



Long-term stability of UHMWPE fibers



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ABSTRACT

The performance of ultra-high molecular weight polyethylene (UHMWPE) fibers for ballistic protection is predicated on the development of a highly aligned molecular structure that allows the polymer to exhibit a superior strength in the axial direction of the fiber. However, even an ideal molecular structure will be subjected to degradation during use, which can reduce the high strength of these fibers, and impact their ability to protect the wearer. In this work, the long term stability of UHMWPE fibers are investigated and the activation energy for this mechanism was calculated to be approximately 140 kJ/mol, in agreement with previous reports. The inclusion of accelerated aging temperatures that encompass the alpha-relaxation temperature introduced physical effects in addition to oxidative degradation that complicate a simple explanation of the changes in properties. Assuming that the shift factors that were used in this analysis are correct, it would take approximately 36 years for the tensile strength of this UHMWPE yarn to fall by 30% at 43 °C. Changes in the oxidation index of this material due to aging are also studied using Fourier Transform Infrared (FTIR) Spectroscopy, and no simple correlation between the retained strength and the oxidation index was found.

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1. Introduction

Ultra high molecular weight polyethylene [1–4] (UHMWPE) is one of the two main types of fibers currently used in ballistic-resistant body armor. UHMWPE is a long-chain polyolefin with a molar mass between 3 million and 5 million. Its tensile strength is reported to be approximately 40% greater than PPTA fiber [5] due to its high crystallinity and highly oriented zig-zag sp^3 conformation. Polyethylene has no functional groups, resulting in superior chemical resistance as compared to other materials [6]. A well-publicized field failure in 2003 of a body armor based on the fiber poly(*p*-phenylene-2,6-benzobisoxazole), or PBO, has prompted our work to better understand the long term stability of other classes of fibers used in body armor when exposed to elevated temperatures [7–9].

Degradation of polyolefins initiates from thermal decomposition of hydroperoxides and peroxides produced due to defects,

unsaturations, and other impurities introduced during processing [10]. The rate of degradation is dependent upon many factors such as the number of free radicals generated, the presence of scavenger compounds (e.g., antioxidants), the presence of oxygen, and the degree of crystallinity of the polymer. UHMWPE fibers used in soft body armor are protected from photo-oxidation by a protective fabric carrier, and exposure to ionizing radiation is not expected to occur during general use. The likely routes to initiate degradation are thermal exposure (from storage and wear) or mechanically-initiated degradation from routine use of the armor. Mechanical degradation initiates free radical formation and can occur at folds [11] due to movement of the armor on the wearer. Once these free radicals are generated they may follow the established free radical reactions such as hydrogen abstraction and hydroperoxide formation resulting in main chain scission, reduction of molecular weight, and oxidation. Each of these short-term exposures results in cumulative damage that may lead to unforeseen performance reductions in the armor over time. Mechanically-induced oxidation is not a commonly explored route for artificial aging of UHMWPE fibers since it can be difficult to quantify and control

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free radical formation via this method. In this study, elevated temperature exposure will be used to accelerate degradation, since the reaction pathways are assumed to be similar once free radicals are initiated. Costa and co-authors have discussed thermal, photo, and mechano-oxidation of UHMWPE in detail, and their work includes a reaction scheme of how oxidation occurs in this material [12,10].

Due to the highly oriented and crystalline microstructure of UHMWPE fibers, it is not immediately clear that accelerating degradation via temperature will follow Arrhenius behavior. The goals of this study are threefold: first, to determine whether elevated temperatures follow the constant acceleration assumption, next to determine whether or not mechanical performance shifts to create a master curve, and finally to determine how the calculated activation energy agrees with a previous study to determine activation energy via elevated temperature exposure [4].

1.1. Methodology of artificial aging

Classically, researchers have extrapolated high temperature behavior to a lower temperature regime using the Arrhenius equation [13–15]. Time-temperature superposition may be used to shift data from different aging temperatures to create a master curve if the increase in temperature increases the rate of degradation by a constant multiplicative factor. When plotted on a logarithmic time graph, all data sets at the various temperatures should have the same overall curve shape. If the data from each elevated temperature can be superposed at a reference temperature by multiplying the aging time by a constant, known as the shift factor, a_t , then the time-temperature superposition is generally regarded as valid. In order to verify the feasibility of time-temperature superposition, a plot of ($\log a_t$ versus $1/T$) should result in a linear dependence upon temperature [13].

Previous work has focused on understanding the long term stability of bulk UHMWPE typically used in orthopedic joint replacement applications [16]. Chabba and coworkers performed artificial aging experiments on UHMWPE fibers, focusing on oxygen uptake as a marker of degradation and calculating the activation energy of this process as being approximately 120 kJ/mol. In this study, the focus is on tensile strength as an indicator of degradation in the fiber, and not oxygen uptake as in Chabba's study. Tensile strength was selected as a metric for this study because it is generally considered to be an easily-studied parameter that is related to ballistic performance [17]. In order to better represent the aging environment for body armor, aging temperatures of 43 °C and 65 °C were chosen to simulate body temperature and potential storage conditions (e.g., the trunk of a car), and 90 °C and 115 °C were used to accelerate degradation.

2. Experimental

2.1. Sample description

Gel spun UHMWPE continuous filament yarns were used in this study. Yarn samples were stored in dark ambient conditions when not being exposed. For the aging experiments, yarns were wound onto perforated spools and placed into ovens at 43 °C, 65 °C, 90 °C, and 115 °C under dry conditions for a predetermined period of time. A series of temperature/relative humidity dataloggers were used to monitor the consistency of the chamber temperature during the exposure period.

2.2. Mechanical properties measurement

An Instron¹ Model 5582 test frame equipped with a 1 kN load cell and pneumatic yarn and cord grips (Instron model 2714-006) was used to measure the breaking strength of UHMWPE yarns. The experiment was performed in accordance with ISO 2062 [18]. A 58.42 cm (23 in) yarn was given 23 twists (1 twist per 2.54 cm) on a custom designed yarn-twisting device, and the level of twist was maintained while transferring the yarn to the pneumatic grips. The gage length was 25 cm and the crosshead speed was 250 mm/min. The strength at break was recorded and each data point represents the mean of at least 7 trials.

2.3. Oxidation measurement

Oxidation of UHMWPE was measured using Fourier Transform Infrared Spectroscopy. A Nicolet Nexus 670 Fourier Transform Infrared Spectrometer (FTIR) equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a SensIR Durascope (Smiths Detection) attenuated total reflectance (ATR) accessory was used in the oxidation measurement. Consistent pressure on the yarns was applied using the force monitor on the Durascope. The final scans represent the average of 128 individual scans with a resolution of 4 cm^{-1} between 650 cm^{-1} and 4000 cm^{-1} , respectively. Spectral analysis, including spectral baseline correction and normalization, was carried out using a custom software package developed at NIST to catalog and analyze multiple spectra. The spectra were baseline corrected and normalized using the peak at 1472 cm^{-1} , which was attributed to the CH_2 bending mode. Typical standard uncertainties for spectral measurement are 4 cm^{-1} in wavenumber and 5% in peak intensity. For the purposes of evaluating the degree of oxidation, the overlapping peaks were deconvolved using the methods available in the instrument software package between 1712 cm^{-1} and 1735 cm^{-1} . This peak ratio is known as the oxidation index and is commonly used in other UHMWPE aging literature [19–21]. The oxidation index will be described in further detail in the results and discussion section of this work.

3. Results and discussion

3.1. Mechanical properties of artificially aged fibers

Fig. 1 shows the change in tensile strength as a function of aging at different temperatures. As anticipated, the reduction in tensile strength was lowest at the aging temperature of 43 °C. Only a slight decrease in the tensile strength (2%) was observed after one week of aging, with virtually no change after the first month of aging. A slow, steady deterioration in the tensile strength was observed throughout the long term aging study. The study was ended at 102 weeks of aging, with a final tensile strength loss of 9%.

The reduction in residual tensile strength was more evident at the aging temperature of 65 °C. The decrease in tensile strength after the first week was approximately 3.0%, and in the first month it was 8%. After 94 weeks of aging, the study was ended, with a final tensile strength loss of over 30%.

The reduction in tensile strength was even more apparent at the higher temperatures. The UHMWPE fibers lost 28% of their initial

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

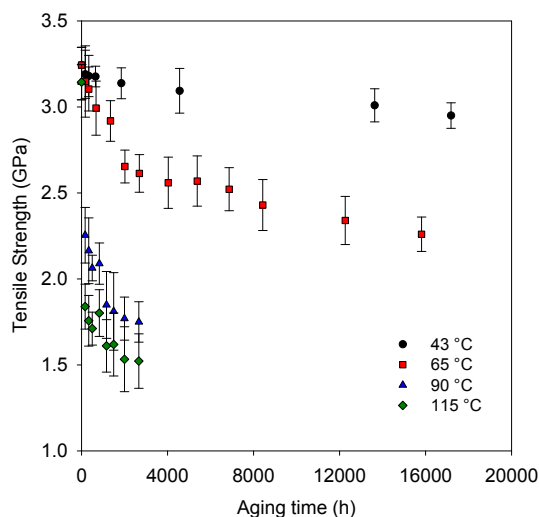


Fig. 1. The decrease in tensile strength of artificially aged UHMWPE fibers at various temperatures over time.

tensile strength at the aging temperature of 90 °C in the first week, and continuously decreased to 56% after 17 weeks. Fibers exposed to the aging condition of 115 °C lost 42% of their original tensile strength after 1 week. The study continued for 17 weeks, after which the fibers had lost 52% of their original tensile strength. However, given the rapid and catastrophic loss of tensile strength in the fibers aged at 90 °C and 115 °C, and the fact that the fibers were unconstrained during this experiment, it is possible that these fibers may have undergone a morphological change during elevated temperature exposure. The loss of orientation in the fiber, combined with scissions in the critical tie chains that are important in carrying load in UHMWPE fibers [22] could be partially responsible for the rapid loss in tensile strength (especially at 1 week of aging time) in the fibers aged at 90 °C and 115 °C, rather than oxidative chain scission. DMTA temperature scans of unaged fibers were previously reported [23] and show reduction in the storage modulus by 30% and 50% at 90 °C and 115 °C, respectively, although the material remains 20 °C away from the transition region. Shrinkage of highly drawn and oriented polyethylene has been widely reported [24,1,25]. Shrinkage was not directly measured or observed in this study, but remains a potential consequence of small changes in polymer morphology when working with such highly drawn fibers at elevated temperatures. Previous work [23] has shown that the UHMWPE fibers used in this experiment undergo an alpha-relaxation above 80 °C, but degradation may be accelerated at higher temperatures. Gillen et al. have also shown these methods to work for Nylon 6,6 material aging at elevated temperatures [14,15,13].

In order to assess the long term stability of UHMWPE fibers, the master curve at 43 °C is presented in Fig. 2. The lowest aging temperature represents the base use condition for the fibers (body temperature). A master curve was created by using 43 °C as the reference temperature, and then horizontally shifting the higher temperature aging data until they superimposed smoothly to form a single curve [4,26,27]. The amount that each curve must be shifted is called the *shift factor*, a_t , and is used in Equation (1) to determine the activation energy of the aging mechanism.

$$\ln a_t = \ln \frac{t_t}{t_0} = -\frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \quad (1)$$

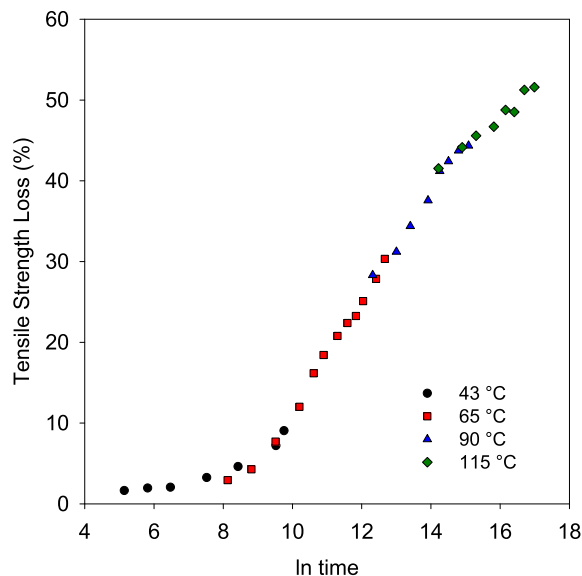


Fig. 2. Master curve for aging of UHMWPE fibers at the reference temperature of 43 °C. Error bars are not shown for clarity of presentation, the standard uncertainty in the data is approximately 5%.

Where a_t is the shift factor, t_0 is the aging time of reference temperature, t_t is aging time after shifting, E_a is the activation energy, R is the universal gas constant, and T_{ref} is the reference temperature. The value of the activation energy as calculated by Equation (1) is found to be 140 kJ/mol, with a standard deviation of approximately 15% (based on the original error in the tensile strength measurements combined with the error in the shift factor calculation), which is approximately 20 kJ/mol higher than previously published results from Chabba [4], which were based on oxygen uptake. This difference is within the error of this measurement. A table of shift factors is given in Table 1 and the shift factors are plotted to show linearity in Fig. 3. The strong linearity of the shift factor plot, even at the high temperatures where shrinkage may occur supports the elevated temperature aging methodology. Assuming that the master curve presented in Fig. 2 is valid, one might predict that it will take approximately 36 years for the tensile strength of this UHMWPE yarn to fall by 30% at 43 °C.

3.1.1. Oxidation analysis

A representative FTIR spectrum of baseline, or unaged, UHMWPE fibers is shown in Fig. 4. The characteristic peaks at 2916 cm^{-1} and 2848 cm^{-1} are identified as sp^3 C–H stretching, 1471 cm^{-1} and 1461 cm^{-1} are assigned to C–H bending, and 731 cm^{-1} and 717 cm^{-1} are in-phase and out-of-phase C–H rocking, respectively. Hydroperoxides were not detected in the ATR-FTIR spectra of the UHMWPE fibers during aging. Gugumus [28–31] has previously shown that FTIR can be used to measure hydroperoxide in LDPE and HDPE films, and that hydroperoxide concentration decreases linearly with film thickness. Temperature has been shown to have a complicated effect on the formation and

Table 1
Shift factors for aging of UHMWPE.

Aging temperature °C	$\ln a_t$	a_t
43	0	1.0
65	3.0	20.1
90	7.2	1339.4
115	9.1	8955.3

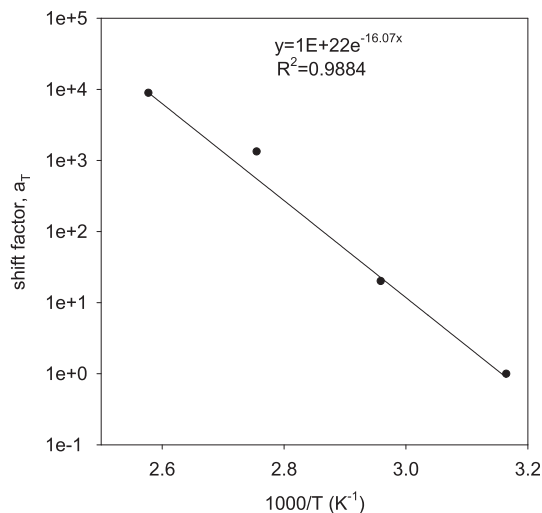


Fig. 3. Plot verifying linearity of the shift factors. Shift factor has no units. Error bars are not shown for clarity of presentation, the standard uncertainty in the data is approximately 5%.

destruction of free and associated hydroperoxides, which may hinder our ability to resolve any hydroperoxides, even though they are expected to form.

The degree of oxidation increases with aging temperature and time, and is identified by the formation of a new peak at 1737 cm^{-1} , which is assigned to an ester. Another shoulder peak is observed at 1713 cm^{-1} , which is identified as a ketone. At least two peaks are superimposed to form a complex FTIR spectrum. Both peaks were treated as Gaussian functions and fitted as shown in Fig. 6. The absorption band around 1737 cm^{-1} is not attributed to a single oxidation product. This band is indicative of the presence of oxidation products from the decomposition of peroxides and hydroperoxides. The baseline oxidation level for this material is evident by the presence of a peak at 1737 cm^{-1} and 1713 cm^{-1} in

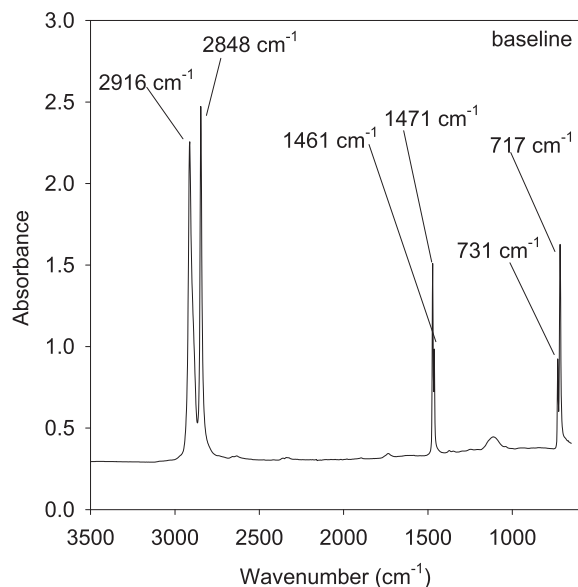


Fig. 4. FTIR spectrum of baseline, or unaged, UHMWPE fiber. The units of absorbance are arbitrary. The characteristic peaks at 2916 cm^{-1} and 2848 cm^{-1} are identified as sp^3 C–H stretching, 1471 cm^{-1} and 1461 cm^{-1} are assigned to C–H bending, 731 cm^{-1} and 717 cm^{-1} are in-phase and out-of-phase C–H rocking, respectively. A small peak around 1125 cm^{-1} is unassigned.

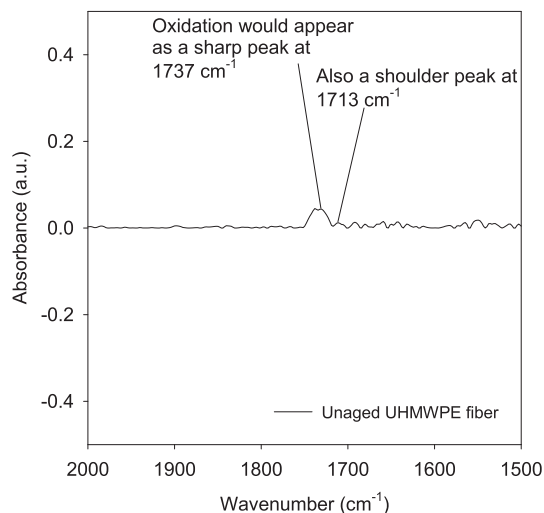


Fig. 5. FTIR spectrum showing baseline oxidation levels for unaged UHMWPE fiber. Standard uncertainty in these measurements is approximately 4 cm^{-1} .

the unaged material, as shown in Fig. 5. It is possible that the peak at 1737 cm^{-1} represents the hindered phenol of an antioxidant. If the antioxidant is present in the baseline material, there are implications for interpreting the oxidation products.

3.1.2. Role of antioxidants in polyethylene

The antioxidants function is based on the hydrogen transfer mechanism, by which the hydrogen atom of the antioxidants hydroxyl group transfers to the polyethylene carbon-centered, peroxy, and alkoxy radicals as shown in Fig. 7 [32–37]. The hindered phenol does not participate in hydrogen transfer reactions, although it may hydrogen bond to some of the oxidation products. The free radical produced from the above reactions is very stable with the alkoxide structure, and is similar to the vitamin E alkoxide radical [38].

The peak analysis presented for $43\text{ }^\circ\text{C}$ in Fig. 6 indicates an increasing of the shoulder at 1713 cm^{-1} . The peak at 1737 cm^{-1} appears to shrink with exposure time. This contradicts the production of multiple hydroxyl containing oxidation products that would increase this peak with time. One suggestion is the decrease in the peak at 1737 cm^{-1} is the consumption of an antioxidant ester. The oxidation analysis of 1713 cm^{-1} (discussed later) does not indicate an induction time for the production of the main ketone band that would be expected for the presence of an antioxidant. However, despite the fact that the oxidation products will continue to increase through various oxidation reactions in the amorphous structure, they will also decompose continuously to CO_2 , CO , and even OH radicals, as shown by the sequence of reactions in Fig. 8 [39]. It should also be mentioned that these reactions take place in the limited amorphous part of the polymer and at the crystalline interfaces. These factors affect the interpretation of the FTIR spectrum in this region. In this material, the available oxygen is limited because the diffusion of oxygen is much lower than the consumption due to the higher crystallinity of this material. Currently, the exact nature of the changes at 1737 cm^{-1} are unknown and remain a convolution of potential degradation or protection mechanisms.

3.1.3. Oxidation index

The intensity of the ketone group generally increases with increasing aging time at $43\text{ }^\circ\text{C}$. Thus, the degree of oxidation of UHMWPE fibers could potentially be quantified by introducing the

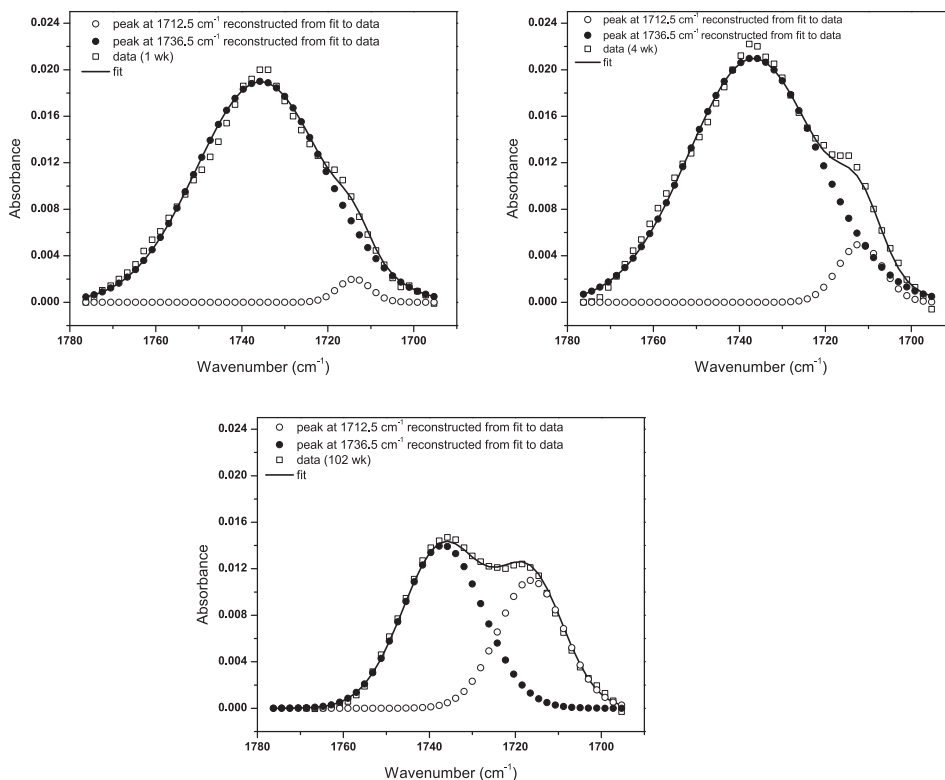


Fig. 6. Curve-resolved FTIR spectra of UHMWPE fiber aged at 43 °C for 1 week (top left), 4 weeks (top right), and 102 weeks (bottom), scale enlarged to show 1680–1780 cm⁻¹ region, where oxidation appears, more clearly. The units of absorbance are arbitrary. The shoulder of this peak is resolved to elucidate the formation of a new peak around 1713 cm⁻¹. Standard uncertainty in these measurements is approximately 4 cm⁻¹.

oxidation index (OI), as used in other artificial aging applications for bulk UHMWPE [3,21,12]. For the purposes of this study, the peak at 1472 cm⁻¹ was used as the reference peak, and the OI is the peak area at 1713 cm⁻¹ divided by the peak area at 1472 cm⁻¹. Equation (2) defines oxidation index. Figs. 9 and 10 show the increase in OI over time for all aging temperatures.

$$OI = \frac{A_{1713\text{cm}^{-1}}}{A_{1472\text{cm}^{-1}}} \quad (2)$$

The OI increased moderately at the lower aging temperatures of 43 °C and 65 °C. For these aging conditions, the OI increased from 0.0002 to 0.0243 and 0.0249, for 43 °C and 65 °C, respectively. For the higher aging temperatures, the OI increased more rapidly. After

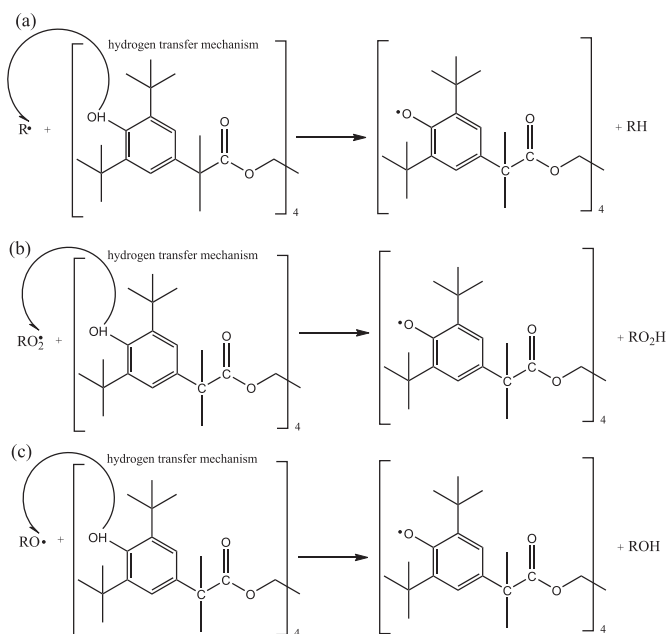


Fig. 7. The hydrogen transfer mechanism by which a common antioxidant, which is likely present in the UHMWPE fiber, works to prevent oxidation [32–37].

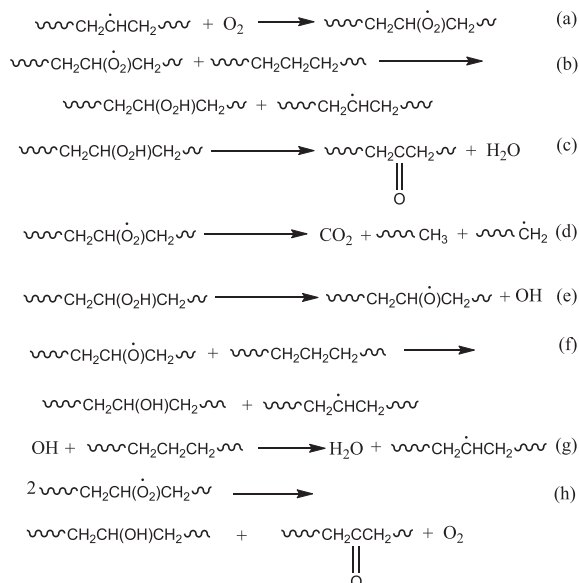


Fig. 8. This series of reactions shows the formation of many of the common scission products due to the oxidation of polyethylene [39].

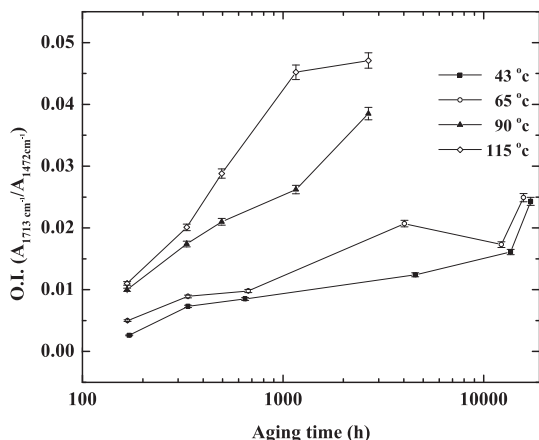


Fig. 9. Changes in oxidation index (OI) for different aging temperatures as a function of time for UHMWPE fibers (log axis). Error bars represent standard combined uncertainty in the FTIR data.

17 weeks of aging at 90 °C, the OI increased from 0.0002 to 0.0385, and for 17 weeks of aging at 115 °C, the OI increased from 0.0002 to 0.0471. Fig. 11 shows the relationship between tensile strength and OI, the higher the aging temperature, the faster the drop in tensile strength, regardless of the OI value. This result might be indicative of changes in morphology at these higher aging temperatures, as described previously.

4. Summary and future work

This work has demonstrated that exposure to elevated temperatures is a valid method for aging UHMWPE fibers. When exposed to elevated temperatures for long periods of time, UHMWPE fibers lose tensile strength, and the Arrhenius model is applicable to predict this phenomenon. However, it is a challenge to identify one aging mechanism responsible for the loss of tensile strength because it is a convolution of oxidation and changes in fiber morphology. This is demonstrated by the behavior of the fibers exposed to 90 °C and 115 °C, which may undergo shrinkage and loss of orientation. Molecular spectroscopy verified that all samples were oxidized by the elevated temperature exposure, however there is not a clear relationship between OI and the change in tensile strength. Therefore, it would be difficult to utilize

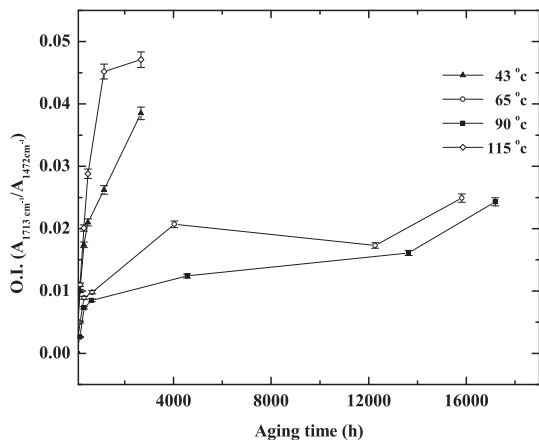


Fig. 10. Changes in oxidation index (OI) for different aging temperatures as a function of time for UHMWPE fibers (linear axis). Error bars represent standard combined uncertainty in the FTIR data.

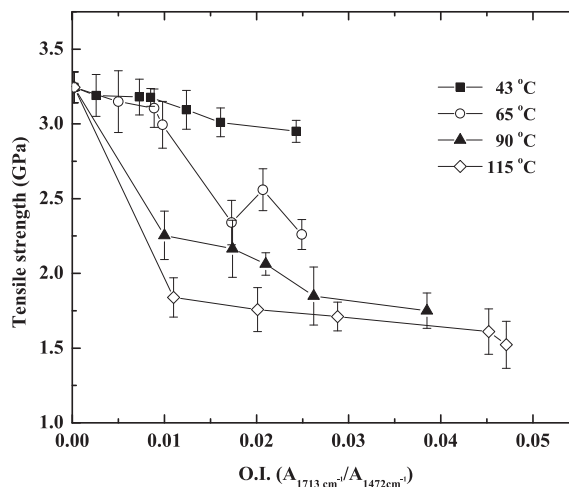


Fig. 11. The relationship between tensile strength and oxidation index at different aging temperatures for UHMWPE fibers. In all cases, as the OI increases, tensile strength decreases. Deviations from the overall in the 65 °C data are not explained. Further work will attempt to measure changes in morphology that may have resulted from this oxidation.

this model to predict failure outside the accelerated environment of the laboratory, unless these two contributing factors can be separately understood and their interactions accounted for in the model. A future paper will detail the changes in thermal properties and morphology of these fibers resulting from this aging experiment, and carefully consider the role of shrinkage. This work verifies that there is potential for oxidation and tensile strength loss in this material when it is exposed to elevated temperatures for long periods of time. These factors should all be considered when using these fibers in applications where this type of environment may be encountered.

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