This manuscript was accepted for publication in Materials Science and Engineering C

Microstructure, thermooxidation and mechanical behavior of a novel highly linear, vitamin E stabilized, UHMWPE

F.J. Medel[a,b], M.J. Martínez-Morlanes[c], P.J. Alonso[b], J. Rubin[b], F.J. Pascual[c], J.A. Puértolas[b,c],

[a] Department of Mechanical Engineering. Engineering and Architecture School, Universidad de Zaragoza, E-50018, Zaragoza, Spain.

[b] Instituto Ciencia de Materiales de Aragón, ICMA, Universidad de Zaragoza-CSIC, E-50018, Zaragoza, Spain.

[c] Department of Materials Science and Technology, Instituto de Investigaciones en Ingeniería de Aragón, I3A, Universidad de Zaragoza, E-50018, Zaragoza, Spain.

*Correspondence to Prof. Francisco J. Medel
Department of Mechanical Engineering
Engineering and Architecture School
Universidad de Zaragoza
C/ María de Luna s/n, 50018, Zaragoza, Spain
Phone: +34 976 762553
Fax: +34 976762670
E-mail: fjmedel@unizar.es

ABSTRACT

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

KEYWORDS: UHMWPE, α-tocopherol (vitamin E), microstructure, thermoxidation, mechanical properties.

INTRODUCTION

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

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

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

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

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

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

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

MATERIALS AND METHODS

Raw Materials

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

Vitamin E detection

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

Differential Scanning Calorimetry

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

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

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

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

Transmission Electron Microscopy

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

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

X-ray diffraction experiments

X-ray diffraction patterns were measured at room temperature using a D-Max Rigaku diffractometer with a Cu rotating anode and working at 40 kV and 80 mA. No filtering of Cu K_β was taken. Data were collected from 2θ = 20º to 80º in steps of 0.03º and 3 second per step.

Thermogravimetry

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

Free radical concentration assessment

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

Mechanical properties

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

Statistical analysis

Student´s t tests were conducted to assess significant differences in thermal, thermooxidation and mechanical properties between material groups. A level of $p < 0.05$ was selected as indicative of significance.

RESULTS

Thermal properties and microstructure

First heating DSC curves exhibited the standard peak associated to the melting process of the polymer. Analysis of the DSC curves provided the transition temperature and enthalpy content, which is related to the degree of crystallinity, for each sample (Figure 2). PE-VE, MG003, specimens exhibited higher crystallinity (61.6±1.1 %) and melting temperature (139.7±1.0 ºC) than GUR 1050 controls (55.0±0.3 %, and 136.2±0.5 ºC, respectively; $p < 0.0003$, statistically significant difference, in both cases). As for the effects of irradiation, a small crystallinity increase was observed for gamma-irradiated 0.1% PE-VE specimens (63.2±1.7 %). The melting transition temperature experienced a small, but statistically significant, increase with irradiation up to 143.3±1.8 ºC ($p<0.03$; Student´s t test). Upon irradiation, GUR 1050 specimens exhibited significantly higher crystallinity (59.9±0.7 %) and melting temperature (140.4±0.3 ºC) with respect to neat GUR 1050 samples ($p \leq 0.001$). The crystallinity of PE-VE-I was still significantly higher than that of irradiated GUR 1050 materials ($p < 0.03$).

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

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

a background to take account non-crystalline contributions. No specific modeling of the background was made to separate the amorphous halo from the total background. The fitted cell parameters were a = 7.398±0.005 Å, b = 4.939±0.004 Å and c = 2.542±0.002 Å for PE-VE, and a = 7.401±0.005 Å, b = 4.939±0.004 Å and c = 2.542±0.002 Å for PE-VE-I. As for GUR 1050 controls, diffractograms showed a more intense amorphous halo around θ = 20° as well as a lower cell parameter a = 7.286±0.004 Å.

Thermogravimetry

The thermogravimetric decomposition curves of PE-VE and PE-VE-I polyethylenes exhibited essentially similar features (Figure 5a). Sample mass remained constant at the beginning of the test, but specimens soon started to weight gain at T_B, reaching the maximum at T_0 (Figure 5b). Then, decomposition began and samples lost mass in a non-linear fashion up to T_1, which lay between 400 and 450 °C depending on the material. 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 until the specimen was almost decomposed. The chemical meaning of each temperature are explained in detail elsewhere[19], but it is worth mentioning that only T_B, and T_0 are the relevant temperatures to rank the oxidation stability of the current polymer systems stabilized with phenolic antioxidant.

A detailed analysis of the thermogravimetric curves revealed some differences between unirradiated and irradiated MG003 polyethylenes. Thus, the onset of thermooxidation, T_B, of PE-VE materials was significantly shifted towards lower temperatures, from 252±2 ºC to 205±2 ºC, upon irradiation ($p<0.0001$; Student´s t test). Likewise, T_0 significantly changed upon gamma irradiation from 261 ± 1 ºC to 234 ± 1 ºC ($p<0.0001$). As for conventional grades, unstabilized GUR 1050 polyethylene exhibited

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

Free radical concentration assessment

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

Mechanical properties

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

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

DISCUSSION

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

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

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

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

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

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

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

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

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

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

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

CONCLUSIONS

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

ACKNOWLEDGEMENTS

Research funded by the Comisión Interministerial de Ciencia y Tecnología (CICYT), Spain. Project: MAT 2010-16175 and Consolider-Ingenio CDS2008-0023 from the Ministerio de Ciencia e Innovación.

REFERENCES

[1] S. Santavirta, V. Hoikka, A. Eskola, Y.T. Konttinen, T. Paavilainen, K. Tallroth, J Bone Joint Surg Br, 72 (1990) 980-984.

[2] S. Santavirta, Y.T. Konttinen, V. Bergroth, A. Eskola, K. Tallroth, T.S. Lindholm, J Bone Joint Surg Am, 72 (1990) 252-258.

[3] S.M. Kurtz, The UHMWPE Biomaterials Handbook: Ultra-High Molecular Weight Polyethylene in Total Joint Replacement and Medical Devices (2nd Edition), Academic Press, Burlington, MA, 2009.

[4] H. McKellop, F.W. Shen, B. Lu, P. Campbell, R. Salovey, J Orthop Res, 17 (1999) 157-167.

[5] V. Premnath, W.H. Harris, M. Jasty, E.W. Merrill, Biomaterials, 17 (1996) 1741-1753.

[6] L. Costa, M.P. Luda, L. Trossarelli, E.M. Brach del Prever, M. Crova, P. Gallinaro, Biomaterials, 19 (1998) 659-668.

[7] J.A. Puertolas, A. Larrea, E. Gomez-Barrena, Biomaterials, 22 (2001) 2107-2114.

[8] F.J. Medel, P. Pena, J. Cegonino, E. Gomez-Barrena, J.A. Puertolas, J Biomed Mater Res B Appl Biomater, 83 (2007) 380-390.

[9] J.A. Puertolas, F.J. Medel, J. Cegonino, E. Gomez-Barrena, R. Rios, J Biomed Mater Res B Appl Biomater, 76 (2006) 346-353.

[10] L. Packer, Am J Clin Nutr, 53 (1991) 1050S-1055S.

[11] E. Oral, S.L. Rowell, O.K. Muratoglu, Biomaterials, 27 (2006) 5580-5587.

[12] S.M. Kurtz, J. Dumbleton, R.S. Siskey, A. Wang, M. Manley, J Biomed Mater Res A, 90 (2009) 549-563.

[13] E. Oral, C.G. Beckos, A.S. Malhi, O.K. Muratoglu, Biomaterials, 29 (2008) 3557-3560.

[14] E. Oral, K.K. Wannomae, S.L. Rowell, O.K. Muratoglu, Biomaterials, 28 (2007) 5225-5237.

[15] C. Wolf, J. Maninger, K. Lederer, H. Fruhwirth-Smounig, T. Gamse, R. Marr, J Mater Sci Mater Med, 17 (2006) 1323-1331.

[16] P. Gijsman, H.J. Smelt, D. Schumann, Biomaterials, 31 (2010) 6685-6691.

[17] F.J. Buchanan, J.R. White, B. Sim, S. Downes, J Mater Sci Mater Med, 12 (2001) 29-37.

[18] F.J. Medel, F. Garcia-Alvarez, E. Gomez-Barrena, J.A. Puertolas, Polym Degrad Stabil, 88 (2005) 435-443.

[19] M.J. Martinez-Morlanes, F.J. Medel, M.D. Mariscal, J.A. Puertolas, Polym Test, 29 (2010) 425-432.

[20] M.D. Ridley, M.S. Jahan, Journal of Biomedical Materials Research Part A, 88A (2009) 1097-1103.

[21] M.S. Jahan, B.M. Walters, Radiat Phys Chem, 80 (2011) 281-285.

[22] M.S. Jahan, Chapter 29 - ESR Insights into Macroradicals in UHMWPE, in: M.K. Steven, P.D. Ph.D.A2 - Steven M. Kurtz (Eds.) UHMWPE Biomaterials Handbook (Second Edition), Academic Press, Boston, 2009, pp. 433-450.

[23] E. Oral, E.S. Greenbaum, A.S. Malhi, W.H. Harris, O.K. Muratoglu, Biomaterials, 26 (2005) 6657-6663.

[24] H. Matsuda, T. Aoike, H. Uehara, T. Yamanobe, T. Komoto, Polymer, 42 (2001) 5013-5021.

[25] J.A. Puertolas, M.J. Martinez-Morlanes, M.D. Mariscal, F.J. Medel, J Appl Polym Sci, 120 (2011) 2282-2291.

[26] J.R. Burns, J Appl Phys, 37 (1966) 2856-&.

[27] G.T. Davis, R.K. Eby, G.M. Martin, J Appl Phys, 39 (1968) 4973-&.

[28] P.R. Swan, J Polym Sci, 56 (1962) 403-&.
[29] D. Barron, C. Birkinshaw, Polym Degrad Stabil, 94 (2009) 1621-1631.
[30] F.J. Medel, C.M. Rimnac, S.M. Kurtz, J Biomed Mater Res A, 89 (2009) 530-538.
[31] I. Krupa, A.S. Luyt, Polym Degrad Stabil, 71 (2001) 361-366.
[32] A. Tidjani, C.A. Wilkie, J Appl Polym Sci, 100 (2006) 2790-2795.
[33] E. Catari, C. Albano, A. Karam, R. Perera, P. Silva, J. Gonzalez, Nucl Instrum Meth B, 236 (2005) 338-342.
[34] R.W.J. Westerhout, J. Waanders, J.A.M. Kuipers, W.P.M. vanSwaaij, Ind Eng Chem Res, 36 (1997) 1955-1964.
[35] S. Al-Malaika, S. Issenhuth, Polym Degrad Stabil, 65 (1999) 143-151.
[36] M.S. Jahan, K.S. McKinny, Nucl Instrum Meth B, 151 (1999) 207-212.
[37] M.J. Martinez-Morlanes, P. Castell, P.J. Alonso, M.T. Martinez, J.A. Puertolas, Carbon, 50 (2012) 2442-2452.
[38] A. Galeski, Prog Polym Sci, 28 (2003) 1643-1699.
[39] L.A. Pruitt, Biomaterials, 26 (2005) 905-915.

FIGURE CAPTIONS

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

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

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

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

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

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

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

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

FIGURE 1

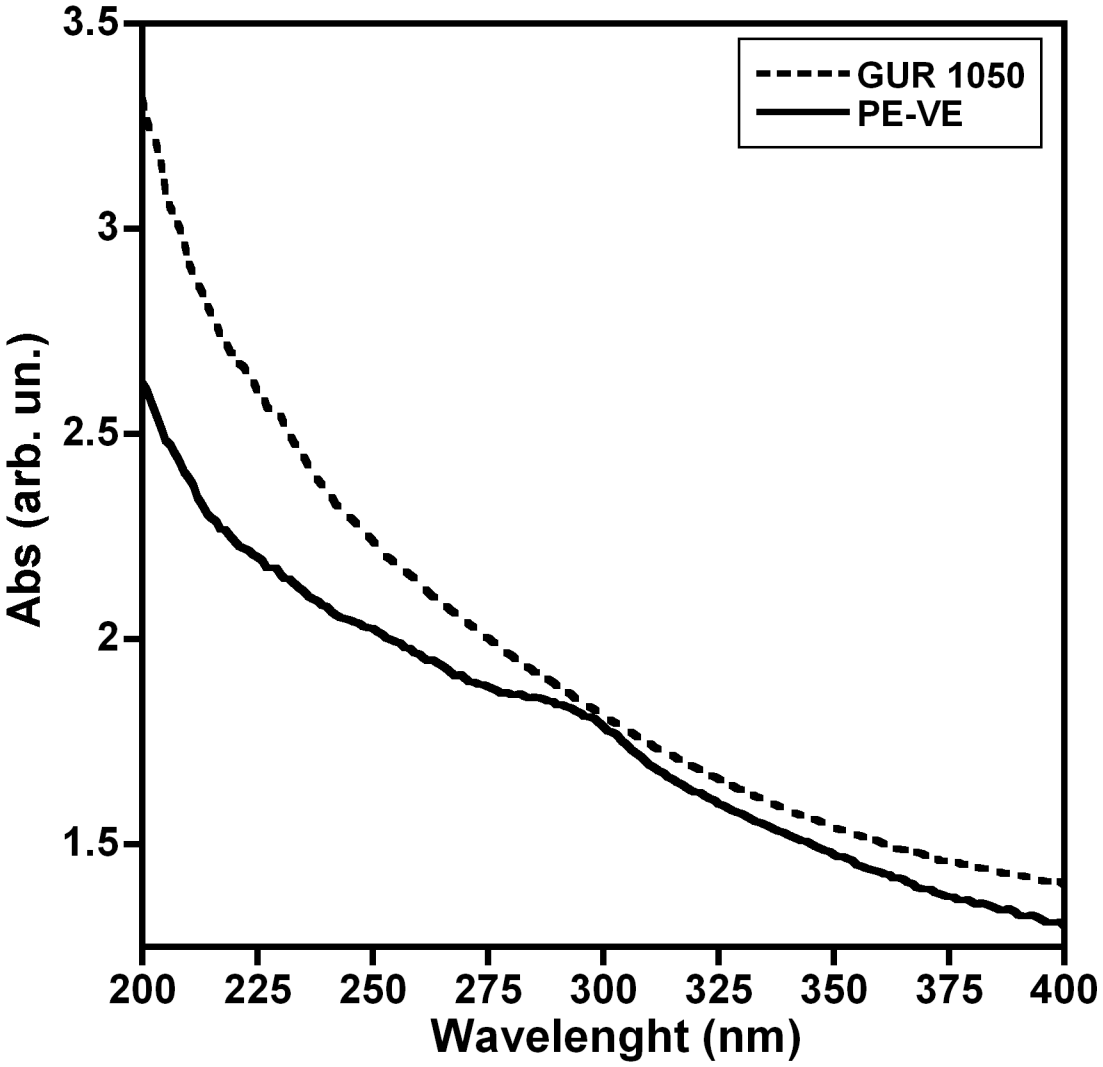
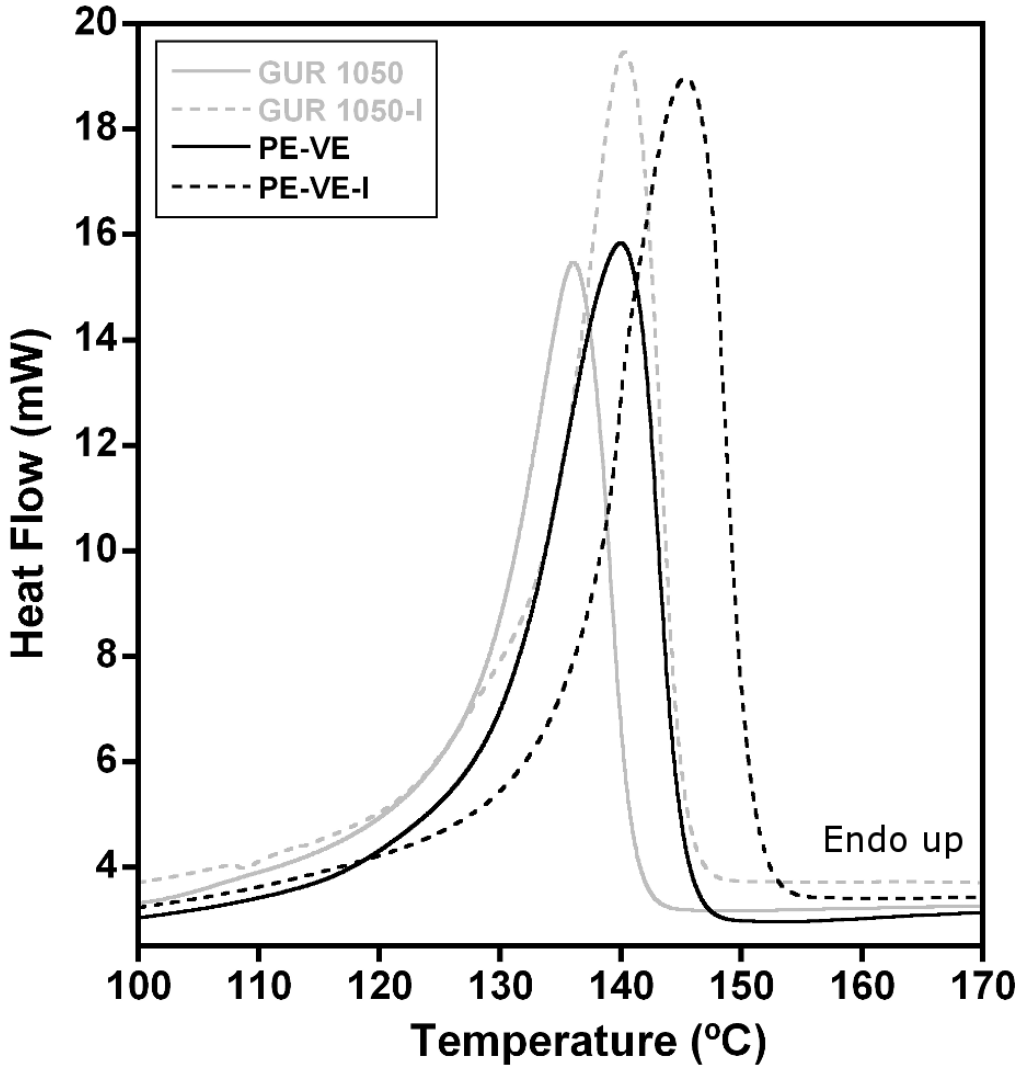

GUR 1050
PE-VE
Abs (arb. un.)
3.5
3
2.5
2
1.5
200
225
250
275
300
325
350
375
400
Wavelenght (nm)

FIGURE 2


GUR 1050
GUR 1050-I
PE-VE
PE-VE-I
Heat Flow (mW)
Temperature (°C)
Endo up
20
18
16
14
12
10
8
6
4
100
110
120
130
140
150
160
170

FIGURES 3A-B

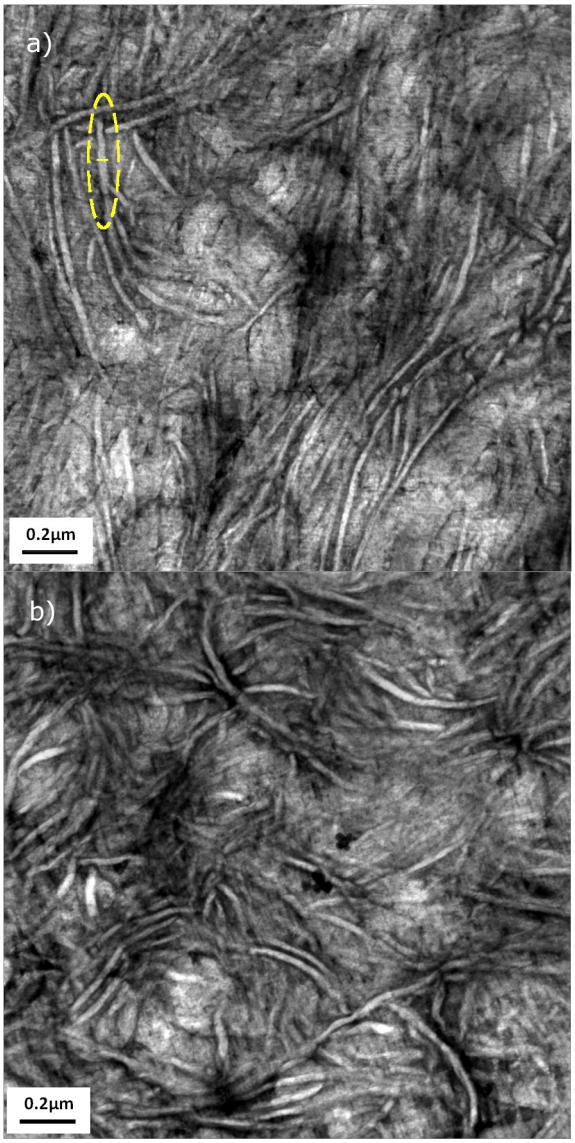
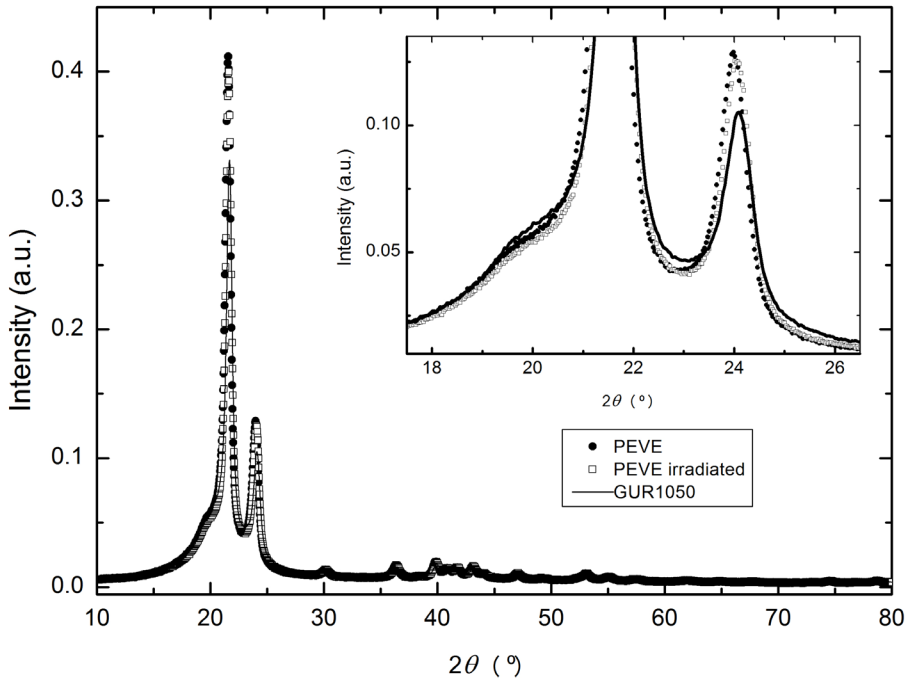
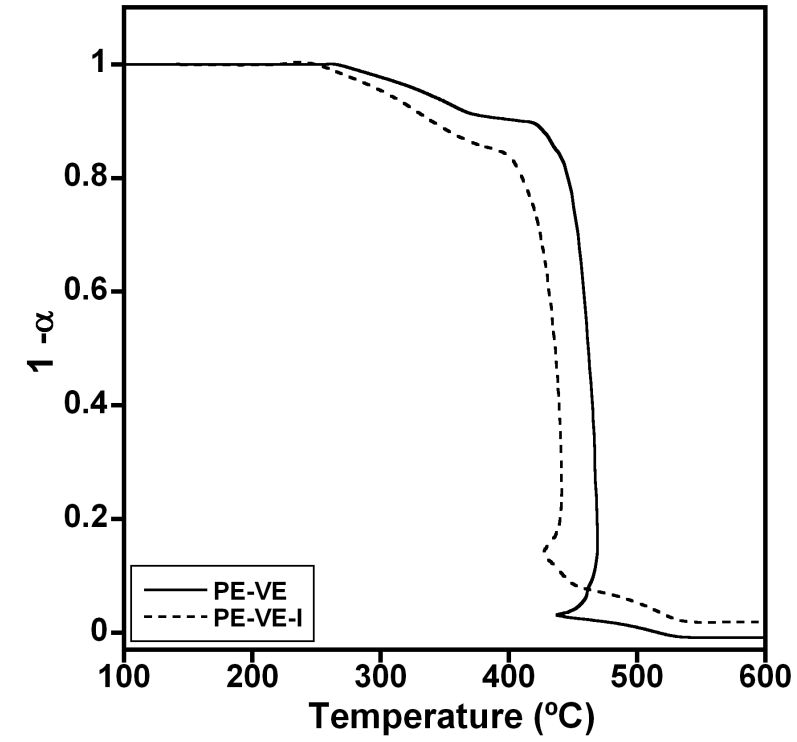


FIGURE 4


Intensity (a.u.)
0.0
0.1
0.2
0.3
0.4
10
20
30
40
50
60
70
80
2θ (°)
Intensity (a.u.)
0.05
0.10
18
20
22
24
26
2θ (°)
PEVE
PEVE irradiated
GUR1050

FIGURES 5A-B


1
0.8
0.6
0.4
0.2
0
1 -α
PE-VE
PE-VE-I
100
200
300
400
500
600
Temperature (ºC)

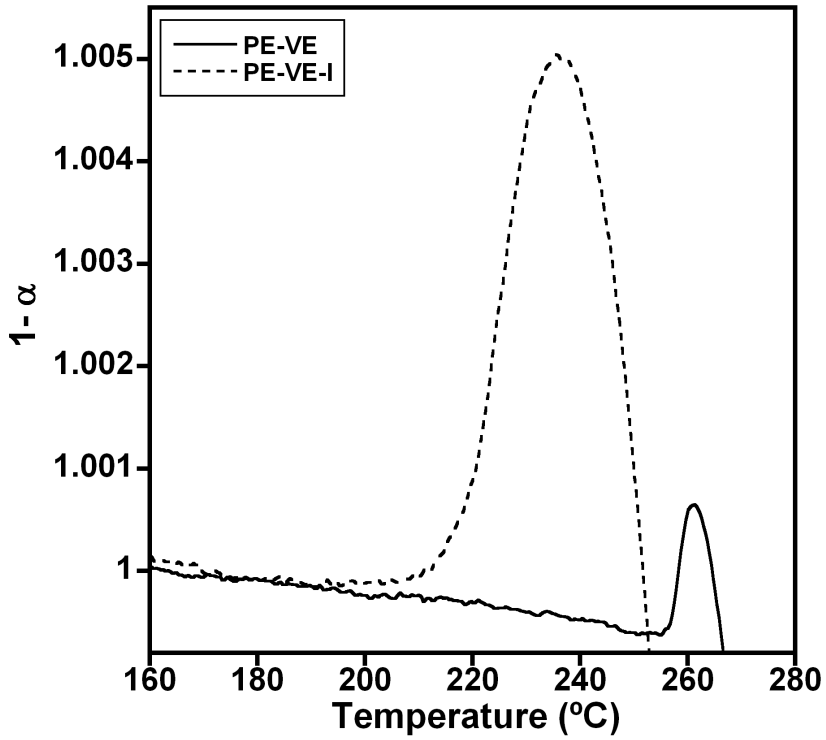

1.005
1.004
1.003
1.002
1.001
1
1- α
PE-VE
PE-VE-I
160
180
200
220
240
260
280
Temperature (ºC)

FIGURE 6

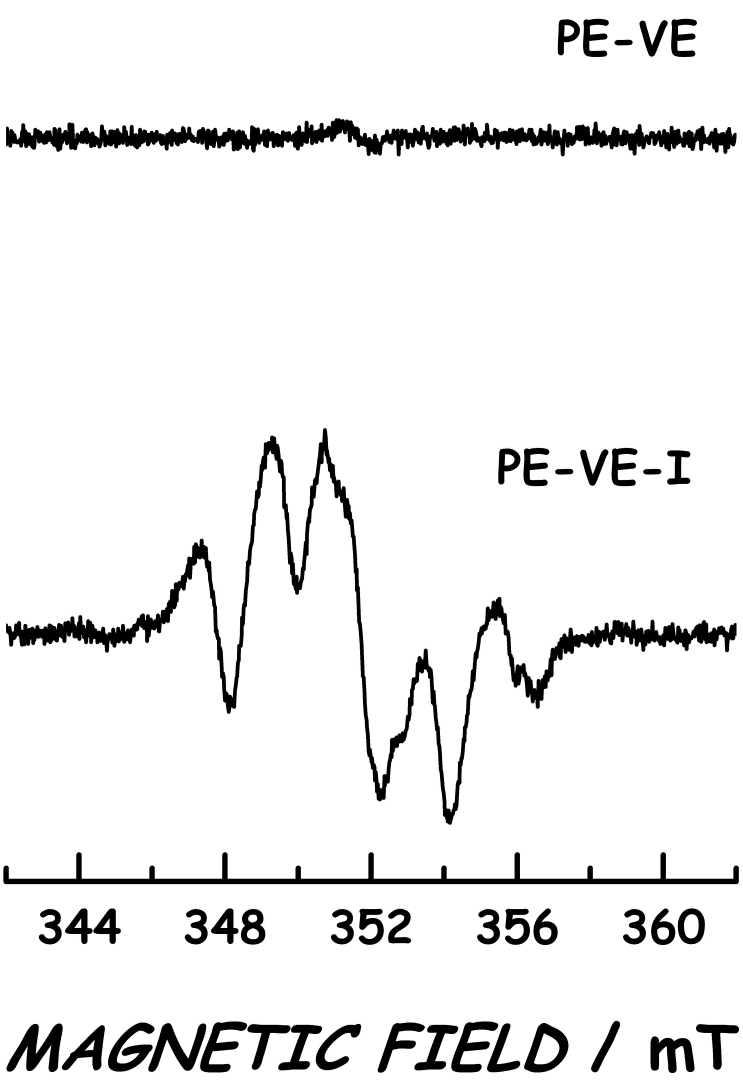


FIGURE 7

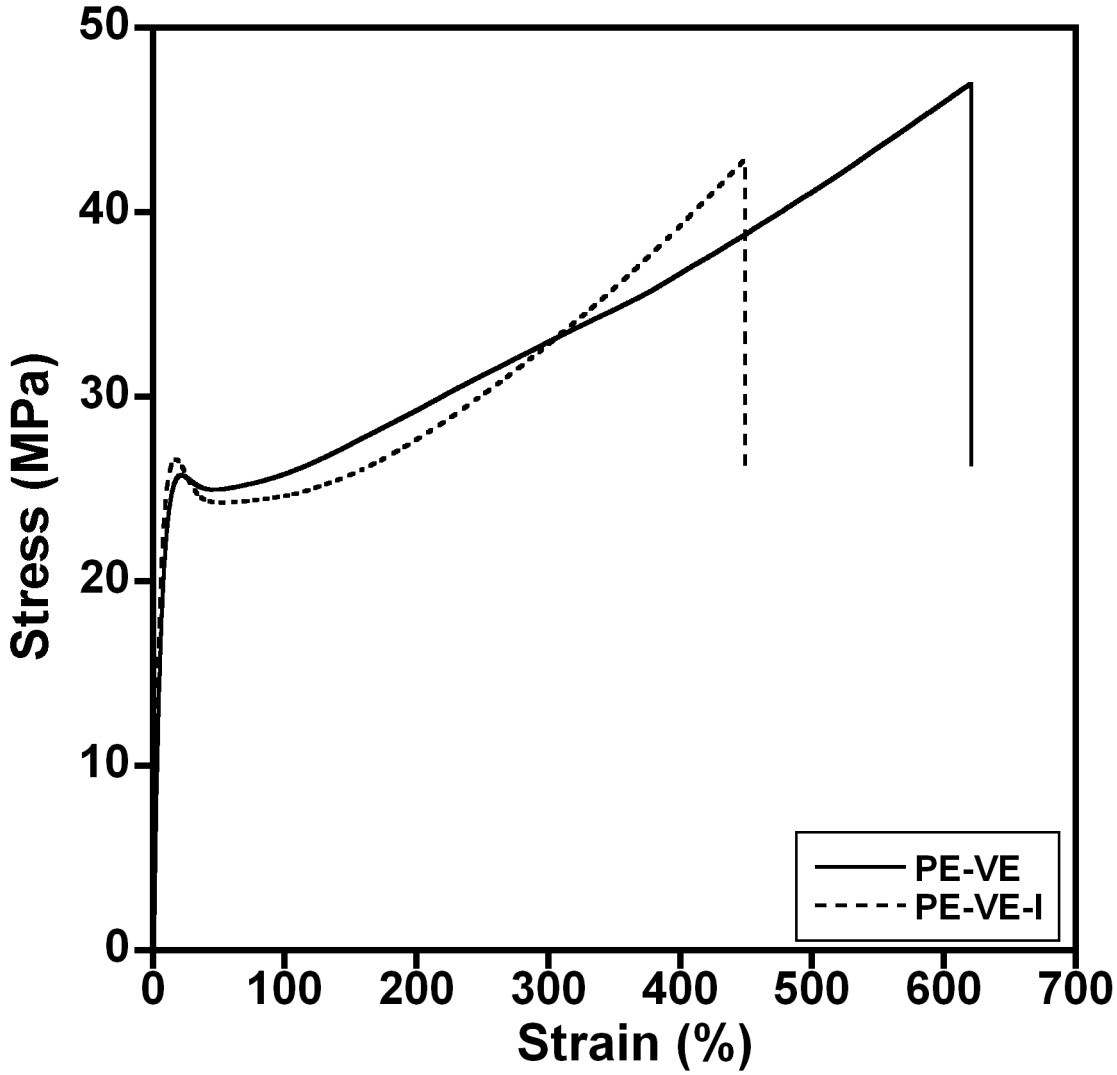

50
40
30
20
10
0
Stress (MPa)
0
100
200
300
400
500
600
700
Strain (%)
PE-VE
PE-VE-I

FIGURE 8