

Thermal and Dynamic Mechanical Properties of Vitamin E Infused and Blended Ultra-High Molecular Weight Polyethylenes

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ABSTRACT: Vitamin E (or α -tocopherol) is an alternative via to thermal treatments to achieve oxidative stability of gamma or electron beam irradiated ultra-high molecular weight polyethylenes (UHMWPE) used in total joint replacements. Our aim was to study the effects of vitamin E on the molecular dynamics and microstructural properties of UHMWPE. We hypothesized that the antioxidant would plasticize UHMWPE. Vitamin E was incorporated into UHMWPE at different concentrations by diffusion and blending and detected by ultraviolet and infrared spectroscopies from 500 ppm and 4000 ppm, respectively. Dynamic mechanical thermal analysis was used to characterize the influence of this antioxidant in the relaxations of the raw material. Differential scanning calorimetry and transmission electron microscopy served to characterize thermal and microstructure properties, respectively. Vitamin E concentrations above 3% by weight significantly reduced the degree of

crystallinity and increased the melting transition temperature of raw UHMWPE. The presence of increasing concentrations of α -tocopherol introduced and/or strengthened the beta relaxation, which was also shifted toward gradually lower temperatures and had rising activation energies up to 188 kJ/mol. In addition, the gamma relaxation remained unaltered on vitamin E addition. Therefore, no plasticizing effects of vitamin E on the molecular dynamics of UHMWPE could be confirmed from mechanical spectroscopy data. However, the α relaxation was modified in intensity and location due to the changes in the degree of crystallinity introduced by the incorporation of vitamin E. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2282–2291, 2011

Key words: polyethylene (UHMWPE); antioxidants (vitamin E/ α -tocopherol); viscoelastic properties (DMTA); molecular mechanics; microstructure

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) remains as the most relevant material used in total joint replacements. However, long-term service of UHMWPE, and thus the life span of the whole joint replacement system are compromised by material limitations. Wear of the UHMWPE component has been accepted as the most prominent drawback in hip arthroplasty, with associated generation of debris particles, subsequent osteolysis, and eventual aseptic loosening of the implant.¹ First-generation highly crosslinked polyethylenes were introduced in orthopaedic implants as a promising

alternative to conventional, gamma sterilized, UHMWPE.^{2–4} Thus, high irradiation doses are used to promote a significant crosslink density within the amorphous phase of the polymer, which is responsible for a dramatic improvement in wear resistance.^{4,5} However, concerns about long-term oxidation of highly crosslinked UHMWPE remain due to the generation of free radicals during irradiation, which may initiate oxidation reactions in the presence of molecular oxygen,^{6,7} which, in turn, convert UHMWPE into a brittle polymer with a significant loss of satisfactory performance.⁸ In the search of a method that would avoid the risk of long-term oxidation, orthopaedic manufacturers have combined the irradiation process with a subsequent thermal stabilization step at temperatures either below (annealing) or above (remelting) the melting transition temperature of UHMWPE. Both thermal stabilization processes seem to retain the wear resistance of highly crosslinked UHMWPEs. Nevertheless, remelting decreases the original crystallinity of the polymer, and therefore, it affects detrimentally some of the polymer's mechanical properties,⁹ whereas annealing preserves them better.¹⁰ However, annealing

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methods may not assure a complete oxidative stability, because less mobile free radicals, located within the crystalline region, are not able to recombine, because crystals do not melt completely during annealing.

An alternative to the foregoing thermal stabilization methods has been found in the use of α -tocopherol (vitamin E). This vitamin is a natural lipid, which acts as an antioxidant *in vivo* by means of the donation of a hydrogen atom to free radical formed on lipids hindering lipid peroxidation in cell membranes.¹¹ In irradiated UHMWPE, vitamin E basically acts as a scavenger of radiation-induced free radicals, allowing for the elimination of postirradiation thermal processes and their associated shortcomings, such as the reduction in toughness and fatigue resistance of the polymer.¹² Two different techniques are currently in use to incorporate vitamin E into highly crosslinked UHMWPE. On one hand, vitamin E is diffused into medical UHMWPE following high dose irradiation in a two stage process.^{13,14} In the first stage, radiation crosslinked UHMWPE is submerged in a vitamin E bath at about 120°C. Then, the polymer is taken out of the bath and subjected again to 120°C to homogenize the antioxidant concentration through the component thickness. On the other hand trace concentrations of vitamin E are blended with medical grade UHMWPE resins before consolidation and irradiation to assure both oxidative stability and high efficiency in the crosslinking generation, as higher vitamin E concentrations are known to inhibit radiation crosslinking.^{15,16} Research on the use of vitamin E as antioxidant for highly crosslinked polyethylenes has resulted in the recent clinical introduction of a second generation of vitamin E stabilized highly crosslinked polyethylenes.

The design of new components for total hip and knee replacements based on these new and promising materials requires good understanding of their microscopic and macroscopic properties. Although the mechanical, toughness, and fatigue behaviors of vitamin E stabilized polyethylenes are well known,^{17–19} the influence of α -tocopherol on the thermal and viscoelastic behaviors as well as molecular dynamics of UHMWPE remains to be established. This work deals with the latter aspect and our purpose was to characterize the thermal and dynamic mechanical responses of vitamin E infused and vitamin E blended UHMWPE materials. Fourier Transform InfraRed (FTIR) and ultraviolet (UV) spectroscopies were used in this study to assess the antioxidant concentration present within the vitamin E infused and blended UHMWPE sections prepared. We hypothesized that the presence of the antioxidant would introduce a plasticization effect in UHMWPE.

MATERIALS AND METHODS

Materials and vitamin E detection methods

The raw materials used in this study were GUR 1020 UHMWPE supplied by Meditech (Fort Wayne, IN) as several thin films and a compression-molded sheet of GUR 1050 UHMWPE (Perplas Medical, Lancashire, UK). Vitamin E was incorporated into the foregoing materials by blending and diffusion, respectively. The first method was used by Meditech to compression mold 0.250 mm thin films from virgin GUR 1020 UHMWPE and from blends of GUR 1020 UHMWPE resin and vitamin E, wherein the antioxidant was said to be present in two concentrations: 0.075 and 0.3% by weight. Hereafter, these materials will be referred to as PE20-E00, PE20-E0075, and PE20-E03, respectively, depending on the amount of vitamin E added to the UHMWPE resin. However, 0.2 mm thin sections were obtained with the use of a Leica SM2000R microtome from cubes ($15 \times 15 \times 15 \text{ mm}^3$), which were, in turn, machined from the GUR 1050 compression-molded sheet. The sections were weighed on a balance (Mettler Toledo; Switzerland) with a resolution of 0.0001 g, and then soaked in a bath of vitamin E (α -tocopherol, Aldrich Chemicals) at 120°C for varying durations, in a nitrogen gas atmosphere. At the end of the diffusion process, the sections were taken out of the vitamin E bath, cleaned and subsequently homogenized at 120°C for 24 h in nitrogen. After vitamin E doping, the sections were weighed again to determine the antioxidant weight percentage. Thus, samples corresponding to concentrations of vitamin E ranging from 2.0 to 9.0% by weight were prepared. Calibration curves for infrared and UV spectroscopies vitamin E indices were obtained using the foregoing UHMWPE sections. FTIR spectroscopy was performed on them using a Perkin-Elmer model 1600 spectrometer (range: $4000\text{--}400 \text{ cm}^{-1}$; 235 repeat scans per sample location; resolution 4 cm^{-1}). Vitamin E was detected in FTIR spectra of infused UHMWPE sections as the vibrational band centered at 1262 cm^{-1} . A vitamin E index (VI) was defined as the area ratio between the absorption peak at 1262 cm^{-1} ($1275\text{--}1230 \text{ cm}^{-1}$) and the reference peak at 1895 cm^{-1} ($1980\text{--}1850 \text{ cm}^{-1}$) corresponding to the polyethylene skeletal absorbance. The vitamin E concentration was also detected by UV spectroscopy using an Aligent 8453 Diode Array spectrophotometer at a range of 1100–190 nm. UV absorption spectra of vitamin-E infused UHMWPE sections revealed the presence of a noticeable peak at 290 nm. To obtain sections with very low antioxidant concentration (0.3% w), the previous vitamin E doping process was performed on cubes. Then, 0.2 mm sections were cut parallel to the cube faces using a microtome. FTIR spectroscopy was

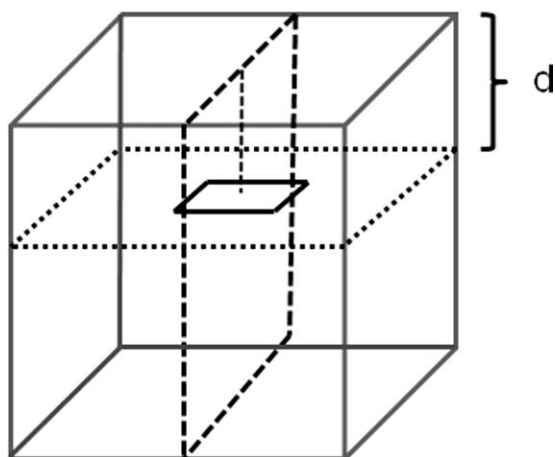


Figure 1 Schematic drawing depicting location of UHMWPE samples with specific vitamin E concentration at a depth d , as measured by means of FTIR spectroscopy.

conducted from the edge of these sections at every 100 μm to characterize the antioxidant concentration through the cube thickness. Once the depth corresponding to the desired vitamin E concentration was determined, perpendicular sections were cut at that depth to obtain samples for further calorimetric and dynamic mechanical analysis (Fig. 1). The vitamin E content was also confirmed by UV spectroscopy for sections with the lowest antioxidant concentrations. In summary, specimens corresponding to raw GUR 1050 UHMWPE and to concentrations of α -tocopherol ranging from 0.3 to 9.0% by weight were prepared for this study. These materials will be designated as PE50-E00, PE50-E03, PE50-E07, PE50-E23, PE50-E46, PE50-E50, PE50-60, PE50-E80, and PE50-E90, respectively.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed to assess thermal properties, namely crystallinity content and melting transition temperatures. Three specimens ($n = 3$) per material group were heated from 20 to 200°C at a rate of 10°C/min in a Differential Scanning Calorimeter (Perkin-Elmer). The area below the thermograms from 50 to 160°C, normalized by 290 J/g as the enthalpy of melting of a 100% crystalline UHMWPE,²⁰ gave the crystallinity percentages for each material.

Transmission electron microscopy

Relevant material groups (PE50-E00, PE50-E23, and PE50-E46 materials) were chosen based on melting transition temperature results. Specimens belonging to those groups underwent specific preparation to obtain Transmission Electron Microscopy (TEM)

images, which allowed the measurement of crystal thickness as well as the detection of changes in morphology caused by the presence of vitamin E in a broad range of concentrations. First, 200 μm sections of UHMWPE were stained with 99% chlorosulphonic acid at 60°C for 5 h, which is thought to stabilize the amorphous regions. Samples were washed with acetone (at 0°C) and rinsed with distilled water. Stained samples were dried at 60°C for 1 h and later embedded in epoxy and cured at 60°C for 2 days. Ultrathin sections (~ 60 nm thick) were cut with a diamond knife and collected in carbon grids. Then, the sections were poststained with uranyl acetate in 1% methanol for 4 min. A Jeol 100CX TEM operating at 100 kV was used to produce micrographs at 20,000x and 60,000x magnifications. The best five TEM preparation samples were chosen from each group and analyzed using the Digital Micrograph 3.3.1 software package (Gatan, Pleasanton, CA). At least 15 measurements of lamellar thickness were done per 60,000x images using the mentioned software. These images allowed the measurement of crystal thickness and the detection of changes in morphology caused by the presence of vitamin E.

Dynamic mechanical thermal analysis

Dynamic mechanical measurements were carried out on $15 \times 4.5 \times 0.2$ mm³ prismatic test specimens using a Dynamic Mechanical Thermal Analyser, model MKII of Polymer Laboratories. All the experiments were conducted working in tensile mode and the heating runs were performed at a rate of 1°C/min from -130 to 125°C. The frequencies used were 0.3, 3, 10, 30, and 50 Hz. Before heating, samples were first cooled down to -135°C inside the cell. These measurements provided information about the dynamic mechanical properties, namely, storage modulus, E' , loss modulus, E'' , and loss tangent, $\tan \delta$. Activation energies were calculated from the temperature of the maximum values of loss modulus and $\tan \delta$ at different frequencies based on an Arrhenius model for β and γ relaxations (Fig. 2). In the case of the α relaxation, the behavior slightly departed from the Arrhenius model.

RESULTS AND DISCUSSION

Infrared and UV spectroscopic detection of vitamin E

In agreement with previous work,²¹ linear correlations were found between the vitamin E concentration as determined by weighing and both the infrared vitamin E index, VI, ($R^2 = 0.96$; Fig. 3) and the area of the UV absorption peak at 290 nm normalized to the film thickness, A/t ($R^2 = 0.98$;

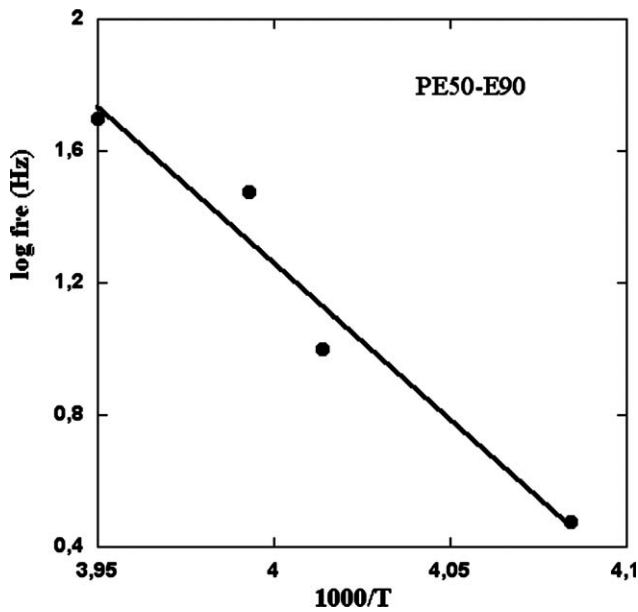


Figure 2 Activation energies corresponding to γ , and β relaxations were obtained by fitting to an Arrhenius model.

Fig. 3). In the case of FTIR, a detection limit of 0.4% by weight of vitamin E was noted, and the use of different reference peaks (1895 and 2020 cm^{-1}) yielded similar linear correlations. However, the linear trend found for the normalized UV absorption, A/t , and the vitamin E content confirmed a Beer's law behavior, $A/t = \epsilon c$, where ϵ is the dielectric constant, and c the concentration of vitamin E in a nonpolar matrix such as UHMWPE. Previous research has also demonstrated that UV spectroscopy performed at temperatures above the

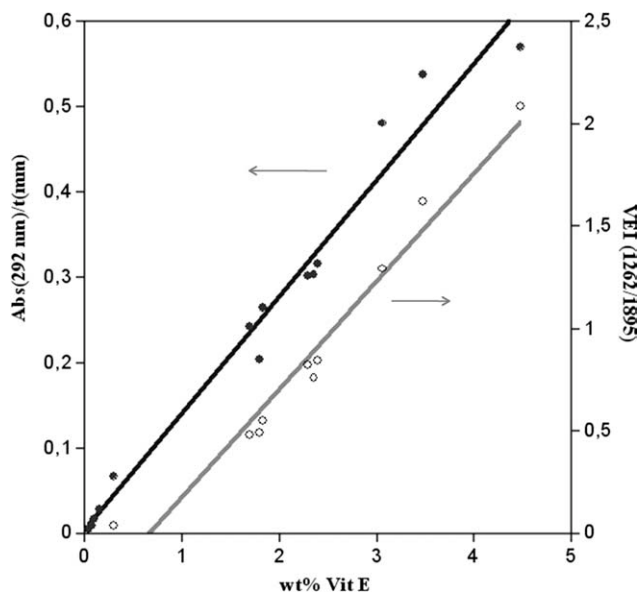


Figure 3 Correlation between Vitamin E index from FTIR and UV peak absorptions as a function of the vitamin E concentration.

melting point of UHMWPE ($\sim 140^\circ\text{C}$) helps to reach increased resolution avoiding the incident light scattering from UHMWPE crystals.²¹

DSC and TEM studies: Crystallinity, melting temperature, and crystal thickness

Analysis of the thermograms provided the crystallinity content and the transition temperature for every material, as reflected in Figure 4(a,b), respectively. The presence of vitamin E at high concentrations provoked two effects on the base material GUR1050, namely a significant drop in the degree of crystallinity and an increase in melting temperature. DSC complementary measurements at samples containing vitamin E concentrations ranging from 4.5% to 9.0% wt % followed similar trends. Because vitamin E was diffused into the amorphous regions of the

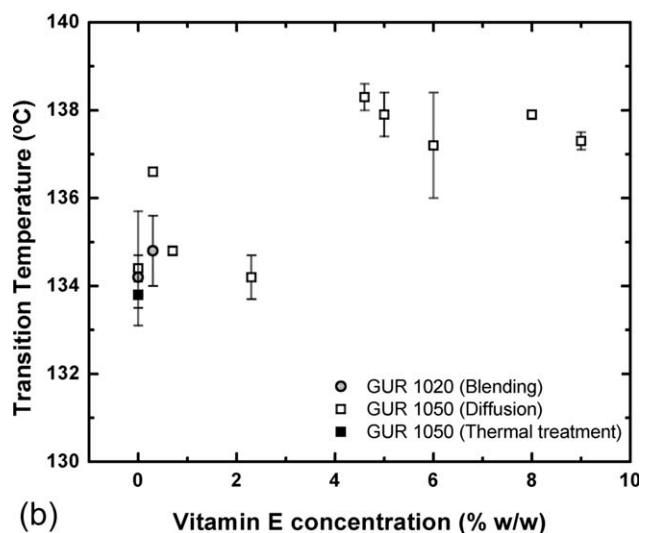
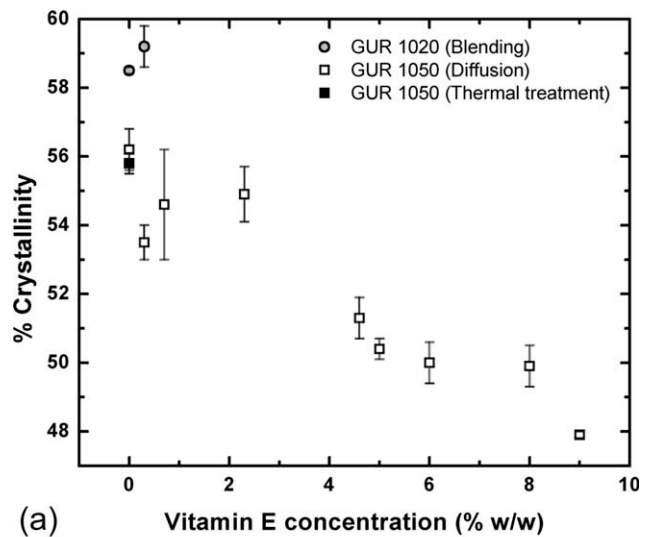


Figure 4 a) Crystallinity content and b) melting transition temperature results obtained from DSC experiments.

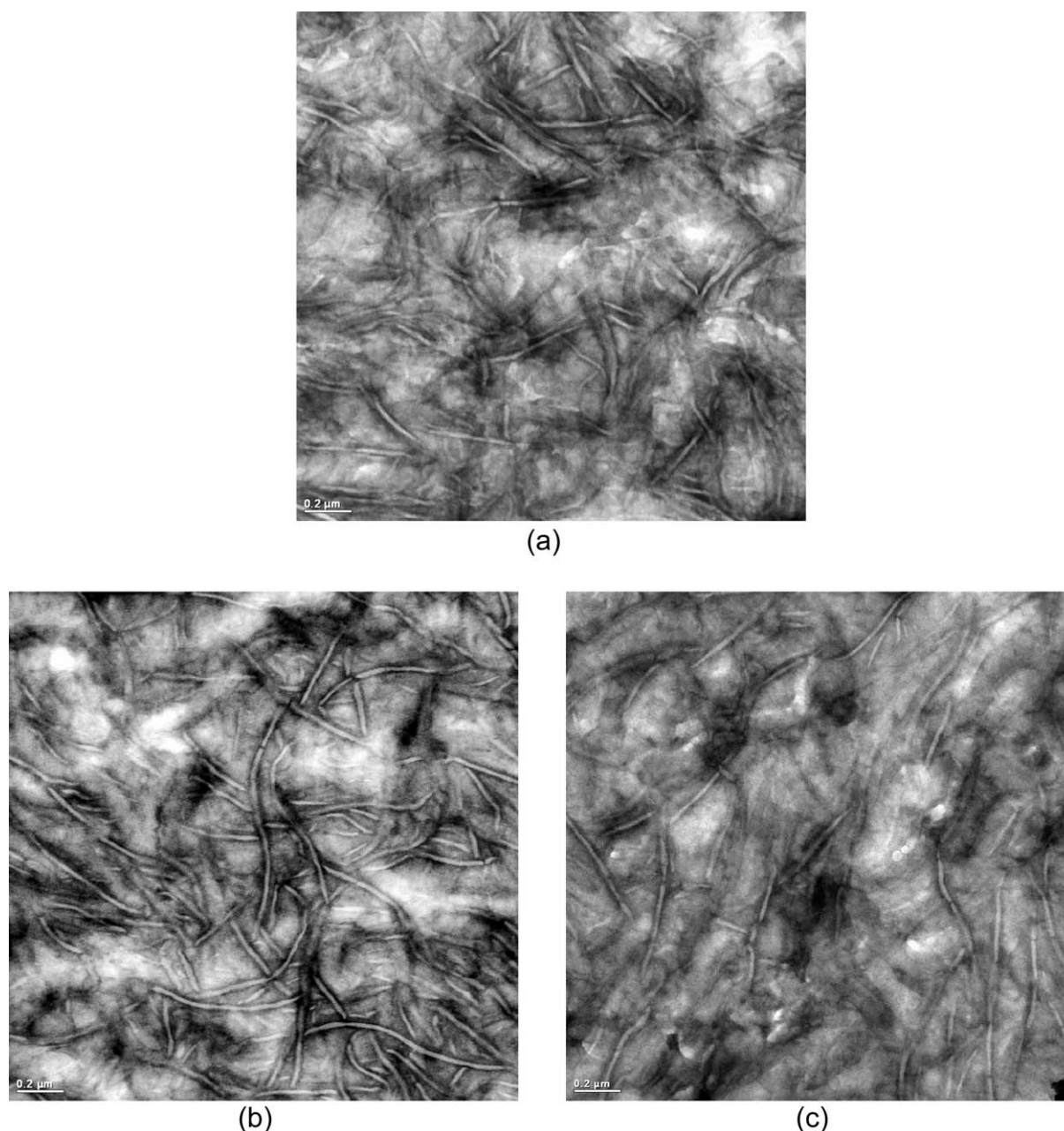


Figure 5 TEM micrographs ($\times 60,000$) of a) PE50-E00, b) PE50-E23, and c) PE50-E46.

semicrystalline polymer, no effects on crystallinity were expected, except for a likely effect on the surface energy of UHMWPE lamellar crystals. The diffusion process, however, was performed at 120°C , and therefore an annealing process took place simultaneously to the diffusion of the antioxidant. In vitamin E free-samples, this thermal process is known to produce a light increase in crystallinity due to lamellar rearrangements activated at the annealing temperature. Furthermore, two different lamellar rearrangement mechanisms have been identified by Matsuda et al.²² depending on the annealing temperature. Thus, low temperature annealing ($T < 120^{\circ}\text{C}$) induces gradual thickening of the

original lamellar crystals without significant melting, whereas high temperature annealing ($T > 125^{\circ}\text{C}$) causes partial melting and then rapid lamellar doubling. These mechanisms competitively coexist on annealing over 120°C , and their balance depends on the annealing temperature. Although the influence of vitamin E in both mechanisms has not been established, the antioxidant might partially inhibit lamellar rearrangements, especially lamellar doubling. However, some gradual thickening may still occur, accounting for the overall lamellar thickening observed in TEM micrographs. This last effect was also corroborated by the rise in transition temperature, T_m , which according to the Thomson-

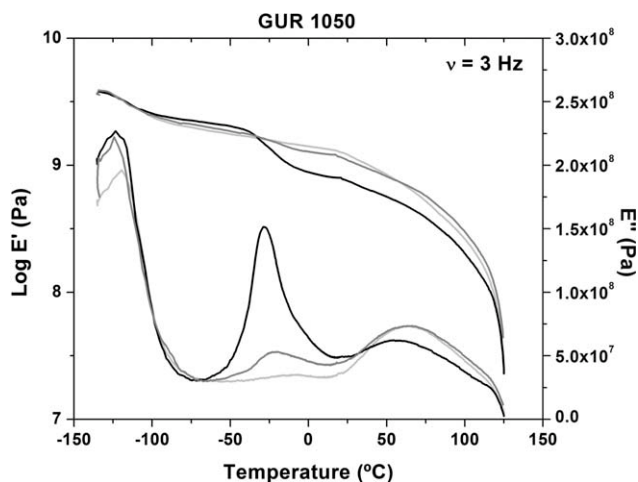


Figure 6 Temperature dependence of storage modulus, E' , and loss modulus, E'' , at 3 Hz for virgin PE50-E00 (light gray line), and vitamin E infused polyethylenes samples PE50-07 (gray line) and PE50-90 (black line).

Gibbs equation involves an increase in lamellar thickness, L_c :

$$T_m = T_{m0}(1 - 2\sigma/L_c\rho_c\Delta H_m^0) \quad (1)$$

where T_m is the melting point of the polymer; 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_m^0 the enthalpy of melting of a perfect crystalline polyethylene. As mentioned before, potential changes in the surface energy of polyethylene lamellar crystals may not be discarded, and they might also influence the melting transition of the polymer. Finally, the reduction in crystallinity content due to the incorporation of vitamin E has been also observed by Oral et al.,¹³ and this effect is more intense when the diffusion temperature approaches the melting point of the polymer.

TEM micrographs of virgin UHMWPE showed the typical features of semicrystalline polymers with randomly oriented crystal lamellae, 26.7 ± 4.2 nm thick, immersed in a dark gray region, which is the amorphous region [Fig. 5(a)]. TEM micrographs of vitamin-E infused polyethylenes showed a small increase in lamellar thickness, with values of 28.0 ± 2.9 nm, and 29.6 ± 3.8 nm for PE50-E23 and PE50-E46, respectively, [Fig. 5(b,c)]. This increase is in agreement with the observed trend for the melting point of samples with the highest vitamin-E contents. However, the qualitative observation of TEM images suggested that the lamellar density corresponding to PE50-E46 samples was lower than those of the PE50-E00 and PE50-E23 materials, in accordance with the fall in crystallinity registered by DSC measurements when vitamin E was present in the material above 1% approximately.

Dynamic mechanical thermal analysis

The dynamic mechanical behavior of the two raw materials, PE50-00 and PE20-00, was basically the same. Two well-expressed relaxations, γ and α , characterized the temperature dependence of dynamic modulus properties. The γ relaxation was reflected by a weak stepwise change in the storage modulus and a maximum in $\tan \delta$ and E'' around -125°C in both raw UHMWPEs regardless of their different molecular weights (Figs. 6 and 7). This relaxation is associated with the amorphous region of the polymer. However, the α relaxation, which is related to the crystalline region, appeared as a strong and wide decrease in E' and a rounded and small maximum in E'' close to 50°C (Figs. 6 and 7). Despite the similar behavior of both polymers regarding the γ and α relaxations, a difference was noted between them, as a weak β relaxation appeared around -10°C only for the higher molecular weight material, PE50-E00.

The incorporation of α -tocopherol into UHMWPE gave rise to a distinct relaxation around -25°C , which was more evident at the highest concentrations (Figs. 6 and 7). Specifically, this “new” beta transition associated with the presence of vitamin E appeared as a noticeable peak in the E'' plots for PE50-E90 samples, and it gradually lost intensity and was shifted toward higher temperatures as the vitamin E concentration decreased for PE50-E07, PE50-E03, PE20-E03, and PE20-E0075 specimens. The activation energy of this transition calculated from the temperature of the maximum in $E''(T)$ plots ranged from 149 to 188 kJ/mol for 0.7 and 9% vitamin E doped GUR 1050 UHMWPEs. Regarding the effect of frequency, essentially similar results were observed at the highest frequencies (10, 30, and

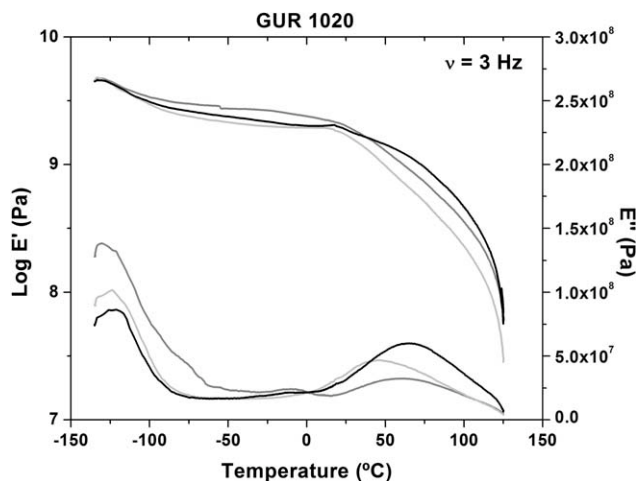


Figure 7 Temperature dependence of storage modulus, E' , and loss modulus, E'' , at 3 Hz for virgin PE20-E00 (light gray line), and vitamin E blended polyethylenes PE20-0075 (gray line) and PE20-03 (black line).

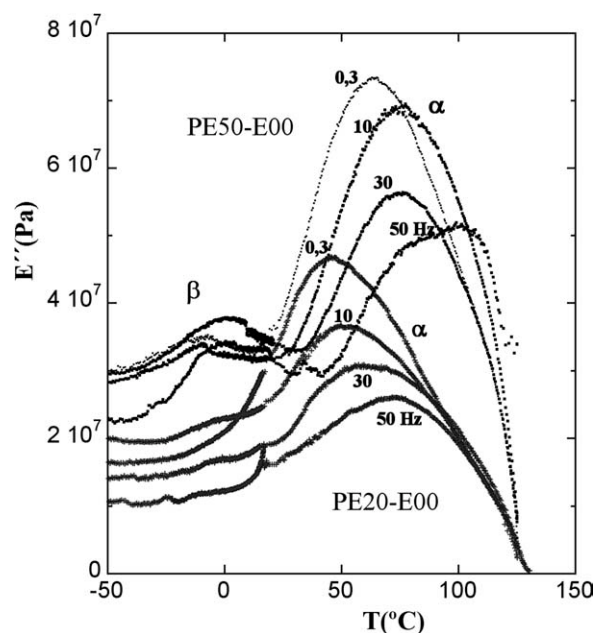


Figure 8 Frequency dependence of loss modulus for virgin PE50-E00 and PE20-E00 samples at 0.3, 10, 30, and 50 Hz.

50 Hz), as can be seen in the isochrone curves of raw and vitamin E stabilized UHMWPEs (Figs. 8 and 9).

The β relaxation has been observed not only in branched low-density polyethylenes (LDPE) but also in some linear polyethylenes in connection with the amorphous phase. However, due to constraints imposed by chain connections to, and confinement by crystal lamellae, the β process is greatly broadened in linear polyethylenes, and therefore much less prominent, in comparison to the main relaxation in wholly amorphous polymers (i.e., the glass transition). Thus, the temperature of the pronounced beta relaxation is generally considered the glass-rubber transition temperature (T_g) for LDPE, whereas the weak or even absent beta relaxation in linear polyethylenes induces to consider T_g as the temperature of the gamma relaxation.²³ Different molecular mechanisms have been proposed to contribute to the β relaxation in specific polyethylenes, in addition to those related to the glass transition.²⁴ In general, the beta relaxation is accepted to stem from the relaxation of chain units in the interfacial region via fold-surface, chain-end, branch-point molecular motions, and chain rotation.²⁵ Therefore, the higher interlamellar content (i.e., lower crystallinity), the stronger the beta relaxation as demonstrated for chlorinated and short-chain branched polyethylenes.^{25–27} Moreover, the beta relaxation is absent in linear high-density polyethylenes (HDPEs) in agreement with their much lower interlamellar content. In the case of high molecular weight polyethylenes, Nitta and Tanaka²⁸ concluded that the β relaxation is a consequence of the activation of loop and loose

tie molecules, because these elements arise in these particular polyethylenes but they do not form in common linear HDPE. The current findings appear to be consistent with this alternative explanation, as a weak β transition was detected in raw GUR 1050 specimens but it was absent in the lower molecular weight GUR 1020 specimens. The activation energy (ΔH) of β transition had a value of 140 kJ/mol for PE50-E00 but with strong uncertainty due to the inherent difficulty to determine the maximum from the plateau shape of this transition. The addition of increasing vitamin E concentrations, however, was responsible for the introduction and/or progressive strengthening of the originally absent or weak β relaxation in vitamin E containing GUR 1020 and GUR 1050 UHMWPEs, respectively. Also, the incorporation of increasing concentrations of the antioxidant resulted in a shift toward lower temperatures of the beta relaxation, although with higher activation energies. The presence of the beta relaxation in these materials seems to be related to the crystallinity drop (i.e., increase in interlamellar content) provoked by the diffusion of the antioxidant. Nevertheless, the existence of this transition cannot be exclusively attributed to the thermal conditions used for antioxidant diffusion, as both GUR 1020 and GUR 1050 UHMWPEs exhibited no changes in both crystallinity and relaxation behavior after thermal treatment at 120°C. The current crystallinity results

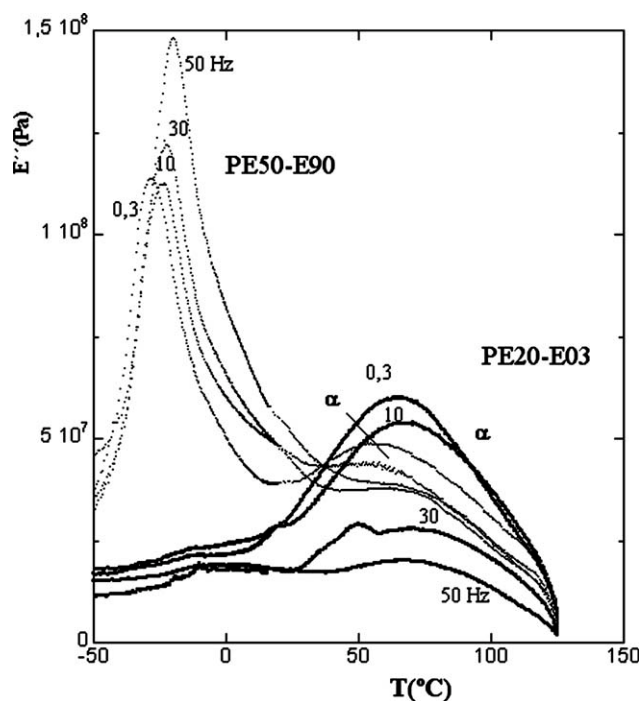


Figure 9 Frequency dependence of loss modulus, E'' , for vitamin E infused, PE50-90, and blended, PE20-E03, samples with maximum antioxidant concentration at 0.3, 10, 30, and 50 Hz.

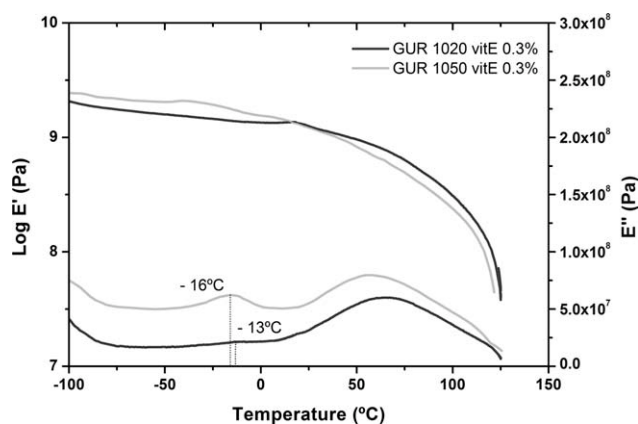


Figure 10 Temperature dependence of storage modulus, E' , and loss modulus, E'' , at 3 Hz for vitamin E blended PE20-03 and vitamin E infused PE50-03 polyethylenes.

along with the relaxation behavior also suggest that, on diffusion at high temperature, vitamin E is preferentially located on crystal surfaces. However, vitamin E doped GUR 1050 and 1020 UHMWPEs with similar antioxidant concentrations (0.3% w/w) exhibited the beta relaxation at different temperatures (Fig. 10).

With regard to a hypothetical role of α -tocopherol as plasticizer, the current results did not provide evidence of such effect for the beta relaxation. In this sense, the effects of various plasticizers on the relaxation behavior of different materials, such as polyvinyl chloride, polyvinyl acetate, polystyrene, composite biopolymer caseinate-pullulan, and blends of poly(3-hydroxybutyrate) and cellulose acetate among others, have been investigated by several researchers.^{23,29–31} The addition of a plasticizer generally results in a shift toward lower temperatures of the corresponding relaxation (in some cases T_g) and a decrease of the apparent energy of activation.²⁹ In our study, the relaxation behavior of vitamin E containing UHMWPE specimens matched the former condition that is decreasing temperatures for the beta relaxation as the antioxidant concentration increased. However, the apparent activation energies were increasingly higher. The relatively high activation energy (188 kJ/mol) of the beta relaxation for the highest vitamin E content suggests a cooperative mechanism, with numerous chain units taking part in the relaxation. Despite the shift toward lower temperatures of the beta relaxation of UHMWPE, no evidence of a plasticizing effect on antioxidant incorporation could be confirmed as the activation energy was increasingly higher. Moreover, vitamin E had no significant plasticizing effects (neither on temperature nor on activation energies) on the relaxation behavior of the present polymeric specimens for concentrations as low as those used in clinically available UHMWPE materials (Fig. 10). The lower intensity of

the beta relaxation in vitamin E blended GUR 1020 would stem from both the much lower concentration of the antioxidant and the lower molecular weight of the raw polymer, which in turn results in a lower fraction of tie and loop molecules.

Regarding the γ relaxation of the raw UHMWPEs, the calculated activation energies of the lower molecular weight material, PE20-E00, reached a value of 65 kJ/mol. The γ relaxation is commonly associated with the motion of polymethylene segments in amorphous regions of the polymer, which results in kink formation, inversion, and migration or crankshaft motion.^{32,33} The temperature location of the γ relaxation is also considered to be the subglass transition temperature for some polyethylenes.^{34,35} Although in some cases differences in the γ transition might be attributed to different crystallinity contents, the similar values of this parameter and intensities of the γ transition for both raw materials suggest that other cause may be involved. However, PE50-E00 and PE20-E00 also showed relatively small differences in the maximum values of the storage modulus (3.2 GPa and 1.6 GPa, respectively), at temperatures below the γ transition. It is also known that the stiffness of polyethylene can be also slightly influenced by molecular weight,³⁶ as occurred in this case. The loose chain ends in the lamella, which are affected by the length of the polymer chains, could be another underlying cause of this different behavior.

With regard to vitamin E infused and blended UHMWPEs, no significant changes were observed in the temperature location, intensity or activation energies of the γ relaxation (Figs. 6 and 7) for these materials. The fact that the presence of vitamin E in different concentrations did not significantly alter the γ transition induces to think that no plasticizing effects take place in vitamin E-UHMWPE systems even at relatively high concentrations of antioxidant. As mentioned above, the incorporation of the antioxidant was responsible for the introduction and/or strengthening of the beta relaxation. However, plasticization of the beta relaxation was also discarded due to the rising activation energies registered for increasingly higher vitamin E amounts. Therefore, our hypothesis tested negative as the present results confirmed both, vitamin E did not alter the internal friction of UHMWPE with regard to the gamma relaxation, and it actually generated more friction in the beta relaxation region especially at high antioxidant concentrations.

The incorporation of vitamin E into UHMWPE provoked changes in intensity and temperature shifts to the α relaxation. These changes depended on the technique used to obtain the vitamin E-UHMWPE system. Although for vitamin E infused UHMWPEs, the α relaxation shifted to lower temperatures and

decreased in intensity with increasing vitamin E concentrations, vitamin E blended UHMWPEs exhibited shifts toward higher temperatures in this transition as the amount of vitamin E increased. The foregoing changes in intensity and temperature shifts were especially pronounced for PE50-E90 (Fig. 6), which was characterized by the lowest crystallinity, close to 40%. However, the effect of vitamin E in the activation energy of the α process was similar for blended and infused UHMWPEs, because in both cases, it increased the activation energies. The activation energies obtained were 92, 166, and 313 kJ/mol for PE20-E00, PE20-E0075, and PE20-E03, respectively, and 83 and 198 kJ/mol for PE50-E00 and PE50-E90, respectively.

The α transition is related to the crystal phase of the material by means of interlamellar shear mechanism, and its temperature location is an indication of the lamellar thickness.^{37,38} Therefore, the shifts toward lower temperatures observed in vitamin E infused materials confirmed lower lamellar thickness in agreement with the present DSC results. This decrease in crystal thickness is probably a direct result of the synergism between the annealing conditions needed to diffuse and homogenize vitamin E into UHMWPE, and the influence of the antioxidant on the recrystallization mechanisms of the polymer. At the highest vitamin E concentration, the activation of recrystallization mechanisms may be not favored and hence partial melting, without further lamellar doubling or gradual thickening, might be responsible for the drop in both crystallinity content and crystal size as well as the decreased intensity of the α relaxation. However, the effect of trace concentrations of antioxidant in the crystallization of UHMWPE during compression molding remains unclear. Thus, although the shift toward higher temperatures of the α transition suggests thicker lamellar crystals regardless of concentration, the intensity variations followed opposite trends for blends with 0.075 and 0.3% by weight of vitamin E. More research is needed to determine the influence of trace concentrations of vitamin E on both crystal nucleation and further crystallization processes during compression molding of vitamin E blended UHMWPEs. In this regard, and although it is logical to expect that the exclusive activation of vitamin E molecules should introduce a new relaxation at the same temperature regardless of polyethylene type and method of incorporation, the physicochemical interaction of the antioxidant and polyethylene molecules may significantly vary with concentrations and production conditions. Finally, more studies must be undertaken to know the effect of radiation-induced crosslinking either by gamma radiation or electron-beam on the molecular dynamics of vitamin E blended UHMWPEs.

CONCLUSIONS

Vitamin E concentrations in blended GUR 1020 UHMWPE and infused GUR 1050 UHMWPE were detected by FTIR and UV from values of 0.3 and 0.075%, respectively. A linear correlation appeared between the vitamin index related with the intensity of specific peaks in IR (1262 cm^{-1}) and UV (290 nm) spectra and the weigh concentration. Vitamin E concentrations above 3% reduced significantly the degree of crystallinity and increased the melting transition temperature of the raw material, aspects which were confirmed by DSC measurements and observation of microstructural features on TEM micrographs.

The dynamical and mechanical thermal analysis showed the presence of two well-expressed relaxations, γ and α , about -125°C and 50°C , which were associated to the amorphous and crystalline parts of these semicrystalline polymers, respectively. A weak β relaxation at -10°C was detected in the high molecular weight GUR 1050 polyethylene. The presence of vitamin E in different concentrations did not significantly alter the intensity and location of the γ transition. The introduction of increasing α -tocopherol amounts generated and/or progressively strengthened the beta relaxation in UHMWPE, the transition being shifted toward lower temperatures and having rising activation energies as the antioxidant concentration increased (up to -25°C , and 188 kJ/mol activation energy for the highest concentration). Because of the unaltered gamma relaxation and the increasing activation energies of the beta transition, potential plasticization effects were discarded in vitamin E-UHMWPE systems. Finally, another effect of the highest vitamin E concentrations in infused UHMWPE is the intensity decrease of the α relaxation, in accordance with the drop of crystallinity content observed in DSC measurements, and the shift toward lower temperatures.

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