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Synthesis of a flexible poly(chloroprene)/methyl red film dosimeter using an environment-benign shear compounding method

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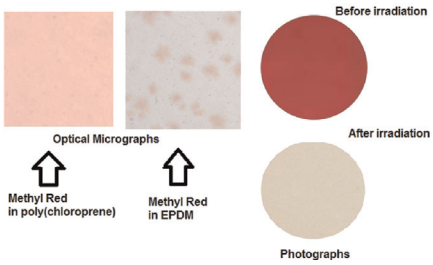
HIGHLIGHTS

- A new film dosimeter was developed through solvent free route.
- The dispersion of dye was homogeneous.
- The dose linearity was observed up to 30 kGy.
- There was no dose rate or temperature dependence.
- No significant dependence on humidity was observed till 75% RH.

GRAPHICAL ABSTRACT



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ABSTRACT

The paper reports synthesis of a new film dosimeter based on a solvent-free route. Methyl red (MR) dye was introduced into poly(chloroprene) (PC) in various concentrations. The films were intensely red with λ_{max} ~515 nm. The absorbance decreased linearly with absorbed radiation dose up to 30 kGy without a significant change in λ_{max}. Color coordinates of the films were also analyzed. Optical micrographs of the films showed no signs of inhomogeneous distribution of MR in the PC matrix, which was attributed to the polarity of PC. Radiation sensitivity, dose response linearity, effects of irradiation temperature and humidity, as well as the rate of fading, were also investigated.

1. Introduction

Radiation processing is a cost-effective, energy-saving and environment-friendly way to develop superior products and technologies (Berejka et al., 2014; Dubey et al., 2011, 2012; M'Garrech and Ezzouch, 2009). There are many large-scale irradiation facilities and research laboratories worldwide where high-energy radiation is extensively used for various purposes (Chmielewski et al., 2014; Dubey et al., 2006, 2013). In all such radiation applications, radiation dosimetry is mandatory because precise and easy measurements of radiation doses are essential for obtaining products with desired properties. However, many of the dosimeters available today are expensive, difficult-to-use, rigid, or require hazardous air pollutants (HAPs) and volatile organic solvents (VOCs) in their manufacturing (Biramontri and Haneda, 1996; Devic, 2011; Dubey et al., 2006; Galante and Campos, 2006; Meiner et al., 2004; Whittaker, 1993). Therefore, there is a need to

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develop inexpensive, flexible, reliable radiation dosimeters by a solvent-free process.

Polymer film dosimeters are widely used in radiation processing. They are usually based on a transparent polymer matrix doped with a dye (Bett et al., 2002; Kattan et al., 2011; McLaughlin, 2003; Tu et al., 2009; Whittaker et al., 1997). During an irradiation, the dye may either change its color (with its λ_{max} shifting) or undergo discoloration due to radiolytic transformations in its chromophoric group, which only decreases the absorbance. In a recent study, Soliman and Abdel-Fattah (2013) explored the potential of leuco crystal violet in a poly(vinyl butyral) film for high-dose radiation dosimetry. They observed a linear response to the dose in the range 0–20 kGy and a non-linear response at higher doses up to 100 kGy. Similarly, Kattan et al. (2011) explored the feasibility of using polyvinyl chloride (PVC) films with bromocresol purple in dosimetry and reported a linear dose response up to 50 kGy.

An azo compound methyl red (MR) is one of the dyes most extensively studied for radiation dosimetry applications, mainly because of its low cost and the discoloration linearly dependent on the absorbed dose (Ajji, 2006; Tu et al., 2009). Ajji (2006) explored performance characteristics of aqueous solutions of MR in the gamma radiation dosimetry. As MR is a pH-sensitive dye, both alkaline and acidic solutions were used to analyze the effect of pH on the dosimetric parameters. The authors observed a remarkable difference between the responses of MR in acidic and alkaline solutions. Al Zahrany et al. (2011) used polyvinyl butyral (PVB) films dyed with MR as radiation dosimeters, while Barakat et al. used MR-doped poly(methyl methacrylate) (PMMA) in such applications (Barakat et al., 2001; Russo et al., 2002a). Although the results were promising, the used procedures of the dosimeter manufacturing were complex and involved solvents (Ajji, 2006; Al Zahrany et al., 2011; Dubey et al., 2011, 2012, 2013; McLaughlin, 2003; Meiner et al., 2004; Russo et al., 2002b; Tu et al., 2009; Whittaker, 1993; Whittaker et al., 1997).

Shear/melt compounding is a method routinely used to mix polymers with desired ingredients. It is a solvent-free process, in which a polymer mix is heated up to a temperature above the melting point of the polymer with continuous shearing (Dubey et al., 2006, 2011, 2012, 2013). Such processes can be used for a solvent-free mixing of dyes and polymers for dosimetric applications. However, in addition to various problems related to degradation of the radiochromic behavior of dyes in a solid matrix, the proper dispersion and distribution of the dye in a polymer matrix are major challenges in developing dosimeters in this way (Dubey et al., 2006, 2011). To the best of our knowledge, there are no reports of using this process in manufacturing radiation dosimeters.

This paper reports a synthesis of a novel film dosimeter using shear compounding. The polymer matrix used is highly flexible poly(chloroprene) (PC). The flexibility made it possible to manufacture detectors usable in multi-dimensional dosimetry and in complex geometries (Babic et al., 2009; Kozicki and Sasiadek, 2012). The dye was incorporated in PC in various concentrations, and the performance characteristics of the resulting products as gamma dosimeters were investigated. Efforts were made to analyze the morphology of the dosimeters, their colorimetric parameters, and the post-irradiation stability of their signals.

2. Material and methods

2.1. Dosimeter preparation

PC and ethylene propylene diene monomer (EPDM) were procured from local suppliers (Polychloroprene M-40, Mooney viscosity 48 ± 5, manufactured by Denki Kagaku Kogyo Kabushiki Kaisha, Japan; EPDM ethylene content 55%, manufactured by DSM, The Netherlands). MR (MW 269.3) from Aldrich was used without further purification. Fig. 1 shows the molecular structures of PC and MR. A series of PC/MB mixtures were prepared by homogeneously mixing PC and MR at 60 °C in a Brabender Plasticorder (Brabender GmbH, Duisburg, Germany). Three five-minute mixing-and-cooling cycles were used to minimize dehydrochlorination and degradation of the components. The weights of the components were carefully chosen based on their bulk density to achieve the desired contributions from the constituents to the total volume, which ensured proper filling of the mixing chamber. The homogeneous mix was cut into small pieces, which were compressed into 0.1-mm-thick 12×12 cm^2 sheets with a compression-molding machine (150 kg/cm^2 pressure for 5 min at 60 °C). In the following text, the concentrations of the dye are expressed in millimoles of the dye per 100 g of the resulted mixture.

2.2. Radiation source

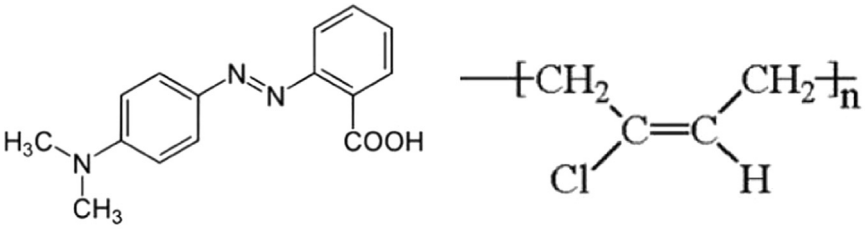
A ^{60}Co source Gamma Chamber GC-5000 (Board of Radiation & Isotope Technology, BRIT, India) with the dose rate of about 1.5 kGy h^{-1} (Fricke dosimetry) was used. Lead attenuators made it possible to reduce the dose rate to 0.75 and 0.375 kGy h^{-1}. Another Gamma Chamber, GC-900 (BRIT, India) was used to irradiate the films at a dose rate of 3.5 kGy h^{-1}.

2.3. Spectrophotometry

The absorbance changes were measured with a Shimadzu UV-2500 spectrophotometer at λ_{max}=515 nm. The dose response was characterized with the percentage change in the absorbance (RCA)

$$RCA = (A_{ui} - A_i)/A_{ui}, \quad (1)$$

where A_{ui} is the absorbance of an unirradiated film and A_i is the absorbance of the irradiated film. The absorbance of each film was measured four times, and two replicate films were used for each dose point. For reproducibility studies, a large number of samples were irradiated to various doses (10 films per dose), and the



Methyl red Polychloroprene

Fig. 1. Molecular structures of the film components.