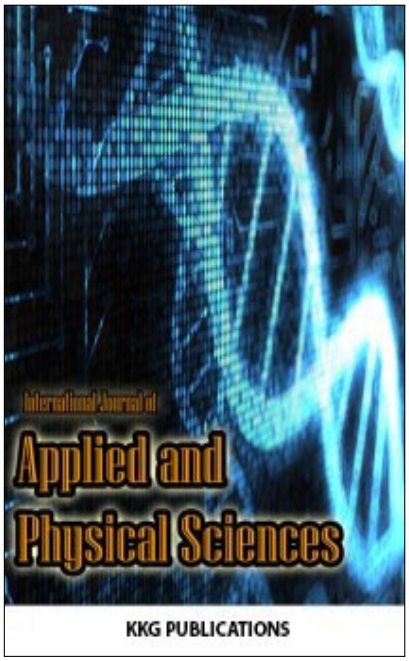

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UV-VISIBLE SPECTROPHOTOMETER ANALYSIS ON POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE

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Abstract. Polymer gel has been used as a dosimeter to determine spatial dose distributions by radiotherapy equipment. This study explores the absorption peak in the UV-visible (UV-vis) spectrophotometer as the relative intensity of polymerization. Theoretically, high intensity of polymerization results in high absorbance. The size of gold nanoparticles (GNPs) and dose of irradiation are expected to affect polymerization. Normoxic polymer gel samples using 2-Hydroxyethyl methacrylate (HEMA) as the monomer were prepared with different sizes of GNPs to study the effect of GNPs with ascorbic acid acting as the oxygen scavenger. Linear accelerator (LINAC) was the source of high irradiation x-ray energy as it is one of the most widely used radiotherapy equipment. The diagnostic x-ray unit acted as a low energy source. One crucial factor in fabricating the sample is the environment temperature. Radiation-induced polymer gel is environmentally sensitive where a low-temperature environment (<5°C) is needed to ensure the structural stability of the gel. The UV-vis analysis shows that the absorbance increases when the irradiation doses increase, while the size of GNPs affects the absorbance value depending on the irradiation dose.

INTRODUCTION

Due to increasing usage of radiotherapy techniques, such as Intensity Modulated Radiotherapy (IMRT) and high dose brachytherapy, the need of better dose verification method is increased. The main dosimeters used are ionizing chamber and Thermo Luminescent Dosimeter (TLD) which is restricted for taking measurement at only one point. Radiographic film can only be used as dosimeters but it can measure 2D dose distribution at its best. An accurate verification technique is needed for 3D high resolution-spatial dose distribution. Polymer gels have been developed as one of the current techniques that shows promise to accomplish this need [1-3].

It was as early as 1950s when polymer gels were being irradiated to see the effect [4], [5], but in 1993 [6] came up with the idea of using Magnetic Resonance Imaging (MRI) to map the 3D dose distribution. The gel used then was polyacrylamide infused in gelatin or agarose matrix. Since then many types of polymer gel were introduced including BANANA (BIS-acrylamide, Acrylamide, Nitrous oxide and Agarose), BANG-1TM (BIS acrylamide, acrylamide, nitrogen, gelatin), BANG-2TM (BIS acrylamide, acrylamide, sodium hydroxide, nitrogen, gelatin), BANG-3TM (BIS acrylamide, methacrylic, sodium hydroxide, nitrogen, gelatin), PAG (polyacrylamide gel), VIPAR (N-vinylpyrrolidone-argon based), and HEA (2-hydroxyethyle acrylate, bis-acrylamide acrylamide gelatin).

Polymer gel is very sensitive towards oxygen, therefore it is vital to prohibit any oxygen molecules from interrupting during polymerization. Water molecules have the tendency to scavenge the free radicals formed during water radiolysis. Therefore, to prevent this event from happening, in this study, polymer gels are prepared under normoxic condition [7-9]. Gold nanoparticles (GNPs) have been recognized as an element with high-Z to have potential in medical field specifically cancer treatment. A research was conducted by injecting 106 EMT-6 syngeneic mammary carcinoma cells into mice's thigh [10, 11]. The result shows that mice with GNPs injected prior to x-ray exposure survive longer with reduced size of tumor cells compared to those without GNPs.

MATERIALS AND METHOD

Sample Preparation

2-Hydroxyethyl methacrylate (HEMA) is used as the monomer and is dissolved in a gelatin solution. Ascorbic acid acts as the anti-oxidant agent to minimize the interaction of oxygen molecules during polymerization, and for the same reason, deionized water is used as the solvent. This type of polymer gel is called normoxic polymer gel. Fong have the details of this kind of polymer gel [8]. Portion for each element used in samples' preparation are as in table 1.

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TABLE 1
LIST OF ELEMENTS AND THEIR COMPOSITIONS

Element composition Portion concentration	(%w/w)
Gelatin	5
2-Hydroxyethyl methacrylate (HEMA)	9
N,N'-Methylene-bisacrylamide (BIS)	3
Deionized water	83
Ascorbic acid	5 mM

Samples were stored at a very low temperature environment (<5°C) overnight before irradiation. This is to ensure the HEMA structure stability which has to be solid at all time. For irradiation purposes, Pantai Hospital Penang has permitted the usage of their Linear Accelerator (LINAC) as the energy source for this study. For low x-ray energy, diagnostic x-ray unit in the Biophysics lab of School of Physics, Universiti Sains Malaysia was used. All samples were kept in low temperature environment immediately after irradiation.

Data Measurement

For this research purpose, UV-visible spectrophotometer (Shimadzu UV-1800) is used as an analysis instrument.

RESULTS AND DISCUSSION

Polymerization of 2-Hydroxyethyl methacrylate (HEMA) can be relatively measured using UV-visible spectrophotometer. Absorbance value recorded by UV-visible spectrophotometer represents relative intensity of polymerization. Linear accelerator (LINAC) uses high energy x-ray as the energy sources. In theory, radiation-induced polymer gels such as HEMA, are sensitive to the irradiation dosage. The intensity of monomer's chain broken to form polymers increases with higher energy of exposure. Higher intensity of polymerization results in higher value of absobance as the polymers will actively absorb lights at certain wavelengths. Based on figure 1, which presents the data of absorbance versus dose, it shows the absorbance value increases with increasing irradiation dose. Numbers of HEMA bonds break at a high intensity upon irradiation with 50 Gray x-ray energy to form (poli) 2-Hydroxyethyl methacrylate (pHEMA). This results in high light absorption by pHEMA due to its complexity of structure. The curve of absorption at 10 Gray of x-ray energy is much lower because the capability to break HEMA bonds is limited compared to 50 Gray x-ray energy.

Referring to figure 2, it is shown that HEMA with GNPs of 15 nm in diameter has the highest absorbance while HEMA with 40 nm GNPs has the lowest. The effect of the size of GNPs towards the polymerization of HEMA can be seen as the size of GNPs is bigger, the polymerization occurs less in intensity thus lowering the absorbance value. For GNPs with size bigger than 40 nm, in this case, 50 nm and 80 nm, absorbance values increase but still do not exceed the absorbance of HEMA with 15 nm and 20 nm GNPs.

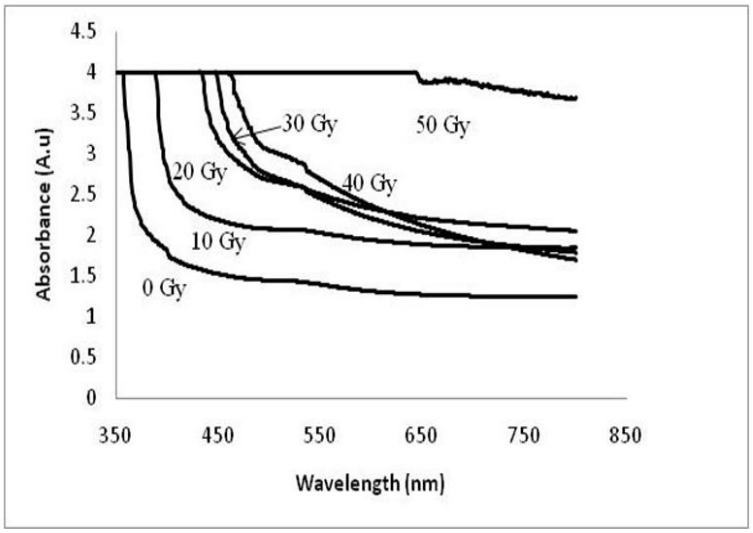

Fig. 1 . UV-Vis representation of absorbance for HEMA doped with 15nm GNPs at different x-ray energy

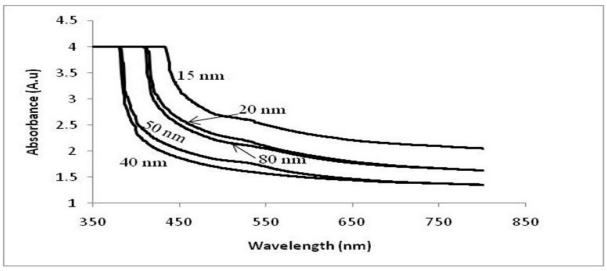

Fig. 2 . UV-Vis representation of absorbance for HEMA doped with different sizes of GNPs at 20 Gray of x-ray energy

For the highest x-ray energy used for study which was 50 Gray, there is a slight difference in Uv-Vis reading of absorbance (figure 3). HEMA with 15 nm and 40 nm of GNPs remains as the highest and lowest value of absorbance respectively. For HEMA doped with 50 nm and 80 nm the reading shows that the intensity of polymerization of both samples is higher compared to 20 nm GNPs. In comparison, upon irradiation with 20 Gray x-ray energy, both have lower absorbance number than 20 nm GNPs. HEMA with 20 nm, 50 nm and 80 nm GNPs is more affected by higher x-ray energy than 15 nm and 40 nm GNPs.

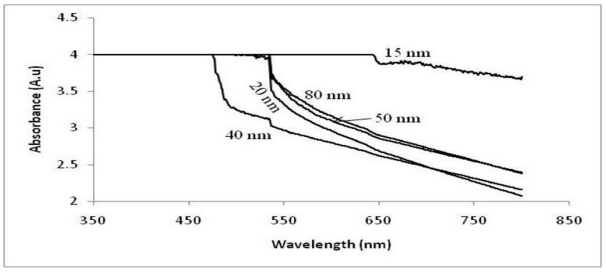

Fig. 3 . UV-Vis representation of absorbance for HEMA doped with different sizes of GNPs at 50 Gray of x-ray energy

For comparison purpose, this study was repeated using the same monomer and preparation techniques but different x-ray energy source. Samples with the same size and amount of GNPs were irradiated with diagnostic x-ray unit. In figure 4, HEMA samples that were irradiated with 40 kVp can be seen as having no significant difference in absorbance value compared to those unirradiated. 40 kVp produces $\sim$0.3 mGy of x-ray energy which is too small compared to energy by LINAC, thus resulting in insignificant intensity of pHEMA formed. As the irradiation energy increased to 60 kVp, there is a slight increase in the absorbance value but it still does not exhibit a significant difference when the energy was increased to 80 kVp. When x-ray energy was increased further until a maximum of 110 kVp, the absorbance value increases but, samples irradiated with 90 kVp have almost the same absorbance value as the 110 kVp irradiation at all wavelengths. This can be observed by the overlapping curves between the two energies. Polymerization still occurs when samples are exposed to low x-ray energy but it is less significant than high x-ray energy such as LINAC.

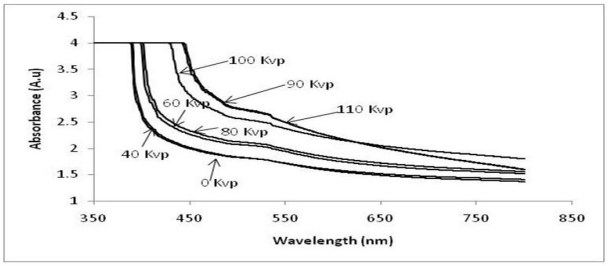

Fig. 4 . UV-Vis representation of absorbance for HEMA doped with 15nm GNPs at different x-ray energy using diagnostic x-ray unit

CONCLUSION

Although it releases ionizing radiation, the energy from diagnostic x-ray unit is not as capable to break monomers bond as high energy x-ray. Absorbance value for HEMA amongst low x-ray energy is not clearly distinguishable meaning at very low x-ray energy, polymerization occurs at very low intensity.

On the other hand, LINAC which irradiates very high x-ray energy causes single monomers to break their bond rapidly at high intensity. Polymerization occurs at higher rate thus influences the absorbance value read by UV-Vis.

Size of GNPs affects the polymerization process with lowest size of GNPs in this study, 15 nm in diameter, shows highest absorbance value while GNPs of 40 nm size has the lowest absorbance value upon irradiation to the same level of x-ray energy. The two largest size of GNPs in this study, 50 nm and 80 nm in diameter, exhibit a polymerization behavior lower than the 20 nm GNPs when irradiated with 20 Gray of x-ray energy. Upon irradiation with 50 Gray of x-ray energy, both 50 nm and 80 nm GNPs samples polymerized at higher intensity than 20 nm GNPs. This shows that both parameters (GNPs' size and X-ray energy) controlled the polymerization of HEMA. To get a clearer explanation regarding this matter, it is best to vary method of analysis in the future.

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