

Phosphorescence of orthopaedic– grade ultra high molecular weight polyethylene

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Isothermal luminescence decay curves have been measured from orthopaedic–standard ultra high molecular weight polyethylene between 35 and 70 °C on the rising edge of the main glow peak at 70 °C. Preparatory peak-shape analysis of the temperature-resolved glow peak at 70 °C measured at 1 °C s⁻¹ gave a geometrical factor close to 0.5 suggestive of second

order kinetics for both the isothermal and thermally stimulated luminescence. The results of analysis of the phosphorescence of transformed monotonic-to-peak isothermal decay curves are also second order, as is the conclusion from thermoluminescence glow-curve de-convolution. All methods of analysis give an activation energy of about 0.7 eV.

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1 Introduction Ultra-high molecular weight polyethylene (UHMWPE) is a thermoplastic used as a prosthetics material in orthopaedics [1]. Before use, UHMWPE is subjected to high dose gamma irradiation which, although effective as a sterilizing agent, de-links polymer bonds creating free-radicals in the process [2].

Free radicals produced following irradiation consist mainly of allyl and alkyl types [1,2]. Some of the free radicals undergo oxidation thus accelerating the degradation of UHMWPE [3]. Such ageing due to oxidation may be minimised or stabilised by annealing, typically below 200 °C, since the heating enables free-radical recombination reactions [1].

Changes in the concentration of free radicals within the UHMWPE matrix may be monitored using thermoluminescence (TL) where any temperature induced charge recombination appears as a set of temperature-resolved glow peaks [4]. The study and interpretation of TL peaks may be done using appropriate kinetics models. Previous analysis of the TL of UHMWPE using a discrete trap model [5] showed that although the method is feasible for investigating changes in the concentration of free-radicals in UHMWPE, conflicting conclusions reached regarding the order of kinetics and values of the activation energy suggested a need for a more complex model appropriate for a material that is known to be only partially crystalline [6].

In order to further improve understanding of luminescence properties of UHMWPE preparatory to development of suitable calculational models, this paper reports measurements and analysis of the phosphorescence of UHMWPE. The analysis of the luminescence was carried out using the transformation of decay curves to peaks as well as curve fitting methods where an *a priori* knowledge of the order of kinetics is not a requirement.

2 Phosphorescence Phosphorescence is the emission of thermally stimulated luminescence at a constant temperature. The emission process is first-order if the time-dependence of the luminescence intensity at temperature T is a simple exponential, i.e.

$$I(t) = I_o \exp(-pt) \tag{1}$$

where p $\alpha \exp(-E/kT)$ is the decay constant, E is the activation energy, I_o is the initial value of the intensity, and k is Boltzmann's constant [4]. Thus first-order behaviour can be identified as a linear semi-log plot of I(t) against time t. On the other hand, 'general order' emission is a dependence of I(t) on t as

$$I(t) = \frac{n_o^b p'}{\left[1 + (b-1)p' n_o^{b-1} t\right]^{\frac{b}{b-1}}}$$
(2)



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where b (\neq 1) is the order of kinetics, n_o is the initial charge concentration in the defect or charge-trap undergoing the isothermal decay, and p' is analogous to p in Eq. (1). Equation (2) reduces to second-order if b = 2. Qualitatively, general-order behaviour is identified as a linear dependence of I^{(1-b)/b} on t whereas the second order characteristic is shown as a linear change with time of [I_o/I(t)]^{1/2} [4].

Despite the kinetics alternatives discussed above, the linear feature could not be convincingly established in preparatory measurements. Methods not dependent on a prior knowledge of the order of kinetics b were therefore used.

3 Experimental Samples used were discs of UHMWPE (Poly Hi Solidur, Germany) of 1 mm thickness and 5 mm diameter. Thermally stimulated luminescence was measured in a nitrogen atmosphere using a RISO Luminescence reader (TL/OSL-DA-15). The luminescence was detected by an Electron Tubes Ltd model 9235QB photomultiplier through a BG-39 band-pass filter (transmission band 340-620 nm FWHM). Phosphorescence was measured at various temperatures between 35 and 70 °C.

Figure 1 shows two separate phosphorescence decay curves, one measured at 40 °C and the other, shown in the inset, at 50 °C. The initial increase in intensity values in each graph is an experimental artefact and is the partial thermoluminescence appearing as the sample stage heats up to set temperature. The line through data points in the main graph is a function of form y = mx + c and is included as a visual guide only. Figure 1, showing a change in the decay from being apparently linear at 40 °C (main graph) to non-linear at 50 °C (inset), is a qualitative indicator of the dynamic nature of the kinetics of the phosphorescence and a justification for not using a constant value for the order of kinetics during analyses of phosphorescence decay curves in UHMWPE.

4 Results and discussion

4.1 Order of kinetics The order of kinetics for the phosphorescence was determined by the peak shape method [4]. The peaks used in this test were not thermoluminescence glow peaks were the luminescence intensity is plotted against temperature [4, 5], but rather phosphorescence decay curves transformed into peaks. In this case, the intensity is plotted as a function of time. The procedure for the transformation will be described in due course.

The peak-shape method, which can be used to determine either the order of kinetics or the activation energy relies on the geometrical division of a TL peak of maximum intensity at temperature T_m into ω , τ and δ . The parameter ω is defined as the width of the peak at half the peak-intensity (i.e at full width half maximum, FWHM). On the other hand, the lower half-width defines τ and the upper half-width δ i.e. $\omega = T_2 - T_1$; $\tau = T_m - T_1$; $\delta = T_2 - T_m$. The order of kinetics is then abstracted from the relationship of b and the Halperin-Braner geometrical factor μ_g where μ_g = δ/ω [4]. In this test, which adapted the method for transformed peaks, measurements at 50, 60 and 70 °C gave μ_g =

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0.55, 0.50, 0.51 respectively all of which are close to 0.5 thus indicating second-order kinetics.



Figure 1 Phosphorescence decay curve at 40° C (open cycles) and in the inset at 50 °C (solid cycles).

4.2 Calculation of activation energy

4.2.1 Peak shape analysis The activation energy was calculated using the peak-shape method on the basis of second order kinetics using the equation

$$E_{\gamma} = C_{\gamma} \left[\frac{kT_{m}^{2}}{\gamma} - b_{\gamma} (2kT_{m}^{2}) \right] \quad (3)$$

where γ is any of ω , τ , or δ and C_{γ} is a reference constant corresponding to any of the three parameters ω , τ , or δ [4]. Since Eq. (3) has temperature rather than time as the variable, the calculations were made on a set of five TL glow peaks measured at 0.6 °C/s between 30 and 200 °C after irradiation to 215 Gy. The average value of the geometrical factor for the set was $\mu_g = 0.52 \pm 0.04$ eV. This is indicative of second order kinetics and is in good agreement with the geometrical analysis of transformed phosphorescence peaks discussed in Section 4.1.

Figure 2 compares values of the activation energy E_{ω} , E_{τ} and E_{δ} evaluated using Eq. (3). It is apparent that although the values are comparable, in general $E_{\omega} < E_{\tau} < E_{\delta}$. The reasons for the systematic difference are not yet clear but could simply be a reflection of the difficulty of subjectively judging accurately the position of data points at FWHM of each peak. The average value for each method for the 5 measurements were found to be $E_{\omega} = 0.60 \pm 0.05$ eV, $E_{\tau} = 0.65 \pm 0.07$ eV and $E_{\delta} = 0.74 \pm 0.05$ eV which are mutually consistent.

Previous measurements on the dependence of the activation energy on irradiation dose made using TL at 1°C/s [5] showed that although the value of the activation energy changed with dose, it was about 0.6 eV around 220 Gy. This is comparable with values in this work made on samples irradiated to 215 Gy but measured at 0.6 °C/s. There have otherwise been little else on calculation of kinetic parameters in UHMWPE using the discrete trap-model although there are several examples of theoretical formula-

tions of analytical methods proposed for polymers in general, e.g. [7]. Of particular interest might be the estimation that the electron affinity in alkyl radicals, which should correspond to the electron trap energy (activation energy) in this study, is of the order of 1 eV [7].



Figure 2 Values of the activation energy for three alternative peak-shape methods described in the text.

4.2.2 Monotonic-to-peak transformation The time-dependent change of phosphorescence can be transformed into a peak with similar kinetics by using the product I(t)t as the dependent variable [4, 8]. For example, the first-order decay curve of Eq. (1) may be transformed into a peak

$$y = \frac{n_o}{\gamma} e^x \exp(-\frac{e^x}{\gamma})$$
(4)

on the y vs x axes where y = It, $x = \ln t$, $\gamma = 1/p$ and n_o is as previously defined in Section 2. Similar expressions may be obtained for the second- and general order cases. The key to the technique is that if phosphorescence is measured at two different temperatures, say, T_1 and T_2 , the peaks will have maxima $\ln \gamma_1$ at T_1 and $\ln \gamma_2$ at T_2 . The difference in temperature produces peaks shifted by Δ on the x axis, that is, on the ln t scale where the shift $\Delta = \ln \gamma_2 - \ln \gamma_1$ can be expressed more explicitly as

$$\Delta = \frac{E}{k} \left(\frac{1}{T_2} - \frac{1}{T_2} \right) \tag{5}$$

from which the activation energy E may be evaluated.

Measurements for the analysis were made at 35, 40, 50, 60, 65 and 70 °C. However, it was found that peaks could only be properly resolved for $\Delta T \ge 20$ °C where ΔT is the temperature difference for two peaks which need not have been measured successively. Figure 3 shows an example of transformed peaks from phosphorescence measured at 60 and 65 °C. Analyses of peak pairs at 40 and 60 °C, and 35-70 °C gave activation energy values of 0.78 eV and 0.74 eV respectively. These values are consistent with values from peak-shape analysis presented earlier.



Figure 3 A comparison of phosphorescence measured at 60 and 65 °C transformed into TL-like shape for kinetic analysis.

4.2.3 Thermoluminescence glow-curve decon-volution In order to provide an independent comparison of results from phosphorescence analyses, thermoluminescence glow curves were measured for analysis using 'general order' computerized glow-curve deconvolution. Since thermoluminescence glow-curves in UHMWPE consist of two peaks [5], curve fitting was carried out using a sum of two terms of form

$$I(T) = I_m b^{\frac{b}{b-1}} \exp\left(\frac{E}{kT} \frac{T - T_m}{T_m}\right) \times \left[(b-1)(1-\Delta) \frac{T^2}{T_m^2} \exp\left(\frac{E}{kT} \frac{T - T_m}{T_m}\right) + Z_m \right]^{\frac{-b}{b-1}}$$
(6)

where I(T) is the thermoluminescence intensity, k is Boltzmann's constant, $\Delta = 2kT/E$, $\Delta_m = 2kT_m/E$ and $Z_m = 1+(b-1)\Delta_m$ [9]. In this method, the activation energy E, the peak-temperature T_m, as well as the order of kinetics b are independent variables that are determined by iteration to a best fit and they therefore provide independent comparable values for the calculations of the preceding sections.

Figure 4 shows a glow-curve measured between 30 and 200 °C at 0.4 °C/s following irradiation to 215 Gy. The solid line through the glow-curve is the best fit of Eq. (6) with $b = 2.00 \pm 0.06$ and $E = 0.80 \pm 0.01$ eV for the main peak, the subject of this study. The results from the deconvolution analysis show that the emergent value of b is second order, in good agreement with peak-shape and transformation techniques. The value of the activation energy is also consistent with calculations from the other methods described. Kinetic parameters obtained using various methods described in the text show that values of the activation energy for a similar order of kinetics are consistent.





Figure 4 Thermoluminescence glow-curve of UHMWPE. The solid line is the best fit of a general-order equation which produces b = 2 and E = 0.80 eV.

5 Summary The phosphorescence of ultra high molecular weight polyethylene has been investigated between 35 and 70 °C on the rising edge of the main glow peak at 70 °C. Peak-shape analysis on both dynamic temperature and transformed isothermal decay curves gave a geometrical factor close to 0.5 suggestive of second-order kinetics, a conclusion supported by results from de-convolution of thermoluminescence peaks. In addition, all methods for calculation of the activation energy are based on the discrete trap model and give similar values of the activation energy at about 0.7 eV for the charge eviction process leading to emission of luminescence in UHMWPE.

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