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POLYMETHACRYLIC GEL (PMAG) AS A POINT DOSIMETER

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ABSTRACT

Polymethacrylic gel (PMAG) of different concentrations of MAA and BIS were irradiated using γ-rays produced by ^{60}Co radionuclide with the absorbed doses ranging from 0 Gy to 19 Gy. Due to the radiation-induced polymerization processes, the formation of Polymethacrylic gel (PMAG) occurs, which causes the dose response mechanism increased in the Nuclear Magnetic Resonance (NMR) relaxation rates of protons. The relaxation rate R_2 ($1/T_2$) are fitted to the functional form y as a function of absorbed dose D was found to have a monoexponential expression in the form; $y = y_0 + A\left(1 - e^{-D/D_0}\right)$. The relaxation rate ($\Delta R_2$) dose sensitivity value (12.5 $\pm$ 0.1 Gy) of MAA monomer by Lepage, *et al* 2001 is comparable with PMAAG experimental value gained which are 12.6 $\pm$ 0.1 Gy. The dose sensitivity, D_0 and half dose, $D_{1/2}$ was found increasing with the concentrations of MAA monomer and BIS crosslinker. The slope parameter $k_{BIS} > k_{MAA}$ indicates that consumption of crosslinker is much faster than monomer. Eventually, UV-Vis spectrophotometer was used to record PMAG degree of absorption. The PMAG has a mean value of absorption of 0.614 at 375 nm. The dose derived from PMAG is comparable to Fricke dosimeter and ionization chamber readings between 4.7 ± 0.1% and 11.6 ± 0.1%. The dose errors of less than 10 ± 0.1% are considered acceptable in radiation processing, an improvement of accuracy less than 5.0 ± 0.1% is acceptable in radiotherapy. This effort is to undertake the study of precision and accuracy associated with the use of Fricke and polymer gel in optimizing the usage of gels for dosimetry.

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INTRODUCTION

The gel dosimeter and its use in combination with nuclear magnetic resonance (NMR) is a new and promising tool, which attempts to satisfy the requirements of the ideal dosimetry system [1]. NMR offers a prospect with regard to identification and localization of healthy and diseased tissue that could be valuable in monitoring and evaluating tissue response to therapy. A full exploitation of the potential in NMR imaging techniques require knowledge of the parameters that govern the imaging process, namely proton spin-lattice relaxation time T_1 and proton spin-spin relaxation time T_2. The nuclear spin-lattice relaxation time T_1 describes the Z component of magnetization (M_z) return to its equilibrium value, while the spin-spin relaxation time T_2 describes the return to equilibrium of the transverse magnetization, M_{xy}[2]. A practical calibration is obtained from a linear fit to the quasi-linear increase of R_1 and R_2 at low doses [3], [4]. The gradient of the quasi-linear increase of relaxation rate versus absorbed dose, at low doses (i.e. the so-called relaxation rate-dose sensitivity), is generally accepted as a parameter to quantify the polymer gel dosimeters performance.

Radiotherapy, including three-dimensional (3-D) dose calculation algorithms, inverse therapy planning, streotactic radiotherapy and radiosurgery are applications, which demand certain special properties of radiation dosimeter. Moreover, treatment planning systems and radiation dose delivery are becoming increasingly complex with the emphasis on precise definition of the target and highly sculpted dose distributions to spare nearby sensitive tissue. The first developments in this field were carried out with gels infused with Fricke solution. More recently, interest has broadened to include polymer gels, which have associated advantages and disadvantages with respect to Fricke gels. Fricke gel and polymer gel dosimeters are important in routine quality control, where information regarding proper radiation doses can replace cumbersome and impracticable end-point testing. Quality control implicates dosimeter standard accuracy and precision. It was decided to accept the use of calibrated ionization chamber as a 'gold standard' as these offer the best accuracy and of any widely available radiation measuring device employed in radiotherapy [5].

Chemical Mechanisms of Polymer Gel Dosimeters

There are three ways of forming a polymer from a monomer: the opening of a ring, the combination of molecules processing two reactive functional groups, or the opening of a double bond with the present of irradiation. The potential of a monomeric species to polymerize is a function of degree of stabilization offered by the newly formed active propagating centre. On their own, free radical species are highly unstable and therefore react with many monomers; most acrylics. The reaction of a free radical with methacrylic acid monomer and N, N'-methylene-bisacrylamide (BIS) crosslinker is an example of a polymerization involving the opening of a double bond, (Figure 1).

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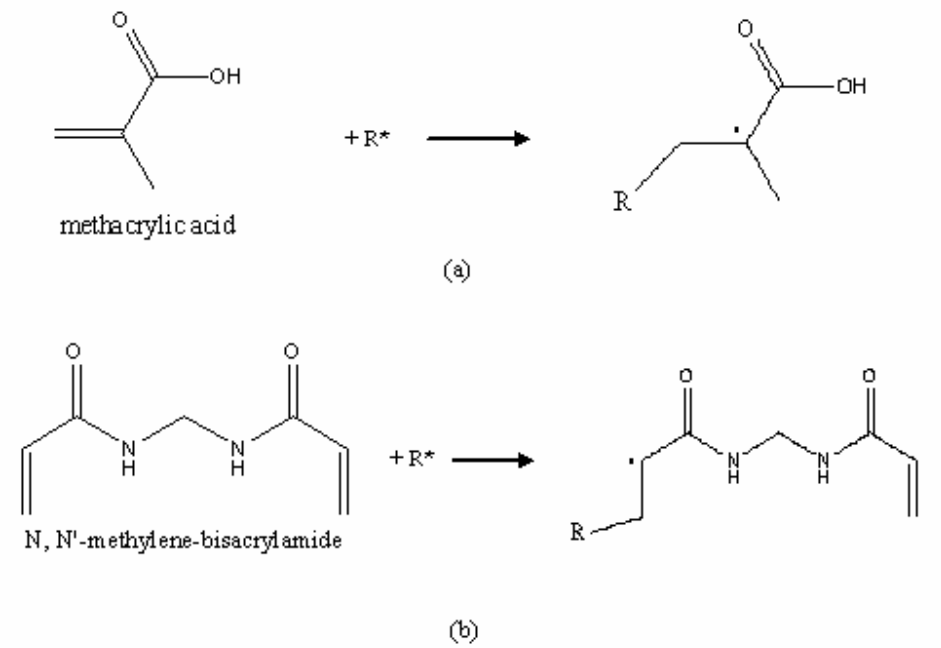

Figure 1: Chemical structure of (a) methacrylic acid monomer and (b) N, N'-methylene-bisacrylamide (BIS) crosslinker performing polymerization.

After the double bond has been opened, the free radical of the monomer can react with a new monomer, opening its double bond and hence propagating the chain reaction. This polymerization will then propagate until the supply of monomer is exhausted, or the active side on the end of a polymer chains terminate. This is called addition polymerization. The general sequences of the polymerization [4] are summarized as follows;

(Initiation)

$$I \rightarrow R^* \tag{1}$$

(Propagation)

$$R^* + M \rightarrow RM^* \tag{2}$$

$$RM^* + M \rightarrow RMM^* \tag{3}$$

$$RMM^* + M \rightarrow RMMM^* ..... \tag{4}$$

(Termination)

$$R(M)_n M^* \rightarrow \textit{Inactive polymer} \tag{5}$$

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EXPERIMENTAL METHOD

Gel preparation

The polymer gels were synthesized in a nitrogen glove-box according to Deene et al. (2000). In this work however, the polymer gel was prepared base on the procedure introduced by Maryanski *et al* (1994). Some modifications were made to suit the facilities available in the laboratory. In the first beaker, the gelatine was dissolved in deionized water and stirred to a constant temperature of 55˚C in a water bath for 2 hours. The N, N'-methylene-bisacrylamide (BIS) was also dissolved in deionized water in another beaker. The solution was stirred at a temperature of 55˚C in a water bath for the duration of 1 hour. Both solutions were bubbled with nitrogen during the dissolving process in order to expel the oxygen, which can induce polymerisation (Maryanski *et al*., 1994). Both solutions were allowed to cool down to room temperature at 27 ˚C for about 1 hour to avoid spontaneous heat-induced polymerization before mixing. In the mixing process, BIS solution was added to the gelatine solution and stirred at room temperature for 30 minutes. Methacrylic acid (MAA) was then added to the solution and stirred for 10 minutes in homogenizing the solution. The beaker was then covered with aluminium foil to protect the gel against light-induced polymerization. The final product was filled into the 5 ml ampoule tubes or "P6" glass vials using a peristaltic pump via Tygothane flexible tubing and sealed the tubes with parafilm. The prepared dosimeters were stored in a refrigerator at low temperature (15˚C) and protected from UV light. It is recommended to irradiate the dosimeters as soon as possible (within days) after preparation in order to avoid damage by oxygen penetrating through the stopper. The polymer gels prepared were composed of 2 to 5% (w/w) MAA as monomers, 2 to 5% BIS as crosslinker, 5% gelatin and are completed with deionized water at the appropriate proposition.

Gel irradiation

Each dosimeter was irradiated at different doses (0-19Gy) using gamma rays produced by Co-60 radionuclide, generated at 1.25MeV energy. Gamma radiation is utilized for fundamental studies and for low-dose rate irradiations with deep penetration. Calibrations of this source are performed using a standard Fricke dosimeter and ionizing chamber.

Measurement

Nuclear Magnetic Resonance instrument (BRUKER, minispec pc100, with operating frequency 20 MHz – crystal controlled) is used in order to observe relaxation rates of proton caused by polymerization process within PMAG dosimeters. An optical spectrophotometer (Camspec M350) measures the absorption of UV-Visible light at each wavelength and presents the spectra in the form of absorbance (*A*) versus wavenumber or photon energy.

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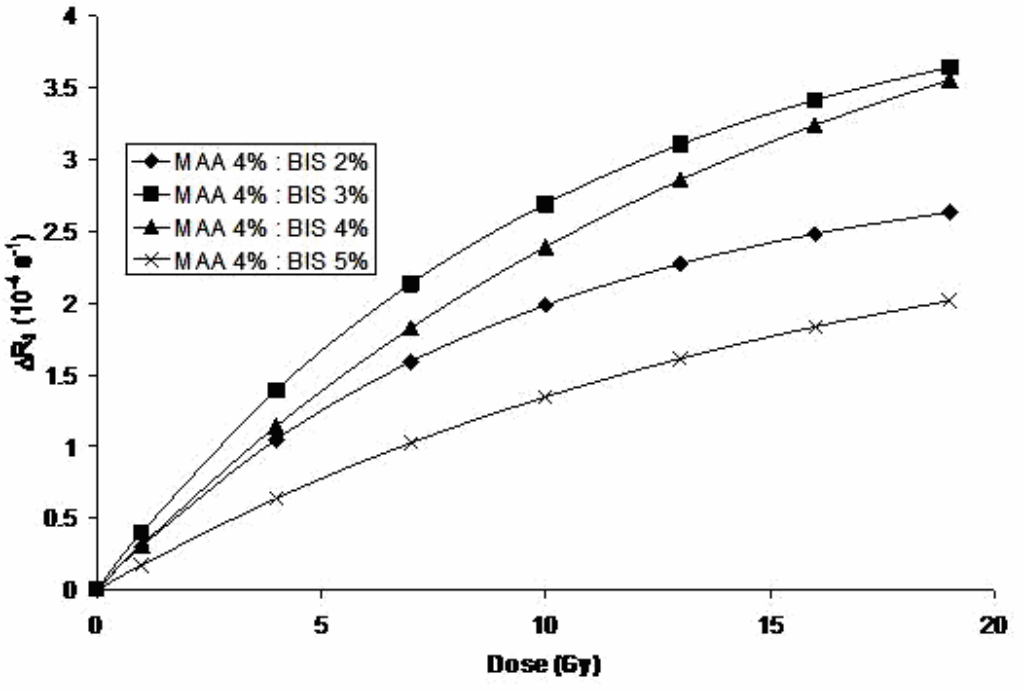
RESULTS AND DISCUSSIONS

Figure 2 (a) shows spin-spin relaxation rate at different BIS compositions and initial composition of MAA in the formation of PMAG. The results were background fitted in order to map the differences in relaxation rate of spin-spin. The relaxation rate R_2 ($1/T_2$) are fitted to the functional form y as a function of absorbed dose D was found to have a monoexponential expression in the form:

$$y = y_0 + A(1 - e^{\frac{-D}{D_0}})$$

The relaxation rates are increasing significantly from 0 Gy to 19 Gy due to mechanism of dose response on the monomer consumption. The spin-spin relaxation rate of the water protons is influenced by the presence of MAA and depends on its relaxitivity determine by composition) and concentration (determine by radiation dose). The presents of BIS enhanced the formation of PMAG makes PMAG more rigid and likely reduces the motional averaging of dipolar interactions among the semisolid pool of protons. Obviously, spin-lattice relaxation rates progressively increase from 0 Gy until 19 Gy due to reduction of water molecules mobility which bound to the monomers by hydrogen bridges in the formation of PMAG. On the contrary, the overlapping of curves can be seen clearly when BIS composition increased. This shows that spin-spin relaxation rates depend on determination of crosslinker composition.



(a)

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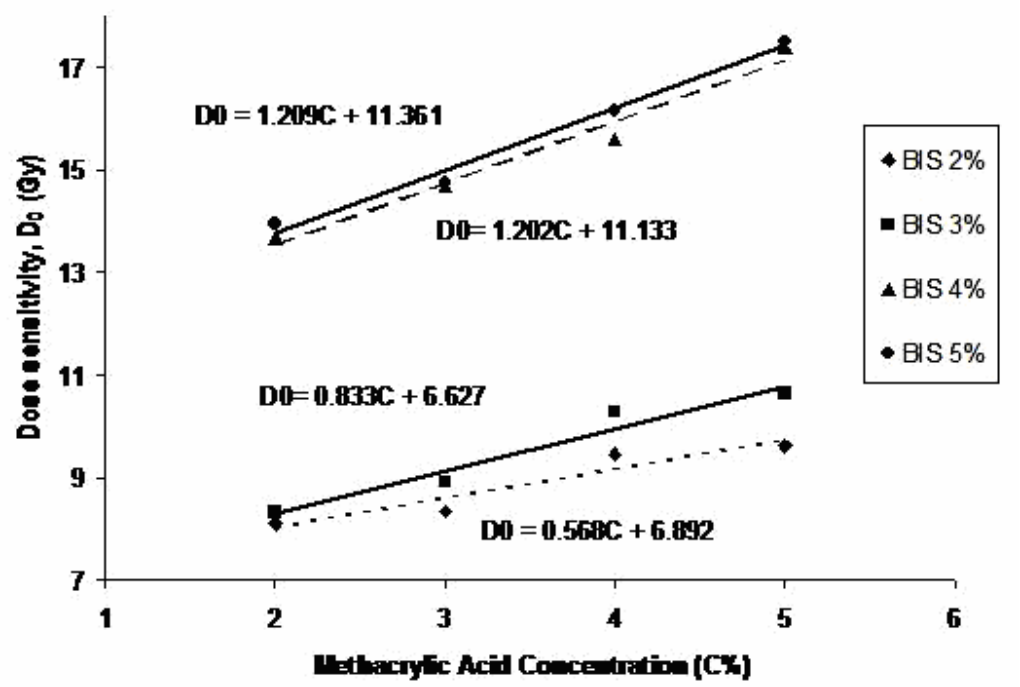
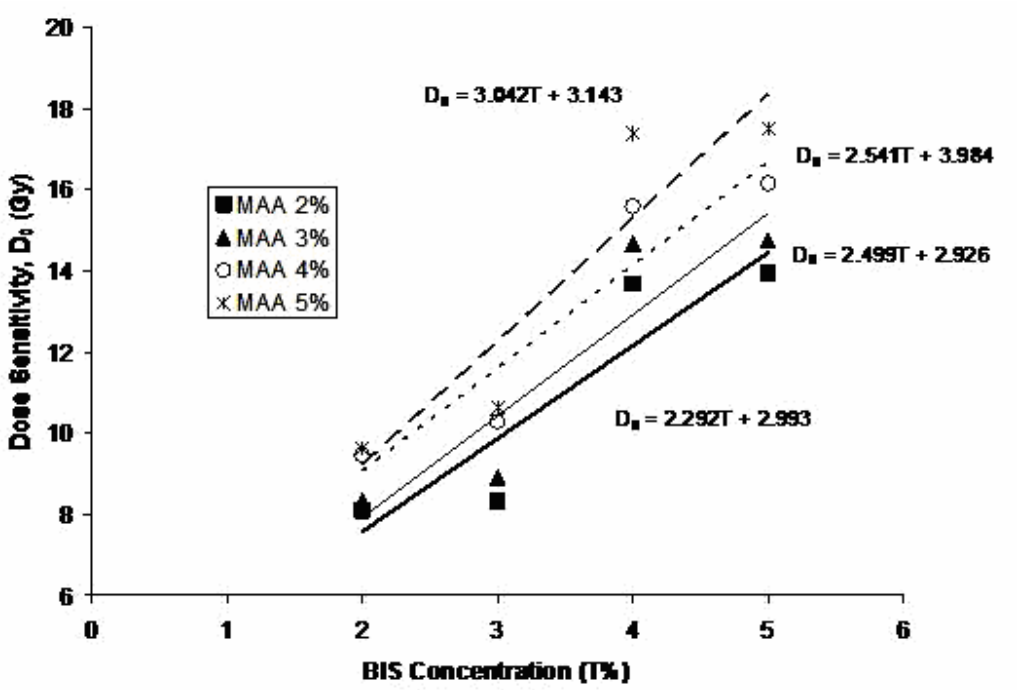


(b)



(c)

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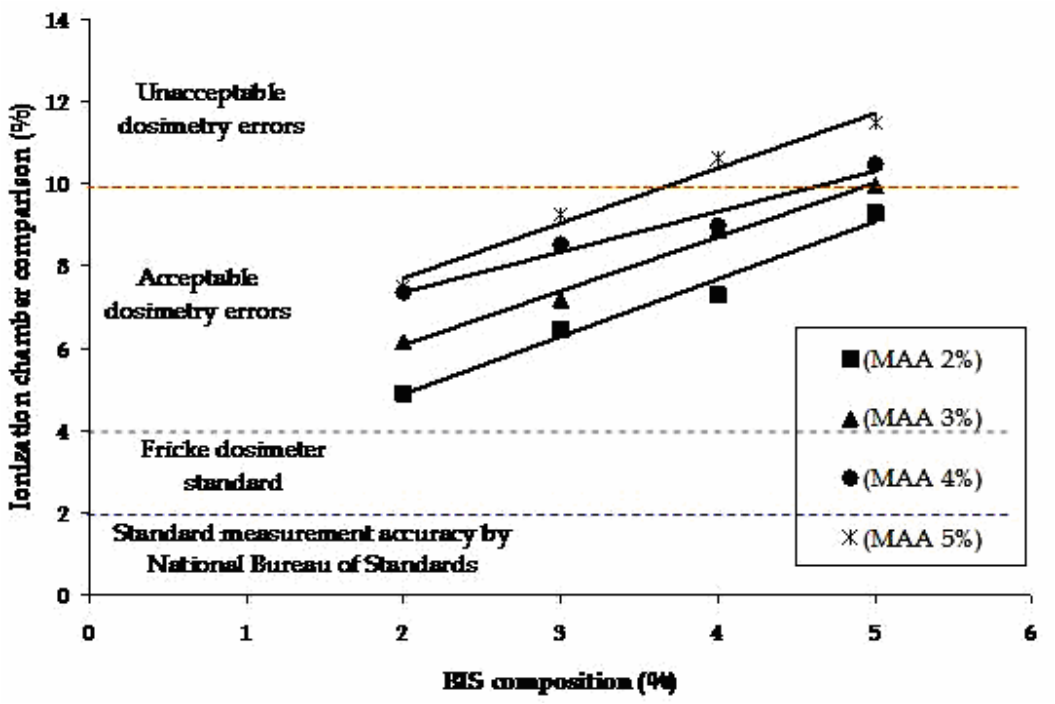

(d)

Figure 2: (a) Normalized NMR spin-spin relaxation rate (ΔR_2) as a function of dose D at various BIS compositions and initial concentration of 4% MAA. (b) Dose sensitivity D_0 of spin-spin relaxation rate ΔR_2 and the initial concentration on MAA for different BIS. (c) Dose sensitivity D_0 of spin-spin relaxation rate ΔR_2 and the initial concentration on BIS for different MAA.

The correlations between dose sensitivity D_0 of spin-spin relaxation rate ΔR_2 and the initial concentration on MAA for different BIS are illustrated in Figure 2 (b). The slope represents the rate of monomer consumption at a given crosslinker concentration and the linear relationship between spin-lattice relaxation rate R_1 and dose sensitivity D_0 value. The dose sensitivity depends on percentage of BIS. Thus, the dose sensitivity D_0 of spin-spin relaxation rate R_1 is a function of both the NMR relaxitivity of crosslinked PMA and the reactivity of MAA. This may oversimplify the description of radiation-induced polymerization. The correlations between dose sensitivity D_0 of spin-spin relaxation rate ΔR_2 and the initial concentration on BIS for different MAA are illustrated in Figure 2 (c). The slope parameter $k_{BIS} > k_{MAA}$, indicating the consumption of crosslinker is much faster than the monomer.

Figure 2 (d) shows the comparison of percentage has been made with ionization chamber. Throughout the results, percentage comparison increases with the increase of N, N'-methylene-bisacrylamide (BIS) concentrations and the increase of monomer, methacrylic acid (MAA). After irradiation, the absorbances (A_i) of irradiated solutions

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of Fricke and PMAG polymer gel were measured using UV-VIS spectrophotometer (Camspec M350) at the absorbance peaks of 305nm for Fricke and 375nm for PMAG. The unirradiated dosimeter solution was used as a reference for unirradiated absorbance A_0 using air path as the 100% transmission.

The equation for calculating the absorbed dose in the Fricke dose meter solution is given by:

$$D = \left(\frac{\Delta A.N_A}{\rho.G.\varepsilon.d\left(1+\xi\left(t-25\right)\right)} \right) \frac{b}{k} \qquad (6)$$

$\Delta A = (A_i - A_0)$ is the change in absorbance at peaks 305 nm (Fricke) and 375 nm (PMAG), where A_i and A_0 are the absorbencies of the irradiated and unirradiated solutions.

N_A = 6.022 x 10^{23} mol^{-1} (Avogadro's number)
ρ = the density of the dosimetry solution
ε = molar extinction coefficient
ζ = temperature coefficient of the molar extinction coefficient
G = G-value of the radiation yield, which is valid for electrons or photons of energy 0.5 to 16 MeV at absorbed dose rates < 2 x 10^7 Gy/s.
d = optical pathlength in the quartz cells
b = energy conversion factor
k = volume conversion factor

Therefore, dose absorbance calculations for Fricke and PMAc gel dosimeter can be determine by using equation (7) and (8).

$$D = \frac{275 \times \Delta A}{1+0.007\left(t-25\right)} Gy \qquad \text{(Fricke)} \qquad (7)$$

$$D = \frac{274.1 \times \Delta A}{1+0.007\left(t-25\right)} Gy \qquad \text{(PMAA gels)} \qquad (8)$$

It was decided to accept the use of calibrated ionization chamber as a 'gold standard' as these offer the best accuracy and of any widely available radiation measuring device employed in radiotherapy. Therefore, the calculations of 3 hours of dosage for ionization chamber have been made in order to compare with dose absorbance results gain from Fricke dosimeter and PMAc gel dosimeter. Although the dosage given to PMAcG is above 20 Gy (> 40 Gy), which is irrelative, however PMAcG has been irradiated up to 100 Gy before saturation of the polymerization occur at 58 Gy. 3 hours exposure is a standard procedure for Fricke dosimeter in order to obtain the minimum dose achievable for the dosimeter. The absorbance can be calculated by referring to equation (8) by replacing the absorbance value of the samples, reference solution and

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other parameters. The dose rate calculations were gained from the radioactive decay law:

$$D = D_0 e^{\left(\frac{-\ln 2.t}{t_{1/2}}\right)} \quad (9)$$

where;
D = rate of active atom at present time t
D_0 = number of active atoms present at the beginning of the observations
$t_{1/2}$ = half-life of radionuclide (Co^{60} = 1926 days)

The calculations were done using the references provided by the Secondary Standard Dosimetry Laboratory (SSDL), Malaysian Nuclear Agency (MNA) at Bangi.

CONCLUSION

Methacrylic acid (monomer) and N, N'-methylene-bisacrylamide (crosslinker) are organic compounds that polymerizes upon interaction of ionizing radiation to form a polymer gel dosimeter. Due to the radiation action, chain-reaction polymerization processes had taken place in the formation of PMAG. The dose sensitivity value (12.5 $\pm$ 0.1 Gy) of MAA monomer by Lepage, *et al* 2001 is comparable with PMAG experimental value gained which are 12.6 $\pm$ 0.1 Gy. The functional group determines both the polymerization rate of the monomers (inversely proportional to the dose sensitivity D_0) and the efficiency of cross-relaxation. Although the alkyl group in MAA does not have a large influence on the cross relaxation efficiency, it alters the polymerization, depends on the initial concentration of crosslinker. The slope $k_{BIS}>k_{MAA}$ indicates that the consumption of crosslinker is much faster than the monomer. Finally, the absorbance of PMAG dosimeter and the dose derived is comparible to Fricke dosimeter and ionization chamber readings between 4.7 ± 0.5% and 11.6 ± 0.5%. Therefore, PMAG gel dosimeter could be used as a point dosimeter in radiation protection. While dose errors of less than 10% are considered acceptable in radiation processing, an improvement of accuracy to less than 5% can be acceptable in radiotherapy.

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