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Evaluation of various polyethylene as potential dosimeters by attenuated total reflectance-Fourier-transform infrared spectroscopy

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HIGHLIGHTS

- Various types of PE films/sheets have been evaluated for use as a potential dosimeter.
- Attenuated total reflectance FTIR spectroscopy was utilized to analyze transvinylene formation in irradiated PE films/sheets.
- PE films/sheets were exposed to ionizing radiation using a 5 MeV high-energy electron beam accelerator.
- Analysis of TV peak formation at the 965 cm^{-1} wavenumber shows an upward trend of TV response to absorbed dose.

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ABSTRACT

Various types of polyethylene (PE) have been evaluated in the past for use as a potential dosimeter, chiefly via the formation of an unsaturated transvinylene (TV) double-bond resulting from exposure to ionizing radiation. The utilization of attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy in characterizing TV formation in irradiated PE for a potential dosimeter has yet to be fully developed. In this initial investigation, various PE films/sheets were exposed to ionizing radiation in a high-energy 5 megaelectron volt (MeV) electron beam accelerator in the 10–500 kilogray (kGy) dose range, followed by ATR-FTIR analysis of TV peak formation at the 965 cm^{-1} wavenumber. There was an upward trend in TV formation for low-density polyethylene (LDPE) films and high-density polyethylene (HDPE) sheets as a function of absorbed dose in the 10–50 kGy dose range, however, the TV response could not be equated to a specific absorbed dose. LDPE film displayed a downward trend from 50 kGy to 250 kGy and then scattering up to 500 kGy; HDPE sheets demonstrated an upward trend in TV formation up to 500 kGy. For ultra-high molecular weight polyethylene (UHMWPE) sheets irradiated up to 150 kGy, TV response was equivalent to non-irradiated UHMWPE, and a minimal upward trend was observed for 200 kGy to 500 kGy. The scatter of the data for the irradiated PE films/sheets is such that the TV response could not be equated to a specific absorbed dose. A better correlation of the post-irradiation TV response to absorbed dose may be attained through a better understanding of variables.

1. Introduction

Historically, beginning with the work of Charlesby et al., the effects of high-energy radiation on various types of polyethylene (PE) have been studied (Charlesby et al., 1964). This includes the formation of a main-chain unsaturated transvinylene (TV) double-bond with peak at 965 cm^{-1} via Fourier-transform infrared (FTIR) spectroscopy (Charlesby et al., 1964; Johnson and Lyons, 1995; Muratoglu et al., 2003). The mechanism for the formation of TV unsaturations during irradiation using a high-energy electron beam is mainly via hydrogen abstraction and to a lesser degree by recombination of two adjacent alkyl radicals on the same chain (ASTM International F 2381-10, 2010; McLaughlin et al., 1999). Other well-known inherent effects noted from PE exposure to ionizing radiation include chain scission, cross-linking and degradation (via production of alkyl and allyl radicals), and formation of carbonyl and other oxidation products when oxygen is present (Charlesby et al., 1964; Cota et al., 2007; McLaughlin et al., 1999; Singh, 1999; Waterman and Dole, 1970a, 1970b). It has also been shown that the concentration of these TV unsaturations formed within the PE backbone as a result of exposure to ionizing radiation is dose-dependent (Charlesby et al., 1964; McLaughlin et al., 1999; Zenkiewicz et al., 2003). Furthermore, the rate of the subsequent

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decay of these TV unsaturations is dependent on various factors as well (Lyons, 2004a, 2004b, 2004c).

PE films have been evaluated for use as potential dosimeters in the past to varying degrees to measure the absorbed dose delivered to healthcare products. These evaluations encompassed various analytical techniques using a variety of wavelengths (Johnson and Lyons, 1995; McLaughlin et al., 1999; Wenxiu et al., 1980, 1989). [A dosimeter is a device having a reproducible, measurable response to radiation, which can be used to measure the absorbed dose in a given system (ANSI/AAMI/ISO 11137-1:2006/(R) (2010))]. The effects of electron beam processing on various PE have also been investigated (Illgen et al., 2009; Muratoglu and Harris, 2001; Muratoglu et al., 2002, 2003; Murray et al., 2012, 2013), with studies ranging from cross-linking in PE foams (Dias and de Andrade e Silva, 2007) to the effects of blending antioxidants into PE to suppress thermal oxidation (Ghaffari and Ahmadian, 2007).

The utilization of attenuated total reflectance (ATR)–FTIR in characterizing TV formation in various irradiated PE films/sheets for potential dosimeters has yet to be fully developed. ASTM International F 2381-10, *Standard Test Method for Evaluating Trans-Vinylene Yield in Irradiated Ultra-High-Molecular-Weight Polyethylene Fabricated Forms Intended for Surgical Implants by Infrared Spectroscopy,* compares the TV peak between 950 and 980 cm^{-1} to a reference band between 1330 and 1396 cm^{-1}, and only mentions ATR-FTIR as an alternative mode of spectra collection (ASTM International F 2381-10, 2010). However, there have been a few published articles demonstrating the use of ATR-FTIR to evaluate [cross-linked] PE (Sugimoto et al., 2013) or TV formation in PE films/sheets exposed to ionizing radiation (Murray et al., 2012, 2013). The majority of published literature reports employing conventional transmission FTIR and FTIR microscopy to investigate this TV formation in irradiated PE (Illgen et al., 2009; Johnson and Lyons, 1995; McLaughlin et al., 1999; Muratoglu and Harris, 2001; Muratoglu et al., 2002, 2003; Pinheiro et al., 2006; Zenkiewicz et al., 2003).

In this initial investigation, low-density polyethylene (LDPE) films, high-density polyethylene (HDPE) sheets, and ultra-high molecular weight polyethylene (UHMWPE) sheets were exposed to different doses of ionizing radiation using a 5 megaelectron volt (MeV) [high-energy] electron beam accelerator. The different PE films/sheets were then analyzed via ATR-FTIR, and the TV peak formation at the 965 cm^{-1} wavenumber was assessed. Studying TV formation in irradiated PE via ATR-FTIR is of considerable interest since it offers unique sampling advantages compared to transmission FTIR, in characterizing these PE films/sheets for potential use as dosimeters in the healthcare product sterilization dose range.

2. Materials and methods

2.1. Materials

Three different types of commonly available PE films/sheets were studied: LDPE film (0.004 in. thickness; McMaster Carr; Robbinsville, NJ), HDPE sheet (0.0625 in. thickness; United States Plastic Corp.®; Lima, OH); UHMWPE sheet (0.062 in. thickness; Plastics International; Eden Prairie, MN). The PE films/sheets were further prepared by cutting them into approximately 5 cm × 5 cm specimens. There was neither pre- nor post-irradiation conditioning for these PE films/sheets; all films were stored in the analytical laboratory at room conditions.

2.2. Electron beam irradiation

Irradiation of the PE films/sheets was performed using a MEVEX 5 MeV, 2 kW electron beam accelerator (Model MB5000; Kanata, Ontario). All PE films/sheets were treated at room temperature in the presence of air at Johnson & Johnson (Raritan, NJ), at two ranges of doses. The first dose range included: 10, 20, 30, 40 and 50 kilograys (kGy). The second dose range included: 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 kGy. The absorbed dose was confirmed using alanine dosimeters traceable to a national standard and measured using a Bruker e-scan electron paramagnetic resonance (EPR) spectrometer (Billerica, MA).

2.3. ATR-FTIR spectroscopy

The PE films/sheets were evaluated using a Bruker ALPHA™ FT-IR spectrometer with Eco-ATR single reflection sampling module and zinc selenide (ZnSe) crystal. ATR is essentially a FTIR sampling technique that is ideal for both solids and liquids, and usually does not require any specialized sample preparation. An IR beam is transmitted through an optically dense crystal, with a high index of refraction, that is in contact with a sample which has a lower index of refraction. This results in an evanescent wave that penetrates past the sample surface, approximately 1–2 μm into the sample, and then is reflected back into the crystal for subsequent detection. ATR addresses concerns about variation in thickness, which is an influence quantity for some optical dosimeters, by examining the first 1–2 μm only. All data was recorded under ambient conditions with 32 scans per sample and at 4 cm^{-1} resolution: the anvil was outfitted with a slip-clutch to deliver a fixed compression of approximately 4000 psi on the sample against the ZnSe crystal. Data analysis was conducted with the Bruker OPUS IR Software (Version 7.2). The IR spectra were evaluated using the internal Integration Mode B – the software draws a straight line between two defined frequency limits and integrates the area above that line. Normalization or other transformations on the IR spectra were not performed, including comparing the area under the curve at 965 cm^{-1} to another reference peak.

3. Results

3.1. Evaluation of PE films/sheets irradiated in the 10–50 kGy dose range

The PE films/sheets (LDPE, HDPE and UHMWPE) were irradiated at room temperature in the presence of air for the first series of target doses: 10, 20, 30, 40 and 50 kGy; only the conveyor speed was adjusted to obtain the desired target dose during a single pass. The PE films/sheets were then analyzed via ATR-FTIR to measure the area under the curve at the TV absorbance peak at 965 cm^{-1} wavenumber. Fig. 1 displays a box-and-whisker plot[1] for the LDPE film data obtained from the median absorbance intensity ($n=10$) versus target dose (kGy), including the TV response for non-irradiated LDPE film. Although an upward trend was observed, the range and resolution of individual data points is such that a TV response could not be equated to a specific absorbed dose. Similarly, Fig. 2[2] displays a box-and-whisker plot for the HDPE sheet data obtained from the median absorbance intensity ($n=10$) versus target dose, including the TV response for non-irradiated HDPE sheet. Again, an upward trend was observed, with a possible outlier at 40 kGy, but the TV response is lower than that of the LDPE film. Furthermore, of the PE films/sheets exposed

[1] In the box-and-whisker plots, the points coinciding with the center lines are the median absorbance intensity ($n=10$) at the different absorbed doses; the boxes below and above are the ranges of the second and third quartiles (respectively), and the 'whiskers' are the standard error.

[2] For better visualization of the data, the absorbance scale in Fig. 2 box and whisker plot is in 10^{-3} resolution in comparison to the other box-and-whisker plots which are in 10^{-2} resolution.