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Research paper



Facile preparation of new polystyrene leucomalachite green thick films and study of their radiochromic behavior for low doses of gamma radiation

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Abstract

Colourless polystyrene-leucomalachite green (PS-LMG) thick films containing a suitable chloroalkane were prepared by a fast and facile casting method, and were investigated for their radio chromic response behavior under the influence of 1.25 MeV γ-radiation. Their gamma response was studied in the 0.05 kGy to 10 kGy range to evaluate their suitability for potential use as the dosimeter in the radiation processing industries. The films were found to undergo a visibly distinct green coloration in the studied range, with the colour intensity increasing with an increase in the total dose. The radiochromic response of these films when investigated as a function of film thickness showed that the colour development as well as the linearity of the response was markedly affected by the thickness of the films. The effect of dye loading and the chloroalkane concentration on the radiochromic response of these films were also investigated. Depending upon the film thickness and reactant concentrations, the films were found to be capable of visually detecting gamma radiation doses as low as few tens of grays.

Keywords: *Polystyrene; Leucomalachite Green, Radiochromic; Thick Films; Low Dose.*

1. Introduction

A diverse range of radiochromic films employing pH-sensitive dyes, leuco dyes and tetrazolium salts have been prepared and investigated for their dosimetric properties for radiation processing applications (McLaughlin et al.1989, Miller et al.1988, Mai et al.2004, Moussa et al.2003). However, most of the dosimeters prepared so far for the radiation processing industry are for monitoring medium and doses of radiation, i.e., 1kGy and higher ranges (Gafar et al.2015, Akhavan et al.2002, Sidney et al.1990). Recently, increase in the processes of treatment of food by radiation has realized the need for routine dosimeters and labels that requires process monitoring at relatively lower doses of radiation. Some of the food irradiation applications (Saylor et al.1988) like sprout inhibition, insect and parasite disinfection, and delay in maturation require dosimetric systems for monitoring at doses lower than 1 kGy (Pourbeigi et al.2005). Very few (McLaughlin et al.1989, Pourbeigi et al.2005) radiochromic films have been reported for such types of low dose applications. Gafchromic films originally developed for medical dosimetry have been used in the radiation processing industries for low dose monitoring, but their routine and extensive use is often restricted by their high cost and availability.

A number of leuco based films have been prepared and investigated for their radio chromic behavior. Out of them, malachite green (MG) and its derivatives has been well studied by previous researchers for the preparation of dosimetric films as well as for 3-D dosimetry. While the polyvinyl chloride (PVC) film with malachite green was studied for high-dose radiation measurements (Kattan et al.2007, Abdel-Fattah et al.1996), polyvinyl butyral film (PVB) based on leucomalachite green (LMG) was investigated as a high-dose dosimeter for gamma radiation processing applications in the dose range of 3-150 kGy (Soliman et al.2014) while a chlorine-containing polymer matrix doped with malachite-green methoxide thin film dosimeter was reported (Akhavan et al.2007) for the dose range of 1–60 kGy. Subsequently, LMG based polyvinyl butyral as low dose dosimeters could be developed for dose measurements of the order of a few hundred Gy level up to 4 kGy doses by Mai and group (Mai et al.2008). PVB with its specific advantages has been used as the polymer matrix by many researchers like Mei and coworkers, however, processibility of PVB is quite difficult, particularly its solubility, requiring the mixture of several high boiling solvents and co-solvents. The use of high boiling solvents not only requires longer time for the casted films to dry, it also restricts the thickness of the films owing to the skin affect as observed by previous researchers (Adamovics et al.2004). On the other hand, polystyrene being easily soluble in many common low boiling organic solvents can facilitate the preparation of much thicker films. Although polystyrene based radiochromic films have been reported earlier, but most of them have been used for the measurements of high radiation doses (McLaughlin et al.1979, Tariq et al.2012, Niroomand-Rad et al.1998).

The present study aims to prepare a new series of radio chromic leuco based polystyrene films for potential use as a dosimeter in radiation processing industry, that can respond to gamma radiation from few tens of Gy onwards, vital for many food-processing applications. For this, we have attempted to develop a new combination of an acid sensitive leuco dye, like LMG, a suitable haloalkane as the sensitivity enhancer and polystyrene as the polymer matrix. Since thicker films are known (Cheung et al.2001) to have

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higher radiation sensitivity, researchers worldwide have been using the multilayer films to improve the radiation sensitivity. Our objective was to prepare a novel formulation in such a way that all the ingredients are soluble in a single low boiling solvent like chloroform, so that faster drying can take place thereby facilitating the formation of thicker film. To the best of our knowledge, there is no such previous publication that has reported the preparation and study of radiochromic behavior of PS-LMG films for measuring low gamma doses starting from few tens of Gy onwards.

2. Materials and methods

2.1. Materials

Leucomalachite green was procured from Sigma Aldrich as colourless powder and used as such without any further purification. Polystyrene (Average MW 28, 0000) was procured from Sigma Aldrich while chloroform was procured from Sigma Aldrich and was purified further according to the reported method by Perin and Perin. Three different chloroalkanes selected for the present study, hexachloroethane, ethyl trichloroacetate and chloral hydrate were procured from Sigma Aldrich and was used without further purification.

The thickness of the solvent casted films was measured using a digital micrometer (Mitsubishi, Japan). The radiation exposure studies were carried out in Gamma Chamber (GC-5000). Fricke dosimeter was used for dose calibration. The optical characterization of the unirradiated and the irradiated films were carried out using an Ocean Optics UV-Vis reflectance spectrophotometer.

2.2. Methods

2.2.1. Preparation of the PS-LMG film

General process for the preparation of the PS-LMG films involves dissolving the three ingredients, i.e., polystyrene, LMG and the chloroalkane in chloroform in the required ratios as per the designed formulations, mixing them properly until a transparent solution is obtained and then casting them on a leveled base in a confined area. The leveling of the base was carried out by spirit level.

For example, in order to prepare a PS-LMG film with 1 phr (parts per hundred parts of resin) of the dye and the chloroalkane ratio at 1:10, the first step was to weigh 1.0 gm of polystyrene pellets and dissolve in 10 ml of chloroform. 10 mg of leucomalachite green was dissolved separately in 2ml chloroform. 100 mg of the chloroalkane was weighed and was slowly added to the dye solution and mixed properly until a clear colorless solution is obtained. This dye solution containing the chloroalkane was then added to the polymer solution and the viscous formulation so obtained was ultrasonicated for 15 minutes. The solution was set aside for 1 hour for the bubbles to settle down, if any. The obtained clear viscous solution was poured into a flat glass plate having 10 x 8 cm^2 confined area under dark room conditions, keeping temperature between 30 - 40 ^{0}C and letting it to dry for 18 hours. After drying, the films were carefully peeled off; thickness measured with a micrometer over multiple points, and then kept in black pouch for protection against light.

Similarly, all the other formulations were made wherein the PS, LMG, chloroalkane contents were varied, casted and dried to obtain their corresponding films. In the experiments where the radiation response as function of film thickness was studied, the formulations were kept the same; the casting area was varied.

2.2.2. Radiation exposure studies

For exposure studies of the prepared radiochromic film, strips were neatly cut from the film, each of size 2 x 1 cm^2. Each strip was irradiated in ^{60}Co gamma chamber at the doses up to 10 kGy. Dose rate at the time of irradiation was 3.0 kGy/h.

2.2.3. UV-VIS Spectrophotometric studies

Quantification of the response behavior was carried out by wavelength scans of exposed and unexposed films obtained using a spectrophotometer. The response of the film was also studied by changing their orientations. A constant time gap of about 24 hours between exposure and evaluation of the film was maintained.

3. Results and discussion

Smooth, bubble free, colourless films of 10 x 8 cm^2 sizes were obtained by the casting method. Films of thickness ranging from 30±5 µm to 300±10 µm and higher were prepared by the method. Although films of thickness up to 1mm could be prepared using the reported formulations and procedure, we have restricted our present study up to 300 µm due to the reasons discussed in the subsequent paragraphs. While the films of 30±5 µm required only 2 hours to dry, the films with 300±10 µm thickness could be obtained in 24-hour time, much lesser time period as compared to films based on other polymers like PVB, PVC and PVA. The films could be peeled off easily from the base substrate and usable as self-standing films. Another advantage of the quick drying to form these films is that the possibility of any premature coloration during the film preparation steps is minimized, resulting in completely colourless thick films.

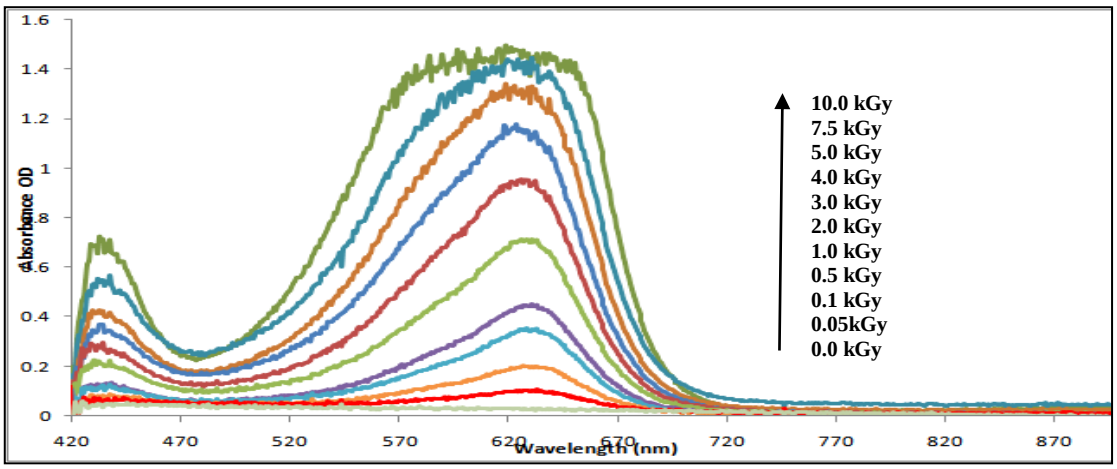


Fig. 1: Optical spectra of gamma irradiated PS-LMG film to increasing dose of radiation from 0.05 kGy to 10 kGy.

All the prepared films were found to respond to ^{60}Co-γ Radiation, the colour changes detectable visually and be easily monitored. On irradiating them with γ-radiation at regular intervals upto 10 kGy ranges, these films became green in colour, the colour intensity increasing with increasing doses of gamma radiation. Fig. 1 shows a typical absorption curve of one of the PS-LMG films (250±10 micron thick with 1phr dye loading and 1:1 dye to hexachloroethane ratio) irradiated to increasing doses of gamma radiation upto 10 kGy.

As can be seen in the Fig.1, absorption peak at 629 nm wavelength was observed in the irradiated films along with another minor absorption peak at 425 nm that corresponded to the absorption characteristics of malachite green dye. As seen in the figure, the absorbance OD of the peak increases with an increase in radiation doses, along with the peak broadening at 629 nm at higher doses. No further significant increase in the Abs OD was observed beyond 10 kGy and the peak signal almost reaching saturation at 629 nm, although the absorbance at 425 nm showed a linear increase till 10 kGy. Since not much colour change was observed visibly beyond 10 kGy, it can be suggested that the colour of the radiochromic film was primarily dictated by the change in absorbance at 629 nm.

A net change in absorbance OD at 629 nm (λ_{max}) of the film as function of gamma doses is plotted (Fig.2). From the plot, it can be clearly seen that the change in absorbance is not linearly proportional to the radiation doses, particularly at higher doses (Fig.2). It was found from the plot that the intensity of colour increases linearly with increasing absorbed doses in the beginning of the dose-response curve then tends to increase with lower rate until reaching saturation at higher doses. The overall dose response function was found to be follow a non-linear trend (2nd polynomial function); however, good linearity was observed at the low-dose ranges, almost upto 5 kGy. However, the linearity range was found to vary with a variation in the film thickness as well as in the formulation as will become evident from the subsequent studies.

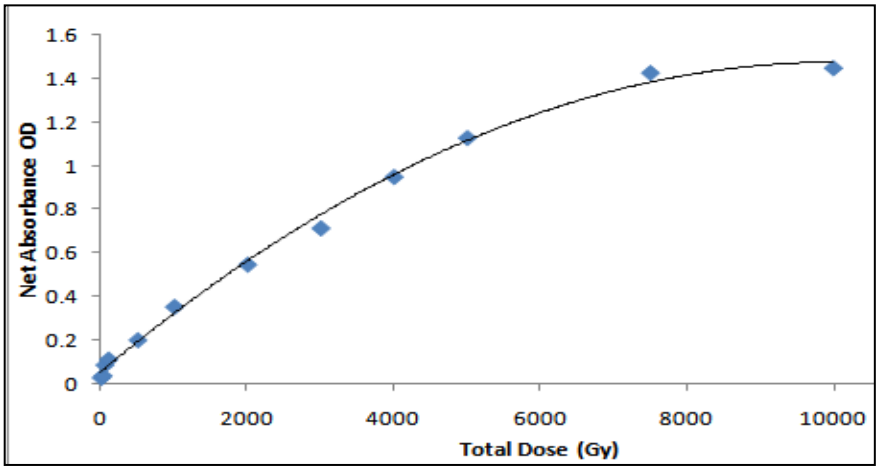


Fig.2. Plot of total dose versus net absorbance OD of the gamma irradiated PS-LMG film from 0.05 kGy to 10 kGy

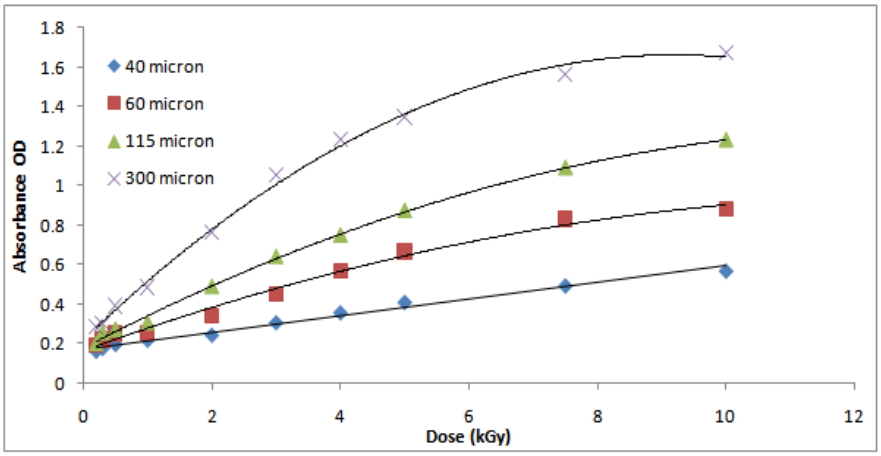


Fig. 3: Plot of Absorbance as function of increasing γ-doses up to 10KGy of PS-LMG films with 40 µm, 60 µm, 115 µm and 300 µm thickness.

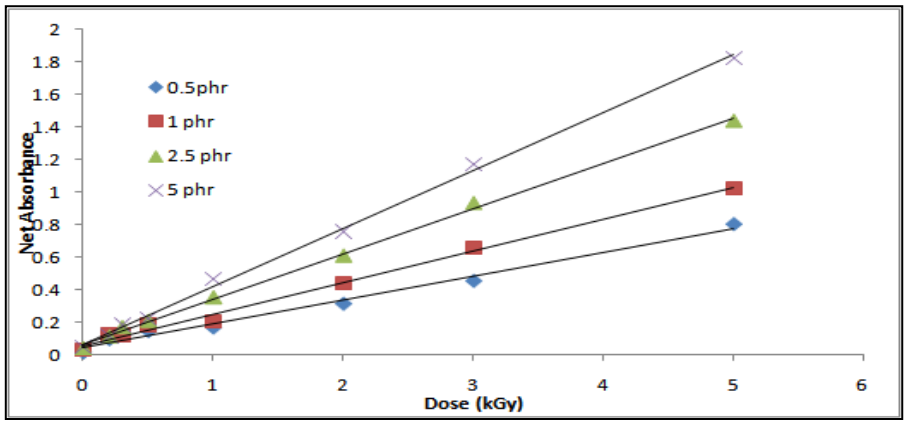


Fig. 4: Plot of Absorbance OD with increasing γ-doses upto 5kGy of LMG-PS films with 0.5phr, 1phr, 2.5phr and 5 Phr of LMG in the films.

In order to study the effect of film thickness on the radiochromic response of these films, films having similar composition but different thickness was irradiated with increasing doses of gamma radiation and their change in absorbance recorded. Fig. 3 shows radiation response of four such films having same composition (1 phr dye and 1:1 dye to chloroalkane ratio) but four different thicknesses, i.e., 40 µm, 60 µm, 115 µm and 300 µm, and irradiated up to 10 kGy doses, keeping all the other irradiation parameters constant. As can be seen in Fig.3, the radiochromic response of the films increase with an increase in film thickness, with the thicker films developing a more intense colour than their thinner counterparts for the same dose. For example, while a detectable colour change was observed very clearly at 50 Gy for a 300 µm film, the 40 µm film gave a detectable colour change only beyond 500 Gy. Also the final colouration of the 300 µm film after the 10 kGy dose irradiation was much more intense than that of the 40 µm film. However, the linear range for the thinner ones is found to be more than the thicker ones as clearly evident from the plot. For instance, the 300 µm film shows a linear response upto 4 kGy whereas fairly good linearity response was observed upto almost 10 kGy for the 40 µm film. Preliminary radiochromic characterization of films thicker than 300 µm film, i.e., upto 1 mm was done in terms of their response range and visually detectable dose limit. Although the colour response was more intense, the films were found to show a very limited response range, some of them saturating even at 2 kGy, without much increase in terms of the minimum detectable dose. Detailed studies with these thicker films are in progress and will be reported subsequently, and are beyond the scope of the present publication.

The gamma sensitivity of these PS films as a function of LMG loading was studied. Films of thickness 80 ± 5 microns having varying dye concentration and 1:1 dye to chloroalkane ratio, was irradiated to gamma radiation doses upto 5 kGy and their increases in colour intensity recorded as a function of increasing doses (Fig.4). The change in sensitivity of PS–LMG film with different concentration of LMG dissolved in PS matrix is shown in Fig. 4. The sensitivity of films increases proportionally to the LMG concentration which was in agreement with the observations by previous researchers (Mai et al.2008).

Since the chloroalkane concentration is known (Adamovics et al.2004) to affect the overall radiochromic response of the films, the gamma sensitivity of these PS films as a function of chloroalkane concentration was studied. We have investigated three different chloroalkanes viz., hexachloroethane, ethyl trichloroacetate and chloral hydrate. All of them were found to enhance the radiochromic response of these PS-LMG films. Fig.5. Shows the radiochromic response behavior of the thick PS-LMG films of 300 µm and dyes loading (1 phr) in presence of hexachloroethane taken in the ratio of 1:1, 1:5, 1:10 and 1:25 with respect to the LMG amount and irradiated to γ Radiation doses upto 2 kGy. As can be seen, there is a significant influence of the dye to chloroalkane ratio on the radiochromic response behavior of these films. With higher concentration of the chloroalkane, the rate of colour change was found to increase proportionally and the

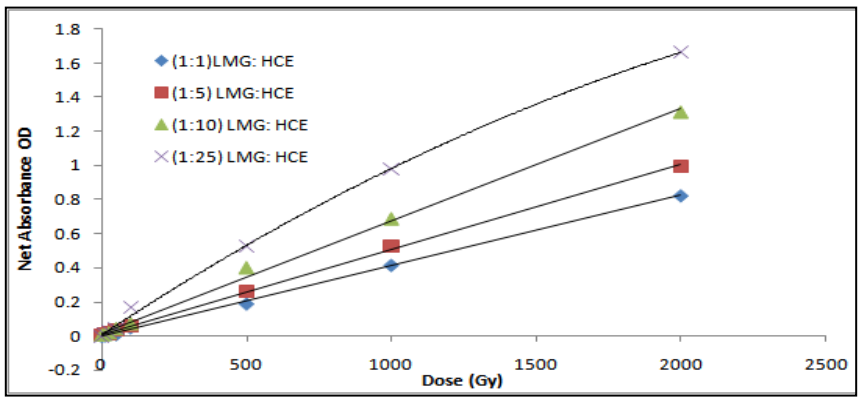


Fig. 5: Plot of Absorbance OD with increasing γ-doses upto 2kGy of PS-LMG films with varying ratio of LMG **:** Hexachloroethane (1:1, 1:5, 1:10 and 1:25).

green coloration of the film becoming more intense. However, with the increase in the chloroalkane to dye ratio, the linearity range of the films is reduced, a behavioral pattern reported earlier in such kind of leuco based systems. Fig. 5 clearly shows how the linearity of the films is decreasing as we move from 1:1 to 1:25 dye to chloroalkane ratio.

The role of dye and chloroalkane in the radiochromic behavior of the films could well be understood from the mechanism of the colour change in the leuco based dosimeter films on interaction with ionizing radiation as investigated by several researchers previously (Abdel-Fattah et al.1996, Mai et al.1998, Whittaker et al.1987).

The dependence of sensitivity could be explained assuming the change in both the number of colored precursors and the concentration of dye and the haloalkane in polymer matrix (Mai et al.2008). The dependence of sensitivity on the concentration of these two ingredients may be written as follows:

$$\frac{D\,[\text{colored dye}]}{d[t]} = k\,[\text{dye precursors}] \times [\text{Haloalkane}] \quad (1)$$

Where [colored dye] is the concentration of dye precursors to be colored, haloalkane is the active concentration of the hexachloroethane that is acting as the free radical initiator and k is the rate constant (s^{-1}).

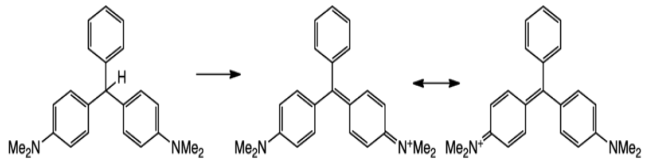


Fig. 6: Structure of LMG (Colourless) and Malachite Green (Colored).

LMG becomes coloured due to radiolytic oxidation. The RC–H bond in LMG get broken by irradiation, and it results in the structure rearrangement at one of the triarylmethane groups leading to the quinonoid chromophore structure of the deep color source as a part of the resonant unsaturated carbon ion (Fig.6) (McLaughlin et al.1977). The mechanism of the radiation induced color change of the LMG from colorless to green may be explained as similar to that of malachite green cyanide which has similar optical absorption spectrum (McLaughlin et al.1977).

The color development of the exposed portions in a radiochromic film is not detectable unless there is a radical initiator like a haloalkane in the formulation that produces radicals during the irradiation. A wide range of chloroalkanes such as chloroform, carbon tetrachloride and methylene chloride have previously demonstrated radiolytic oxidation of triphenylmethanes in liquid systems (Miyaji et al.2001) while the action of chloral hydrate have been well studied in a number of solid dosimeter films (Ebraheem et al.2013, El-Kelany et al.2012). Although not much details on the radiation induced decomposition of hexachloroethane is reported, it can be hypothesized that its radiolysis leads to the formation of chloride radicals as one of the intermediates, which in turn oxidizes the LMG and color change of the film takes place. The following mechanism for the radiolytic decomposition of hexachloroethane is proposed:

$$C_2Cl_6 \longrightarrow C_2Cl_6^{*}, C_2Cl_6^{+}, e^{-} \quad (2)$$

$$C_2Cl_6 + e^{-} \longrightarrow C_2Cl_6^{-} \longrightarrow {}^{\bullet}C_2Cl_5 + Cl^{-} \quad (3)$$

$$C_2Cl_6^{+} + Cl^{-} \longrightarrow C_2Cl_6 + {}^{\bullet}Cl \quad (4)$$

$$Cl + {}^{\bullet}Cl \longrightarrow Cl_2 \bullet^{-} \quad (5)$$

$${}^{\bullet}C_2Cl_5 + {}^{\bullet}Cl \longrightarrow C_2Cl_6 \quad (6)$$

Hexachloroethane provided oxidative species CI • and $Cl_2 \bullet^{-}$ during irradiation, and then LMG was oxidized:

$$CI \bullet + LMG \longrightarrow MG^{+} + Cl \quad (7)$$

$$Cl_2 \bullet^{-} + LMG \longrightarrow 2C1^{-} + MG^{+} \quad (8)$$

The high sensitivity of the developed leuco films may be attributed to high rate of oxidation of the leuco dye to its coloured form which in turn is probably due to the availability of large active concentration of the oxidative species $CI^{\bullet}$ and $Cl_2^{\bullet -}$ formed in theradiolytic decomposition of hexachloroethane.

Therefore, it can be seen from the above observations that the thick films of PS-LMG prepared and reported here were highly sensitive towards lower dose ranges of gamma radiation. In order to establish these prepared PS-LMG films for use as dosimeters in the radiation processing industries, further studies are in progress to evaluate the effect of irradiation dose rate, temperature, humidity along with their pre- and post-irradiation stability; and will be reported in subsequent publications after the completion of the study. As mentioned earlier, the present work is mainly focused on the noble strategy adopted in terms of its preparative route and designing of formulation for the development of suitable radiochromic films that can respond to low doses of gamma radiation i.e., lesser than 1 kGy.

4. Conclusions

A new series of polystyrene based dosimeter films were prepared that were sensitive to low doses of gamma radiation in the 0.05 - 10 kGy range, with a minimum visually detectable dose in few tens of grays. This polystyrene based film incorporating leucomalachite green (LMG) and a chloroalkane like hexachloroethane with their thickness ranging from 30 to 300 microns was prepared using a fast and facile solvent casting method in a low boiling organic solvent like chloroform. The radiochromic response of the films, i.e., their rate of colour development and linearity range was found to be dependent on the film thickness, LMG loading as well as the concentration of chloroalkane used. Depending upon a particular radiation processing application, the radiation sensitivity of these films can be tuned by tailoring these three parameters. These films can find potential applications both as a dosimeter as well as indicator films for the food irradiation and other radiation processing industries. While a thicker PS-LMG film with higher dye loading and a higher dye to chloroalkane ratio can find its use as a colour indicator and as a low dose dosimeter for measuring doses from few tens of grays, the thinner films with lesser content of dye and lower dye to chloroalkane ratio will be more suitable for dose measurements in the relatively higher ranges, ie., from few hundreds of grays upto more than 10 kGy of gamma doses.

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