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Oxidative degradation in polyethylene: the microscopic properties responsible for macroscopic weathering

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Polyethylene, HDPE, UHMWPE, Mechanical Properties, Thermal Properties, Creep, Oxidation, Crosslinking, Radiation

ABSTRACT: Radiation-initiated crosslinking of polyethylene has proven to be an effective method of reducing creep and wear. This has allowed polyethylene to find widespread use in engineering and medical sectors where extreme conditions would otherwise cause it to degrade. However, despite their resilience, irradiated polyethylene products are still vulnerable to oxidative degradation in some long-term applications. A good deal of literature exists to discuss the effects that irradiation and oxidative degradation have on polyethylene's mechanical properties, but not much literature exists to describe the microscopic properties that make irradiated polyethylene susceptible to this process. This review presents a micro-scale look at polyethylene's morphology and chemistry, with the intention of describing which characteristics make the material more or less favorable for oxidation. By describing the factors that make irradiated polyethylene vulnerable to oxidation in the first place, the hope is to provide insight on how to mitigate oxidation in future applications.

1) Introduction

Since its discovery over 120 years ago[1], polyethylene (PE) has become one of the most widely-used polymers on the planet. From use in WWII radars to modern-day packaging, engineering, and even medical prosthetics[1–4], PE owes its popularity to its many inherent properties. It is lightweight, chemically inert, and in certain forms such as ultra-high molecular weight polyethylene (UHMWPE), it is quite resistant to wear and creep[2,5–7]. These properties make PE a very useful manufacturing material in many industries, but despite all of these benefits the material is still not immune to creep, wear, and fragmentation in extreme conditions or long-term use[6–8].

Eventually, a solution to this problem came in the form of crosslinking PE. Crosslinking is the process of binding separate polymer chains together by forming chemical bonds between them, changing the internal structure from something analogous to a polymer spaghetti bowl into something more akin to a web. Crosslinked materials are sometimes referred to as *thermosets*; their many internal bonds restrict individual chains from flowing, and therefore the material takes on more rubbery characteristics at higher temperatures. When exposed to conditions above its melt temperature, a thermoset will degrade before it ever flows like a liquid.

There are two common methods of crosslinking polymers: chemical crosslinking and exposure to ionizing radiation. Chemical crosslinking is a relatively straightforward process that uses a chemical initiator, such as peroxides, to generate free radicals. These radical initiators trigger free radical interactions between the polymer chains, which in turn causes them to crosslink where radicals meet. Chemical initiators cannot generally diffuse through a polymer once it's solidified, so they must be added while the material is melted and unformed[9–11].

Radiation-based crosslinking, on the other hand, generates free radicals by exposing polymers to ionizing radiation. Typically, gamma irradiation or beta irradiation (in the form of electron bombardment) is used to trigger radical formation. High-energy particles from the radiation collide with atoms in the polymer, causing them to enter an excited state. In some cases, the bonds between an excited atom and a neighbor will undergo homolytic cleavage, breaking the bond and creating two radical sites. When different radical sites come into contact with each other, they react to form a new chemical bond. This phenomenon occurs homogenously wherever the radiation can penetrate, and can be done after a material is cured. Both radiation and chemical-based crosslinking are viable methods, but for the purposes of this discussion, radiation-based crosslinking will be the primary focus.

Radiation-crosslinked PE has since been researched and utilized in many engineering applications, such as using highly crosslinked UHMWPE in medical prostheses during the late 1990's, and crosslinked UHMWPE remains the industry gold standard even today[7]. For most manufacturing purposes, crosslinking has been capable of reducing creep and wear in both high-density polyethylene (HDPE) and UHMWPE, but research over the last two decades has shown that this improvement may be making crosslinked PE (XPE) more vulnerable to oxidation in the long term via a process called *oxidative degradation*[5–8]. Abundant literature exists to describe the effects of crosslinking on PE's thermal and mechanical properties, some of which was covered in a recent mini-review[12], but the amount of literature that describes oxidative degradation and its effect on XPE's mechanical properties is relatively small in comparison. In the last 20 years, over 200,000 documents have been

published in relation to XPE's mechanical properties, while only some 40,000 works have been published regarding oxidative degradation.*

In a study of radiation's effect on HDPE's oxidative stability, S.S. Cota et al. described HDPE's physical behavior as a "macroscopic effect of multiple phenomena that occur on a microscopic scale"[8]. This statement rings true in every aspect of materials science, and that is why it is so surprising to find comparatively less discussion of how XPE is different from virgin PE on a micro scale, how these differences make XPE more susceptible to oxidation over time, and how oxidation degrades a polymer's mechanical properties. The goal of this work is to pull together information on PE's microstructure, including its morphology and internal chemistry, followed by a discussion of how radiation changes those attributes. It will then explore how these changes affect the material's oxidative stability, oxidative degradation's impact on chemical makeup and morphology, and finally how those changes circle back to change PE's bulk properties.

2) Current understanding of polyethylene's microstructure

2.1: Crystalline and amorphous phases

We'll begin with a short review of morphology. In general, it is commonly acceptable to describe semicrystalline polymers as consisting of two phases: crystalline and amorphous. According to the folded-chain lamella theory, the crystalline phase consists of polymer chains folded in an accordion-like manner to form thin platelets, called *lamellae*[13]. As polymers crystallize, chains of lamellae, called *lamellar fibrils*, begin growth at a nucleus and expand outward in all directions. From this radial growth a *spherulite* is formed, and a single spherulite will grow until it contacts another. Spherulites will vary in size for different polymers, but in general, a bulk polymer will consist of many thousands or hundreds of thousands of spherulites, each one made of lamellar fibrils radiating outward in all directions from the center. The amorphous phase exists as the space between lamellar fibrils, as represented by **Figure 1**[13]. In this space, chains have no regular order and are packed in a relatively loose tangle. The inability to pack into an ordered structure means that the amorphous phase is comparatively less dense than the crystalline phase.

A polymer's degree of crystallinity, X_c, will vary depending on its chemical makeup, physical characteristics, and thermal history. For example, PE is generally considered to be an easily-crystallizing polymer because in an ideal case, its chemical structure is simply one long hydrocarbon chain. The ideal PE has no pendant or main chain groups to create steric bulk or an inhomogeneous charge distribution, and therefore it can fold easily to form crystal lamellae[13]. No PE is truly ideal though; branches are inevitably formed which limit PE's packing ability.

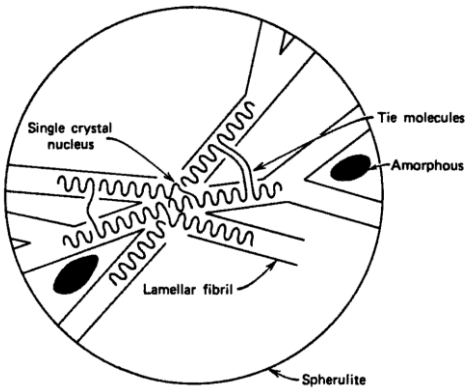

Figure 1: From G. Odian[13], illustration of a spherulite. Crystallization starts at a single nucleus and chains grow into lamellar fibrils. Some chains branch between fibrils and are called tie molecules. Spaces between the tightly packed fibrils consist of randomly arranged polymer strands, better known as the amorphous phase

Low-density polyethylene (LDPE) is the most branched variety, consisting of many long branches off the main chain which restrict packing. This is the reason that LDPE has a lower X_c than some of its counterparts and is less dense in general. HDPE, on the other hand, tends to have very short branches coming off its main chains that offer little resistance to packing. Finally, there is the case of UHMWPE, whose main chain is much longer than HDPE and LDPE's. Their exceptional length makes UHMWPE chains more prone to knots and entanglements, similar to Christmas lights. This abundance of knots in UHMWPE's internal structure makes it difficult for chains to reptate and fold into each other, therefore giving UHMWPE a lower X_c than HDPE[14]. All of these attributes still assume a general case, however. In reality, two identical PE specimens could have very different degrees of crystallinity depending on how they were processed. Crystallization is a thermodynamic phenomenon that is controlled by a macromolecule's translational, rotational, and vibrational energy[13]. When that energy slowly dissipates during cooling, chain segments are allowed to fold into the most energetically favorable conformation. The result is a material with a comparatively high X_c. If that energy is taken away suddenly, like in flash-cooling, then all of that movement energy is lost before the chain segments can fold together. The resulting polymer will therefore have a comparatively low X_c.

The information presented here is by no means a complete description of polymer morphology and the energetic factors that dictate crystallization or the glass transition, but it is vital that this level of understanding be laid down before continuing to discuss the effects of radiation and oxidation on a polymer's bulk properties. Microscopic alterations are felt all the way up to the macroscopic level, and a discussion of macroscopic effects will be meaningless without an understanding of the microstructural changes which are induced by irradiation and oxidation.

*Statistics only consider primary journal articles and reviews. Data gathered via SciFinder keyword search: "crosslinked polyethylene, mechanical properties" and "oxidative degradation, crosslinked polyethylene" for works covering mechanical properties and oxidative degradation, respectively.

2.2: The phases, radiation, and crosslinking

Irradiation-initiated crosslinking of PE is generally triggered by exposing the material to ionizing radiation. In this process, high-energy particles from the radiation excite electrons in the target molecules and cause the chain to cleave into two free radical segments. These segments are formed homogeneously throughout the polymer, and they can split into either two halves of a main chain or a whole chain and an ejected hydrogen. The case of hydrogen ejection is important because it is capable of abstracting other protons in the polymer and leaving as H_2[15]. Cleaved segments are free to relax and move throughout their space with less restriction, wherein they will fold into a nearby crystal lamella, encounter another radical segment and form a bond, or undergo both processes respectively. When a new bond is formed via this process, crosslinking occurs. An outline of the crosslinking process is shown below in **Figure 2**[10,11].

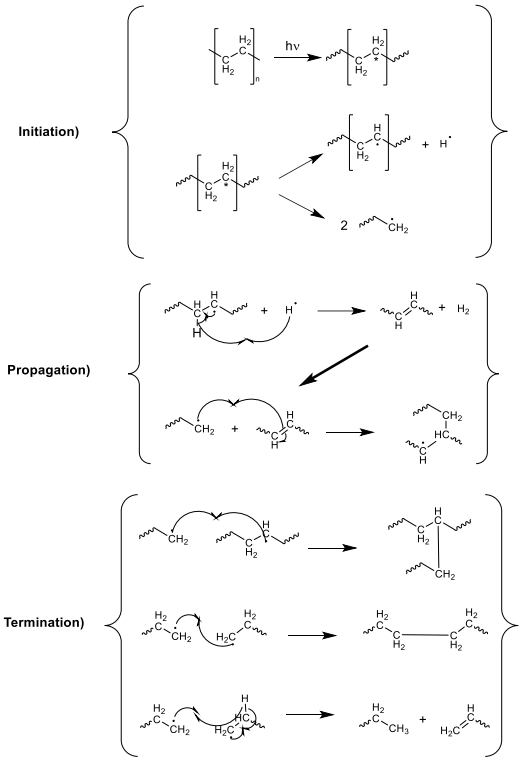

Figure 2: Adapted from Khonakdar et al.[10,11] Mechanisms of radical initiation, propagation, and termination. Initiation begins when ionizing radiation excites an atom, causing it to undergo homolytic cleavage. Note the formation of unsaturated bonds in propagation. These bonds can react with radicals to form a crosslink while simultaneously generating another radical. Termination occurs when two radicals meet each other and form a crosslink. Mechanistically, it is also possible for a radical to abstract hydrogen from a neighboring radical chain rather than crosslink. Theoretically, this will lead to permanent chain scission and the formation of an unsaturated site.

Compared to the crystalline phase, the amorphous phase has been recognized as the more ideal environment for crosslinking due to its lower density[15–17]. Cleaved segments have more open space to move and interact with other radicals, so crosslinking tends to dominate here over the crystalline region. In fact, the crystalline phase is so comparatively restrictive that radicals have been found to exist in PE's crystalline phase for more than 4.5 years without terminating[18]. These radicals, along with other chemical changes caused by irradiation, are theorized to be the reason PE seems more vulnerable to oxidative degradation after radiation treatment.

2.3: Oxidation and its effects

It is well-documented that when polyethylene is exposed to radiation, two complimentary and competing phenomena occur: these are crosslinking and chain scission[2,4,8,15,19,20]. Referring back to **Figure 2**, we see that these processes happen due to ionizing radiation triggering the homolytic cleavage of either C-C or C-H bonds in polyethylene, forming CH_x• and H• radical species[5,10,11]. Once radicals are formed by this initial scission step, they react with each other to form crosslinks throughout the polymer matrix. In this respect, scission and crosslinking are complimentary steps. However, competing reactions with oxygen can induce the formation of oxygen-containing groups, like hydroperoxides, ketones, hydroxides, and acids[5,8]. The formation of these species terminates radicals without creating crosslinks, and this form of termination is oxidative degradation.

Oxidative degradation is problematic because it reduces the overall molecular weight of a polymer, thereby making it brittle and subject to fragmenting[5–8,21]. Ultimate tensile strength and crosslink density tend to decrease as well, implying that oxidation itself is cleaving molecular chains[5,6]. At the time of writing, the exact mechanism by which oxidation cleaves crosslinks isn't fully understood. To complicate the problem, evidence also suggests a reduction in X_c stemming from oxidative degradation. A study performed in 1999 by Han et al. examined the effects of oxidation on HDPE's crystallinity, and they found that after being held above melt temperature (T_m) for 1000 hours, the material's X_c had significantly decreased compared to virgin material[21]. Another sample was held in a vacuum oven under the same conditions, and although some loss of crystallinity was observed, it is nowhere near the reduction seen in the open-air sample[21]. The decrease in crystallinity seen in the vacuum sample is likely the result of remelting the polymer after crosslinks had formed. By nature, crosslinks act like junctions in a net: they restrict chain motion, and therefore hinder the kind of accordion-like folding that is required to create crystal lamellae[10]. Above a polymer's T_m, its chains have enough energy to break free from their lamellae. In other words, a melted polymer is completely amorphous. Any radicals trapped within lamellae are free to move and form new crosslinks, and all of the crosslinks in the polymer will prevent crystallization as the material cools. The outcome of this is that a polymer that's been crosslinked and remelted will almost certainly see a lower X_c than if it had not been remelted.

2.4: Mechanisms of oxidative degradation

On paper, polyolefins like PE are comprised strictly of alkyl groups that tend to be nonreactive when exposed to most foreign substances, like oxygen. This is why polyolefins are inert to most chemicals, and why oxidation usually doesn't occur without extreme conditions or the significant passage of time. However, no manufactured material is free of microscopic defects, and it is these defects that will cause materials to react and break down over time. In the case of irradiated PE, these defects are cleaved radicals and transvinylene, also known as *unsaturated*, bonds[5–8,22]. Referring back to **Figure 2**, we see that the cleaving of chains and the

abstraction of protons can form radical chain ends and unsaturated carbons, respectively.

2.4.1: Radical oxidation

It is generally accepted that oxygen will react with radical species to form ketones, peroxides, and alcohol, along with other groups[5,8]. Under ambient conditions it is rare for alkyl bonds to gain the energy required to separate into radical chain ends[22], but exposure to ionizing radiation naturally provides the energy for homolytic bond cleavage and free radical formation. Because radicals can stay trapped inside a specimen for weeks or even years, radical termination is often promoted by annealing PE below its $T_{m,}$ or completely melting it above T_m and recrystallizing. These annealing and remelting processes provide the energy for chains in the amorphous and crystalline phases, respectively, to move and interact with each other. This interaction allows radicals to meet and therefore terminate by forming crosslinks. Naturally, remelting is more efficient at removing radicals because it releases the chain ends that are trapped in the crystal lamellae, but since oxygen has a difficult time penetrating the tight folding of the crystalline phase[21–23], remelting is not always deemed necessary.

Despite efforts to mitigate oxidation by post-irradiation thermal treatment though, a polymer may still be vulnerable to oxidation during the irradiation process. In order for free radical oxidation to occur in PE, two reactants are needed: available radicals and oxygen diffused within the polymer. In most cases, oxygen doesn't diffuse past the first 1-2mm of a polymer's surface; which means that oxidative degradation is largely a surface effect[5], but this can still be problematic in instances where wear and fragmentation cause complications, like medical implants. Beneath the surface though, crosslinking dominates because there is very little oxygen for the radicals to interact with. They are only able to react with each other, and crosslinking dominates over chain scission as a result.

In cases where it is important to mitigate surface oxidation as much as possible, the simplest way to prevent polymers from oxidizing during radiation is to irradiate them under an inert atmosphere. Both vacuum and nitrogen atmospheres have shown decreased oxidation when compared to irradiation in open air[8,24–27]. When irradiation under inert atmosphere isn't possible, however, there are still measures that can be taken to mitigate the oxidative degradation. For example, one study by Cota et al. examined the effect that radiation dose rate would have on total oxidation and mechanical properties[8]. They found no correlation between oxidation and dose rate under vacuum, but in open air they saw that yield stress was negatively correlated to maximum dose at low dose rates, specifically 115 Gy/h. As dose rates increased (500 and 1000 Gy/h), yield stress also showed an initial decrease as maximum dose increased, but that decrease promptly reversed itself and turned into an increase as maximum dose exceeded 200 kGy. The authors attribute this steady decrease at low dose rates, as well as the initial decrease at higher dose rates, to comparatively high amounts of oxygen within the polymer. They speculate that at low dose rates, oxygen has time to diffuse from the air and into the PE, wherein they will react with radicals that are forming at a similar rate. With both reactants present, chain scission and oxidative degradation will dominate. When the dose rate is increased, however, then the rapid generation of radicals will cause any oxygen present in the polymer to react very quickly. This quick reaction causes the initial decrease in yield stress seen with higher dose rates, but once the initial oxygen is used up radicals will continue to form faster than new oxygen can diffuse into the polymer. With nothing to react with except each other, the radicals will meet to form bonds, and crosslinking will dominate.

2.4.2: Oxidation via unsaturation

Besides free radicals, recent studies have found that radiation enables another mechanism for oxidation that can't be disabled by remelting or high dose rates. In the last 20 years, emerging studies have found that UHMWPE medical inserts are experiencing long-term oxidation and chain scission in vivo, even though these inserts were completely remelted before clinical use[5–7]. Since remelting removes all detectable traces of free radicals, oxidation must be occurring via some alternative mechanism.

Investigations into this phenomenon led to several revelations. Firstly, several studies have reported a correlation between the degree of oxidation and maximum dose used to irradiate the UHMWPE inserts[5–7]. Secondly, there seems to be a critical radiation dose at which oxidation will occur more readily. In an artificial aging study conducted by Fung et al., samples of UHMWPE exposed to radiation doses of 0, 50, 75, and 100 kGy were monitored to track their oxidation[5]. Virgin and 50 kGy samples experienced nearly identical degrees of oxidation all throughout the 10-week study, but the 75 kGy and 100 kGy specimens began to see increased levels of oxidation proportional to radiation dose after 6 weeks of aging. The results of this study are visually represented in **Figure 3**[5]. Finally, the degree of oxidation seems to be correlated with a decrease in crosslink density. In a study of UHMWPE tibial bearings, Reinitz et al. found a correlation between oxidation, time spent in vivo, and the degradation of crosslink density[6]. These observations are important because they imply that radiation makes materials more susceptible to oxidation even after radicals have been removed, and that the mechanism of oxidation cleaves existing polymer chains.

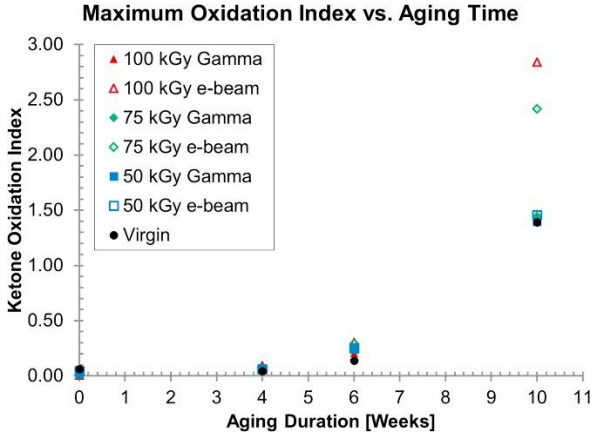

Figure 3: From Fung et al.[5] Shown here is the maximum oxidation index observed in UHMWPE (represented by ketone index as detected by Fourier transform infrared spectroscopy, FTIR) as a function of artificial aging duration. Note that there is little difference between virgin and 50 kGy specimens for the full 10 weeks of aging. Meanwhile, the 75 kGy and 100 kGy samples show much more oxidation between 6 and 10 weeks, especially those irradiated by electron beam (β) radiation. This implies a critical dose value at which oxidation proceeds faster than virgin samples.

The exact mechanisms of in vivo and subsequent ex vivo oxidation are still being explored, but recent theories suggest that oxidation is occurring due to unsaturated bonds formed by irradiation[5]. Unsaturated sites provide reactive centers for oxidation, and the oxidation of unsaturated sites under ambient conditions is frequently seen in other materials, like unsaturated lipids[22,28]. Ozone is generally accepted as an oxidizer for these molecules, but other forms such as singlet oxygen ($^1O_2$), an electrophilic state of oxygen that can be generated in ambient conditions, have demonstrated the capacity to form oxidized groups as well[28]. A proposed mechanism for both ozone-based and singlet oxygen-based oxidation is shown in **Figure 4**. The schemes drawn do not account for all of the possible functional groups that could be formed by oxidation, but they do demonstrate how chain scission can occur in both mechanisms. Furthermore, these mechanisms only provide a potential explanation for oxidation of unsaturated UHMWPE ex vivo. In vivo oxidation is theorized to be caused by oxidizing compounds in the body, but an exact cause is more difficult to pin down[6,7].

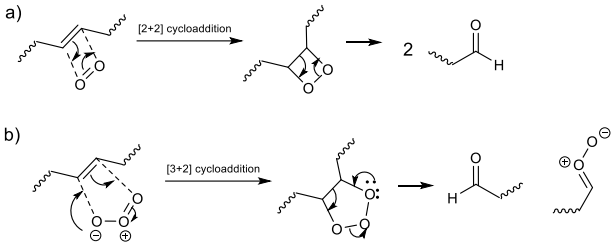

Figure 4: Unsaturated bond oxidation mechanisms via singlet oxygen (a) and ozone (b) are shown above. Mechanisms employ cycloadditions followed by retrocycloaddition to explain chain scission. These are only two of several potential reactions, and products generated in the schemes above could theoretically undergo further oxidation.

Finally, it is important to mention that even though irradiation-based crosslinking may make UHMWPE more vulnerable to oxidation in the long term, it is still more resistant to weathering and mechanical changes than virgin UHMWPE. Virgin UHMWPE is still vulnerable to oxidation over time, but it is far more sensitive to oxidation's effects than crosslinked UHMWPE. In the same study by Fung et al. mentioned earlier, a comparison of mechanical properties as a function of oxidation was performed[5]. The results are described in **Figure 5**, and they show a degradation in ultimate tensile strength and elongation at break occurring at much lower oxidation levels in virgin UHMWPE compared to crosslinked UHMWPE.

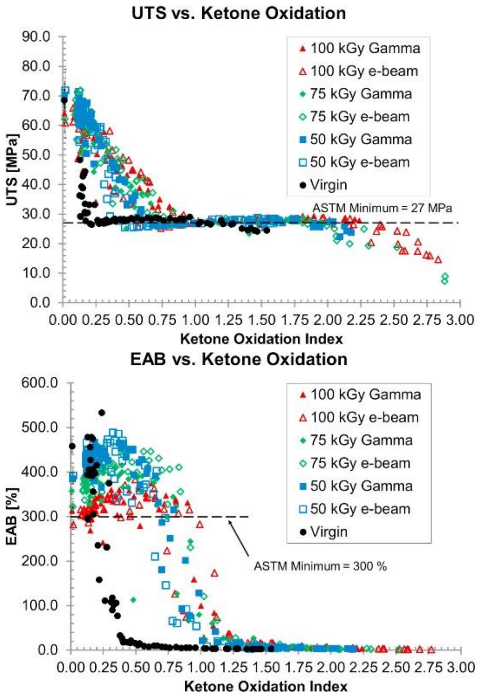

Figure 5: From Fung et al.[28] Shown here are ultimate tensile strength (top) and elongation at break (bottom) in UHMWPE tibial inserts as a function of oxidation. Different radiation doses and sources are marked in the legend. Note that virgin PE experiences a much more sudden decrease in mechanical properties than the crosslinked materials.

3) Conclusions and Future Directions:

Radiation-based crosslinking has proven to be an effective method of reducing wear and creep in PE. This makes the PE much more resilient in conditions of long-term use or high stress, but it can also make the polymer more vulnerable to oxidative degradation over time. Vulnerability to oxidative degradation, as well as its effects, are largely determined by microscopic factors such as a polymer's morphology and internal chemistry. More work is needed to understand the exact mechanism of oxidative degradation by unsaturated bonds, but knowledge of free radical oxidation, morphological effects, and the effect of dose rate allow for significant protection from oxidation during and after irradiation.

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ABBREVIATIONS

PE, Polyethylene; HDPE, High density polyethylene; LDPE, Low density polyethylene; UHMWPE, Ultra high molecular weight polyethylene; X_c, degree of crystallinity

REFERENCES

(1) Spalding, M. A.; Chatterjee, A. M. Handbook of Industrial Polyethylene and Technology : Definitive Guide to Manufacturing, Properties, Processing, Applications and Markets; Hoboken, NJ : John Wiley & Sons: Hoboken, NJ, 2017.

(2) Birkinshaw, C.; Buggy, M.; Daly, S.; O'Neill, M. The Effect of γ Radiation on the Physical Structure and Mechanical Properties of Ultrahigh Molecular Weight Polyethylene. Journal of applied polymer science **1989**, 38 (11), 1967–1973. https://doi.org/10.1002/app.1989.070381101.

(3) Lee, J.-G.; Jeong, J.-O.; Jeong, S.-I.; Park, J.-S. Radiation-Based Crosslinking Technique for Enhanced Thermal and Mechanical Properties of HDPE/EVA/PU Blends. Polymers **2021**, 13 (16), 2832. https://doi.org/10.3390/polym13162832.

(4) Roe, R. J.; Grood, E. S.; Shastri, R.; Gosselin, C. A.; Noyes, F. R.; Roe, R.-J.; Grood, E. S.; Shastri, R.; Gosselin, C. A.; Noyes, F. R. Effect of Radiation Sterilization and Aging on Ultrahigh Molecular Weight Polyethylene. Journal of biomedical materials research. 15 (2), 209–230. https://doi.org/10.1002/jbm.820150209.

(5) Fung, M.; Bowsher, J. G.; Van Citters, D. W. Variation of Mechanical Properties and Oxidation with Radiation Dose and Source in Highly Crosslinked Remelted UHMWPE. Journal of the Mechanical Behavior of Biomedical Materials **2018**, 82, 112–119. https://doi.org/10.1016/j.jmbbm.2018.03.005.

(6) Reinitz, S. D.; Currier, B. H.; Levine, R. A.; Van Citters, D. W. Crosslink Density, Oxidation and Chain Scission in Retrieved, Highly Cross-Linked UHMWPE Tibial Bearings. Biomaterials **2014**, 35 (15), 4436–4440. https://doi.org/10.1016/j.biomaterials.2014.02.019.

(7) Currier, B. H.; Van Citters, D. W.; Currier, J. H.; Carlson, E. M.; Tibbo, M. E.; Collier, J. P. In Vivo Oxidation in Retrieved Highly Crosslinked Tibial Inserts. J. Biomed. Mater. Res., Part B **2013**, 101B (3), 441–448. https://doi.org/10.1002/jbm.b.32805.

(8) Cota, S. S.; Vasconcelos, V.; Senne Jr., M.; Carvalho, L. L.; Rezende, D. B.; Côrrea, R. F. Changes in Mechanical Properties Due to Gamma Irradiation of High-Density Polyethylene (HDPE). Braz. J. Chem. Eng. **2007**, 24, 259–265. https://doi.org/10.1590/S0104-66322007000200010.

(9) Muratoglu, O. K.; Bragdon, C. R.; O'Connor, D. O.; Jasty, M.; Harris, W. H.; Gul, R.; McGarry, F. Unified Wear Model for Highly Crosslinked Ultra-High Molecular Weight Polyethylenes (UHMWPE). Biomaterials **1999**, 20 (16), 1463–1470. https://doi.org/10.1016/s0142-9612(99)00039-3.

(10) Khonakdar, H. A.; Jafari, S. H.; Taheri, M.; Wagenknecht, U.; Jehnichen, D.; Häussler, L. Thermal and Wide Angle X-Ray Analysis of Chemically and Radiation-Crosslinked Low and High Density Polyethylenes. Journal of applied polymer science **2006**, 100 (4), 3264–3271. https://doi.org/10.1002/app.23073.

(11) Khonakdar, H. A.; Jafari, S. H.; Wagenknecht, U.; Jehnichen, D. Effect of Electron-Irradiation on Cross-Link Density and Crystalline Structure of Low- and High-Density Polyethylene. Radiation physics and chemistry. **2006**, 75 (1), 78–86. https://doi.org/10.1016/j.radphyschem.2005.05.014.

(12) Matthew DeSmith. Radiation-Initiated Crosslinking of Polyethylene: The Effects on Physical, Thermal, and Mechanical Characteristics, 2022.

(13) Odian, G. G. Introduction. In Principles of Polymerization; Wiley Online, L., Ed.; Hoboken, N.J. : Wiley-Interscience: Hoboken, N.J., 2004; pp 1–38. https://doi.org/10.1002/047147875X.ch1.

(14) Bistolfi, A.; Bellare, A. The Relative Effects of Radiation Crosslinking and Type of Counterface on the Wear Resistance of Ultrahigh-Molecular-Weight Polyethylene. Acta Biomaterialia **2011**, 7 (9), 3398–3403. https://doi.org/10.1016/j.actbio.2011.05.018.

(15) Keller, A.; Ungar, G. Radiation Effects and Crystallinity in Polyethylene. Radiation Physics and Chemistry (1977) **1983**, 22 (1), 155–181. https://doi.org/10.1016/0146-5724(83)90201-7.

(16) Kömmling, A.; von der Ehe, K.; Wolff, D.; Jaunich, M. Effect of High-Dose Gamma Irradiation on (U)HMWPE Neutron Shielding Materials. Radiation physics and chemistry. **2018**, 142, 29–33. https://doi.org/10.1016/j.radphyschem.2017.02.014.

(17) Perez, C. J.; Vallés, E. M.; Failla, M. D. The Effect of Post-Irradiation Annealing on the Crosslinking of High-Density Polyethylene Induced by Gamma-Radiation. Radiation Physics and Chemistry **2010**, 79 (6), 710–717. https://doi.org/10.1016/j.radphyschem.2010.01.005.

(18) Naheed, N.; Jahan, M. S.; Ridley, M. Measurements of Free Radicals over a Period of 4.5 Years in Gamma-Irradiated Ultra-High Molecular Weight Polyethylene. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **2003**, 208, 204–209. https://doi.org/10.1016/s0168-583x(03)00645-1.

(19) Lopez-Gonzalez, E.; Salmazo, L. O.; Lopez-Gil, A.; Laguna-Gutierrez, E.; Rodriguez-Perez, M. A. Analysis of the Foaming Mechanisms of Materials Based on High-Density Polyethylene (HDPE) Crosslinked with Different Irradiation Doses. Journal of Applied Polymer Science **2018**, 135 (22), 46276. https://doi.org/10.1002/app.46276.

(20) Wang, H.; Xu, L.; Li, R.; Hu, J.; Wang, M.; Wu, G. Improving the Creep Resistance and Tensile Property of UHMWPE Sheet by Radiation Cross-Linking and Annealing. Radiation Physics and Chemistry **2016**, 125, 41–49. https://doi.org/10.1016/j.radphyschem.2016.03.009.

(21) Han, S. O.; Lee, D. W.; Han, O. H. Thermal Degradation of Crosslinked High Density Polyethylene. Polymer Degradation and Stability **1999**, 63 (2), 237–243. https://doi.org/10.1016/s0141-3910(98)00098-6.

(22) Grause, G.; Chien, M.-F.; Inoue, C. Changes during the Weathering of Polyolefins. Polymer Degradation and Stability **2020**, 181, 109364. https://doi.org/10.1016/j.polymdegradstab.2020.109364.

(23) Bracco, P.; Costa, L.; Luda, M. P.; Billingham, N. A Review of Experimental Studies of the Role of Free-Radicals in Polyethylene Oxidation. Polymer Degradation and Stability **2018**, 155, 67–83. https://doi.org/10.1016/j.polymdegradstab.2018.07.011.

(24) Ferreto, H. F. R.; Oliveira, A. C. F.; Gaia, R.; Parra, D. F.; Lugão, A. B. Thermal, Tensile and Rheological Properties of High Density Polyethylene (HDPE) Processed and Irradiated by Gamma-Ray in Different Atmospheres. AIP Conference Proceedings **2014**, 1593 (1, Proceedings of PPS-29, 2013), 236–239. https://doi.org/10.1063/1.4873771.

(25) Okada, Y. Effect of Atmosphere on Radiation-Induced Crosslinking of Polyethylene. Part I. Depressive Effect and Accelerating Effect. Journal of Applied Polymer Science **1963**, 7 (2), 695–701. https://doi.org/10.1002/app.1963.070070224.

(26) Gao, C.; Li, S.; Song, H.; Xie, L. Radiation-Induced Crosslinking of Ultra High Molecular Weight Polyethylene Fibers by Means of Electron Beams. Journal of Applied Polymer Science **2005**, 98 (4), 1761–1764. https://doi.org/10.1002/app.22360.

(27) Hamilton, J. V.; Schmidt, M. B.; Greer, K. W.; Shah, C. Improved UHMWPE through the Control of Sterilization Dose and Atmosphere. Radiation Physics and Chemistry **1998**, 52 (1–6), 283–288. https://doi.org/10.1016/s0969-806x(98)00154-6.

(28) Zhou, Y.; Park, H.; Kim, P.; Jiang, Y.; Costello, C. E. Surface Oxidation under Ambient Air—Not Only a Fast and Economical Method to Identify Double Bond Positions in Unsaturated Lipids But Also a Reminder of Proper Lipid Processing. Anal. Chem. **2014**, 86 (12), 5697–5705. https://doi.org/10.1021/ac404214a.