12-2-2013

Radiation Effects on Medical Grade Polycarbonate Urethane

Rudra Gnawali

Recommended Citation

Gnawali, Rudra, "Radiation Effects on Medical Grade Polycarbonate Urethane" (2013). *Electronic Theses and Dissertations*. 833.
https://digitalcommons.memphis.edu/etd/833

RADIATION EFFECTS ON MEDICAL GRADE POLYCARBONATE URETHANE (PCU)

by

Rudra Gnawali

A Thesis

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

Major: Physics

The University of Memphis

December 2013

ACKNOWLEDGEMENTS

I would like to give my appreciation to Dr. M. Shah Jahan for all of the help and guidance he has provided me with throughout my college career. Our innumerable discussions have taught me to focus and to be a better researcher.

I would like to thank my co-supervisor Dr. Hai Trieu, and committee members Drs. Sanjay R. Mishra and John W. Hanneken, for taking time out of their busy schedules to participate as members of my thesis. My special thanks go to Mr. Benjamin M. Walters and Mahesh Singh Dhar (CERI, U of Memphis) for their support. I am also grateful to all of my professors in the Department of Physics, University of Memphis for their help. I am indebted to my parents, relatives, and friends for supporting me, encouraging me, and for their inspiration for me to pursue my higher study.

Most of all I would like to thank my wife, Bijeta Pokharel, for her patience and understanding in supporting me to complete this endeavor.

Abstract

Rudra Gnawali, M.S. The University of Memphis, December 2013. Radiation Effects on Medical grade Polycarbonate Urethane (PCU). Major Professor: M. Shah Jahan, Ph.D.

Polycarbonate urethane (PCU) is a material of growing prominence for use as a biocompatible material for joint replacements. PCU has good wear properties, is easy to lubricate, and is very compatible with natural tissues. Extensive studies still have not been performed to fully investigate the radiation effects on PCU components. Thermally stimulated luminescence (TSL) spectroscopy is a powerful tool to study radiation-induced defects in materials, while electron spin resonance (ESR) is a technique to directly detect free radicals in a material. To better investigate radiation effects on PCU materials, we have subjected PCU to X-and UV-irradiation and analyzed the thermally-stimulated luminescence (TSL) and radiation-induced free radicals. The materials used for the study were Bionate hip liners obtained from Active Implants Corporation. The resulting TSL and ESR data were analyzed to obtain new insights into the molecular properties of polycarbonate urethane.

TABLE OF CONTENTS

Chapter

LIST OF TABLES

LIST OF FIGURES

Figure Page

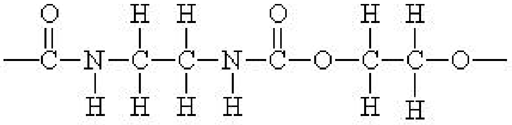
CHAPTER 1

INTRODUCTION

Introduction of Polycarbonate Urethane

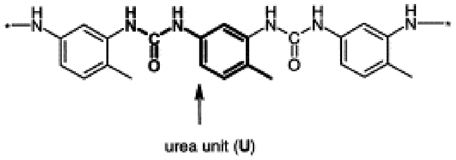
Polycarbonate urethane is a rapidly growing material in the field of orthopedic and other industrial applications. Development of this material from polyurethane began with the development of polyester urethane (PEU), which was found to be more resistant to oxidative environments, in part due to stabilization with antioxidants. Researchers further developed this material into, a new class of polyurethane named polycarbonate urethane (PCU). In the orthopedic and medical devices, this PCU has properties said to be superior to PEU and polyethylene (PE). PCU has polycarbonate soft segments with superior oxidation resistance, as found in several in vitro and early in vivo studies [1, 2]. PCU is synthesized from a methylene di (-phenyl isocyanate) hard segment chain extended with butane diol and poly (1, 6 hexyl 1, 2 ethyl carbonate) soft segments. In relation to oxidation in ultra-high molecular weight polyethylene (UHMWPE) - a commonly used material for similar orthopedic uses such as hip cups - PCU shows similar oxidative resistance, and it has been reported that wear particles which do happen to occur do not affect the body as negatively as those of UHMWPE [2]. The laboratory where this study on PCU was conducted has studied similar radiation-induced oxidative processes in UHMWPE for over 25 years and can therefore provide a good analysis of similar processes in PCU. Therefore, the objective of this study – to gain further knowledge of radiation-induced processes in PCU can be carried out to its maximum potential.

One unique aspect of this project’s testing involves immediate testing after exposure to ionizing radiation. Radiation treatment procedures, especially involving higher-energy radiation such as the gamma or e beam irradiation, typically involve treating the samples at a particular location out of town, and then transporting the materials back and forth, while losing valuable information in these elapsed time periods immediately after radiation exposure. Our in-house UV- and X-irradiation abilities, however, enable measurements to begin within minutes of such radiation treatments. This should provide a unique insight of molecular level which would not be possible otherwise. The structural formulas for Polyurethane and Polycarbonate Urethane are listed below in Figure 1-1. PCU is manufactured in different brand names as listed in Table 1 [3].

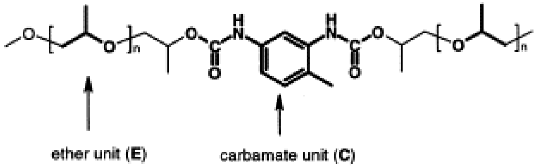


Polyurethane

Polyurea Stucture



Polyurethane Structure



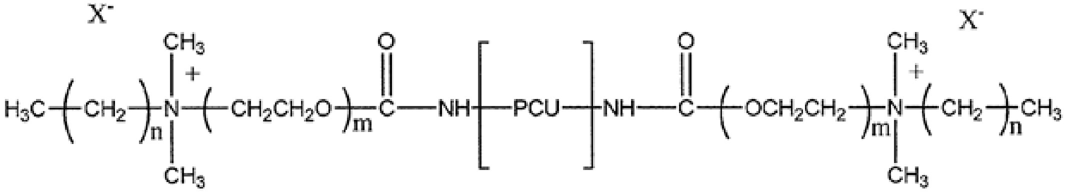


Figure 1-1. Structures of Polyurethane and Polycarbonate Urethane (PCU)

Table 1-1. Different brand names of Polyurethane [3]

	Material	Soft Segment	Hard segment	Molecular Weight (MW)	Polydispersity	Advancing Water contact angle
Elasthane 80A	PEU	PTMO	MDI/BD	292,000	2.02	70± 4^o
Bionate 80A	PCU	PHEC	MDI/BD	314,000	2.17	69± 4^o

PTMO = poly(tetramethylene oxide ; PHEC = poly(1,6-hexyl 1,2-ethyl carbonate) ; MDI = methylene di(p-phenyl isocyanate); BD = butane diol.

PCU vs. UHMWPE

Ultra-high molecular weight polyethylene (UHMWPE) is a type of plastic that is used as an orthopedic biomaterial as a cartilage simulator in hip and knee replacements. The primary problem with UHMWPE is that it wears away over time, creating small particles that a body reacts to and is generally the cause for implant failure. This wear is usually caused by oxidative degradation of the UHMWPE components. The oxidation is reportedly caused which results free radicals by radiation cross linking or sterilization. The goal of this study is to evaluate more closely the effects of radiation on polycarbonate Urethane, by electron spin resonance which can directly detect free radicals created by ionizing radiation (in this case, X- and UV-irradiation). This work also investigating thermoluminescence behavior which can provided additional information on about radiation effects on PCU. Recent studies show that PCU materials developed for cardiovascular applications have properties superior to UHMWPE [4]. As compared to UHMWPE and PEU, PCU is found to have better friction properties and is easier to lubricate than UHMWPE because PCU is a hydrophilic in nature, whereas UHMWPE is hydrophobic [4]. As for the aforementioned wear problem with UHWMPE, PCU has been found to have equal to or better wear properties than UHMWPE [5, 6]. PCU material can therefore be successfully used as an articulating surface that protects the bone and a source of lubrication to improve motion within medicinal joints [2, 7]. In addition, studies have found that the modulus of elasticity of PCU materials is similar to that of cartilage. In all, PCU materials provide good compatibility with natural tissues, are easy to lubricate, and have good wear properties, providing for a viable alternative to the traditional UHMWPE [4, 5, 6, 7, 8, 9].

Literature Review

In the family of polycarbonate urethane, Bionate™ is a brand of PCU, which is used for this study. It is described as an elastomer formed by polymerizing the ‘‘soft-segment’’ component poly (1,6-hexyl-1,2-ethyl carbonate) diol with 4,40-methylene bisphenyl diisocyanate and the chain extender butanediol. Bionate™ has been used in regions outside the United States as an acetabular component for total hip replacement [10, 11]. To more fully describe of the history of the development of PCU, polyurethane itself was first implemented as an acetabular medical device component in 1960 by making cups. Due to the biostability of refined carbon composite polymers, PCU was seen as a reliable alternative to hip replacement materials such as UHMWPE. Polycarbonate urethane then began its introduction to use because of longer degradation time and a thinner degraded layer in comparison to polyurethane. Several techniques were used to investigate and characterizations of novel properties. FTIR techniques, for example, were used to characterize common oxidation mechanisms for polycarbonate urethane and polyurethane [4, 12]. Investigations confirming biostability of PCU were performed by Khan et al., with both in-vivo and in-vitro studies [5, 13], however there is little information evaluating long-term degradation of PCU – only that deformation of the surface can occur upon crosslinking, depending on material thickness, which could possible lead to degradation, although the surface damage on expanded PCU films was not extensive [13]. The conclusion that PCU was more oxidative stable than PEU was obtained primarily via FTIR studies, and PCU was thought to undergo some biodegradation due to oxygen radicals released from adherent cells but at a much slower rate than PEU [4, 14]. As for the specific Bionate™ used in our study, previous research [15] of Bionate™ suggests a greater oxidative stability than UHMWPE, and note that the differences in stability may be associated with the chemical structures of the two materials. PCU which was more oxidative stable than PEU was obtained primarily via FTIR studies, and PCU was thought to undergo some biodegradation due to oxygen radicals released from adherent cells but at a much slower rate than PEU. The researchers [15] also found development in the toughness (6-22%) of irradiated-and-aged PCU and suggested this might be the consequence of microstructural alteration.

Thermally Stimulated Luminescence (TSL) and Electron Spin Resonance (ESR)

Thermally stimulate luminescence (TSL), also known as thermoluminescence (TL), will be referred to from this point as only "TSL". TSL is used to evaluate the activation energies, or trap depth, along with associated frequency factors [16]. TSL in polymers was first reported in 1955, where at temperatures of 77K, TSL was detected in polymers which had been exposed to ionizing radiation that was thought to have produced positive ions and trapped electrons. The electrons are de-trapped through onset of molecular motion from thermal stimulation due to the application of heat. The de-trapped electrons may be re-trapped if other traps exist along its path to the luminescent center. When the electron finally recombines, it induces an excited state of a natural luminescent center which then emits a photon as it decays to the ground state [16]. Early work suggested TSL for low temperature. But if TSL output was observed above 250K it was thought to be due to a lack of luminescence to the de-excitation of luminescence through collision processes [16]. Luminescence was not thought to be governed by free radicals because of radical recombination reactions being inhibited by the low temperatures used in these experiments.

Electron spin resonance (ESR), also called electron paramagnetic resonance (EPR), will be referred to from this point as only “ESR.” As mentioned earlier, ESR can detect free radicals in a material. If fact, it is the only method to directly detect free radicals (whereas other methods only imply the existence of free radicals). Our lab (Biomaterial Research Lab., U of Memphis) has extensively studied free radicals with this ESR technique for over 25 years.

Purpose of Study

The previously mentioned studies of PCU indicated that PCU is a good candidate for worldwide use in medical implant applications which typically involve UHMWPE. The objective of this project is to gain more knowledge about radiation induced processes in PCU. For rapid tests, in house radiation sources such as x-ray and UV were used. This may allow us to understand or reveal the primary events in this polymer immediately following irradiation. For gamma or e-beam radiation, the samples are sent out to outside vendors, and by the time samples are received for measure, most of the initial events are almost completed. To do this, PCU are subjected to various doses of X- and UV-irradiation and analyze with TSL and ESR.

CHAPTER 2

METHOD OF STUDY

Various methods have been applied in the past to study PCU including differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FTIR). With these methods, various properties of PCU have been determined in the past decades. However, thermally stimulated luminescence has not been used as much as the other methods to study the post irradiation oxidation process in PCU. Therefore, in this thesis TSL and ESR methods are used.

Radiation Effects on Biomaterials

Radiation is used widely in the biomaterials science for surface modification sterilization and to improve the bulk properties. The most common energy source of irradiation of biomaterials is gamma or electron beam, however, ultraviolet, x- ray and visible light are also used for specific purpose [17]. Surface modification involves placement of selective chemical moieties on the surface of materials by chemical reactions to improve biointeraction for cell adhesion and prolification, hemocompatibility and water absorption. The radiation exposure to the polymers can lead to cross linking with change in bulk surface properties. Sterilization by irradiation is designed to inactivate most pathogens from the surface of biomedical devices [18]. The radiation dose response can be observed in the TSL glow peaks. In solid state luminescence, energy is released by molecules or atoms upon heating following initial excitation (by irradiation) [19]. The way of excitation is denoted by the prefix of the luminescence effect. For example, photoluminescence refers to excitation by optical photons; radioluminescence is excitation by ionizing radiation; cathodoluminescence is excitation by bombardment with cathode rays; electroluminescence is excitation by the application of electric field; triboluminescence is excitation by application of mechanical stress. The exclusion to this rule is emission by recombination of trapped charges that are created by ionizing radiation and released by thermal stimulation. In this mechanism the sample is exposed to exciting radiation, such as particle or electromagnetic radiation at a fixed temperature. At the end of excitation the sample will be placed in the oven and heated at constant rate and the light output from the sample (or the resulting luminescence) is recorded by either a photomultiplier tube (PMT) or Optical Multi-Channel Analyzer (OMA).

Theory of Thermally Stimulated Luminescence

There are various phenomena in spectroscopy these ate depends upon the excitation and their life time in excited state. For example in fluorescence have 10^{-8} sec life time in excited state while 10^{-4} is allowed for phosphorescence. There are other luminescence in spectroscopy, among them thermally stimulated luminensence is the phenomena based on excitation of electron in a material. The properties are measured as a function of temperature and dose rate [20, 21] which becomes trapped and thermally stimulating the electrons to de excite to lower energy level [22, 23]. The properties are measured as a function of temperature. Most of the cases linear heating rate is used. The thermally stimulated luminescence (TSL) is the powerful instruments in order to study de-trapping and relaxation processes in organic materials [22, 23]. TSL technique is very useful to differentiate between deep and shallow trapping states. The analytical solution of two different de-trapping regimes, include or exclude subsequent re-trapping effects. The first order kinetics solutions explain the no-retrapping phenomena are occurred. The electron released from a localized level recombines with a hole in a recombination center and its re-trapping probability, before to recombine, is negligible. The second order equation explains the phonon assisted release of an electron which is followed by multiple trapping. In this second order kinetic regime the probability of a released electron to get re-trapped is very high. These solutions may deal the energy depth of the traps calculated with respect to the conduction band edge and the frequency factor. Another importance is explaining these solutions for the escape frequency of electron from localized level.

Five definitions of TSL are as follows:

1. All transition in or out of the localized states involve passage of charge (electron or hole) through the delocalized band.

2. The useful definition of trapping states to be those which the possibility of thermal excitation from level into respective delocalized band is greater than the probabilities of recombination of trapped charge. Conversely recombination center is defined as one in which the possibility of recombination with an opposite sign charge carriers is greater than that thermal excitation of trapped carriers. Thus, the demarcation level for electron E_{Dn} and one for $E_{Dn.}$

3. For electron $E_c > E > E_{Dn}$ nonradiative emitting phonons. Similarly for hole transition $E \leq Ev$ to hole trap at $E_{Dp} > E > E_v$ are also nonradiative .Hence E_c and E_v are the bottom of conduction band and top of valance band.

4. Transition of free electrons from $E > E_c$ to trapped hole recombination sites at $E_f > E > E_{Dp}$. Or free holes from $E \leq E_v$ to trapped electron recombination centers at $E_{Dn} > E > E_f$ are radiative, emitting photons.

5. Once a trap is emptied the free carriers can no longer distinguish between it and all other traps of same type [22]. The following Figure 2-1 shows the demographic schematics of electron, hole center and recombination process.

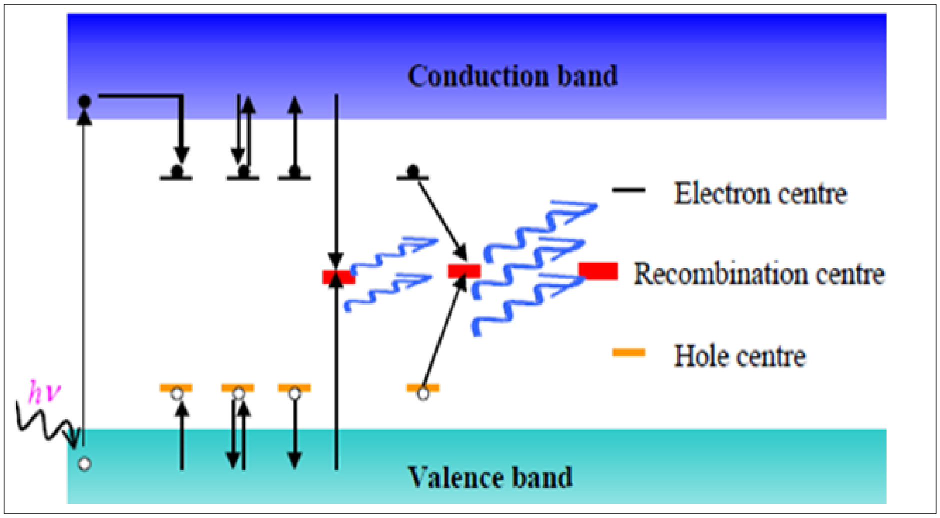


Figure 2-1. Electron hole recombination processes

Order of Kinetics

In TSL theory, there are two types of glow curve kinetics in the elementary theory. The first order kinetic process was developed by Rendall and Wilkins [24, 25] and has been explained as slow re-trapping during thermal excitation while the second order has been explained as fast re-trapping. Rendall and Wilkins suggested that the rate at which the electrons escape the traps for first order kinetics is directly proportional to the intensity of the flow curve which has been explained mathematically in equation 1.

$$\frac{-\mathrm{dn}}{\mathrm{dt}} = \mathrm{ns}\ \exp\left\{\frac{-\mathrm{E}}{\mathrm{K_B T}}\right\} = \mathrm{I_{TL}} \tag{1}$$

Where n is the number of electrons trapped at time t.

After integrating equation 1, we can write

$$\mathrm{I_{TL}} = \mathrm{n_o s}\ \exp\left\{\frac{\mathrm{E_t}}{\mathrm{K_B T}}\right\} \exp\left\{-\left(\frac{\mathrm{S}}{\beta}\right)\int_{\mathrm{T_0}}^{\mathrm{T}} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\} \mathrm{d}\theta\right\}, \tag{2}$$

where n_o is initial concentration of the trapped electrons, n at t = 0, β is the constant rate of heating, and θ represents the arbitrary value of temperature [22, 23, 24].

The possibility of fast trapping has been explained by Garlick and Gibson and suggested the expression of equation 3 for the rate of decay [22].

$$\frac{-\mathrm{dn}}{\mathrm{dt}} = \left(\frac{n^2}{N}\right) s\ \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\} = \mathrm{I_{TL}} \tag{3}$$

Integrating equation 3, we get

$$\mathrm{I_{TL}} = \left(\frac{\mathrm{n_0}^2}{\mathrm{N}}\right) \mathrm{s}\ \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\}\left[1 + \left(\frac{\mathrm{n_o s}}{\beta \mathrm{N}}\right)\int_{\mathrm{T_0}}^{\mathrm{T}} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\} \mathrm{d}\theta\right]^{-2} \tag{4}$$

where, N is the number of trapped electrons. There are possible intermediate orders, so an empirical expression to give a general order of kinetics was developed by Rasheedy et al. [27]; this expression can be written as

$$\frac{-\mathrm{dn}}{\mathrm{dt}} = \left(\frac{\mathrm{n}^{\mathrm{b}}}{\mathrm{N}^{\mathrm{b}-1}}\right) \mathrm{s} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\} = \mathrm{I_{TL}} \tag{5}$$

where b is the order of kinetics [22,26,27]

$$\mathrm{I_{TL}} = \mathrm{n_0}^{\mathrm{b}}\ \mathrm{s} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\} \mathrm{N}^{(1-\mathrm{b})} \left[1 + \left(\frac{\mathrm{S}(\mathrm{b}-1)\left(\frac{\mathrm{n_0}}{\mathrm{N}}\right)^{(\mathrm{b}-1)}}{\beta}\right) \int_{\mathrm{T_0}}^{\mathrm{T}} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\} \mathrm{d}\theta\right]^{\frac{-b}{b-1}} \tag{6}$$

It seems that, in equation 6, as b→1, it reduces to equation 7 (below), but for b = 1, equations 2, 3, 4, and 5 will become invalid. To explain the TSL phenomena in a material for a single trapping level and single type of recombination center, above equations are sufficient. For multiple trapping sites, more complex formulations are needed. For such phenomena, the rate of decay equation now becomes

$$\frac{-\mathrm{dn}}{\mathrm{dt}} = \left(\frac{\mathrm{S_n}}{\mathrm{N+h}}\right) (\mathrm{n} + \mathrm{h}) \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B T}}\right\} = \mathrm{I_{TL}} \tag{7}$$

where n is the number of trapped electrons, which equals the number of holes (m). In some cases, n+h = m, where h is the concentration of electrons in deeper traps. Integrating equation 7, we get

$$\mathrm{I_{TL}} = \left(\frac{\mathrm{S}}{\mathrm{N+h}}\right) \mathrm{nh} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B T}}\right\} \frac{\mathrm{S}}{(\mathrm{N+h})} \mathrm{n}^2 \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B T}}\right\} \tag{8}$$

Equation 8 has components of first and second order kinetics [22], and integrating equation 8, with respect to time, as shown in equation 9, the activation energy of an electron to escape a trap is explained:

$$\mathrm{I_{TL}} = \frac{\mathrm{S'h2}\propto \exp\left\{\frac{\mathrm{h}S'}{\beta} \int_{\mathrm{T_0}}^{T} \exp\left\{-\frac{E_t}{\mathrm{K_B}\theta}\right\} \mathrm{d}\theta\right\} \exp\left\{-\frac{\mathrm{E_t}}{\mathrm{K_B}\theta}\right\}}{\left[\exp\left\{\frac{\mathrm{h}S'}{\beta} \int_{\mathrm{T_0}}^{T} \exp\left\{-\frac{E_t}{\mathrm{K_B}\theta}\right\} \mathrm{d}\theta\right\} - \propto\right]^2} \tag{9}$$

where s’ = $\frac{\mathrm{S}}{(\mathrm{N+h})}$, $\propto = \frac{\mathrm{n_0}}{\mathrm{n_0+h}}$, and $\mathrm{E_t} = [2.52+10.2(\mu_g - 0.42)]\left(\frac{K_B T_M}{W}\right) - 2K_B T_M$.

Regarding equation 9, the full width of half maxima is W = $\partial + \tau$, where ∂ and τ are the high and low temperature half widths, respectively, and μ_g= ∂/W is an asymmetric parameter of glow curve which determines the kinetics order [19]. Similarly, T_m is the maximum peak temperature. For first order kinetics, μ_g = 0.42, and E_t of equation 9 reduces to

$$E_t = 2.52 \left(\frac{K_B T_M}{W}\right) - 2K_B T_M \qquad (10)$$

Electron Spin Resonance (ESR)

ESR is only the technique that can directly detect free radicals. Unpaired electrons can have paramagnetic behavior. The atoms or molecules which have unpaired electrons in their outermost shell are called free radicals. Free radicals are typically very unstable and react quickly with other compounds in an attempt to capture electrons to regain stability. Free radicals can be formed by ionization energy used to cross-link or sterilize a polymeric solid. Free radicals can further break down the polymer backbone by selecting hydrogen from the polymer chain, which creates radicals from the once stable molecules. In the presence of an external magnetic field, the magnetic dipole of the unpaired electron with a spin angular momentum of ± ½ will align parallel (M_s=-1/2) or antiparallel (M_s=1/2) to the magnetic field. This interaction of unpaired electrons in the sample with a magnetic field is called the Zeeman Effect. The two energy state will occur, the lowest energy state when the electron is aligned parallel to the magnetic field and the highest energy state when the electron is aligned antiparallel to the external magnetic field. Transitions can be induced between these spin states. Electromagnetic energy is supplied in the microwave range of frequencies. The dipoles parallel to the field will absorb the microwave energy and the dipoles anti-parallel to the field will release energy. Overall, microwave energy will be absorbed from the microwave field since there are more parallel aligned magnetic dipoles than anti-parallel. The energy associated with the transition is expressed in terms of the applied magnetic field (B), the electron spin g-factor (g), the constant μ_B and by equating with the absorbed microwave frequency ($h\nu$) we can obtain the electron spin g-factor by

$$\Delta E = h\nu = g\mu_B \mathrm{B} \rightarrow g = h\nu / B\mu_B \tag{11}$$

ESR signals are recorded as a derivative of the absorption, which occurs when equation 11 is satisfied. By integrating these ESR spectra and comparing to a known standard, we can estimate a corresponding quantity per gram of free radicals.

CHAPTER 3

MATERIAL AND METHODS

Thermally Stimulated Luminescence

This experiment investigates thermally stimulated luminescence (TSL) of medical-grade polycarbonate urethane (PCU). The non-irradiated PCU was in the form of acetabular cups in sealed packages. These cups were cut in to films of approximately 150 microns in thickness and heated at a constant rate, at 1°C per second, and luminescence was observed at specific temperatures between 40°C to 300°C. The samples were labeled as in Tables 3-1 through 3-5.

Table 3-1. PCU non-irradiated Samples

Samples	Irradiation environment	Mass (mg)
Sample 1	No irradiation	2.1
Sample 2	No irradiation	2.0
Sample 3	No irradiation	2.2
Sample 4	No irradiation	2.2
Sample 5	No irradiation	2.1
Sample 6	No irradiation	2.0

Table 3-2. PCU Samples X- irradiated in air for 20 Minutes

Samples	Irradiation Environment	Mass(mg)
Sample 1	Air	2.0
Sample 2	Air	2.1
Sample 3	Air	2.0
Sample 4	Air	2.1
Sample 5	Air	2.3
Sample 6	Air	2.2

Table 3-3. PCU Samples X- irradiated in air for 30 minutes

Samples	Irradiation Environment	Mass(mg)
Sample 1	Air	2.0
Sample 2	Air	1.9
Sample 3	Air	2.0
Sample 4	Air	2.1
Sample 5	Air	2.0
Sample 6	Air	2.2

Table 3-4. PCU Samples X- irradiated in air for 40 minutes

Samples	Irradiation Environment	Mass(mg)
Sample 1	Air	2.0
Sample 2	Air	2.1
Sample 3	Air	2.0
Sample 4	Air	2.1
Sample 5	Air	2.3
Sample 6	Air	2.2

Table 3-5. PCU Samples X- irradiated in air for 60 minutes

Samples	Irradiation Environment	Mass(mg)
Sample 1	Air	2.0
Sample 2	Air	2.1
Sample 3	Air	2.0
Sample 4	Air	2.2
Sample 5	Air	2.3
Sample 6	Air	2.0

Electron Spin Resonance

The samples for free radical measurements were cut to a size of $3\times3\times8$ mm^3 each. Prior to irradiation treatments, they were cleaned with isopropyl alcohol. The samples were x-irradiated and UV-irradiated at different doses (times of exposure). Upon X-irradiation, it appeared that the PCU material may have turned slightly yellow. Upon UV-irradiation, it was more conclusively observed that the PCU materials did turn significantly yellow, as presented below in Figures 3-1 and 3-2.

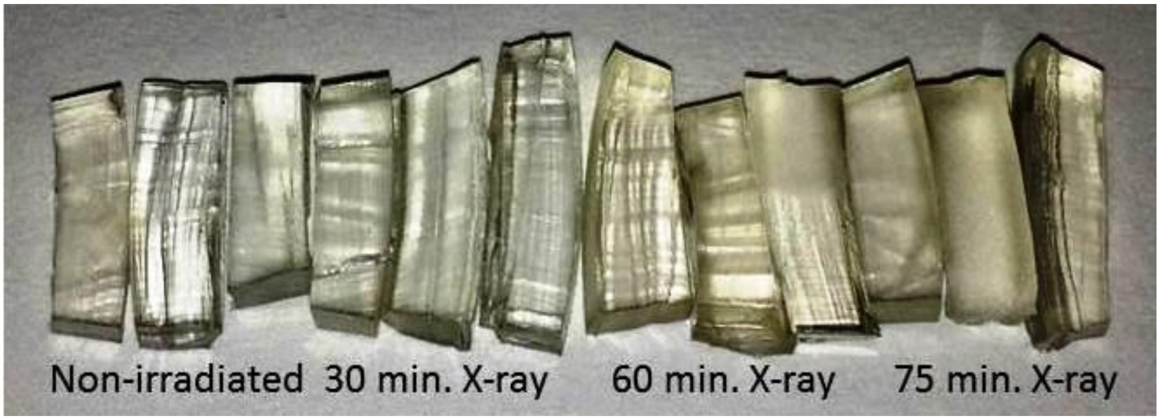


Figure 3-1. PCU specimens with X-irradiation, prepared for subsequent ESR-testing

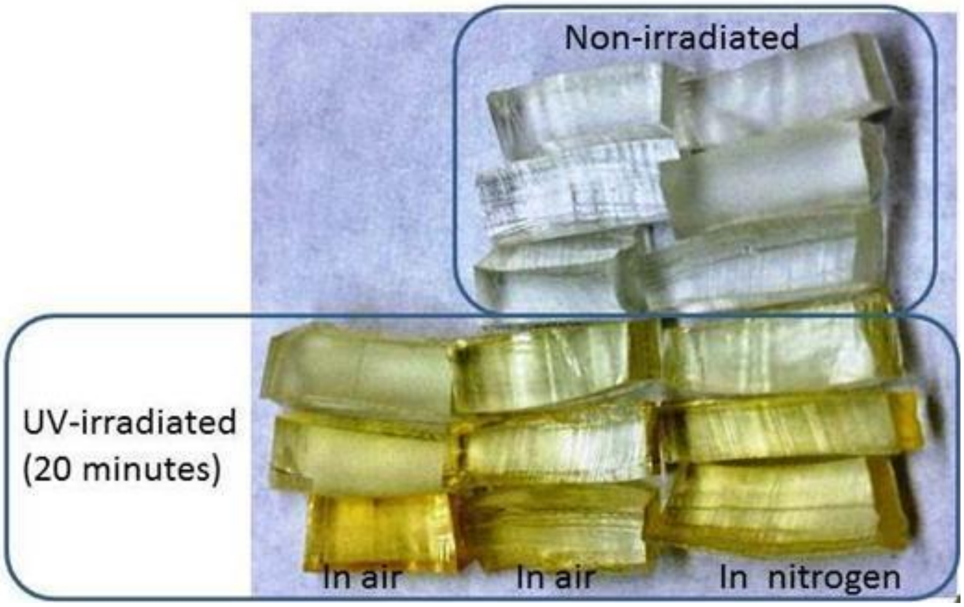


Figure 3-2. PCU specimens with UV-irradiation, prepared for subsequent ESR-testing

TSL Measurements

Thermally stimulated luminescence (TSL) measurements were made using a commercial dosimeter (Harshaw QS 3500) operating at 727 V and 12 mA. These PCU material was cut in to films of approximately 150 microns in thickness and heated at a constant rate, at 1°C per second. Luminescence was recorded at specific temperatures between 40°C to 300°C; resulting spectra ("glow curves") were then deconvoluted into individual glow peaks using PeakFit™ software. The glow peak parameters of the individual peaks were then calculated using additional software (TSL CurveFit™). A block diagram of the TSL reader is shown in Figure 3-3 below.

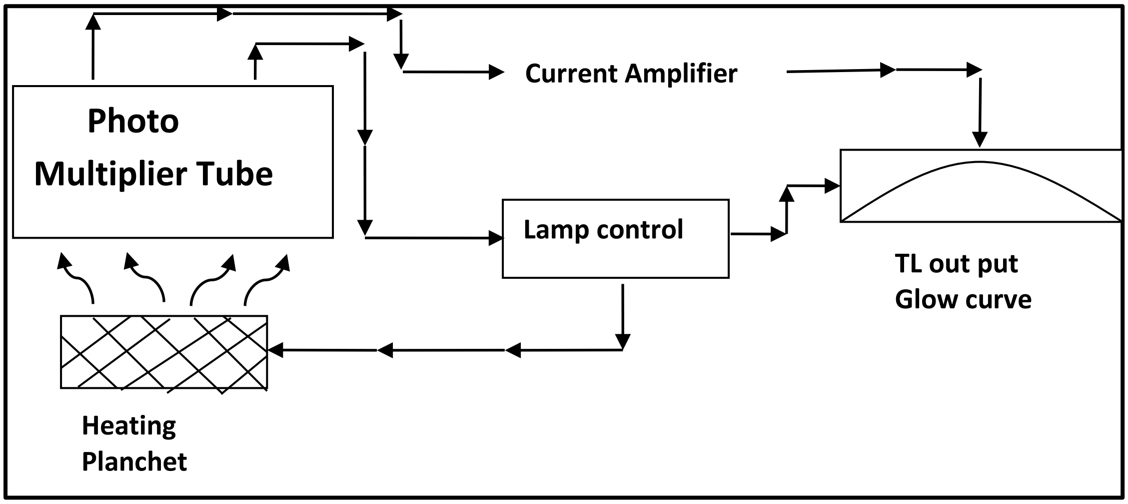


Figure 3-3. TSL experimental setup diagram

An example TSL glow curve is shown below Figure 3-4.

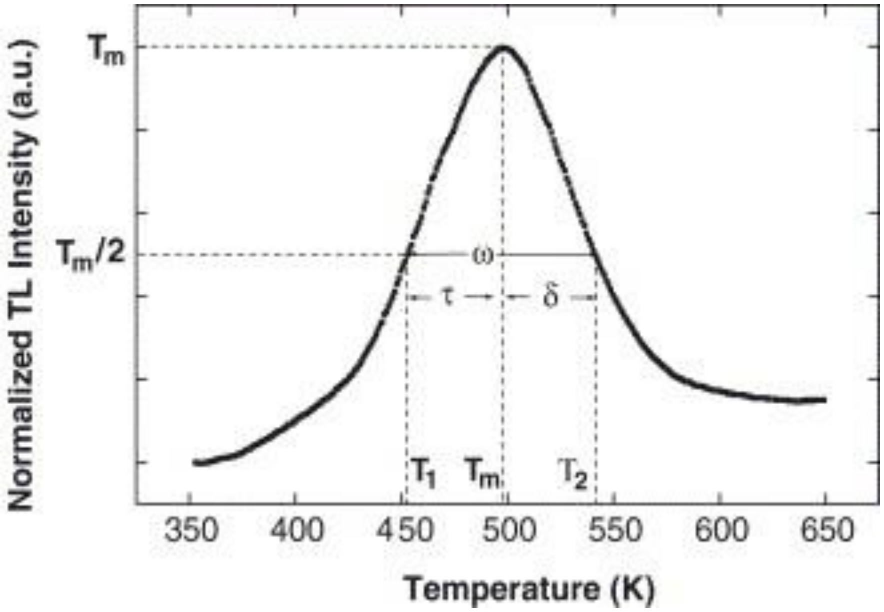


Figure 3-4. An example TSL glow curve

ESR (Free Radical) Measurements

An X-band electron spin resonance (ESR) spectrometer (EMX300 by Bruker) operating at 9.8 GHz microwave frequency was used to detect free radicals. The ESR spectra (first derivative) of three sets of PCU samples were recorded at 1mW microwave power and 5 Gauss modulation amplitude.

CHAPTER 4

TSL - RESULT AND DISCUSSION

In this work, ESR and TSL testing is performed to evaluate the effects of different doses of X-irradiation on PCU.

TSL of non-irradiated and x-irradiated PCU

Thermally-stimulated luminescence glow curves of non-irradiated PCU are shown in Figure 4-1. The TSL glow curves show small luminescence output before the sample is irradiated. The two major peaks (Peaks 1 and 4) are obtained near 139℃ and 224℃ . By using the curve-fitting software, we deconvoluted the curve to reveal additional peaks 3 and 4, near 95℃ and 164℃ respectively.

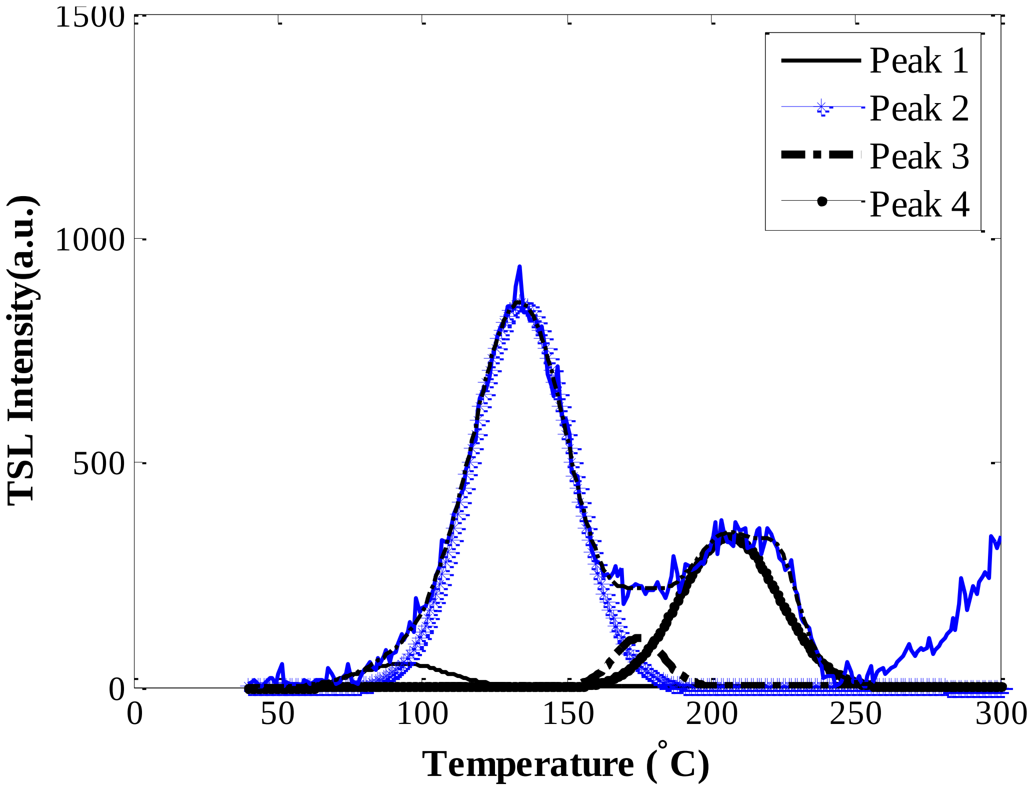


Figure 4-1. TSL glow curve of non-irradiated sample

Figure 4-2 shows a representative glow curve from TSL of PCU after 20 minutes of X-irradiation. Glow peaks 1,2,3,4 and 5 are represented by peak temperatures of nearly 97, 140, 191, 217 and 267℃.

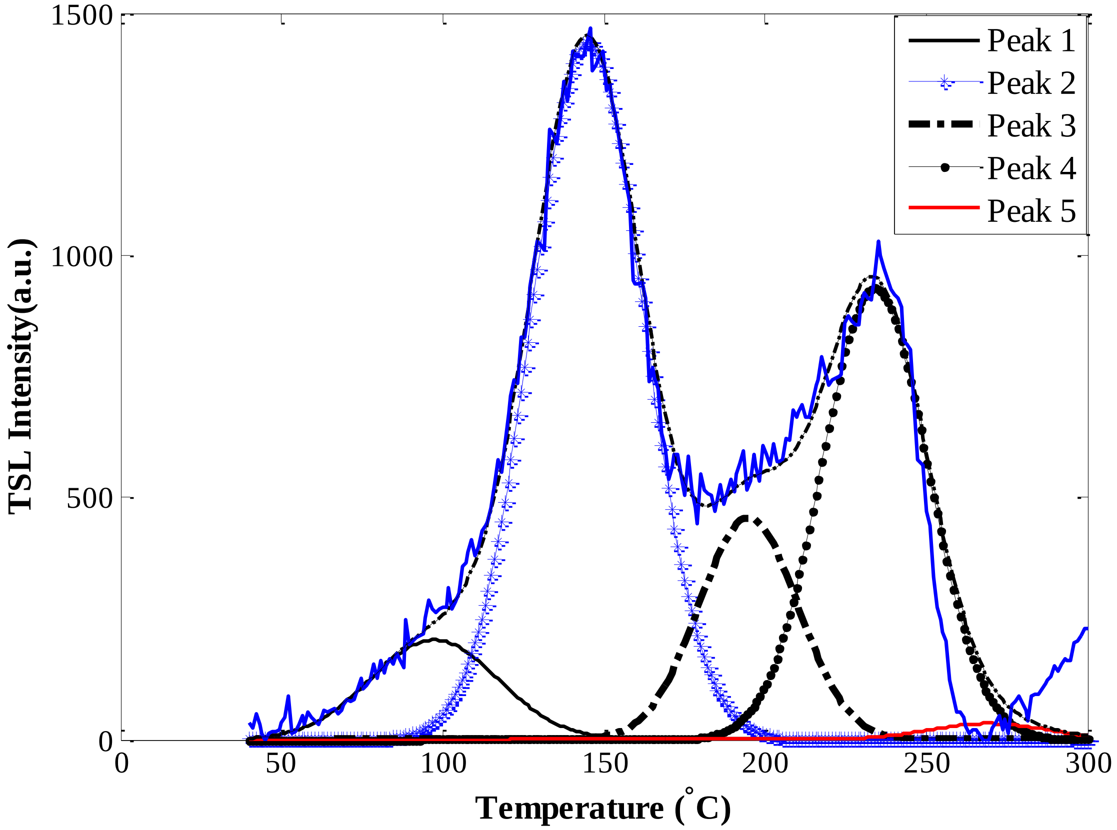


Figure 4-2. TSL glow curve of x- irradiated in air for 20 min

The glow peaks in the Figure 4-3 show peak temperatures of nearly 108, 116,149,216, and 230℃ respectively.

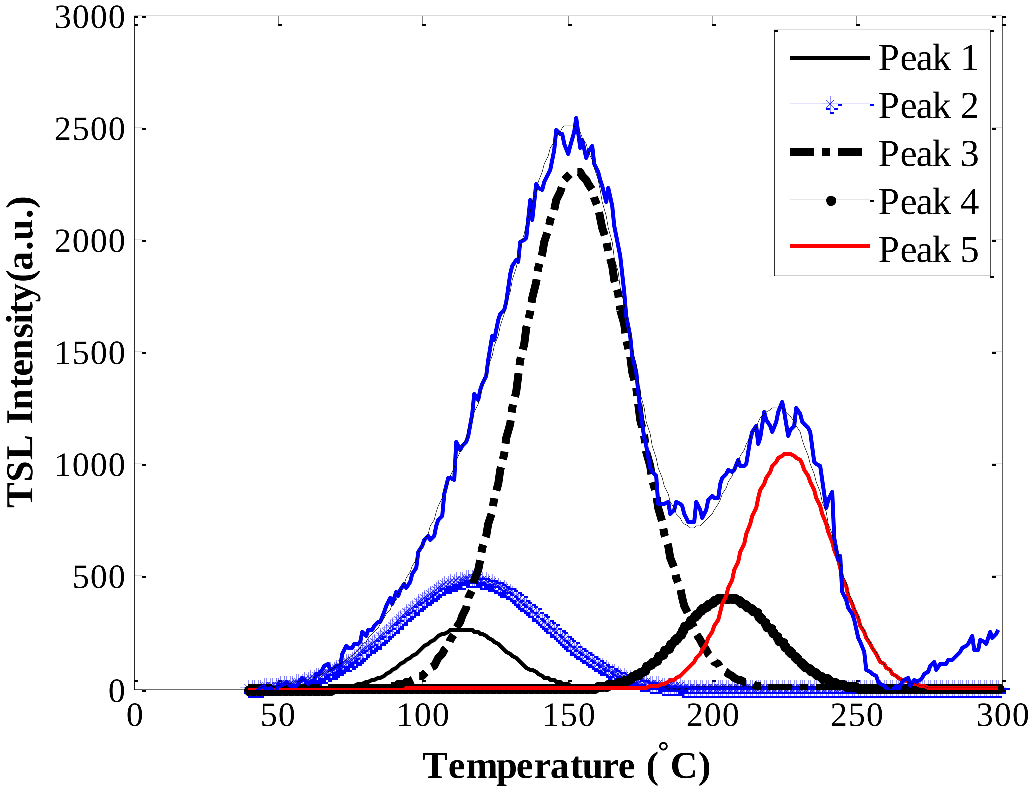


Figure 4-3. TSL Glow curve of x- irradiated for 30 min

In Figure 4-4 the glow peaks 1 to 5 show peak temperatures near 106, 116, 114, 217, and 229°C, respectively.

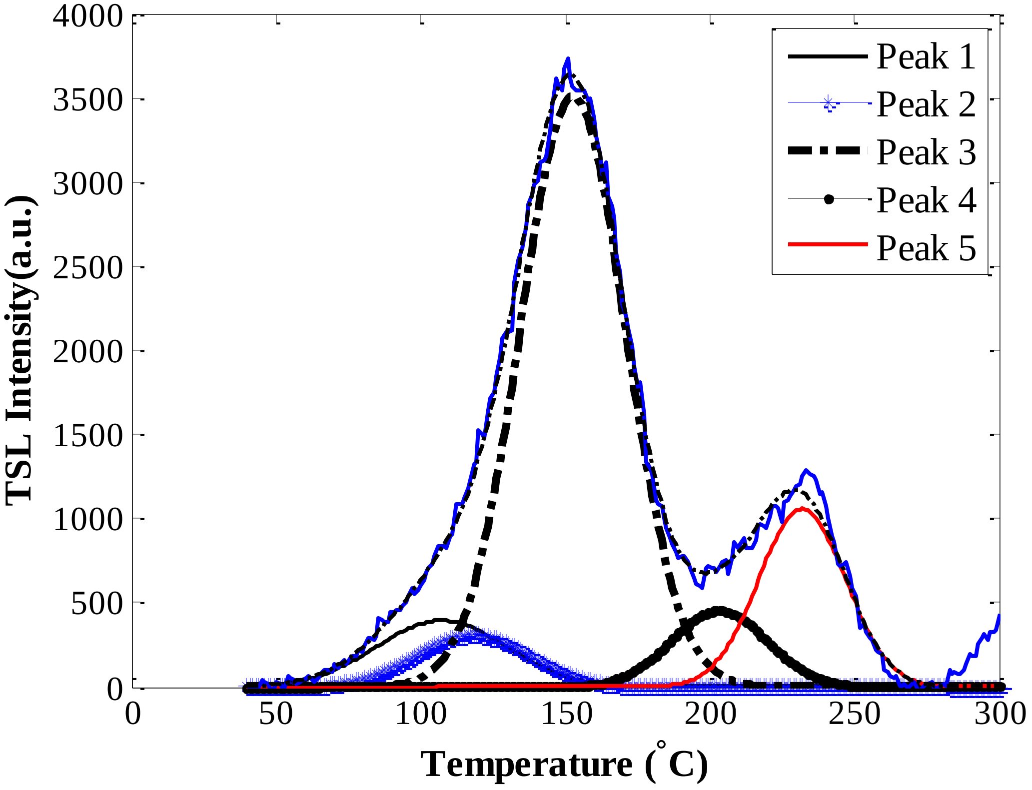


Figure 4-4. TSL glow curve of x- irradiated for 40 min

In Figure 4-5, glow peaks 1 to 3 show peak temperatures near 109,130, and 217℃, respectively.

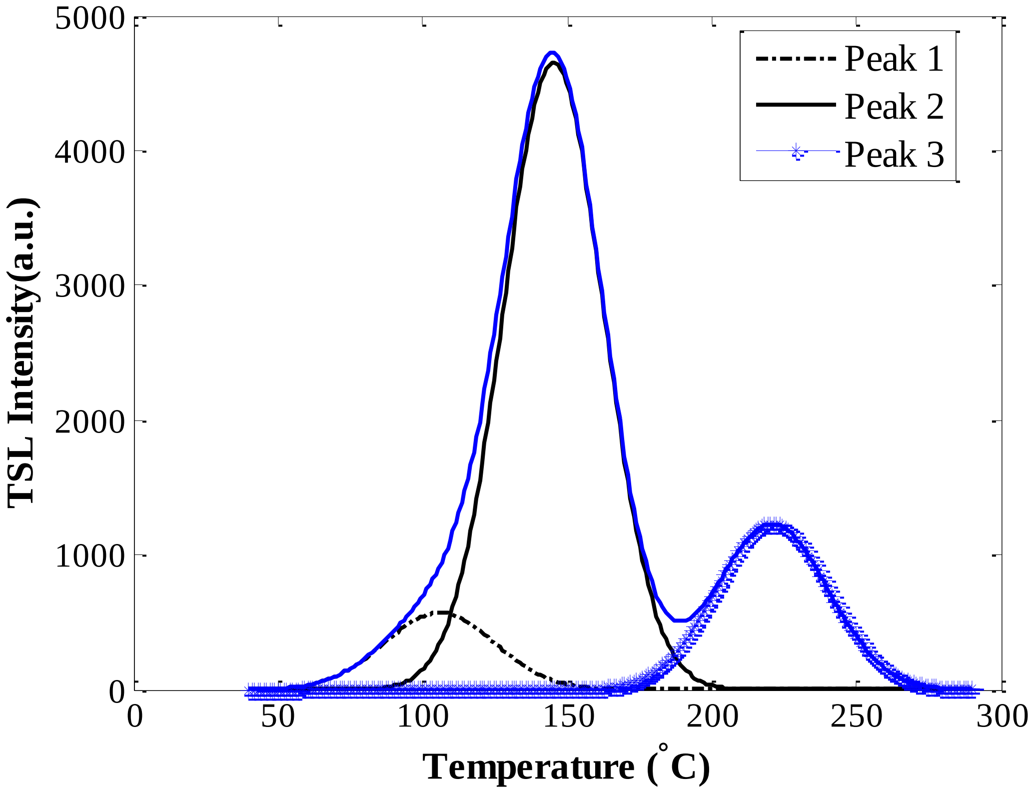


Figure 4-5. TSL Glow curve of x- irradiated for 60 min

The peak intensity changes as a function of radiation dose, as in Figure 4-6. However, the shift in temperature between the samples could arise due to experimental error.

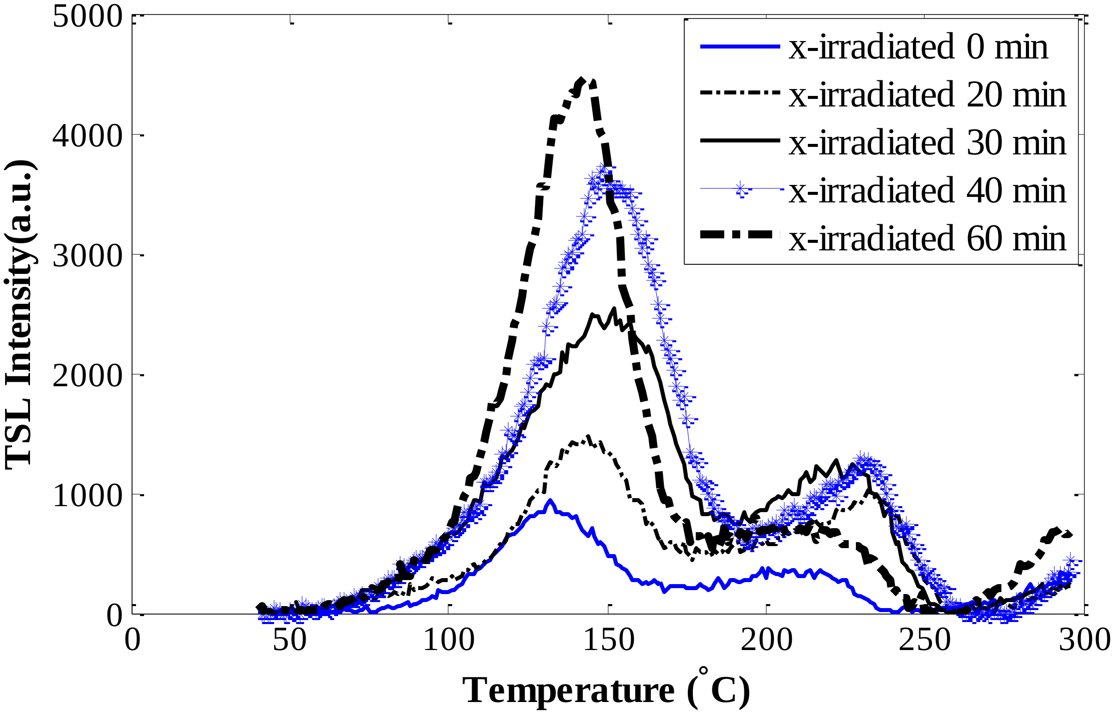


Figure 4-6. TSL intensity with dose of X-irradiation

The peak temperatures of TSL output vary slightly after irradiation: Luminescence for non-irradiated samples occurred at 140°C and 225°C, while luminescence of x-irradiated PCU occurred at (140, 217), (118, 200), (144, 229) and (130, 217)°C, respectively for 20-, 30-, 40- and 60-minute exposure times.

Peak Maximum Temperature (T_{max}) and Activation Energy

The temperature at which the TSL maxima occur is understood to be related to a thermal release mechanism of the trapped carriers from their various regions [27]. These temperatures have been associated with the relaxation temperature at which particular polymer chain motions become possible. Activation energy is the energy required to stimulate the de-trapping of electrons. The following Tables 4-1, 2, 3, 4, and 5 summarize the maximum temperature and the activation energy associated with each glow peak of non- irradiated sample and irradiated sample for different dose. The activation energy these samples for individual peaks ranges from 0.474ev to 2.228ev. The activation energy for all different dose samples are listed in Tables 4-1 through 4-5 below.

Table 4-1. Glow Curve Parameters for non-irradiated PCU

Peak	**Peak Temperature (ºC)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(eV)**	**Frequency Factor**
1	95	18.5	17.9	0.492	1.59	0.943	1.002e+012
2	139	14.8	13.9	0.484	1.51	1.33	3.264e+016
3	164	16.6	14.9	0.473	1.39	1.343	2.41e+015
4	224	13.7	12.1	0.469	1.358	1.856	2.427e+020

Table 4-2. Glow Curve Parameters for 20-minute-x-irradiated PCU

Peak	**Peak Temperature(ºC)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(eV)**	**Frequency Factor**
1	97	22.2	21.7	0.494	1.618	0.815	7.399e+009
2	140	19.6	18.8	0.49	1.566	1.185	1.504e+013
3	191	15.8	15	0.487	1.538	1.85	1.108e+019
4	217	19.6	18.6	0.487	1.537	1.747	2.103+016
5	267	20.6	19.7	0.489	1.558	1.906	4.608+016

Table 4-3. Glow Curve Parameters for 30-minute-x-irradiated PCU

Peak	Peak Temperature(°C)	τ	δ	μ_g	Kinetic Order	Activation Energy(ev)	Frequency Factor
1	108	24	23.7	0.492	1.6	0.775	9.769e+007
2	116	21.6	20.1	0.482	1.486	0.933	5.007e+011
3	149	24	22.2	0.481	1.471	0.977	2.196e+019
4	216	15.7	13.9	0.470	1.364	2.228	2.201e+022
5	230	17.7	16.6	0.484	1.506	1.95	1.563e+017

Table 4-4. Glow Curve Parameters for 40-minute-x-irradiated PCU

Peak	Peak Temperature(°C)	τ	δ	μ_g	Kinetic Order	Activation Energy(ev)	Frequency Factor
1	106	24.4	23.7	0.493	1.6	0.774	9.769e+008
2	116	21.6	20.1	0.482	1.486	0.923	5.007e+010
3	144	24	22.2	0.481	1.471	0.977	2.196e+020
4	217	15.7	13.9	0.47	1.364	2.128	2.201e+020
5	229	17.7	16.6	0.484	1.506	1.922	1.563e+018

Table 4-5. Glow Curve Parameters for 60-minute-x-irradiated PC

Peak	Peak Temperature(°C)	τ	δ	μ_g	Kinetic Order	Activation Energy	Frequency Factor
1	109	21.3	20.8	0.494	1.615	0.892	4.719e+009
2	130	20.5	19.8	0.491	1.585	1.137	3,483e+012
3	217	22.5	21.6	0.490	1.586	1.445	3.751e+013

The TSL in PCU samples, compared with the radiation exposure levels, is described in Figures 4-7 and 4-8. These results show that this luminescence increases with dose. Supplementary information to compare is in Tables 4-1 to 4-5, which includes trap parameters.

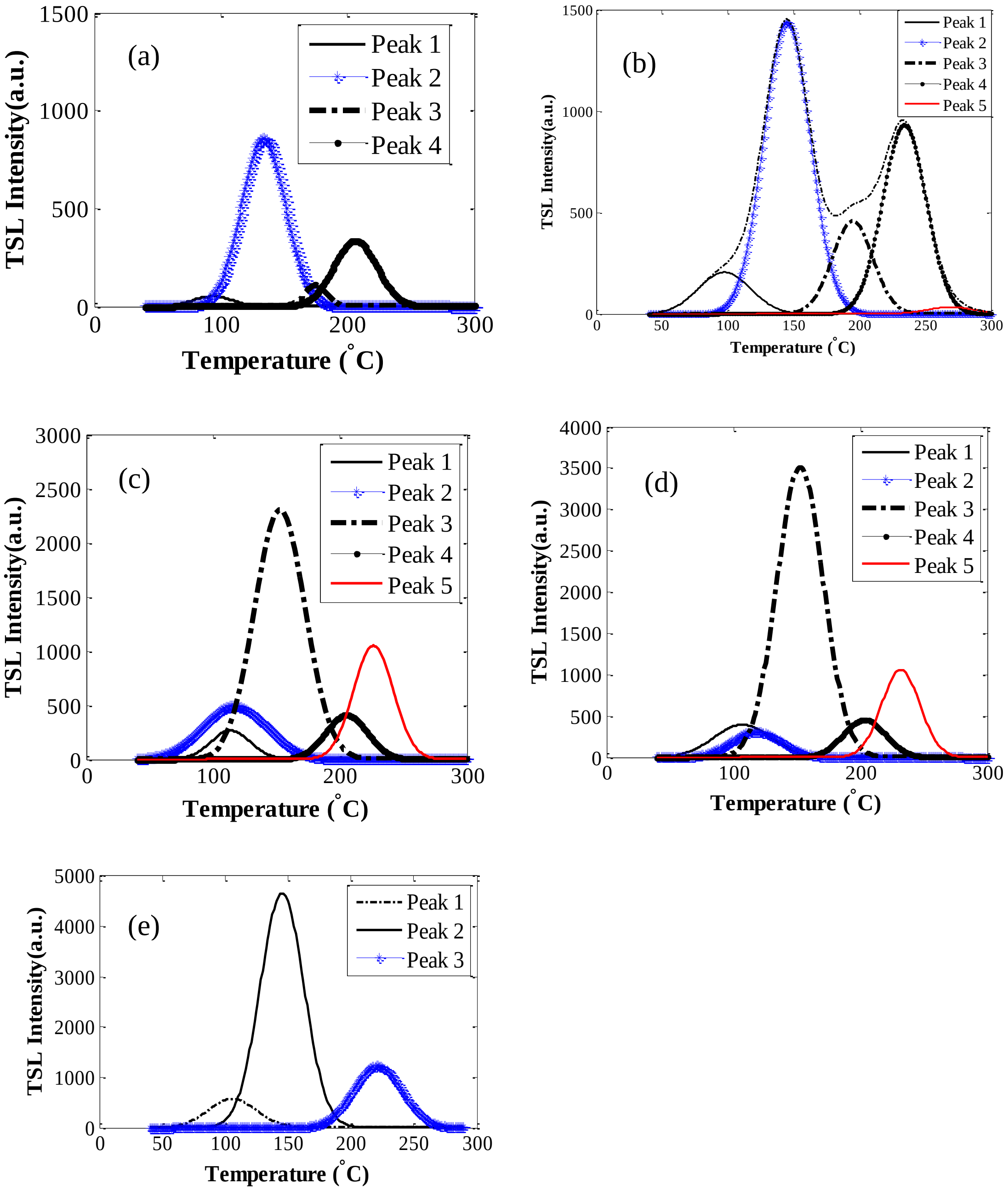


Figure 4-7. TSL deconvulated curves after (a) no X-Irradiation, (b) X-irradiation for 20 min, (c) X-irradiation for 30 min, (d) X-irradiation for 40 min, and (e) X-irradiation for 60 min.

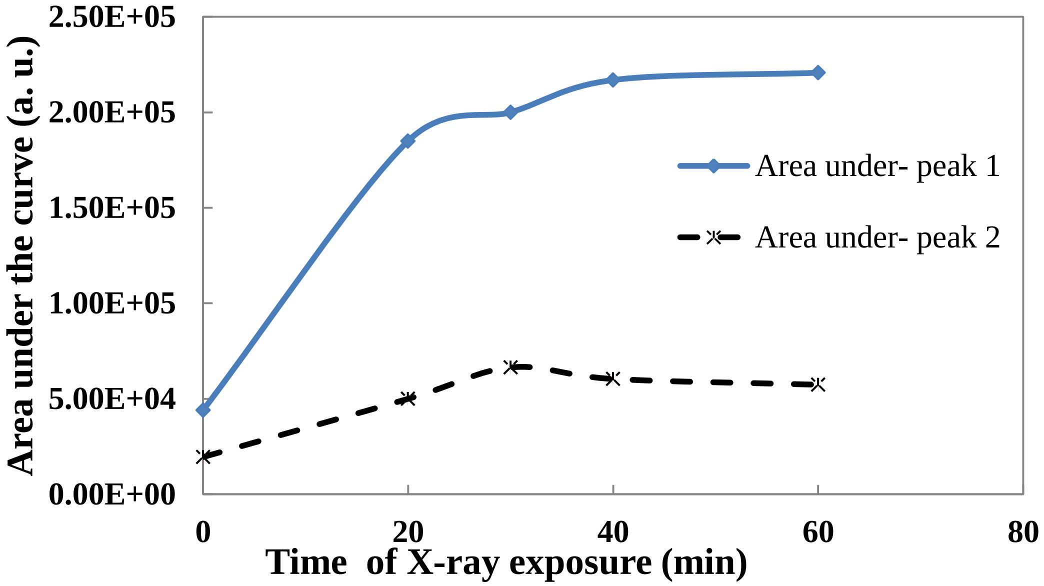


Figure 4-8. Area under the curve vs. time of exposure in minutes

We observed the TSL glow curves produced within 10 minutes of X-irradiation treatments, as well as after 20, 30, 40, and 60 minutes. While the temperature at which luminescence primarily occurred did not change significantly, the quantity of this luminescence decreased with time, indicating some detrapping occurs fairly quickly while at room temperature. This correlates well with ESR results which show free radical quantities similarly decreasing quickly within the first couple of hours –much more than for UHMWPE.

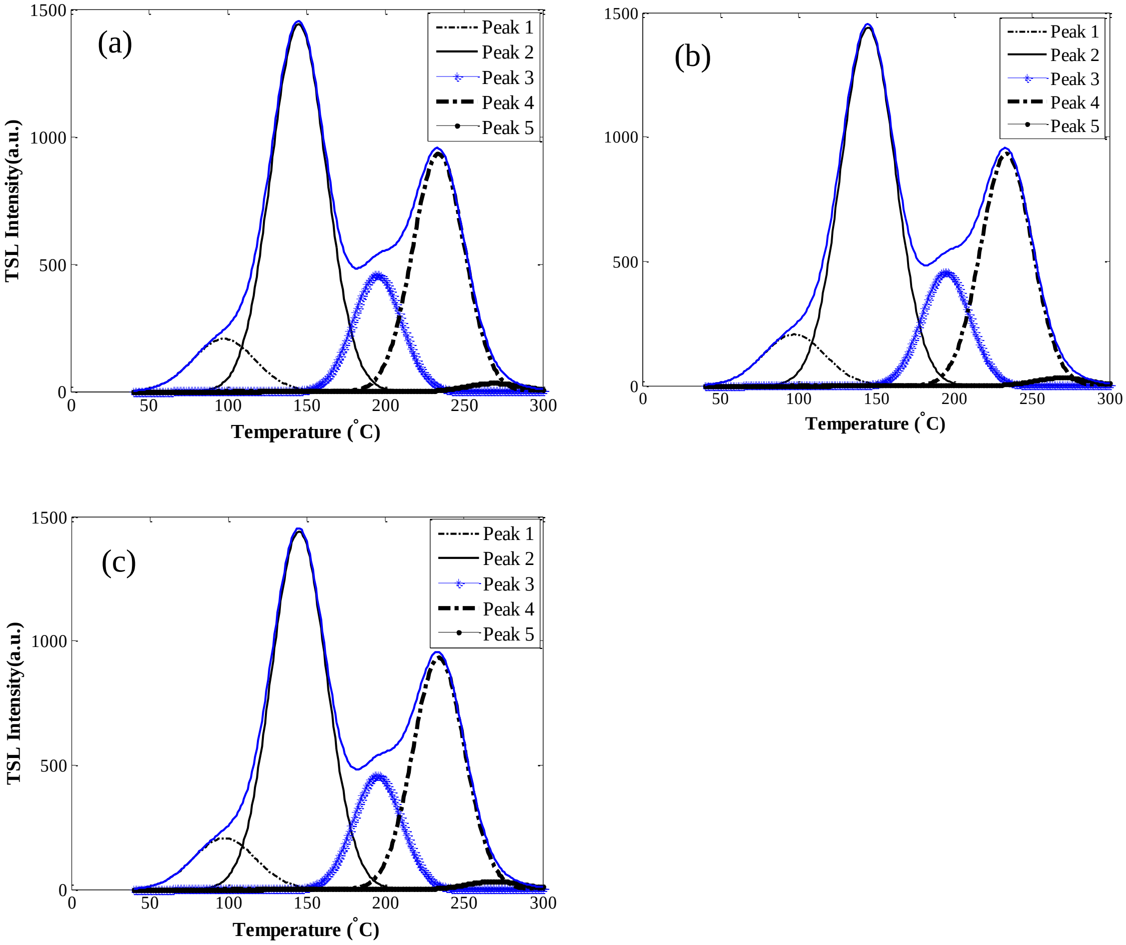


Figure 4-9. TSL glow curves of PCU which was X-irradiated for 20 minutes, and then tested (a) immediately, (b) tested after 10 minutes in air, and (c) tested after 20 minutes

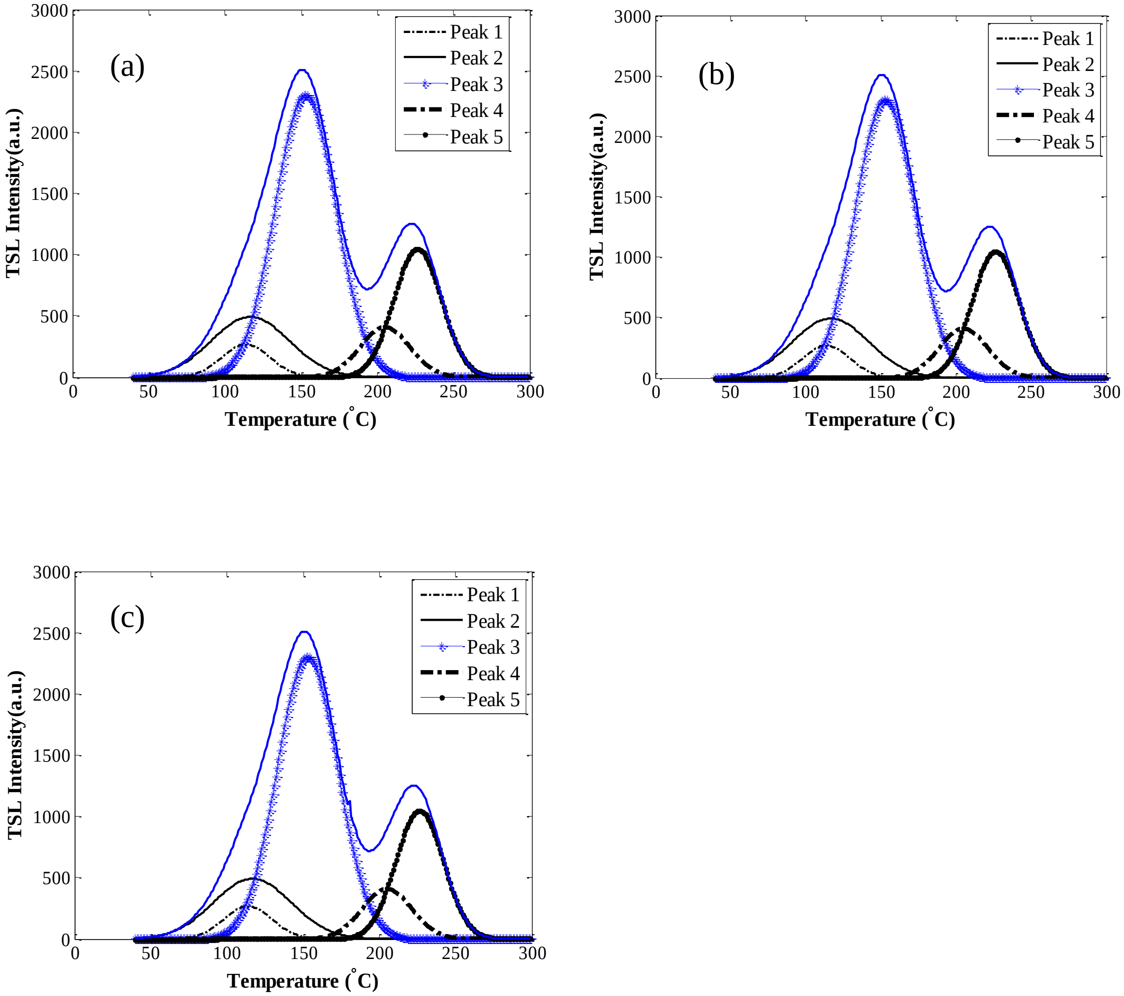


Figure 4-10. TSL glow curves of PCU which was X-irradiated for 30 minutes, and then tested (a) immediately, (b) tested after 10 minutes in air, and (c) tested after 20 minutes.

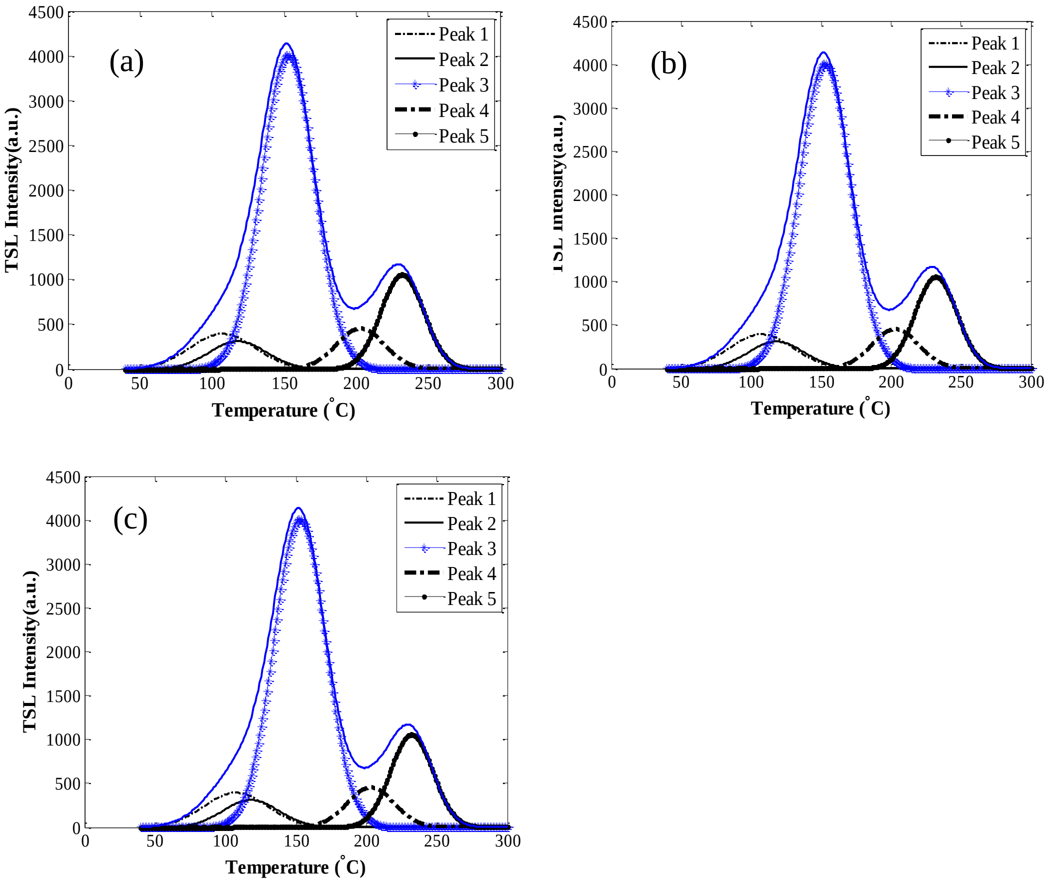


Figure 4-11. TSL glow curves of PCU which was X-irradiated for 40 minutes, and then tested (a) immediately, (b) tested after 10 minutes in air, and (c) tested after 20 minutes.

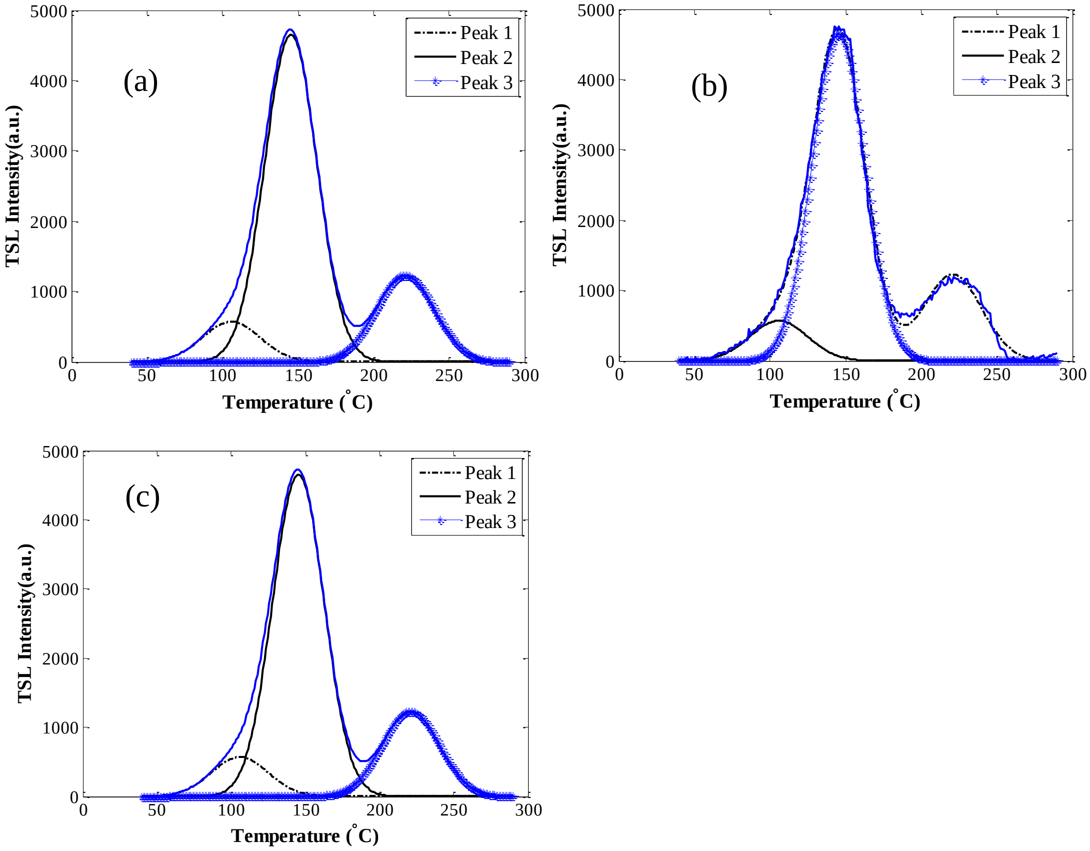


Figure 4-12. TSL glow curves of PCU which was X-irradiated for 60 minutes, and then tested (a) immediately, (b) tested after 10 minutes in air, and (c) tested after 20 minutes.

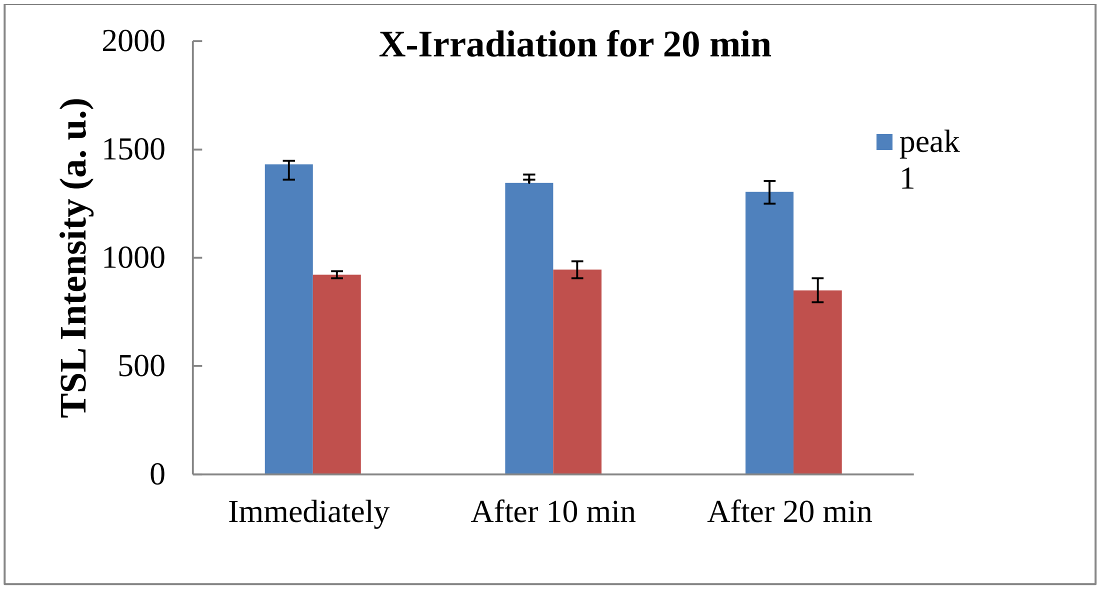


Figure 4-13. TSL intensity vs. 20-min. x-ray exposure

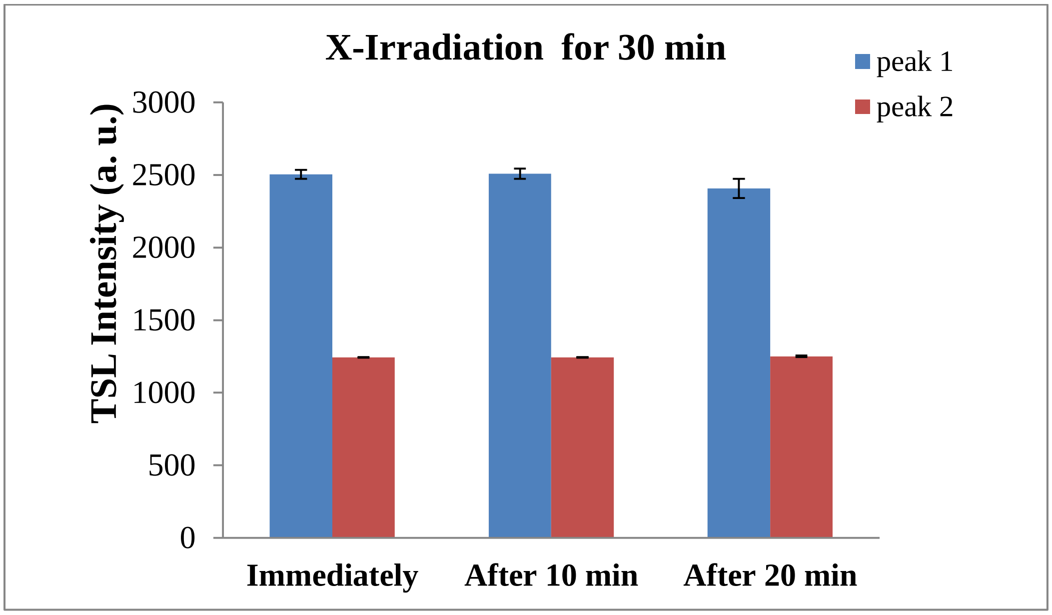


Figure 4-14. TSL intensity vs. 30 min. x-ray exposure

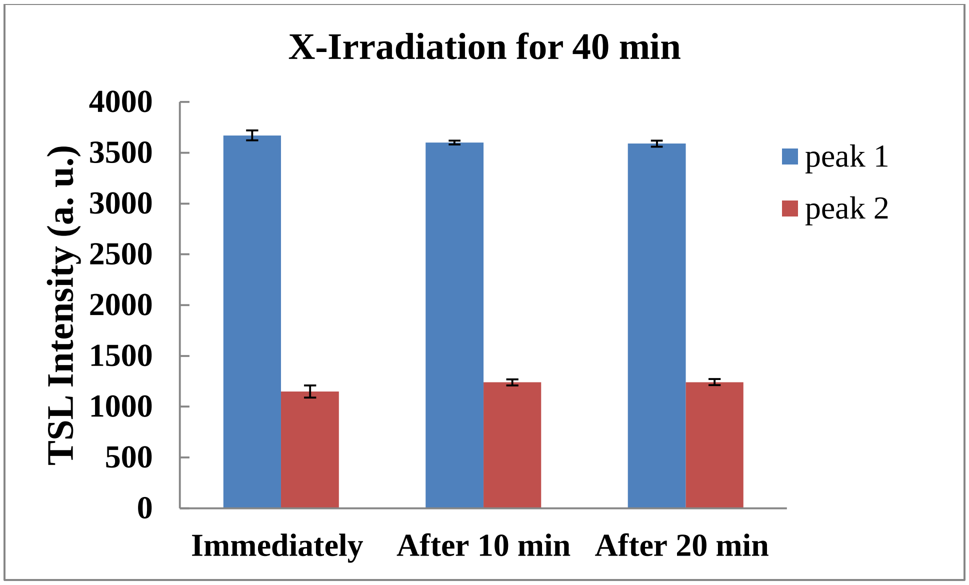


Figure 4-15. TSL intensity vs. 40 min. x-ray exposure

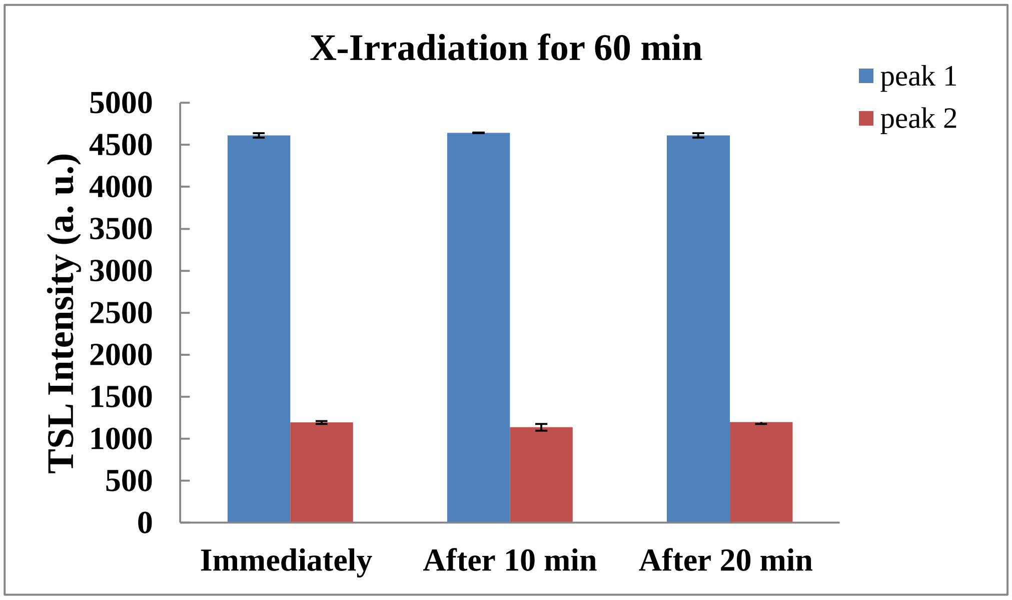


Figure 4-16. TSL intensity vs. 60 min. x-ray

We examined the TSL output for various dose of x-irradiation. We have demonstrated the TSL peak intensity for immediately, after 10 minutes and 20 minutes of irradiated time and we obtained no more change in intensity in luminescence but some intensity were varied and slightly go down, when time elapsed. The decay of intensity is shown in Figure 4-17.

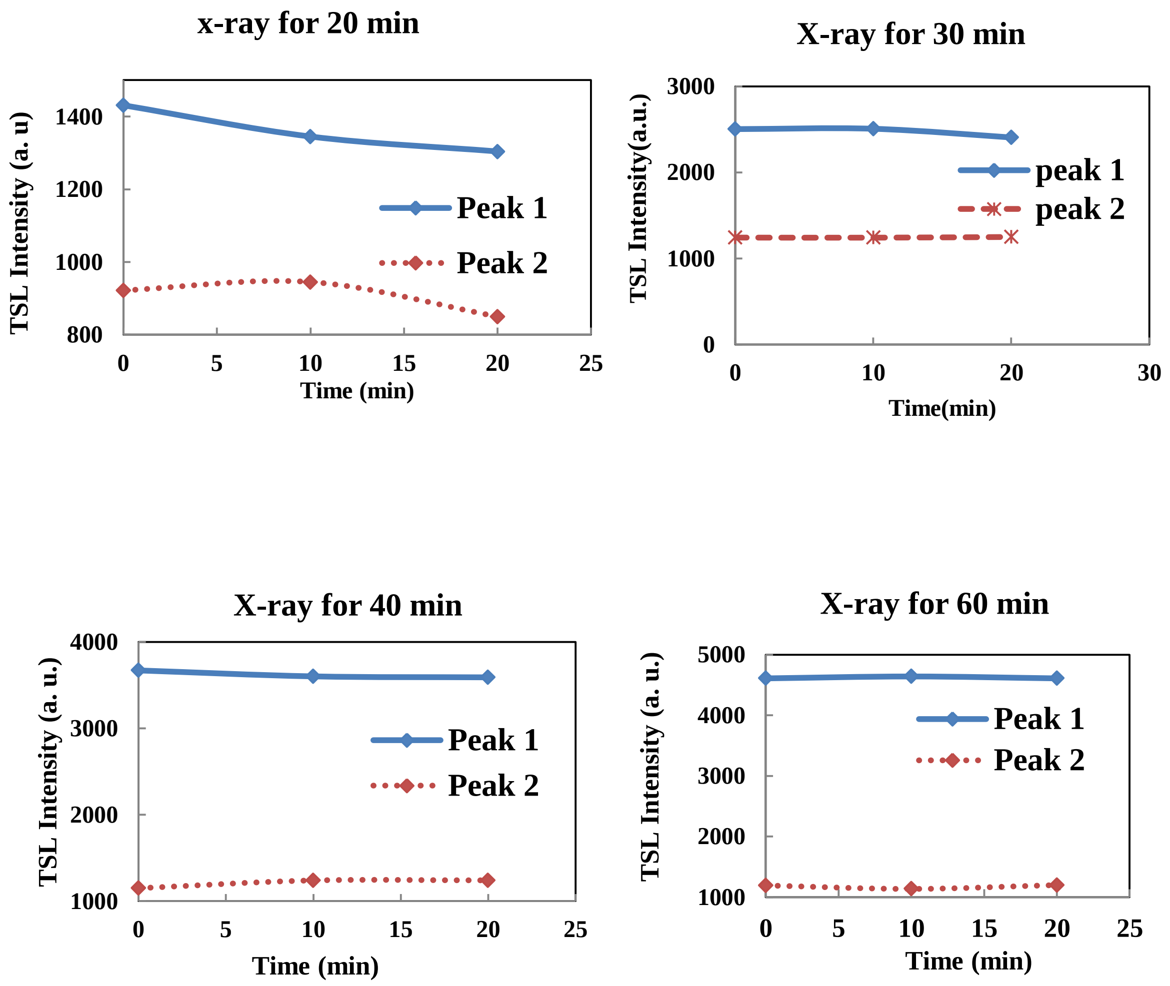


Figure 4-17. TSL intensity decay profile

CHAPTER 5

ESR - RESULT AND DISCUSSION

The ESR spectra of PCU were recorded in air at room temperature. The representative spectra are shown in Figures below. These results show an increase in free radicals with dose (irradiation time at a constant dose rate). In contrast, a measureable presence of free radicals was not observed in non-irradiated samples. For UV-irradiation, we initially observed that the PCU material turned a yellowish in color upon exposure, and thought that this may be reflective of interactions with air/oxygen. Therefore, additional UV-exposures were performed within a nitrogen gas environment. However, the UV-induced color change did not vary significantly with environment. Still, we determined from ESR results that free radicals were significantly created with UV irradiation in both air and nitrogen environments. For X-ray 60 vs. 75 minutes, we observed similar free radical concentrations (see in Figure 5-7), indicating that free radical accumulation had reached its maximum/saturation level upon one-hour exposure. To assess further the status of these radicals with time, retesting was performed after 10 weeks. The graphs and data pertaining to this discussion are shown below.

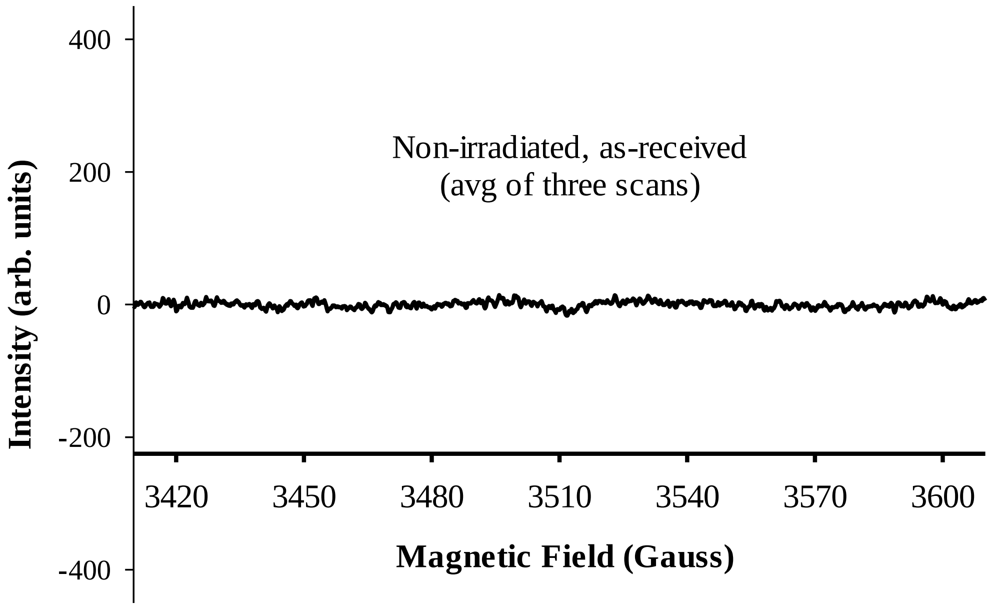


Figure 5-1. ESR spectra of non-irradiated PCU

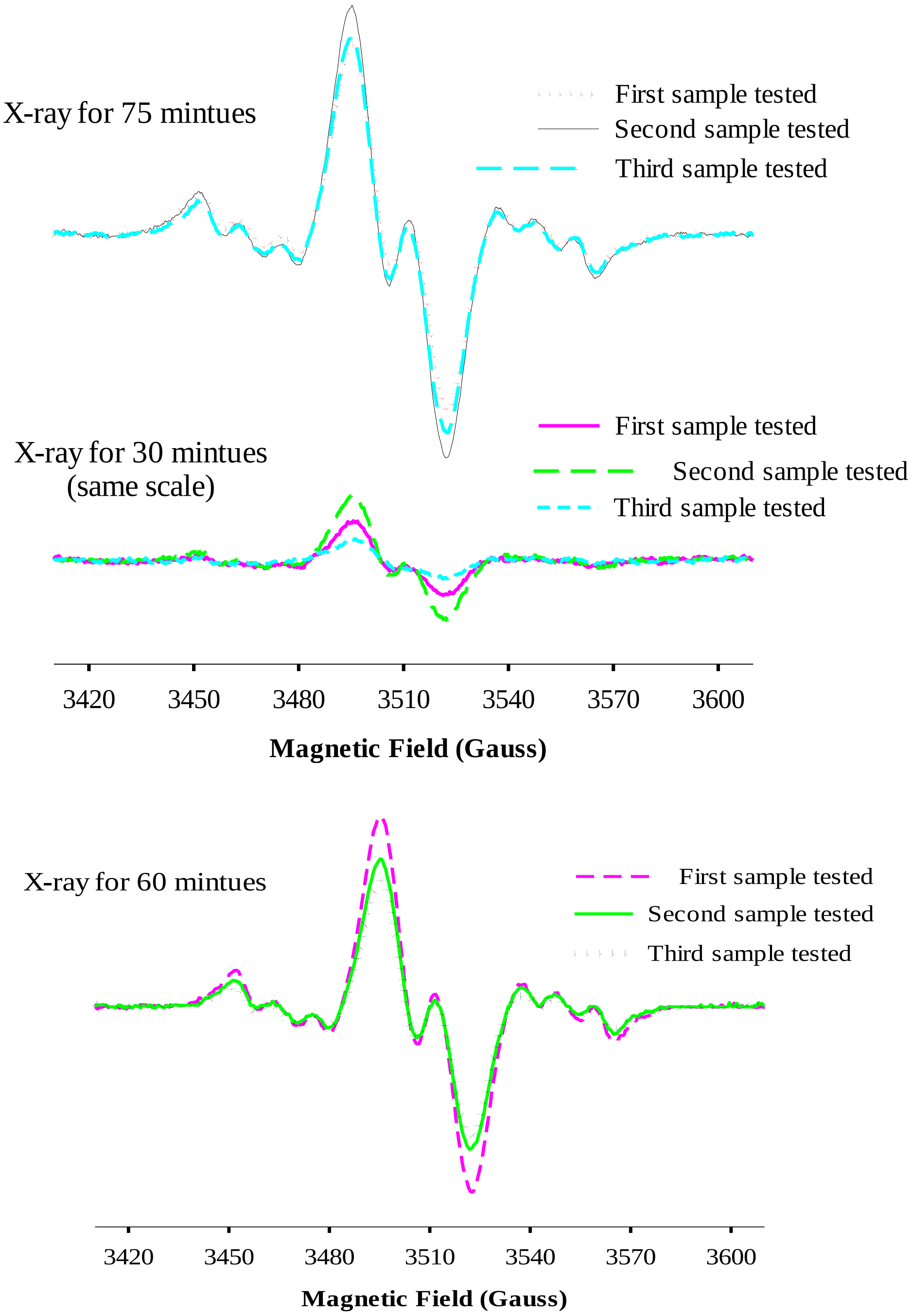


Figure 5-2. ESR spectra immediately after treatment

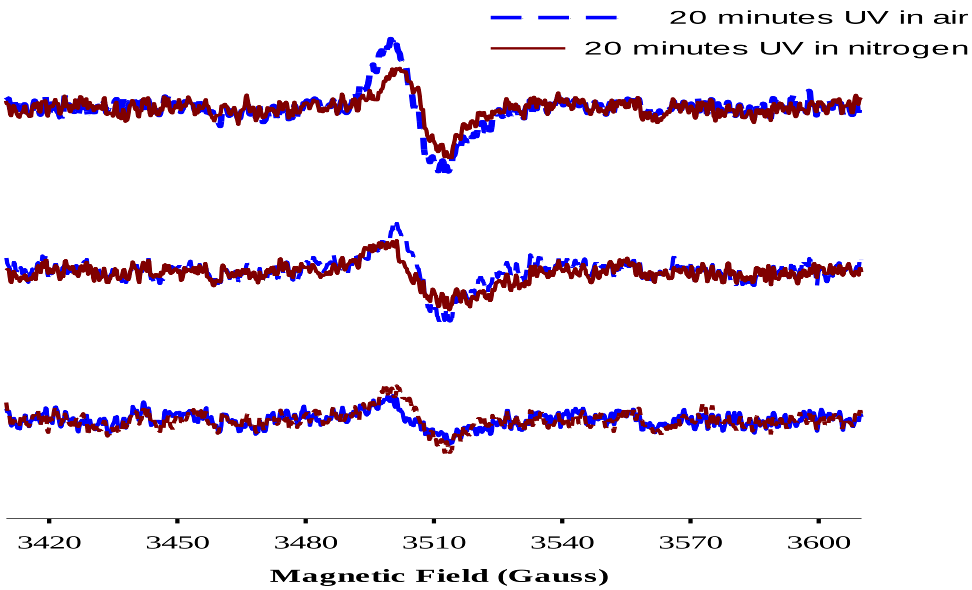


Figure 5-3. ESR spectra immediately after UV- treatments

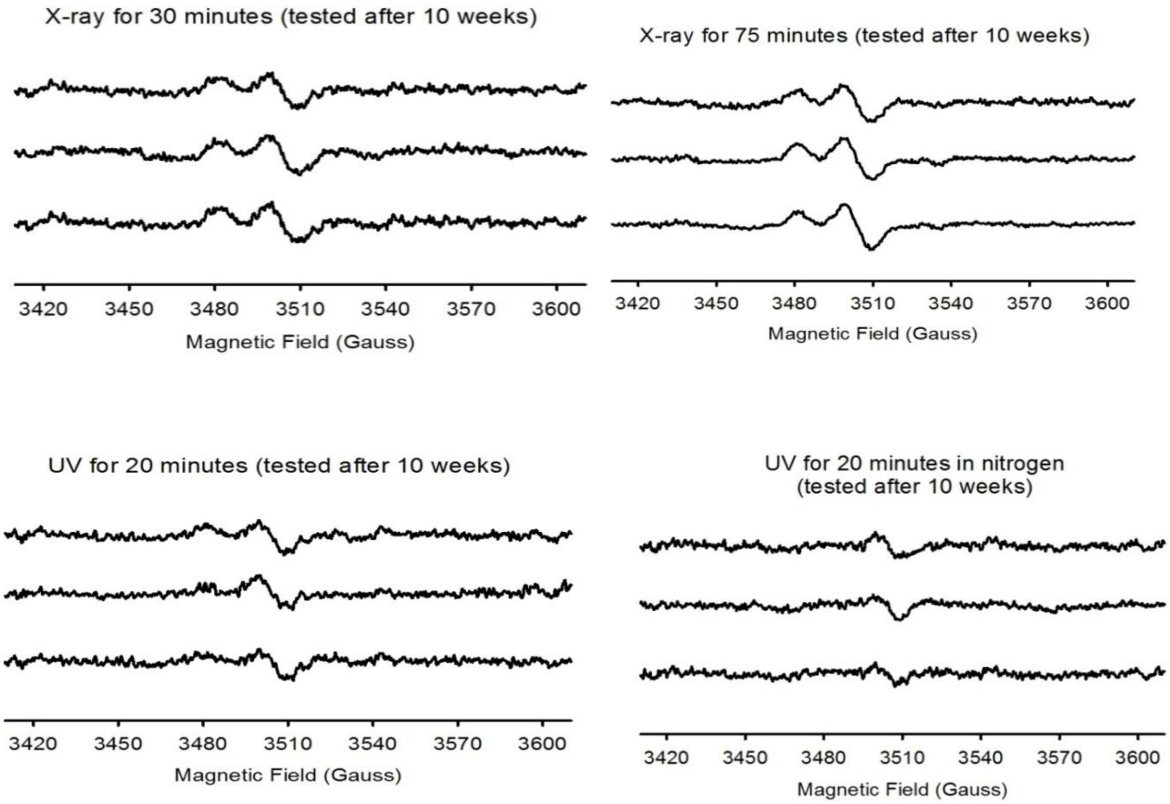


Figure 5-4. ESR spectra 10 weeks after treatments

While the structure of PCU radicals is yet to be determined, ESR spectral intensity was found to increases with x-ray and UV-exposures. The resulting free radical concentrations were calculated and are displayed in the Figure 5-7. In addition, we calculated the peak-to-peak distances as in order to better distinguish the ESR spectra. These data are shown in Figure 5-5.

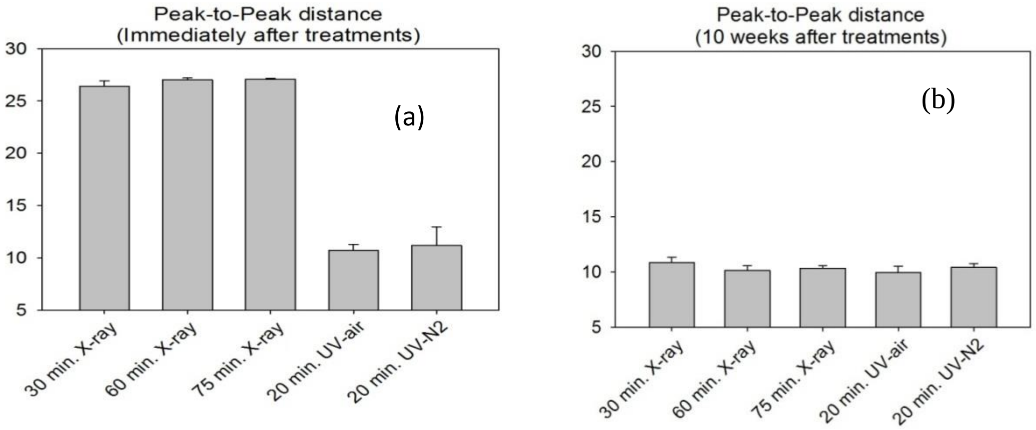


Figure 5-5. ESR spectral details of (a) peak-to-peak distances immediately after treatments vs. (b) peak-to-peak distances 10 weeks after treatments

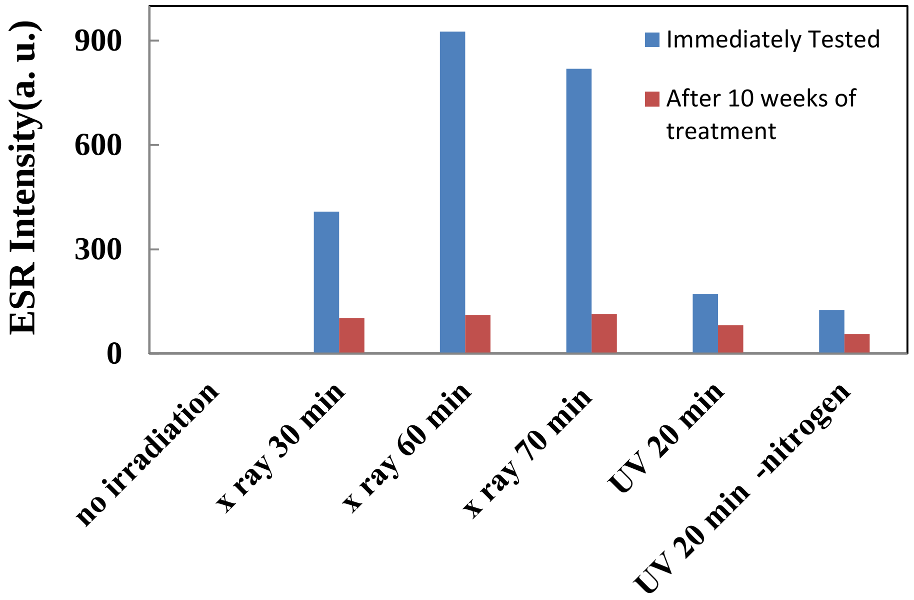


Figure 5-6. ESR intensity vs. irradiation exposures

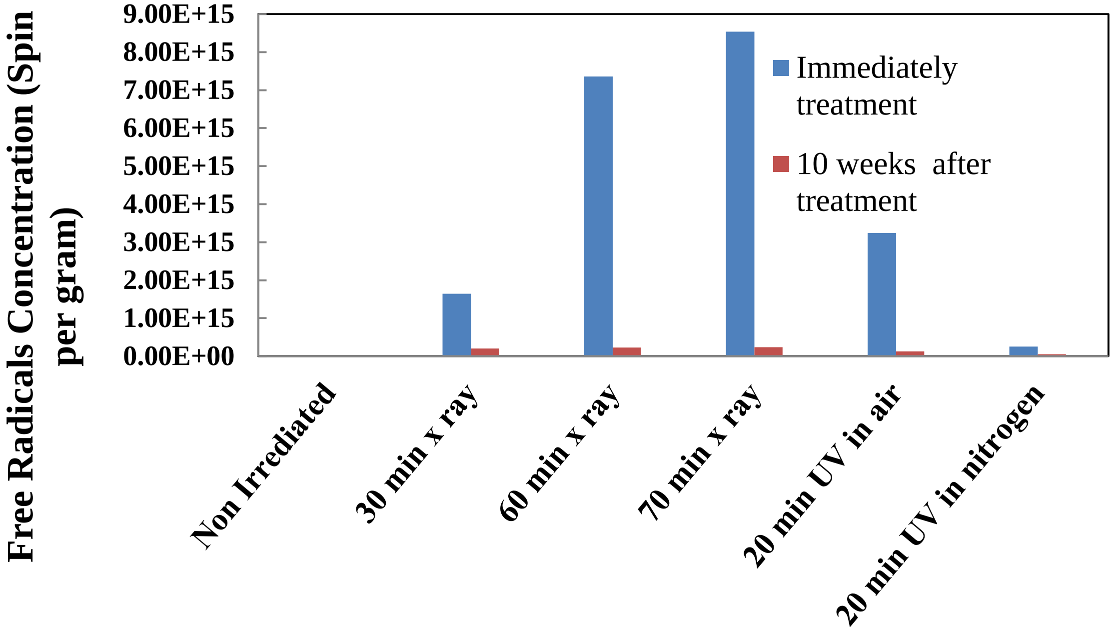


Figure 5-7. Free Radicals estimates

.

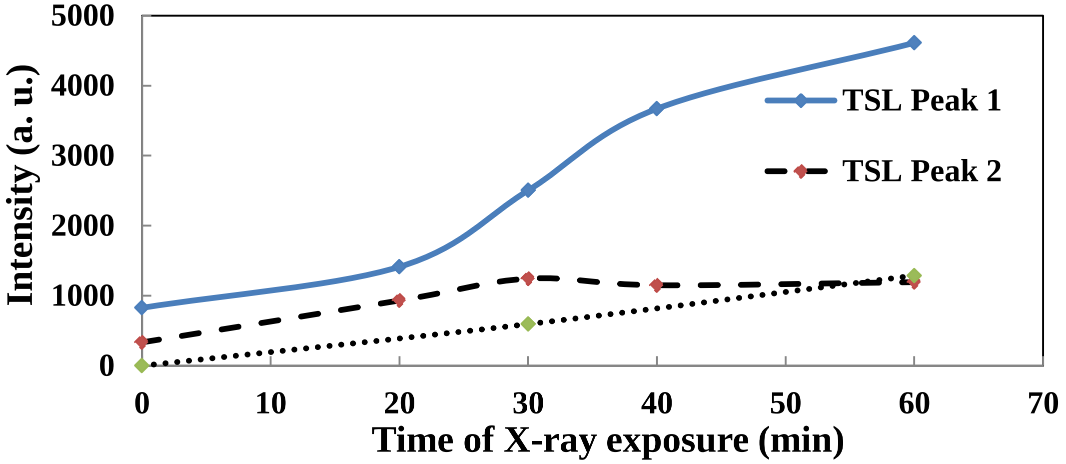
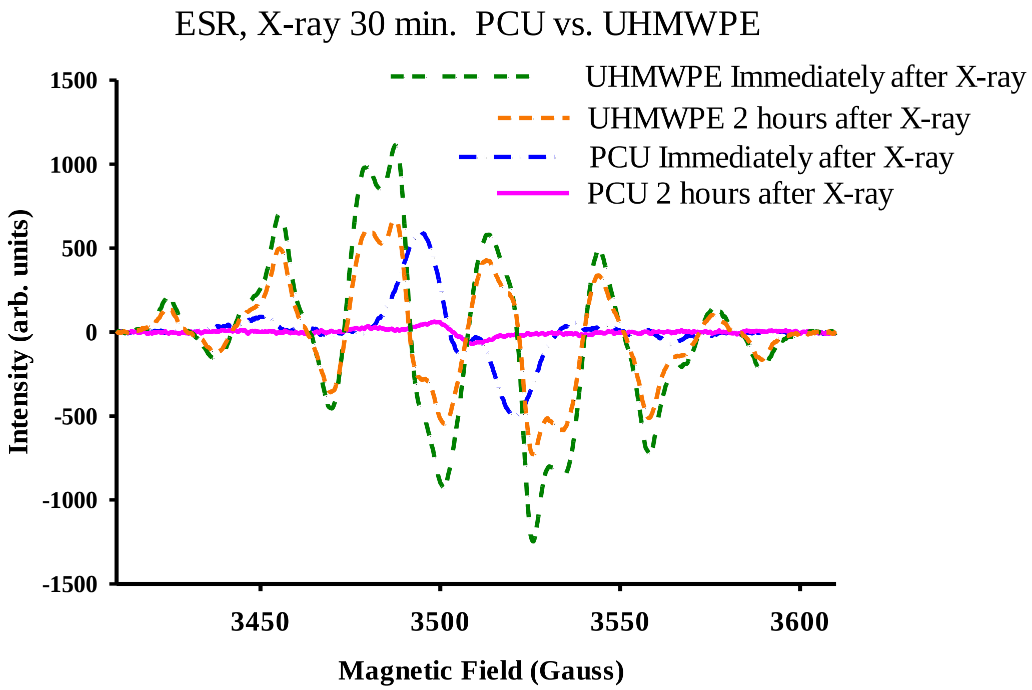


Figure 5-8. Comparative Study of TSL and ESR

We observed ESR intensity is maximum at 60 min irradiation and similar result also obtained for TSL intensity. The ESR report showed that more free radicals are induced for high dose. After 10 weeks of initial treatment the radical concentration significantly decreased. The peak to peak distances (splitting line) are similar for 30, 60 and 75 minutes irradiation suggesting production of similar or identical radicals. But in 10 weeks in air after irradiation, ESR line intensity and line separation decrease significantly. We also compared the ESR intensity for PCU and UHMWPE. The ESR spectra and free radical concentrations are presented in Figure 5-9 and 5-10.



(PCU and UHMPWE samples were
of equal mass, 55.0 mg each)

Figure 5-9. ESR intensity PCU vs. UHMWPE

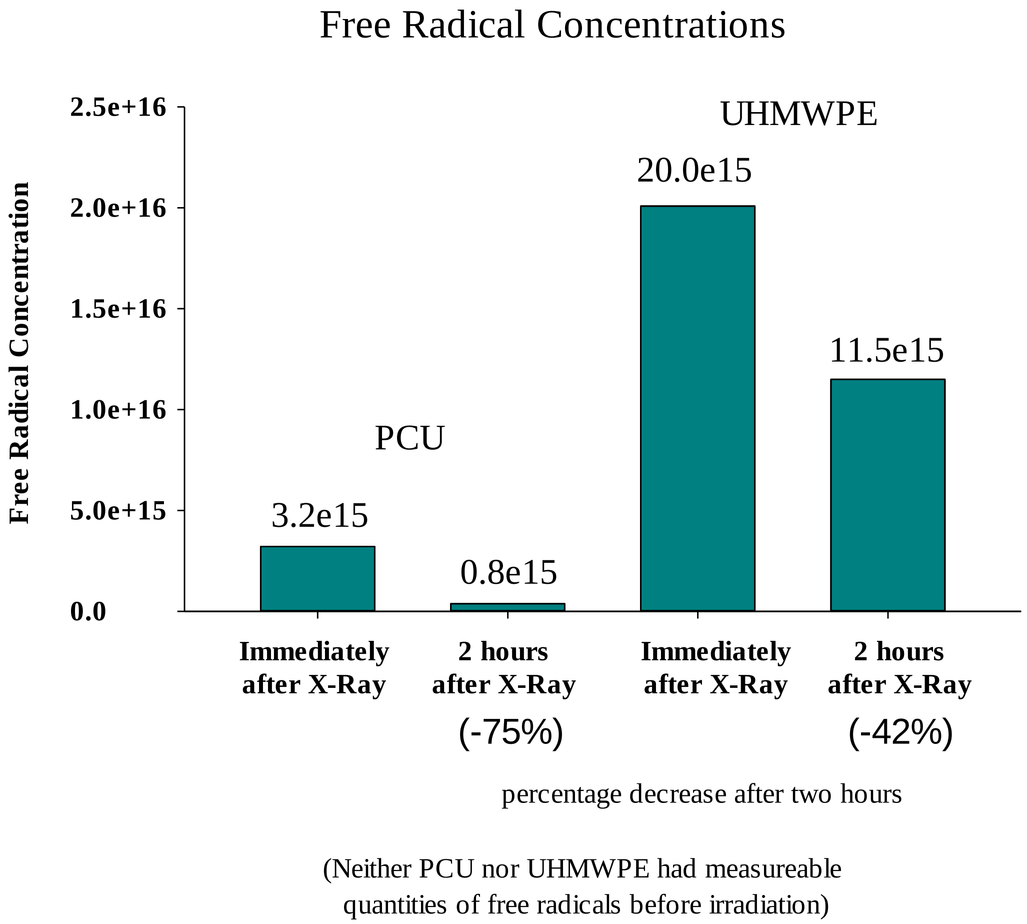


Figure 5-10. Free Radical estimates for PCU & UHMWPE

We observed no detectable free radical in PCU & UHMWPE before irradiation, but, after irradiation, the free radicals are present, there is more concentration of radical in UHMWPE than in PCU. When the same samples were left in air for 2 hour after irradiation the radicals in PCU decreased by 75% and in UHMWPE by 42%.

CHAPTER 6

CONCLUSION

TSL glow curves of non-irradiated PCU contained two major peaks: one near 140°C and the other near 225°C. However, these two peaks were actually made up of additional peaks which were revealed via deconvolution of the curves, using PeakFit ™ software. After X-irradiation, TSL peaks of higher intensities were observed as expected from absorbed radiation; these peaks were also near 140°C and 225°C. Upon calculation of the TSL parameters, it was found that the activation energy was between 0.474ev to 2.228ev while the kinetic order was between 1 and 2.

ESR showed radiation-induced free radicals for both X- and UV-irradiation, while non-irradiated PCU did not contain a measureable presence of free radicals. However, TSL did show measureable luminescence for non-irradiated PCU. As for free radical quantities, it was found that, compared to UHMWPE, PCU incurred significantly less free radical accumulation with X-irradiation and this quantity also decreased much faster than with the UHMWPE.

RECOMMENDED FUTURE WORK

Polycarbonate Urethane has a strong potential to be a very successful component for medical devices as well as other applications. Future work involving FTIR and related oxidation analyses, as well as investigations of effect of gamma-irradiation may yield additional understanding of PCU so that broadening of its uses may be realized. In addition, analyses of crosslinking via various means including chemical and electron-beam may be beneficial. These studies would additionally benefit from concurrent free radical analysis via ESR.

REFERENCES

[1] I. Khan, N. Smith, E. Jones, D. S. Finch, R.E Cameron, Analysis and Evaluation of Biomedical Polycarbonate Urethane Tested in an in Vitro Study and an Ovine Arthoplasty Model. Part 1 Materials Selection and Evaluation26 (2005) 621-631.

[2] M. Kraft, N.G Smith, K.F Pirker, C.W .M. Kay, Evaluation of Effects of Gamma sterilization on Biomedical Polyeurethanes for Implant use, European Cells and Materials 22 (2011), 23

[3] E. M .Christenson, J.M. A. A. Hiltner, Oxidative Mechanism of Polycarbonate Urethane and Polyether Urethane Biodegradation In vivo and In Vitro Correlation (2004) 245-255.

[4] S. C. Scholes, I. C. Burgess, H. R. Marsden, A. Unsworth, E. Jones, N. Smithl, Compliant Layer Acetabular Cups Friction Testing of a Range of Materials and Designs for a New Generation of Prosthesis that Mimics the Natural Joint, Proc. Inst. Mech Eng 5 (2006) 583-596.

[5] S. L. Smith, H. E. Ash, and A. Unsworth , A Tribological Study of UHMWPE Acetabular Cups and Polyurethane Compliant Layer Acetabular Cups, J Biomater Res Part A, 53 (2000) 710-716.

[6] L. Caravia, D. Dowson, and J. Fisher, Start Up and Steady State Friction of Thin Polyurethane Layers,Wear, 160, (1993)191-197.

[7] I. Khan, N. Smith, E. Jones, D. S. Finch, R.E. Cameron, Analysis and Evaluation of Biomedical Polycarbonate Urethane Tested in an In Vitro Study and an Ovine Arthoplasty Model. Part II Materials Selection And evaluation 26(2005) 633-642.

[8] F.P. Quigley et al, Selection of Elastomeric Materials for Complaint-Layered Total Hip Arthroplasty, Proc. Inst. Mech. En. 216 (2002) 77-83.

[9] E.M. Christenson, M. Dadsetan, M. Wiqqins, J. M. Anderson, and A. Hiltnerl, Poly(Carbonate Urethane) and Poly(ether Urethane) Biodegradation: In Vivo Studies, Journal of Biomaterials Research Part A, 69 (2004) 407-416.

[10] K.Gorna,S.Gogolewski, The Effect of Gamma Radiation on Molecular Stability and Mechanical Properties of Biodegradable Polyeurethane for Medical Application 79(2003) 465-474

[11] E.M. Christenson, J.M. Anderson, and A. Hiltner, Oxidative Mechanism of Polycarbonate Urethane and Polyether Urethane Biodegradation, In vivo and in Vitro Correlation. (2004) 246-255.

[12] E.M. Christenson, J.M.A. A. Hiltner, Oxidative Mechanism of Polycarbonate Urethane and Polyether Urethane Biodegradation (2004) 407-416.

[13] E. M.Christenson, J.M A. A. Hiltner, Antioxidant Inhibition of Polycarbonate Urethane In Vivo Biodegradation (2005) 481-489.

[14] S. Fare, P.Petrini, M.A.A Cigada , M. Tanzi, Synergistic Effect of Oxidative Environments and Mechanical Stress on In Vitro Stability of Polyeurathenes and Polycarbonate Urethane 45(1999) 62-74

[15] S.M Kurtz, R. Siskey, M.Reitman, Accelerated Aging, Natural Aging, Small Punch Testing of Gamma Air Sterilized Polycarbonate Urethane Acetabular Components (2010) 442-447.

[16] R.J. Fleming and J.Hagekyriakou, Thermoluminescence in Polymers, Radiation Protection Dosimetry 8 (1984) 99-116.

[17] R.S. Benson,Use of Radiation in Biomaterials Science 191 (2002) 752-757.

[18] A.S. Hoffman, Radiation Technology for Immobilization of Bioactive Materials, IAEA Publication Vienna 1988.

[19] M. Oberhofer and A. Scharmann, Applied Thermolumnescence Dosimetry, Adam Hilger Ltd, Bristol 1979.

[20] A.J J. Bos, Theory of Thermoluminescence 41(2006) S45-S56.

[21] D.R. Vij, Luminescence of Solids, Plenum Press, New York 1998.

[22] R. Chen and Stefens,Theory of Thermoluminescence and Related Phenomena. , World Scientific, Singapore 1997.

[23] P.D Townsend, A.P Townsend, A.P Rowlands and G.Corradi, Thermoluminescence During a Phase Transition 1997.

[24] J.T. Randall and W. MHF, Phosphorescence and Electron Traps I. The study of Trap Distribution 184 (1945), 365-389

[25] J.T. Randall and W. MHF, Phosphorescence and Electron Traps II. The Interpretation of Long Period Phosphorescence.184 (1945)390-407

[26] C. E Mary and Partridge JA, Thermoluminescent Kinetics of Alpha, Irradiated Alkali Halids 40(1964), 1401-1409

[27] M.S. Rasheedy, A New Method for Obtaining the Order of Kinetics and the Activation Energy of Thermoluminescence Glow Peak,8 (1996), 1291

APPENDIX

TABULATION OF CALCULATED GLOW CURVE PARAMETERS

Table 4-6.Glow curve parameter of X- irradiated (20 min)- Immediately

Peak	Peak Temperature(°C)	τ	δ	μ_g	Kinetic Order	Activation Energy(eV)	Frequency Factor
1	95	21.2	21	0.494	1.614	0.805	6.399e+010
2	140	18.6	18	0.49	1.456	1.175	1.504e+012
3	191	15	14.8	0.487	1.523	1.75	1.108e+018
4	217	19.6	18	0.487	1.023	1.857	2.103+015
5	267	20.3	19	0.489	1.512	1.802	4.608+016

Table 4-7.Glow curve parameter of X- irradiated (20 min)- After 10 min

Peak	Peak Temperature(°C)	τ	δ	μ_g	Kinetic Order	Activation Energy(eV)	Frequency Factor
1	96	21	20	0.493	1.613	0.806	6.299e+011
2	140	17	16	0.490	1.457	1.20	1.604e+012
3	191.5	15	14	0.486	1.423	1.71	1.508e+018
4	218	19	18.2	0.484	1.023	1.843	2.303+015
5	268	20	19	0.482	1.515	1.80	4.208+015

Table 4-8.Glow Curve Parameter of X-irradiated (20 min)- After 20 min

Peak	Peak Temperature(°C)	τ	δ	μ_g	Kinetic Order	Activation Energy(eV)	Frequency Factor
1	95	20.2	19.8	0.494	1.617	0.815	6.399e+010
2	140	18.6	17	0.491	1.459	1.175	1.204e+012
3	191	15	14.8	0.587	1.556	1.80	1.308e+018
4	218	19	18	0.687	1.023	2.00	2.203+015
5	266	21.3	19	0.389	1.412	1.702	4.808+016

Table 4-9.Glow Curve Parameter for X-irradiated (30 min)- Immediately

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(ev)**	**Frequency Factor**
1	108	24	22.5	0.492	1.6	0.775	9.769e+007
2	116	21.6	20.3	0.482	1.486	0.933	5.007e+011
3	149	24	22.2	0.481	1.471	0.977	2.196e+019
4	216	15.7	13.9	0.470	1.364	2.228	2.201e+022
5	230	17.7	16.6	0.484	1.506	1.95	1.563e+017

Table 4-10.Glow Curve Parameter for X-irradiated (30 min)- After 10 min

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(ev)**	**Frequency Factor**
1	108	24	23	0.482	1.60	0.774	9.769e+008
2	116	21	20	0.472	1.381	0.823	5.007e+011
3	149	23	22	0.482	1.471	1.124	2.196e+019
4	216	15	14	0.470	1.363	2.118	2.201e+023
5	230	17	16.5	0.483	1.406	2.0	1.563e+018

Table 4-11.Glow Curve Parameter for X-irradiated (30 min) - After 20 min

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(ev)**	**Frequency Factor**
1	108	24.5	23.7	0.492	1.6	0.775	9.769e+007
2	116	21	20.1	0.482	1.486	0.933	5.007e+011
3	149	24.5	22.2	0.481	1.471	0.977	2.196e+021
4	216	15	13.9	0.470	1.364	2.228	2.201e+022
5	230	17	16.6	0.484	1.506	1.95	1.563e+015

Table 4-12.Glow Curve Parameter for X-irradiated (40 min) - Immediately

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(ev)**	**Frequency Factor**
1	106	24	23.7	0.498	1.610	0.984	7.769e+009
2	116.5	21	20.5	0.472	1.287	0.813	6.007e+011
3	144	24	23	0.482	1.572	0.876	4.196e+018
4	217	15.4	13	0.571	1.963	2.228	1.201e+021
5	229	17.8	16.7	0.428	1.705	2.0	1.563e+018

Table 4-13.Glow Curve Parameter for X- irradiated (40 min) - After 10 min

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(ev)**	**Frequency Factor**
1	107	24	23.6	0.494	1.60	0.784	5.769e+010
2	116	22	20.1	0.488	1.487	0.933	9.007e+012
3	143	24	23.5	0.487	2.123	0.967	3.196e+020
4	220	15	14.0	0.470	1.423	1.138	2.201e+020
5	227	17.9	16.8	0.483	1.511	1.982	3.564e+019

Table 4-14.Glow Curve Parameter for X- irradiated (40 min) - After 20 min

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy(ev)**	**Frequency Factor**
1	106	26	25.6	0.433	1.613	0.474	8.769e+009
2	116	22.8	22	0.492	1.846	0.832	5.006e+010
3	144	25	24.5	0.471	1.714	0.978	3.354e+020
4	217	15.8	13.6	0.478	1.436	2.129	2.211e+021
5	229	17	16.6	0.424	1.615	1.981	2.553e+019

Table 4-15.Glow Curve Parameter for X irradiated (60 min)-Immediately

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy**	**Frequency Factor**
1	109	21	20.8	0.675	1.713	1.342	3.719e+009
2	130	20	19.2	0.945	1.682	1.101	3.203e+011
3	217.5	23.4	22.6	0.842	1.591	1.66	2.751e+012

Table 4-16.Glow Curve Parameter for X irradiated (60 min) - After 10 min

Peak	**Peak Temperature(°C)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy**	**Frequency Factor**
1	110	25	24.5	0.490	1.345	1.832	6.101e+009
2	132	21.4	20.5	0.488	1.80	1.453	2.433e+010
3	217	22	21.6	0.581	1.274	1.882	4.132e+013

Table 4-17.Glow Curve Parameter for X irradiated (60 min)- After 20 min

Peak	**Peak Temperature(ºC)**	**τ**	**δ**	**μ_g**	**Kinetic Order**	**Activation Energy**	**Frequency Factor**
1	111	26	25	0.834	1.762	1.987	6.719e+0010
2	130	21	20.7	0.761	1.562	1.124	5.483e+011
3	218	22	21.6	0.890	1.223	1.762	3.751e+013