Thermally Stimulated Luminescence in Oxidized Gamma Sterilized Ultra High Molecular Weight Polyethylene

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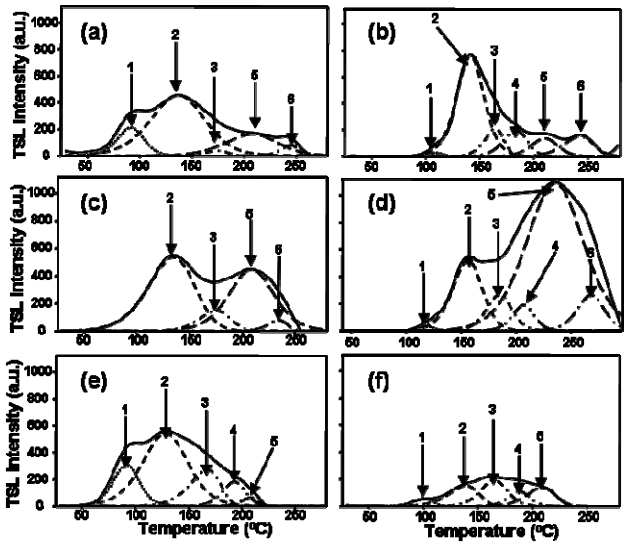
Introduction: Thermally stimulated luminescence (TSL) and chemiluminescence (CL) have been used by many to understand the mechanisms of luminescence in polymers.[1,2] TSL is used to investigate luminescence due to irradiation, whereas, CL is used to study luminescence due to oxidation. It is important to note that CL may occur during TSL provided the material has been previously oxidized. Jahan *et al* used TSL to investigate aging of orthopedic ultra-high molecular weight polyethylene (UHMWPE) following gamma sterilization in air and subsequent storage in air, liquid N_2 or saline solution.[3] Blakey *et al* reported that CL in PE is due to oxidized species within the polymer.[2] TSL has been primarily attributed to free radicals that remain trapped in the polymer matrix following aging or oxidation. In this report, samples were sterilized and stored in N_2, and the resulting TSL glow (total luminescence as a function of temperature) was compared with that detected in samples sterilized and stored in air. Also, samples were thermally oxidized to compare CL to TSL.

Methods: Conventional UHMWPE of resin 1050 (ram extruded) was used in this study. TSL measurements were conducted on films (~60μm) prepared using a Microm 360 Microtome (Richard-Allan Scientific). Samples were irradiated with gamma (~3 Mrad ^{60}Co). Three separate groups (I, II, III) of samples were irradiated and aged in N_2, irradiated and aged in air, and irradiated in N_2 and aged in air, respectively. TSL measurements were performed using a commercial dosimeter (Harshaw QS 3500) in which the heating chamber was continuously purged with dry, filtered N_2. The samples were heated from 30°C to 280°C at a rate of $1^oC\ s^{-1}$, and the resulting TSL intensity was recorded as a function of temperature using a WinREMS software interface. For analyses, the glow curve of a control sample (sample with no irradiation) was subtracted from that of each test sample, yielding difference TSL (dTSL). In conjunction with a curve-fit program (Los Alamos National Lab), simulation of the glow curves provided TSL parameters characterizing each individual peak (deconvoluted). For detection of CL using the same TSL apparatus, as described above, bars and films were thermally oxidized at 160 °C for 1 hour in the presence of air (oxygen). The same procedure was repeated in the presence of N_2.

Results / Discussion: Shown in Figure 1 are the initial and final dTSL of aged GUR 1050 films. Six glow peaks are apparent from the figure. Peaks 1, 2, and 5 are of main interest because they are distinguishable without fitting. CL, conducted for the first time in this lab using the TSL setup, has shown the existence of two peaks at approximately 100 °C (Peak 1) and 210 °C (Peak 5) from thermally oxidized UHMWPE, which have previously been attributed to oxidized species.[4] Peak 2 (~140 °C) has been previously attributed to radical annihilation in the crystalline region of the polymer.[5,6] The narrowing of Peak 2 from (a) to (b) can be ascribed to the varying rate of oxidation (by migration) of radicals trapped in crystalline lamella of different sizes. During early stages of oxidation the size distribution can be heterogeneous; and the resulting TSL (Peak 2) broad. After prolonged oxidation, radicals may stay trapped only in large, homogeneously distributed lamella, and as a result Peak 2 becomes narrow. Peak 5 grows in air-irradiated samples (d) but not in nitrogen irradiated ones (b or f) most likely due to production of oxides during irradiation. The samples aged in nitrogen showed minimum luminescence because of the lack of oxides, although radical concentration could be high. The Peaks 3, 4 and 6 are yet to be identified.

Figure 1: GUR 1050 Representative Fitted Glow Curves (a) γ in N_2 10 sec in air; (b) γ in N_2 70 days in air; (c) γ in air day 2 in air (d) γ in air day 81 in air; (e) γ in N_2 day 1 in N_2; (f) γ in N_2 day 81 in N_2



Conclusions: In summary, both γ induced and thermal oxidation produce peaks at approximately the same temperatures. Also, irradiation and aging environment play an important role in the TSL output. Glow curve analyses provide thermal activation energy and frequency factors for each glow peak (not shown).

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