UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

1. **Nama Ketua Penyelidik:** Azhar bin Abdul Rahman
   Name of Research Leader

   ☐ Profesor Madya/ *Assoc. Prof.* ☑ Dr./ *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):** School of Physics
   School/Department

3. **Nama Penyelidik Bersama:**
   Name of Co-Researcher
   1. Prof. Mohamad Suhaimi Jaafar
   2. Dr. Iskandar Shahrim Mustafa

4. **Tajuk Projek:** Characterization and Clinical Study of 'Normoxic' Polymer Gel
   Title of Project

5. **Ringkasan Penilaian/***Summary of Assessment*:	Tidak Mencukupi *Inadequate*		Boleh Diterima *Acceptable*	Sangat Baik *Very Good*	
	1	2	3	4	5
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☑	☐
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☑	☐
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☑	☐
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☐	☑	☐
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☐	☐	☑
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☑	☐

6. Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris.** Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research

(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Polymer gel has been used as a dosimeter to determine spatial dose distributions by radiotherapy equipments. In this project, various kind of polymer gels are used to see the dose distribution of diagnostic X-Ray and Linear Accelerator (LINAC). Normoxic polymer gel from four different bases namely methacrylic acid (MAGAS), acrylamide (PAGAS), 2-hydroxyethyl methacrylate (HEMA), and 2-Hydroxyethyl acrylate (HEA) are used. The analyses are done using FT-Raman spectroscopy, magnetic resonance imaging (MRI) and UV-visible Spectroscopy. It is expected that the intensity of polymerization will be increasing with the radiation energy. Based on the results obtained, polymerization occurs more rapidly with increasing energy and it is shown that polymer gel is suitable to be used as dosimeter for absorbed dose measurement.

Gel polimer telah digunakan sebagai dosimeter dalam penentuan taburan dos bagi alat-alat radioterapi. Dalam projek ini, beberapa jenis gel polimer digunakan untuk menentukan taburan dos dalam mesin Sinar-X diagnostik dan juga pemecutlinear (LINAC). Gel polimer 'normoxic' dari empat jenis bahan berbeza digunakan, iaitu methacrylic acid (MAGAS), acrylamide (PAGAS), 2-hydroxyethyl methacrylate (HEMA), and 2-Hydroxyethyl acrylate (HEA). Analisis pempolimeran pula dilakukan dengan menggunakan tiga kaedah iaitu spektroskopi FT-Raman, pengimejan resonans magnetik (MRI) dan spektroskopi UV-visible. Keputusan yang dijangkakan adalah bahawa kadar pempolimeran akan lebih tinggi dengan meningkatnya teanga sinaran. Berdasarkan keputusan yang diperoleh, kadar pempolimeran lebih tinggi dengan meningkatnya tenaga sinaran dan gel polimer amat sesuai digunakan sebagai dosimeter untuk pengukuran dos terserap

7. Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Sila gunakan kertas berasingan]
Applicant are required to prepare a Comprehensive Technical Report explaning the project. (This report must be appended separately)

- Please refer attachment -

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Gel polimer	*Polymer Gel*
Radioterapi	*Radiotherapy*
Dos Terserap	*Absorbed Dose*

8. Output dan Faedah Projek
Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

1. Nur S. O., Jaafar M. S., **Azhar A. R.** and Ernee S. O. 2010. Fabrication of Tissue Mimicking Phantom for Abdominal Ultrasound. Seminar Kebangsaan Fizik Perubatan Ke 7, 16 Disember 2010, Kota Bharu, Kelantan.

2. Aifa A. R., Jaafar M. S. and **Azhar A. R.** 2010. Investigation of Ascorbic Acid as an Oxygen Scavenger in Polyhydroxyethylacrylate Gel Dosimeter. Seminar Kebangsaan Fizik Perubatan Ke 7, 16 Disember 2010, Kota Bharu, Kelantan.

3. Aifa Afirah Rozlan, Mohamad Suhaimi Jaafar, and **Azhar Abdul Rahman**. 2011. Development and Characterization of Normoxic Polyhydroxyethylacrylate (PHEA) Gel Dosimeter using Raman *Spectroscopy, World Academy of Science, Engineering and Technology*. **74**, 121-125.

4. Nur Shakila Othman, Muhamad Suhaimi Jaafar, **Azhar Abdul Rahman**, Ernee Sazlinayati Othman, and Aifa Afirah Rozlan. 2011. Ultrasound Speed of Polymer Gel Mimicked Human Soft Tissue within Three Weeks, *International Journal of Bioscience, Biochemistry and Bioinformatics*. **Vol. 1, No. 3**, 223-225.

5. Muhd. Hazwan H.H., Azhar A.R. & Iskandar S.M., 2012, Characterization of Methacrylic Acid (MAGAS) Polymer Gel Using Low Energy X-Ray. *Technology, Science, Social Sciences and Humanities International Conference 2012 (TESSHI)*, Langkawi, Kedah, Malaysia.

b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

Tiada

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

i. NUR SHAKILA BINTI OTHMAN , M.Sc(Research), Fabrication of Tissue Equivalent Phantom for Liver Ultrasound Imaging. Tamat Pengajian

ii. AIFA AFIRAH BINTI ROZLAN ,M.Sc(Research), Fabrication And Characterization Of Normoxic Polymer Gel Dosimeter By Using Raman Spectroscopy At Low X-Ray Energies. Tamat Pengajian.

iii. NIK NOOR ASHIKIN BT NIK AB RAZAK ,Doktor Falsafah (PhD), Preliminary Study of PAGAT and MAGAT Polymer Gel Dosimeter in Radiotherapy Clinical Applications. Aktif (Dijangka tamat pengajian 2014)

iv. MUHD HAZWAN HAKIM BIN HISHAM ,M.Sc(Research). Aktif (Dijangka tamat pengajian 2013)

ii) Lain-lain:
Others

9. Peralatan yang Telah Dibeli:
Equipment that has been purchased

Tiada

Tandatangan Penyelidik
Signature of Researcher

14/1/2013
Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Diperakukan

- output dan produk yang dijanjikan sangat memberangsangkan.

- Beliau wajar diberikan pencapaian gaji yang baru.

PROFESOR MOHD. ZUBIR MAT JAFRI
Timbalan Dekan (Penyelidikan)
Pusat Pengajian Sains Fizik
Universiti Sains Malaysia
11800 Pulau Pinang

30/1/2013

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

Tarikh
Date

Comprehensive Technical Report

A. Project number: 304/PFIZIK/6310068

Project Title: Characterization and Clinical Study of 'Normoxic' Polymer Gel

Project Leader: Dr Azhar Abdul Rahman

Tel: 04-6533888 ext. 5104/3655

B. Summary

Polymer gel has been used as a dosimeter to determine spatial dose distributions by radiotherapy equipments. In this project, various kinds of polymer gels are used to see the dose distribution of diagnostic X-Ray and Linear Accelerator (LINAC). Normoxic polymer gel from four different bases namely methacrylic acid (MAGAS), acrylamide (PAGAS), 2-hydroxyethyl methacrylate (HEMA), and 2-Hydroxyethyl acrylate (HEA) are used. The analyses are done using FT-Raman spectroscopy, magnetic resonance imaging (MRI) and UV-visible Spectroscopy. It is expected that the intensity of polymerization will be increasing with the radiation energy. Based on the results obtained, polymerization occurs more rapidly with increasing energy and it is shown that polymer gel is suitable to be used as dosimeter for absorbed dose measurement.

C. Objectives Achievement

- **Original project objectives**

  1) To study the spatial dose distribution in various kinds of polymer gels.
  2) To determine the difference in dose distribution for diagnostic X-Ray and linear accelerator (LINEAR).

- **Objectives Achieved**

  1) The dose distribution in both X-Ray and LINAC follow according to the theory where polymerization rate increased with increasing dose.
  2) There difference in dose distribution in X-Ray and LINAC

- **Objectives not achieved**
  None

D. Technology Transfer/Commercialisation Approach

1) 1 Ph.D and 3 M.Sc students trained in the latest techniques in "Normoxic" polymer gel dosimeter preparation and characterization.

E. Assessment Of Project Structure

- **Project team**

  Every member of the project team was active but the amount of contribution from each member varies.

- **Collaboration**

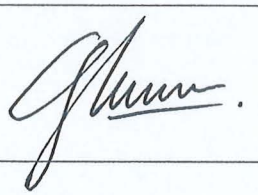
  Each of the institutions involved was responsible in either providing the samples (synthesis), data collection (data processing), data interpretation or submitting manuscripts for publication to international journals.

F. Assessment Of Research Approach

Before data collection:
Sample preparation: All sample preparations were done in the Biophysics Lab, School of Physics, USM.

After data collection:
All the data collections and analysis of the result were done by the group at UPM lab and USM NOR Lab. The publication of the results in reputable international journals was undertaken by all members of the groups.

Date: 14/1/2013 **Signature:**



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Characterization of Methacrylic Acid (MAGAS) Polymer Gel Using Low Energy X-Ray

Muhd. Hazwan H.H.[1], Azhar A.R.[2] & Iskandar S.M.[3]

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Abstract

Polymer gel has been used as a dosimeter to determine spatial dose distributions by radiotherapy equipments. In this study, the dose distribution of diagnostic x-ray machine will be determined using polymer gel. A Normoxic Polymer Gel of Methacrylic Acid Base (MAGAS) is prepared. It is prepared with gelatin, deionized water and for the anti-oxidant agent, ascorbic acid is used. The analysis is done using FT-Raman spectroscopy. It is expected that the intensity of polymerization will be increased with X-Ray energy. Even though a low X-Ray energy was used, polymerization occurred according to the theory.

Keywords: dose distribution, polymer gel, FT-Raman.

1. Introduction

1.1. Polymer Gel Dosimetry

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 dosimetries 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 (Oldham *et al* 1998, Low *et al* 1999, Pfaender *et al* 1999,).

It was as early as 1950s when polymer gels were being irradiated to see the effect (Alexander and Fox 1954, Feng 1958), but in 1993 Mayanski *et al* 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 gelatine or agarose matrix. Since then many types of polymer gel were introduced including BANANA (BIS-acrylamide, Acrylamide, Nitrous oxide and Agarose), BANG-1™ (BIS-acrylamide, acrylamide, nitrogen, gelatin), BANG-2™ (BIS-acrylamide, acrylamide, sodium hydroxide, nitrogen, gelatin), BANG-3™ (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 (Fong *et al* 2001).

1.2. FT-Raman

Due to several restrictions and limitations, polymer gel has not been used in routine clinical environments. To date, MRI is the most used analyzing technique for dose distribution in polymer gel. In 1928, Chandrasekhara Venkata Raman discovered a light-scattering phenomenon which is known by Raman Effect (Raman and Krishnan 1928). It is more convenient to analyze the data of 3D dose distribution.

2. Materials and Methods

2.1. Sample Preparation

Methacrylic acid is used as the monomer and is dissolved in a gelatine 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 *et al* (2001) has the details of this kind of polymer gel. Each sample has a varied amount of methacrylic acid and each sample is exposed with different energy level of x-ray.

2.2. Sample Irridiation

After being left in a very low temperature environment ($<10^0$C) overnight, polymer gels are irradiated in a quick pace to avoid the gels from liquidize. The voltage of x-ray tube used ranging from 40 kVp – 140 kVp. Ionizing chamber is then used to get the measurement of dose in mGy for each tube voltage.

2.3. *Data Measurement*

A few hours after irradiation, measurements with FT-Raman should be done. It is to give time for the sample to stabilize from the polymerization.

3. Result and Discussion

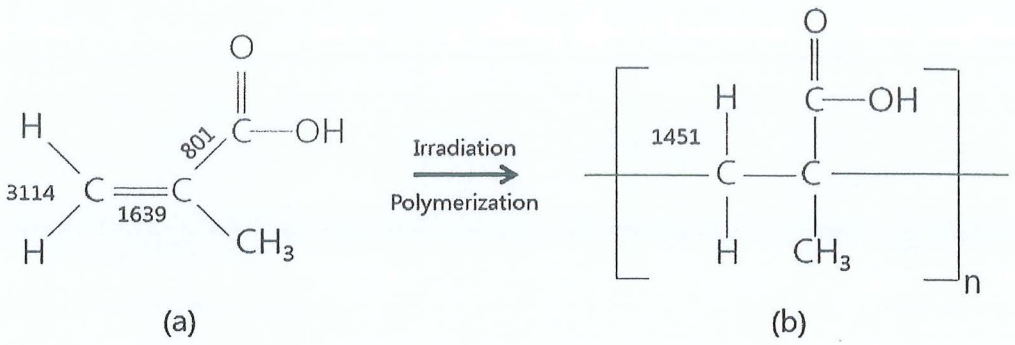

Figure 1. Structural formula (a) methacrylic acid before polymerization and (b) polymethacrylic acid.

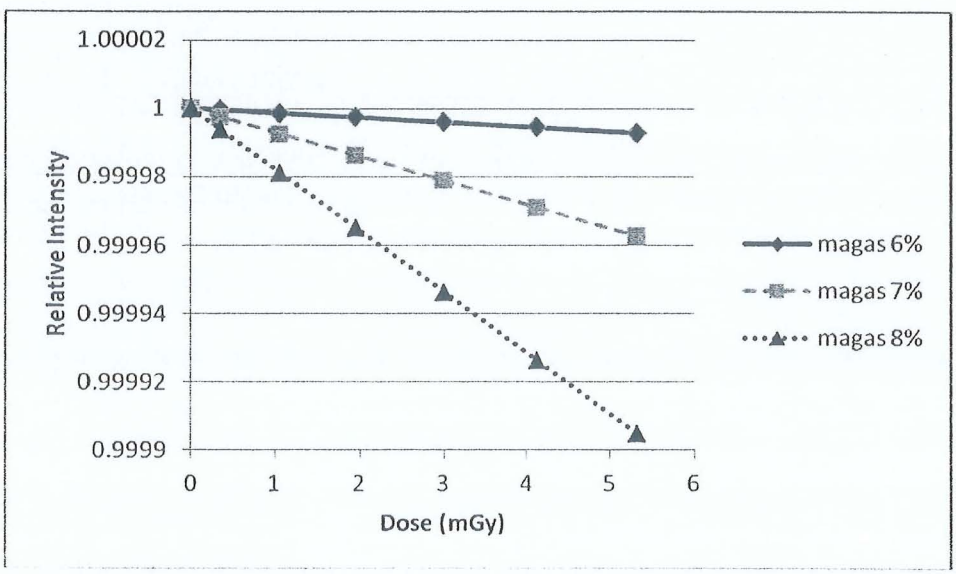

Figure 2. Normalized Raman intensity for C-C stretch at 801cm^{-1}

Upon irradiation, methacrylic acid started to polymerize and a band at wave number 801 cm^{-1} is where C-C bond stretching properties is determined. It occurs because of a symmetric stretching mode of C-COOH which corresponds to a bond between carboxylic carbon and double bond carbon (Halamus and Wojciechowski 2007). As shown in Figure 2, increment in the irradiated dose causes C-C stretching to happen more rapidly. Thus, with increasing polymerization, as expected the intensity of monomer decreases.

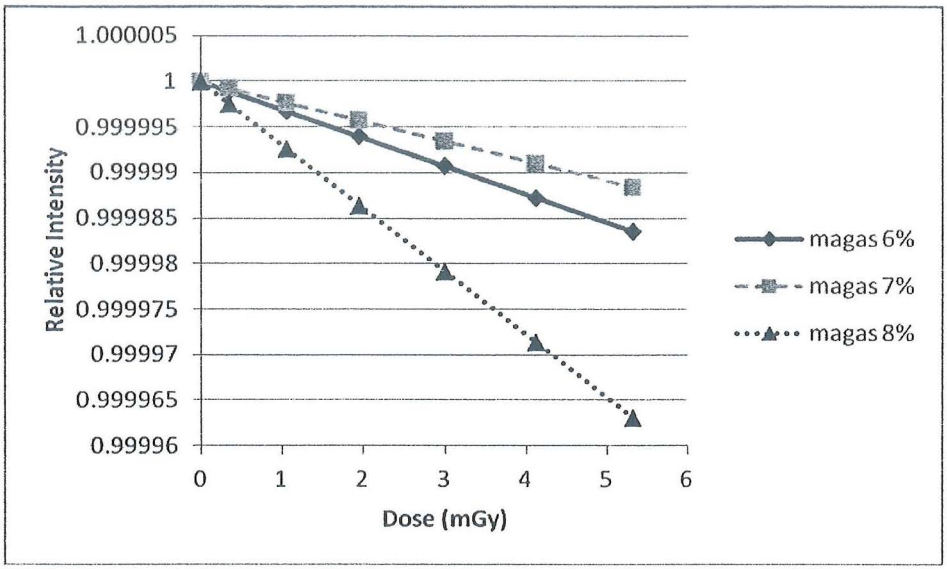

Figure 3. Normalized Raman intensity for C=C stretch at 1639cm^{-1}

A band at 1639cm^{-1} is caused by the C=C bond stretching vibrational mode (Halamus and Wojciechowski 2007). As polymerization took place, the C=C bond gradually transformed into a single bond thus, weakening the band which is indicated by the decreased in intensity as shown in Figure 3. The same phenomenon happens to C-H bond as shown in Figure 4.

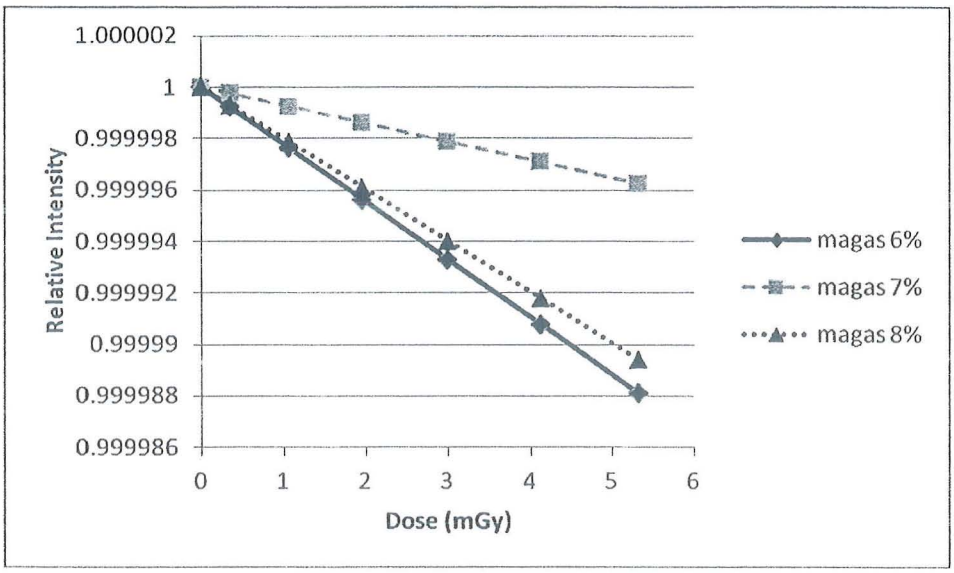

Figure 4. Normalized Raman intensity for C-H stretch at 3114cm^{-1}

The only increasing Raman reading is at the 1451cm^{-1} wave number as shown in Figure 5. This wave number indicates the bending mode of CH_2 bond in the polymethacrylic acid (Figure 1). With the increased value of irradiated dose, polymerization of methacrylic acid happened a lot more which strengthens this band. From Figure 5, it is also proven that the higher amount of monomer causes polymerization to happen rapidly.

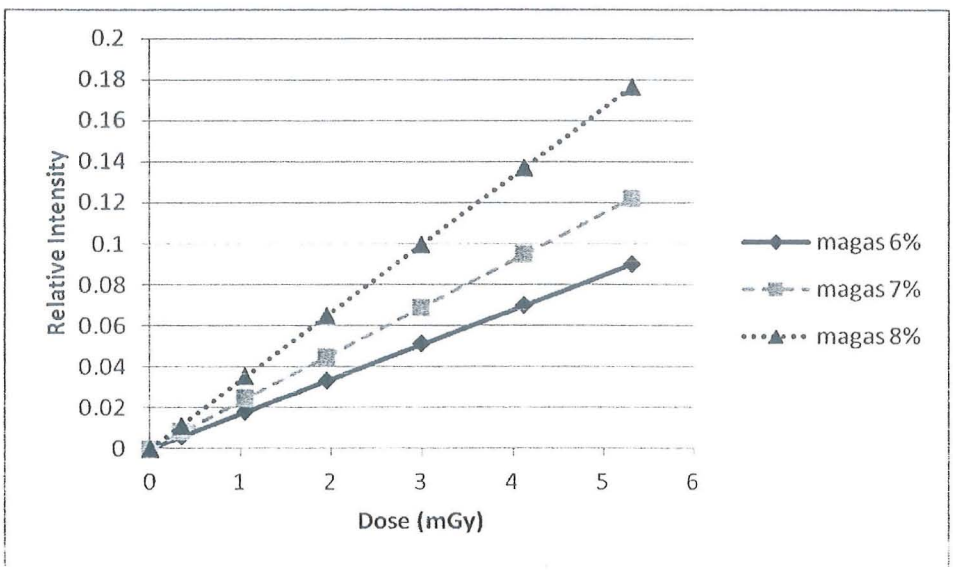

Figure 5. Normalized Raman intensity for C-H stretch at 1451cm^{-1}

4. Conclusions

From the result obtained, it is shown that different x-ray energy, should give different effect to the intensity of a particular bond. The difference in intensity symbolizes increment or decrement of that particular bond. Higher dose causes the polymerization to occur actively thus, will consume more of the monomer.

The increasing amount of monomer in a sample should cause the consuming of it to increase as well. But due to the low range of energy, it is hard to get a distinguishable reading as shown in Figure 3 and Figure 4.

Based on the previous research (Pappas *et al*), 3D dose distribution analysis using FT-Raman is more suitable for high energy dose.

5. Acknowledgement

The authors are grateful to be funded by the research grant 304/PFIZIK/6310068.

References

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Oldham M, Baustert I, Lord C, Smith T, McJury M, Warrington A, Leach M and Webb S. (1998). An investigation into the dosimetry of a nine-field tomotherapy irradiation using BANG-gel dosimetry *Phys. Med. Biol.* **43** 1113–32.

Pfaender M, Grebe G, Budach V and Wurm R. (1999). *Proc. 1st Int. Workshop on Radiation Gel Dosimetry (Lexington, Kentucky, USA)* ed L John Schreiner (Edmonton, Alberta: Canadian Organization of Medical Physicists) pp 190–2.

Halamus T, Wojciechowski P *Polym. Adv. Technol.* (2007), **18** 411.

Development and Characterization of Normoxic Polyhydroxyethylacrylate (PHEA) Gel Dosimeter using Raman Spectroscopy

Aifa Afirah Rozlan, Mohamad Suhaimi Jaafar, and Azhar Abdul Rahman

***Abstract*—**Raman spectroscopy are used to characterize the chemical changes in normoxic polyhydroxyethylacrylate gel dosimeter (PHEA) induced by radiation. Irradiations in the low dose region are performed and the polymerizations of PHEA gels are monitored by the observing the changes of Raman shift intensity of the carbon covalent bond of PHEA originated from both monomer and the cross-linker. The variation in peak intensities with absorbed dose was observed. As the dose increase, the peak intensities of covalent bond of carbon in the polymer gels decrease. This point out that the amount of absorbed dose affect the polymerization of polymer gels. As the absorbed dose increase, the polymerizations also increase. Results verify that PHEA gel dosimeters are sensitive even in lower dose region.

***Keywords*—**normoxic polymer gel, ascorbic acid, Raman spectroscopy, radiation dosimetry.

I. Introduction

RECENT development of complex radiotherapy treatment techniques has emphasized on a need of dosimetric system that has the ability to measure absorbed dose distributions in three dimensions (3D). Current dosimeters, such as ionization chamber, radiographic films and thermo luminescent dosimeter (TLD) can only measure in one or two dimension, and therefore are inadequate to integrate dose over three dimensional volumes. Hence, polymer gel dosimeter has been introduced to overcome this problem. Polymer gel dosimetry is therefore, a technique to determine high spatial resolution 3D dose distributions to verify a complex radiotherapy treatment plans prior to the actual radiotherapy treatment. Polymer gel dosimeters are fabricated from radiation sensitive chemicals which, upon radiation, polymerize as a function of the absorbed radiation dose. The first polymer gel was introduced by [1] for recording dose distributions in 3D using MRI. It is basically a hydrogel, which composed of acrylamide and bis-acrylamide co-monomers and gelatine dissolved in 80-90% water and is called PAG or BANG-1®. When irradiated with ionizing radiation, polymerization of the monomers occurs and the resultant polymer is retained in the gelatin matrix. This initial study have proposed several formulations and acronyms for polymer gel such as BANANA (Bis-acrylamide, Acrylamide, Nitrous Oxide and Agarose), PAG (Polyacrylamide gel) and BANG™ (Bis-acrylamide, Acrylamide, Nitrogen and Gelatin).

However, the use of polymer gel dosimeter has a significant limitation due to the nature of their free radical chemistry. The presence of atmospheric oxygen inhibits the polymerization process of the polymer gel [2]. To expel the oxygen from the gel, anti-oxidant is used to bind the free oxygen in the gel compositions [3]. Although some oxygen effects may still be experienced, these new normoxic gels are very capable as gels dosimeters. This type of polymer gel is known as normoxic polymer gel dosimeters.

Due to several limitations, these gel dosimeters have not reached the requirements to be accapted in routine clinical environments. Difficulties with image acquisitions and incomplete understanding of dose response mechanism are some of the limitations of these dosimeters. The most popular imaging modality for polymer gel is MRI, but this modality is not readily available to all radiotherapy clinics. A number of options have been proposed to address these problems. Optical and x-ray computed tomography (CT) protocol was developed to both imaged polymer gels and extract relative dose information [4, 5]. Still, the response of gel to radiation are not fullt understood. [6] introduced the use of Raman spectroscopy to demonstrate different rates of consumption of monomer and cross-linker. However, the quantifications and understanding of this difference is not complete. Studies of polymer gel using Raman spectroscopy has been further explored by [7, 8, 9].

Raman spectroscopy has the potential to directly monitor individual constituents within the gel sample [9]. In this study, Raman spectroscopy is used to characterize the radiation induced changes in polyhydroxyethylacrylate (PHEAG) gel dosimeters with varying the total amount of monomer (%M). The monomer consumption as a function of absorbed dose was studied using Raman spectroscopy.

II. Materials And Methods

A. Gel Manufacture

All gels were manufactured under normal atmospheric conditions without the use of a glove box. Gels were made under a fume hood using gelatin (bovine skin, Type B, Sigma Chemical Co), 2-hydroxyethylacrylate (HEA) (97%, ACROS Organics), *N, N'* –methylenebisacrylamide (BIS) (Sigma Chemical Co), ascorbic acid (AA) (Hamburg Chemical) and deionized water. The concentrations of the monomer are varied while other chemical constituents are constant.

Aifa Afirah Rozlan, Mohamad Suhaimi Jaafar and Azhar Abdul Rahman are with the Department of Medical Physics, University of Science Malaysia, 11800 USM, Penang, Malaysia.

Corresponding author: Aifa Afirah Rozlan is a master student in Department of Medical Physics, University of Science Malaysia, 11800 USM, Penang, Malaysia. (E-mail: aar09_phy024@student.usm.my).

The gelatin was given to 40% of the total amount of deionized water and allowed to swell for half an hour at room temperature. Then the gelatin solution was stirred and heated to 55°C using a magnetic stirrer/hot plate unit until a clear solution is obtained. The BIS solution and the ascorbic acid solution were prepared in separate beakers of 50% and 10% of the total amount of water. The total amount of compositions should be 100% during the preparation in order to control the parameter used. The gelatin solution was cooled down to about 35°C. BIS solution was added to the gelatin solution. Subsequently, the HEA solution was added into the solution and a homogeneous mixture was achieved by continuous stirring. Finally, the AA solution was added in order to minimize the amount of additional O_2 infiltrating the gel during the time when the anti-oxidant is active.

The solution was finally poured into ampoule tube and sealed with parafilm tape in order to minimize O_2 contamination through the cap of the tube. The gels were placed in a refrigerator at low temperature to solidify. Once set, gels were removed from refrigerator and allowed to equilibrate to room temperature.

B. Gel Irradiation

Gels were irradiated ~12h post-manufactured. All irradiations were performed on a Toshiba KX-50 X-ray Machine using 100 cm source to surface distance (SSD) set-up and 15 x 15 cm^2 field size. Stack of Perspex slab with dimensions of 30 x 30 x 1 cm were used as the phantom. One tube in each batch was left unirradiated, as a control and the remaining sample were irradiated to 50 and 70 kVp tube voltages and tube current of 10 mAs at depth of maximum dose.

C. Raman Spectroscopy of PHEAG

Raman spectroscopy was undertaken for batches in section C after the irradiation of the gels were performed. All Raman spectra were acquired on a Horiba Jobin Yvon LabRAM HR 800 Raman Spectrometer. An 514.5nm Ar^+ laser was used as the excitation source.

III. Results and Discussions

A. Raman Spectroscopy Analysis

Raman spectroscopy was used to monitor the monomer and cross linker consumption after the polymerization of the polymer gel. Raman spectroscopy involves inelastic light scattering process. The sample absorbed the difference in energy between the incident and scattered radiation in the form of molecular vibrations. Each molecule has a characteristic set of vibrational and/or bending modes of covalent bonds it posses. By measuring the intensity of scattered as a function of difference in wavelength between incident and scattered radiation, a chart of molecular constituents within a sample can be done. In this study, the polymer gel dosimeters have been investigated by monitoring the consumption of monomer HEA and cross linker BIS.

Raman frequencies of PHEAG were characterized by referring the table of characteristics frequencies of functional groups in the Raman spectra of complex molecules from [11] and literature reports [7, 10, 11]. The consumption of cross linker BIS and monomer HEA were determined at wave number 1640 cm^{-1} and 1716 cm^{-1} assigned to carbon covalent bond (C=C) stretching mode of BIS and HEA respectively. The vinyl CH_2 bending mode of BIS (1440 cm^{-1}) and HEA (1268 cm^{-1}) are also chosen. All of these four peaks are chosen as the primary signatures of the monomer and cross linker as the peaks are well defined, relatively intense and not covered by other peaks in the same frequency range.

In general, as the polymer gel dosimeter is irradiated, monomer and cross linker are consumed (see fig. 6 of [7]). Fig. 2 shows the Raman spectra for one of the batch of PHEAG gels. The spectra are in the range of 500 cm^{-1} to 2800 cm^{-1}. Observation of figure exhibit the decrease in peak intensity for all four assigned peaks as the tube voltage is increased. This phenomenon indicates the amount of C=C bonds for the consumption of HEA and BIS decreased with increasing tube voltage. This is due to the breaking of carbon covalent bonds to single bonds and the stretching of methylene group during polymerization and cross linking of PHEAG gel.

Fig. 3 shows the peak intensities values as a function of tube voltage for all assigned peak. The peak intensities correspond to the consumption of HEA and BIS during polymerization. Fig. 3(a) and 3(b) shows the intensity representing the amount of vinyl CH_2 stretching for both HEA and BIS at 1268 cm^{-1} and 1440 cm^{-1} respectively. Observation shows that the intensity decreased as the concentration of HEA is increased. This is due to the stretching of vinyl group CH_2 in the HEA and BIS, hence the consumption of HEA and BIS is increased. Similar finding was also reported by [8].

Fig. 3(c) and 3(d) shows the intensity representing the amount of C=C stretching for both HEA and BIS at 1640 cm^{-1} and 1716 cm^{-1} respectively. Observation shows that the intensity decreased as the concentration of HEA is increased. This is due to the stretching of C=C bonds in the HEA and BIS, hence the consumption of HEA and BIS is increased.

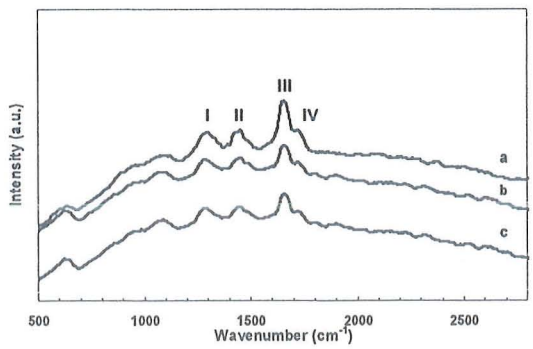

Fig. 2. Raman spectra for one of the PHEAG gels with 3% (w/w) of HEA. (a) indicates the control sample, (b) indicates sample irradiated to 50 kVp, (c) indicates sample irradiated to 70 kVp. Peak I refers to vinyl CH_2 stretch mode of HEA. Peak II refers to vinyl CH_2 stretch mode of BIS. Peak III refers to C=C of BIS. Peak IV refers to C=C of HEA. Spectra corresponding to each amount of HEA were obtained, but for clarity only a few are shown here.

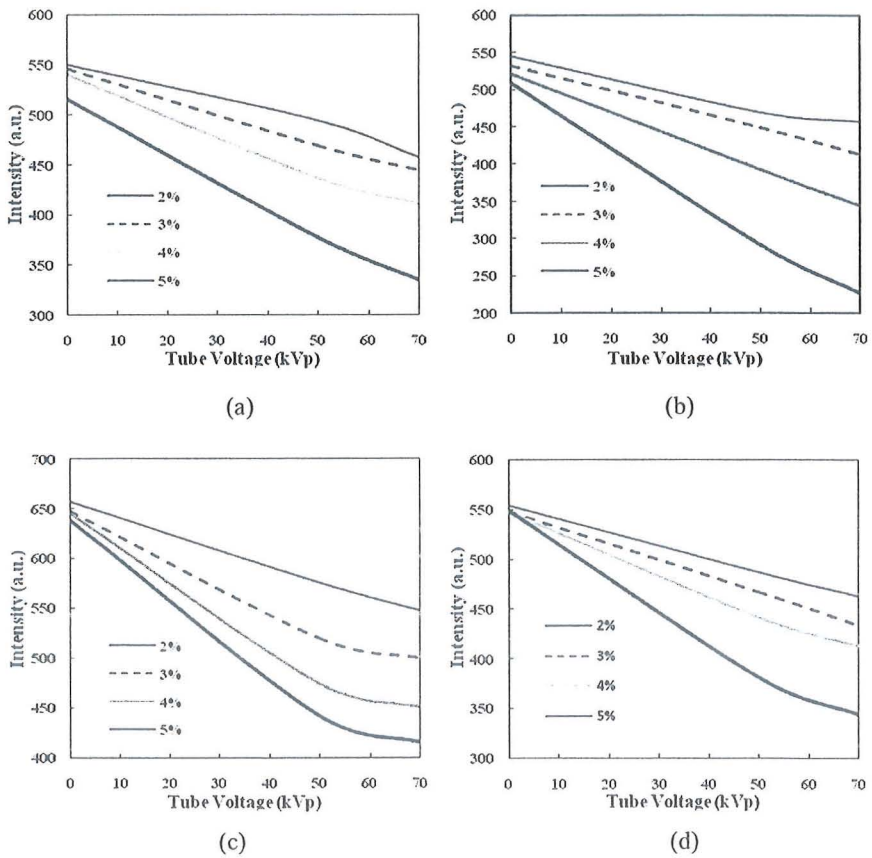

Fig 3. The value of peak intensity as a function of tube voltage, measured using Raman spectroscopy. (a) Peak intensity of vinyl CH_2 stretch mode of HEA (1268 cm^{-1}) with varying HEA amount. (b) Peak intensity of vinyl CH_2 stretch mode of BIS (1440 cm^{-1}) with varying HEA amount. (c) Peak intensity of C=C of BIS (1640 cm^{-1}) with varying HEA amount. (d) Peak intensity of C=C of HEA (1716 cm^{-1}) with varying HEA amount.

B. Polymerization Process

It is of very significant to discuss the mechanism of polymerization process of polyhydroxyethylacrylate in the formation of PHEAG. Fig. 4 shows the chemical structures of HEA and BIS and the initial PHEAG structure formed after irradiated with x-rays. When x-rays interacts with polymer gel dosimeter, the radiolysis of water molecules takes place to produce radical species of hydrogen $H^{\cdot}$ and hydroxyl $OH^{\cdot}$. On their own, these free radical species are highly unstable and reactive, which then react with the co-monomers (HEA and BIS) to open up their C=C stretching double bonds as shown in fig. 5 (a) and (b) for HEA and BIS respectively. The circles in fig. 4 indicate the affected stretching double bonds of co-monomers likely to be broken down into stretching single bonds during polymerization. The free radicals of co-monomers then react with the new co-monomers and hence propagating the chain reaction in the formation of PHEAG. The free radicals also initiate the crosslinking between copolymers of HEA and BIS by sharing electrons to produce a crosslink between two copolymer chains as shown in fig. 5 (c) . The polymerization and crosslinking will then propagate until the supply of monomer and crosslinker is exhausted, or the active side on the end of a polymer chains terminated. The general sequences of the polymerization can be summarized in the following sequences:

Radiolysis of water

$$H_2O + h\nu \rightarrow H^* + OH^*$$

Initiation of co-monomer radicals

$$RH + OH^* \rightarrow R^* + H_2O$$

$$RH + H^* \rightarrow R^* + H_2$$

Propagation of active co-polymer radicals

$$R^* + M_1(HEA) \rightarrow RM_1^*$$

$$R^* + M_2(BIS) \rightarrow RM_2^*$$

Termination of inactive polymer

$$R(M_1^*)_n + (RM_2^*)_m \rightarrow R(M_1)_n(M_2)_m \rightarrow$$

inactive polymer

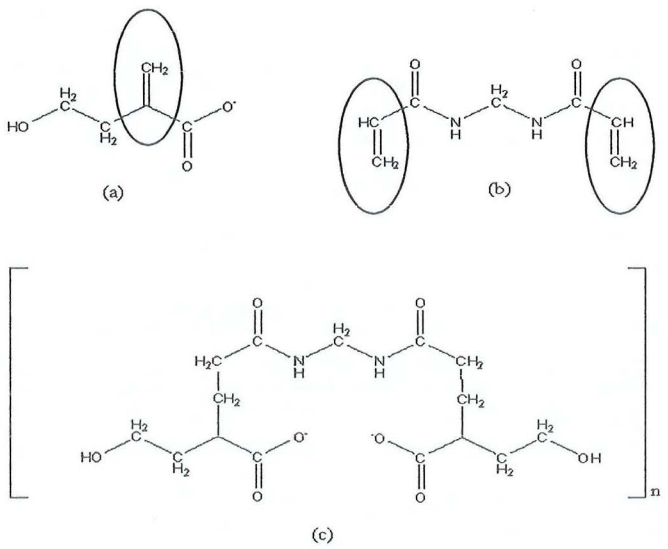

Fig. 4. Chemical structures of (a) 2-hydroxyethyl acrylate (HEA); (b) N, N'-methylene-bisacrylamide (BIS); (c) Polyhydroxyethylacrylate (PHEA). The circles indicate the affected stretching double bonds of co-monomers likely to be broken down into stretching single bonds during polymerization

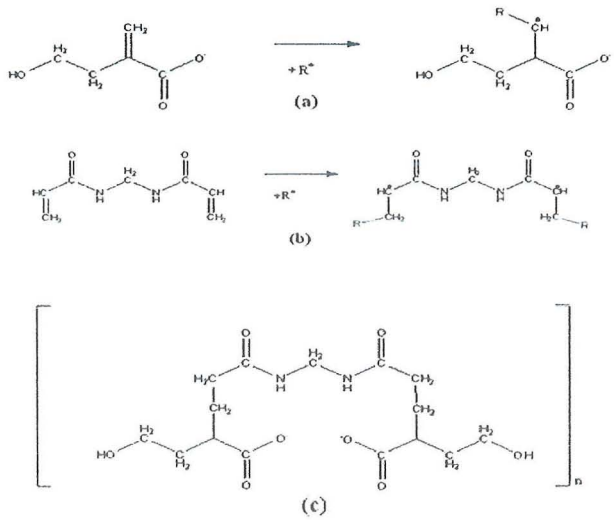

Fig. 5 Initiation of chemical structure (a) HEA; (b) *N, N'*-methylene-bisacrylamide (BIS) and (c) propagation of PHEAG

IV. Conclusions

The oxygen scavenging rate for polymer gels with varying amount of ascorbic acid and HEA concentration were evaluated. It is shown that the scavenging rate is dependent to the amount of ascorbic acid used during manufacturing of gels. Moderate amount of ascorbic acid is sufficient enough (e.g. 10 mM) to deplete O_2 to level suitable for full gel polymerization. Variation of HEA concentration does not affect the rate of oxygen scavenging by ascorbic acid. Polymer gels with varying amount of HEA concentrations and irradiated to 50 and 70 kVp tube voltage were evaluated using Raman spectroscopy. The Raman spectroscopy analysis presented the effect of initial composition of monomer and cross linker in the polymerization of PHEAG gel dosimeters. The gels demonstrate increasing polymerization with tube voltage and monomer concentrations.

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Ultrasound Speed of Polymer Gel Mimicked Human Soft Tissue within Three Weeks

Nur Shakila Othman, Muhamad Suhaimi Jaafar, Azhar Abdul Rahman, Ernee Sazlinayati Othman, and Aifa Afirah Rozlan

Abstract—**A Polymer gel mimicked human soft tissue was being fabricated using a monomer named 2-Hydroxyl-Ethyl-Acrylate (HEA) with the present of gelatin. The readymade gel which is the concentration for HEA fixed at 5% was then undergoes an ultrasonic evaluation to test for the propagation of sound speed through it. Sonic Waves Analyzer is absolutely the most accurate technique to determine the aims (changes of speed as function of polymer structure /stiffness over time). The fixed frequency of transducers involved is at 500 kHz by using the seismic reflection concept. In the observation of relationship between the ultrasound propagation speeds as the day increased, the propagation speed still varies between 1390 to 1500 m/s which is still in the range of speed of sound for human tissue.**

Index Terms—**Tissue mimicking, ultrasound phantom, abdominal ultrasound, ultrasound propagation speed**

I. Introduction

The ultrasound propagation speed of polymer gels was being characterized. Ideally, the word 'mimics' here can be explained as simulating the specific part of human tissue or this simulation purpose more familiarizes called as phantom. Tissue-mimicking phantom serve an important role in ultrasound research and development without the required to use human or animals in experiment. The fabrication of the gel used monomer type 2-Hydroxyl-Ethyl-Acrylate (HEA), gelatin as the gelling agent to control the phantom stiffness [1] and ascorbic acid functioning as the anti-oxidant. The special design was created and fabrication of this tissue equivalent phantom should mimics human soft tissue. Tissue mimicking phantom also is a substitute of any material that simulates a body tissue.

The phantom used for characterization and calibration of US imaging system. The evaluation of accuracy and performance of ultrasound machine systems usually involve tissue mimicking phantoms.

In the range of medical application, there are some tissues phantoms available commercially [2]. The comparison between the multipurpose manufactured phantoms such as (Zerdine™from CIRS Inc., condensed-milk-based gel from Gammex RMI and urethane-rubber-based from ATSLabs)[3]were made, this fabricated phantom has several advantages, i.e the phantom is easily made, low cost, less fragile, and the preparation using less hazardous chemical, and can last within three weeks (23 days) based on visual inspection from the ultrasound image and direct observation.

However, there are lots of tissues mimicking materials for ultrasound phantoms, including agar (polysaccharide), oil gel [4], polyvinyl alcohol gel (PVA) [5], poly acryl amide gel (PAA) [6],

Since 1993, polymeric materials have been used widely in many industries. Among them are transportation, energy production, agriculture, the building industry, retail, packaging consumer goods, foods, and the health and pharmaceutical industries. Some types of polymer like polyolefin, poly (vinyl chloride), polystyrene and synthetic rubbers have been used for more than half of the century in such industrial marketing. Monomer is the core materials in the polymer formation. There are several types of monomers have been used as tissue mimicking material such as acrylamide, acrylic acid, meth acrylic acid, 2-hydroxyl-methyl-acrylate (HEMA), 1-vinyl-2 pyrrolidinone, and including 2-hydroxyl-ethyl-acrylate (HEA).The previous study has also using HEA for biomedical application [4] especially as hydrogel but the important thing is the gel need to polymerize to obtain polymers.

Polymer gel phantom were manufactured consisting of 5% (by volume/weight) 2-Hydroxylethyl Acrylate (HEA), 3% N,N' – Methylene – bis – Acrylamide comonomers dissolve in aqueous gelatin (5% gelatin by total weight and 89% de-ionized water). By using the ultrasound machine, the imaging evaluation was applied to the gel to ensure whether it can simulate the real condition of human soft tissue similar like the several readymade phantoms (manufactured) depend on the image obtained from the screen.

At constant room temperature, the most important thing is the speed of sound through the gel must be in the range of human tissue 1460 m/s to 1650 m/s[7] within three weeks (21 days). The measurement for ultrasound speed was made by using Sonic Waves Analyser (SWA). The Multichannel Analyser (MCA) software and collimated radiation beam photon from a ^{241}Am source were used to measure the linear attenuation coefficient, μ of the polymer gel [8]. Furthermore, density measurement showed that this polymer gel phantom is equivalent to human soft tissue. This polymer gel tissue

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phantom still undergoes some characterizations and these preliminary results proved that the polymer gel is equivalent to human tissue.

The acoustic properties were measured by using a through-transmission water-substituting method. Regarding to the absolute results of mechanical and acoustic properties; the copolymer-in-oil phantom is equivalent with soft tissue. The results for the ultrasound speed and density reported were from 1420-1464 m/s and 0.90 ± 0.04 g/cm^3 respectively. The fabricated phantom materials used here consist of mineral oil and mixture of copolymer, completed with some additives for acoustic scattering purposed [9].

II. Material and Method

A. Polymer gel dosimeter manufacture

Preparation of polymer gel phantoms by using 5% (by volume)(HEA) (Sigma Aldrich,) completed by comonomers, 3% N,N' – methylene – bis –acrylamide (BIS) (Sigma) dissolved in aqueous gelatin (8% gelatin by total volume) and 84% of de-ionized water. After the production finished, the gel were left to cool down to room temperature (22 °C) by maintaining the stirring rate. The gel were poured into ependorf tube, sealed with parafilm tape (Sigma) (to minimize the oxygen contamination inside gel) for linear attenuation coefficient measurements or into small empty vials for density and speed of sound measurement. Then, the remainder gels were poured into the designed container for ultrasound diagnostic imaging. Lastly, those three samples with different shape were then kept in a refrigerator with appropriate condition at approximately 10 °C for 2 hours until a visual detection concluded that the gel already solidified.

B. Ultrasound Propagation Speed Measurements

Ultrasound is the name given to high-frequency sound waves, which are exactly greater than human hearing range. The frequency is beyond the audible frequency range which is 20,000 Hz or higher. As shown in Figure 1, the measurement was done by using the Sonic Waves Analyzer (SWA) under room temperature with the assistance of TDS 1012B Oscilloscope completed by LABVIEW software. The SWA consist of two transducers which act as transmitter and receiver. The sound will be reflected back to the transducer and the remainder will travel through the gel. This is a pulse echo principle from the sequence of events. The propagation speed is the speed measured at whenever the sound moves through a medium which depends on the density of the gel. Generally, the value is highest in solids, average in liquids and lowest in gases.

The longitudinal speed in the pulse echo mode is defined as

$$v = d/t \tag{1}$$

where v = longitudinal speed, m s^{-1}, d = thickness of gel in vial, m, t = time of flight [10]

There are two 6 mm transducers involve in this experimental method, transmitter and receiver. The transducers were aligned properly, and the vial occupied with the gel, was located in between those transducers. Before the measurement started, the coupling transmission gel was covered by all the sensor area of transducer. Then, a dampening circuit was used to reduce the transmitted signal length to a sinusoid of one cycle. The maximum reflected signal received by the transmitting transducer is 500 kHz in frequency. Each signal detected by transducers was displayed on a digitizing oscilloscope (Tektronics TDS 1012B). The sinusoidal signal from oscilloscope was digitized and transferred to a PC for some processing steps such as some noise of the waves were filtered by using special LabView software (version 2.5.1). The repetitions were done three times to determine the ultrasound pulse echo *(time of light, t)* from the average signal. The propagation speed was calculated with the time of light, t, obtained from the waves generated to PC.

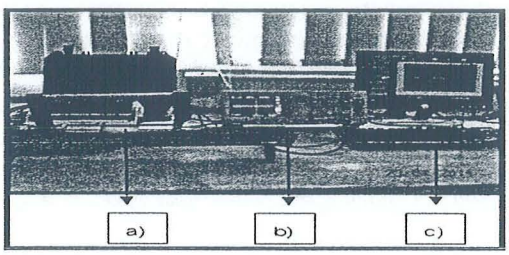

Fig. 1(a). Sonic Wave Analyzer (b) Oscilloscope c) PC with LabView Software

III. Results and Discussion

Based on the results, the propagation speed increase for the first seven days and maintain in the range between 1390 to 1500 m/s within 16 days afterwards. This gel is without sound scatter additives. The density of the sample increased as the day increased. This is may be due to some changes in the elastic properties of the polymer gel, which given as K, bulk elastic modulus once mentioned by V A et al 1997 in [11]:

$$K = v^2 p \tag{2}$$

where p is bulk density and v is acoustic speed. Elastic properties of the material (gel) are also able to be known here as the compressibility of the material. Regarding to equation (2), an increase in elastic modulus will result in increase in the acoustic speed, compared to density because the compressibility plays more important role to determine the sound speed through media An increase in density which should leads to decrease in the propagation speed as in Figure 2 (a), actually didn't affect much of the value of the sound speed. Every five days each, the physical condition of those polymer gels was being observed while the sound speed was measured. As the day increased, the result proved that there are some changes in polymer structure based, in other words, the polymerization was occurred (formation of cross-linked) naturally and absolutely tends to increase the elastic modulus and also rigidity inside the gel. The value of acoustic speed is not expected to be fluctuated in case there is any distorted of ultrasonic pulse through the gel in the experimental procedure.

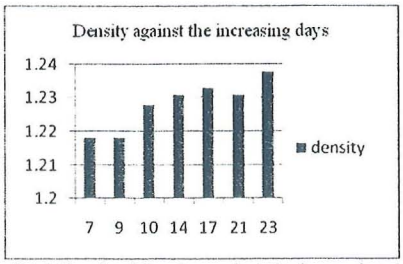

Fig. 2 (a).Graph of density against the increasing days

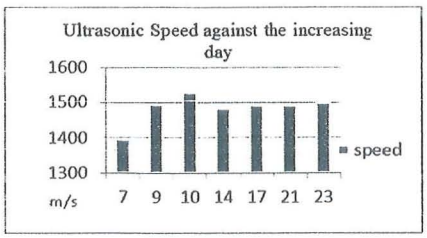

Fig. 2 (b).Graph of ultrasonic speed against the increasing days

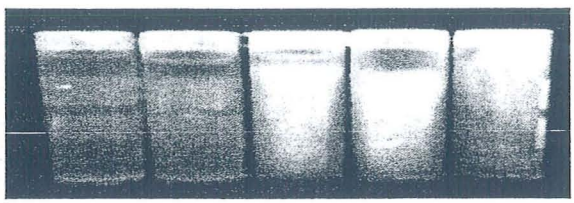

Fig. 3.The physical condition of polymer gels

Based on observation towards the increasing days of the gels being left stand up for almost 23 days, (from left to right, 5th day until 23rd day) (Figure 3), the gel are slowly turning from yellow transparent to milky white. Starting from 15th to 20th day and afterwards, there are some white solid appeared inside the gel and the presence increase by the day. This shows that the polymerization was coming to the saturated level. Nevertheless, the values of acoustic speed of the gel were maintained for the last 14 days. Even though the gel went through the polymerization process, the compressibility of the gel does not become greater, as expected. The presence of white solid inside the gel on the 23th days, (Figure 4(b)), is now considered as 'disturbance' in the ultrasound image.

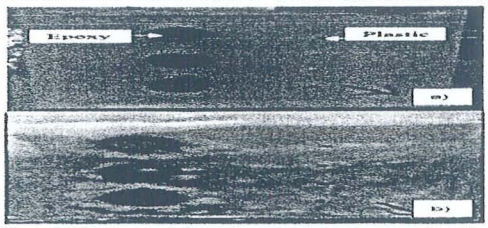

Fig . 4. The substitute materials surrounded by polymer gel inside Perspex container (a) before polymerized (b) after polymerized.

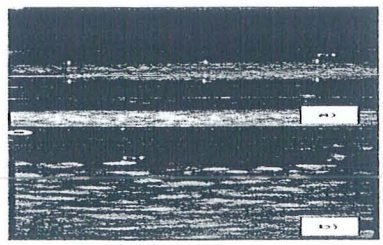

Fig. 5. The ultrasound B-mode image obtained (a) before polymerized (b) after polymerized. The dark background regions show the homogeneous echogenicity of the phantom.

As shown in Figure 5, the ultrasound evaluation was applied by using 10 MHz frequency for the best resolution and contrast to obtain image. Regarding to Figure 5 (a), the image illustrated the epoxy inside the gel in parallel alignment with the linear probe while in Figure 5 (b), the ultrasound image is displayed with lots of small 'bloom' which is originated from Figure 4 (b).

This type of gel is considered match to the acoustic properties of human soft tissue based on the ultrasonic propagation speed and density of the material. Through ultrasound screen, the epoxy material can be seen as the simulation of the human bone.

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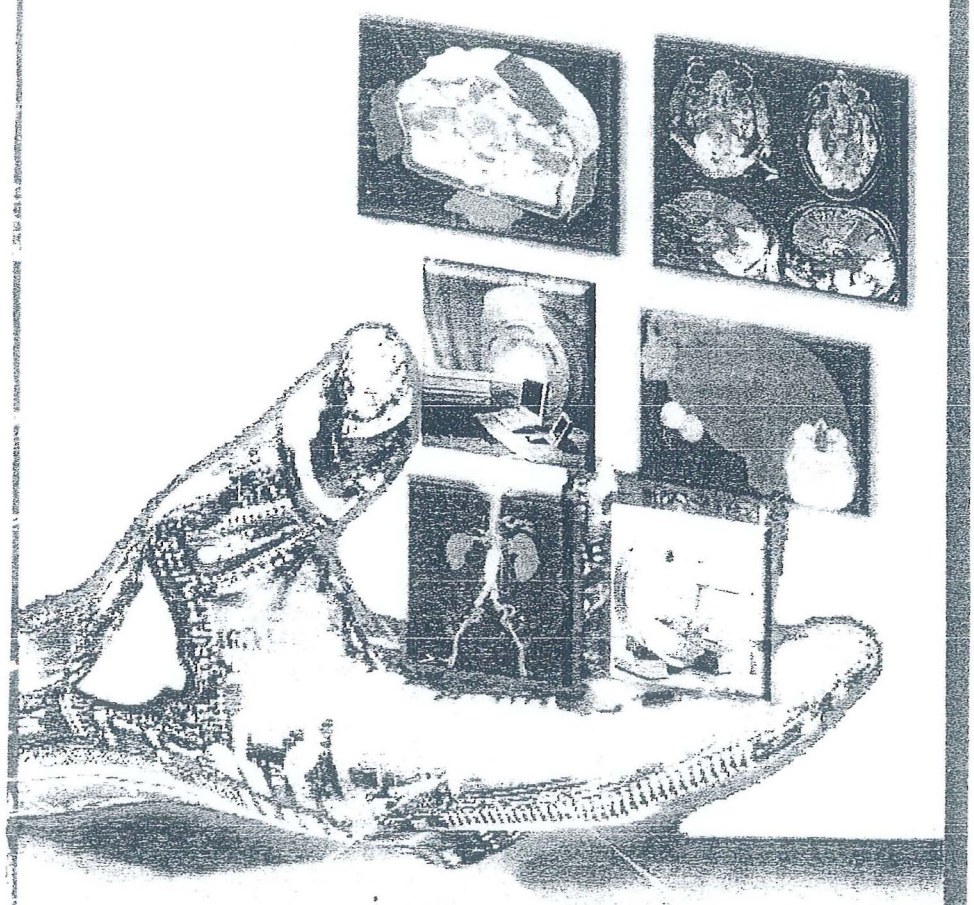

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INVESTIGATION OF ASCORBIC ACID AS AN OXYGEN SCAVENGER IN POLYHYDROXYETHYLACRYLATE GEL DOSIMETER

Aifa Afirah Rozlan, Muhammad Suhaimi Jaafar and Azhar Abdul Rahman

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ABSTRACT

Since 1950's, polymer gel dosimeter has been examined as a clinical dosimeter. Polymer gel dosimeters are fabricated from radiation sensitive chemicals which, upon radiation, polymerize as a function of the absorbed radiation dose. However, their use has significant limitation due to the nature of their free radical chemistry. The atmospheric oxygen inhibits the polymerization process of the polymer gel. The introduction of polymer gel that can be manufactured on the bench top in the laboratory known as normoxic polymer gel dosimeters have overcome this limitation. The scavenging of atmospheric oxygen in normoxic polymer gel dosimeters is achieved through the introduction of an oxygen scavenger (anti-oxidant) in the gel solution. One of the anti-oxidant used to scavenge oxygen is ascorbic acid. Ascorbic acid has been shown to hold great promise as an anti-oxidant due to its effective oxygen scavenging abilities. In this study, we investigate the use of ascorbic acid as an anti-oxidant for polyhydroxyethylacrylate gel (PHEAG) dosimeters used in conjunction with low energy x-ray machines. The composition of the gel was varied and its oxygen scavenging rate was evaluated. Dissolve oxygen meter measurements in solution provide an easy way to get a first impression on the rate of oxygen scavenging. It is found that ascorbic acid was able to bind the oxygen and can thus be used as an anti-oxidant in PHEAG dosimeters. It was also shown that 2-Hydroxyethyl acrylate (HEA) operates as a catalyst in the oxidation of ascorbic acid.

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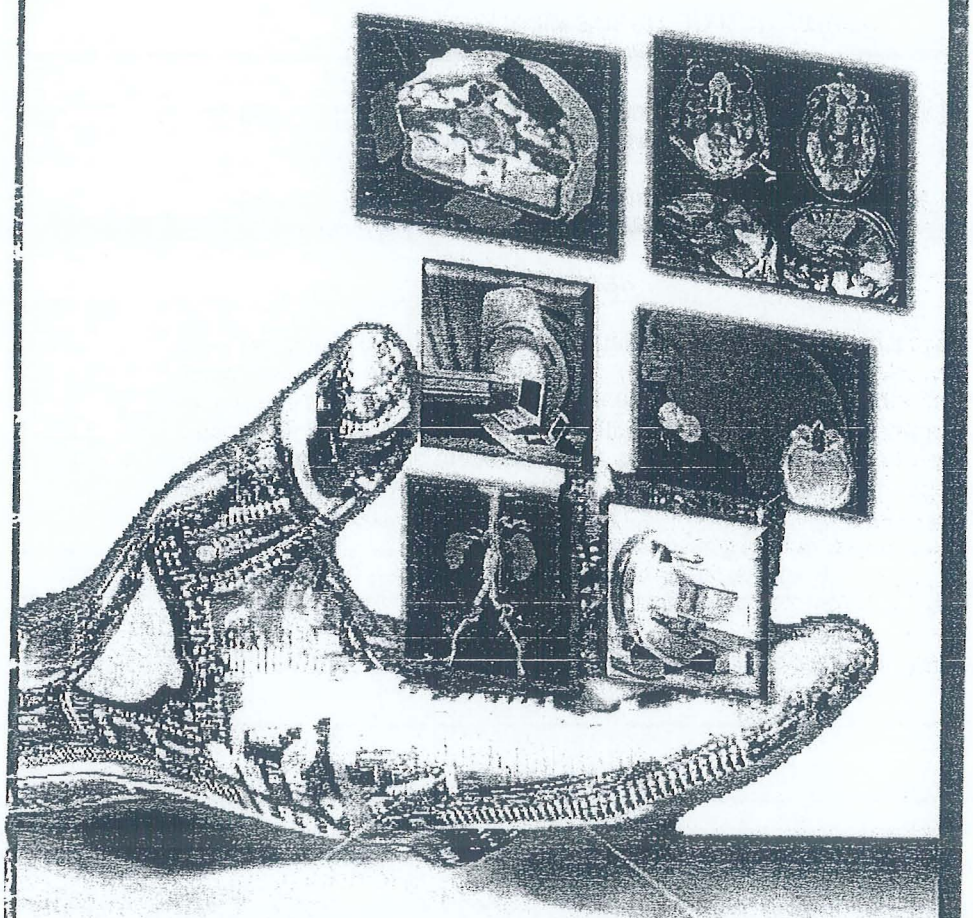

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FABRICATION OF TISSUE MIMICKING PHANTOM FOR ABDOMINAL ULTRASOUND

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ABSTRACT

Tissue mimicking ultrasound phantom was fabricated using monomer 2-hydroxylethyl acrylate (HEA) and ascorbic acid as the anti-oxidant. This fabrication of tissue equivalent phantom is mimics to the human liver and was then compared with manufactured phantoms. The results show that the properties of this tissue phantom are disposable, easily-made, low cost, and less fragile. Furthermore, density analysis showed this phantom is equivalent to real liver, while the speed of sound is in the range of human tissue at constant temperature. This polymer gel tissue phantom still undergoes characterizations and these preliminary results proved that the polymer gel is equivalent to human tissue.

(Keywords: tissue mimicking, phantom, abdominal ultrasound)