Effect of Long-Term Natural Aging on the Thermal, Mechanical, and Viscoelastic Behavior of Biomedical Grade of Ultra High Molecular Weight Polyethylene

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ABSTRACT: In the total joint prostheses, Ultra High Molecular Weight Polyethylene (UHMWPE) may undergo an oxidative degradation in the long term. The overall properties of UHMWPE are expected to be altered due to the oxidative degradation. The goal of this study is to investigate the effects of natural aging up to 6 years in air on the thermal, mechanical, and viscoelastic properties of UHMWPE that was used in total joint replacement. The changes in UHMWPE properties due to aging are determined using Differential Scanning Calorimetry (DSC), uniaxial tensile tests, and Dynamic Mechanical Analysis (DMA). The DSC results show that the lamellar thickness and degree of crystallinity of UHMWPE specimens increase by 38% and 12% due to aging. A small shoulder region in the DSC thermograms is remarked for aged specimens, which is an indication of formation of new crystalline forms within their amorphous region. The tensile properties of aged and nonaged UHMWPE specimens show a significant decrease in the elastic modulus, yield, fracture stresses, and strain at break due to aging. The DM testing results indicate that the storage modulus and creep resistance of UHMWPE specimens decrease significantly due to aging. Also, it is remarked that the α relaxation peak for aged UHMWPE specimens occurs at lower temperature compared to nonaged ones. The significant reduction in the strength and creep resistance of UHMWPE specimens due to aging would affect the long-term clinical performance of the total joint replacement and should be taken into consideration during artificial joint design. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 17–24, 2010

Key words: natural aging; UHMWPE; DSC; DMA; tensile properties

INTRODUCTION

Ultra High Molecular Weight Polyethylene (UHMWPE) has been the material of choice for polymer-on-metal bearing surfaces in joint replacement implants for the last three decades.[1] Its microstructure, based on extremely high molecular weight, confers optimal properties such as high wear and fatigue resistance and high fracture toughness.[2] These properties make UHMWPE the preferred candidate to articulate against metallic or ceramic femurs. Therefore, the growing demand for UHMWPE as a bearing material for total joint replacement has led to active research for the characterization and the development of its mechanical and tribological properties.[3–9] However, wear and degradation of UHMWPE in the artificial joint still limit the in vivo service and duration of total joint replacement.[10,11]

It is known that UHMWPE has a viscoelastic behavior even under normal loading conditions and its overall mechanical properties change over a period of time due to natural aging either on shelf or in vivo. The natural aging of UHMWPE causes subsurface oxidative degradation (between 1 and 2 mm) under the polymer surface.[2] This oxidative degradation causes embrittlement of the polymer and loss of its overall mechanical properties. The characterization of natural aging effects on the elastic and viscoelastic behavior of UHMWPE will help in the determination of the in vivo penetration nature of the metallic femur in UHMWPE cup. The changes in polymer properties due to aging will results in change in the penetration depth and accordingly the contact stress at the UHMWPE cup. The changes of contact stress at UHMWPE cup affects the wear rate of total joint prostheses that is considered the main reason of joint failure.[12–14] Therefore, the changes in UHMWPE mechanical and viscoelastic behavior due to long-term natural aging are thought to play an important role in the long-term clinical performance of the total hip joint replacement.

Because oxidation of UHMWPE (due to natural aging) takes months or years to reach an appreciable

level at ambient or body temperature, thermal aging techniques have been developed to accelerate the oxidation of UHMWPE with the expectation that the material behavior after accelerated aging will be comparable to naturally aged ones. Based on this assumption, accelerated thermal aging has been widely used by many researchers to investigate the resistance of UHMWPE to aging.[1,15–17] Using this aging technique, from 5 to 10 years of shelf aging can be simulated within a time period of one week. Also, the aging of polymer that performed at 80°C for 23 days has found to be equivalent to approximately 8 years shelf aging.[1] Meanwhile, many researchers have highlighted certain limitations of accelerated thermal aging techniques.[18,19] For example, thermal aging of UHMWPE is considered as a severe oxidative process compared to natural aging. Also there are substantial differences between the crystalline microstructure of thermally aged and naturally aged UHMWPE. Due to such limitations, the author thought that it is important to study the effects of real time natural aging on the properties of UHMWPE. This will help in understanding the long-term performance of the artificial hip joint especially for more active patients and limit the revision operations of the hip joint replacement.

The main goal of this research is to study the effects of long-term natural aging in air for 6 years (instead of accelerated aging) on the thermal, mechanical, and viscoelastic behavior of UHMWPE. Identifying the UHMWPE behavior after long-term natural aging will help in understanding the long-term performance of artificial joints that contain UHMWPE.
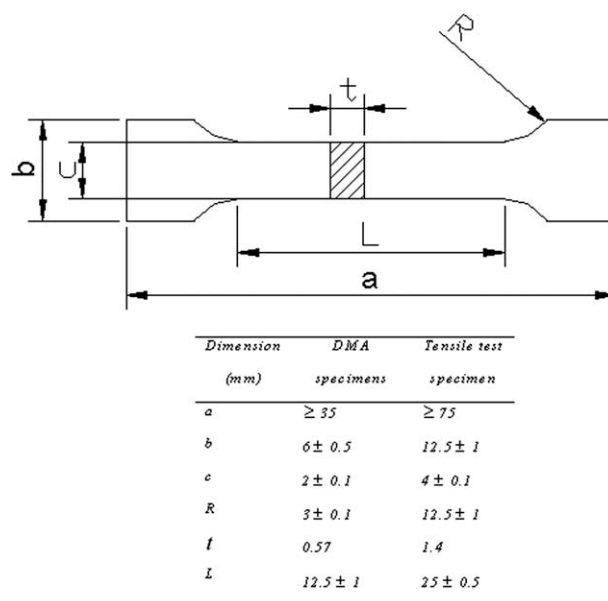
EXPERIMENTAL WORK

Material and specimen preparation

The UHMWPE material (GUR 410 Medical grade) used in the present study is supplied by Junfer Company, Vienna, Austria. This material is available in sheet form with thickness of 0.57 mm and various lengths. The material is made by pressure-less belt sintering technique followed by compression to form the UHMWPE sheets with the required thickness. The reported molecular weight of GUR 410 varies from 5 to 6×10^6 g/mol. The density of the melt-crystallized polymer is about 0.94 g/mm^3. The specimens used for mechanical and viscoelastic properties characterization are formed using a sharp knife die with the standard dimensions as shown in Figure 1.

Aging procedure

Real time natural aging of UHMWPE specimens is performed (in Egypt) at 25 ± 3°C and humidity of 80% ± 5 for a period of 6 years in air with the aim of increasing the diffusion of oxygen into the tested specimens. The characterizations of nonaged

Dimension (mm)	DMA specimens	Tensile test specimen
a	≥ 35	≥ 75
b	6 ± 0.5	12.5 ± 1
c	2 ± 0.1	4 ± 0.1
R	3 ± 0.1	12.5 ± 1
t	0.57	1.4
L	12.5 ± 1	25 ± 0.5

Figure 1 Tensile specimens (a) quasi-static and (b) DMA specimens (EN ISO 527-2).

UHMWPE specimens are performed in 2003.[20] The aged UHMWPE specimens are tested in 2009. Although several researches argued that 2 years natural aging of PE is sufficient to cause remarkable changes in their properties, the author thinks that 6 years natural aging will have more remarkable effects on the tested material properties.

Characterization methods

Calorimetric measurements for aged and nonaged UHMWPE specimens are performed by means of Differential Scanning Calorimetry (DSC-7 series, Thermal Analysis System, Perkin Elmer, Covina, California, USA). Each sample of UHMWPE (5–10 mg) is sealed in an aluminum pan and heated from 25 to 145°C at rate of 5°C/min, then cooled down to 30°C at cooling rate of 5°C/min. The DSC samples are taken from the cross section of UHMWPE sheet, which has 0.57 mm thickness. Previous results indicated that the natural aging causes subsurface degradation under the polymer surface up to 2 mm in depth.[2] So, the oxidation is expected to be homogenous through the UHMWPE specimen thickness. The heat of fusion is calculated by integrating the area under the DSC endothermic peak for the first heat. The melting temperature is registered as the maximum point of the endothermic melting peak. The percent crystallinity is calculated by normalizing the heat of fusion to that of 100% crystalline PE (290 J/g). By measuring the melting point of UHMWPE, the crystalline lamellar thickness, L$_c$ is estimated using the Thomson-Gibbs equation.[21,22]

$$T_m = T_{mo} \left(1 - \frac{2\sigma}{L_c \Delta H_m^o} \right)$$

where T_m is the melting point of the polymer, T_{mo} is the equilibrium melting point of perfect crystalline polyethylene, σ is the specific surface energy and ΔH_m^0 is the enthalpy of melting of a perfect crystalline polyethylene. Lamellar thickness is estimated by considering $T_{\mathrm{mo}} = 145.7°C$, σ 93×10^{-7} J/cm^2 and ΔH_m^0 is taken to be 89.3 J/cm^3 ≈ 290 J/g.[2,22]

Tensile tests of aged and nonaged UHMWPE specimens are carried out on a universal testing machine at cross head speed of 3 mm/min up to fracture at room temperature. The elastic modulus, yield stress, fracture stress, and strain at break are calculated according to Ref. 20. At least three specimens are tested for each group of UHMWPE specimens and displayed as mean ± standard deviation.

The viscoelastic behavior (storage, loss modulus, and creep-recovery behavior) of aged and nonaged UHMWPE specimens is characterized by using Dynamic Mechanical Analysis (DMA Model 2980 TA Instrument, New Castle, Delaware, USA). The UHMWPE specimens are tested over a frequency range from 0.01 to 100 Hz at temperature ranges from 30 to 100°C using a heating rate of 1°C/min.

The DMA is also used to measure the creep-recovery behavior of aged and nonaged UHMWPE specimens by applying a stress of 2.5, 5, and 10 MPa for a period of time equal to 240 min at 37°C (human body temperature). The recovery behavior of UHMWPE specimen is measured for a period of 240 min after removing the applied stress. The creep compliance $J(t)$ is also frequently applied to describe the creep performance of material. The creep compliance is defined as the time dependent strain $\varepsilon(t)$ divided by the applied stress σ as follows:

$$J(t) = \frac{\varepsilon(t)}{\sigma}$$

In the present work, the recoverable creep compliance $J_r(t)$ is determined after load removal for aged and nonaged UHMWPE as a function of time according to the following equation:

$$J_r(t) = \frac{\varepsilon_r(t)}{\sigma} = \frac{\varepsilon_c(t) - \varepsilon_f(t)}{\sigma}$$

where $\varepsilon_c(t)$ is total creep strain just before stress removal, $\varepsilon_f(t)$ is the residual strain after strain removal, and $\varepsilon_r(t)$ is the recovery strain.[23]

RESULTS AND DISCUSSIONS

Calorimetric analysis

In the present work, the DSC thermograms of tested material are divided into two groups. The first is the nonaged UHMWPE specimens that shows an endothermic peak at $T = 132.8°C$, average enthalpy ΔH of 159.5J/g, a crystallinity percentage of 55% and estimated lamellar thickness of 23.5 nm. The second is the 6 years natural aged UHMWPE specimens that shows an endothermic peak at $T = 136.3°C$, average enthalpy ΔH of 194 J/g, a crystallinity percentage of 67%, and estimated lamellar thickness of 32.6 nm. The values of percentage crystallinity, melting temperature as well as the estimated lamellar thickness for aged and non-aged UHMWPE specimens are presented in Table I. From these results, it can be concluded that the melting temperature, enthalpy, and crystallinity percentage after 6 years of natural aging are 3%, 22%, 12% higher than their values for nonaged specimens, respectively. Also the estimated lamellar thickness increased by 38% due to long-term aging. In general, larger lamellar thickness corresponds to higher melting temperature, chain regularity and crystallinity, and vice versa.[2,22,24] The changes in the aged UHMWPE DSC results can be attributed to the oxidation and chain scission of the tested material due to long-term natural aging. The tested polymer chain scission process allows further crystal perfection and growth to occur. Therefore, the aged UHMWPE has higher degree of crystallinity compared to nonaged material.[24]

A comparison between the DSC thermograms for the first heat of aged and nonaged UHMWPE specimens is shown in Figure 2. The small shoulder in the DSC thermograms of aged UHMWPE may reflect the presence of new crystallites produced by chain scission process that generates shorter molecular chains. As a result, new crystallization can occur in the amorphous region with crystals shorter than the original lamella. The chain scission produces an overall decrease in tie molecules, allowing for lamellar rapprochement and reordering resulting in an increase of the melting temperature as indicated in the DSC results.[23]

Tensile tests results

The engineering stress-strain behavior of nonaged UHMWPE specimens at quasi-static conditions is

TABLE I
Tensile and Thermal Properties of Nonaged and Aged UHMWPE Specimens

Property	Young's modulus (MPa)	Yield stress (MPa)	Fracture stress (MPa)	Fracture strain	Crystallinity	Melting temperature (°C)	Lamellar thickness, L_c (nm)
Nonaged specimen	1136 ± 30	20.4 ± 0.25	25 ± 0.3	1157 ± 40	55%	132.84	23.5
Aged specimen	790 ± 12	18.2 ± 0.33	20.1 ± 0.4	880 ± 31	67%	136.3	32.6
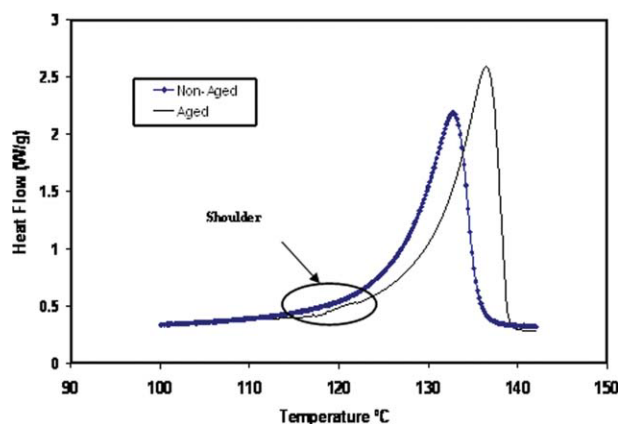
Figure 2 Thermograms of aged and nonaged specimen of UHMWPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

studied before by the author in 2003.[20] Herein, additional results for the tensile behavior of 6 years naturally aged UHMWPE material are reached to give sufficient data about the behavior of UHMWPE. Compared to nonaged specimens, the long-term natural aging of UHMWPE results in significant changes in the tensile behavior of the tested material. These changes are characterized by a remarkable reduction in the elastic modulus, yield stress, fracture stress, and ductility of aged UHMWPE specimens compared to nonaged ones. Table I contains the mean values and standard deviations of elastic modulus, yield stress, fracture stress, and strain at break that obtained from the tensile testing of UHMWPE specimens. The tensile tests show that all aged and nonaged UHMWPE specimens are deformed in a ductile manner with formation of neck in the specimen central region. The neck is expanded to the specimens gauge length with deformation. The yield, fracture stresses and strain at break are shifted to lower values due to aging. A significant decrease in the value of the elastic modulus is recorded for aged specimens compared to nonaged ones. From Table I, it can be found that the elastic modulus and yield stress after 6 years of natural aging are 49% and 8% lower than their corresponding values for the nonaged specimens, respectively. Also, the fracture stress and strain at break of aged specimens are 25% and 18.5% lower than their corresponding values for nonaged specimens, respectively. Similar results are obtained by Edidin et. al.[18] where, the fracture stress, yield stress, and strain at break showed a remarkable decrease in their values due to natural and accelerated aging. In contrast with the present results, only the values elastic modulus that obtained by Edidin et. al.[18] showed an increase in their values due to aging. These differences in the elastic modulus results can

be attributed to the different aging technique that used by Edidin et. al.[18] compared to the present aging method.

The reductions in the mechanical properties of long-term naturally aged UHMWPE specimens are regarded to the material oxidation and its corresponding chain scission. The chain scission process results in an increase of polymer crystallinity (due to lamella thickening), breakage of the polymer long chains, reduction of tie molecules, reduction in the tested material molecular weight, increasing material brittleness, and weakening their properties.[25] On the other hand, it is known that the elastic modulus is essentially determined by the proportion of extended chain tie molecules that produce links in the axial direction between crystalline blocks (spherulites).[26] The aging of polymer results in chain scission, which produces an overall decrease in the tie molecules. Therefore, the reduction in the elastic modulus that remarked in the present study is regarded to the decrease in the tie molecules due to long-term aging.

Dynamic mechanical properties

Storage and loss modulus

The tensile dynamic mechanical properties of nonaged UHMWPE are studied before by the author underlining the issue of preheat treatment effects on the tested material properties.[20] Herein, additional results are presented, mainly the effects of long-term natural aging on the viscoelastic properties of the tested polymer. Plots of the storage modulus (E′) and the loss modulus (E″) at different frequencies for aged and nonaged UHMWPE material are presented in Figure 3. These results are carried out at frequencies ranging from 0.01 to 100 Hz at normal body temperature (37°C). The results show a strong dependence of the tested material viscoelastic behavior on the testing frequency (loading rate). The storage modulus increases significantly due to increasing the testing frequency while the loss modulus significantly decreases. These results confirm that the viscoelastic behavior of UHMWPE is strain rate dependent. Compared with the nonaged UHMWPE specimen response, long-term natural aging results in significant reduction on the tested material storage modulus for all testing frequencies as indicated in Figure 3. Similar reduction in UHMWPE loss modulus is also remarked due to aging, especially at low testing frequencies. At higher frequencies, there are no remarkable effects for natural aging on the loss modulus. The reduction in the tested material storage and loss modulus due to aging can be justified by the polymer chain scission and the
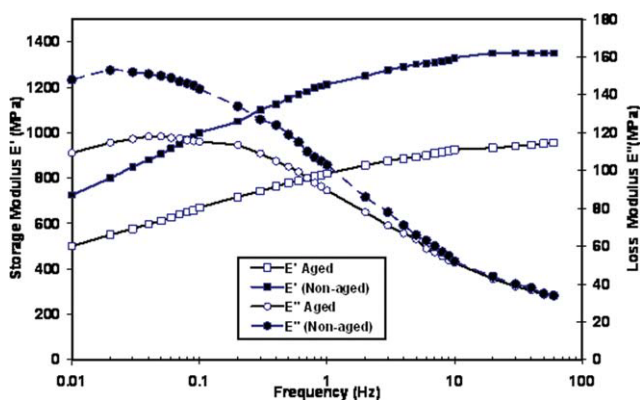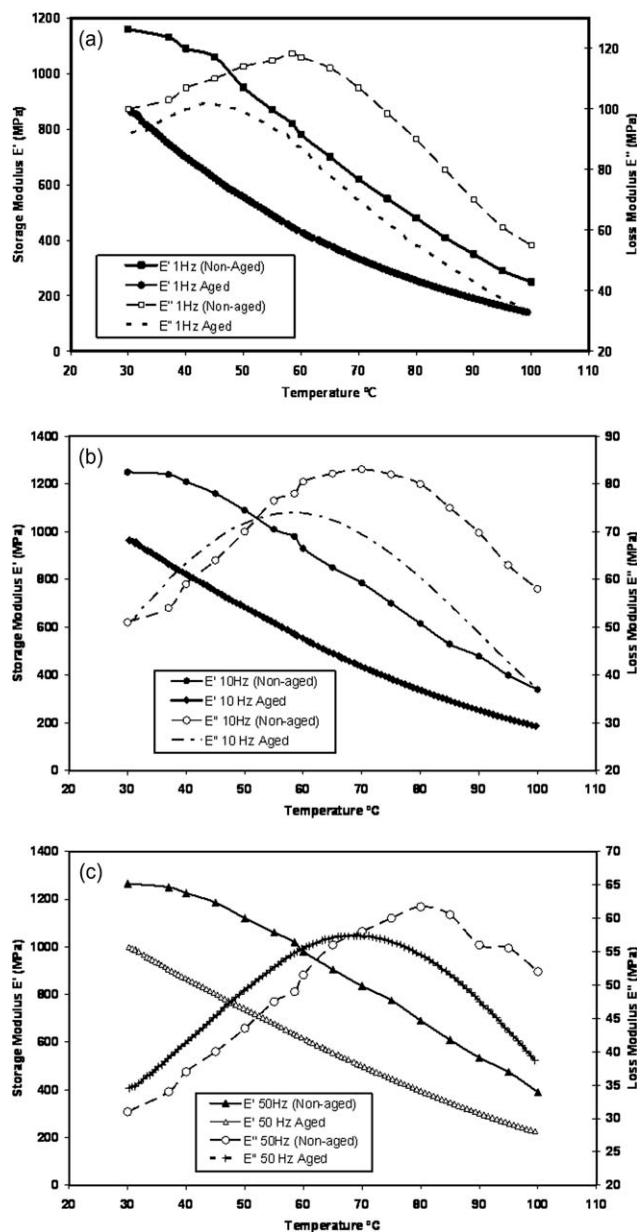
Figure 3 Comparison between storage and loss modulus for aged and nonaged UHMWPE against frequency at 37°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

corresponding reduction of tie molecules due to long-term natural aging.

A comparison between the storage and loss modulus results for aged and nonaged UHMWPE specimens with temperatures at frequencies of 1, 10, and 50 Hz are shown in Figure 4(a–c), respectively. The results show that for all testing frequencies, the storage modulus of aged UHMWPE specimens has lower value than that for the nonaged specimens at the same testing conditions. Significant reduction in the loss modulus results is remarked due to aging especially at higher temperature. Also, the results show that the storage modulus for both aged and nonaged UHMWPE specimens increases with increasing the testing frequency and decreases with increasing the testing temperature. The increase of storage modulus with increasing the testing frequency is regarded to the strain rate dependent nature of the tested polymers. The reduction in the values of storage and loss modulus that obtained at higher temperature can be justified by the higher mobility of polymer chains at elevated temperature.

From the loss modulus results that shown in Figure 4, an α relaxation (indicating strong mobility of polymer molecules) is obviously remarked for both aged and nonaged UHMWPE specimens. It is known that the relaxation of polymer is usually associated with motion of loose folds at lamella surface. The α relaxation is associated with interlamellar shear process and indicated by the peak in the loss modulus curves.[27] The UHMWPE α relaxation occurs at temperatures ranging from 58 to 88°C for nonaged specimen and from 43 to 71°C for aged UHMWPE specimen depending on the testing conditions. The relation between α relaxation temperature and testing frequency for aged and nonaged UHMWPE specimens is plotted in Figure 5. It is evident in Figures 4 and 5 that as the frequency

increases the position of α relaxation moves to higher temperature for both aged and nonaged UHMWPE specimens. This phenomenon indicates that the polymer chains need more energy to respond to the shorter timescale stresses imposed at higher frequencies. These results agree with,[27] where the α relaxation of different types of PE occurs at temperatures ranging from 50 to 120°C depending on the testing frequency. The reduction in α relaxation temperature due to aging can be regarded to

Figure 4 (a) Comparison of storage and loss modulus for aged and nonaged UHMWPE at 1 Hz against temperature. (b) Comparison of storage and loss modulus for aged and nonaged UHMWPE at 10 Hz against temperature. (c) Comparison of storage and loss modulus for aged and nonaged UHMWPE at 50 Hz against temperature.
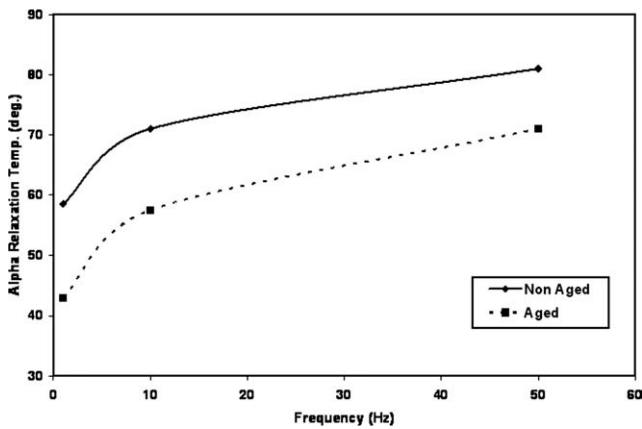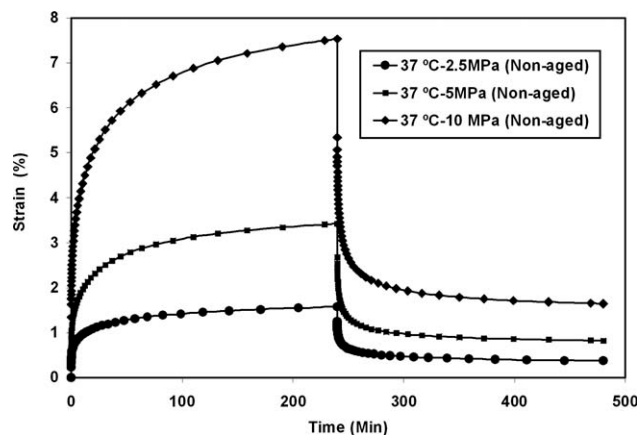
Figure 5 Variation of a relaxation temperature with frequency for aged and nonaged UHMWPE specimens.

Figure 7 Creep and partial recovery strain after removal of the stress for aged UHMWPE against time at different stress levels at 37°C.
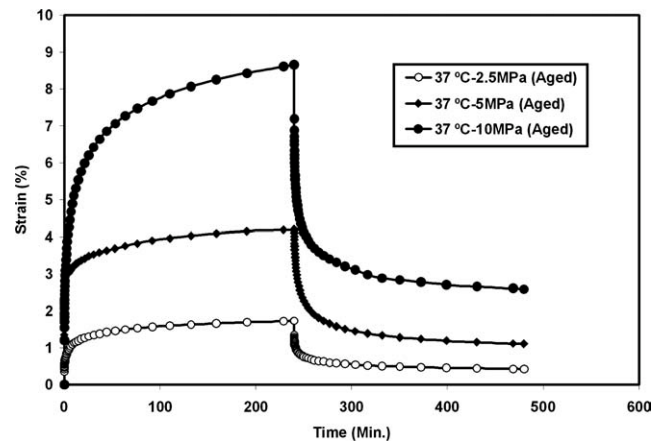
the chain scission which results in the reduction of the quantity and effectiveness in supporting load of the available tie molecules, breakage of the polymer long chains, reduction in the tested material molecular weight, increasing material brittleness, and weakening their properties.

Creep and recovery behavior

Figures 6 and 7 show the creep-recovery response of nonaged and aged UHMWPE specimens that obtained at different loading conditions. The tests are carried out at constant stress levels of 2.5, 5, and 10 MPa and at temperature of 37°C (human body temperature). The results show an initial elastic deformation and following this, the strain slowly increases as long as the stress is maintained. After stress removal (at 240 min of loading), the elastic strain is quickly recovered, and the portion of the creep strain is recovered slowly in the course of

time. The creep test results indicated that the creep strain for both nonaged and aged UHMWPE increases (or the creep resistance decreases) with increasing the applied stress. The total creep strain at 240 min (end of loading duration) at stress of 10 MPa was nearly twice its corresponding value at 5 MPa. Also the total creep strain at 240 min at stress of 5 MPa equals twice its corresponding value at 2.5 MPa.

For all the testing conditions, it can be remarked that the creep resistance of UHMWPE decreases significantly due to long-term aging. The creep strain of aged UHMWPE after 240 min of loading at stress level 2.5, 5, and 10 MPa increases by 15%, 17.7%, and 10%, respectively when compared with nonaged specimen. Also, the residual remaining strain for aged UHMWPE increases by 12%, 34%, and 56%, respectively when compared to nonaged specimens at the same testing conditions. The reduction of creep resistance of aged UHMWPE specimens can
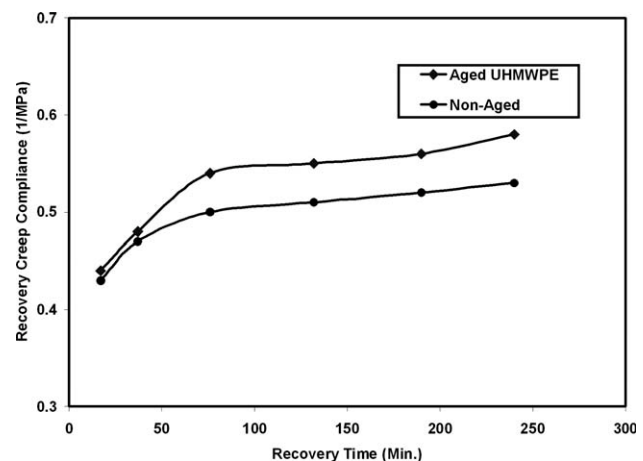

Figure 6 Creep and partial recovery strain after removal of the stress for nonaged UHMWPE against time at different stress levels at 37°C.
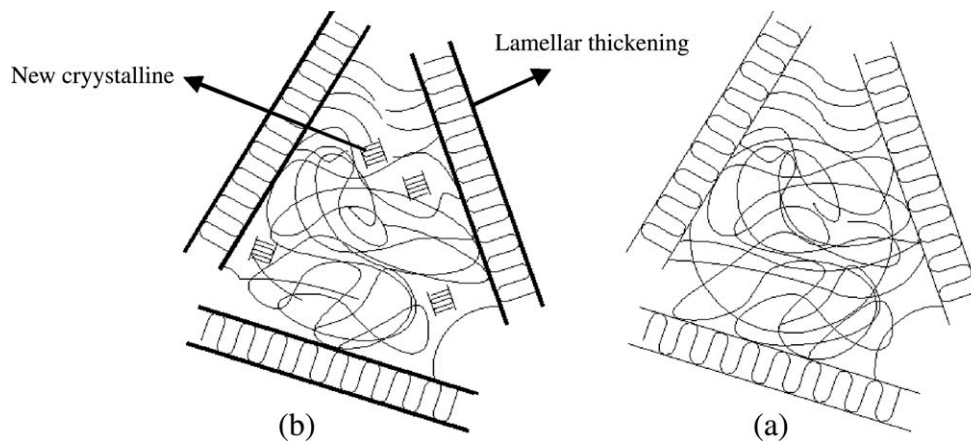

Figure 8 Variation of recovery creep compliance with time for aged and nonaged UHMWPE after stress removal at 37°C.

Figure 9 Schematic drawings of UHMWPE proposed model for microstructure (a) nonaged specimens (b) 6 years aged specimens.

be regarded to the reduction of tie molecules in the polymer amorphous region due to aging.

It is known that, the recoverable creep is usually associated with stretching in the amorphous region. Therefore, it is expected that the amorphous region in the aged UHMWPE will be more stretchable than the nonaged one. This expectation is confirmed by the recovery creep compliance results for aged and nonaged UHMWPE that shown in Figure 8. The recovery creep compliance of aged UHMWPE has higher value than that for nonaged ones confirming the chain scission expectation and reduction of tie molecules in the aged UHMWPE.

Proposed degradation mechanism

In the present work, the proposed degradation mechanism of UHMWPE can be schematically represented as indicated in Figure 9(a,b). Figure 9(a) shows the nonaged UHMWPE microstructure that is considered as any semi-crystalline polymer with crystalline and amorphous phases. The crystalline phase consists of folded long chains added to thin orthorhombic crystals (lamellae). These lamellae are randomly oriented and connected with tie molecules that form the amorphous phase. These tie chain improves the mechanical properties of UHMWPE.

Due to long-term aging a lamella thickening is observed as indicated in Figure 9(b). In the meantime, the chain scission results in shorter molecules with higher mobility. Those few chains tend to recrystallize during the aging time resulting in an increase of the total crystallinity of polymer. The scission of tie molecules that connects the lamellae results in reduction of the tie molecules quantity and effectiveness in supporting load and then reduction of the material mechanical properties. The possibility of the presence of small crystallites within the amorphous region due to aging is expected for aged specimens. This expectation is supported by the presence of small shoulders in the DSC results of aged UHMWPE specimens.

CONCLUSIONS

Based on the experimental findings of this work, it can be concluded that the increase of the degree of crystallinity of UHMWPE due to long-term natural aging can be justified by the lamella thickening phenomenon. This phenomenon stems from the chain scission of UHMWPE chains during aging. This chain scission results in shorter molecules with higher mobility. Those few chains tend to recrystallize during the aging time resulting in an increase in the UHMWPE total crystallinity. The phenomenon of chain scission during aging also results in the reduction of the quantity and effectiveness in supporting load of the available tie molecules, breakage of the polymer long chains, reduction in the tested material molecular weight, increasing material brittleness, and weakening their properties. The changes in the above parameters justify reduction of α relaxation temperature, elastic and storage modulus, yield and fracture stresses, and creep resistance in spite of the increase in the tested material crystallinity.

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