, at 10^{-9} Torr, with a take-off angle of 90°. The XPS analysis reported values are the average of measurements

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