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2 **Microstructure, thermooxidation and mechanical behavior of a**
3 **novel highly linear, vitamin E stabilized, UHMWPE**
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1 **ABSTRACT**

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3 A novel, vitamin E-stabilized, medical grade ultra-high molecular polyethylene, MG003
4 (DSM Biomedical; The Netherlands), has been very recently introduced for use in total
5 joint replacements. This homopolymer resin features average molecular weight similar to
6 that of conventional GUR 1050 resin ($5.5-6 \times 10^6$ g/mol), but a higher degree of linearity.
7 The aim of this study was to characterize the microstructure, thermal and thermooxidation
8 properties as well as the mechanical behavior of this novel MG003 resin before and after
9 gamma irradiation in air to 90 kGy. For this purpose, a combination of experimental
10 techniques were performed including differential scanning calorimetry (DSC),
11 thermogravimetry (TG), transmission electron microscopy (TEM), X-Ray Diffraction,
12 electron paramagnetic resonance (EPR), and uniaxial tensile tests. As-consolidated
13 MG003 materials exhibited higher crystalline contents (~62%), transition temperatures
14 (~140 °C), crystal thickness (~36 nm), yield stress (~25 MPa) and elastic modulus (~400
15 MPa) than GUR 1050 controls (55%, 136 °C, 27 nm, 19 MPa, and 353 MPa, respectively).
16 Irradiation produced similar changes in both MG003 and GUR 1050 materials,
17 specifically increased crystallinity (63% and 60%, respectively), crystal thickness (39 nm
18 and 30 nm), yield stress (27MPa and 21 MPa), but, above of all, loss of elongation to
19 breakage (down to 442 and 469%, respectively). Thermogravimetric and EPR results
20 suggest comparable susceptibilities to oxidation for both MG003 and GUR 1050
21 polyethylenes. Based on the present findings, MG003 appears as a promising alternative
22 medical grade polyethylene and it may satisfactorily contribute to the performance of total
23 joint replacements.

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30 **KEYWORDS:** UHMWPE, α -tocopherol (vitamin E), microstructure, thermooxidation, mechanical
31 properties.

1 INTRODUCTION

2 Since the 1960s, ultra-high molecular weight polyethylene (UHMWPE) remains as
3 one of the most relevant materials used in total joint replacements (TJR). However, wear
4 processes unavoidably generate UHMWPE debris particles, which, in turn, trigger
5 osteolytic reactions that eventually may lead to the aseptic loosening of the implant [1-2].
6 Several physical, chemical and microstructure modifications have been introduced in the
7 last 50 years aiming at reducing the wear of UHMWPE components to thus extend the life
8 span of total joint prostheses.

9 The most significant and positive microstructure modification made to
10 conventional, gamma sterilized, UHMWPE was the introduction of crosslinks between
11 polymer chains by means of high doses of gamma or electron beam irradiation [3]. This
12 microstructural feature is responsible for the remarkable improvement in wear resistance
13 exhibited by modern first-generation highly crosslinked polyethylenes [4]. However, post-
14 irradiation annealing or remelting treatments are needed to eliminate radiation-induced
15 free radicals that do not take part in crosslinking generation. The rationale for this
16 additional process is to prevent that free radicals can initiate, in the presence of molecular
17 oxygen, the long-term oxidation cycle [5-7] that eventually turns UHMWPE into a brittle
18 polymer. Nevertheless, both thermal treatments introduce a significant loss in the
19 mechanical performance [8-9], particularly in toughness and fatigue behavior, albeit to
20 different extent.

21 Second generation highly crosslinked polyethylenes have been developed on the
22 basis of α -tocopherol (vitamin E) addition as an alternative to thermal stabilization
23 methods. This vitamin is a natural lipid, which acts as an antioxidant *in vivo* by means of
24 the donation of the hydrogen atom to free radical formed on lipids hindering lipid
25 peroxidation in cell membranes[10]. In irradiated UHMWPE, vitamin E basically acts as a

1 scavenger of radiation-induced free radicals, allowing elimination of post-irradiation
2 thermal processes and their associated shortcomings[11]. Two different methods are
3 currently in use to incorporate vitamin E into UHMWPE. One of them involves the
4 addition of trace concentrations of vitamin E to medical grade UHMWPE resins, which
5 are physically blended prior to consolidation and irradiation [12-13]. The other technique
6 entails diffusion of vitamin E into consolidated UHMWPE after radiation crosslinking
7 [14-15]. Although the latter method avoids the loss of efficiency in crosslinking generation
8 experienced by blended vitamin E-UHMWPE systems, it, however, introduces a lack of
9 homogeneity in the through-thickness vitamin E concentration.

10 Different UHMWPE resins have been used to produce conventional, as well as
11 first- and second-generation highly crosslinked polyethylenes. Thus, calcium stearate free
12 GUR 1020, GUR 1050 (Ticona) and 1900H (Basell) have been the common resins used by
13 orthopaedic manufacturers. Differences in average molecular weight, average resin
14 particle size, size distribution as well as morphology of resin particles explain variations
15 between the material properties of converted UHMWPE.

16 A novel medical UHMWPE resin, MG003, has been very recently introduced for
17 total joint arthroplasty components by DSM Biomedical (The Netherlands). This
18 homopolymer resin features an average molecular weight similar to that of GUR 1050
19 resin but a higher degree of linearity than both GUR resins. To make this material resistant
20 to oxidation and suitable for radiation-crosslinking, trace concentrations of alpha-
21 tocopherol have been added to MG003 to develop a vitamin E stabilized medical
22 UHMWPE resin. Although trace concentrations of this antioxidant confer good oxidative
23 stability and preservation of mechanical properties, some drawbacks have been reported
24 [16]. The aim of this study was to characterize microstructure, susceptibility to oxidation,

1 as well as the thermal and mechanical behavior of this material before and after gamma-
2 irradiation in air.

3

4 **MATERIALS AND METHODS**

5 *Raw Materials*

6

7 A compression molded sheet of MG003 UHMWPE blended with 0.1 % by weight
8 vitamin E was kindly provided by DSM Biomedical (The Netherlands). According to
9 DSM product information, the molecular weight of MG003 resin is close to $7 \cdot 10^6$ g/mol
10 based on calculations using the Margolies equation ($M_w = 5.37 \cdot 10^4 \cdot [\eta]^{1.49}$, being η the
11 intrinsic viscosity as determined by ISO 1628-3). This polymer will be denoted PE-VE
12 hereafter. In addition to neat samples, specimens were also prepared for further gamma-
13 irradiation in air to a final dose of 90 kGy (Aragogamma, Barcelona; Spain), and they will
14 be referred to as PE-VE-I. When possible, GUR 1050 and irradiated GUR 1050 specimens
15 were used as controls.

16 *Vitamin E detection*

17

18 The vitamin E concentration was detected by ultraviolet (UV) spectroscopy using
19 an Aligent 8453 Diode Array spectrophotometer working in the 1100-190 nm range. UV
20 absorption spectra of vitamin-E stabilized MG003 UHMWPE sections revealed the
21 presence of a band at 290 nm (Figure 1).

22 *Differential Scanning Calorimetry*

23

24 Differential Scanning Calorimetry (DSC) was performed to assess thermal
25 properties, namely crystallinity content and melting transition temperatures. Indium
26 standards were used for heat calibration before running experimental tests. Samples (mass

1 ~6 mg) were heated from 20 to 200 °C at a rate of 10 °C/min in a Differential Scanning
2 Calorimeter (Perkin Elmer). At least three scans were taken for all materials. The area
3 below the DSC curves from 80 to 150 °C, normalized by 290 J/g as the enthalpy of
4 melting of a 100 % crystalline UHMWPE [17], gave the crystallinity percentages for each
5 material. Estimations of lamellar thickness, L_c , were computed introducing the
6 experimental values of the transition temperature, T_m , into the Thomson-Gibbs equation:

$$7 \quad T_m = T_{m0} (1 - 2\sigma / L_c \rho_c \Delta H_{m0}) \text{ (eq. 1)}$$

8 where T_{m0} , is the equilibrium melting point of a perfect crystalline polyethylene, σ the
9 specific surface energy, ρ_c the crystallinity phase density and ΔH_{m0} the enthalpy of melting
10 of a perfect crystalline polyethylene.

11 *Transmission Electron Microscopy*

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13 Polyethylene specimens underwent specific preparation, reported in previous
14 studies, to obtain Transmission Electron Microscopy (TEM) micrographs [18]. First, 200
15 μm sections of UHMWPE were stained with 99% chlorosulphonic acid at 60°C for 5
16 hours, which is thought to stabilize the amorphous regions. Samples were washed with
17 acetone (at 0°C) and rinsed with distilled water. Stained samples were dried at 60°C for 1
18 hour and later embedded in epoxy and cured at 60°C for 2 days. Ultrathin sections (~ 60
19 nm thick) were cut with a diamond knife and collected in carbon grids. Then, sections
20 were post-stained with uranyl acetate in 1% methanol for 4 minutes. A Jeol 100CX TEM
21 (operating at 100 kV) was used to produce micrographs at 20000x and 60000x
22 magnifications. The best 5 TEM preparation samples were chosen from each set of
23 materials and analysed using Digital Micrograph 3.3.1 (Gatan Inc., Pleasanton, CA, USA).
24 At least fifteen measurements of lamellar thickness were done per 60000x images using

1 the mentioned software. These images allowed the measurement of crystal thickness as
2 well as detection of changes in morphology caused by the presence of vitamin-E.

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X-ray diffraction experiments

8 X-ray diffraction patterns were measured at room temperature using a D-Max
9 Rigaku diffractometer with a Cu rotating anode and working at 40 kV and 80 mA. No
10 filtering of Cu K β was taken. Data were collected from $2\theta = 20^\circ$ to 80° in steps of 0.03°
11 and 3 second per step.

12

Thermogravimetry

14

15 To evaluate the decomposition behavior of unirradiated and gamma-irradiated
16 vitamin E-UHMWPE systems, thermogravimetric experiments were conducted in air on a
17 TA Instruments thermobalance (accuracy: 10^{-4} mg) from room temperature to 700°C at a
18 heating rate of $10^\circ\text{C}/\text{min}$. Samples weighed approximately 7.0 mg, and again, at least
19 three scans were taken for all materials. Analysis of the thermogravimetric traces was
20 conducted as reported elsewhere[19]. Specifically, the temperatures (T_B and T_0)
21 corresponding to the onset of mass increase and maximum mass reached, respectively,
22 served to evaluate the susceptibility to oxidation as they are associated to the induction of
23 thermooxidation processes in the polymeric melt. In addition, the temperature (T_1) from
24 which the purely thermal degradation prevailed in the decomposition behavior of the
25 polymeric samples was used to confirm radiation-induced changes in microstructure.

26

1 *Free radical concentration assessment*

2

3 Electron Paramagnetic Resonance (EPR) measurements were taken at room
4 temperature, before and after irradiation, in a Bruker Elexsys E580 spectrometer working
5 at X-band. The microwave power was 0.2 mW and the modulation amplitude 0.1 mT.
6 Prismatic shape samples (2x2x10 mm³) were fixed with vacuum grease to a methacrylate
7 sample holder. No signals due either to the sample holder or to the vacuum grease were
8 detected. At least two samples were measured for both control and PE-VE materials. The
9 intensity of the EPR signal was reproducible within 5% in all the cases.

10

11 *Mechanical properties*

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13 Uniaxial tensile tests were carried out at room temperature according to ASTM
14 D638M (UNE-EN ISO 527-2). Thus, bone-shaped samples were tested to failure at a
15 crosshead speed of 5 mm/min in an Instron machine (model 5565). All tests were
16 performed at 23°C ±2 °C. Yield stress, σ_y , elastic modulus, E, ultimate tensile stress, σ_{ult} ,
17 and elongation to breakage, ϵ_{ult} , were deduced from the raw load-displacement data.

18 *Statistical analysis*

19 Student's t tests were conducted to assess significant differences in thermal,
20 thermooxidation and mechanical properties between material groups. A level of $p < 0.05$
21 was selected as indicative of significance.

22

1 RESULTS

3 *Thermal properties and microstructure*

5 First heating DSC curves exhibited the standard peak associated to the melting
6 process of the polymer. Analysis of the DSC curves provided the transition temperature
7 and enthalpy content, which is related to the degree of crystallinity, for each sample
8 (Figure 2). PE-VE, MG003, specimens exhibited higher crystallinity (61.6 ± 1.1 %) and
9 melting temperature (139.7 ± 1.0 °C) than GUR 1050 controls (55.0 ± 0.3 %, and 136.2 ± 0.5
10 °C, respectively; $p < 0.0003$, statistically significant difference, in both cases). As for the
11 effects of irradiation, a small crystallinity increase was observed for gamma-irradiated
12 0.1% PE-VE specimens (63.2 ± 1.7 %). The melting transition temperature experienced a
13 small, but statistically significant, increase with irradiation up to 143.3 ± 1.8 °C ($p < 0.03$;
14 Student's t test). Upon irradiation, GUR 1050 specimens exhibited significantly higher
15 crystallinity (59.9 ± 0.7 %) and melting temperature (140.4 ± 0.3 °C) with respect to neat
16 GUR 1050 samples ($p \leq 0.001$). The crystallinity of PE-VE-I was still significantly higher
17 than that of irradiated GUR 1050 materials ($p < 0.03$).

18 TEM micrographs of PE-VE specimens showed the typical microstructure features
19 of a semicrystalline polymer with randomly oriented crystal lamellae, 36 ± 3 nm thick,
20 immersed in a dark grey region, which was the amorphous region (Figure 3a). The
21 lamellar thickness registered for GUR 1050, 27 ± 4 nm, was remarkably lower than that of
22 PE-VE. Gamma-irradiated MG003, PE-VE-I, experienced a little increase in lamellar
23 thickness, with an average value of 39 ± 6 nm (Figure 3b).

24 X-ray patterns of PE-VE and PE-VE-I materials were almost identical (Figure 4),
25 except for a slightly lower intensity of the amorphous halo around $\theta = 20^\circ$ in the case of
26 PE-VE-I. The patterns were fitted by the Rietveld method with an orthorhombic phase and

1 a background to take account non-crystalline contributions. No specific modeling of the
2 background was made to separate the amorphous halo from the total background. The
3 fitted cell parameters were $a = 7.398 \pm 0.005 \text{ \AA}$, $b = 4.939 \pm 0.004 \text{ \AA}$ and $c = 2.542 \pm 0.002 \text{ \AA}$
4 for PE-VE, and $a = 7.401 \pm 0.005 \text{ \AA}$, $b = 4.939 \pm 0.004 \text{ \AA}$ and $c = 2.542 \pm 0.002 \text{ \AA}$ for PE-
5 VE-I. As for GUR 1050 controls, diffractograms showed a more intense amorphous halo
6 around $\theta = 20^\circ$ as well as a lower cell parameter $a = 7.286 \pm 0.004 \text{ \AA}$.

7

8 *Thermogravimetry*

9 The thermogravimetric decomposition curves of PE-VE and PE-VE-I
10 polyethylenes exhibited essentially similar features (Figure 5a). Sample mass remained
11 constant at the beginning of the test, but specimens soon started to weight gain at T_B ,
12 reaching the maximum at T_0 (Figure 5b). Then, decomposition began and samples lost
13 mass in a non-linear fashion up to T_1 , which lay between 400 and 450 °C depending on the
14 material. In this region, the slope of the mass loss changed, becoming less pronounced at
15 temperatures inferior but close to T_1 . Afterwards, sample weight dropped linearly from T_1
16 until the specimen was almost decomposed. The chemical meaning of each temperature
17 are explained in detail elsewhere[19], but it is worth mentioning that only T_B , and T_0 are
18 the relevant temperatures to rank the oxidation stability of the current polymer systems
19 stabilized with phenolic antioxidant.

20 A detailed analysis of the thermogravimetric curves revealed some differences
21 between unirradiated and irradiated MG003 polyethylenes. Thus, the onset of
22 thermooxidation, T_B , of PE-VE materials was significantly shifted towards lower
23 temperatures, from $252 \pm 2 \text{ °C}$ to $205 \pm 2 \text{ °C}$, upon irradiation ($p < 0.0001$; Student's t test).
24 Likewise, T_0 significantly changed upon gamma irradiation from $261 \pm 1 \text{ °C}$ to $234 \pm 1 \text{ °C}$
25 ($p < 0.0001$). As for conventional grades, unstabilized GUR 1050 polyethylene exhibited

1 significantly lower thermooxidation temperatures both before ($T_B=185\pm3$ °C, and
2 $T_0=228\pm3$ °C) and after irradiation ($T_B=157\pm3$ °C, and $T_0=222\pm1$ °C) in comparison with
3 PE-VE materials ($p<0.0001$ in both cases). On the other hand, the beginning of the purely
4 thermal degradation was unexpectedly brought forward upon irradiation for PE-VE as T_1
5 significantly decreased from 447 ± 5 °C to 410 ± 16 °C ($p<0.005$). GUR 1050 polyethylenes
6 thermally decomposed at significantly lower temperatures (411 ± 13 °C; $p<0.006$ with
7 respect to PE-VE) and experienced a borderline increase upon irradiation (433 ± 9 °C;
8 $p=0.06$ with respect to unirradiated GUR 1050).

9 *Free radical concentration assessment*

10 No Electron Paramagnetic (EPR) signal was detected in PE-VE samples prior to
11 irradiation. However, a complex signal was observed after irradiation (Figure 6). It was
12 similar to that described in research authored by Oral and co-workers[11], and Jahan and
13 co-workers [20-22], who revealed the formation of some radiation-induced free radicals
14 within vitamin E stabilized GUR 1050 polyethylenes.

15 *Mechanical properties*

16 The engineering stress-strain curves of all studied materials followed the typical
17 uniaxial tensile behavior of conventional UHMWPE and modern first-generation highly
18 crosslinked polyethylenes (Figure 7). Significantly higher yield stress and elastic modulus
19 characterized PE-VE (25 ± 1 ; $p<0.0001$ and 393 ± 27 MPa; $p<0.01$, respectively) in
20 comparison with GUR 1050 specimens (19 ± 1 and 353 ± 8 MPa). PE-VE materials also had
21 significantly higher stress to rupture than GUR 1050 polyethylenes (48 ± 2 and 36 ± 2 MPa,
22 respectively; $p<0.0001$), but, in contrast, they exhibited significantly lower elongation to
23 breakage (650 ± 32 and 867 ± 53 %, respectively; $p<0.0001$). Upon irradiation, yield stress
24 and elastic modulus properties significantly increased with irradiation for MG003,

1 reaching 27 ± 1 and 473 ± 17 MPa ($p < 0.0001$ in both cases with respect to PE-VE),
2 whereas GUR 1050 polyethylenes experienced a significant increase in yield stress, but
3 not in elastic modulus (21 ± 1 , and 371 ± 45 MPa; $p < 0.0001$ and $p < 0.25$, respectively).
4 Both irradiated materials experienced a significant loss of ductility as reflected by
5 decreases in ultimate strain down to 442 ± 55 % ($p < 0.0001$) in the case of PE-VE and
6 down to 469 ± 14 % ($p < 0.0001$) for GUR 1050 polyethylene. As for fracture stress
7 properties following irradiation, PE-VE materials experienced a small, yet significant,
8 decrease from 48 ± 2 to 42 ± 4 MPa ($p < 0.002$), whereas this property remained essentially
9 the same, 37 ± 1 MPa, in the case of GUR 1050 materials.

10

11 **DISCUSSION**

12 The current DSC results confirm that this new medical grade UHMWPE presents a
13 relatively high crystallinity, close to 60 %. This crystalline content is, however, lower than
14 that of UHMWPEs produced by hot isostatic pressing of ram-extruded rods (ArCom
15 UHMWPE; Biomet, Warsaw; Indiana) or by high-pressure crystallization (Hylamer;
16 DePuy Dupont Orthopaedics, Warsaw, IN), which exhibit crystallinities within 65-71 %.
17 Nevertheless, the crystallinity of MG003 is higher than that of conventional low-pressure
18 sintered UHMWPE (50-55 %). The high linearity of this new polymer may facilitate the
19 crystallization of polymeric chains into thicker lamellae due to the absence of branching.
20 In this sense, the sharp melting peaks observed in DSC experiments suggest the existence
21 of a narrow lamellar size distribution, as reflected by TEM micrographs. The average
22 lamellar thicknesses, L_c , measured directly from TEM images, around 36 ± 3 nm, are
23 coherently in agreement with the values calculated using the Thomson-Gibbs equation,
24 which grew with melting temperature. These crystal thickness values are higher than those
25 associated to conventional GUR 1050 and 1020 consolidated forms, wherein average

1 lamellar thickness is near 26 nm, which also corresponds to lower values of the transition
2 melting temperature.

3 The presence of trace concentrations of vitamin E provokes no significant changes
4 on the raw material from a microstructure point of view, except for a slight increase in the
5 degree of crystallinity and lamellar thickness. These phenomena have been observed for
6 blended vitamin E-GUR 1050 systems at antioxidant concentrations similar to that used in
7 MG003 resins[23]. Following irradiation, the present PE-VE samples experienced a slight
8 increase in crystallinity, which results from the radiative chain scission of molecules and
9 further rearrangement into crystals. On the other hand, concentrations of vitamin E as low
10 as 0.1% are needed to not inhibit crosslinking generation in UHMWPE due to the free
11 radical scavenger role of the phenolic antioxidant[13]. In the case of vitamin E infused
12 UHMWPE, the thermal processes used to incorporate vitamin E are performed at
13 temperatures over 120 °C, and this implies that an annealing process takes place
14 simultaneously to the diffusion of the antioxidant. Thermal annealing is known to produce
15 a small increase in the crystallinity of UHMWPE associated to the gradual thickening of
16 lamellar crystals [24], and this also occurs to vitamin E infused UHMWPEs as long as the
17 antioxidant concentration does not exceed 0.4 % by weight[25].

18 Our X-ray diffraction findings point out that the novel pristine MG003, UHMWPE
19 - vitamin E blend, presents the same crystalline structure that conventional GUR
20 UHMWPEs, although the *a* and *b* cell parameters are slightly shorter than those obtained
21 for polyethylene by Burns[26], but are in agreement with Davis and Swan[27-28]. The
22 lower *a* cell parameter and the less intense amorphous halo around $\theta=20^\circ$ found for GUR
23 1050 polyethylene indicate the conventional grade was less crystalline than PE-VE
24 materials, in agreement with the present DSC results. Irradiation introduced no substantial
25 changes in the diffractograms as compared to those of unirradiated PE-VE. Nevertheless, a

1 slight decrease in the background or amorphous halo was noticed upon irradiation,
2 suggesting PE-VE-I materials had crystallized better. The area ratios of the fitted
3 backgrounds versus the experimental patterns indicated an increase in crystallinity of
4 about 3%, confirming again the microstructure findings obtained by DSC and TEM.
5 Barron and Birkinshaw have recently reported evidence of radiation-induced crystallinity
6 increases in GUR 1020 and 1050 grades by a combination of techniques, namely DSC,
7 SAXS and Raman spectroscopy[29]. They interpreted their results considering UHMWPE
8 as a three phase material, fully crystalline (local ordered chain folded molecules, i.e.
9 crystal lamellae), fully amorphous (disordered molecules), and all-trans amorphous
10 (interfacial molecules). Upon irradiation, interfacial molecules experience chain scission
11 and become mobile enough so they are either able to incorporate into the original crystals
12 or to develop a second, thinner, crystal population. Consequently, the rearrangements of
13 the aforementioned interfacial molecules upon irradiation give rise to crystallinity and
14 melting temperatures increases. The present findings are in agreement with the three phase
15 model and its evolution upon irradiation, regardless of the polyethylene resin. The three
16 phase model has been also successfully utilized by other researchers in the assessment of
17 microstructure, oxidation-induced, changes in moderately oxidized polyethylene knee
18 retrievals, but its applicability to highly oxidized polyethylene was questioned[30].

19 The current thermogravimetric experiments confirmed that vitamin E had a
20 beneficial antioxidant role for MG003 UHMWPE. Thus, T_B , the temperature at which the
21 thermooxidation processes induce a small but detectable mass increase, was shifted
22 towards remarkably higher values upon vitamin E incorporation with respect to
23 conventional unstabilized GUR 1050. Following gamma irradiation, however, T_B
24 experienced a 19 % decrease in vitamin E-MG003 materials, suggesting some loss of
25 oxidative resistance in comparison with the unirradiated system. As with regards to the

1 beginning of the purely thermal decomposition, gamma irradiation shifted T_1 towards
2 higher temperatures in the case of GUR 1050. In a previous study, the thermal
3 decomposition of electron-beam irradiated GUR 1050 UHMWPEs was also observed to
4 be progressively delayed with increasing radiation doses as compared to unirradiated
5 materials[19]. This delay was attributed to the generation of increasing crosslink densities
6 in agreement with Krupa and Tidjani [31-32]. The more stable crosslinked networks might
7 hinder thermal scissions and therefore the depolymerization and evaporation of volatile
8 products. In contrast, gamma-irradiated vitamin E-MG003 experienced an 8% reduction in
9 T_1 , which is in apparent contradiction with the expected trend. Moreover, fracture strain
10 results of PE-VE-I specimens did support the creation of the crosslinked network. A
11 similar decrease in the initial degradation temperatures has been reported for LLDPE
12 when diethyl maleate was grafted to it using gamma irradiation[33]. This behavior is not
13 unexpected on the basis of the higher breakage rate of carbon atoms adjacent to side
14 chains during thermogravimetric experiments[34]. In the case of the highly linear MG003
15 polyethylene, grafting of vitamin E or its byproducts might be occurring during gamma
16 irradiation[35], thus explaining the change in the thermal decomposition behavior.

17 The absence of EPR signals in unirradiated PE-VE samples (Figure 6) strongly
18 suggests that processing did not introduce a significant amount of radicals in the blended
19 system. On the contrary, EPR experiments of PE-VE-I specimens confirmed the presence
20 of radiation-induced free radicals upon gamma-irradiation in air (Figure 6). Furthermore,
21 the EPR spectrum of PE-VE-I showed marked differences when compared with those of
22 irradiated GUR UHMWPE samples that did not contain vitamin E (trace a and b in Figure
23 6). In the last case, the EPR spectra of GUR 1050 was dominated by the allyl signals,
24 since the outermost lines distance was about 8.5 mT, although the existence of some
25 polyenyl radicals may be responsible for the strongly overlapped central part of the
26 spectrum[20-22]. In PE-VE-I samples, besides the foregoing primary radical signals,

1 another signal showing a barely resolved hyperfine structure was observed in the central
2 part of the spectra. This signal could be associated with α -tocopheroxyl radicals [20-22]. It
3 is worth noting that the absolute intensity of the primary allyl radicals is lower in PE-VE-I
4 samples than in vitamin E free GUR resins, at least by a factor of twelve. The signal due to
5 α -tocopheroxyl radicals (trace c in Figure 8) was obtained by subtraction of trace a and b,
6 the last one being multiplied by a suitable factor; some spurious signals in both high and
7 low magnetic field sides of the EPR spectra could be due to the vinyl radicals[36-37].
8 These results indicate that the addition of vitamin E to UHMWPE significantly decrease
9 the primary radical production during irradiation.

10

11 The influence of trace concentrations of vitamin E on the mechanical properties of
12 pristine MG003 UHMWPE was practically negligible. However, the yield and ultimate
13 tensile stresses as well as the elongation to breakage underwent changes when the vitamin
14 E-UHMWPE system was irradiated. Thus, PE-VE-I samples experienced a 10% increase
15 in yield stress, σ_y , with respect to unirradiated specimens, whereas the ultimate tensile
16 strength, σ_{ult} , dropped a 12 %, and so did the fracture strain by a 30 %. Therefore, gamma
17 irradiation provoked a significant loss of toughness. This behavior is qualitatively similar
18 to that recently reported for 0.1 wt% α -tocopherol blended GUR 1050 UHMWPE upon
19 gamma irradiation to 100-kGy doses [13, 23]. However, in the present case, the increase in
20 σ_y was only 5 %, and the decreases in ultimate stress and strain, σ_{ult} and ϵ_{ult} , were higher,
21 18 % and 50 % respectively[23]. As for modern first generation highly crosslinked
22 UHMWPEs, denoted hereafter by XLPE, these mechanical parameters, σ_y , σ_{ult} , and ϵ_{ult}
23 have been reported to undergo 1%, 21% and 28% reductions[8], respectively, upon
24 electron beam irradiation to 100 kGy and post-irradiation annealing. When a post-
25 irradiation remelting treatment is used, these reductions become sharper, namely 17%,

1 12%, 11%, respectively[8]. The higher yield stresses exhibited by PE-VE-I specimens
2 compared with the unirradiated material coherently correlates with the higher lamellar
3 thicknesses measured in TEM micrographs, since this mechanical parameter is governed
4 by crystal thickness according to Galeski[38]. However, the reduction of σ_{ult} , and ϵ_{ult} and,
5 therefore, the associated work to fracture, would be more influenced by the level of
6 radiation-induced crosslinking generated by irradiation. The elevated crosslink density is
7 most probably responsible for the foregoing toughness loss since it introduces constraints
8 to the amorphous deformation modes of the polymer and, therefore, it diminishes its
9 ductile capability[39]. More research is needed to confirm this trend in the toughness
10 response of vitamin E stabilized MG003 UHMWPE, including additional impact and J-
11 integral experiments.

12

13 **CONCLUSIONS**

14 MG003 materials present microstructure, thermal, thermoxidation and mechanical features
15 comparable to those of conventional medical UHMWPE, both before and after irradiation.
16 The higher degree of linearity of MG003 is responsible for elevated crystallinity and, in
17 turn, superior elastic modulus and yield stress values as compared to those of GUR 1050
18 converted forms. Irradiation in air caused similar effects in both MG003 and GUR1050
19 polyethylenes, especially a significant loss in ductility as measured by elongation to
20 breakage results in uniaxial tensile tests. Gamma irradiation in air also yielded measurable
21 free radicals in vitamin E stabilized MG003 materials, being this behavior essentially
22 similar to that of irradiated vitamin E doped GUR 1050 polyethylenes. From a materials
23 science point of view, the novel MG003 medical polyethylene is confirmed as a suitable
24 alternative to conventional GUR resins, and a satisfactory contribution to the performance
25 of metal-polyethylene total joint replacements is anticipated.

1 **ACKNOWLEDGEMENTS**

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4 Ministerio de Ciencia e Innovación.

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1 **FIGURE CAPTIONS**

2

3 Figure 1. Ultraviolet spectra of unstabilized GUR 1050, and vitamin E stabilized MG003
4 polyethylenes. A distinct band at 290 nm was observed for the stabilized material.

5 Figure 2. DSC curves of unirradiated GUR 1050, MG003 (PE-VE), as well as of 90 kGy
6 gamma irradiated, GUR 1050-I and PE-VE-I, materials.

7 Figure 3. TEM micrographs (60.000x) of a) as-consolidated PE-VE sample and b) 90 kGy
8 gamma irradiated PE-VE-I sample. As an example, a crystal thickness measurement (see
9 text) is schematically depicted for a single lamella.

10 Figure 4. X-ray diffraction patterns of GUR 1050, PE-VE and PE-VE-I materials.

11 Figure 5. a) Typical decomposition curves from control PE-VE and 90 kGy gamma
12 irradiated PE-VE-I samples. b) A close-up view revealed a small but noticeable weight
13 gains before the beginning of volatilization with maxima at T_0 . The onset of this weight
14 gain was designated as T_B .

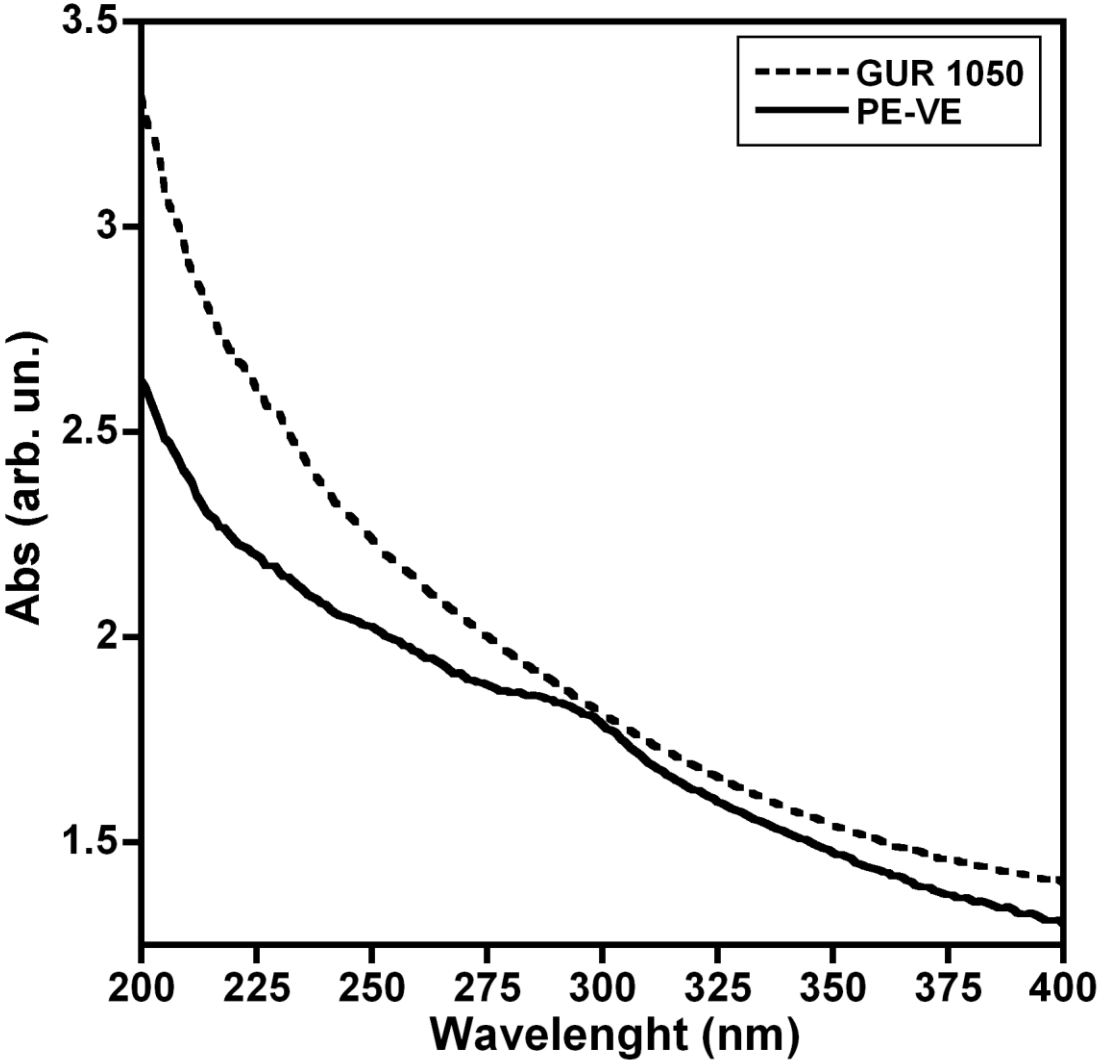
15 Figure 6. Room temperature X-band EPR spectrum of a) as-received sample PE-VE b)
16 and 90 kGy gamma irradiated samples, PE-VE-I.

17 Figure 7. Stress-strain curves in the uniaxial tension test for as-consolidated, PE-VE, and
18 90 kGy gamma irradiated in air, PE-VE-I.

19 Figure 8. Room temperature X-band EPR spectra measured of a) 90 kGy gamma
20 irradiated sample, PE-VE-I. b) Vitamin E free GUR 1050 UHMWPE irradiated in the
21 same conditions; in this case the signal intensity has been divided by a factor twelve in
22 order to make easy the comparison of signals due to primary radicals (see text). c) gives
23 the difference of the a) and b) and points out the presence of alpha-tocopheroxyl radicals.

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FIGURE 1

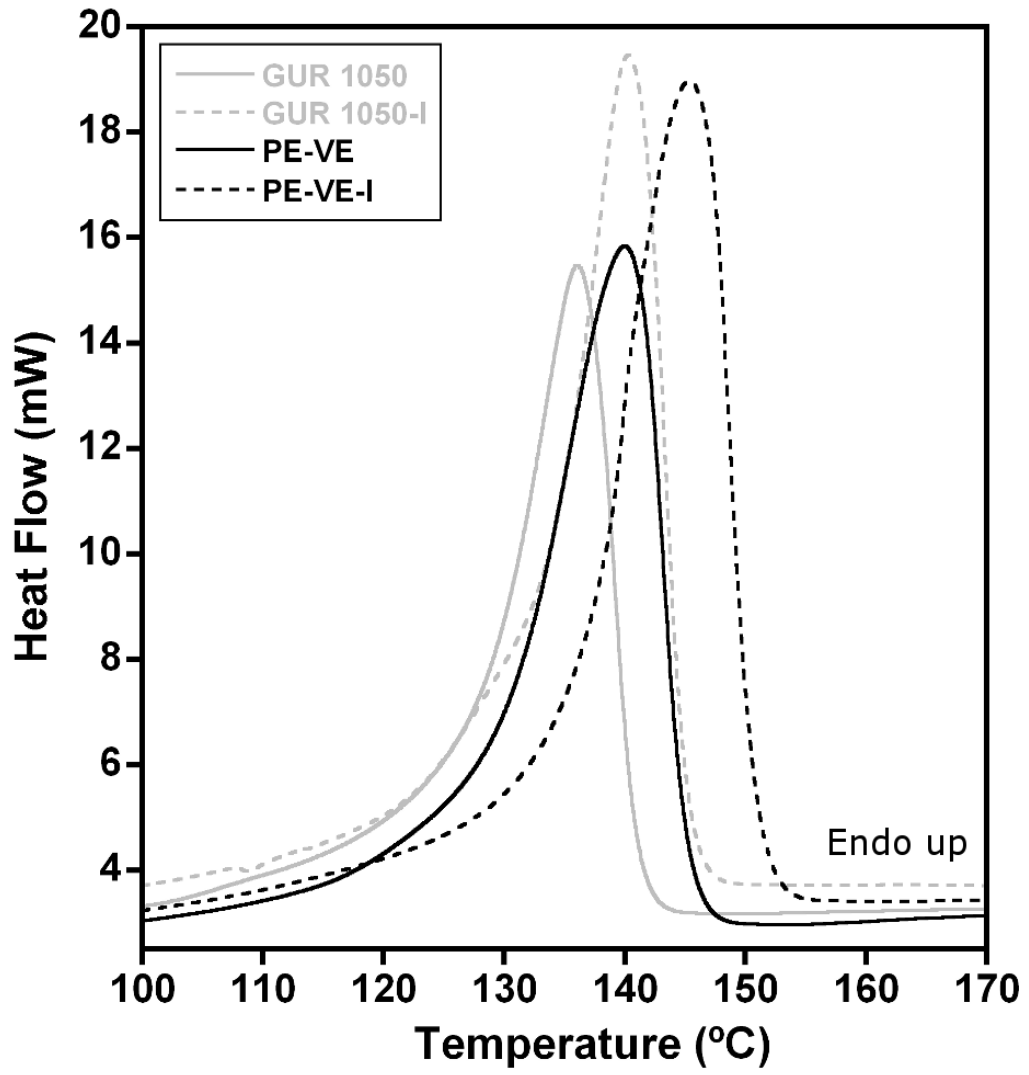


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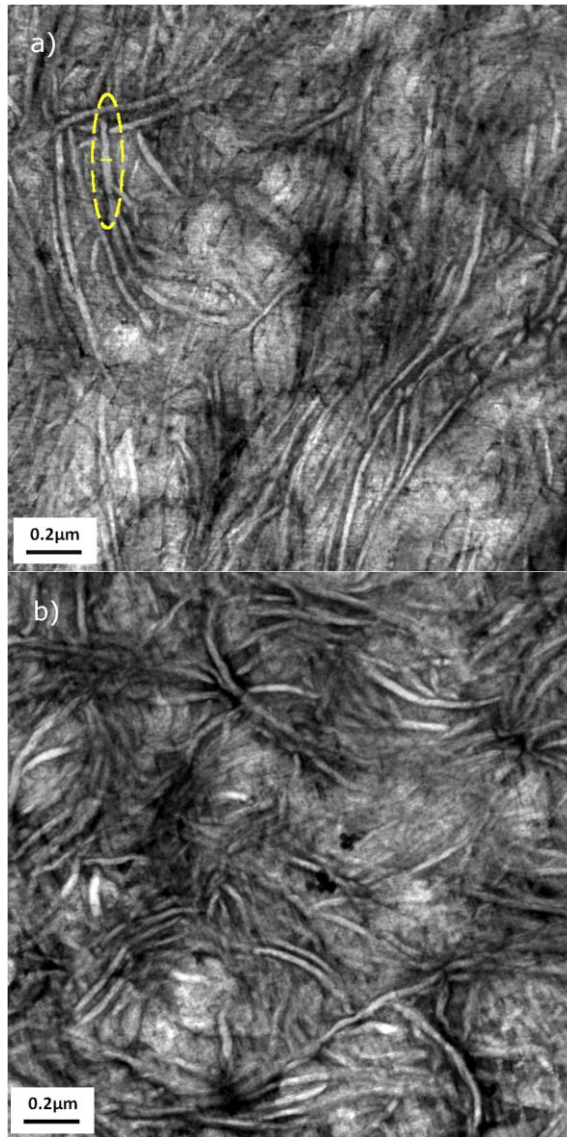
FIGURE 2



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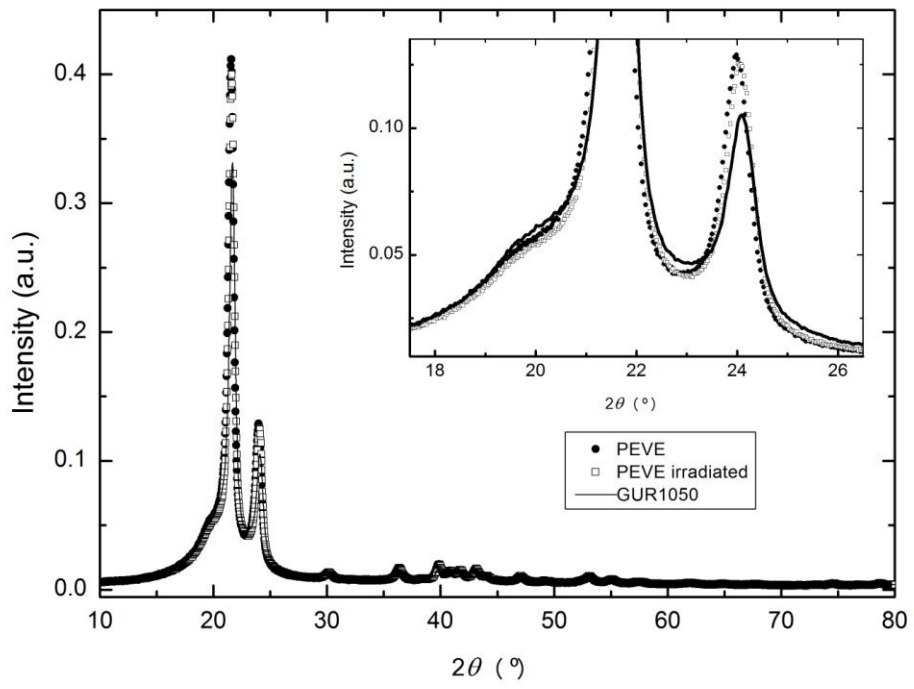
FIGURES 3A-B



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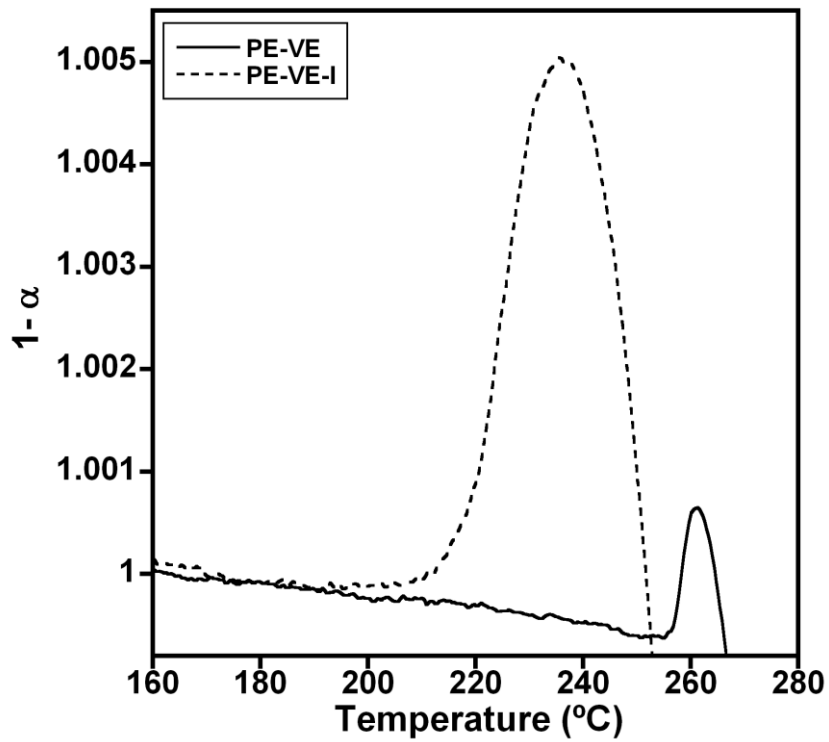
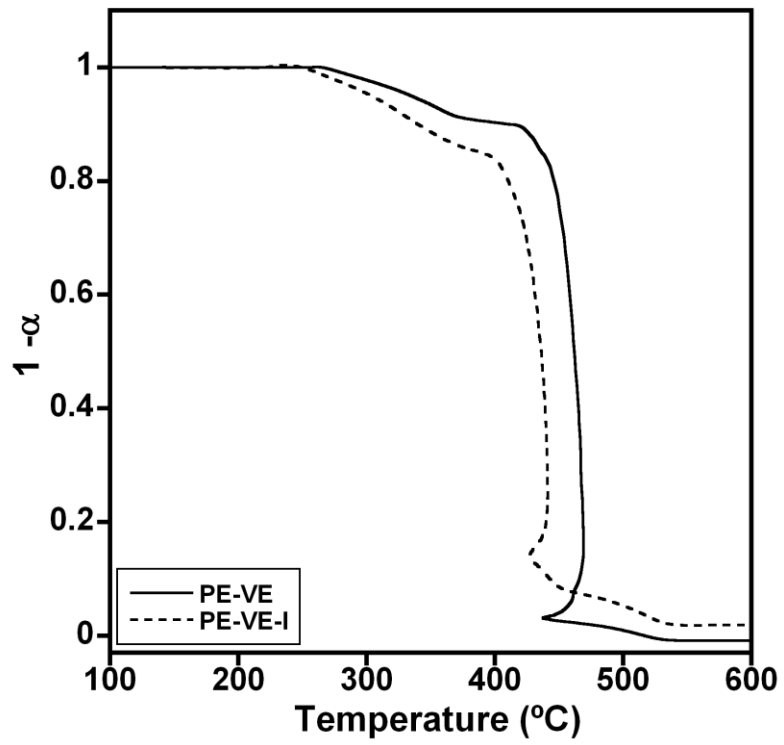
FIGURE 4



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FIGURES 5A-B



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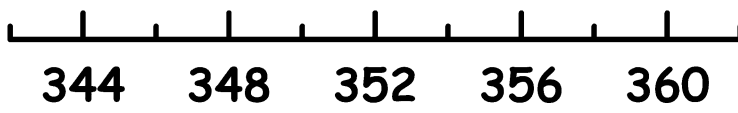
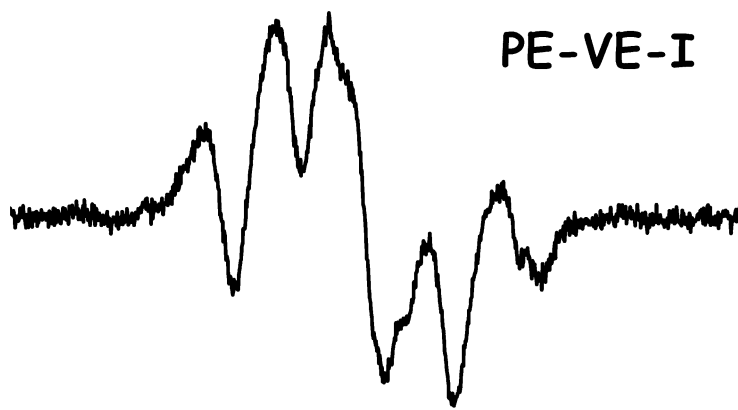
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FIGURE 6

PE-VE



PE-VE-I

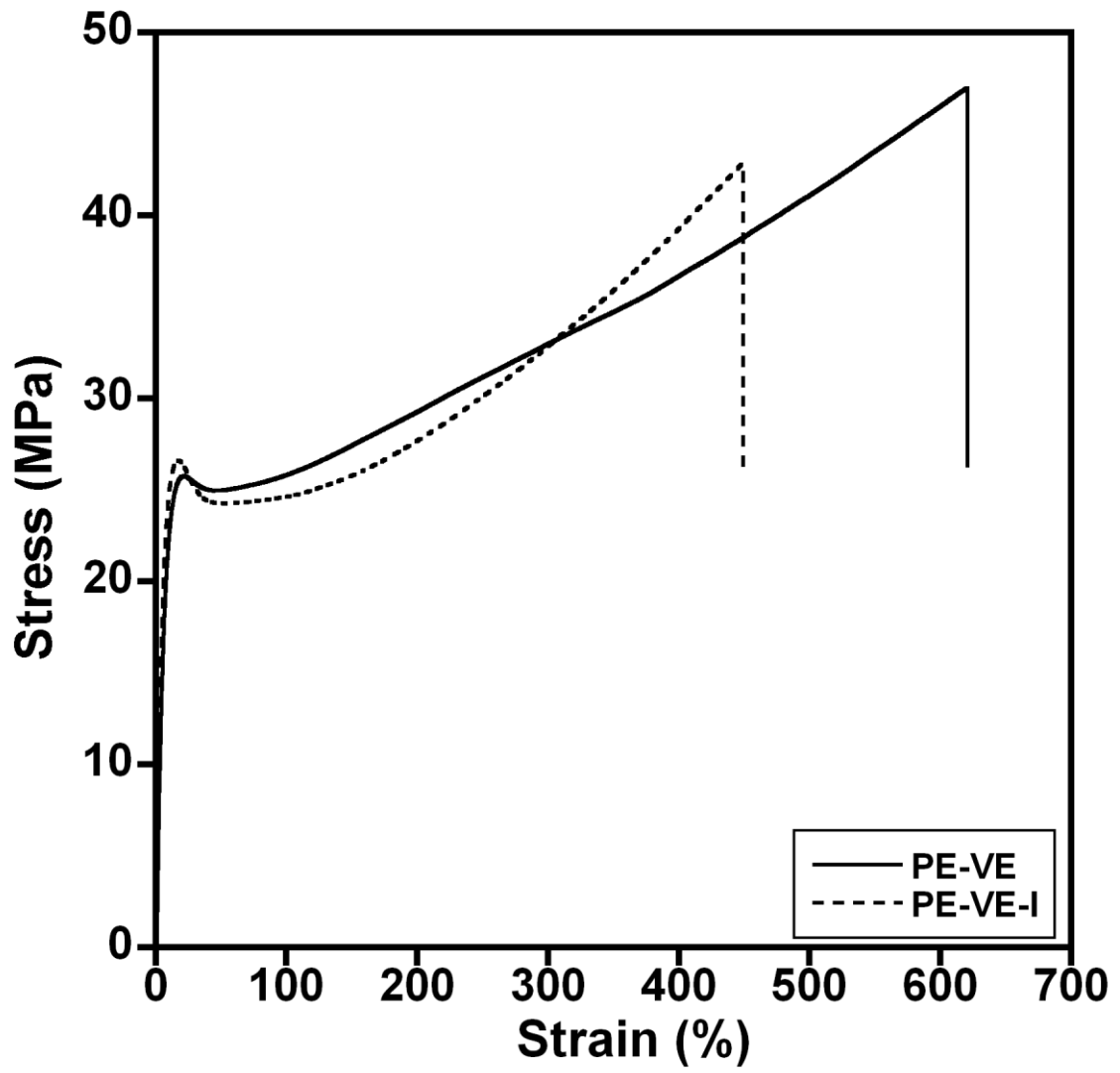


MAGNETIC FIELD / mT

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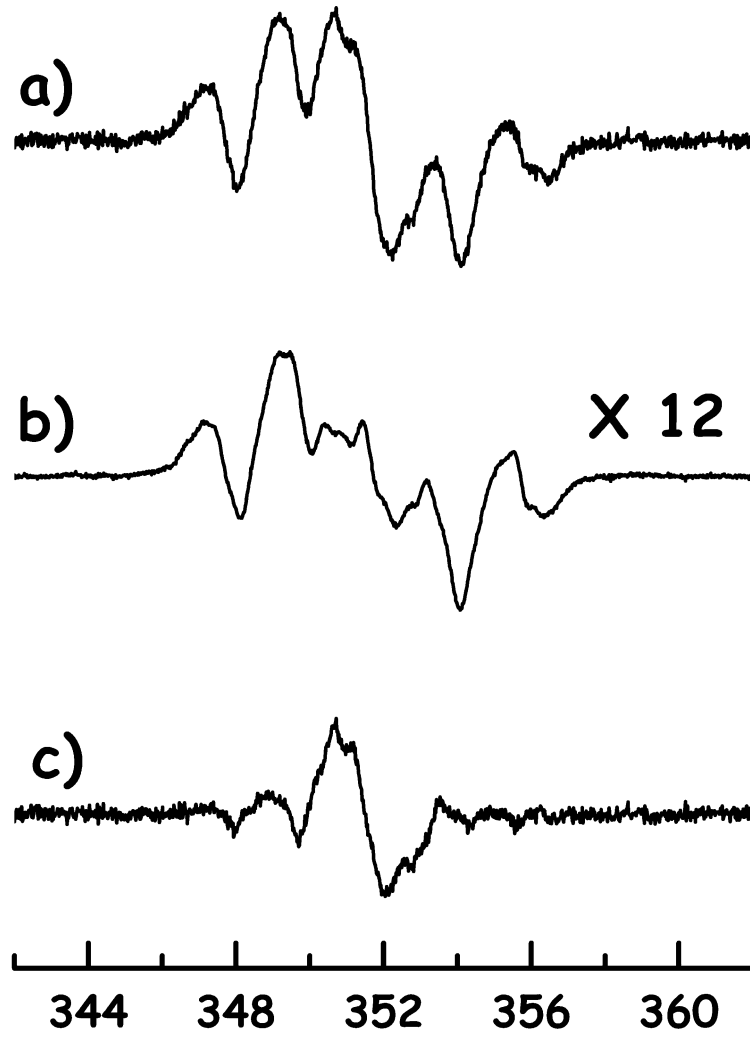
FIGURE 7



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FIGURE 8



MAGNETIC FIELD / mT