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# Thermally Stimulated Luminescence Study of Vitamin-E Containing Ultra-High Molecular weight Polyethylene(UHMWPE)

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# THERMALLY STIMULATED LUMINESCENCE STUDY OF VITAMIN-E CONTAINING ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE)

by

Dereje Nigatu Abdi

A Thesis

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# Abstract

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Oxidative degradation of ultra-high molecular weight polyethylene (UHMWPE) due to gamma- irradiation has been a major concern in total hip and knee joint arthroplasty. Irradiation (gamma or electron beam) is used for sterilization or crosslinking of UHMWPE. However, in the past decade the use of the biocompatible stabilizer alpha-tocopherol (vitamin-E) has been introduced to reduce or eliminate radiation-induced oxidation of UHMWPE. In conjunction with electron spin resonance (ESR) and Fourier Transform infrared (FTIR) spectroscopy, thermally stimulated luminescence (TSL) technique was employed in this study. TSL of gamma irradiated UHMWPE with or without vitamin E shows multiple glow peaks originating from the species resulting from reaction of free radicals with oxygen following irradiation. Major peaks near 140, 210, and 240$^{o}$C are observed only in UHMWPE, whereas an additional strong peak near 180 $^{o}$C is observed in vitamin-E containing UHMWPE. The glow peaks in UHMWPE-without-vitamin E are weak when irradiation is performed in nitrogen; they subsequently start to grow as a function of aging in air, suggesting that these peaks (or luminescence at these temperatures) are produced by species formed after the reaction of oxygen with the free radicals. However, in the presence of vitamin E, these peaks are found to decrease in intensity as a function of aging. The antioxidation effect of vitamin E is found to be more pronounced in the TSL data than in those obtained from ESR or FTIR measurements.

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# CHAPTER 1

# INTRODUCTION

Ionization energy is used for many industrial purposes, including treatment of medical equipment, sterilization of food and polymer processing. The dose used for sterilization of polymer to eradicate microorganisms can reach up to 40 KGy and the dose used for crosslinking can reach up to 100 KGy [1]. However gamma irradiation used for sterilization of ultra-high molecular weight polyethylene (UHMWPE), as well as the mechanical stress and chemical interactions within the body after implantation may contribute to degradation of the material [2-4]. The effect caused by gamma-irradiation on UHMWPE has been discussed since the late 1968, including the study of various irradiation methods such as dose rates and irradiation environment.

Ultra-high molecular weight polyethylene (UHMWPE), a semi crystalline polymer with a molecular weight of approximately 2-6 million grams per mole is commonly used for components of total hip and knee joint replacements. It serves as a load bearing or articulating surface in the joint replacement [5]. The very high molecular weight, extremely low coefficient of friction, high wear resistance and lack of the reactivity in the body makes UHMWPE a material of choice in arthroplasty. The melting point of UHMWPE is above 120 $^{o}$C and the viscosity of the melt is so high that it cannot be processed with a normal processing technique such as extrusion and injection moulding. The material is instead compression moulded or ram-extruded into blocks; such as acetabular cups are then machined from these blocks.  Medical grade UHMWPE is a linear polymer with low concentration chain imperfection and it is generally additive free, in compliance with ASTM F648-07 [6].

Reports published in the last few decades do show some failure of UHMWPE components in medical devices [9-14]. The major cause of these failures may be the absence of stabilizing additives for the oxidation process may be caused by free radicals remaining in irradiated UHMWPE, ultimately resulting in oxidative degradation of components. Therefore, stabilization of UHMWPE has been of primary relevance and in the recent past, ASTM F2656-07 introduced the possibility to use alpha-tocopherol (α-T) - or synthetic vitamin-E, a natural antioxidant [7]. Studies done in the past suggest no oxidation or limited oxidation in vitamin E stabilized medical grade UHMWPE [16-18]. Techniques including electron spin resonance (ESR), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) have been used to explore the stabilizing effect of vitamin E and the mechanisms involved in the post-irradiation oxidation process. However, for this study we have used thermally stimulated luminescence (TSL), to investigate the post-irradiation oxidation process in vitamin E containing medical grade UHMWPE. A number of papers have been published in the past on both low and high temperature TSL of high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) [30-32]. During storage of irradiated UHMWPE in oxygen or air, the polymer begins to degrade due to oxidation and an oxidation product is produced in the polymer. The oxidized species produced as a result of oxidation are carbonyl, hydroperoxide and peroxy, and these species greatly affect the luminescence output.

Since the first report of Randall and Wilkins on phosphorescence properties of organic polymers, a number of researchers have worked to understand the mechanisms and origin of TSL from different types of polymers [30, 31]. A thermally stimulated luminescence technique involves the heating of a material at a constant rate to observe the emission of light, known as luminescence, from a material previous absorption of energy from an exciting radiation source. The origin of TSL of irradiated polyethylene is the recombination of trapped charges, which are formed during the irradiation of the material; the trapped charges are then released by molecular motion caused by the heating of the sample. The Charlesby and Partridge TSL model of irradiated polyethylene shows that three TSL peaks are related to two known transition region of polyethylene, the crystalline and amorphous regions [34]. They suggest that this TSL is due to a previously ionized carbonyl group - probably attached to the ends of molecular chain or end sides of a chain of polyethylene, capturing a thermally de-trapped electron and then shifting to an excited state and then de-exciting by emitting a photon which creates the luminescence [33-36]. Another model, proposed by K. Jacobson, involves UHMWPE that is oxidized by heating in oxygen environment; suggest that TSL output is due to the decomposition of peroxide or hydroperoxides into excited carbonyl groups [37-39].

Based on the above two models, this thesis will try to understand the mechanism of TSL in medical grade UHMWPE powder resin which has been blended with vitamin E and apply TSL techniques to systematically study the oxidation process in the material. Furthermore we will also use ESR in a complementary manner to better analyze the process subsequent to irradiation in these materials.

Existing literature primarily contains information about consolidated UHMWPE (UHMWPE powder resin which has been compression molded into a solid form). However in this thesis we have studied UHMWPE resin powder in an attempt to obtain a more basic under-standing of the activity, radiation-induced or the free radical-induced in UHMWPE. More importantly, since oxygen can diffuse into powder relatively easily, the purpose of this study is to gain a better understanding of the oxidation mechanism during post-gamma aging in the presence of oxygen (air). The experimental work is done on GUR 1050 and GUR 1050-E. GUR 1050 is a type of UHMWPE resin powder made by Ticona and GUR 1050-E is GUR 1050 containing 1000 ppm vitamin E via blending method.

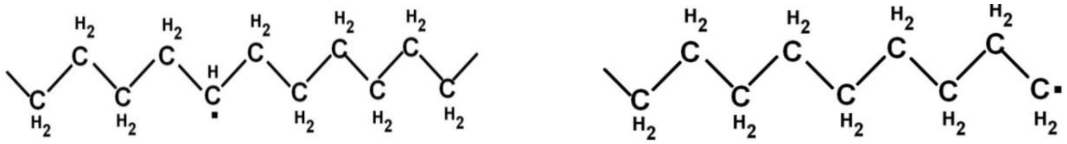
# CHAPTER 2

# BACKGROUND

## 2.1 Effect of sterilization

As the name implies, ultra-high molecular weight polyethylene (UHMWPE) is made up of extremely long chain of polyethylene monomers with molecular weight of 2-6 million g/mole, density ranging from 0.94-0.97 g/ml, and tensile strength of 21 MPa [5]. Prior to implant within the body, UHMWPE must be sterilized to prevent contamination. The methods applied for sterilizations includes, gamma irradiation, electron beam irradiation (e-beam), ethylene oxide gas treatment (Eto), gas plasma treatment and most recently proton irradiation [9-12] . Gamma irradiation is one of the most common methods of sterilization currently in use and the common source is cobalt ($^{60}$Co) and the photon in this case has energies of 1.17-1.33 MeV [13, 14].

Gamma sterilization involves irradiation of the polymer component with gamma rays. When the high energy photons are incident on the polymer, they start to interact with the atoms in the polymer being penetrated, causing electron or electrons to be set in motion with some kinetic energy. The energy transferred in the medium is called KERMA (Kinetic Energy Released in the Medium) [14]. These high energy electrons will start to transfer their energy to the polymer matrix by exciting and ionizing of other electron(s), breaking the C-C and C-H bonds and forming unwanted species called free radicals. The destructive effect of the electron will stop when it is captured by the ions in the medium. So the electron may immediately recombine with the ion or become trapped in the polymer matrix. Three types of primary radicals will be formed immediately upon irradiation namely alkyl, allyl, and polyenyl as shown in Figs. 2-1, 2-2, and 2-3 below [15].



Chain type

End type

Fig. 2-1. The chemical structure of alkyl radicals.

Chain type

End type

Fig. 2-2. The chemical structure of allyl radicals.

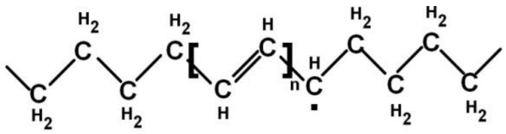


Fig. 2-3. The chemical structure of polyenyl radicals.

The various radicals resulting from irradiation will differ in their mobility. For example, hydrogen radicals formed by the cleavage of C-H bonds is the most mobile, whereas the radicals formed during cleavage of the backbone are less mobile [14]. The mobility of radicals is also limited by the amount of free volume available in the polymer matrix. Crystalline areas will not allow much chain mobility, whereas amorphous areas will allow chain mobility and radicals reaction are fast. Therefore, radical reactions depend on the mobility and available free volume, availability of other free radicals and accessibility of other reactive species like oxygen. At room temperature the generation of free radicals and the reaction of free radicals will occur simultaneously, resulting in the formation of carbon-carbon double bonds, which is postulated to be a result of the occurrences of two end type alkyl radicals next two each other.

If free radicals are not stabilized, they may react with oxygen, resulting in the formation of oxidation products while oxygen penetrates the material via diffusion. Immediately after irradiation alky radical can react with oxygen and form peroxy radicals (See Fig. 2-4a). These peroxy radicals (due to high electron affinity) then abstract hydrogen from the polyethylene chain, creating primary free radicals, which then react with oxygen to further cascade the oxidation process [16]. When peroxy radicals are hydrogenated, they will form hydroperoxides (see Fig. 2-4b), which are not stable and degrade over time into oxidation products - mainly ketones, esters and carboxylic acids (see Fig. 2-5) [22]. These oxidation products will result in chain scission and decrease the molecular weight of the polyethylene, leading to oxidative degradation of the polymer and deteriorations of its mechanical properties. Therefore, antioxidant additives have been introduced to stabilize free radicals.

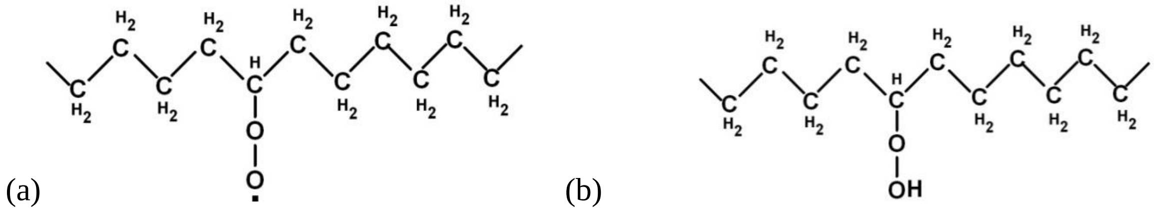


Fig. 2-4. The chemical structure of: (a) Peroxy radicals and (b) hydroperoxides.

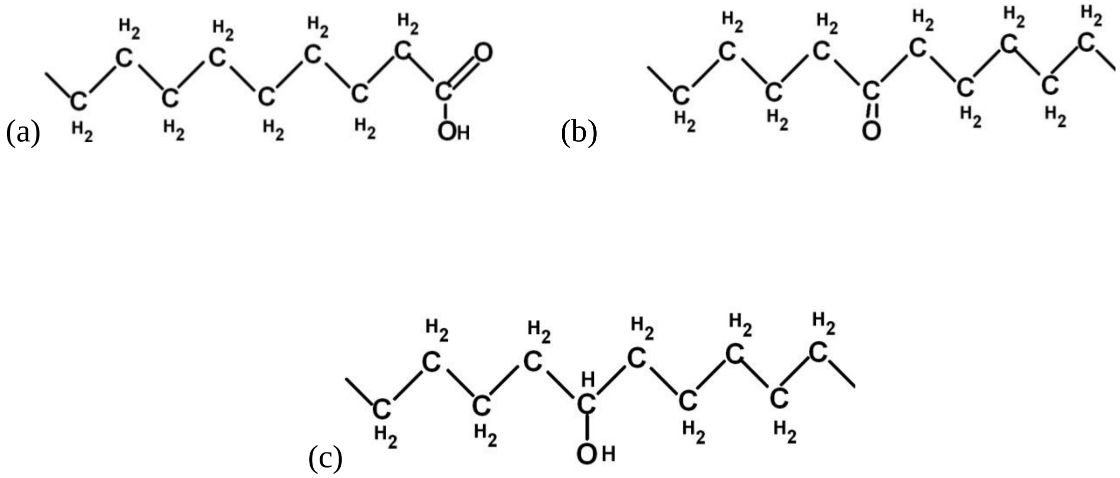


Fig. 2-5. The chemical structure of the major oxidation products in irradiated polyethylene: (a) carboxylic acid, (b) ketone and (c) ester.

## 2.2 Vitamin E as antioxidant

Antioxidants are molecules which can safely react with free radicals and terminate the chain reaction before vital molecules are damaged. Although there are several enzyme systems within the body that scavenge free radicals, the principal micronutrient (vitamin) antioxidants are vitamin E, beta-carotene, and vitamin C. Vitamin E is found naturally in some foods, added to others, and available as a dietary supplement. "Vitamin E" is the collective name for a group of fat-soluble compounds with distinctive antioxidant activities. Vitamin exists in eight chemical forms (alpha-, beta-, gamma-, and delta-tocopherol and alpha-, beta-, gamma-, and delta-tocotrienol) that have varying levels of biological activity. Alpha- (or α-) tocopherol is the only form that is recognized to meet human requirements. Due to its biocompatibility and low toxicity [16-18], vitamin E (α-tocopherol (α-T)) has been used in UHMWPE to fight oxidative degradation and its stabilizing effect has been investigated for the past 10 years, most studies show limited or no oxidation in vitamin E containing UHMWPE depending on the concentration [19,20].

Vitamin E is incorporated into UHMWPE by two different methods, blending and diffusion [15, 21, 24]. For blending method, the UHMWPE resin is mixed with vitamin E then it can be molded in to a solid by compression and heat, and then further processing radiation crosslinking or sterilization may be applied. However, with diffusion, the UHMWPE resin is first compression molded in to a solid sample, then the sample is typically cross-linked by radiation, and then the sample is immersed in to a bath of hot vitamin E for diffusion until the desired amount is incorporated in the material. Finally, the material will be removed from the hot vitamin E bath and will be heated to allow the vitamin E to spread throughout the material, this process is called homogenization. Alpha-Tocopherol is an antioxidant and its main role in vivo or in vitro is to stabilize the active free radicals resulting from the oxidation of polyunsaturated fatty acids in the cell membranes or the oxidation of UHMWPE chain respectively. Alpha-tocopherol long lipophilic chain (termed as "phytyl tail") provides compatibility with UHMWPE chain and the chroman head donates its phenolic hydrogen to stabilize the free radicals in UHMWPE [17]. The chemical structure of alpha-tocopherol and alpha-tocopherol radical is shown in Fig. 2-6.

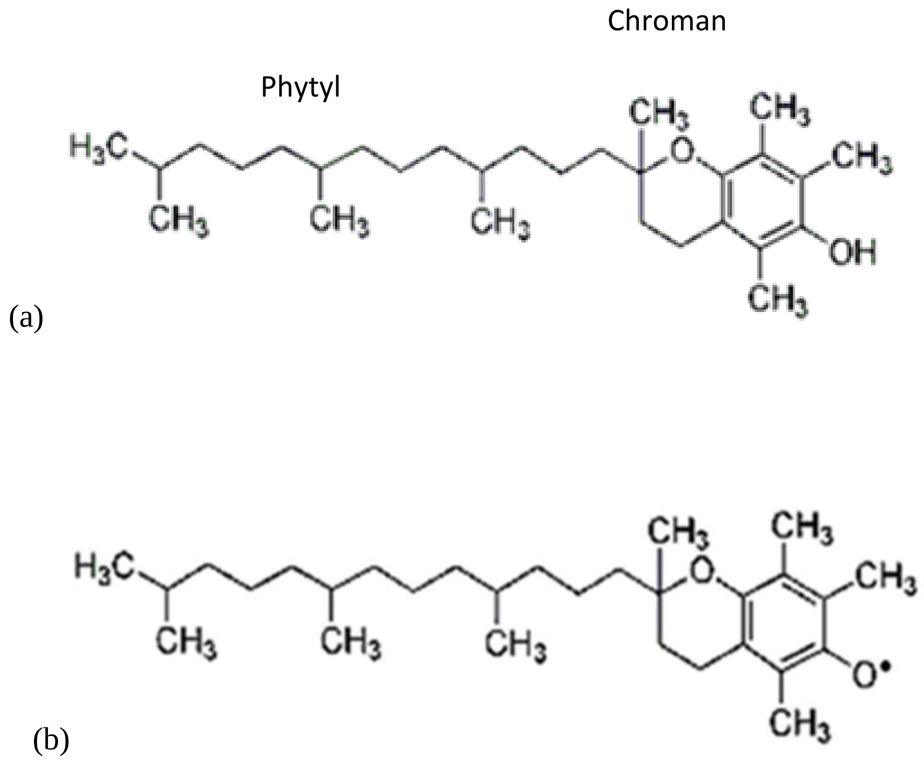


Fig. 2-6. The chemical structure of: (a) Alpha-tocopherol (α-T) and (b) an alpha-tocopherol radical (α-T-O$^*$).

## 2.3 Methods of study

Several methods have been applied in the past to study polyethylene including differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), Electron spin resonance (ESR), and Imaging chemiluminescence (ICL). With these methods, various properties of polyethylene 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 UHMWPE (with or without vitamin E). Therefore, in this thesis, in addition to ESR and FTIR, TSL method is used in detail to study UHMWPE. A brief outline of each method is discussed in the following sections.

### 2.3.1 Thermally Stimulated Luminescence (TSL)

#### Radiation Effect

Solid state luminescence is a process in which energy is released by molecules or atoms upon heating following initial excitation (typically by irradiation) by a source of energy [27]. The means 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 exception to this rule is emission by recombination of trapped charges that are created by ionizing radiation and released by thermal stimulation. This type of emission is known as thermally stimulated luminescence (TSL), sometimes called thermoluminescence (TL).

The mechanism of TSL involves two steps [28]. In the first step 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). The intensity of the luminescence as a function of temperature, which possibly exhibit several maxima, is called a thermally stimulated luminescence (or thermoluminescence) glow curve. This glow curve reveals information about the traps created by radiation such as the number of initial sites and trap depth. The glow curve characteristics, such as the number of peaks, peak shape, the peak emission spectral composition which is dependent on the given sample, and the nature of the initial excitation source such as UV light, gamma ray or electron beam. The glow curve also depends on the excitation dose and the dose rate [29].

The interaction of radiation with matter produces numerous changes in both the indigenous lattice ion and the impurities present in a solid. The most noticeable effect of these interactions during radiation is the resultant crystalline defects (ionic defects), the energy released from the increased number of electrons free to move about until trapped (electronic defects), and dislocation loops and voids (gross imperfection). When radiation is applied to the solid the valence electrons of the lattice and the impurities atom will be excited. As a result electrons will be excited to the conduction band and holes to the valence band. In the electronic defects the valence state of both the impurities and lattice defects can be changed by trapping electrons and holes created elsewhere in the lattice by radiation. In ionic defects the vital role is played by the vacancies which are produced when an atom or ion is missing from its normal site in the crystal structure. Vacancies are one of the most known products of radiation damage.

## Theory of thermally stimulated luminescence

In thermally stimulated luminescence solid which has been exposed to exciting radiation will be heated at a constant rate. During warming, thermal relaxation will occur and the electrons and holes may escape from metastable states or traps. The probability of thermal excitation of charge carrier from the traps is expressed using Boltzmann factor and is given by the equation [27]

$$P=s\ \exp\left(-\frac{E}{kT}\right) \qquad 2\text{-}1$$

Where s is a pre-exponential factor on the order of $10^{11}\ s^{-1}$-$10^{14}\ s^{-1}$ which is the frequency of the lattice vibration and is called frequency factor, E is the thermal activation energy required to liberate a trapped electrons, k is the Boltzmann constant and T is absolute temperature. The number of electrons released per unit time is also proportional to the total concentration of trapped electrons (n). [30,31]The rate of production of emitted photons in the Randall-Wilkins model which involves a single trap and recombination center is therefore given by

$$I_{TL} = -\frac{dn}{dt} = ns\exp\left(-\frac{E}{kT}\right) \qquad 2\text{-}2$$

After solving this equation for n and substituting for n will result in the equation

$$I_{TL} = sn_o\ \exp\left(-\frac{E}{kT}\right)\exp\left\{-\left[\frac{s}{\beta}\right]\int_{To}^{T}\exp\left\{-\frac{E}{K\theta}\right\}d\theta\right\} \qquad 2\text{-}3$$

Where $n_o$ is the initial concentration of the trapped electrons, θ represents the varying temperature, and β is the constant rate of heating. This model does not allow for any retrapping of free electrons or even their spending time in the conduction band before recombining with holes. This equation is the Randall-Wilkins first order expression of TL glow curve intensity. In another model, Garlick and Gibson considered an alternative possibility that retrapping dominates and derived the expression for the rate of decay as follows [25]

$$I_{TL} = -\frac{dn}{dt} = (\frac{n^2}{N}) S \exp(-\frac{E}{kT}) \qquad 2\text{-}4$$

Integrating and substituting for n yields

$$I_{TL} = \frac{(n_o^2/N) \, S \exp(-\frac{E}{kT})}{[1+[\frac{ns}{\beta N}] \int_{To}^{T} \exp\left\{-\frac{E}{K\theta}\right\} d\theta]\hat{}2} \qquad 2\text{-}5$$

where N is the number of trapped electrons. In equation 2-3 and 2-5, the order of kinetics is specified as 1 and 2, respectively. [41]The general order of kinetics was later formulate by Partridge and May the decay equation with, b being the order of kinetics, is given by

$$I_{TL} = -\frac{dn}{dt} = (\frac{n^b}{N^{b-1}}) S \exp(-\frac{E}{kT}) \ . \qquad 2\text{-}6$$

Integrating and substituting for n yields

$$I_{TL} = \frac{n_o^2\hat{}b \; S \exp(-\frac{E}{kT}) N^b}{[1+[\frac{(b-n)s(\frac{n^b}{N^{b-1}})}{\beta}] \int_{To}^{T} \exp\left\{-\frac{E}{K\theta}\right\} d\theta]\hat{}b/b-1} \qquad 2\text{-}7$$

From a TSL experiment we can determine the glow peak parameters such as activation energy, order of kinetics and frequency factor [28]. The temperature-dependent activation energy (E) of an electron to escape a trap was determined to be

$$E = \left[2.52 + 10.2(\mu_g - 0.42)\right]\left(\frac{KT_m}{\omega}\right) - 2KT_m \qquad 2\text{-}8$$

Where ω = δ + τ is the full width half maximum and δ and τ are the high and low temperature half widths respectively as shown Fig 2-7. $\mu_g = \delta/\omega$ is an asymmetric parameter of a glow curve which determines the kinetic order and $T_m$ is the maximum peak temperature. For first order kinetics the symmetric factor $\mu_g$ is approximatelly 0.42 [26] and the above equation can reduce into

$$E = [2.52]\left(\frac{KT_m}{\omega}\right) - 2KT_m \qquad 2\text{-}9$$

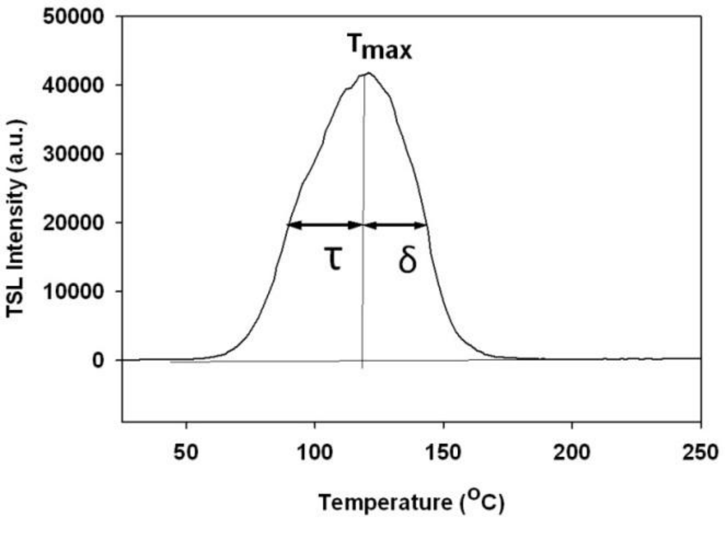


Fig. 2-7. A schematic TSL peak showing the maximum temperature $T_{max}$, the derived low temperature half width τ, and high temperature half width δ.

### 2.3.2 Electron Spin Resonance (ESR)

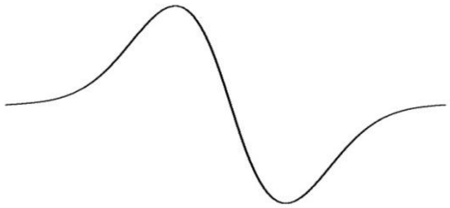
The molecules of solid can exhibit paramagnetism as a result of unpaired electron spins. The atoms or molecules which have an unpaired electron in their outer most shell are called free radicals. Free radicals are typically very unstable and react quickly with other compounds, trying to capture the needed electron to regain their stability. Free radicals can be created by ionization energy used to cross-link or sterilize a polymer solid. Free radicals can further break down the polymer backbone by abstracting hydrogen from the polymer chain, which creates radicals from the once stable molecules. The only instrument that can directly detect free radicals in a given material is electron spin resonance (ESR) spectrometer, also known as Electron paramagnetic resonance (EPR). When an external magnetic field (B) is applied, 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. Hence, two states will be formed as a result, 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 by supplying electromagnetic energy, usually 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 $\mu_B$ and by equating with the absorbed microwave frequency $(h\nu)$ we can obtain the electron spin g-factor, which is

$$E = g\mu_B \mathrm{B} M_s = \pm\frac{1}{2} g\mu_B B$$

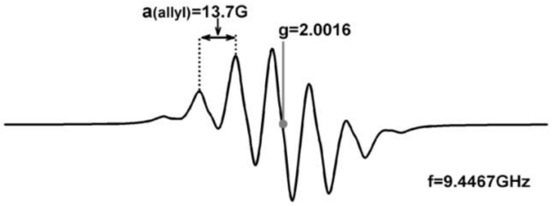
$$\Delta E = h\nu = g\mu_B \mathrm{B}$$

$$g = h\nu / B\mu_B \qquad 2\text{-}9$$

polyenyl radical



Allyl radical



Alkyl radical

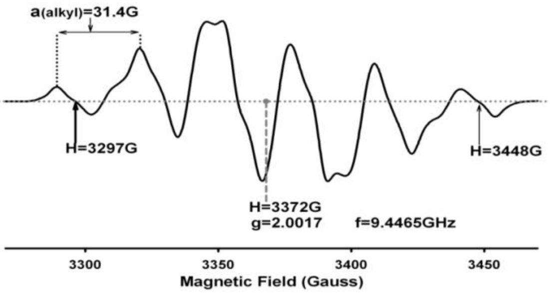


Fig. 2-8. The ESR spectra of primary radicals.

The ESR signal is the first or second derivative of the absorption spectrum generated from the net loss energy; by integrating the ESR spectra we can estimate the quantity of free radicals for a given sample. The ESR spectra of polyethylene radicals are shown in Fig. 2-8, the ESR spectrum of vitamin-E (α-tocopherol) radical is shown in the Fig. 2-9.

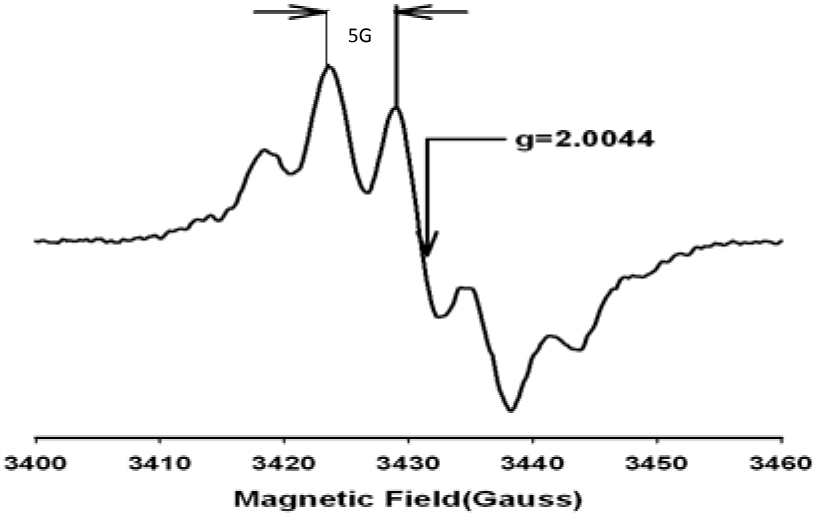


Fig. 2-9. The ESR spectra of Alpha-Tocopehrol (vitamin-E) radical.

### 2.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is the preferred method of infrared spectroscopy in which infrared light is passed through the sample whereby some of the infrared light will be absorbed by the sample and some of it is passed through (transmitted). The infrared spectrum represents a finger-print of a sample with absorption peak(s) which correspond to the frequencies of vibration between the bonds of atoms making up the material. The resulting spectrum will provide information about the sample, including the identity of the unknown material, the quality or consistency of the sample, and determine the amount of particular component within a mixture. FTIR can be used to determine the extent of oxidation in UHMWPE. Hydroperoxide, ketones, carboxylic acids and alcohols are formed as a result of post oxidation processes in UHMWPE. The degree of oxidation can be determined by the ketone absorption at 1718 $cm^{-1}$, the hydrogen bonded hydroperoxides absorption at 3420 $cm^{-1}$ and the non-hydrogen bonded hydroperoxide absorption at 3605 $cm^{-1}$ [22]. According to the ASTM F2102-06 an oxidation index (OI) for a solid sample is defined as the ratio of the area of the carbonyl absorption peak(s) centered near 1720 $cm^{-1}$ to the area of the absorption peak(s) centered near 1370 $cm^{-1}$.Fig. 2-10 represent the FTIR spectrum of UHMWPE.

$$\text{Oxidation Index (OI)} = \frac{area\ under\ absorption\ peak\ centered\ at\ 172\ cm^{-1}}{area\ under\ absorption\ peak\ centered\ at\ 1370\ cm^{-1}}$$

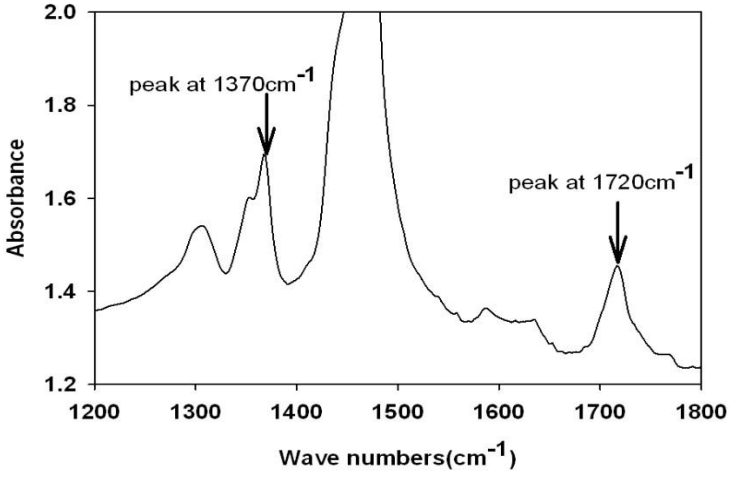


Fig. 2-10. FTIR spectrum of UHMWPE (ASTM F2102 06).

## 2.4 Literature Review

### TSL in polyethylene

TSL in irradiated inorganic materials has been a subject of study for over 60 years, especially since the work of Randall and Wilkins. Randall et al. studied the phosphorescence properties of different types of powder phosphor which are excited first with a short wave-length ultra-violet light from quartz mercury arc while kept cold in liquid air [30]. After all the traps in the powder were filled, the mercury arc was switched off and the sample was heated at a constant rate; the glow produced during heating was then observed. They found that the thermal glow curves of phosphors activated by different types of metals shows different peaks centered at different maximum temperatures, which corresponds to different activation energies of the trap depth.

In 1990, R.J. Fleming studied the origins of TSL in different types of polymers and suggested that their luminescence was due to the recombination of electrons at luminescence centers which were escaping from their traps upon heating [32]. He conducted his experiment on polyethylene at low temperature and found that the TSL glow curve contains three different peaks at different maximum temperatures. Fleming proposed that the peak near 100 K was due to oscillatory or rotational motion of short side chains attached to the main chain, and that the peak near 160 K was due to crank shaft motion of short main-chain segments between sterically-permitted configurations, and that the peak near 225 K was due to the glass transition. Fleming also suggested that all these peaks were due to the properties of the amorphous regions of the sample.

In their 1960’s papers, Charlesby and Partridge conducted experiments on the TSL of irradiated polyethylene and other polymers [33-36]. Their experiments involved irradiating different types of polymers at liquid nitrogen temperature (77 K) using a $^{60}$Co Ɣ-source at a maximum dose of 0.6 Mad/h; the light output from the samples was detected by heating the sample. All of the polymers investigated in their experiments showed some degree of luminescence once the samples reached room temperature. According to their observations the most interesting glow curve was that of the polyethylene which contained multiple peaks, and their sensitivity to oxygen. Charlesby and Partridge also investigated the dependence of these peaks on irradiation dose, the presence of oxygen and the heating rate. They showed that intensity of the luminescence start to decrease after an irradiation dose of 1 Mrad, and suggested these decreases cannot ascribed to saturation, but due to the damaging effect of radiation. They also showed that, in the presence of oxygen, the oxygen molecule acts as a trap for the electron, thereby affecting the glow peak of irradiated polyethylene.

TSL studies of polyethylene, both at low and high temperature, have shown three major peaks when in the absence of oxygen and four peaks in the presence of oxygen [40-43]. Jahan et al. studied gamma irradiated medical grade UHMWPE using TSL techniques to understand the effect of post-irradiation storage condition such as liquid nitrogen(LN), saline solution at 37 $^{o}$C, and a dry atmosphere at RT. They observed three high temperature peaks (near 140, 220, and 240 $^{o}$C) in which the appearance of each peak was dependent on the storage environment [43]. They asserted that the peak near 140 $^{o}$C is attributed to the alkyl radicals, and they speculate that the 220 and 240 $^{o}$C peak may be associated with the bond-scission and cross-linking processes.

Meggitt and Charlesby investigated the TSL of untreated samples of low density polyethylene and biphenyl-treated samples at low temperatures. They observed three peaks, with the largest peak centered near 231 K, for the untreated samples and a very prominent high temperature peak centered at 217 K for the biphenyl treated samples [40]. Their investigation suggests that in samples treated with biphenyl, the biphenyl captures electrons and luminescence occurs when the holes, trapped in the polymer matrix following irradiation, are released thermally and migrate towards the biphenyl.

### ESR and FTIR of Polyethylene

Polyethylene has been studied intensively in the past in terms of radicals generated by irradiation and the subsequent oxidation of the material [10-14, 26]. Early studies showed that gamma irradiation of UHMWPE leads to the formation free radicals which can persist even after a long shelf-life, especially if irradiation takes place in an oxygen free environment. These free radicals can react with oxygen such as from tissue fluids, which can lead to oxidative degradation of the implant in vivo [14]. However, the diffusion of reactive species like oxygen, entering into the implant surface in vivo is much lower due to the lower concentration of oxygen in the tissue fluid compared to the oxygen concentration in the air. If shelf aged in air, the oxygen diffusing into the polymer matrix will result in the post-irradiation oxidative degradation of UHMWPE, affecting the wear performance of the polyethylene [22,30]. Due to the free radicals have limited mobility in the crystalline region, where they remain for long time unchanged. It has been suggested that irradiation in air and subsequent storage in air will increase both the long term and short term oxidation. Higher wear rates have been observed with aging of UHMWPE in, where oxidative degradation and chain scission predominate. Premnath et al. have suggested that sterilization by irradiation in an inert atmosphere or vacuum will reduce the degree of oxidation [14]. Costa et al. studied the effects of irradiation dose on the formation of oxidation products using FTIR showing that hydroperoxide concentration increases proportionally up to a dose of 30 kGY and then plateaus, suggesting that at 30 kGY the production of hydroperoxides is limited by the quantity of radicals in the polymer while for higher irradiation doses, there are excess free radicals and therefore oxygen diffusion becomes the limiting factor in the production of hydroperoxides [11].

The motivation for crosslinking of ultra-high molecular weight polyethylene with a high energy radiation and heat treatment has been developed in the past to improve oxidation degradation in the material [1, 37, 38]. Oral and Muratoglu studied oxidation, wear and fatigue resistance bearing surface made from highly cross-linked UHMWPE (XLPE) [1]. They suggest that to optimize both wear resistance and fatigue strength, UHMWPE must be cross-linked at radiation doses ranging from 50 to 100 kGy. They also suggest that thermal treatment of highly cross-linked UHMWPE above the melting point subsequent to irradiation results in better wear resistance and oxidative stability of the UHMWPE. The high temperature will melt the crystalline region, allowing the recombination of the trapped free radicals in these regions. Once the polymer is re-crystallized and the free radicals have been eliminated, wear resistant and oxidation-resistant UHMWPE will be achieved. However, Oral and Muratoglu also found that post-irradiation melting further decreases the fatigue strength of UHMWPE due to the decrease in the crystallinity accompanying the melting of the polymer.

The stabilizing effect of vitamin E upon polyethylene free radicals has also been investigated in depth over the past 10 years [16-19]. Bracco et al. studied the effect of vitamin E as an antioxidant and they observed that alpha-tocopherol blended UHMWPE shows a loss of the phenol groups and they suggest two different ways of reaction [18]. The first begin a direct reaction between the phenol and alkyl macroradicals formed by irradiation (Fig. 2-10, reaction 5) [17]; the second being between macro-alkyl radicals and oxygen and producing peroxy macroradical, fixed in a defined position on the plymer chain, which can only abstract a hydrogen atom to form a hydroperoxide and a macro-alkyl radical( Fig. 2-11, reaction 7). This second reaction is inhibited in the presence of vitamin E due to the limited availability of macro-alkyl radicals and the reactions of peroxy radical with vitamin E is unlikely-this suggest that, in the presence of vitamin E there will be a limited amount of peroxide available. Oral et al. studied oxidation of UHMWPE – which, while in the powder form, was blended with vitamin E, and then compression-molded into a solid form before any irradiation treatments; they found that such blended material offered considerable oxidation resistance when the material is irradiated [16]. However, such blending with vitamin E before irradiation prevents the material from achieving an adequate crosslink density required for mechanical strength; the crosslink density is decreased because the vitamin E eliminates the radicals before they can serve to crosslink the polyethylene [emailed ref]. Jahan and Walters ESR studies of 1 and 10 wt.% α-tocopherol-blended UHMWPE samples show that the vitamin E was found to partially quench polyethylene radicals after irradiation (before exposure to air). They also suggested that the remaining polyethylene radicals decayed to oxygen induced radicals (OIR) and the sample which contained the vitamin E produced a relatively lower concentration of OIR [15]. Peltzer et al. studied elongation at break properties of compression molded UHMWPE and found an increase in flexibility with the addition of α-tocopherol; they suggested this was an important feature for food packaging material because the increase in flexibility would provide to a more versatile material to contain fresh and processed foods [23].

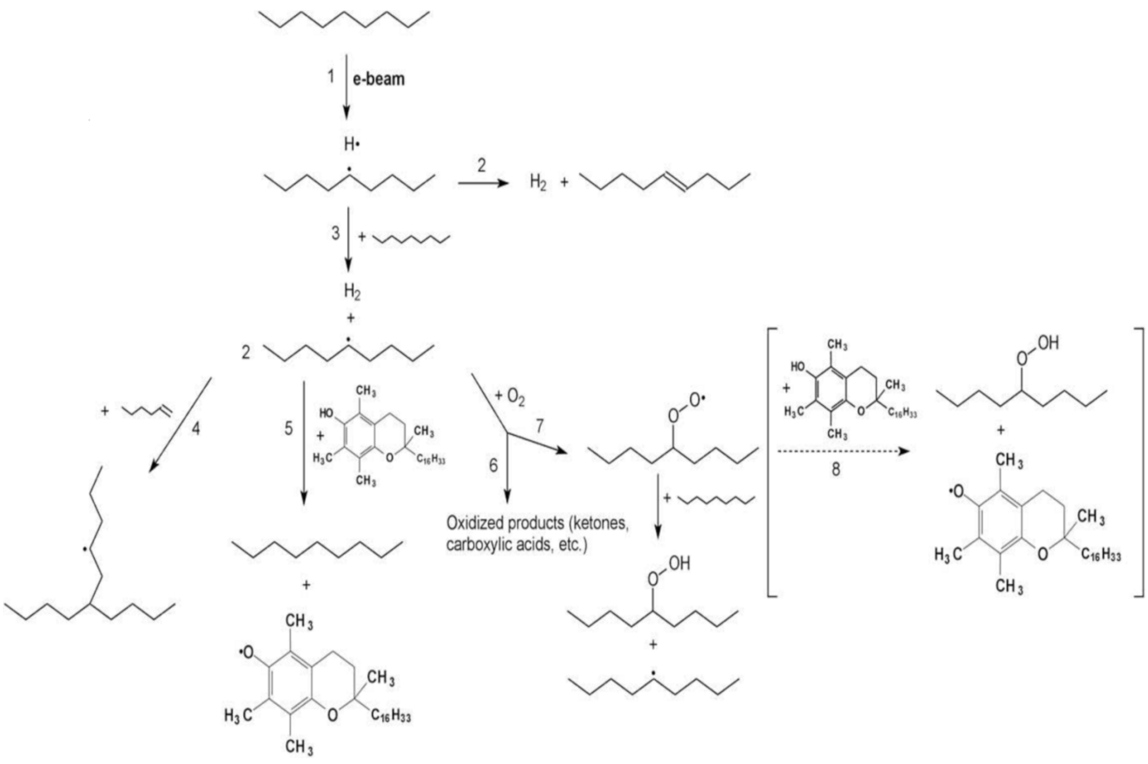


Fig. 2-11. The reaction mechanism of alpha-tocopherol and polyethylene radicals and the formation of hydroperoxides [Bracco et al.].

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Ultra-High Molecular Weight Polyethylene (UHMWPE)

For this project two sets of medical grade UHMWPE resin powder was used which is manufactured by Ticona (Oberhausen, Germany). The first set contains no vitamin E additive (GUR 1050) and the second set contains 1000ppm alpha- tocopherol (α-T) vitamin E (GUR 1050-E). GUR is a polyethylene with a very high degree of polymerization. Its molecular weight can range between 3.9 and 10.5 million gram per mole. This material is best candidate for many industrial applications especially for orthopedic implant due to its exceptionally high notched impact strength, high energy absorption capacity at high stress levels, very low wear, low friction loss, high stress crack resistance, and excellent chemical resistance to acids, alkalis and aggressive gases. A large number of literatures can be found on consolidated UHMWPE solid sample. We studied powder UHMWPE in order to obtain a more basic understanding of the activity in un-consolidated resin powder. The samples were irradiated using gamma ray at a dose of 30 kGy.

### Irradiation by gamma rays

The samples were gamma irradiated, which is a cobalt 60 ($^{60}$Co) source provided by STERIS-ISOMEDIX Services (Grove Park, OH, USA) and each sample received a radiation dose of 30 kGy which is commonly used for sterilization of medical implants.

There was no attempt made to remove the oxygen from the samples before irradiation. Before irradiation each set of samples was packed in polyethylene bags respective to the irradiation environment. One set of GUR 1050 samples was irradiated in nitrogen and stored in nitrogen for 69 days. The second set of samples was irradiated in nitrogen and stored in air for 90 days. The last set of samples was irradiated in air and stored in air for 90 days. The samples blended with vitamin E also irradiated and stored in a similar fashion.The initial measurement was done 10 days after the irradiation day. Samples are labeled as follows and are listed in the following tables. The GUR 1050 samples which are not blended with vitamin E are labeled nn1-nn5,na1-na6 and aa1-aa6 as samples irradiated in nitrogen and stored in nitrogen for 69 days (Table 3-3), samples irradiated in nitrogen and stored in air for 90 days (Table 3-2) and samples irradiated in air and stored in air for 90 days (Table 3-1), respectively. The samples blended with vitamin E are labeled nne1-nne5, nae1-nae6 and aae1-aae6 as samples irradiated in nitrogen and stored in nitrogen for 69 days (Table 3-6), samples irradiated in nitrogen and stored in air for 90 days (Table 3-5) and samples irradiated in air and stored in air for 90 days respectively (Table 3-4).

Table 3-1

GUR 1050 samples irradiated in air aged in air

| Samples | Irradiation Environment | Storage time in air |
|---|---|---|
| aa1 | Air | On arrival |
| aa2 | Air | 1 day |
| aa3 | Air | 14 days |
| aa4 | Air | 43 days |
| aa5 | Air | 69 days |
| aa6 | Air | 90 days |

Table 3-2

GUR 1050 samples irradiated in nitrogen aged in air

| Samples | Irradiation Environment | Storage time in air |
|---|---|---|
| na1 | $N_2$ | On arrival |
| na2 | $N_2$ | 1 day |
| na3 | $N_2$ | 14 days |
| na4 | $N_2$ | 43 days |
| na5 | $N_2$ | 69 days |
| na6 | $N_2$ | 90 days |

Table 3-3

GUR 1050 samples irradiated in nitrogen and stored in nitrogen

| Samples | Irradiation Environment | Storage time in nitrogen |
|---|---|---|
| nn1 | $N_2$ | On arrival |
| nn2 | $N_2$ | 1 day |
| nn3 | $N_2$ | 14 days |
| nn4 | $N_2$ | 43 days |
| nn5 | $N_2$ | 69 days |

Table 3-4

GUR 1050E samples irradiated in air aged in air

| Samples | Irradiation Environment | Storage time in air |
|---|---|---|
| aae1 | Air | On arrival |
| aae2 | Air | 1 day |
| aae3 | Air | 14 days |
| aae4 | Air | 43 days |
| aae5 | Air | 69 days |
| aae6 | Air | 90 days |

Table 3-5

GUR 1050E samples irradiated in nitrogen aged in air

| Samples | Irradiation Environment | Storage time in air |
|---|---|---|
| nae1 | $N_2$ | On arrival |
| nae2 | $N_2$ | 1 day |
| nae3 | $N_2$ | 14 days |
| nae4 | $N_2$ | 43 days |
| nae5 | $N_2$ | 69 days |
| nae6 | $N_2$ | 90 days |

Table 3-6

GUR 1050E samples irradiated in nitrogen and stored in nitrogen

| Samples | Irradiation Environment | Storage time in nitrogen |
|---|---|---|
| nne1 | $N_2$ | On arrival |
| nne2 | $N_2$ | 1 day |
| nne3 | $N_2$ | 14 days |
| nne4 | $N_2$ | 43 days |
| nne5 | $N_2$ | 69 days |

### 3.2 TSL measurements

TSL measurements were performed using a commercial dosimeter (Harshaw QS 3500) operated at 727 V and 12 mA. The heating chamber was continuously purged with dry, filtered nitrogen gas ($N_2$) to avoid the production of thermally oxidized radicals and moisture .A powder sample about 2.0 mg was placed in a DSC pan and leveled gently on the surface and heated from room temperature to 300 $^0$C at rate of 1 $^0$C/s. The resulting TSL glow curve was recorded as a function of temperature using the WinREMS software. Each of the glow curves were then deconvoulated into an individual glow peaks using peak-fit software. The glow peak parameters of the individual peaks were then calculated using curve fitting software from Los Almos National Laboratory. A block diagram of the TSL reader is shown in Fig. 3-1 below.

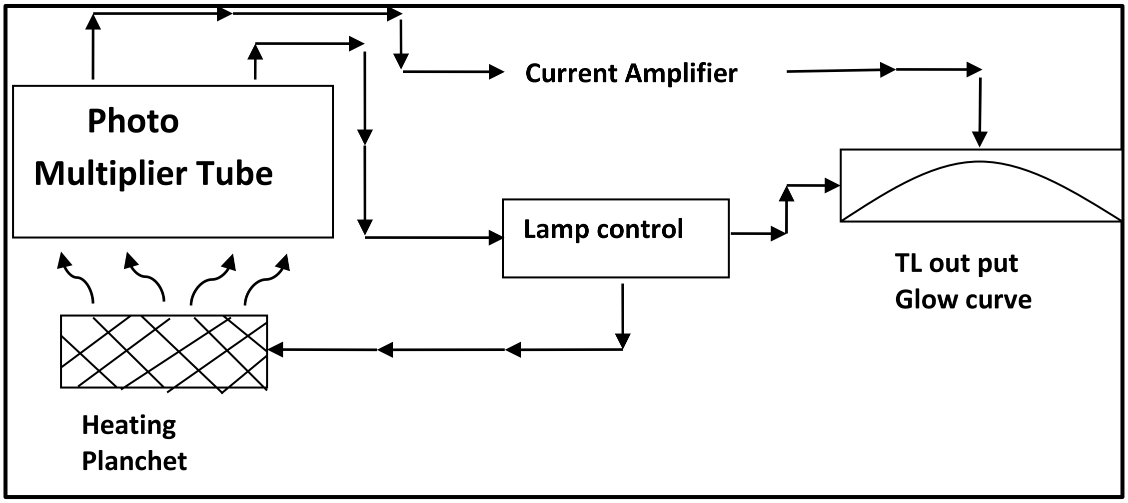


Fig. 3-1. TSL experimental setup diagram.

### 3.3 FTIR measurements

The extent of the oxidation of the polymer after 90 days of exposure in nitrogen and air were studied using an FTIR Auto Image microscopy (Perkin-Elmer). According to ASTM F2102-06 standard the extent of oxidation in a solid sample is determined by the oxidation index (OI) which is defined as the ratio of the area of carbonyl absorption peak(s) centered near 1720 $cm^{-1}$ to the area of the absorption peak(s) centered near 1370 $cm^{-1}$. However the sample we used for this study are powders, which is not addressed by ASTM, so measurement method may not applicable to this study. Nonetheless, the ASTM method may provide a relative oxidation index amongst the sample. Three sets of powder sample were tested based on 128 resolution scan.

### 3.4 Free radical measurements

For free radical measurements or detection, a very high sensitivity x-band electron spin resonance (ESR) spectrometer (EMX 300 by Bruker) was employed. The mixed mode resonator cavity of the spectrometer operates near 9.8 GHz microwave frequency, and the resonance absorption signal is detected at 100 KHz by modulating the external magnetic field at the same frequency(100 KHz).The ESR spectra(first derivative) of the three sets of each powder sample were recorded at 1mW microwave power and 5 G modulation amplitude. The ESR measurement setup is shown in Fig. 3-2 below.

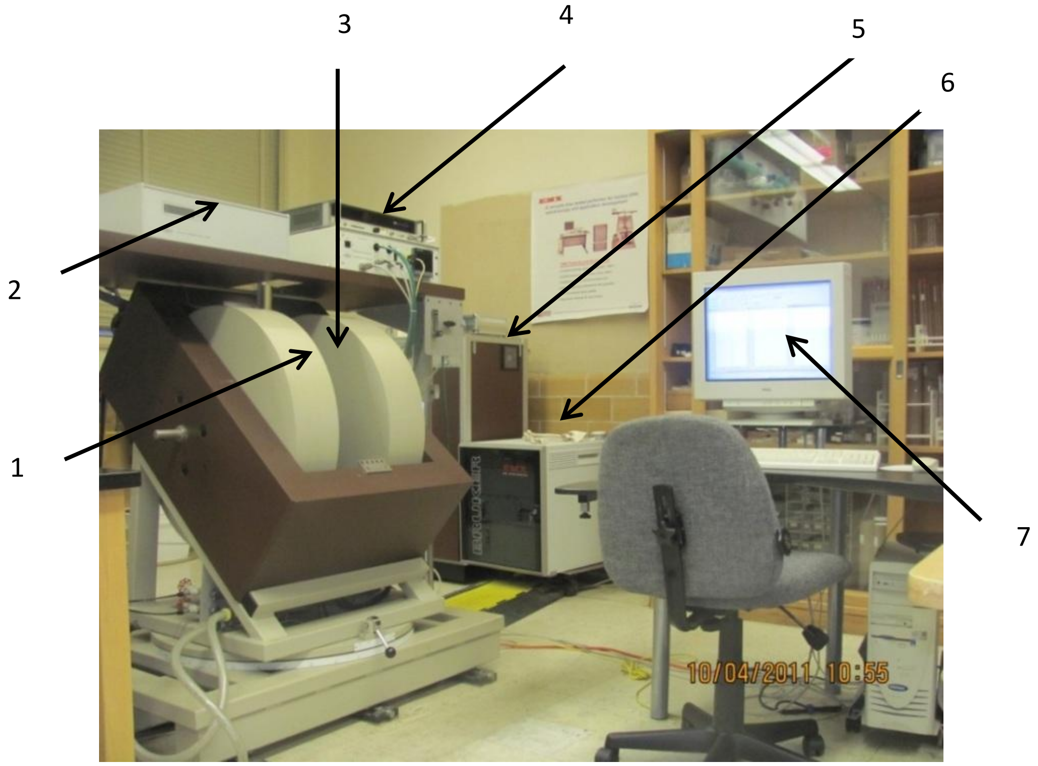


Fig. 3-2. ESR measurement setup: (1) ESR magnet, (2) X-band microwave source, (3) ESR cavity, (4) Temperature and nitrogen flow control unit, (5) Power supply, (6) Console, and (7) Data acquisition Computer.

# CHAPTER 4

## Results and Discussion

Based on the models of TSL in UHMWPE, oxidized species must be present for luminescence to occur [33, 37]

1. UHMWPE is oxidized
    a. By free radical reaction following irradiation with ionizing radiation
    b. By heating in the presence of oxygen
2. Carbonyl group or groups must pre-exist in the polymer

### 4.1 Thermally Stimulated Luminescence (TSL) of GUR 1050 and GUR 1050-E

Thermally stimulated luminescence glow curves of non-irradiated UHMWPE powder are shown in Fig. 4-1. The TSL glow curve of GUR 1050 sample has no luminescence output before the sample is irradiated. This result suggests that GUR 1050 sample has no active species responsible for light emission before undergoing irradiation. However UHMWPE containing vitamin E (GUR 1050-E) shows very minimal luminescence output before the sample is irradiated with gamma ray. This weak luminescence output in GUR1050-E sample in the temperature region 120-200 $^{o}$C might be produced by vitamin E radicals. Glow curve of gamma irradiated UHMWPE sample is shown in Fig. 4-2. The glow curve of GUR 1050 shows major peaks near 110 ,140 and 280 $^{o}$C and curve fit analysis shows additional (minor) peaks near 160 $^{o}$C and 210 $^{o}$C when irradiation is done in inert atmosphere (Fig. 4-2a) (in the presence of Nitrogen).

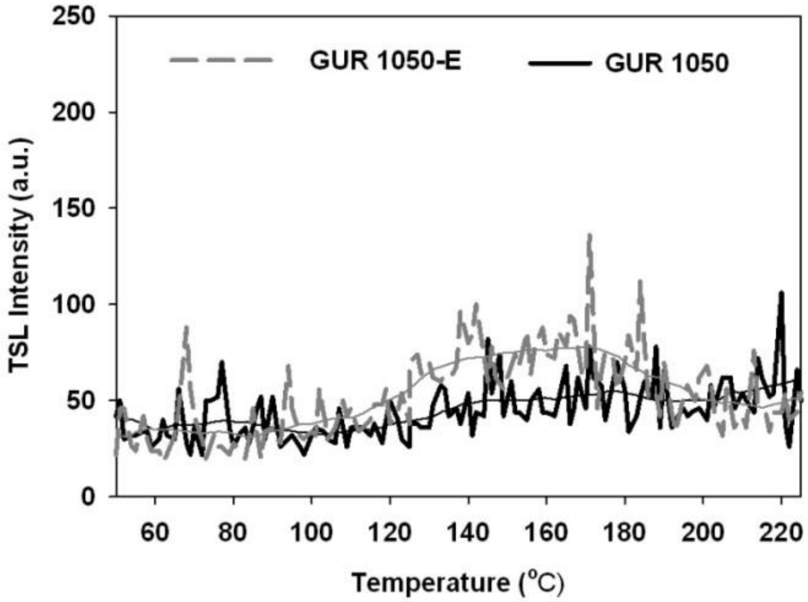


Fig. 4-1. TSL Glow curve of non-irradiated UHMWPE (GUR 1050 and GUR 1050-E).

When irradiation is done in the presence of oxygen (air) (Fig. 4-2b) one additional major peak is observed near 240 $^{o}$C and the peak near 210 $^{o}$C is also more intense. The peaks near 110, 160 and 280 $^{o}$C do not seem to be affected by the irradiation environment. The peak near 140 $^{o}$C is almost 50 % lower in intensity when irradition is done in nitrogen than air. The peak near 200 $^{o}$C is almost minimal in nitrogen and increases significantly when irradiation is done in air. The peak which is affected most by the irradiation environment is the peak near 240 $^{o}$C . This peak is almost minimal or non-existance when irradiation is done in $N_2$ . When GUR 1050 sample is irradited in air this peak apears to have relativelly high intensity. Therefore the peaks near 200 and 240 $^{o}$C might be due to species produced by oxygen-radical reaction. Thermally stimulated luminescence glow curve of GUR 1050-E is shown in Fig. 4-3. For GUR 1050-E the major peak is centered near 180 $^{o}$C and another shoulder peaks near 140 $^{o}$C, 240 and 280

$^{o}$C. Glow peak analysis also shows another small peak near 200 $^{o}$C. The overall TSL intensity of the sample which contains vitamin E is large compared to that the sample containing no vitamin E. The peak near 180 $^{o}$C is observed in the sample which contains vitamin E only; hence it must be the characteristics of the vitamin E radicals.

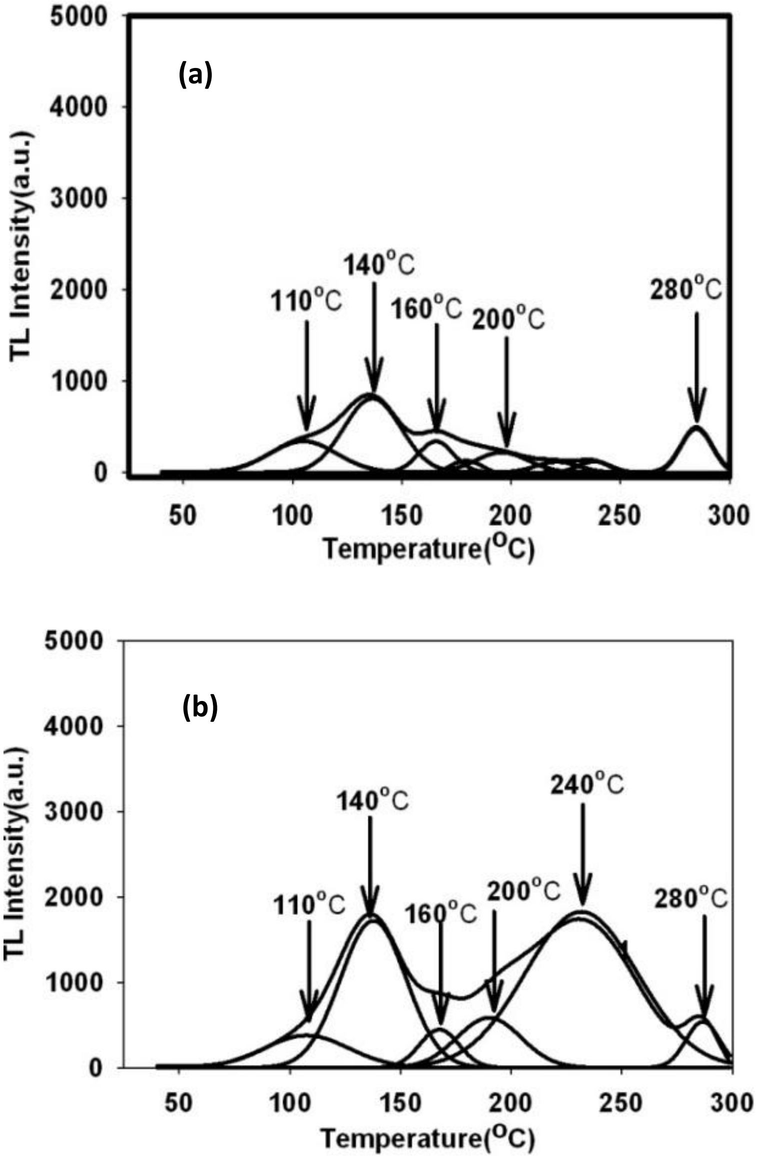


Fig. 4-2. TSL Glow curve of GUR 1050 gamma irradiated (a) in Nitrogen (b) in air.

ESR also able to detect the vitamin E radicals in gamma irradiated UHMWPE-E. The peak near 140 $^{o}$C in these two glow curves appears to be equal in intensity and does not seem to be affected by the irradiation environment. Peak near 180 $^{o}$C is about 10% lower in intensity when irradiation is performed in $N_2$ than in air. The peak near 240 $^{o}$C has almost 40% higher intensity when irradiation is done in air than in nitrogen.

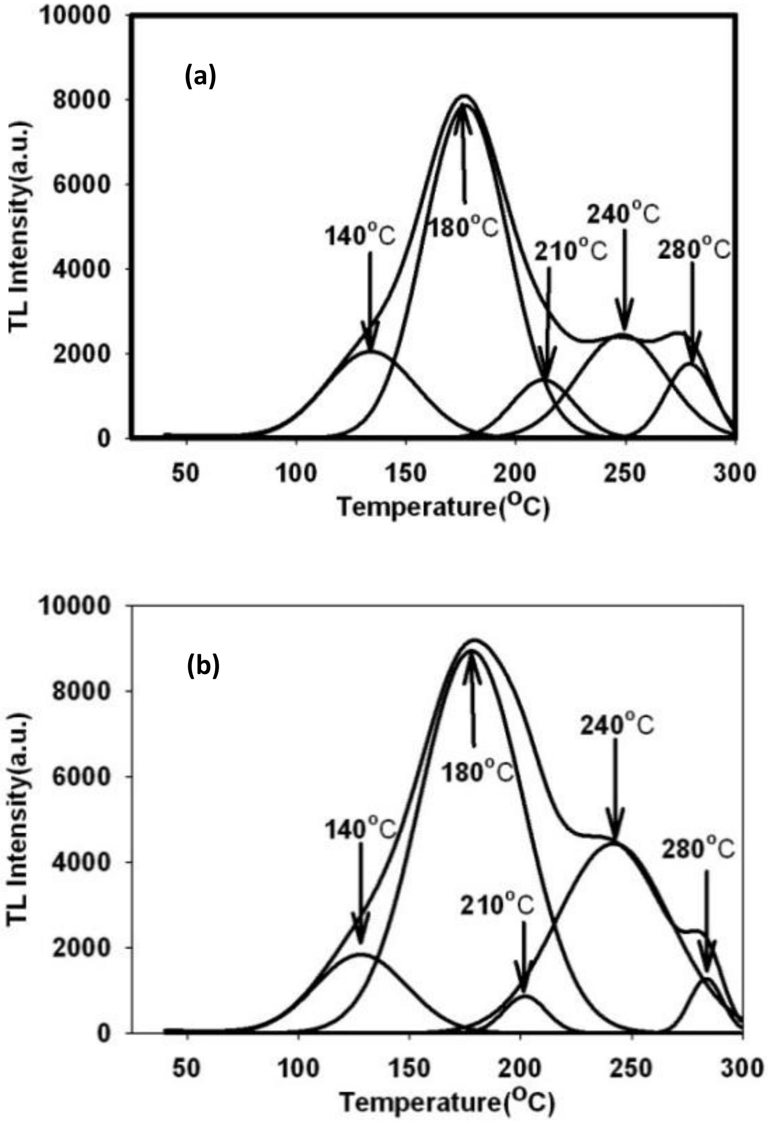


Fig. 4-3 The TSL fitted Glow curve of GUR 1050-E gamma irradiated (a) in $N_2$ and (b) in air.

## 4.2 GUR 1050 and GUR 1050-E: peak maximum temperature ($T_{max}$) and activation energy

The temperature at which the TSL maxima occur is believed to be the characteristics of the thermal release mechanism of the trapped carriers from their various regions [33]. 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. Tables 4-1 and 4-2 summarize the maximum temperature and the activation energy associated with each glow peak of GUR 1050 and GUR 1050-E. The activation energy of GUR 1050 samples for individual peaks ranges from 27-84 kCal/mole. The average activation energy for peak 2 near 140 $^{o}$C is about 1.768 eV or 40 kCalmole$^{-1}$. The activation energy of the 140 $^{o}$C peak in GUR 1050-E sample (Table 4-2) is about 22 kCalmole$^{-1}$. Naheed find the activation energy of the primary radical as 16 kCalmole$^{-1}$ and Deng et al. found their activation in the range between 50-100 kCalmole$^{-1}$. So the activation energies we found for the TSL peaks are consistent with those obtained by others. The activation energy of the peak near 180 $^{o}$C is approximately 24 kCalmole$^{-1}$.

Table 4-1
Glow curve parameters of UHMWPE (GUR 1050)

| **Peak** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| **$T_{max}$ ($^{o}$C)** | 110 | 140 | 160 | 180 | 200 | 240 | 280 |
| **E(eV)** | 1.1825 | 1.768 | 2.766 | - | 1.6425 | 1.2159 | 3.641 |
| **E(kCal/mole)** | 27.25 | 40.74 | 63.74 |  | 37.85 | 28.02 | 83.91 |

Table 4-2

Glow curve parameters of UHMWPE (GUR 1050-E)

| **Peak** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| **$T_{max}$ ($^oC$)** | - | 140 | - | 180 | 210 | 240 | 280 |
| **E(eV)** | - | 0.958 | - | 1.033 | 2.334 | 1.4487 | 4.134 |
| **E(kCal/mole)** | - | 22.08 | - | 23.80 | 53.77 | 33.38 | 80.14 |

### 4.3 Glow peak of GUR 1050 and 1050-E as a function of aging (oxidation) in a given storage environment

#### GUR 1050

The glow peak as a function of aging time in different environments for GUR 1050 sample is shown in the Fig. 4-4.The initial peak near 210 and 240 $^oC$ are minimal or almost non-existence in samples irradiated in nitrogen and stored in air or nitrogen (Fig. 4-4 (b and c)). These two peaks are oxidation peaks formed in the polymer during oxidation. For the samples irradiated in nitrogen and stored in room temperature after the initial measurement, these two peaks appear to grow (Fig. 4-5(a)). Initially due to the limited availability of oxygen these peaks are very weak. However when exposed to air, oxygen diffuses in to the sample and reacts with free radicals to form the oxidation products. After 90 days in air, the intensity of the TSL peaks near 210 and 240 $^oC$ increases approximately by 81% and 84%, respectively. For GUR 1050, gamma irradiated in air, the peak intensity of the 210 and 240 $^o$ C peaks increase approximately by 58% and 18% respectively. For the samples irradiated in air there is a significant amount of oxidized species to start with due to the availability of oxygen and additional growth in intensity could occur when further diffusion of oxygen takes place (Fig. 4-5 (b)). Evidently, this later growth is much less in the pre-oxidized materials (irradiated in air) than in the un-oxidized (irradiated in $N_2$) ones.

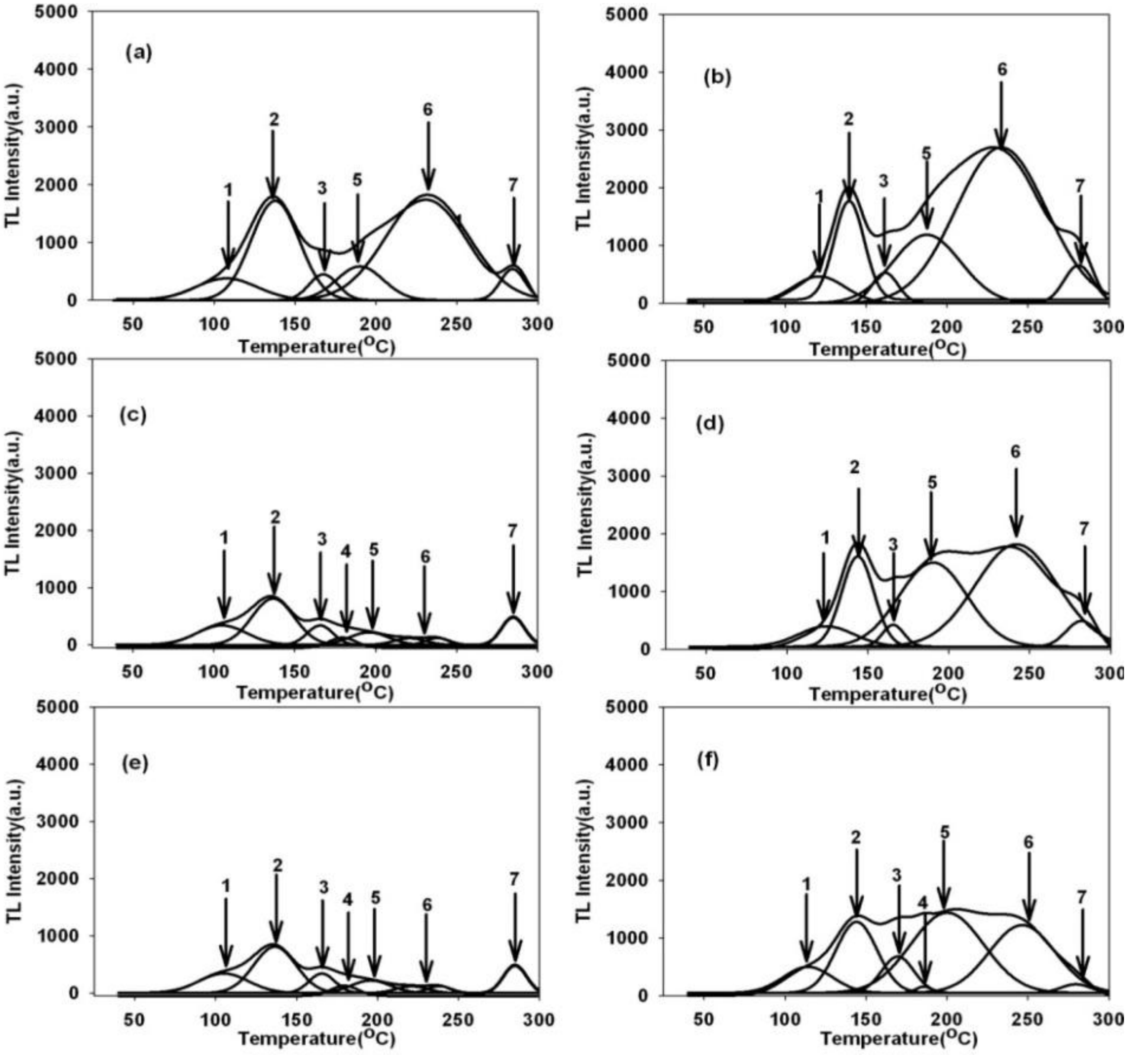
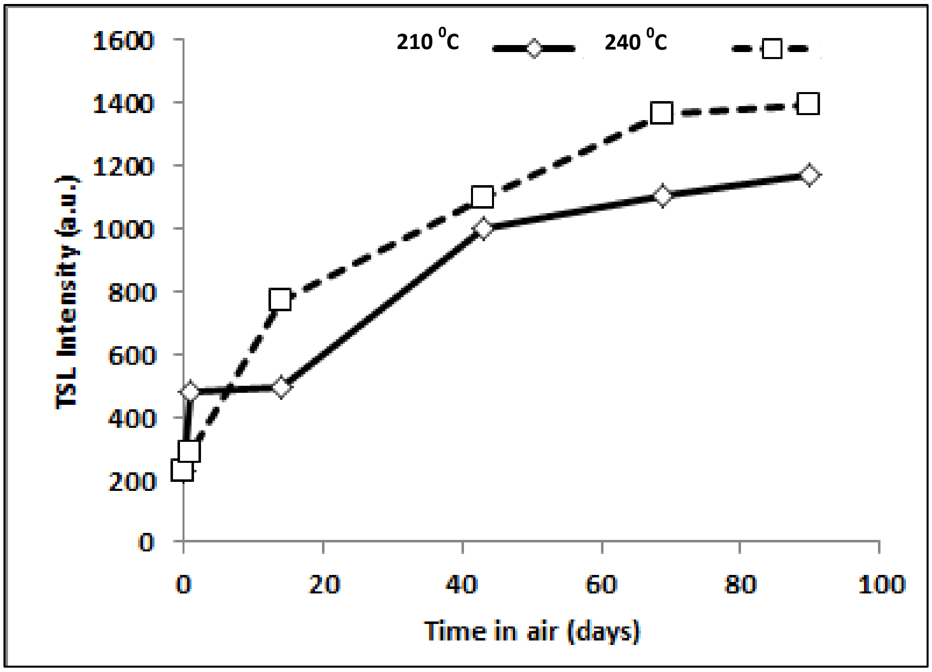
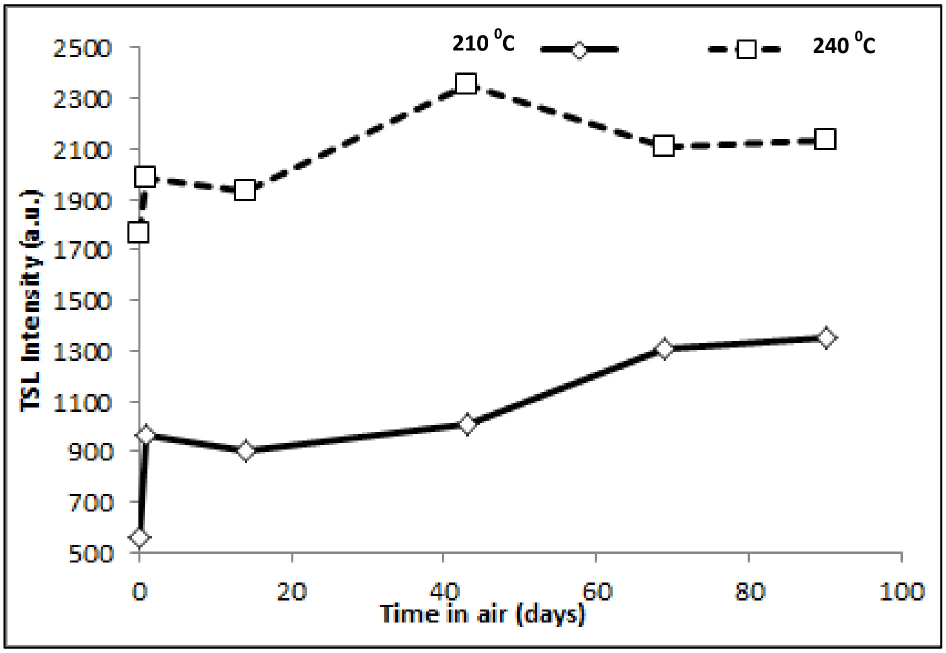


Fig. 4-4. Deconvoulated TSL glow curve of GUR 1050 (a) gamma in air stored in air on arrival; (b) gamma in air stored 90 days in air; (c) gamma in $N_2$ stored in air 10 minutes; (d) gamma in $N_2$ stored in air for 90 days; (e) gamma in $N_2$ stored in air for 10 minutes;(f) gamma in $N_2$ stored in $N_2$ for 69 days.



(a) Gamma in $N_2$ stored in air



(b) Gamma in air stored in air

Fig. 4-5. TSL intensity of the peak near 210 and 240 °C as function of aging time.

The peak near 140 °C increases up to an approximate 40 days of aging at room temperature for both sets of sample irradiated in air or nitrogen (Fig. 4-6). The samples irradiated in nitrogen were kept in nitrogen for 10 days before the initial measurement and there was no or limited free radical activity for these days (not shown). For the sample irradiated in $N_2$ the 140 °C peaks increases approximately by 25% after 40 days in air.

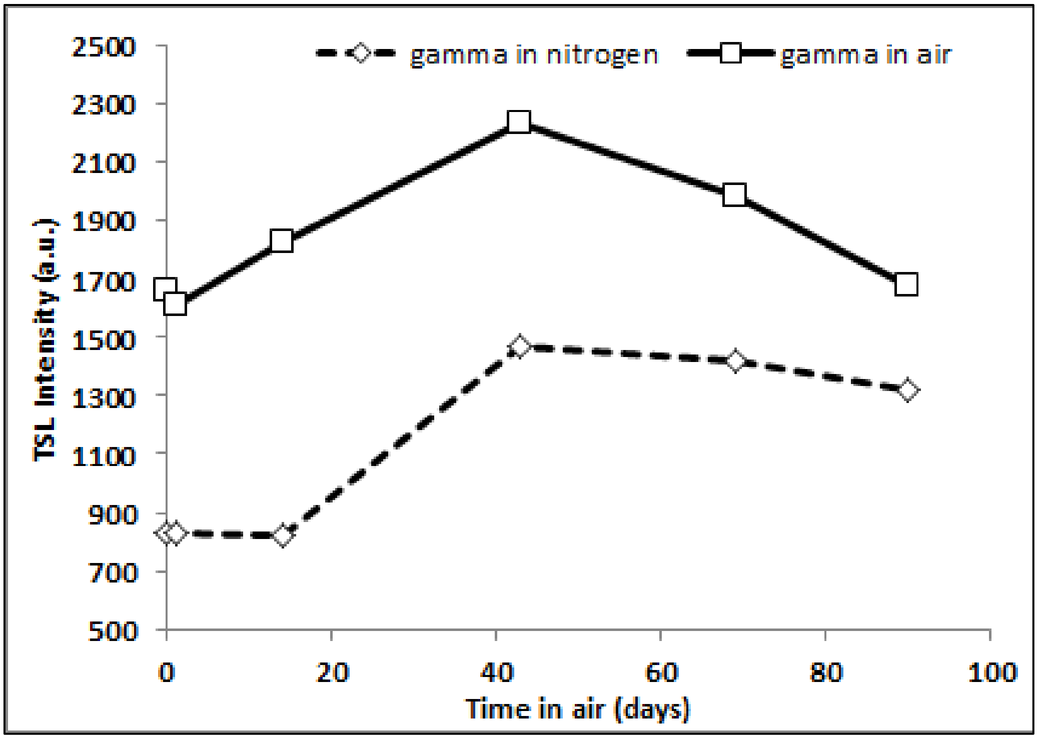


Fig. 4-6. Glow peak near 140 °C of GUR 1050 gamma irradiated in $N_2$ or air and stored in air.

**GUR 1050-E**

Fig. 4-8 shows the TSL intensity in GUR 1050-E as a function of aging time of the samples irradiated and stored in their respective environment. All peaks have relatively larger TSL intensity compared to GUR 1050. Fig. 4-7 illustrates the intensity decay with respect to time in air of peak 4 (near 180 $^{o}$C) of GUR 1050-E. Recall that, this peak is due to the thermal annihilation of the vitamin E radicals and the intensity of this peak is decreasing as function of aging time. Shown in Fig. 4-9 the intensity of peak 2 (near 140 $^{o}$C) also decreases as a function of aging in air for the samples irradiated in nitrogen and air.

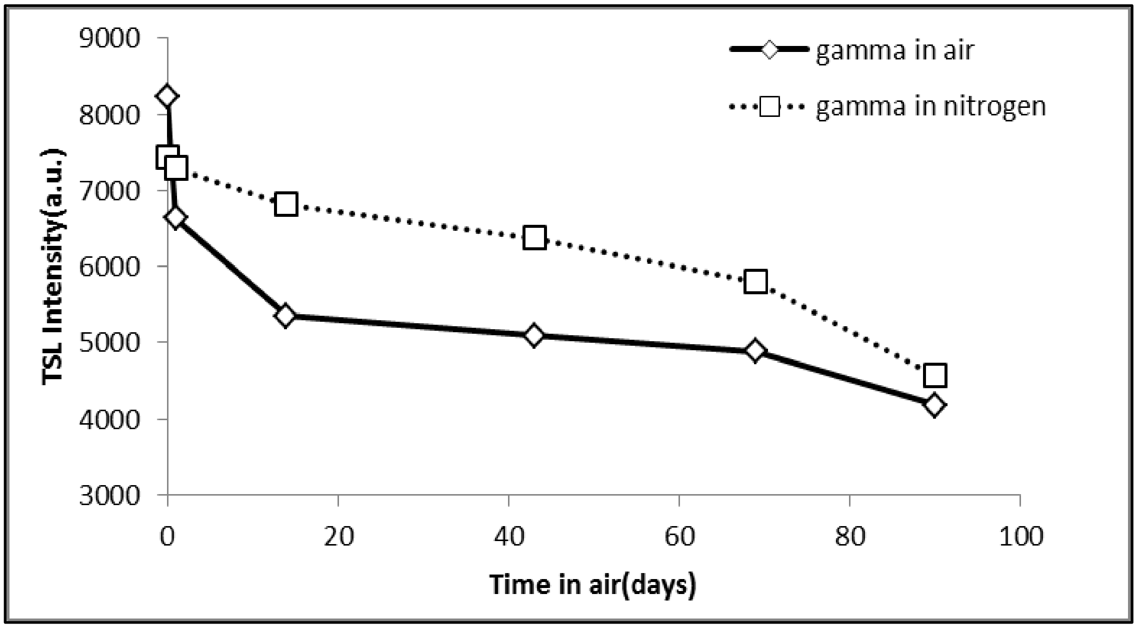


Fig. 4-7. Glow peak near 180 $^{o}$C of GUR 1050-E gamma irradiated in $N_2$ or in air, and stored in air.

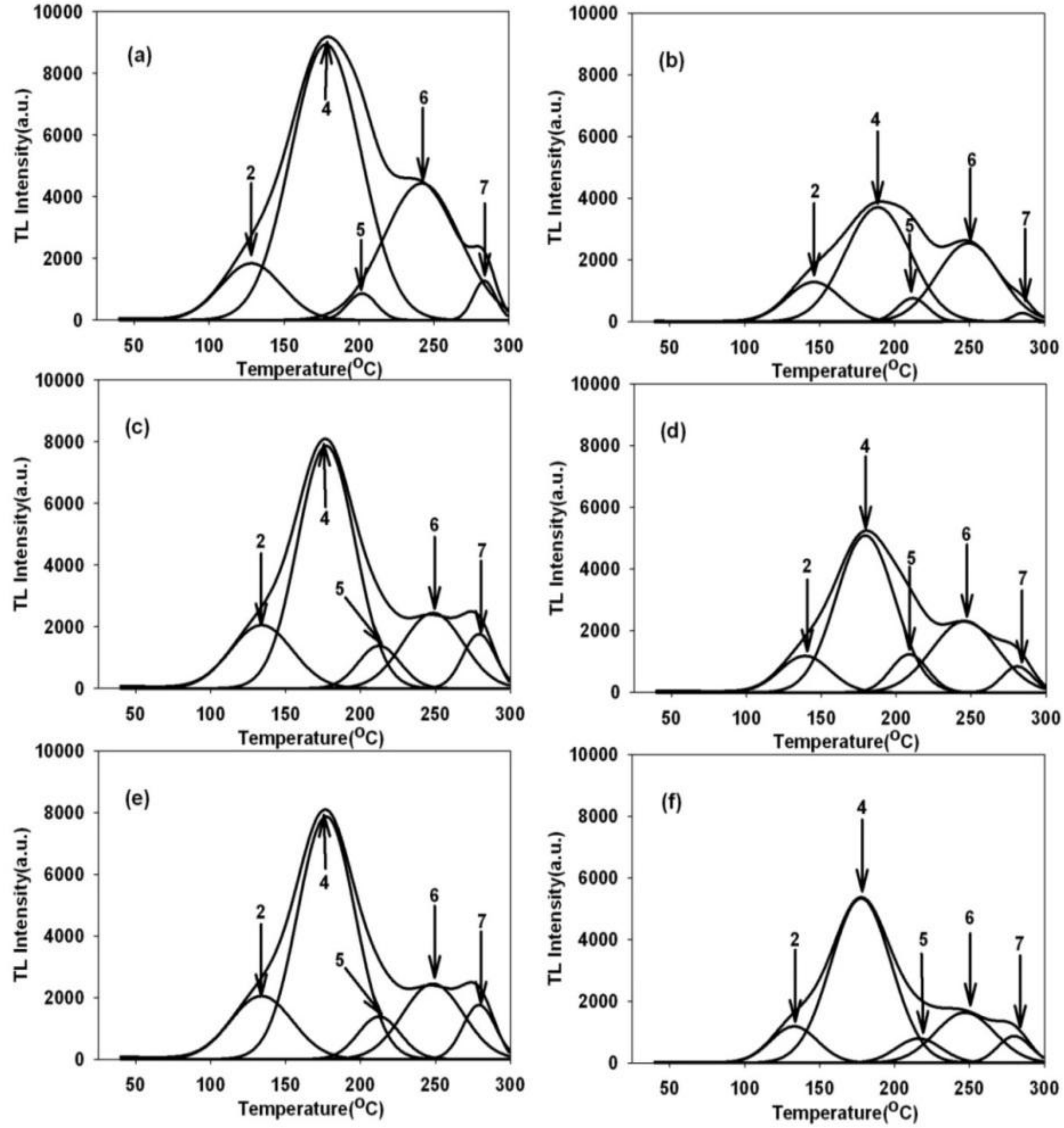


Fig. 4-8. Deconvoulated TSL glow curve of GUR 1050-E (a) gamma in air stored in air on arrival; (b) gamma in air stored 90 days in air; (c) gamma in $N_2$ stored in air 10 minutes; (d) gamma in $N_2$ stored in air for 90 days; (e) gamma in $N_2$ stored in air for 10 minutes;(f) gamma in $N_2$ stored in $N_2$ for 69 days.

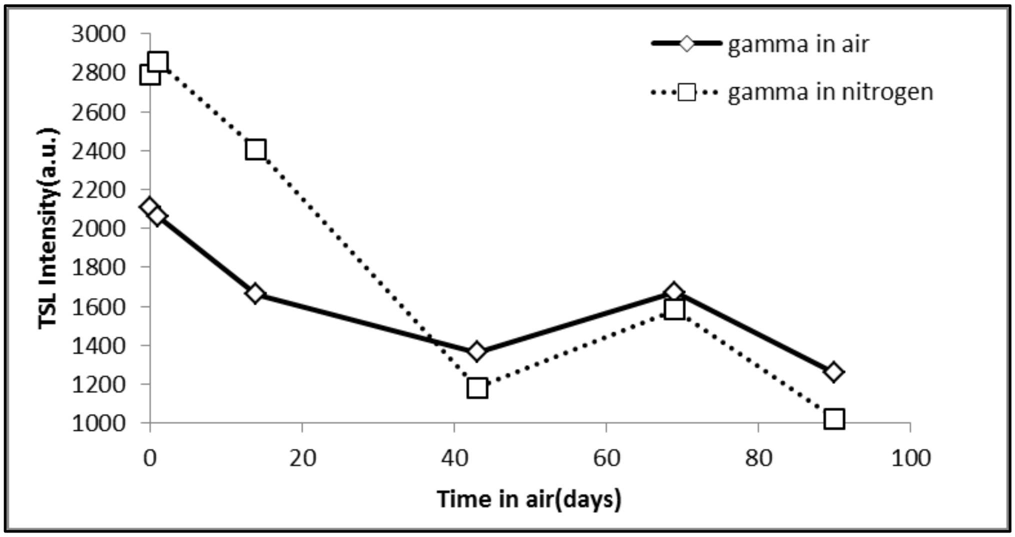


Fig. 4-9. Glow peak near 140 °C of GUR 1050-E gamma irradiated in $N_2$ or air and stored in air.

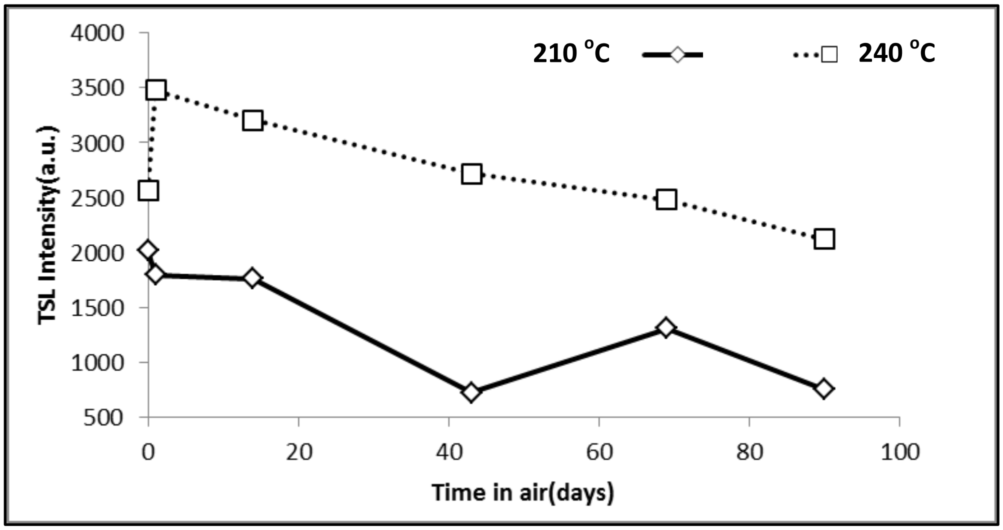


Fig. 4-10. Glow peak near 210 and 240 °C of GUR 1050-E gamma in $N_2$ and stored in air.

As shown Fig. 4-9, the peak near 140 °C of GUR 1050-E sample is decreasing with time in air when irradiation is done air or $N_2$. We recall that this peak is due to the thermal annihilation of the oxidation products. However in the presence of vitamin E due to the stabilization of the radicals, the concentration of the oxidation products decreases as a function of aging-time. The peak near 210 and 240 °C of GUR 1050-E, also decrease as function of aging as shown in Fig. 4-10. Hence further degradation effect of the primary radicals and production of oxidation species will be limited by the presence of vitamin E. Fig. 4-11 shows the total luminescence output of each set of samples as a function of oxidation time in air. The total TSL output of GUR 1050-E gamma irradiated in air or $N_2$ decreases by a significant amount over the 90 days oxidation time. This might be due to the decay of the vitamin E radicals as well as the limited amount of oxidation products. In non-vitamin-E samples (GUR 1050) total TSL remains constant, although peak intensity of the peaks at 210 and 240 °C was found to increase with time.

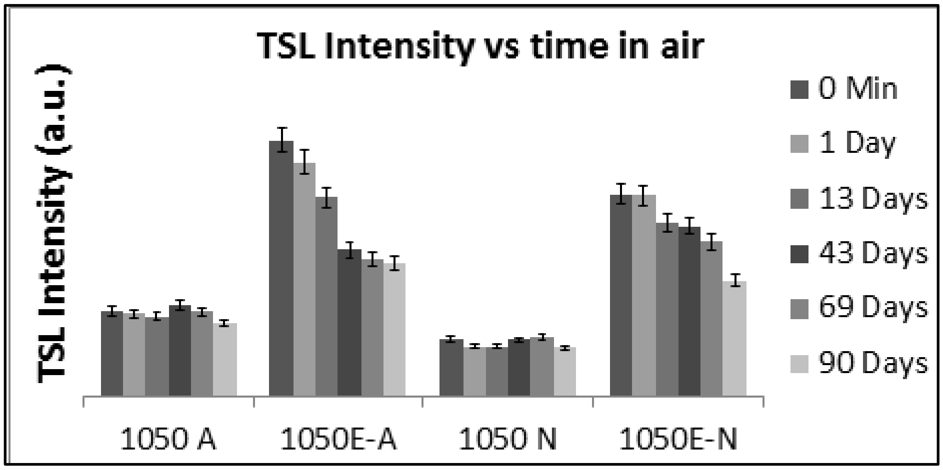


Fig. 4-11. Total luminescence as a function of aging of UHMWPE.

### 4.3 ESR analysis of GUR 1050 and GUR 1050-E

Shown in Fig. 4-12 are the ESR spectra recorded as a function of time in air for GUR 1050 and GUR 1050-E. The samples were irradiated 10 days prior to the first day measurement and named as “first measurement” and “upon opening to air” due to being the first day that the samples were opened to air and kept in air after this day.

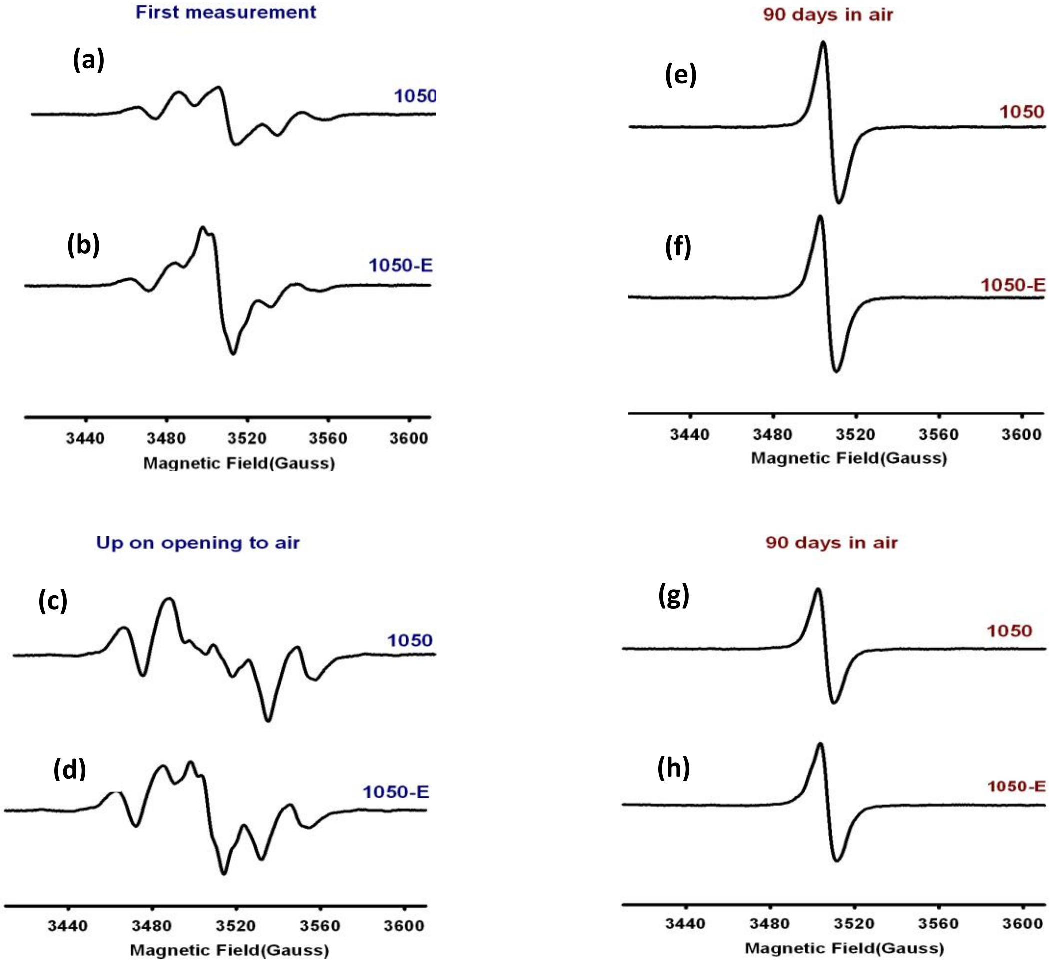


Fig. 4-12. ESR spectra of GUR 1050 and GUR 1050-E gamma irradiated in air and in $N_2$.

GUR 1050-E samples (Fig. 4-12(b and d)) show a different pattern due to the presence of the vitamin E. After exposure of the samples to air, the polyethylene radical starts to react with oxygen. This can be observed from the representative spectra recorded after the initial measurement. The figure also shows identical spectra recorded after 90 days of oxidation in air. Furthermore, after 90 days, in all sample no measurable difference is found in the radical concentrations in the samples (Fig. 4-13).

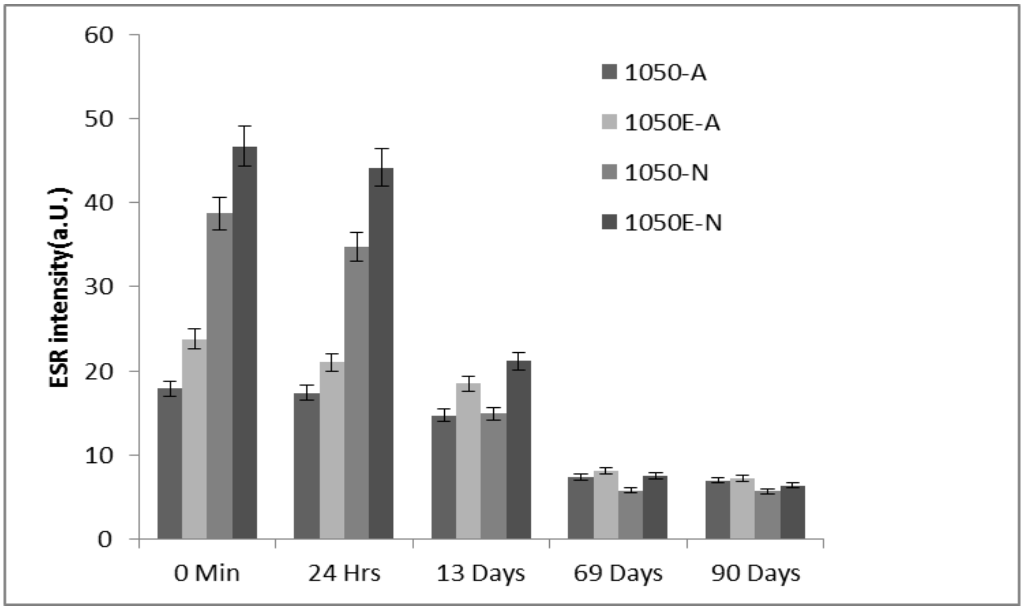


Fig. 4-13. Integrated ESR intensity as function of time in GUR 1050 and GUR 1050-E.

### 4.4 FTIR analysis of GUR 1050 and GUR 1050-E

Shown in Fig. 4-14 are the FTIR spectra of UHMWPE powder samples. According to ASTM standard the absorption peak near 1720 cm$^{-1}$ is due to the vibration of the carbonyl group and it measures the oxidation extent of polyethylene by comparing this peak with the absorption peak near 1370 cm$^{-1}$. The FTIR spectrum shown in the Fig.

4-14(a) does not have any detectable peak near 1720 $cm^{-1}$.Because this sample is not irradiated and there is no free radical available to produce oxidation products.

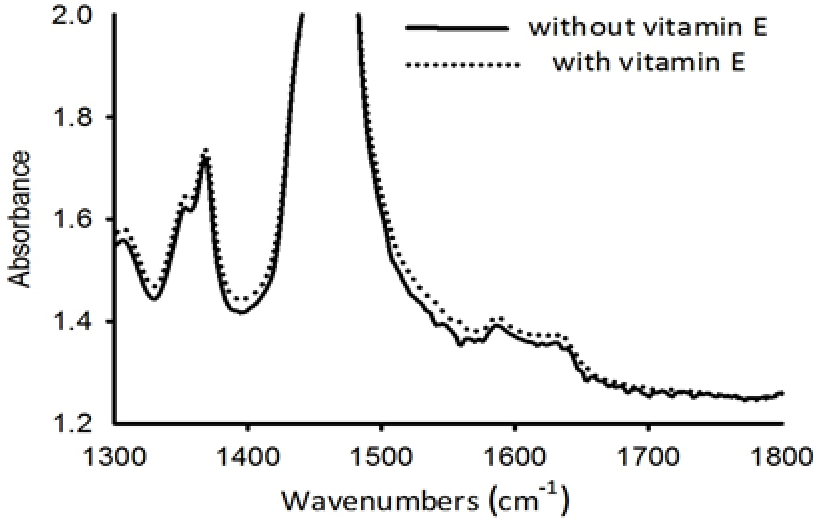


Fig. 4-14. FTIR spectrum of un-irradiated UHMWPE powder sample.

However when UHMWPE, with or without vitamin E, is gamma irradiated in air or $N_2$ and stored in air for 90 days, an absorption peak near 1720 $cm^{-1}$ is detected (Fig. 4-15(a and b)). Even though according to ASTM F2102-06 the oxidation index is used to measure the oxidation extent of UHMWPE for only consolidated solid sample, we used this method for powder sample only for comparison purpose. Nonetheless, Table 4-3 shows that UHMWPE containing alpha-tocopherol has relatively low oxidation value compared to the one that does not contain vitamin E, though the difference is very small. This result similar to previous study confirms that vitamin E is effective in reducing the oxidation process [15-17].

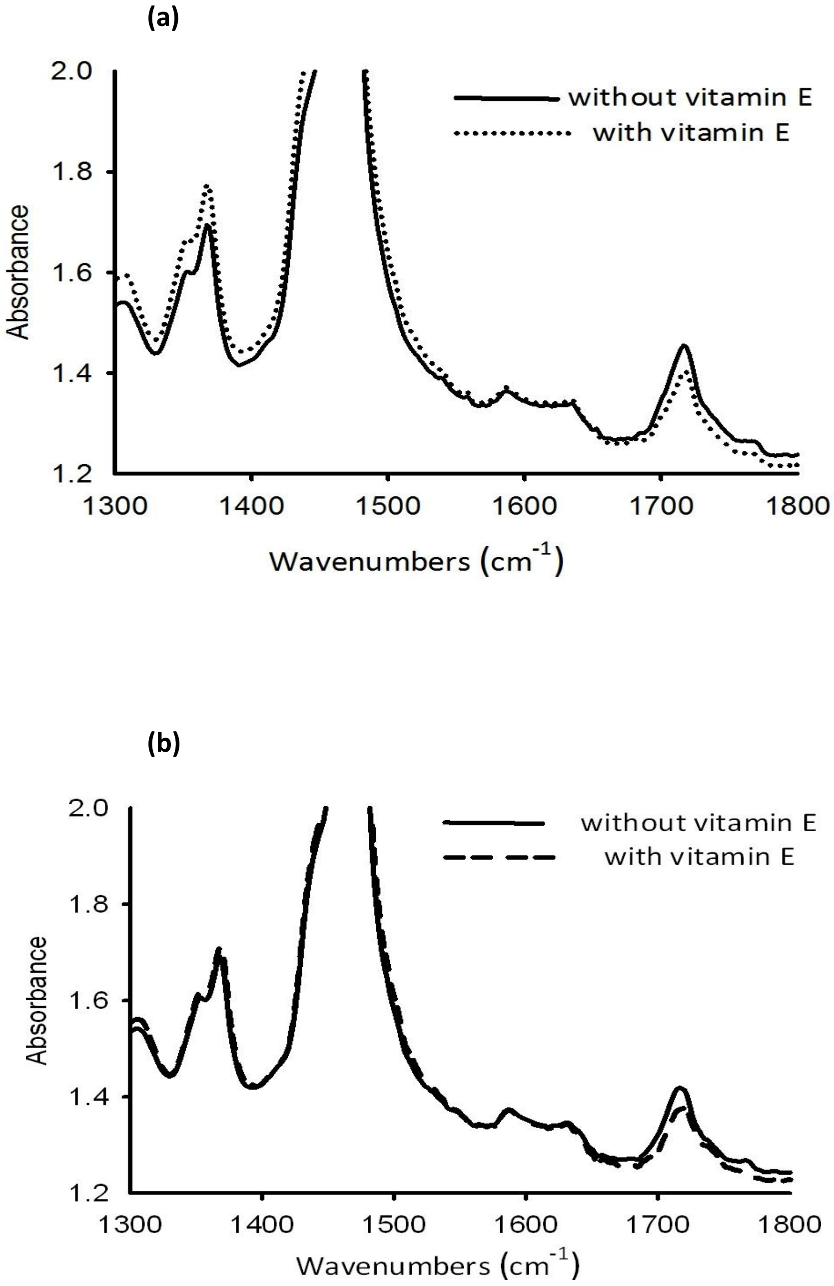


Fig. 4-15. FTIR spectrum of UHMWPE powder sample (a) gamma in air and stored 90 days in air, and (b) gamma in $N_2$ and stored 90 days in air.

Table 4.3
A relative oxidation value of UHMWPE powder sample

| Powder | Irradiated | Oxidation (Arb. Value) | Standard Deviation |
|---|---|---|---|
| 1050 | None | None | - |
| 1050-E | None | None | - |
| 1050 | Air | 0.87 | 0.02 |
| 1050-E | Air | 0.60 | 0.07 |
| 1050 | Nitrogen | 0.71 | 0.04 |
| 1050-E | Nitrogen | 0.64 | 0.03 |

# Conclusion and Future work

## Conclusion

Thermally stimulated luminescence of medical grade UHMWPE containing 1000ppm alpha-tocopherol (GUR 1050-E) is studied in this work. TSL glow curve of GUR 1050-E contains a major peak centered near 180 $^oC$ and shoulder peaks approximately near 140, 210, 240 and 280 $^oC$. The peak near 180 $^oC$ is observed only in irradiated 1050-E sample and the study shows that this peak is due to the thermal annihilation of the more stable vitamin E radicals.

Although FTIR measurements are routinely used to determine the oxidation level (oxidation index) of post-irradiation specimens, the difference in oxidation indices between non-vitamin-E and vitamin-E UHMWPE (GUR 1050 and GUR 1050-E) is found to be very insignificant. ESR tests used in this study do not find any measurable difference between the spectra in vitamin-E and non-vitamin-E UHMWPE (GUR 1050 and GUR 1050-E). TSL tests on the other hand, find significant difference between these two groups of samples. During aging in air (oxidation), TSL intensities at 140, 210, and 240 $^oC$ increases as a function of time in GUR 1050 and decreases in GUR 1050-E. Additional work is needed to explain these observation with respect to the primary events of free radical reaction.

## Future work

For future, an experiment involving FTIR study of UHMWPE as a function of oxidation time is needed in conjunction with TSL to better understand the oxidation mechanism of the material. Future experiment is recommended also to include different concentration of vitamin E to better investigate the effectiveness of vitamin E as antioxidant. It is also recommended to study different types of antioxidants as free radicals quenchers.

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# APPENDIX-I: TABULATION OF CALCULATED GLOW CURVE PARAMETERS FOR GUR 1050

Table 1-1
γ -irradiated in air aged 1 minute in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **Ʈ($^{o}$C)** | **δ($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 110 | 23 | 23 | 0.495 | 1.631 | 0.868 | 1.75 E10 |
| **2** | 139 | 18 | 18 | 0.488 | 1.554 | 1.282 | 4.08 E14 |
| **3** | 168 | 10.5 | 10.5 | 0.483 | 1.494 | 2.528 | 1.16 E28 |
| **4** | - | - | - | - | - | - | - |
| **5** | 191 | 17.5 | 17.3 | 0.487 | 1.535 | 1.674 | 1.35 E17 |
| **6** | 235 | 31 | 31 | 0.495 | 1.625 | 1.127 | 7.42 E09 |
| **7** | 287 | 9 | 9 | 0.453 | 1.216 | 4.164 | 4.63 E36 |

Table 1-2
γ -irradiated in air aged 1 day in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **Ʈ($^{o}$C)** | **δ($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 112.5 | 21.5 | 21.5 | 0.491 | 1.587 | 0.936 | 1.23 E11 |
| **2** | 136 | 16.4 | 16.4 | 0.486 | 1.525 | 1.379 | 9.66 E15 |
| **3** | 162 | 10.7 | 10.7 | 0.481 | 1.472 | 2.404 | 1.05 E27 |
| **4** | - | - | - | - | - | - | - |
| **5** | 196 | 24.3 | 24.2 | 0.491 | 1.586 | 1.229 | 1.03 E12 |
| **6** | 237.5 | 25.8 | 25.7 | 0.491 | 1.58 | 1.377 | 2.36 E12 |
| **7** | 280.5 | 14.8 | 14.7 | 0.482 | 1.49 | 2.832 | 6.53 E24 |

Table 1-3
γ -irradiated in air aged 14 days in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **Ʈ($^{o}$C)** | **δ($^{o}$C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 107 | 24.7 | 24.2 | 0.495 | 1.622 | 0.793 | 2.03 E09 |
| **2** | 136 | 16 | 16 | 0.489 | 1.555 | 1.434 | 4.56 E16 |
| **3** | 162 | 8.6 | 8.6 | 0.475 | 1.419 | 3.024 | 2.05 E34 |
| **4** | - | - | - | - | - | - | - |
| **5** | 195 | 19.2 | 19.2 | 0.488 | 1.547 | 1.554 | 4.34 E15 |
| **6** | 236.5 | 30.5 | 30.5 | 0.496 | 1.634 | 1.161 | 1.53 E10 |
| **7** | 278.5 | 12.7 | 12.7 | 0.48 | 1.461 | 3.259 | 7.44E28 |

Table 1-4
$\gamma$ -irradiated in air aged 43 days in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **$\tau$($^{o}$C)** | **$\delta$($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 121 | 13.6 | 13.4 | 0.481 | 1.473 | 1.542 | 5.99 E18 |
| **2** | 140.3 | 10.8 | 10.8 | 0.481 | 1.473 | 2.146 | 2.15 E25 |
| **3** | 163.3 | 9.7 | 9.7 | 0.481 | 1.479 | 2.68 | 1.46 E30 |
| **4** | - | - | - | - | - | - | - |
| **5** | 189.5 | 22 | 21.5 | 0.486 | 1.523 | 1.313 | 1.83 E13 |
| **6** | 233 | 36.5 | 36.5 | 0.499 | 1.666 | 0.95 | 1.22 E08 |
| **7** | 279 | 11.4 | 11.4 | 0.484 | 1.507 | 3.705 | 9.24 E32 |

Table 1-5
$\gamma$ -irradiated in air aged 69 days in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **$\tau$($^{o}$C)** | **$\delta$($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 121 | 13 | 13 | 0.488 | 1.549 | 1.646 | 1.35 E20 |
| **2** | 139.5 | 9.7 | 9.7 | 0.478 | 1.45 | 2.382 | 2.05 E28 |
| **3** | 157.5 | 8.8 | 8.8 | 0.482 | 1.49 | 2.887 | 1.11 E33 |
| **4** | - | - | - | - | - | - | - |
| **5** | 197.5 | 17.8 | 17.4 | 0.484 | 1.504 | 1.696 | 1.26E17 |
| **6** | 236.5 | 27.8 | 27.8 | 0.494 | 1.619 | 1.275 | 2.324E11 |
| **7** | 279 | 11.3 | 11.3 | 0.479 | 1.458 | 3.681 | 5.68 E32 |

Table 1-6
$\gamma$ -irradiated in air aged 90 days in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **$\tau$($^{o}$C)** | **$\delta$($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 128.5 | 16.8 | 16.8 | 0.489 | 1.561 | 1.31 | 2.60 E15 |
| **2** | 147 | 12 | 12 | 0.481 | 1.471 | 1.987 | 9.04 E22 |
| **3** | 168.5 | 8.7 | 8.7 | 0.482 | 1.487 | 3.073 | 2.17 E34 |
| **4** | - | - | - | - | - | - | - |
| **5** | 212.5 | 20 | 20 | 0.484 | 1.511 | 1.579 | 1.90 E15 |
| **6** | 248.5 | 24 | 24 | 0.491 | 1.585 | 1.553 | 6.63 E13 |
| **7** | 286 | 10.2 | 9.8 | 0.474 | 1.406 | 4.205 | 1.27 E37 |

Table 1-7
$\gamma$ -irradiated in $N_2$ aged 1 minute in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **ʈ($^{o}$C)** | **δ($^{o}$C)** | **$\mu_g$** | **Kinetic Or.** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 109 | 22.7 | 22.1 | 0.488 | 1.552 | 0.868 | 1.91 E10 |
| **2** | 138 | 14.7 | 14.7 | 0.486 | 1.526 | 1.57 | 1.90 E18 |
| **3** | 163 | 8.8 | 8.8 | 0.482 | 1.49 | 2.962 | 3.08 E33 |
| **4** | - | - | - | - | - | - | - |
| **5** | 208 | 17.5 | 17.5 | 0.487 | 1.535 | 1.798 | 6.48 E17 |
| **6** | 240 | 17.5 | 17.4 | 0.485 | 1.52 | 2.028 | 7.44 E18 |
| **7** | 262 | 8.2 | 8.2 | 0.446 | 1.157 | 4.1 | 3.51E37 |

Table 1-8
$\gamma$ -irradiated in $N_2$ aged 1 day in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **ʈ($^{o}$C)** | **δ($^{o}$C)** | **$\mu_g$** | **Kinetic Or.** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 108.5 | 20.4 | 20.4 | 0.494 | 1.61 | 0.974 | 5.50E11 |
| **2** | 139 | 15.4 | 15.4 | 0.486 | 1.533 | 1.503 | 2.42 E17 |
| **3** | 163.5 | 9 | 8.7 | 0.473 | 1.4 | 2.898 | 5.02 E32 |
| **4** | - | - | - | - | - | - | - |
| **5** | 222.5 | 27.4 | 27 | 0.49 | 1.575 | 1.219 | 1.40 E11 |
| **6** | 245 | 9.6 | 9.6 | 0.481 | 1.477 | 3.835 | 3.33 E36 |
| **7** | 285.5 | 10.8 | 10.4 | 0.468 | 1.349 | 3.884 | 1.61 E34 |

Table 1-9
$\gamma$ -irradiated in $N_2$ aged 14 days in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **ʈ($^{o}$C)** | **δ($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 118.7 | 25.8 | 25.8 | 0.496 | 1.636 | 0.806 | 1.37 E09 |
| **2** | 138.5 | 14.4 | 14.2 | 0.484 | 1.503 | 1.604 | 4.79 E18 |
| **3** | 167.5 | 10 | 10 | 0.479 | 1.457 | 2.604 | 2.54 E29 |
| **4** | - | - | - | - | - | - | - |
| **5** | 186.7 | 17.4 | 17.4 | 0.487 | 1.534 | 1.652 | 1.16 E17 |
| **6** | 232 | 30 | 30 | 0.495 | 1.623 | 1.155 | 1.74 E10 |
| **7** | 281.5 | 12.5 | 12.5 | 0.48 | 1.461 | 3.295 | 1.09 E29 |

Table 1-10
$\gamma$ -irradiated in $N_2$ aged 43 days in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **$\delta$(°C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 122 | 19.7 | 19.7 | 0.492 | 1.593 | 1.08 | 4.78 E12 |
| **2** | 142 | 12.4 | 12.4 | 0.485 | 1.521 | 1.902 | 1.56 E22 |
| **3** | 170 | 13 | 13 | 0.484 | 1.507 | 2.055 | 3.22 E22 |
| **4** | 197.5 | 20 | 20 | 0.487 | 1.538 | 1.501 | 9.33 E14 |
| **5** | 239 | 23.8 | 23.5 | 0.488 | 1.547 | 1.502 | 3.99 E13 |
| **6** | 259 | 10 | 10 | 0.482 | 1.485 | 3.886 | 1.02 E36 |
| **7** | 280.7 | 11.7 | 11.7 | 0.482 | 1.489 | 3.588 | 6.11 E31 |

Table 1-11
$\gamma$ -irradiated in $N_2$ aged 69 days in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **$\delta$(°C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 125 | 17.4 | 17 | 0.482 | 1.484 | 1.227 | 3.02E14 |
| **2** | 144 | 12 | 12 | 0.481 | 1.471 | 1.958 | 6.01 E22 |
| **3** | 168.5 | 13.5 | 13.5 | 0.483 | 1.492 | 1.967 | 3.27 E21 |
| **4** | - | - | - | - | - | - | - |
| **5** | 192 | 22 | 22 | 0.491 | 1.576 | 1.34 | 2.33 E13 |
| **6** | 239.5 | 32.4 | 32.4 | 0.496 | 1.637 | 1.1 | 3.14 E09 |
| **7** | 283.5 | 9 | 9 | 0.453 | 1.216 | 4.112 | 2.66 E36 |

Table 1-12
$\gamma$ -irradiated in $N_2$ aged 90 days in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **$\delta$(°C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 134 | 17 | 17 | 0.486 | 1.53 | 1.317 | 1.86 E15 |
| **2** | 147 | 10.8 | 10.8 | 0.481 | 1.473 | 2.223 | 6.38 E25 |
| **3** | 169 | 8 | 8 | 0.481 | 1.471 | 3.35 | 3.14 E37 |
| **4** | - | - | - | - | - | - | - |
| **5** | 196 | 28 | 28 | 0.493 | 1.609 | 1.067 | 1.53 E10 |
| **6** | 245.5 | 26.5 | 26 | 0.488 | 1.549 | 1.381 | 1.56 E12 |
| **7** | 286 | 9 | 9 | 0.453 | 1.216 | 4.149 | 3.95 E36 |

Table 1-13

$\gamma$ -irradiated in $N_2$ aged 1 minute in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 109 | 22.7 | 22.1 | 0.488 | 1.552 | 0.868 | 1.91 E10 |
| **2** | 138 | 14.7 | 14.7 | 0.486 | 1.526 | 1.57 | 1.89 E18 |
| **3** | 163 | 8.8 | 8.8 | 0.482 | 1.49 | 2.962 | 3.08 E33 |
| **4** | 180 | 14.5 | 14.5 | 0.484 | 1.505 | 1.926 | 2.86 E20 |
| **5** | 208 | 17.5 | 17.5 | 0.487 | 1.535 | 1.798 | 6.48 E17 |
| **6** | 240 | 17.5 | 17.4 | 0.485 | 1.52 | 2.028 | 7.44 E18 |
| **7** | 262 | 8.2 | 8.2 | 0.446 | 1.157 | 4.1 | 3.51 E37 |

Table 1-14

$\gamma$ -irradiated in $N_2$ aged 1 day in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kinetic Or.** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 105 | 19.4 | 19.2 | 0.492 | 1.591 | 1.011 | 2.32 E12 |
| **2** | 137 | 16.8 | 16.8 | 0.489 | 1.561 | 1.368 | 6.08 E15 |
| **3** | 163 | 9 | 9 | 0.48 | 1.463 | 2.884 | 3.81 E32 |
| **4** | - | - | - | - | - | - | - |
| **5** | 183.5 | 28.4 | 28.4 | 0.495 | 1.63 | 0.995 | 5.25 E09 |
| **6** | 236.5 | 32.4 | 32.4 | 0.496 | 1.637 | 1.087 | 2.68 E09 |
| **7** | 274 | 11.4 | 11.4 | 0.482 | 1.486 | 3.561 | 8.90E31 |

Table 1-15

$\gamma$ -irradiated in $N_2$ aged 14 days in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | 110.5 | 20.2 | 20.2 | 0.491 | 1.581 | 0.987 | 7.07 E11 |
| **2** | 138 | 13.8 | 13.4 | 0.477 | 1.435 | 1.659 | 2.49 E19 |
| **3** | 159.5 | 8.4 | 8.4 | 0.475 | 1.419 | 2.991 | 1.32E34 |
| **4** | 171 | 10 | 10 | 0.479 | 1.457 | 2.863 | 4.49E29 |
| **5** | 188.5 | 19.4 | 19.4 | 0.489 | 1.562 | 1.503 | 2.09 E15 |
| **6** | 235.5 | 29.8 | 29.4 | 0.492 | 1.593 | 1.181 | 2.64 E10 |
| **7** | 281.5 | 10.2 | 10 | 0.474 | 1.408 | 4.097 | 2.65 E36 |

Table 1-16
$\gamma$ -irradiated in $N_2$ aged 43 days in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **$S(s^{-1})$** |
|---|---|---|---|---|---|---|---|
| **1** | 114 | 21.4 | 21.4 | 0.493 | 1.6 | 0.95 | 1.68 E11 |
| **2** | 145 | 18 | 18 | 0.488 | 1.554 | 1.32 | 7.13 E14 |
| **3** | 169 | 8 | 8 | 0.481 | 1.471 | 3.358 | 3.48E37 |
| **4** | 190 | 18 | 18 | 0.488 | 1.545 | 1.537 | 4.33 E15 |
| **5** | 222 | 17 | 17 | 0.486 | 1.53 | 1.971 | 1.06E19 |
| **6** | 251.5 | 18 | 18 | 0.488 | 1.554 | 2.106 | 1.51E19 |
| **7** | 284 | 11 | 10.4 | 0.466 | 1.331 | 3.785 | 2.35 E33 |

Table 1-17
$\gamma$ -irradiated in $N_2$ aged 69 days in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **$S(s^{-1})$** |
|---|---|---|---|---|---|---|---|
| **1** | 116 | 19 | 18 | 0.476 | 1.425 | 1.066 | 5.17 E12 |
| **2** | 145 | 15.4 | 15.4 | 0.486 | 1.533 | 1.548 | 4.63 E17 |
| **3** | 169 | 12 | 12 | 0.485 | 1.516 | 2.248 | 4.86 E24 |
| **4** | - | - | - | - | - | - | - |
| **5** | 203 | 27.2 | 27.2 | 0.494 | 1.618 | 1.125 | 4.63 E10 |
| **6** | 248.5 | 24.5 | 24.5 | 0.491 | 1.577 | 1.484 | 1.36 E13 |
| **7** | 280 | 11 | 11 | 0.479 | 1.452 | 3.795 | 5.52 E33 |

# APPENDIX- *Π*: TABULATION OF CALCULATED GLOW CURVE PARAMETERS FOR GUR 1050E

Table 2-18
$\gamma$ -irradiated in air aged 1 minute in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **$\delta$(°C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **$S(s^{-1})$** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 138 | 29.8 | 29.4 | 0.496 | 1.642 | 0.767 | 1.32 E08 |
| **3** | - | - | - | - | - | - | - |
| **4** | 183 | 28.4 | 28 | 0.491 | 1.578 | 0.985 | 4.25 E09 |
| **5** | 204 | 11.4 | 11.4 | 0.482 | 1.484 | 2.715 | 7.15 E27 |
| **6** | 244 | 27.5 | 27.5 | 0.493 | 1.607 | 1.323 | 4.60 E11 |
| **7** | 283 | 11 | 11 | 0.479 | 1.452 | 3.834 | 8.36 E33 |

Table 2-19
$\gamma$ -irradiated in air aged 1 day in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **$\delta$(°C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **$S(s^{-1})$** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 138 | 31.5 | 30.7 | 0.494 | 1.615 | 0.722 | 3.47 E07 |
| **3** | - | - | - | - | - | - | - |
| **4** | 181 | 28.8 | 28.7 | 0.495 | 1.62 | 0.971 | 3.19 E09 |
| **5** | 201 | 12.4 | 11.8 | 0.472 | 1.383 | 2.482 | 3.39 E25 |
| **6** | 244.5 | 28.4 | 24.2 | 0.491 | 1.579 | 1.278 | 1.51 E11 |
| **7** | 279.5 | 14.2 | 14 | 0.48 | 1.463 | 2.935 | 6.58E25 |

Table 2-20
$\gamma$ -irradiated in air aged 13 days in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **$\delta$(°C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **$S(s^{-1})$** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 143 | 21.4 | 21.4 | 0.493 | 1.6 | 1.104 | 1.73 E12 |
| **3** | - | - | - | - | - | - | - |
| **4** | 189 | 27.7 | 27.5 | 0.492 | 1.597 | 1.042 | 1.28 E10 |
| **5** | 215.7 | 15.7 | 15.4 | 0.482 | 1.482 | 2.076 | 2.54 E20 |
| **6** | 253.5 | 19.5 | 19.5 | 0.485 | 1.521 | 1.931 | 2.40 E17 |
| **7** | 283 | 6.6 | 6.6 | 0.401 | 1.483 | 2.819 | 3.40 E24 |

Table 2-21
$\gamma$ -irradiated in air aged 43 days in air

| **Peak** | **$T_{max}$ ($^{o}C$)** | **$\tau$($^{o}C$)** | **$\delta$($^{o}C$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 141.5 | 22.8 | 22.8 | 0.492 | 1.592 | 1.02 | 1.72 E11 |
| **3** | - | - | - | - | - | - | - |
| **4** | 182.5 | 26.8 | 26.5 | 0.491 | 1.583 | 1.049 | 2.29 E10 |
| **5** | 201 | 10 | 10 | 0.479 | 1.457 | 3.061 | 5.74 E31 |
| **6** | 268.5 | 29.5 | 29.5 | 0.495 | 1.622 | 1.224 | 5.13 E10 |
| **7** | 281 | 11 | 10.4 | 0.466 | 1.328 | 3.772 | 2.89 E33 |

Table 2-22
$\gamma$ -irradiated in air aged 69 days in air

| **Peak** | **$T_{max}$ ($^{o}C$)** | **$\tau$($^{o}C$)** | **$\delta$($^{o}C$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 140 | 22.5 | 22.5 | 0.493 | 1.604 | 1.034 | 2.85 E11 |
| **3** | - | - | - | - | - | - | - |
| **4** | 182 | 26.5 | 26.5 | 0.493 | 1.605 | 1.058 | 3.03 E10 |
| **5** | 202 | 15 | 15 | 0.484 | 1.511 | 2.058 | 6.42 E20 |
| **6** | 242 | 25.5 | 25.5 | 0.491 | 1.579 | 1.423 | 4.69 E12 |
| **7** | 272 | 12 | 12 | 0.481 | 1.471 | 3.377 | 2.22 E30 |

Table 2-23:
$\gamma$ -irradiated in air aged 90 days in air

| **Peak** | **$T_{max}$ ($^{o}C$)** | **$\tau$($^{o}C$)** | **$\delta$($^{o}C$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 148 | 22 | 22 | 0.493 | 1.602 | 1.098 | 9.77 E11 |
| **3** | - | - | - | - | - | - | - |
| **4** | 191.5 | 26.8 | 26.8 | 0.493 | 1.605 | 1.091 | 3.94 E10 |
| **5** | 212.5 | 12 | 12 | 0.481 | 1.471 | 2.673 | 7.02 E26 |
| **6** | 251.5 | 25.5 | 25.5 | 0.491 | 1.58 | 1.463 | 6.93 E12 |
| **7** | 285 | 9 | 9 | 0.453 | 1.216 | 4.134 | 3.37 E36 |

Table 2-24
$\gamma$ -irradiated in $N_2$ aged 1 minute in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **δ(°C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 142.5 | 23.7 | 23 | 0.485 | 1.521 | 0.983 | 5.36 E10 |
| **3** | - | - | - | - | - | - | - |
| **4** | 177.5 | 19.4 | 18.9 | 0.482 | 1.489 | 1.417 | 5.71 E14 |
| **5** | 206.5 | 17.3 | 17.3 | 0.488 | 1.548 | 1.827 | 1.44 E18 |
| **6** | 252 | 26 | 26 | 0.492 | 1.592 | 1.449 | 4.86 E12 |
| **7** | 281 | 12.7 | 12.4 | 0.473 | 1.397 | 3.253 | 5.07E28 |

Table 2-25
$\gamma$ -irradiated in $N_2$ aged 1 day in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **δ(°C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 139 | 27.4 | 27.4 | 0.498 | 1.661 | 0.841 | 1.08 E09 |
| **3** | - | - | - | - | - | - | - |
| **4** | 177 | 21.5 | 21.5 | 0.49 | 1.573 | 1.29 | 2.03 E13 |
| **5** | 206.5 | 14.7 | 14.7 | 0.484 | 1.508 | 2.133 | 2.78 E21 |
| **6** | 242 | 28 | 28 | 0.494 | 1.619 | 1.296 | 2.65 E11 |
| **7** | 279.5 | 13.4 | 13 | 0.474 | 1.409 | 3.095 | 1.99E27 |

Table 2-26
$\gamma$ -irradiated in $N_2$ aged 13 days in air

| **Peak** | **$T_{max}$ (°C)** | **$\tau$(°C)** | **δ(°C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 147.7 | 28.7 | 28.7 | 0.497 | 1.651 | 0.835 | 5.43 E08 |
| **3** | - | - | - | - | - | - | - |
| **4** | 176.5 | 18.4 | 18.4 | 0.489 | 1.556 | 1.498 | 5.29 E15 |
| **5** | 201 | 16 | 16 | 0.484 | 1.504 | 1.905 | 1.72 E19 |
| **6** | 242 | 30 | 30 | 0.496 | 1.634 | 1.187 | 2.08 E10 |
| **7** | 280 | 15 | 15 | 0.483 | 1.493 | 2.789 | 2.28 E24 |

Table 2-27
$\gamma$ -irradiated in $N_2$ aged 43 days in air

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 135.5 | 26 | 26 | 0.495 | 1.625 | 0.867 | 2.96 E09 |
| **3** | - | - | - | - | - | - | - |
| **4** | 182 | 30 | 30 | 0.497 | 1.643 | 0.936 | 1.19 E09 |
| **5** | 204 | 14 | 14 | 0.483 | 1.499 | 2.224 | 3.31 E22 |
| **6** | 249.5 | 29 | 29 | 0.494 | 1.611 | 1.283 | 1.26 E11 |
| **7** | 281 | 10.5 | 10 | 0.469 | 1.362 | 3.98 | 2.42 E35 |

Table 2-28
$\gamma$ -irradiated in $N_2$ aged 69 days in air

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 144 | 23 | 23 | 0.494 | 1.618 | 1.033 | 2.00 E11 |
| **3** | - | - | - | - | - | - | - |
| **4** | 182 | 23.2 | 23.2 | 0.492 | 1.594 | 1.216 | 1.96 E12 |
| **5** | 209.7 | 15.7 | 15.7 | 0.487 | 1.536 | 2.038 | 1.89 E20 |
| **6** | 249 | 26.4 | 26 | 0.489 | 1.56 | 1.408 | 2.32 E12 |
| **7** | 280.5 | 12 | 12 | 0.481 | 1.474 | 3.428 | 2.09 E30 |

Table 2-29
$\gamma$ -irradiated in $N_2$ aged 90 days in air

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 141 | 20.5 | 20.5 | 0.491 | 1.582 | 1.139 | 5.50 E12 |
| **3** | - | - | - | - | - | - | - |
| **4** | 181.5 | 24 | 24 | 0.491 | 1.585 | 1.167 | 5.62 E11 |
| **5** | 209.5 | 15 | 15 | 0.484 | 1.511 | 2.116 | 1.31 E21 |
| **6** | 248 | 26.5 | 26.5 | 0.492 | 1.595 | 1.38 | 1.28 E12 |
| **7** | 281.5 | 12.4 | 12.4 | 0.481 | 1.478 | 3.385 | 7.34 E29 |

Table 2-30
$\gamma$ -irradiated in $N_2$ aged 1 minute in air

| **Peak** | **$T_{max}$ ($^{o}$C)** | **$\tau$($^{o}$C)** | **$\delta$($^{o}$C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 142.5 | 23.7 | 23 | 0.485 | 1.521 | 0.983 | 5.36 E10 |
| **3** | - | - | - | - | - | - | - |
| **4** | 177.5 | 19.4 | 18.9 | 0.482 | 1.489 | 1.417 | 5.71 E14 |
| **5** | 206.5 | 17.3 | 17.3 | 0.488 | 1.548 | 1.827 | 1.44 E18 |
| **6** | 252 | 26 | 26 | 0.492 | 1.592 | 1.449 | 4.86 E12 |
| **7** | 281 | 12.7 | 12.4 | 0.473 | 1.397 | 3.253 | 5.07E28 |

Table 2-31
$\gamma$ -irradiated in $N_2$ aged 1 day in $N_2$

| **Peak** | **$T_{max}$ ($^{o}$C)** | **$\tau$($^{o}$C)** | **$\delta$($^{o}$C)** | **$\mu_g$** | **Kin Order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 136 | 24.8 | 24.8 | 0.496 | 1.635 | 0.921 | 1.35 E10 |
| **3** | - | - | - | - | - | - | - |
| **4** | 176.5 | 22.7 | 22.7 | 0.491 | 1.58 | 1.207 | 2.31 E12 |
| **5** | 214.4 | 17.7 | 17.7 | 0.487 | 1.536 | 1.831 | 7.42 E17 |
| **6** | 252 | 21.8 | 21.8 | 0.489 | 1.561 | 1.746 | 4.12 E15 |
| **7** | 277.5 | 14.6 | 14.2 | 0.478 | 1.45 | 2.826 | 7.92E24 |

Table 2-32
$\gamma$ -irradiated in $N_2$ aged 13 days in $N_2$

| **Peak** | **$T_{max}$ ($^{o}$C)** | **$\tau$($^{o}$C)** | **$\delta$($^{o}$C)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 139 | 22.8 | 22.8 | 0.492 | 1.592 | 1.008 | 1.43 E11 |
| **3** | - | - | - | - | - | - | - |
| **4** | 174 | 18.4 | 18.4 | 0.489 | 1.556 | 1.481 | 4.22 E15 |
| **5** | 199.2 | 15.8 | 15.8 | 0.485 | 1.519 | 1.931 | 4.04 E19 |
| **6** | 242 | 30.5 | 30.5 | 0.496 | 1.634 | 1.183 | 1.89 E10 |
| **7** | 280.5 | 11.2 | 11.2 | 0.482 | 1.486 | 3.648 | 2.24 E32 |

Table 2-33
$\gamma$ -irradiated in $N_2$ aged 43 days in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 135 | 23 | 23 | 0.493 | 1.605 | 0.984 | 9.46 E10 |
| **3** | - | - | - | - | - | - | - |
| **4** | 178 | 23.4 | 23.4 | 0.493 | 1.598 | 1.134 | 2.99 E11 |
| **5** | 212 | 17 | 16.8 | 0.483 | 1.497 | 1.882 | 3.30 E18 |
| **6** | 246.5 | 30 | 30 | 0.493 | 1.604 | 1.219 | 3.43 E10 |
| **7** | 282 | 11.3 | 10.7 | 0.469 | 1.36 | 3.706 | 5.84E32 |

Table 2-34
$\gamma$ -irradiated in $N_2$ aged 69 days in $N_2$

| **Peak** | **$T_{max}$ ($^oC$)** | **$\tau$($^oC$)** | **$\delta$($^oC$)** | **$\mu_g$** | **Kin order** | **E(eV)** | **S($s^{-1}$)** |
|---|---|---|---|---|---|---|---|
| **1** | - | - | - | - | - | - | - |
| **2** | 133 | 18.7 | 18.5 | 0.486 | 1.528 | 1.188 | 4.64 E13 |
| **3** | - | - | - | - | - | - | - |
| **4** | 181 | 26.5 | 26.5 | 0.493 | 1.605 | 1.053 | 2.84 E10 |
| **5** | 215 | 138 | 13.2 | 0.473 | 1.395 | 2.348 | 1.90 E23 |
| **6** | 246.5 | 25.9 | 25.7 | 0.49 | 1.569 | 1.42 | 3.57 E12 |
| **7** | 280.5 | 12 | 12 | 0.481 | 1.471 | 3.485 | 7.04 E30 |