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Radiation induced Free Radical Stability and Degradation Behavior in GUR resin and 1900 resin types UHMWPE over 20 years of aging

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Abstract

Radiation-induced free radical stability was evaluated using Electron Spin Resonance (ESR) for two medical-grade Ultra High Molecular Weight Polyethylene (UHMWPE) resins, GUR 4150 and 1900H, after 20 years of aging in air and vacuum at 23 °C, 37 °C, and 75 °C. Spectral analysis revealed oxygen-induced radicals in samples aged in air at 23 °C and 37 °C, with higher concentrations at 23 °C, whereas vacuum-aged samples retained primary radiation-induced radicals that decreased progressively with increasing temperature; no radicals were detected in air-aged samples at 75 °C. Overall, radical concentration decreased by about two orders of magnitude over 20 years. At 23 °C, 1900H exhibited lower FRC than GUR 4150 by about two-thirds, indicating improved oxidative stability. After air aging at 23 °C, 1900H also showed reduced carbon-centered polyenyl radicals (R1, 0.6×) and oxygen-induced polyenyl radicals (R2, 0.5×) compared to GUR 4150. X-ray diffraction (XRD) confirmed the crystalline structure of both materials through the characteristic orthorhombic peaks at Bragg angles $2\theta = 22^\circ$ (110) and 24° (200). The average crystallite sizes for GUR 4150 were 21.76, 20.24, and 21.84 nm, while for 1900H they were 17.14, 20.22, and 21.56 nm at 23 °C, 37 °C, and 75 °C, respectively. Fourier Transform Infrared Radiation measurements revealed oxidation index values of 11.3%, 17.7%, and 38.2% for GUR 4150, compared with significantly lower values of 5.2%, 7.4%, and 10.5% for 1900H, indicating enhanced oxidation resistance of 1900H after 20 years of aging.

Keywords: UHMWPE, gamma sterilization, free radicals, ESR, oxidation, annealing

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1. Introduction

Hip and knee joint replacements are common surgical interventions for managing joint degeneration due to aging, trauma, or disease. Ultra-high molecular weight polyethylene (UHMWPE), a commonly used material that serves as an articulating surface in joint replacement surgeries and acts as a cartilage substitute in components such as the socket of a ball-and-socket hip joint, has become a top choice for these implants due to its exceptional mechanical, tribological, and biocompatible properties [1,2]. However, the wear debris formed in the articulating surfaces are known to have negative effect on the performance of the liners. One of the causes of the formation of such wear debris and the associated oxidative degradation of the articulating surfaces is known to arise from free radical reactions. When UHMWPE (a semi-crystalline polymer) is subject to high-energy radiation, which is often used to sterilize the implants (e.g., 30kGy gamma radiation is a common dosage) or to crosslink its molecular chains for added strength (for which 100kGy is a common dose), free radicals (molecules with unpaired electrons) are formed due to breakage of molecular bonds. The broken molecules with free radicals in the amorphous regions are able to get cross-linked through recombination processes, both immediately, as well as over time [5]. However, the free radicals which are generated in the crystalline regions stay trapped and gradually induce oxidative cascade reactions, resulting the oxidative embrittlement of the irradiated UHMWPE in the long term [4-10]. These trapped radicals, often referred as “residual radicals” may react more or less with oxygen depending on the types of UHMWPE, thereby more or less oxidation, thereby more or less wear, and thereby more or less success/life of the implant, before it fails due to oxidation-induced osteolysis [3, 4].

GUR Resin (Two types: GUR 4150 and GUR 4120) and 1900 Resin (designated as Himont 1900) are two major types of medical grade UHMWPE (although Himont 1900 is not as common today), have been historically used to consolidate components in joint replacements. These two types of UHMWPE resin (GUR Resin and 1900 Resin) are different in chemical composition depending on the trace level of residuals and ash contents during polymerization [17, 25]. Due to the difference in chemical contents, two types of resins possess different morphological properties (average molecular weight, mean particle size, and crystalline properties) and play a critical role in generation, mobility and persistence of free radicals formed during irradiation, crosslinking, free radical mediated oxidation and wear resistance during storage and use [17-19]. For instance, variations in crystallinity may influence the diffusion of oxygen and mobility of free radicals, while differences in molecular weight distribution can alter the rate of radical recombination or oxidation.

GUR 4150 UHMWPE is typically characterized by a more ordered lamellar crystalline structure with a relatively higher degree of crystallinity, which has been reported to restrict molecular mobility and promote the retention of irradiation-induced residual free radicals. Over long-term aging, such trapped radicals may contribute to oxidative degradation. In contrast, Himont 1900H UHMWPE, whose production was discontinued in the early 2000s, exhibits a less ordered,

predominantly spherulitic crystalline morphology [17], which is associated with increased chain mobility and may facilitate faster radical diffusion and recombination.

Radiation sterilized UHMWPE products are often shelf stored prior to use as implant component [11]. If the products are stored in air permeable packaging, material degradation can occur rapidly due to oxidative reaction of the free radicals [12]. Vacuum or inert-gas packaging is, therefore, an alternative approach to minimize the oxidation during the storage period [13], still the radicals are there to react with oxygen later when exposed to, such as when implanted [14, 15]. However, Post-irradiation thermal treatments—annealing (below melting point) and remelting (above melting point)—reduce residual radicals and improve oxidation resistance but compromise toughness and fatigue strength [16]. Such research was initiated in 1998 under the auspices of the NSF-Industry/University Center for Biosurfaces (IUCB), a partnership program between the State University of New York at Buffalo (SUNY Buffalo) and the University of Memphis. The primary objective was to estimate the long-term oxidative reaction due to free radicals and the annealing effect in quenching the free radicals in gamma irradiated (30 kGy) UHMWPE resins: GUR 4150 (GUR resin) and 1900H (Himont 1900) in open air and vacuum conditions at room temperature (23°C), body temperature (37°C), and elevated temperatures (75°C). Since the root cause of wear is free radical, it is important to know how different types of UHMWPE may be correlated to the top reasons for implant failure in the long-term, such as the amount of real years that today's implants are expected to last (~20 years), and in real-time aging conditions, whose data are preferred to artificially accelerated aging (e.g., oxygen-pressure chambers). To our knowledge, no studies have been performed to compare the free-radical induced oxidation processes in different types of UHMWPE for 20 years or longer.

So, even if a type of UHMWPE is no longer commercially used in current implement manufacturing, such as 1900H in this study, the information may be used to learn how to make better UHMWPE types in the future, which may be less susceptible to oxidation, similar to the effect of an antioxidant but without requiring the antioxidant (which may have additional advantages, as the antioxidant may interfere with crosslinking, for example).

2. Chemical Background of UHMWPE

UHMWPE is a high-density polyethylene, made up of more than 200,000 ethylene monomeric units. The molecular weight of UHMWPE is measured around $(2-6) \times 10^6$ g/mol and has a density of 0.94-0.97 g/ml [17, 20]. The crystallinity of UHMWPE is around 30–40%, and crystalline regions are randomly oriented with respect to each other [17,20]. Overlaps can exist between the long molecular chains, which allow transfer of large shear forces from molecule to molecule [17]. Gamma irradiation, used for crosslinking and sterilization, breaks polymeric chains, some of which recombine to form crosslinks, and there are others that remain as radicals. The well-studied radicals in UHMWPE are Alkyl: $[-CH_2-\dot{C}H-CH_2-]$, Allyl: $[-CH_2-CH=CH-\dot{C}H-CH_2-]$ and Polyenyl: $[-CH_2-HC\dot{\cdot}-(CH=CH)_n-CH_2-]$ [20]. These primary radicals can recombine over time in the UHMWPE aging in air, or in nitrogen. However, some trapped radicals

in the crystalline region convert to short-lived secondary or tertiary radicals, which are precursors to the oxidation process in UHMWPE. The secondary or tertiary radicals are: Peroxy: [$\text{—CHO}_2\bullet$], Alkoxy: [$\text{—CHO}\bullet$] and Vinyl: [$\text{>CH}\bullet\text{CH}_2\text{—}$]. In the presence of oxygen, two additional types of radicals, R1: $\text{—}\bullet\text{CH—}[\text{CH}=\text{CH—}]_m\text{—}$, polyenyl with $m > 3$ and R2: $\text{—}\bullet\text{OCH—}[\text{CH}=\text{CH—}]_m\text{—}$, called oxygen induced radicals (OIR) with $m = 2$ or 3 (dienyle or trienyle), can remain trapped in the irradiated UHMWPE for a very long time [11].

3. Materials and Methods

3.1. Selected samples

Solid UHMWPE made from the aforementioned resin types (GUR 4150 and 1900H) of 10 mm length and 2 mm diameter, machined from ram extruded rod, were provided by Industry/University Center for Biosurfaces (IUCB) for free radical measurements using Electron Spin Resonance (ESR) technique. The samples were categorized into two groups and stored in open air or vacuum-sealed ESR sample tubes evacuated to 1 mTorr or better. Prior to storage, all samples received 30 kGy gamma irradiation at room temperature. In 1998, the ESR spectrum of each sample was recorded and labeled as initial (time $t=0$) spectrum, which provided information about the initial or the primary radicals. Following the initial measurements, samples were stored at room temperature (23°C), body temperature (37°C) and at elevated temperature (75°C).

3.2. Experimental Characterization

3.2.1. X-ray diffraction (XRD)

The crystalline properties of GUR 4150 and 1900H types of UHMWPE aging in air at three different temperatures (23°C, 37°C, and 75°C) for 20 years, were analyzed using a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). XRD data were collected with a tube voltage of 40 kV and a current of 40 mA over a 2θ range of 20° to 70°, using a step size of 0.0484° and a counting time of 2 s per step. A solid-state VANTEC detector was used for data acquisition.

3.2.2. Fourier Transform Infrared Radiation (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was employed to analyze the chemical composition of GUR 4150 and 1900H UHMWPE samples aged in air at 23 °C, 37 °C, and 75 °C for 20 years, with absorbance spectra recorded over the wavenumber range of 400–4000 cm^{-1} using a Nicolet iS10 spectrometer (Thermo Fisher Scientific).

3.2.3. Electron Spin Resonance (ESR)

The free radical test of GUR 4150 and 1900H types UHMWPE aging in air at three different temperatures (23°C, 37°C, and 75°C) for 20 years, was performed by analyzing ESR spectra which were recorded using an X-band Bruker EMX 300 spectrometer operating at 9.8 GHz microwave frequency and 100 kHz magnetic field modulation frequency. The samples were tested over 200

Gauss sweep width, centered at 3510 Gauss. Each category of sample contained at least three specimens. Free radical concentrations (spins/g) were determined by double integrating the ESR absorption spectra and comparing the results to calibration standards of known spin concentration. Microwave power was varied to detect the types of radicals (carbon-centered polyenyl, R1) and (oxygen-centered dienyl or trienyl, R2) by studying the power saturation behavior of radicals. Modulation amplitude were varied to optimize signal to noise ratio. The relative composition of radical species was determined by spectral simulation and deconvolution using a multi-component fitting approach. Experimental ESR spectra were fitted by linear combination of reference spectra corresponding to individual radical species. The weighting factors of each component were iteratively adjusted using least-squares minimization until the simulated spectrum reproduced the experimental line shape and hyperfine features with minimal residual error. The optimized weighting coefficients were used to estimate the fractional contribution of each radical type.

4. Result and Discussion

4.1. X-ray Diffraction (XRD) Measurements

The X-ray Diffraction (XRD) patterns shown in **Figure 1 (a, b)** represents strong signals from two orthorhombic peaks at the Bragg angle of $2\theta = 22^\circ$ (110) and 24° (200) for both GUR 4150 and 1900H UHMWPE aging at 23°C , 37°C and 75°C for 20 years [24]. Some small peak signals were also observed close to $2\theta = 37^\circ$ (020), 41° (310) and 44° (220) respectively for both types of the UHMWPE samples. No significant peak shifts were observed in the XRD patterns of the samples after heat treatment at 37°C and 75°C compared to the room temperature (23°C) condition. The sharp and intense diffraction peaks in the XRD pattern confirmed the dominance of crystalline regions within the UHMWPE samples, while the absence of peak broadening indicated a minimal contribution from the amorphous phase. The average crystallite sizes of GUR 4150 and 1900H were determined using the Debye Scherrer approximation as described below.

$$\text{Crystallite Size, } D = \frac{K\lambda}{\beta \cos\theta} \quad \dots \text{Equ. (1)}$$

Where, $K \sim 0.9$ is the shape factor, λ represents the wavelength ($\text{CuK}\alpha$), β = Field-Width-Half-Maximum (FWHM).

The crystallite sizes of GUR 4150 samples stored at 23°C , 37°C and 75°C were calculated as 21.76 nm, 20.24 nm, 21.84 nm respectively. In comparison, the crystallite sizes of 1900H samples stored at the same temperatures were determined as 17.14 nm, 20.22 nm, and 21.56 nm, respectively. At room temperature (23°C), GUR 4150 exhibited a larger crystallite size compared to 1900H, reflecting its higher degree of crystallinity and denser molecular packing. However, at an elevated temperature of 75°C , 1900H showed a significant increase in crystallite size, from 17.14 nm to 21.56 nm, suggesting thermal reorganization driven by increased molecular mobility in its more amorphous matrix.

On the other hand, GUR 4150, being more crystalline compared to 1900H at the beginning, undergone less pronounced crystallite growth, and even a slight dip at 37°C. This could be due to partial chain scission and the competing effects of oxidative degradation and recrystallization before further increase at 75°C, as a result of thermal annealing. These negligible variations of the crystallite sizes can be demonstrated from the reduction of scatterings at grain boundaries that existed inside the UHMWPE samples. Also, enhanced phonon generated from the lattice vibrations may transport into amorphous regions sandwiched between crystallites. After heat stretching, the boundary roughness got decreased that allows more phonon scattering replacing diffuse scattering, which potentially reduced the differences of the crystallite sizes between GUR 4150 and 1900H stored at 23°C, 37°C, 75°C temperatures [25]. The overall trend confirmed that thermal aging promoted crystallite growth in both types of UHMWPE, especially in more spherulitic 1900H.

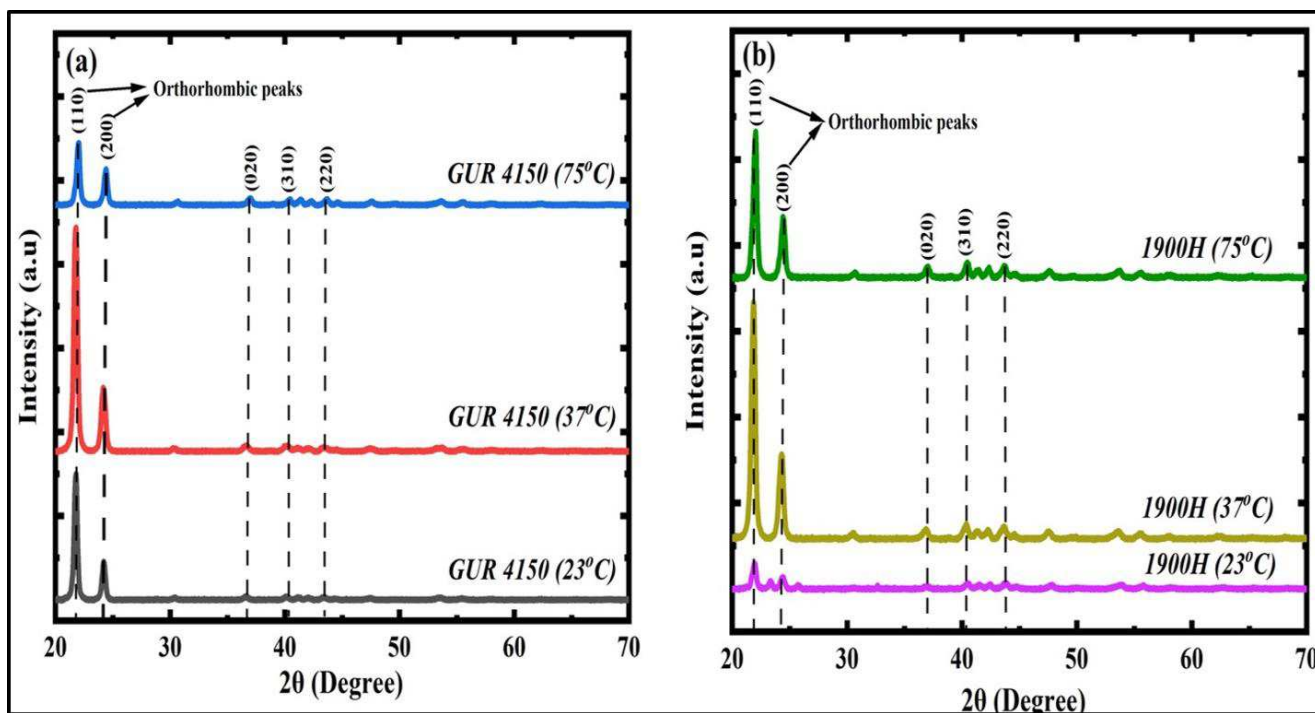


Figure 1: X-ray diffraction (XRD) patterns of (a) GUR 4150 and (b) 1900H UHMWPE samples after 20 years of aging in air at 23°C, 37°C, and 75°C.

4.2. FTIR Spectrums

The Fourier Transform Infrared Radiation (FTIR) measurements were performed to study the vibrations of the chemical bonds activated in GUR 4150 and 1900H after 20 years of aging in air at three different temperatures (23°C, 37°C and 75°C). The FTIR spectrums as shown in **Figure 2** (a, b) represent the identical absorbance peaks for both types of UHMWPE samples stored at 23°C, 37°C and 75°C. The sharp peak signals that appeared at 717 cm^{-1} are due to the bending such as rocking vibrations of C-C bonds from $-(\text{CH}_2)_n-$ chain. The peaks at 1458 cm^{-1} can be attributed to the C-H deformation such as scissoring vibration from the methylene group $-(\text{CH}_2)_n-$. Stretching

vibration modes were observed from each UHMWPE sample at 1593 cm^{-1} and 1730 cm^{-1} from the C=C alkene and C=O carbonyl functional groups [26]. Moreover, the two absorption peaks found about 2908 cm^{-1} and 2835 cm^{-1} respectively are due to the C–H asymmetric and symmetric stretching vibrations in the $-\text{CH}_2-$ group. In addition, small signals were also observed near 3785 cm^{-1} for both GUR 4150 and 1900H, can be attributed to the stretching vibration of O–H functional groups. In this study, oxidation index of both GUR 4150 and 1900H were further calculated from the ratio of peak area (1730 cm^{-1} , carbonyl group as C=O) to the referenced peak area (2908 cm^{-1} , as C–H can be assumed to remain relatively stable during oxidation process) to investigate the degradation of these UHMWPE samples stored at 23°C , 37°C and 75°C over 20 years period of time [27].

The calculated oxidation index (OI) values were obtained as 34%, 40%, 54% for GUR 4150 and as 5%, 12%, 14% for 1900H over 20 years of aging in air at 23°C , 37°C and 75°C respectively. From the calculated OI of two different types of UHMWPE, it has been observed that GUR 4150 oxidized significantly more at all temperatures compared to 1900H. This can be a possible effect of the higher lamellar crystalline morphology of GUR 4150 indicating higher crystallinity, where the residual radicals (which were not recombined through gamma induced crosslinking) remain trapped within crystalline lamellae and slowly react with diffusing oxygen over the years. In contrast, the lower oxidation of 1900H compared to GUR 4150 might be due to the presence of less ordered spherulitic crystalline morphology (lower crystallinity and higher amorphous content) that allows faster radical recombination, limiting the availability of radicals to sustain prolonged oxidation [17]. However, the OI of GUR 4150 stored at room temperature (23°C) exhibited a greater percentage with rising temperatures (37°C and 75°C) compared to 1900H, which could be attributed to the formation of microvoids or interfacial defects under thermal stress, promoting increased oxygen permeability and deeper oxidation [28]. The OI increased significantly with storage temperature for both GUR 4150 and 1900H samples, which might be the effect of higher molecular kinetic energy accelerating the oxidation reactions, along with the thermally enhanced diffusion of oxygen into the material.

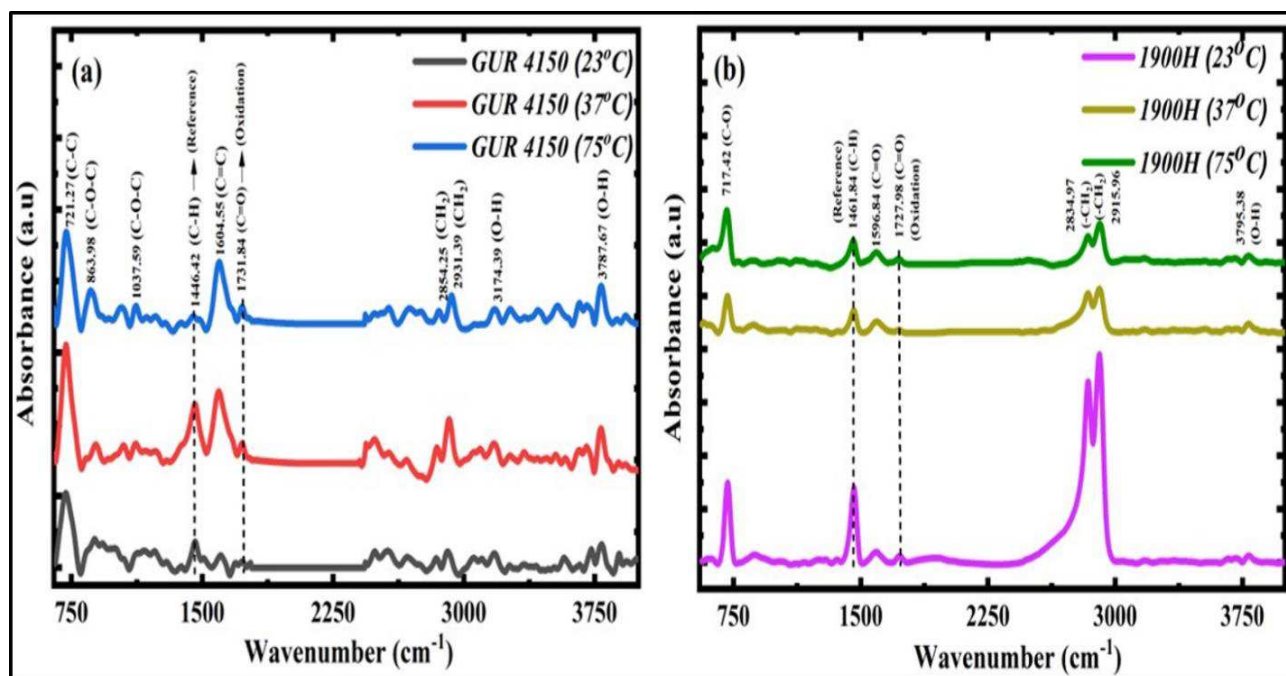


Figure 2: FTIR spectra of (a) GUR 4150 and (b) 1900H UHMWPE samples after 20 years of aging in air at 23°C, 37°C, and 75°C.

4.3. ESR spectra of GUR 4150 and 1900H types UHMWPE

ESR spectra of GUR 4150 and 1900H samples after 20 years of aging in open air and vacuum-sealed conditions at 23°C, 37°C, and 75°C are shown in **Figure 3 (a-f)**. In both types, the open-air samples aged at 23°C and 37°C indicated the conversion of primary gamma-induced radicals into oxygen-induced polyenyl radicals. The absence of radicals in both GUR 4150 and 1900H at 75°C suggests that, irrespective of the difference in mean particle size, molecular weight distribution and crystalline properties, both types of UHMWPE respond in a similar manner to the moderate thermal annealing. At 75°C, both types of UHMWPE samples could have increased mobility of molecular chains and subsequent stabilization of free radicals through further recombination [16]. All vacuum-sealed samples at all three different temperatures contained primary alkyl type radicals, suggesting no oxidation had occurred.

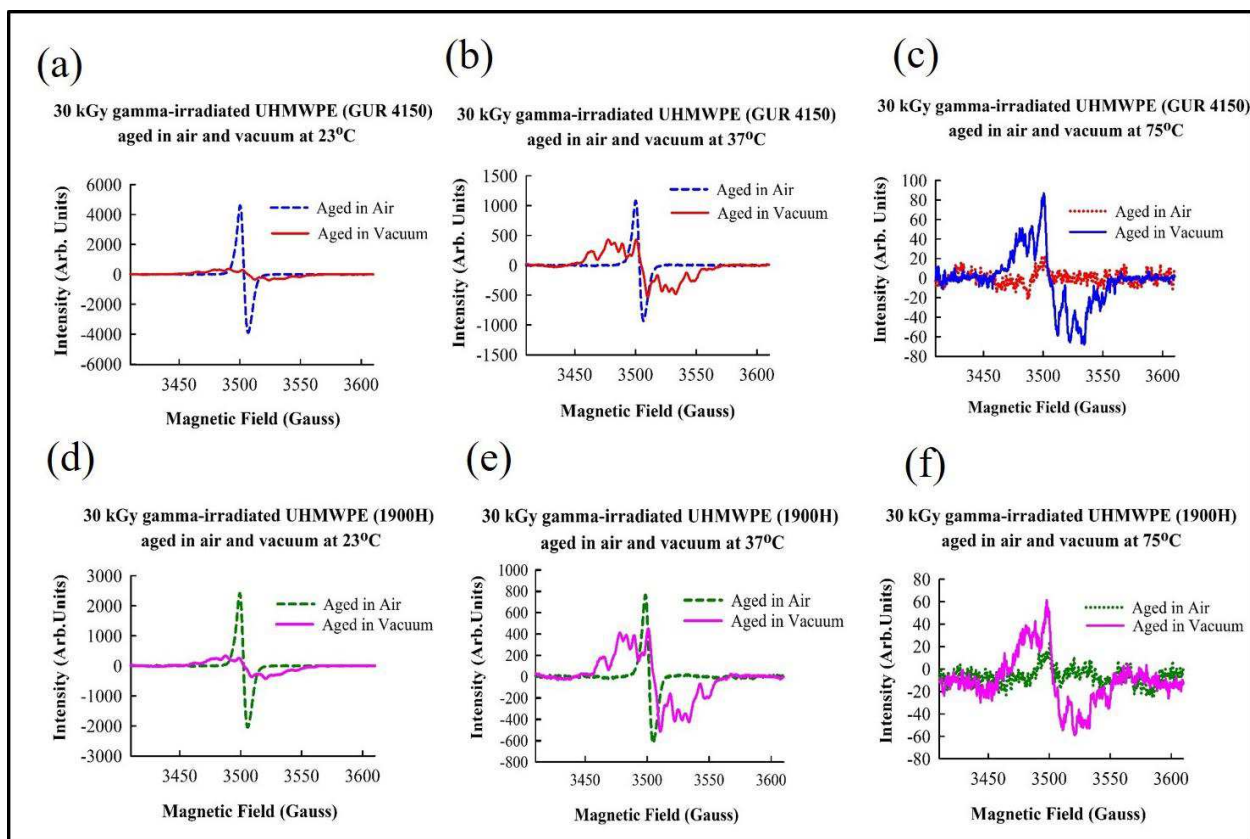


Figure 3: ESR spectra of GUR 4150 (a-c) and 1900H (d-f) followed by 20 years of aging at 23°C, 37°C and 75°C temperature in air and vacuum-sealed conditions.

4.4. Detection and extraction of free radicals

The types of free radicals associated with primary (gamma-induced) radicals in a particular sample were identified and their relative percent compositions were estimated, as shown in Table 1.

Table 1: Percent (%) composition of radical types detected in GUR 4150 and 1900H after 20 years of aging in vacuum-sealed condition at different temperatures

Radical Type	23°C		37°C		75°C	
	GUR 4150	1900H	GUR 4150	1900H	GUR 4150	1900H
Alkyl	14 ± 3	16 ± 4.5	14 ± 2.03	12 ± 1.2	14 ± 0.6	18 ± 3.2
Allyl	39 ± 6	42 ± 8	47 ± 3.33	51 ± 1.76	34 ± 10.3	19 ± 5.5
Polyenyl	47 ± 3	22 ± 11.5	27 ± 10.03	18 ± 4.4	0	0
Dienyl	0	21 ± 1	20 ± 5.5	19 ± 4.7	52 ± 10.5	63 ± 2.4
Trienyl	0	0	0	0	0	0

For alkyl and allyl radicals, no significant difference was found between GUR 4150 and 1900H at 23°C, but 1900H at 23°C showed lower concentration of polyenyl (22/47) and the presence of dienyl (21/0) and no trinyl (0/0). At 37°C, 1900H showed an approximately equal concentration of alkyl (12/14), allyl (51/47), and less polyenyl (18/27), and a similar concentration of dienyl (19/20) and no trinyl (0/0). 1900H at 75°C showed an approximately equal amount of alkyl (18/14), less allyl (19/34), no polyenyl and a higher concentration of dienyl (63/52). The conversion of primary radicals into dienyl (oxygen centered polyenyl) components in 1900H sealed in 23°C might occur due to the difference in size and molecular weight of 1900H at room temperature, as compared to GUR 4150. In addition, the conversion of primary radicals into dienyl components might increase with the increase in temperature, due to the thermal motion of the polyethylene molecules.

4.5. Detection and Quantification of R1 and R2 radical

The ESR spectral features due to two additional types of radicals exist in UHMWPE; R1: $\bullet\text{CH}-[\text{CH}=\text{CH}-]_m-$, polyenyl with $m > 3$ (carbon centered polyenyl) and R2: $-\text{OCH}-[\text{CH}=\text{CH}-]_m-$, Oxygen induced radicals (OIR) with $m = 2$ or 3 (Oxygen centered polyenyl) were observed for GUR 4150 and 1900H samples after 20 years of aging in open air at room temperature (23°C), as shown in **Figure 4**. The spectral features, recorded as a function of microwave power (ESR test parameter), were similar for both types of samples. For each type, the ESR spectrum due to carbon centered polyenyl radical (R1) was observed as a symmetric isolated signal that was detected at very low microwave power (0.01 mW). As the microwave power increased, the ESR signal indicated the presence of another type of radical with a different resonance factor, which is known as the R2 oxygen-induced radical. At 160 mW microwave power, the resonance ESR spectra consisted of two different radical species: R1 and R2. Similar detection of R1 and R2 radical had also been observed earlier for GUR 4150 aged in open air [21].

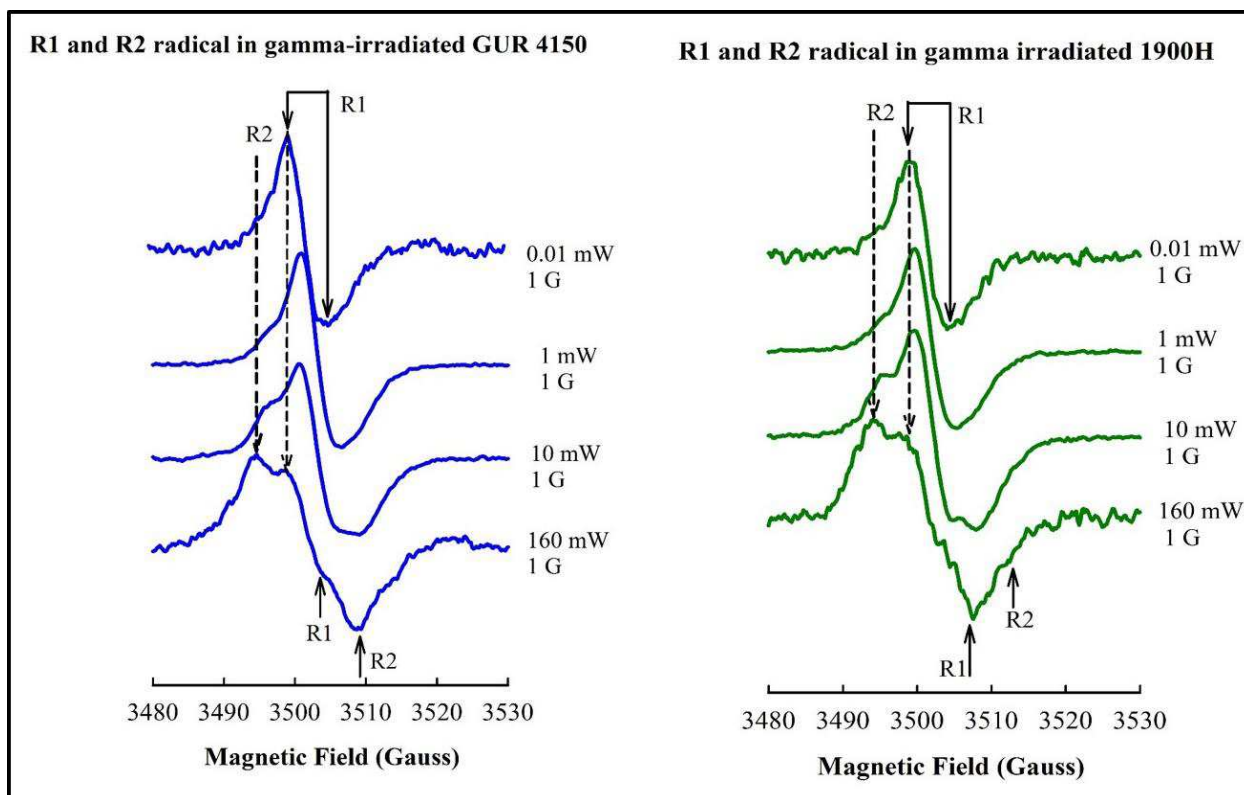


Figure 4: ESR spectra recorded for (a) GUR 4150 and (b) 1900H with varying power (mW) and constant modulation amplitude (1 Gauss) to detect R1 and R2 radicals after 20 years of aging in vacuum at room temperature.

The relative concentrations of R1 and R2 were studied between GUR 4150 and 1900H and presented in **Figure 5**. Analyses of the ESR data revealed that 1900H (compared to GUR 4150) contained lower concentrations of R1 (0.6x) and R2 (0.5x). This result indicates a possible increased oxidation protection in 1900H samples, as fewer oxygen-induced radicals were generated. The spherulitic crystalline morphology of 1900H, typically associated with slightly lower molecular weight polyethylene compared to GUR 4150 (having lamellar crystalline morphology) might have increased mobility of molecular chains and subsequent recombination of free radicals [17, 22].

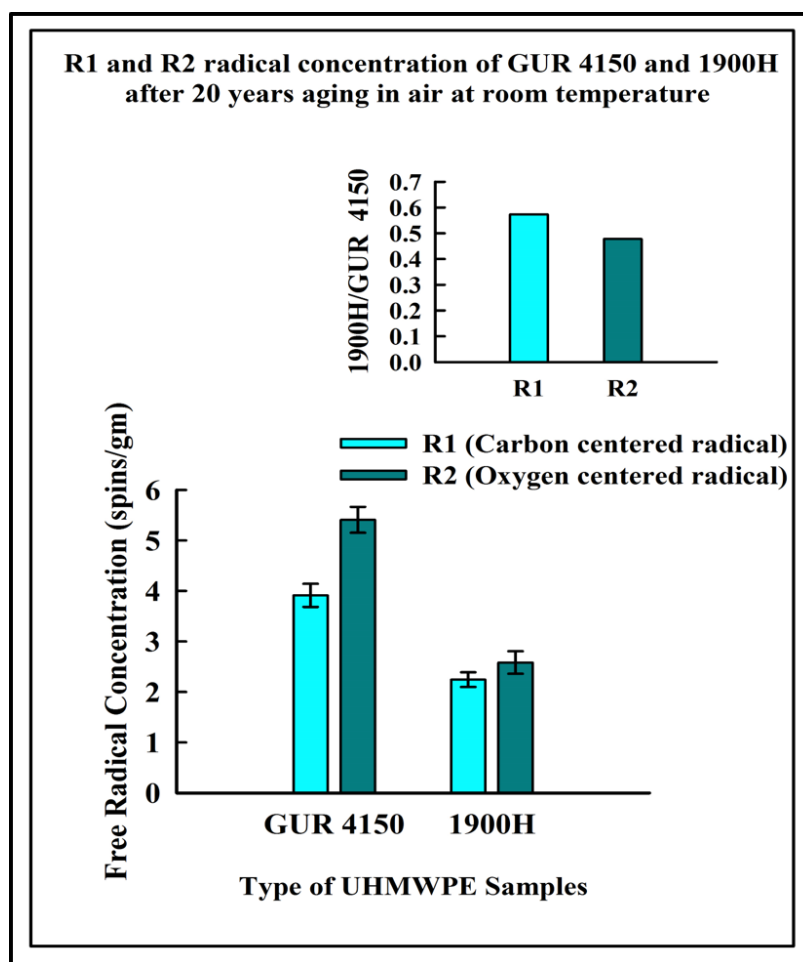


Figure 5: Relative Free Radical Concentration (FRC) of R1 and R2 radicals of GUR 4150 and 1900H after 20 years of aging in air at room temperature.

4.6. Quantification of Free radical concentration

The Free Radical Concentrations (FRC) (spins/g) were quantified and are shown in **Figure 6**. The bar chart of FRC (spins/g) clearly presented that, at 23°C, the open air 1900H sample contains less FRC (spins/g) compared to GUR 4150, by a factor of 2/3, which might be an effect of free radical conversion to the non-radical species. In vacuum environments, both GUR 4150 and 1900H showed slightly higher concentration at 23°C than at 37°C. 1900H might have less recombination of free radicals in vacuum condition at 37°C which causes slightly more radical concentration compared to GUR 4150 under the same condition. In addition, the ratios of free radical concentration between these two types of UHMWPE shown in the inset graph of **Figure 6** demonstrated that, compared to GUR 4150, 1900H contains 0.6, 0.9, 1.0, 1.1 and 1.3 times more radicals at 23°C (air), 37°C (air), 23°C (vacuum), 37°C (vacuum) and 75°C (vacuum), respectively. However, all the samples except those stored in air at 75°C, had quantifiable radical contents remaining after 20 years. The difference in rate of recombination of gamma induced primary types of free radicals between two types of UHMWPE might be caused by the difference

in mean particle size, molecular weight distribution and crystalline morphology between two major types of UHMWPE resin [17].

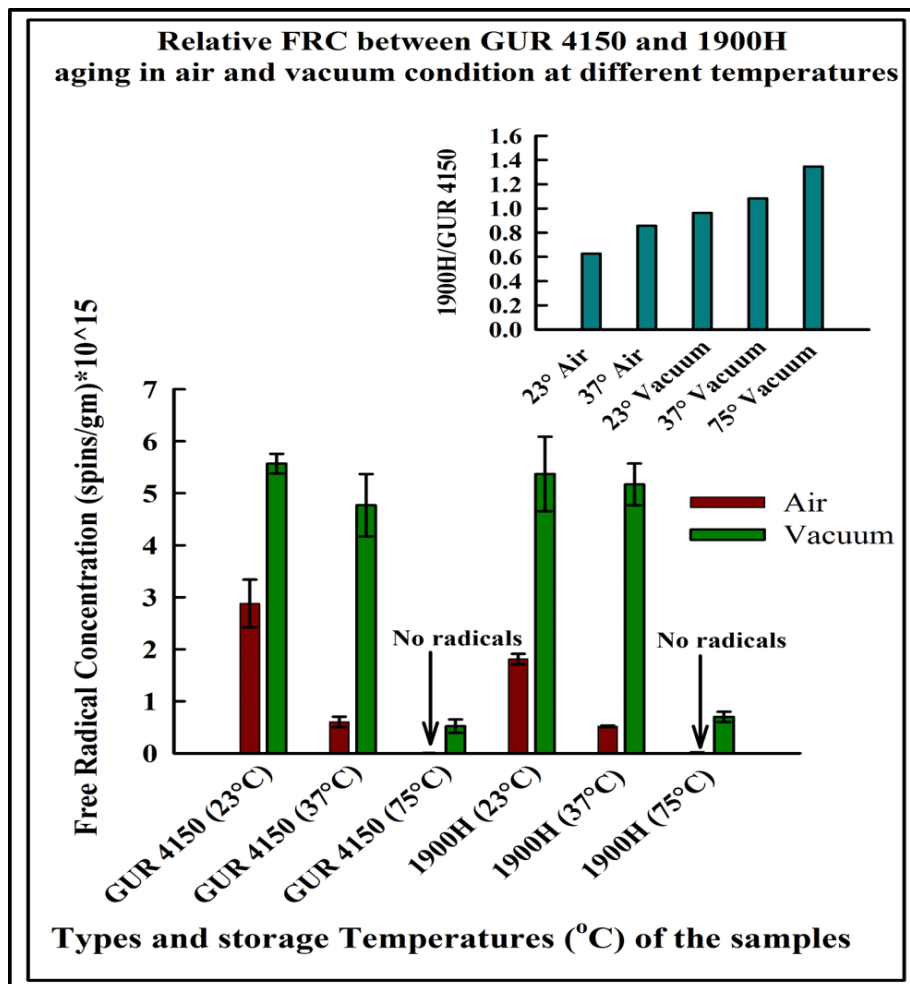


Figure 6: Relative free radical concentration (FRC) between GUR 4150 and 1900H followed by 20 years of aging in air and vacuum environment at 23°C, 37°C and 75°C temperature.

In addition, the free radical concentrations (FRC) (spins/g) of both types of UHMWPE: GUR 4150 and 1900H samples followed by 20 years of aging in air and vacuum environment at room temperature (23°C), were quantified and compared to the initial radical concentrations measured immediately after gamma irradiation at time $t=0$ (20 years ago), which is presented in **Figure 7**. From the FRC (spins/g) bar chart of **Figure 7**, it was found that the total concentration of radicals in all samples decreased by two orders of magnitude over 20 years. The reduction of FRC (spins/g) in both GUR 4150 and 1900H samples, aging in air and vacuum at room temperature (23°C), may be caused by prolonged exposure of samples to the low level of ultraviolet (UV) radiation,

potentially emitted by the fluorescent or LED light used in the laboratory [23]. The ratio of FRC of GUR 4150 and 1900H samples aging in air at room temperature (23°C) for 20 years (t=20) to that of initial condition (t=0) were shown in the inset graph of Figure 6. It was found that after 20 years GUR 4150 showed 0.28 times more FRC, whereas 1900H showed 0.18 times more FRC, as compared to their initial states. The higher stabilization rate of free radicals in 1900H can be an effect of the difference in crystalline morphologies between two types of resins. It has been reported that GUR resin (GUR 4150) possesses more ordered and compact lamellar crystalline structure, whereas 1900 resin (1900H) resin possesses less-organized spherulitic crystalline structures [17]. The prolonged exposure to the fluorescent light of 1900H samples may promote enhanced molecular mobility in the amorphous region of less organized spherulitic crystalline structure, inducing the higher recombination of primary gamma induced radicals.

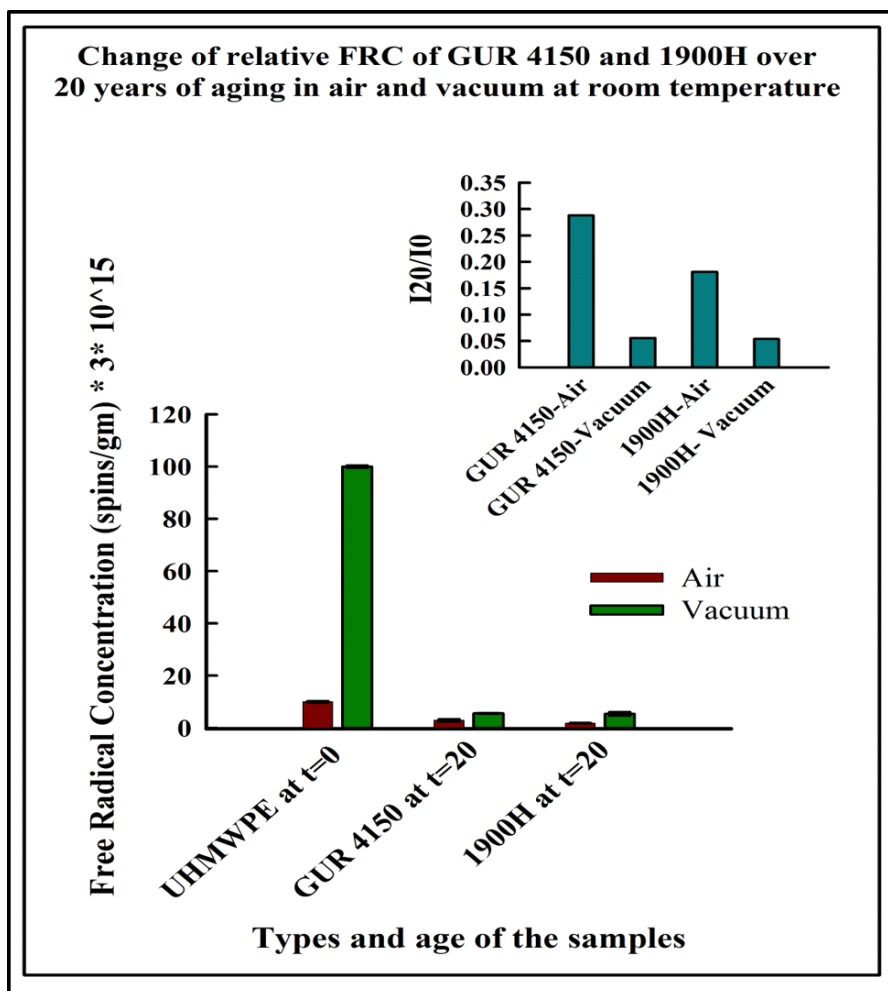


Figure 7: Change in Free radical concentration (FRC) in UHMWPE (GUR-4150 and 1900H) followed by 20 years of aging in air and vacuum sealed condition compared to initial condition.

Conclusion

Although 1900H types of polyethylene are now less common (more typical in current use are GUR1020 and GUR1050, for example), these results can give insights as to possible oxidation-preventative measures to implement in future manufacturing, beyond simply adding antioxidants or adjusting heat treatments.

GUR 4150 and 1900H (and their associated makeup due to their manufacturing) in open air at all temperatures indicated a conversion of primary radicals to oxygen-induced radicals, whereas vacuum-sealed all indicated a presence of primary radicals (initially produced upon original gamma-irradiation treatment 20 years ago), demonstrating that even 75°C heat is not sufficient to completely eliminate radicals generated from 30kGy gamma irradiation. It is therefore assumed that additional dose such as 100 kGy would yield more radicals which would remain in inert environments unless undergoing additional heat or other treatment (e.g., antioxidants). The detection and extraction analyses of radicals in both types of UHMWPE showed a percent conversion of primary radicals into dienyl (oxygen-centered polyenyl) components in 1900H over 20 years of aging in vacuum at 23°C, whereas, no such conversion was detected for GUR 4150 samples aged in similar conditions. This conversion of less stable primary radicals into the dienyl radicals (containing conjugated double bond which helps to delocalize the unpaired electron making the radical more stable) in 1900H samples indicates the presence of higher recombination of radicals and possible improved wear resistance, compared to GUR 4150. In addition, the lower amount of carbon-centered polyenyl (R1) and oxygen-centered polyenyl (R2) radicals in 1900H, compared to GUR 4150, after 20 years of aging in air at room temperature (23°C) suggests possible increased oxidation protection in the 1900H samples, as fewer oxygen-induced radicals were generated. This observation was further supported by the calculated oxidation index (OI), where 1900H consistently demonstrated lower OI values, indicating a reduced extent of oxidative degradation. The relatively lower formation of carbonyl species in 1900H suggests enhanced oxidation resistance compared to GUR 4150. XRD analysis provided further structural insights, revealing higher crystallinity and denser packing of GUR 4150 compared to 1900H. The SEM images also revealed a more pronounced ordered arrangement of crystalline lamellae in GUR 4150 samples aged in air at room temperature for 20 years, compared to 1900H samples aged in same temperature and condition.

The FRC analyses as a function of temperature and condition also indicated that both types (GUR 4150 and 1900H) in all conditions (air and vacuum sealed at 23°C, 37°C and 75°C), showed descending FRC (spins/g) with increase in temperature, as would be expected with the assumption that temperature decreases radical quantities in general. This result indicates the possible recombination of radicals due to the increase in mobility of molecular chain with increase in temperature. It was also observed that, 1900H contains a smaller number of FRC (spins/g) by a factor of 2/3 compared to GUR 4150 over 20 years. Although, compared to initial (at t=0, immediate after gamma irradiation) measurements, the present FRC (spins/g) of all samples (GUR 4150 and 1900H of all conditions) were found to decrease by two orders of magnitude, and there

are still quantifiable radicals remaining in all the samples except those stored in air at 75°C. The semi-crystalline lamellar structure of GUR 4150, stored at higher temperatures have undergone more oxidation due to their long-term radical stability and reactive interfacial amorphous zones. Whereas 1900H spherulites semi-crystalline nature exhibited less degradation due to the characteristics of lower radical retention. The integrated analyses from ESR, FTIR, XRD, and SEM consistently indicated that 1900H exhibits greater oxidative stability and structural retention over long-term aging compared to GUR 4150. This behavior is associated with 1900H's intrinsic molecular structure and manufacturing processes, which govern its radical recombination pathways and mitigate oxidative degradation.

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Author's contributions

Afsana Sharmin contributed to the experimental design, performed ESR experiment, data analysis and article writing. Farhan Azim performed XRD and FTIR measurements, data analysis and writing. Benjamin M. Walters provided analytical guidance and contributed to the review and editing of the manuscript. Muhammad S. Jahan developed the research concept, supervised the project, contributed to data interpretation and discussion, and critically revised the manuscript prior to submission.

Conflict of Interest

There is no conflict of interest in this work.

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