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4 **ON THE ASSESSMENT OF OXIDATIVE STABILITY OF**  
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7 **POST-IRRADIATION STABILIZED HIGHLY**  
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10 **CROSSLINKED UHMWPES BY THERMOGRAVIMETRY**  
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4 **ABSTRACT**  
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10           The characterization of the oxidative resistance of contemporary UHMWPE  
11 formulations currently relies upon time-consuming accelerated aging protocols and  
12 subsequent FTIR assessment. The potential of thermogravimetric analysis (TGA) for this  
13 purpose, however, remains mostly unknown. To study radiation and stabilization-induced  
14 changes in the decomposition process, TGA curves corresponding to virgin, e-beam  
15 irradiated, and post-irradiation stabilized UHMWPE materials were registered and  
16 analyzed. TGA traces of most materials exhibited similar features, with two weight  
17 increases before an initially non-linear decomposition and a portion of linear  
18 volatilization starting near 400 °C. After irradiation, the onset of the second weight  
19 increase shifted to lower temperatures and the linear volatilization stage began at higher  
20 temperatures. While post-irradiation annealing did not introduce significant changes in  
21 TGA curves, remelting delayed the onset of the second weight gain. Furthermore, this  
22 weight increase disappeared after vitamin E diffusion. Energies of activation of the  
23 initially predominant thermooxidation and the subsequent thermodegradation processes  
24 were also calculated from fraction of conversion and reciprocal of temperature plots. As  
25 opposed to TGA, FTIR assessment of oxidation following accelerated aging at 120 °C for  
26 36 hours appeared to be less sensitive to discriminate between the different materials.  
27 This study confirms TGA as a promising technique to characterize the oxidative  
28 resistance of medical grade UHMWPEs.  
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58 **KEYWORDS:** highly crosslinked UHMWPE; oxidation; vitamin E; stabilization; FTIR; TGA.  
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4 **INTRODUCTION**  
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10       Oxidation of ultra-high molecular weight polyethylene (UHMWPE) components  
11 remains as one of the most relevant concerns in total joint arthroplasty (TJA).  
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14 Historically, gamma sterilization and prolonged storage in air were soon associated with  
15 oxidative degradation and mechanical deterioration of UHMWPE bearings [1, 2]. By the  
16 mid 90s, orthopedic manufacturers abandoned gamma sterilization in air and introduced  
17 packaging in an inert gas to reduce the susceptibility to oxidation of gamma irradiated  
18 UHMWPE [3]. Other non-radiative sterilization methods, such as ethylene oxide and gas  
19 plasma, were also reconsidered since they do not induce the oxidation of UHMWPE, but  
20 without the attractive improvement in wear resistance that radiation sterilization brings  
21 about. Thus, gamma inert sterilized UHMWPE is currently considered as the  
22 conventional formulation for use in TJA. Following the introduction of conventional  
23 UHMWPE, the development and clinical introduction of first-generation highly  
24 crosslinked polyethylenes aimed at producing formulations with superior wear resistance  
25 and good oxidative stability, as provided by elevated crosslink densities that high  
26 radiation doses impart to UHMWPE and post-irradiation thermal treatments, respectively  
27 [4]. However, conventional gamma inert sterilized UHMWPE retrievals have been shown  
28 to exhibit in vivo oxidation mechanisms similar to those of historical gamma air sterilized  
29 UHMWPE components [5, 6]. Also, the oxidative stability of first-generation highly  
30 crosslinked polyethylenes has been demonstrated to be formulation dependent. Both  
31 gamma inert sterilization and high-dose irradiation followed by submelt annealing  
32 treatments leave behind residual free radicals within UHMWPE, which initiate the in  
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4 vivo oxidation process as molecular oxygen dissolved in body and tissue fluids becomes  
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6 available [7]. On the contrary, post-irradiation remelting treatments reduce radiation-  
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8 induced free radicals to undetectable levels, but at the expense of crystallinity and  
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10 mechanical properties, such as fatigue crack propagation resistance [8-10]. To  
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12 simultaneously avoid long-term oxidation and mechanical concerns of first-generation  
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14 highly crosslinked polyethylenes, second-generation vitamin E stabilized highly  
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16 crosslinked polyethylenes have been developed and very recently introduced for clinical  
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18 use in total hip arthroplasty [11, 12].  
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26 To date, the efficacy of changes in packaging, sterilization and stabilization  
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28 strategies with regard to the oxidative stability of contemporary polyethylene  
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30 formulations is being established *in vitro* by means of time-consuming accelerated aging  
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32 protocols and subsequent FTIR characterization of oxidation [13, 14]. Standard  
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34 accelerated aging protocols (ASTM International F2003-00 and F2003-02) try to mimic  
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36 the spatial distribution of physical and chemical changes caused by oxidation within  
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38 UHMWPE based on thermal aging at temperatures below the onset of melting. Thus,  
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40 accelerated aging has been performed either in air at 80 °C for three weeks or at 70 °C  
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42 and elevated oxygen pressure (5 atm) for two weeks, and then the levels of oxidation  
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44 products, namely carbonyl-containing compounds, are determined by FTIR per ASTM  
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46 F2102-06e1. Also, other alternative methods are being employed to reproduce the effects  
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48 of natural aging in UHMWPE. Thus, severe oxidative challenges performed at 120 °C for  
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50 up to 36 hours succeed to promote subsurface high oxidation areas as reflected in the  
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52 presence of white banding in fracture surfaces of artificially aged UHMWPE tensile  
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4 specimens [15]. In any case, the long-term degradation that UHMWPE formulations  
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6 undergo in vivo and the thermally induced oxidation are two different processes, and  
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8 although they might be correlated, extrapolations from accelerated aging results should  
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10 be drawn carefully.  
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16 Thermogravimetric analysis (TGA), on the other hand, is a useful technique in the  
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18 characterization of the thermal decomposition of polymeric materials and their  
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20 composites [16-29]. In particular, the thermal degradation of LDPE and HDPE and the  
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22 underlying kinetic models have been matter of intense research since the 1960s [19, 22,  
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24 23]. Surprisingly, and despite the relevance and wide range of applications of UHMWPE,  
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26 few studies have been published on the thermal stability of this polymer as assessed by  
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28 TGA [17, 20, 30-33]. To the authors' knowledge, the works by Slouf et al., Peltzer and  
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30 colleagues, and Koleva and coworkers represent the only publications on this topic for  
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32 the last two years [20, 30, 31]. Therefore, the potential of TGA to evaluate the thermo-  
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34 oxidative stability of contemporary UHMWPE for orthopedic use remains mostly  
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36 unknown. In this sense, the presence of radiation-induced free radicals within gamma  
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38 sterilized UHMWPE and highly crosslinked polyethylenes may alter the decomposition  
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40 reactions and kinetics of UHMWPE, and this might be reflected in TGA experiments.  
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42 The objective of the present study was to evaluate the suitability of TGA in  
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44 characterizing the oxidative stability of various highly crosslinked polyethylene  
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46 formulations. We hypothesized that TGA would discriminate between UHMWPEs  
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48 irradiated to different doses and stabilized by thermal treatments and natural antioxidants.  
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4 Additionally, potential correlations between the features of TGA decomposition curves  
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6 and levels of oxidation after a severe oxidative challenge were explored.  
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## 10 11 12 13 14 **MATERIALS AND METHODS**

### 15 16 17 *Materials*

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20         Rectangular prisms (63.5x12.7x6.35 mm<sup>3</sup>) were machined out of a compression-  
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22 molded sheet of raw UHMWPE GUR 1050 (Perplas Medical, Ltd; UK), and then  
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24 electron-beam irradiated in air to three different doses: 50, 100 and 150 kGy. A 10-MeV  
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26 Rhodotron TT 200 accelerator (Ionmed Esterilización S.A., Tarancón, Spain) was used to  
27  
28 perform the single side irradiation in 25 kGy passes. After irradiation, some samples  
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30 underwent thermal stabilization by either annealing at 130 °C or remelting at 150 °C for 2  
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32 hours in a vacuum oven (Weiss-Gallenkamp, Loughborough, UK) followed by a final  
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34 slow cooling stage (0.5 °C/min) to room temperature. On the other hand, other specimens  
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36 were infused with alpha-tocopherol (vitamin E). For that purpose, 200 microns thin  
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38 sections were obtained using a microtome from non-irradiated (virgin), and e-beam  
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40 irradiated UHMWPE samples, and vitamin E was diffused into them at 120 °C for 10  
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42 min. The final concentration of vitamin E averaged 6.5 percent by weight, as measured  
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44 by means of FTIR. Although much lower concentrations (~ 0.4%) are considered for  
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46 stabilization purposes of commercial vitamin E containing UHMWPEs, the foregoing  
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48 concentration was chosen to emphasize the role of this antioxidant. In summary, 13  
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50 material groups were included in this study, namely, non-irradiated UHMWPE (NI), as-  
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52 irradiated UHMWPEs ( $\beta$ 50,  $\beta$ 100, and  $\beta$ 150, for 50, 100 and 150 kGy of absorbed  
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4 radiation dose, respectively), annealed UHMWPEs ( $\beta$ 50A,  $\beta$ 100A,  $\beta$ 150A), remelted  
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6 UHMWPEs ( $\beta$ 50R,  $\beta$ 100R, and  $\beta$ 150R), and vitamin E-infused UHMWPEs (NI-VE,  
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8  $\beta$ 50-VE,  $\beta$ 100-VE, and  $\beta$ 150-VE).  
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### 11 12 13 14 **Methods**

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16 Thermogravimetric experiments were conducted in air on a TA Instruments  
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18 thermobalance (accuracy:  $10^{-4}$  mg) from room temperature to 600 °C at a heating rate of  
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20 10 °C/min. In all cases, specimens were prepared from the center of microtomed sections  
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22 of the rectangular prisms. The initial sample weight was approximately 6 mg, and at least  
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24 three samples per material group were tested, giving a total of 76 experiments. The main  
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26 features of decomposition curves were documented and analyzed for all materials. Our  
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28 main interest was not to study the behavior of UHMWPE at temperatures far above the  
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30 typical service and processing temperatures of UHMWPE in TJA, but rather to gain  
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32 insight into the effects of irradiation and thermal stabilization on UHMWPE properties  
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34 (oxidative resistance, microstructure, etc.) as reflected by TGA experiments.  
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42 Energies of activation were determined from fraction of conversion,  $\alpha = W_i -$   
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44  $W_T/W_i$ , against the reciprocal temperature plots, where  $W_i$  is the initial weight, and  $W_T$  is  
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46 the weight at temperature T. As  $\alpha$  vs.  $1/T$  curves were clearly non-linear in all cases, the  
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48 Coats-Redfern method was chosen to obtain activation energies from specific  
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50 temperature ranges. The Coats-Redfern technique uses the following relationship to  
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52 determine energies of activation:  
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$$56 \ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{qE_A} - \frac{E_A}{RT} \quad (\text{eq. 1})$$

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4 where T is the temperature, A pre-exponential factor, R the gas constant, q the heating  
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6 rate, and  $E_A$  the activation energy. The algebraic function,  $g(\alpha)$ , depends on the kinetic  
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8 model chosen to describe the thermal degradation reactions in the solid state. If the  
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10 correct  $g(\alpha)$  function is used, the plot of the left term in equation 1 against the reciprocal  
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12 of temperature should be a straight line in the selected range. Various  $g(\alpha)$  were tested to  
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14 find the best fit to the experimental fraction of conversion curves obtained for the  
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16 materials included in this study.  
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24 To investigate the oxidative stability of pristine and highly crosslinked  
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26 polyethylenes, sections were microtomed from all the materials and then subjected to a  
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28 severe oxidative challenge. Thus, UHMWPE sections underwent thermal aging in air at  
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30 120 °C for 36 hours [15]. The levels of final oxidation products (carbonyl groups) were  
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32 measured at the center of the sections by FTIR spectroscopy, and oxidation indices were  
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34 calculated as the area ratio of the carbonyl band centered at  $1718\text{ cm}^{-1}$  and the reference  
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36 band at  $1360\text{ cm}^{-1}$  following ASTM F2102 guidelines.  
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44 Statistical analysis was conducted to explore significant differences and potential  
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46 correlations between the parameters of TGA curves, energies of activation and oxidation  
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48 levels for the different materials. Student's t-tests, and general linear models with  $p <$   
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50 0.05 as level of significance were used.  
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## RESULTS AND DISCUSSION

### *Thermogravimetric curves*

First, attention was paid to the thermogravimetric behavior of non-irradiated and as-irradiated UHMWPEs. Decomposition curves corresponding to virgin UHMWPE exhibited 5 regions demarcated by four temperature points,  $T_0$ ,  $T_1$ ,  $T_2$ , and  $T_3$ , as indicated in Figure 1A. Sample mass remained constant at the beginning of the heating run, but specimens soon started to gain weight, reaching the maximum at  $T_0$ . More detailed observations confirmed not only the foregoing weight increase, but also a previous and much lower mass gain at temperatures close to the melting point of the polymer. After this minor increase, the sample mass gently decreased from  $T_A$  to  $T_B$ , which was the onset of the subsequent weight gain with maximum at  $T_0$  (Figure 1B). Once the greatest weight was reached at  $T_0$ , the decomposition began and samples lost mass in a non-linear fashion up to  $T_1$ . In this region, the slope of the mass loss changed, becoming less pronounced at temperatures inferior but close to  $T_1$ . Afterwards, sample weight dropped linearly from  $T_1$  to  $T_2$ . From the latter temperature a non-linear and less steep weight loss took place, and complete volatilization was reached at  $T_3$ .

Irradiation was responsible for noticeable changes in the location of  $T_A$ ,  $T_B$ ,  $T_0$  and  $T_1$  (see Table 1), but the shape of the decomposition curves was essentially identical to that of NI samples (Figures 1A-B). As-irradiated materials experienced the first weight maximum,  $T_A$ , at temperatures significantly higher than that of virgin UHMWPE ( $p <$

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4 0.0001). In contrast, the onset of the second weight gain,  $T_B$ , occurred at temperatures 30  
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6 degrees lower than in the non-irradiated material ( $p < 0.0001$ ). Likewise, as-irradiated  
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8 materials reached maximum weights at significantly lower  $T_0$  temperatures than virgin  
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10 UHMWPE (~236 °C versus 242 °C, on average, respectively). The maximum weight at  
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12  $T_0$ ,  $W_{T_0}$ , however, was the same (100.8%) for both virgin and as-irradiated UHMWPEs.  
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14 No significant differences in  $T_A$ ,  $T_B$  and  $T_0$  were observed within as-irradiated materials  
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16 regardless of radiation dose. Besides, the linear weight loss stage began earlier in the case  
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18 of virgin UHMWPE (average  $T_1 = 404$  °C), and  $T_1$  gradually increased with radiation  
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20 dose up to 422 °C at the highest dose ( $p < 0.0001$ ). As-irradiated materials also had  
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22 significantly higher remaining weights (4-7% higher) at the onset of the linear  
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24 decomposition stage than NI samples ( $p < 0.0001$ ). Once the linear weight loss was over  
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26 at  $T_2 \sim 475$  °C, as-irradiated materials weighed 2% less than virgin UHMWPE ( $p <$   
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28 0.0001). The temperature of complete volatilization significantly decreased at the highest  
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30 radiation dose (average  $T_3 = 573$  °C for  $\beta 150$ ) compared to NI UHMWPE (average  $T_3 =$   
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32 583 °C).  
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44 Post-irradiation annealed and remelted materials presented thermogravimetric  
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46 traces similar to those of virgin and as-irradiated materials. On the contrary, vitamin E-  
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48 infused UHMWPEs started to lose weight sooner than thermally stabilized materials  
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50 (Figure 2A) since they did not gain weight after the minor increase with maximum at  $T_A$   
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52 (Figure 2B). With regard to the first weight gain, the stabilization treatments had distinct  
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54 effects on the location of  $T_A$ . Annealing at 130 °C significantly increased  $T_A$  with respect  
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56 to the polymer irradiated at low and intermediate doses ( $p \leq 0.04$ ), as shown in Table 1.  
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4 On the other hand, remelting significantly decreased  $T_A$  ( $p \leq 0.002$ ), regardless of  
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6 radiation dose. Concerning the second mass increase, the behavior of annealed materials  
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8 closely resembled that of as-irradiated UHMWPEs, whereas remelted UHMWPEs were  
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10 closer to NI specimens. Thus, the onset,  $T_B$ , and maximum,  $T_0$ , of the second weight gain  
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12 did not significantly vary after annealing, but strongly increased in remelted UHMWPEs  
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14 as compared with as-irradiated materials ( $p \leq 0.0001$  and  $p < 0.009$  for  $T_B$  and  $T_0$ ,  
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16 respectively; Table 1). Remelted UHMWPEs generally had significantly lower  $W_{T_0}$  (0.1-  
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18 0.2%) than annealed and as-irradiated materials ( $p < 0.007$  in both cases). The effects of  
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20 irradiation and stabilization on  $T_B$  are summarized in Figure 3A. On the other hand, all  
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22 the stabilization methods generally retarded the onset of the linear decomposition stage,  
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24 making  $T_1$  to increase with respect to non-stabilized UHMWPEs. This effect was  
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26 especially noticeable after vitamin E stabilization, as  $T_1$  registered a significant rise  
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28 between 6 and 15 °C ( $p \leq 0.03$  with respect to 50 and 100 kGy as-irradiated UHMWPEs;  
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30 Figure 3B). Findings concerning the remaining weight at the beginning of the linear  
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32 volatilization stage,  $W_{T_1}$ , pointed out generally higher values for vitamin E infused  
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34 materials with respect to annealed and remelted UHMWPEs, and also for the non-  
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36 irradiated but vitamin E-stabilized polyethylene (10% heavier than NI on average).  
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38 Finally, the end of the linear weight loss stage,  $T_2$ , remained close to 475 °C for all the  
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40 stabilized materials, and no clear trend was observed for  $T_3$ , that is the temperature at  
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42 which volatilization was complete (see Table 1).  
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The previous thermogravimetric behavior can be interpreted on the basis of three processes which are most likely involved in the decomposition and volatilization of

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4 UHMWPE in air. These mechanisms manifest themselves in the thermogravimetric  
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6 curves and will be discussed in the following lines. The first process is the dissolution of  
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8 a small amount of air into the UHMWPE sample as crystalline regions become melted.  
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10 This phenomenon might explain the first weight increase noted for all materials,  
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12 regardless of irradiation and stabilization treatments, as well as the shift towards higher  
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14 temperatures of this maximum in the case of higher crystallinity materials (i.e. as-  
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16 irradiated UHMWPEs) [34]. The other two processes are the oxidation cycle and the  
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18 purely thermal degradation, which take place simultaneously from the beginning of the  
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20 experiment. Both processes are explained on the basis of complex free radical chain  
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22 mechanisms, but oxidation implies the incorporation of oxygen into the molecular chains  
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24 provided free radicals are available for reaction. After the initial incorporation of oxygen,  
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26 oxidation results in chain scission and creates more radicals that further react with  
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28 oxygen, fueling the complex oxidation cycle [35, 36]. On the other hand, thermal  
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30 degradation generates macroradicals by thermal scission of molecular chains, and then it  
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32 is responsible for a gradual decrease in the molecular weight of the polymer (or  
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34 depolymerization), giving place to the eventual volatilization of low molecular weight  
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36 compounds [23]. Therefore, oxidation entails an initial weight increase of the sample  
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38 because of the oxygen uptake, whereas thermal degradation creates no mass gain.  
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40 Keeping the foregoing in mind, the different initial states of non-irradiated, as-irradiated,  
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42 and stabilized UHMWPEs might be responsible for changes in the features of the  
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44 thermogravimetric traces. Thus, non-irradiated UHMWPE possesses no free radicals (or a  
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46 negligible amount) at the beginning of the experiment, but the thermal degradation effect  
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48 originates macroradicals that are able to react with oxygen, resulting in the second weight  
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4 increase with maximum at  $T_0$  in the decomposition curve. Radiation-induced free radicals  
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6 are present within as-irradiated UHMWPEs and they could react with oxygen from the  
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8 very beginning of the thermogravimetric experiment, and for that reason  $T_B$ , the onset of  
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10 the mass increase with maximum at  $T_0$ , occurred much before than in virgin UHMWPE  
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12 (see Figures 3A). The effect of stabilization methods on the oxidation and thermal  
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14 degradation processes depends on their efficacy. Annealing appeared to not be able to  
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16 completely extinguish radiation-induced free radicals, and the parameters of the second  
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18 weight gain remained mostly unchanged as compared with as-irradiated UHMWPE.  
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20 Remelting, however, succeeded to eliminate radiation-induced free radicals, and the  
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22 oxygen uptake happened only after some thermal degradation that originates some  
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24 volatilization and macroradicals, which can react with oxygen, as occurred in non-  
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26 irradiated UHMWPE. Vitamin E and its derivatives arisen in the melt state (dimeric and  
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28 trimeric products) may neutralize not only radiation-induced free radicals in the polymer  
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30 [37, 38], but also a significant amount of both thermal and oxidative macroradicals  
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32 generated during the thermogravimetric experiment. This fact might be reflected in the  
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34 absence of the second weight gain in vitamin E infused materials, and in the typically  
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36 higher remaining weight of vitamin E-infused UHMWPEs immediately before the linear  
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38 volatilization stage at  $T_1$ . However, vitamin E may not be able to completely avoid the  
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40 thermal depolymerization and some volatilization of UHMWPE, as the shape of the  
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42 associated thermogravimetric curves remained essentially the same. Also, the oxidation  
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44 process cannot be discarded because if oxidation was totally absent in the experiment, the  
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46 decomposition trace should resemble the typical thermogravimetric curve found for  
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48 experiments in nitrogen atmosphere [30].  
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4           Concerning the effect of the radiation dose, the influence of this factor was more  
5  
6 noticeable on the onset of the linear volatilization at  $T_1$ . This linear volatilization could be  
7  
8 considered as a stage in which oxidative degradation becomes negligible with respect to  
9  
10 the thermal degradation mechanism that prevails from  $T_1$  and later on. The present  
11  
12 findings confirmed that the higher the radiation dose the later the linear volatilization  
13  
14 started, so that irradiated materials were more thermally stable. In this sense, Tidjani and  
15  
16 Krupa have reported a better thermal stability of LLDPE crosslinked by gamma  
17  
18 irradiation based on TGA experiments in nitrogen [21, 26]. Probably, the more stable  
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20 crosslinked networks might hinder thermal scissions even at relatively high temperatures,  
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22 being this influence especially noticeable at high radiation doses (150 kGy), that is, when  
23  
24 the crosslink density saturates [39]. Finally, irradiation and stabilization methods appear  
25  
26 to have no significant effects on the final volatilization stage (i.e. on  $T_2$ , and  $T_3$ ) of  
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28 UHMWPE.  
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### 35 36 37 38 *Energies of activation* 39 40 41 42

43           Koleva and colleagues have recently investigated the suitability of the most  
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45 common kinetic models and the associated algebraic expressions in describing the  
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47 thermal degradation of carbon fiber and aramid fiber UHMWPE composites [20]. They  
48  
49 found that the kinetic model that best fitted the thermal degradation of the foregoing  
50  
51 UHMWPE composites was a diffusion mechanism expressed algebraically as the  
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53 Zhuravlev-Lesokhin-Tempelmann equation:  
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$$\ln \left( \frac{(1-\alpha)^{-1/3} - 1}{T^2} \right) = \ln \frac{AR}{qE_A} - \frac{E_A}{RT} \quad (\text{eq. 2})$$

This model describes the kinetic of processes limited by the diffusion of the reagent (or products) through the layer of the final product. Similarly, and after trials with all the algebraic function tested by Koleva and coworkers, the Zhuravlev-Lesokhin-Tempelmann equation also best fitted the fraction of conversion against the reciprocal temperature curves for all the materials included in the present study. The representation of fraction of conversion and reciprocal temperature plots revealed two regions that followed an almost linear behavior ( $R^2$  ranged from 0.94 to 1.00; Figure 4). These regions corresponded to processes taking place in the oxidation-dominated phase of the TGA experiment (from  $T_0$  to  $T_1$ ), and in the thermodegradation stage (i.e. the linear volatilization from  $T_1$  and  $T_2$ ). Energies of activation corresponding to both processes were calculated.

The use of the Coats-Redfern method and the Zhuravlev-Lesokhin-Tempelmann equation for the thermoxidative process confirmed significantly lower activation energies for as-irradiated materials with respect to non-irradiated UHMWPE ( $p < 0.003$ ; Student's t-test; Table 2). The differences between the activation energies of as-irradiated UHMWPEs, however, were not significant ( $p > 0.3$ ). While thermal stabilization methods did not introduce significant variations to the activation energies of the thermo-oxidative decomposition ( $p > 0.5$ ), vitamin E infused polyethylenes, in contrast, exhibit significantly higher activation energies ( $p \leq 0.001$ ). Concerning the thermodegradation process, activation energies significantly increased after every 50 kGy-radiation dose

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4 increment ( $p < 0.008$ ). Furthermore, activation energies of both thermally stabilized and  
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6 vitamin E infused UHMWPEs were generally higher than those of as-irradiated  
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8 UHMWPEs. In general, remelting yielded slightly higher activation energies than  
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10 annealing for the thermodegradation process, regardless of the radiation dose. Finally, the  
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12 presence of vitamin E also increased the activation energies of both non-irradiated and  
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14 as-irradiated polyethylenes, especially at the highest concentration. In fact, the highest  
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16 activation energy was obtained for  $\beta$ 100VE polyethylenes ( $p < 0.003$  as compared with  
17  
18 materials irradiated at 100 kGy). General linear models confirmed the significant  
19  
20 influences of both radiation dose and stabilization methods on the activation energies  
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22 corresponding to thermodegradation processes ( $p < 0.0001$  in both cases, respectively).  
23  
24 However, stabilization methods, but not irradiation, had a significant influence on the  
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26 activation energies of the thermoxidation processes according to linear models ( $p = 0.04$ ;  
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28 and  $p = 0.25$ , respectively). Despite the previous findings, linear models did not revealed  
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30 significant differences when the analysis was confined to the thermoxidative and  
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32 thermodegradation activation energies of annealed and remelted polyethylenes ( $p \geq 0.7$ ).  
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43         The mechanisms involved in the oxidative and thermal degradations that probably  
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45 took place in the present TGA experiments corresponded with a three-dimensional  
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47 diffusion mechanism described by Zhuravlev's equation, and previously validated by  
48  
49 Koleva and colleagues for thermal degradation of carbon fiber UHMWPE composites.  
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51 The activation energy of the oxidative process seems to be controlled more by irradiation  
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53 than by post-irradiation thermal treatments. The vitamin E presence strongly increases the  
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4 activation energies of both thermooxidative and thermodegradative processes, confirming  
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6 the efficacy of this additive as antioxidant and radical-quencher during TGA experiments.  
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### 10 11 *Correlation between oxidation and thermogravimetric parameters* 12 13 14

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17 After severe oxidative challenge, all materials exhibited non-zero levels of  
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19 oxidation, regardless of the stabilization method (Table 3). Nonetheless, as-irradiated  
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21 UHMWPEs had significantly higher oxidation indices (up to 2) than the other materials  
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23 (oxidation indices ranged from 0.2 to 0.5), the only exception being the  $\beta$ 150A  
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25 specimens. Post-irradiation annealing was not able to provide UHMWPEs irradiated to  
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27 150 kGy with sufficient oxidation resistance (oxidation index: 1.5), whereas remelting  
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29 stabilized all as-irradiated materials regardless of the radiation dose (oxidation indices ~  
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31 0.3). Vitamin E infused materials showed slightly higher oxidation indices, 0.5, than  
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33 remelted and annealed polyethylenes (0.2-0.3), with the mentioned exception for the  
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35 highest radiation dose in the latter case. The measurable oxidation levels observed after  
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37 thermal aging for virgin UHMWPE in the present study were not unexpected since  
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39 Edidin and colleagues previously reported non-zero oxidation for pristine UHMWPE  
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41 after standard accelerated aging [40]. Costa and coworkers also observed similar findings  
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43 following accelerated aging for both virgin and post-irradiation vitamin E stabilized  
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45 UHMWPE [38]. General linear models confirmed significant effects of radiation dose  
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47 and stabilization method on oxidation ( $p < 0.0001$  in both cases). In the case of non-  
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49 stabilized UHMWPEs,  $T_0$  was significantly correlated with the oxidation index after  
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51 accelerated aging ( $p = 0.01$ ). On the contrary, no correlation existed between the  
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4 oxidation indices measured after severe oxidative challenge, and TGA parameters or  
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6 energies of activation calculated for post-irradiation stabilized UHMWPEs. This could be  
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8 related to the fact that vitamin E stabilized materials exhibited a different TGA behavior  
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10 and the highest activation energies. This finding might also be in agreement with the fact  
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12 that the oxidation index quantifies the amount of carbonyl groups, but not other oxidation  
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14 products like alcohols or hydroperoxides. Hydroperoxides are intermediate oxidation  
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16 products and they represent the oxidation potential for UHMWPE as they eventually  
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18 decompose into carbonyl compounds [41].  
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## 26 **CONCLUSIONS**

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32 This study indicates that TGA may be a suitable tool for characterization of the  
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34 oxidative stability of different medical grade UHMWPEs. Noticeable changes in the  
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36 features of decomposition curves were observed after irradiation and post-irradiation  
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38 stabilization methods. Specifically, as-irradiated UHMWPEs experienced a characteristic  
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40 weight increase at the beginning of the thermogravimetric experiment sooner than  
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42 pristine UHMWPE. Also, the onset of the linear volatilization stage in TGA traces  
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44 occurred at higher temperatures for increasing radiation doses. Among thermal  
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46 stabilization methods, annealing did not change the behavior of the weight increase  
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48 behavior found in as-irradiated UHMWPEs, but remelting significantly retarded the onset  
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50 of this mass gain. Interestingly, vitamin E stabilized UHMWPEs exhibited no weight  
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52 gain before decomposition, suggesting a good effectiveness as antioxidant and radical  
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54 quencher. The combined use of the Coat-Redferns method and Zhuravlev-Lesokhin-  
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Tempelman equation allowed calculation of energies of activation for two linear regions as observed in fraction of conversion and reciprocal temperature plots. These linear regions corresponded to thermoxidation and thermodegradation processes. Lower energies of activation were found for the thermooxidation process after irradiation, whereas vitamin E diffusion significantly augmented the activation energy of this mechanism. Thermodegradation was also found to exhibit higher activation energies after irradiation, and they were further increased after remelting and vitamin E stabilization. Overall, TGA appeared to be more sensitive than infrared assessment of oxidation following accelerated aging at 120 °C in air for 36 hours to determine the oxidative stability of medical grade UHMWPE formulations.

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6 **FIGURE CAPTIONS**  
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8 **Figure 1A-B.** Typical decomposition curves for control GUR 1050 UHMWPE (NI), and  
9 e-beam irradiated UHMWPE materials, (1A). A close-up view revealed two small but  
10 noticeable weight gains before the beginning of volatilization and with maxima at  $T_A$  and  
11  $T_0$ . The onset of the second weight gain was designated as  $T_B$ , (1B).  
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17 **Figure 2A-B.** Typical decomposition curves for e-beam irradiated UHMWPE at 100 kGy  
18 and subsequently stabilized by annealing, remelting and vitamin E diffusion (2A). In a  
19 close-up view (2B), annealed and remelted materials also experienced two weight gains  
20 with maxima at  $T_A$  and  $T_0$  prior to decomposition. Vitamin E infused materials, however,  
21 immediately lost mass following the weight increase at  $T_A$ .  
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28 **Figure 3A-B.** Effect of irradiation and stabilization methods on the onset,  $T_B$ , of the  
29 second weight increase found in thermogravimetric curves (3A), and on the beginning,  
30  $T_1$ , of the linear volatilization stage (3B).  
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36 **Figure 4.** Fraction of conversion against the reciprocal temperature curves obtained for  
37 B100 and B100 vit E UHMWPEs from thermogravimetric experiments using the  
38 Zhuravlev-Lesokhin-Tempelmann equation. As opposed to non-irradiated, as-irradiated  
39 materials, and thermally stabilized polyethylenes, post-irradiation vitamin E infused  
40 materials gave slightly different plots (curves have been shifted vertically for the sake of  
41 clarity).  
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Figure 1A  
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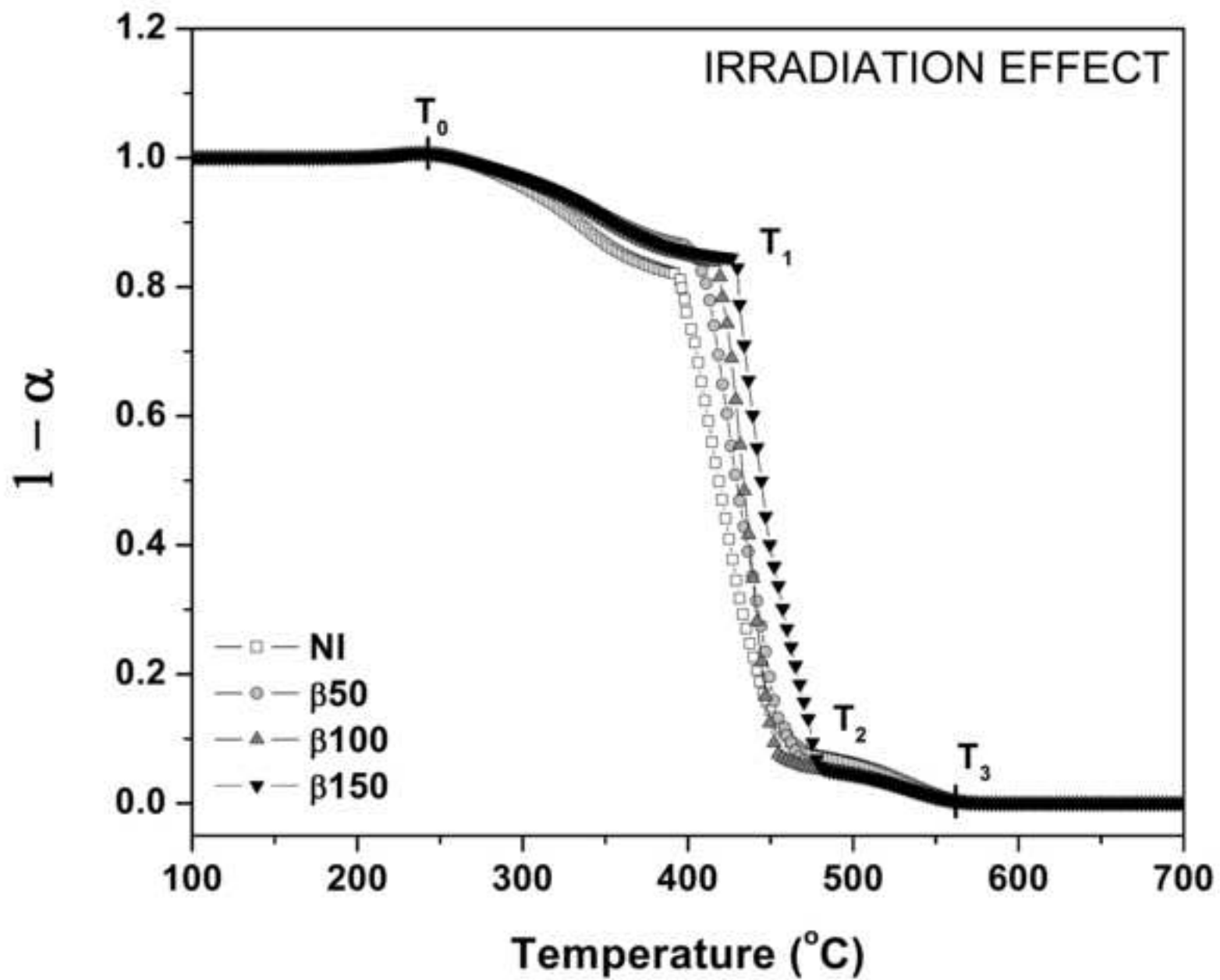




Figure 1B  
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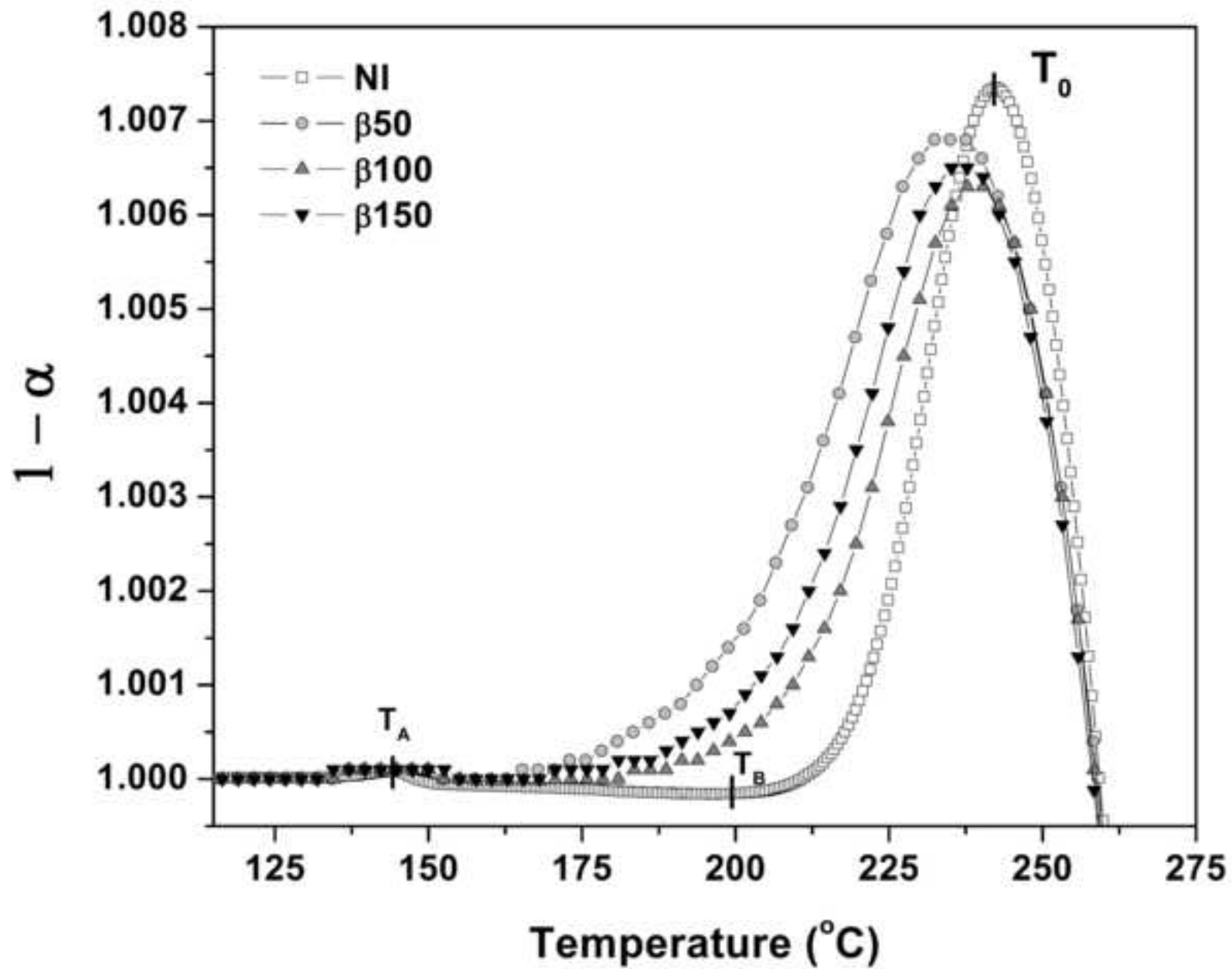


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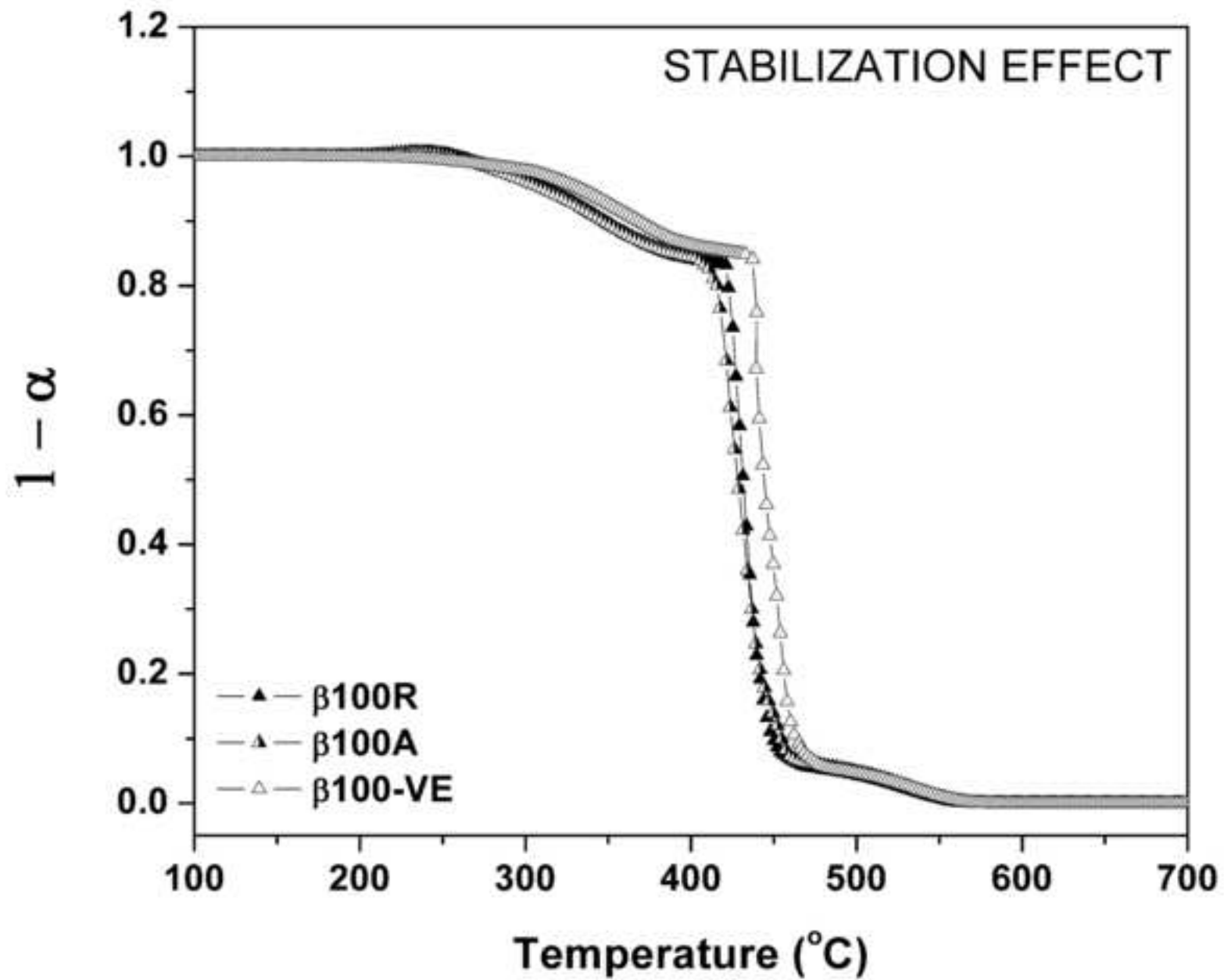


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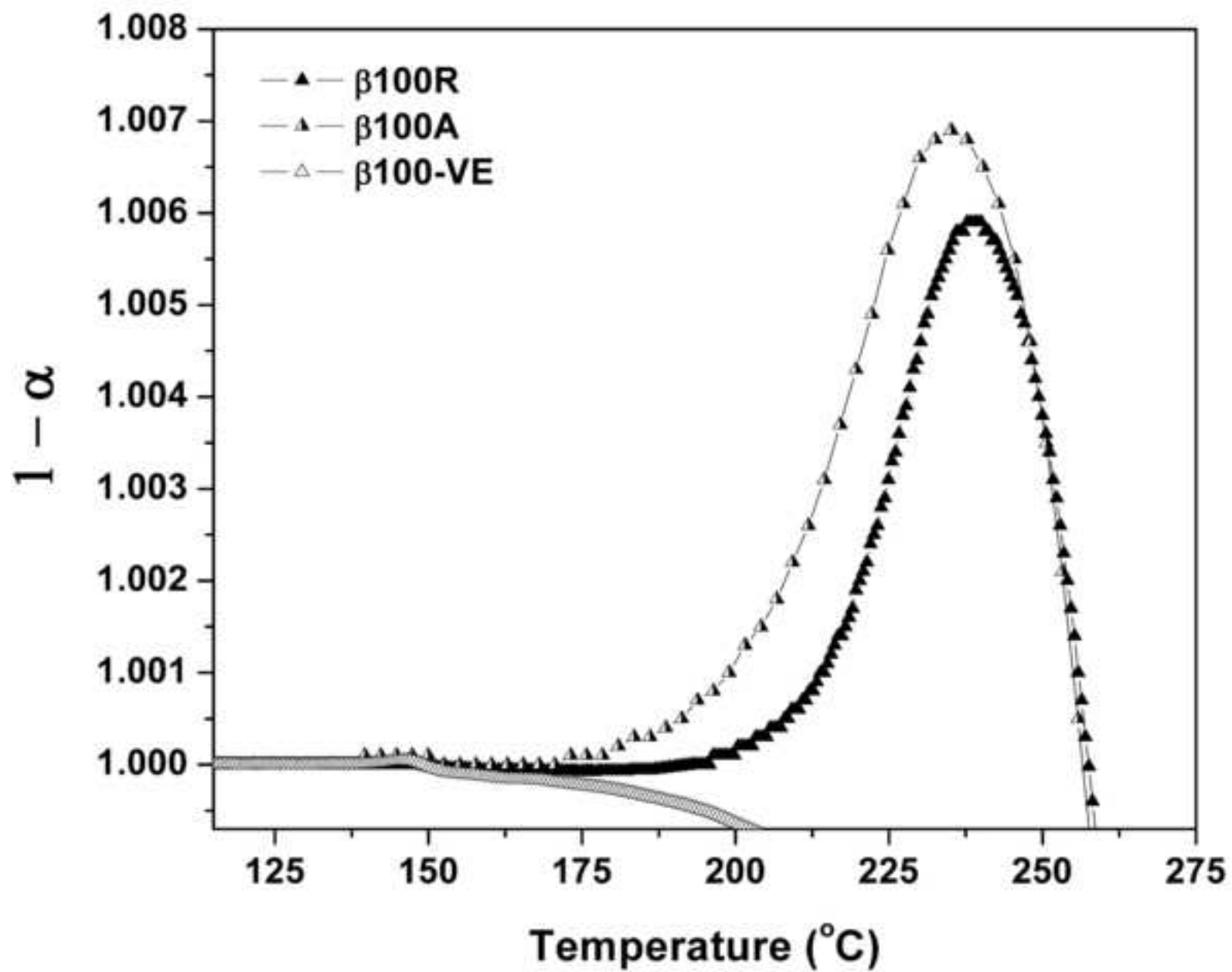


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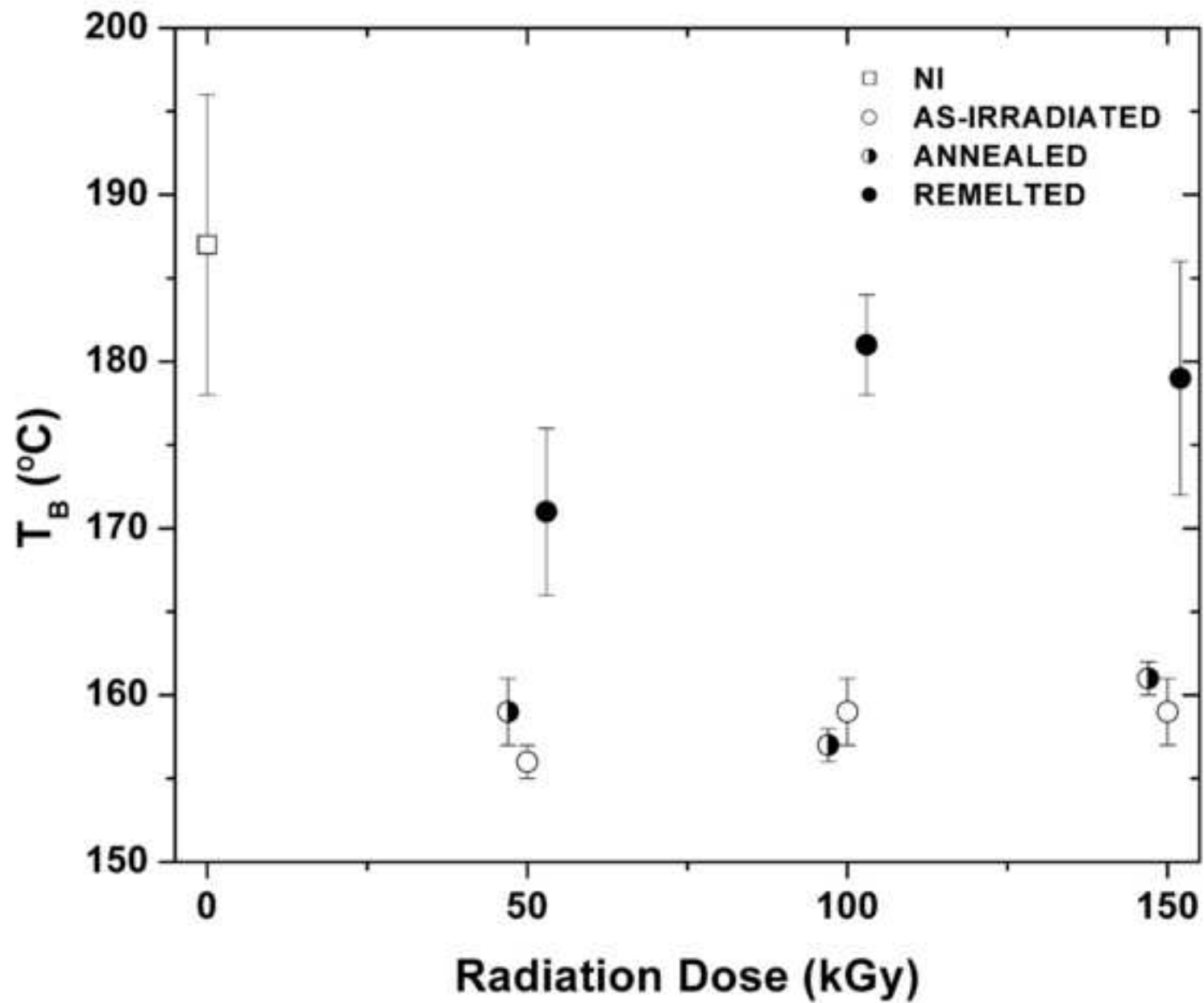


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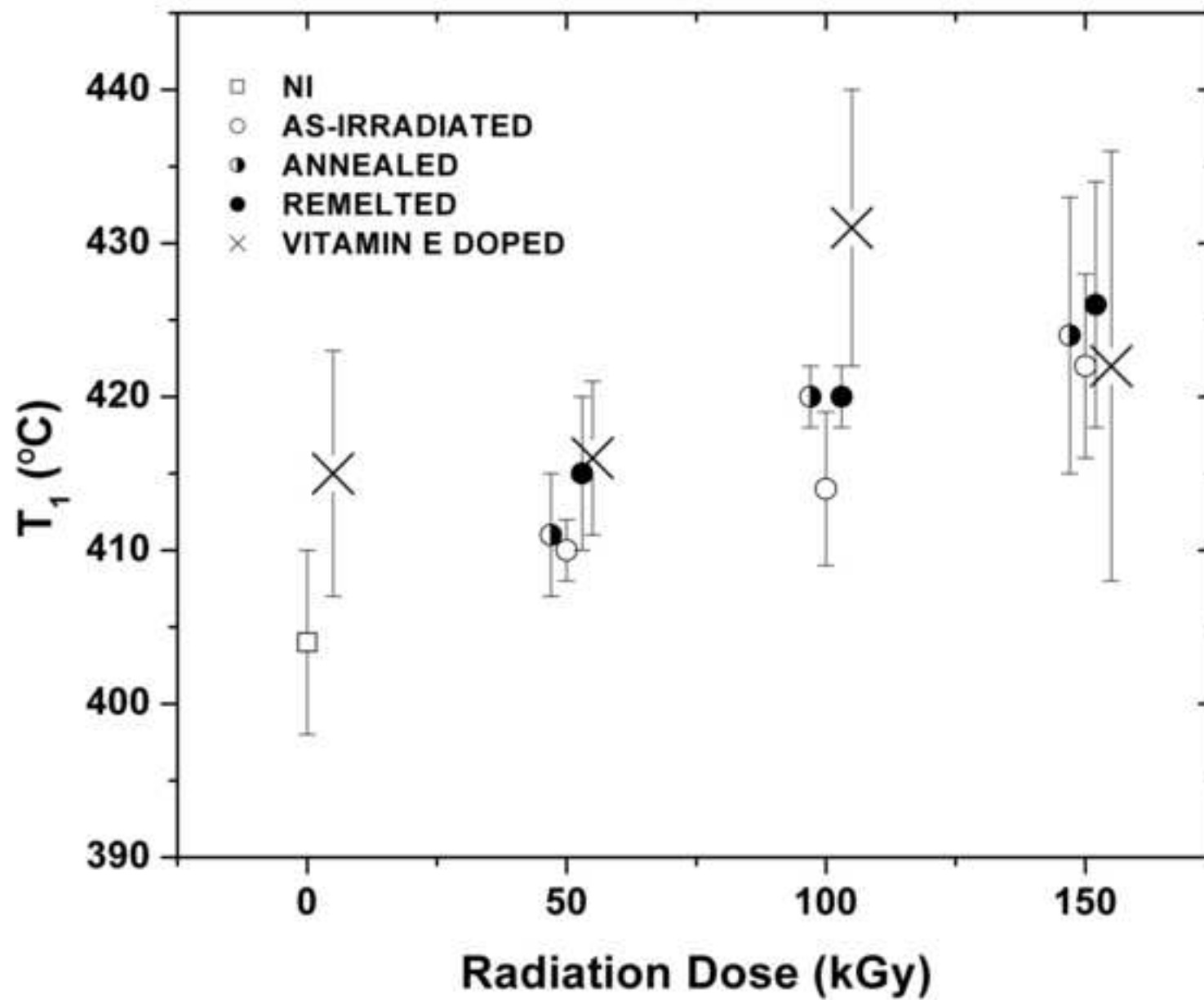
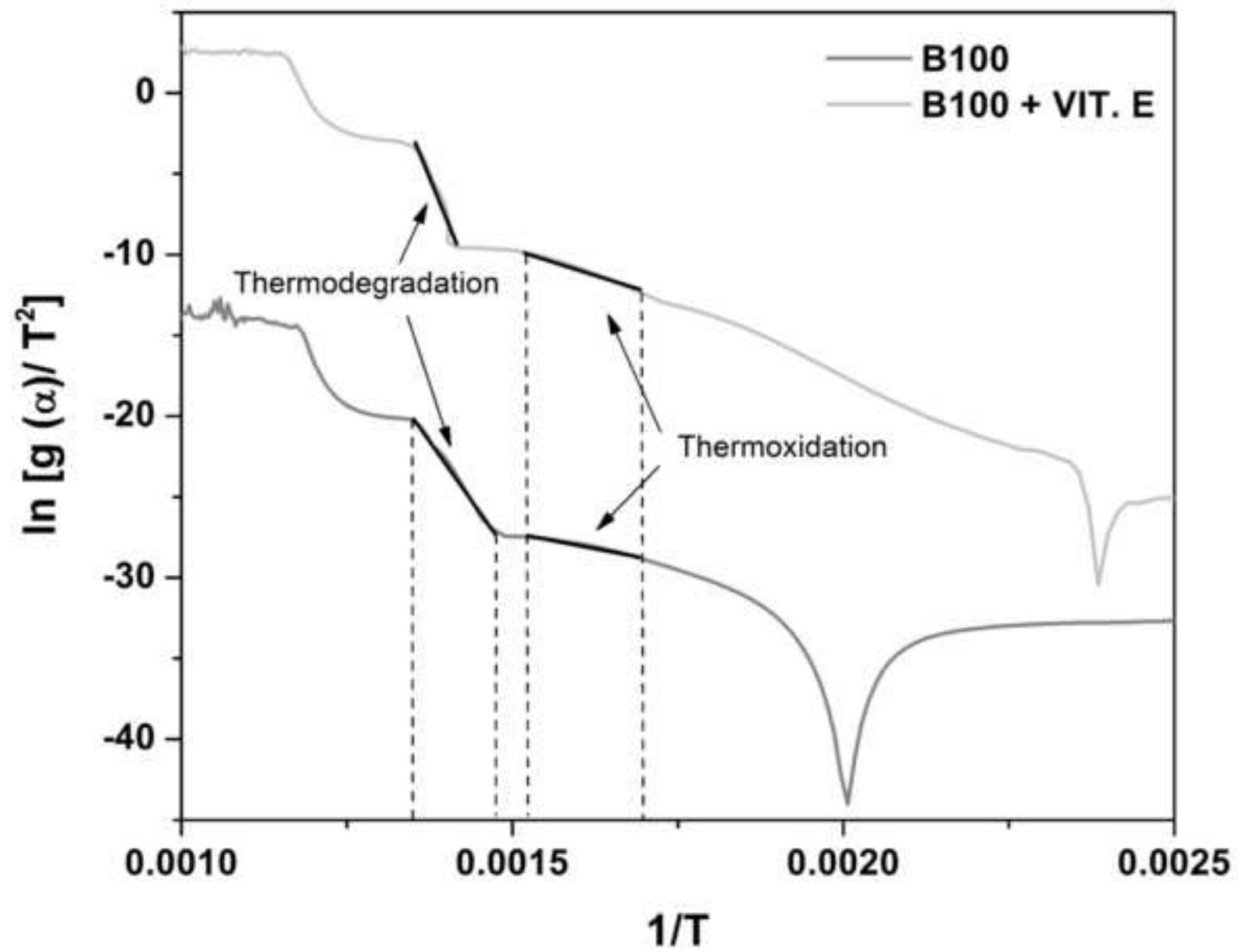


Figure4

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**Table 1.** Decomposition temperatures and remaining weights (average $\pm$ SD) obtained from thermogravimetric experiments for control, irradiated, irradiated and stabilized, and vitamin E-infused materials.

MATERIAL GROUP	T <sub>A</sub> (°C)	T <sub>B</sub> (°C)	T <sub>0</sub> (°C)	W <sub>T0</sub> (%)	T <sub>1</sub> (°C)	W <sub>T1</sub> (%)	T <sub>2</sub> (°C)	W <sub>T2</sub> (%)	T <sub>3</sub> (°C)
<b>NI</b>	143.4 $\pm$ 0.5	187 $\pm$ 9	242 $\pm$ 1	100.802 $\pm$ 0.004	404 $\pm$ 6	79.7 $\pm$ 1.4	473 $\pm$ 1	8.2 $\pm$ 0.2	583 $\pm$ 3
<b>B50</b>	147.4 $\pm$ 1.0	156 $\pm$ 1	235 $\pm$ 2	100.733 $\pm$ 0.052	410 $\pm$ 2	86.7 $\pm$ 1.3	473 $\pm$ 2	5.9 $\pm$ 0.3	587 $\pm$ 1
<b>B100</b>	147.9 $\pm$ 0.4	159 $\pm$ 2	237 $\pm$ 2	100.730 $\pm$ 0.082	414 $\pm$ 5	84.9 $\pm$ 2.0	481 $\pm$ 7	5.5 $\pm$ 0.5	578 $\pm$ 6
<b>B150</b>	148.0 $\pm$ 1.9	159 $\pm$ 2	236 $\pm$ 1	100.700 $\pm$ 0.001	422 $\pm$ 6	84.4 $\pm$ 0.5	474 $\pm$ 6	5.7 $\pm$ 0.3	573 $\pm$ 6
<b>B50A</b>	148.6 $\pm$ 0.8	159 $\pm$ 2	236 $\pm$ 1	100.775 $\pm$ 0.050	411 $\pm$ 4	84.6 $\pm$ 0.8	472 $\pm$ 6	6.0 $\pm$ 0.3	563 $\pm$ 10
<b>B100A</b>	148.5 $\pm$ 0.5	157 $\pm$ 1	235 $\pm$ 1	100.760 $\pm$ 0.055	420 $\pm$ 2	83.5 $\pm$ 1.0	471 $\pm$ 2	5.8 $\pm$ 0.6	577 $\pm$ 2
<b>B150A</b>	149.7 $\pm$ 0.5	161 $\pm$ 1	236 $\pm$ 1	100.775 $\pm$ 0.050	424 $\pm$ 9	82.6 $\pm$ 0.5	475 $\pm$ 4	6.0 $\pm$ 0.6	578 $\pm$ 6
<b>B50R</b>	141.5 $\pm$ 1.0	171 $\pm$ 5	239 $\pm$ 1	100.625 $\pm$ 0.050	415 $\pm$ 5	84.6 $\pm$ 0.5	468 $\pm$ 3	6.1 $\pm$ 0.3	577 $\pm$ 2
<b>B100R</b>	143.8 $\pm$ 0.6	181 $\pm$ 3	242 $\pm$ 3	100.575 $\pm$ 0.050	420 $\pm$ 2	82.8 $\pm$ 1.8	469 $\pm$ 3	5.9 $\pm$ 0.2	578 $\pm$ 4
<b>B150R</b>	144.5 $\pm$ 0.7	179 $\pm$ 7	238 $\pm$ 1	100.680 $\pm$ 0.045	426 $\pm$ 8	82.9 $\pm$ 1.5	476 $\pm$ 6	5.7 $\pm$ 0.2	579 $\pm$ 6
<b>NI-VE</b>	144.2 $\pm$ 0.5	N/A	N/A	N/A	415 $\pm$ 8	90.0 $\pm$ 0.7	476 $\pm$ 4	5.6 $\pm$ 0.3	584 $\pm$ 2
<b>B50-VE</b>	146.4 $\pm$ 0.4	N/A	N/A	N/A	416 $\pm$ 5	85.5 $\pm$ 1.0	478 $\pm$ 6	5.8 $\pm$ 0.5	578 $\pm$ 6
<b>B100-VE</b>	146.9 $\pm$ 0.4	N/A	N/A	N/A	431 $\pm$ 9	84.5 $\pm$ 0.6	475 $\pm$ 7	6.1 $\pm$ 0.5	572 $\pm$ 13
<b>B150-VE</b>	150.5 $\pm$ 0.4	N/A	N/A	N/A	422 $\pm$ 14	76.7 $\pm$ 3.9	481 $\pm$ 5	9.2 $\pm$ 1.9	584 $\pm$ 10

N/A Not applicable. The second mass increase was absent in vitamin E stabilized UHMWPEs.

**Table 2.** Energies of activation (average±SD) calculated for linear regions from the fraction of conversion versus the reciprocal temperature plots corresponding to control, irradiated, irradiated and stabilized, and vitamin E-infused materials.

<b>MATERIAL GROUP</b>	<b>E<sub>oxidation</sub> (kJ/mol)</b>	<b>E<sub>thermodegradation</sub> (kJ/mol)</b>
<b>NI</b>	124 ± 3	329 ± 22
<b>B50</b>	111 ± 3	466 ± 26
<b>B100</b>	109 ± 3	540 ± 9
<b>B150</b>	112 ± 8	609 ± 33
<b>B50A</b>	112 ± 1	534 ± 47
<b>B100A</b>	110 ± 4	664 ± 29
<b>B150A</b>	108 ± 1	590 ± 6
<b>B50R</b>	110 ± 1	632 ± 16
<b>B100R</b>	111 ± 2	643 ± 32
<b>B150R</b>	106 ± 1	610 ± 35
<b>NI-VE</b>	104 ± 5	553 ± 31
<b>B50-VE</b>	145 ± 11	526 ± 87
<b>B100-VE</b>	130 ± 11	822 ± 80
<b>B150-VE</b>	168 ± 28	797 ± 83



**Table 3.** Oxidation indices (average±SD) calculated for control, as-irradiated and stabilized UHMWPEs after severe oxidative challenge at 120 °C for 36 hours.

<b>MATERIAL GROUP</b>	<b>OI</b>
<b>NI</b>	0.07 ± 0.01
<b>B50</b>	1.62 ± 0.04
<b>B100</b>	2.01 ± 0.60
<b>B150</b>	2.26 ± 0.01
<b>B50A</b>	0.32 ± 0.15
<b>B100A</b>	0.28 ± 0.05
<b>B150A</b>	1.51 ± 0.53
<b>B50R</b>	0.19 ± 0.01
<b>B100R</b>	0.35 ± 0.06
<b>B150R</b>	0.33 ± 0.08
<b>NI-VE</b>	0.16 ± 0.06
<b>B50-VE</b>	0.40 ± 0.14
<b>B100 -VE</b>	0.45 ± 0.03
<b>B150-VE</b>	0.56 ± 0.21