



Enhanced interfacial shear strength in ultra-high molecular weight polyethylene epoxy composites through a zinc oxide nanowire interphase

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ABSTRACT

The mechanical properties of fiber-reinforced composites are largely dictated by fiber-matrix interactions, where a well-adhered interface is desired. Ultra-high molecular weight polyethylene (UHMWPE) fibers suffer from poor interfacial properties due to their smooth and inert surface. Therefore, enhancing the interfacial properties of such composites will lead to an increased use in structural applications where high modulus, tenacity, low density, high impact and abrasion resistance properties are needed. In this work, an interfacial modification process consisting of an oxygen plasma surface functionalization followed by the grafting of zinc oxide nanowires (ZnO NWs) onto the UHMWPE fiber surface is investigated to improve the fiber-matrix interaction in UHMWPE composites. The UHMWPE fiber surface is subjected to varying oxygen plasma treatment durations such that the surface oxygen content can be increased to improve ZnO NW adhesion. Through single fiber pullout testing, the interfacial shear strength (IFSS) of oxygen plasma functionalized and ZnO NW coated UHMWPE fibers was shown a maximum increase of 135% with a 30 s plasma treatment prior to ZnO NWs. This increase in IFSS is attributed to an increased surface area interaction and mechanical interlocking between the fiber and matrix. The results detailed in this work demonstrate a benign, simple, and effective way to significantly improve the interfacial properties of UHMWPE fiber reinforced composites.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) fibers have gained significant attention as a suitable material in a wide range of industries including automotive, aerospace, marine, forestry, medical and military applications [1–8]. UHMWPE fibers are implemented in these industries primarily due to their tenacity, high-impact and abrasion resistance, low density, low fatigue and creep propagation and low moisture absorption [1–8]. However, due to their low surface energy, high crystallinity, and chemical inertness, UHMWPE fibers suffer from poor resin wetting and weak adhesion to the matrix which limits the structural applications of their corresponding polymer-matrix composites [6,9,10]. As a result, failure in UHMWPE composites is typically initiated at the level of the fiber-matrix interface due to the absence of chemical bonding and a lack of mechanical interlocking, severely weakening their performance in structural applications [11–13]. Consequently, it is important to modify the fiber-matrix interactions in UHMWPE fiber-reinforced composites, such that their overall

performance is improved and their potential applications are expanded.

In an effort to improve the fiber-matrix interface of UHMWPE composites, researchers have employed various treatments: dry chemical, wet chemical and multiscale fiber surface modifications. Wet and dry chemical treatment methods introduce functional groups and roughness to the UHMWPE fiber surface to increase chemical bonding and mechanical interlocking with the polymer matrix. Dry chemical treatment techniques include plasma treatment [14–18], corona discharge [19–21], ultraviolet-irradiation [22,23], and gamma irradiation [24]. Wet chemical treatment techniques include chemical grafting [25,26], oxidative acid etching [27,28], and coating treatments [29–31]. Multi-scale fiber surface modification consists of the application of nano-material reinforcements which add enhanced surface area and mechanical interlocking interactions with the matrix. Shanmugam et al. coated UHMWPE fibers with 0.03% of multiwalled carbon nanotubes (MWCNTs) that were embedded in a dopamine solution. Through transverse fiber bundle testing, it was shown that the bonding between the UHMWPE fibers and the matrix was improved by 42.5%, relative to

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untreated UHMWPE fibers [32]. However, higher weight fractions of MWCNTs resulted in a heavily entangled uneven coating that led to poor resin wetting. Ahmadi et al. modified the epoxy matrix of UHMWPE composites with MWCNTs that were chemical treated with glycidyl methacrylate (GMA) and amino-thiol using free radical polymerization, which produced an interfacial shear strength (IFSS) increase of 336% [33]. Mohammadalipour et al. grafted GMA onto the UHMWPE fibers, modified the polymer matrix with nano clay, and used microdroplet tests to show that with 3% nano clay, the IFSS increased by 228% [34]. Zhang et al. trapped nano-silicon dioxide (1%) on the surface and diffused into the UHMWPE fibers during the gel spinning process. The IFSS, measured through a single fiber pullout test, increased by 148% relative to untreated UHMWPE fibers, but an increase in the nano-silicon dioxide concentration resulted in a decrease in the fiber's mechanical properties [35].

Alternatively, researchers have demonstrated the effectiveness of zinc oxide nanowires (ZnO NWs) as a reinforcing material in fiber-reinforced composites [36–43]. Lin et al. demonstrated that by providing enhanced mechanical interlocking abilities and increased surface area interaction, a ZnO NW interphase can improve the IFSS of carbon fiber reinforced composites by 133% [38]. The ZnO NWs also reduced the stiffness gradient, resulting in a reduction of stress concentrations at the interface between the varying fiber and matrix materials [44]. Later, Galan et al. optimized the nanowire morphology and improved the IFSS of ZnO NW reinforced carbon fiber composites by 228% [39]. It was also demonstrated that the use of ZnO NWs can enhance the IFSS of aramid fiber reinforced composites by 51% [41]. Swaminathan et al. reported that a ZnO NW interphase with a glass fiber reinforcement could increase the IFSS by 430% [43]. Nasser et al. evaluated ZnO NW coated carbon and glass fiber-reinforced composites under varying strain rates during single fiber pullout tests. This testing showed that the IFSS increased at low strain rates (benefiting structural performance) and decreased at high strain rates (beneficial under ballistic loading conditions), therefore demonstrating the use of ZnO NWs as a multifunctional material [36,37]. These results clearly highlight the use of a ZnO NW interphase to improve the IFSS of fiber-reinforced composites and indicates a potential reinforcement for UHMWPE fiber composites.

This work characterizes the interfacial properties of oxygen plasma treated and ZnO NW coated UHMWPE fiber-reinforced composites. The UHMWPE fibers were functionalized by oxygen plasma for various treatment durations to introduce oxygen functional groups to the UHMWPE fiber surface. The post-functionalized surface chemical structure is examined using Fourier-transform infrared spectroscopy (FTIR), while the concentration and types of oxygen functional groups on the surface of the UHMWPE fiber were characterized by X-ray photoelectron spectroscopy (XPS). Through a hydrothermal growth method, the ZnO NWs were then grown on the oxygen plasma treated fiber and the morphology and uniformity of the growth were characterized using a scanning electron microscope (SEM). The mechanical properties of the fibers were tested using single fiber tensile tests, which demonstrated the property preservation post oxygen plasma treatment. The IFSS of the ZnO NW coated UHMWPE fiber with various oxygen plasma functionalization durations was measured through the use of single fiber pullout tests and the IFSS was shown to increase when compared to untreated UHMWPE fibers. Finally, SEM images of the surface following pullout were taken to analyze the interfacial failure mechanism. The results of this work demonstrate a simple and effective surface functionalization and nanowire coating of the UHMWPE fiber-reinforced composite, which significantly increases the IFSS.

2. Experimental

2.1. UHMWPE surface functionalization and ZnO NWs growth

UHMWPE fibers were first cleaned to remove any contaminants

through sonication in acetone and then ethanol, followed by drying in an oven at 80 °C for 1 h. The fibers were then functionalized through an oxygen plasma treatment to introduce oxygen functional groups onto the UHMWPE surface. The fibers were treated for varying treatment durations (15 s, 30 s, 60 s and 90 s) in an SPI Plasma Prep II with an oxygen atmosphere of 99.6% purity. The effect of the plasma functionalization treatment on the chemical structure of the UHMWPE fiber surface was investigated through FTIR using a Nicolet iS50 spectrometer with a SMART diamond ITR attachment. To investigate the presence and concentration of oxygen functional groups added to the surface of the UHMWPE fiber after plasma functionalization, XPS was performed using a Kratos Axis Ultra XPS with an X-ray neutralizer that compensated for any charge loss and an Al K α (1486 eV) monochromatic X-ray source. All binding energy peaks were constrained to a full width-half max of 1.1 eV–1.7 eV and the curves were fitted using CASA XPS software with a Gaussian 70%-Lorentzian 30% curve mixture.

Following the plasma treatment, single UHMWPE fibers were attached to a Teflon frame using 5-min epoxy, with one end of the fiber left unbonded and free (Fig. 1). The Teflon frame was then dipped in a ZnO nanoparticle (NP) seeding solution [45]. The ZnO NP solution was prepared of 0.0014 M of zinc acetate (Zn(CH₃CO₂)₂) and 0.0057 M of sodium hydroxide (NaOH) at a mixing ratio of 18:7, respectively. The Teflon frame with the fibers attached was then dipped into the seeding solution 3 times with annealing at 85 °C for 10 min in between dipping. After dipping, the fibers were dried for 1 h at 85 °C. The ZnO NWs were then grown on the UHMWPE fibers using a hydrothermal growth method, where the hydrothermal growth solution consisted of an aqueous solution of 2 mM of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 2 mM of hexamethylenetetramine (C₆H₁₂N₄), and 2 mM of polyethyleneimine (H(NHCH₂CH₂)_nNH₂). The UHMWPE fibers on the Teflon frame was placed inside a glass beaker that was filled with the ZnO NW hydrothermal growth solution and placed into an oven at 85 °C for 5 h. After the growth, the fibers were rinsed with deionized water and dried at 85 °C for 2 h. The full process schematic is shown in Fig. 1. The uniformity and morphology of the ZnO NWs grown on the UHMWPE fibers were then examined through SEM using a JEOL JSM-7800FLV.

2.2. Tensile and interfacial shear strength tests

The tensile strength preservation of plasma functionalized and ZnO NW coated UHMWPE fibers was evaluated using single fiber tensile tests. The UHMWPE single fibers were placed between two 38 mm × 13 mm sandpaper tabs at gauge length of 12.7 mm and bonded using a high shear strength epoxy (Loctite® 9430™ Hysol), cured at 82 °C for 1 h. The samples were then loaded on a 5982 Series Instron load frame and clipped with alligator clips to ensure that no slipping occurred during testing. The samples were tested with a 5 N load cell at a rate of 0.016 mm/s (Fig. 5A).

The single fiber pullout method was used to measure the IFSS of the plasma functionalized and ZnO NW coated UHMWPE fibers embedded in an epoxy matrix. The free end of the UHMWPE fibers from the Teflon frame were inserted into a slit in a silicon mold and the embedded length was modified using an optical microscope. Epon 862 resin and Epikure 3230 curing agent, at a ratio 100:35, were added to the silicon mold and cured at 80 °C for 8 h. Once the samples were cured, the epoxy block with the UHMWPE fiber embedded were removed from the silicon mold, and the same Epon 862 and Epikure 3230 epoxy mixture (ratio 100:35) was used to create tabs on the free end of the fiber (Fig. 6A). A large tab, a minimum of 33x larger than the fiber embedded length, was constructed to ensure fiber pullout occurred instead of fiber slippage within the tab. The single fiber pullout samples were mounted on a 5982 Series Instron frame, clipped with an alligator clip and tested using a 5 N load cell at a rate of 0.016 mm/s, as seen in Fig. 6A.

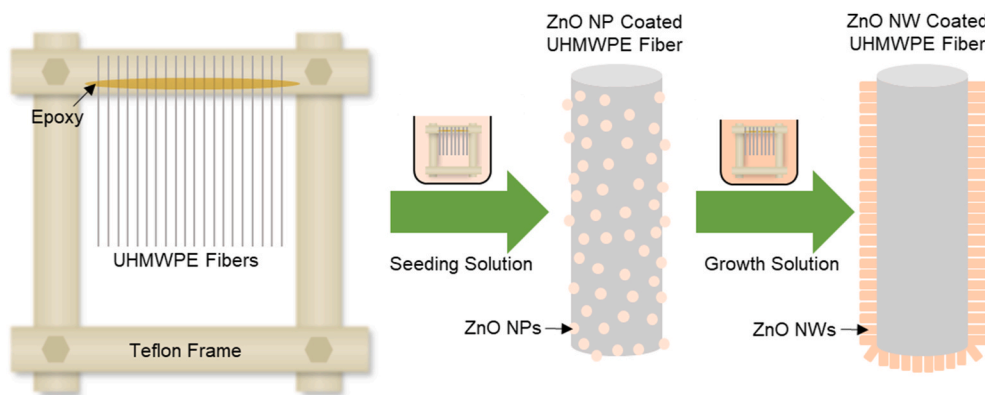


Fig. 1. Hydrothermal growth method schematic.

3. Results and discussion

3.1. UHMWPE surface functionalization and ZnO NWs growth

To understand the effect the oxygen plasma treatment has on the UHMWPE chemical structure, fibers with varying treatment durations were investigated via FTIR. Untreated UHMWPE has distinct absorbance peaks at 2914 cm^{-1} , 2848 cm^{-1} , 1472 cm^{-1} , and 716 cm^{-1} corresponding to C–H stretching. After plasma treatment, these C–H peaks remain visible, in addition to new oxygen containing groups which occur at wavenumbers of 1736 cm^{-1} , 1644 cm^{-1} , 1353 cm^{-1} , and 1113 cm^{-1} [46], as seen in Fig. 2. It is important to note that after the plasma treatment, there are no significant C–H peak shifts indicating that the chemical structure of the UHMWPE fiber is not altered by the fiber surface treatment. When comparing fibers that are plasma treated for various durations, the absorbance peaks remain relatively the same. This can attribute to such differences between the varying treatment durations are difficult to observe when compared to the large interaction volume measured during FTIR. Nonetheless, oxygen functional groups have been reported to aid in the adhesion between ZnO NWs and surface of fibers [40]. Therefore, the presence of these oxygen functional groups on the surface of the UHMWPE fiber highlights the potential for enhanced chemical bonding with the ZnO NWs.

XPS was used to further characterize the chemical composition of the UHMWPE fiber surface after oxygen plasma treatment. To investigate the concentrations of the oxygen functional groups on the surface of the UHMWPE fiber, the C1s spectrum was obtained from fibers with

varying oxygen plasma treatment durations. The C1s peaks were fitted at energy bands of 284.5–285.5 eV, 285.5–287.0 eV, 286.5–288. eV, and 288.0–290.0 eV, which corresponds to C–C, C–OH (hydroxyl), C=O (ketone), and COOH (carboxyl) functional groups, respectively. Fig. 3 displays the peak fitting for each oxygen plasma treatment duration and Table 1 shows the corresponding concentration percentages. The carbon percentage (C–C%) decreases drastically after a 15-s plasma treatment and introduces ketone and carboxyl functional groups to the UHMWPE

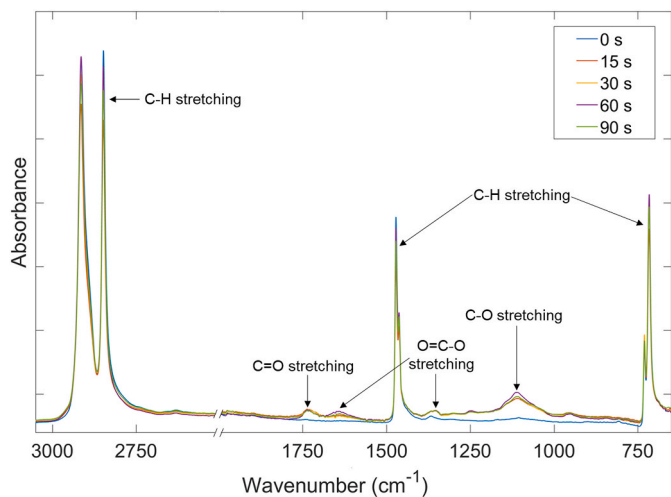


Fig. 2. FTIR of the UHMWPE fiber surface with varying oxygen plasma treatment durations with oxygen functional group peaks labeled.

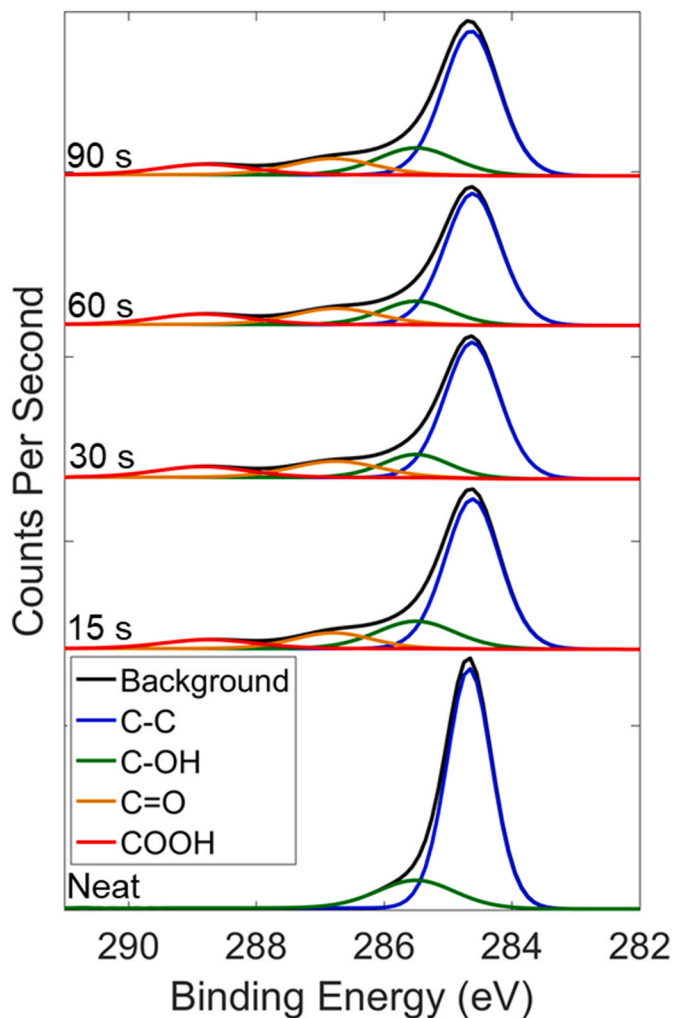


Fig. 3. Deconvoluted C1s XPS spectra for varying oxygen plasma treatment durations of UHMWPE fiber.

Table 1

XPS C1's concentrations of carbon, hydroxyl, ketone, and carboxyl functional groups for varying oxygen plasma treatment durations of UHMWPE fiber.

| Plasma-Treatment Durations (s) | C-C% (Carbon) | C-OH% (Hydroxyl) | C=O% (Ketone) | COOH% (Carboxyl) |
|--------------------------------|---------------|------------------|---------------|------------------|
| 0 | 88.40 | 16.60 | 0 | 0 |
| 15 | 66.24 | 17.34 | 9.85 | 6.57 |
| 30 | 65.54 | 13.49 | 12.45 | 8.52 |
| 60 | 65.09 | 14.32 | 12.15 | 8.44 |
| 90 | 64.80 | 16.60 | 10.96 | 7.64 |

fiber surface. When treated with 30 s oxygen plasma, the ketone and carboxyl functional groups reach their peak concentrations of 12.45% and 8.52%, respectively. When the plasma treatment was increased to a duration greater than 30 s, the concentrations of the ketone and carboxyl functional groups decrease while the hydroxyl group concentration increases. Initially the weak UHMWPE surface layers are removed, as the highly active ionized O₂ in the oxygen plasma chamber reacts with the UHMWPE surface to introduce oxygen functional groups. When the treatment period is short the dominant role of the plasma is to introduce active functional groups on the surface of the UHMWPE fiber [47–50]. With a 15 s treatment duration, the introduction of C–OH group is the dominate active functional group introduced onto the UHMWPE surface. When the treatment increases to 30 s, more active groups are introduced onto the surface, specifically C=O and COOH. However, when the treatment is prolonged, surface etching effect becomes the dominate role, thus removing a portion of the active functional groups introduced onto the UHMWPE surface in the beginning stage of plasma treatment [47–50]. Thus, after a 30 s plasma treatment duration, the recently grafted C=O and COOH bonds are cleaved, causing a reduction in their concentrations and an increase in C–OH concentration. The ketone functional group has been shown to have the highest compatibility with ZnO NWs due to its lack of steric hindrance, which allows for the highly-polar lone pair of electrons on the ketone oxygen atom to be accessible to the zinc ions [40]. The 30 s plasma treated UHMWPE fiber surface had the highest ketone concentration that could potentially provide the strongest adhesion to the ZnO NWs.

The morphology, uniformity and quality of the ZnO NW growth on the surface of the UHMWPE fiber is imperative to ensure consistent interfacial properties and was characterized using SEM. As seen in Fig. 4A–B, the surface of untreated UHMWPE is initially smooth, which offers little opportunity for mechanical interactions with the epoxy matrix. With no prior plasma treatment, the ZnO NWs do not adhere well to the inert surface of the UHMWPE, as highlighted by the non-uniform growth on the fiber surface causing poorly adhered ZnO NW sheets to easily fall off (Fig. 4C–D). After the oxygen plasma treatment, the UHMWPE fiber surface is found to have an increased population of oxygen functional groups (confirmed by FTIR and XPS), which aid in the adhesion of the ZnO NWs to the surface and allow for a well-adhered uniform growth on the UHMWPE fiber surface (Fig. 4E–H). The morphology, uniformity and quality of growth of the ZnO NWs grown on the surface of the UHMWPE fiber are observed to be unaffected by the varying oxygen plasma treatment durations. As seen in Fig. 4E–H, the nanowires for all varying oxygen plasma treatment durations are measured to be approximately 1 μm long with diameters ranging between 40 and 80 nm and rounded ends, thus demonstrating the uniformity in ZnO NW morphology across various treatment durations. The nanowires are also well aligned and radiating outward from the fiber surface and have similar growth densities between UHMWPE fibers with varying oxygen plasma durations. Similar characteristic has been observed in prior work where the ZnO NW growth morphology and uniformity was unaffected by surface functionalization [40,51]. The modified surface morphology offers a substantial increase in surface area compared to the originally smooth surface and has the potential to improve the IFSS by providing a larger bonding area and introducing mechanical interlocking with the epoxy matrix.

3.2. Tensile and interfacial shear strength tests

It is important to ensure that the mechanical properties of the UHMWPE fibers remain intact after any surface functionalization. The effect the oxygen plasma treatment and ZnO NW growth have on the tensile properties of the UHMWPE fibers were investigated through single fiber tensile testing. A modified testing method to prevent fiber slippage was developed for the smooth inert surface of the untreated UHMWPE fiber. Through single fiber tensile testing, the tensile strength for oxygen plasma treated and ZnO NW coated UHMWPE fibers was observed to be unchanged, regardless of the treatment duration (Fig. 5B). These results are expected as the short oxygen plasma treatment durations allow for functionalization of the surface without damaging the UHMWPE fiber surface, along with other studies in literature demonstrating the benign nature of the plasma treatment to the UHMWPE fiber [14–18]. Previous work has also shown that the ZnO NW growth is benign when applied to polymer fibers, as it has been reported that the hydrothermal growth method does not affect the tensile properties of the fiber [36–43]. Therefore, an oxygen plasma treatment is an efficient method to introduce oxygen functional groups to the surface of the UHMWPE fiber while also preserving the tensile properties.

Single fiber pullout tests were performed to measure the effect of a ZnO NW interphase and oxygen plasma surface functionalization on the interfacial properties of UHMWPE fiber-reinforced composites. Fiber-matrix debonding is a common failure mode in fiber-reinforced composites, and it can be studied using single fiber pullout tests which allow for direct load measurement during debonding without external interference from the bulk material characteristics [52,53]. The single fiber pullout test setup can be seen in Fig. 6A, where a large epoxy tab was used to ensure that the UHMWPE fiber pulled out of the epoxy block before slipping through the tab. Single fiber pullout tests were performed for untreated and oxygen plasma treated UHMWPE fibers for durations of 15 s, 30 s, 60 s and 90 s with and without ZnO NWs. Due to the smooth inert surface of the UHMWPE fiber (Fig. 4A–B), untreated UHMWPE specimens exhibited a IFSS of 3.13 MPa. When only the plasma treatment was applied to the UHMWPE fiber, the IFSS was found to increase to 4.75 MPa after a 90 s oxygen plasma treatment. This slight increase can be attributed to an increase in the chemical interaction between the UHMWPE fiber and the epoxy matrix due to the addition of oxygen functional groups on the surface of the UHMWPE fiber. Therefore, to increase the IFSS, ZnO NWs were grown on the oxygen plasma treated UHMWPE fiber. When a 30 s oxygen plasma surface treatment was applied in combination with a ZnO NW interphase, the IFSS was found to increase to 7.35 MPa, which corresponds to a 135% improvement, relative to untreated fibers. When the oxygen plasma treatment was further increase to 60 s and 90 s, smaller IFSS improvements of 120% and 108% were observed, respectively, relative to untreated fibers. The increase in IFSS can be attributed to the mechanical interlocking and increased surface area between the UHMWPE fiber and the epoxy matrix, as the ZnO NWs coated on the fiber are firmly embedded in the epoxy matrix. The ZnO NWs also improve the load transfer during fiber pullout by reducing the stiffness gradient between the fiber and the matrix. Due to the fact that the morphology, uniformity and quality of the ZnO NW interphase on the UHMWPE fiber are unaffected by the oxygen plasma treatment, it can be concluded that the IFSS of the specimen is dictated by the adhesion between the ZnO NWs and the UHMWPE fiber surface. Therefore, a comparison between the oxygen functional groups concentrations and IFSS can provide further insight into the performance of the ZnO NW interphase in UHMWPE composites.

Through experimental and molecular dynamics simulations it has been proven that the ketone functional group has the strongest affinity to the ZnO NWs [40]. This is due to fact that the ketone functional group has lone pair of electrons which are accessible to the zinc ions and are not blocked by protons elsewhere on the molecule. Similar interactions

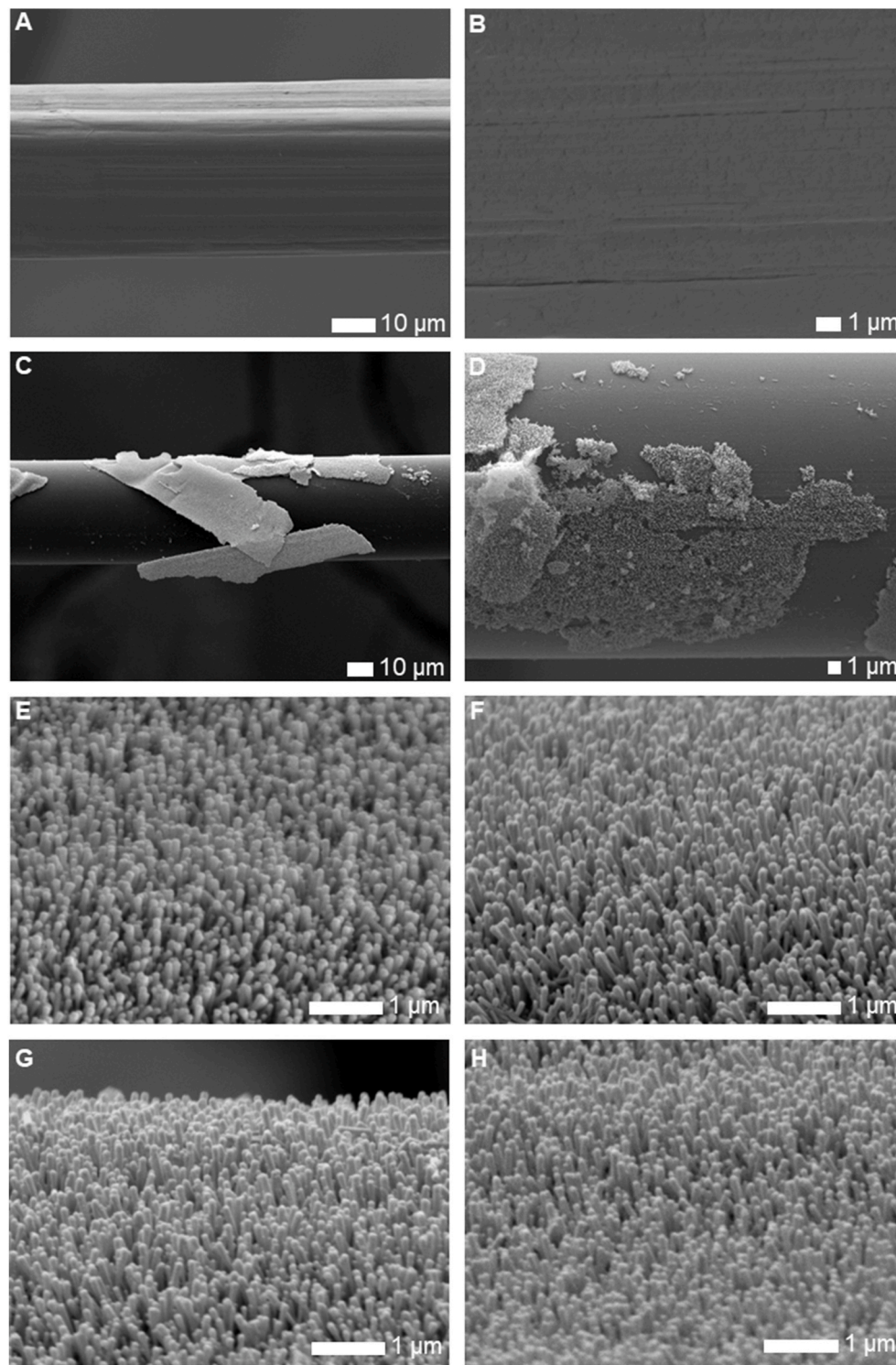


Fig. 4. SEM images of A & B) untreated UHMWPE fibers. ZnO NWs grown on plasma treated UHMWPE fibers with oxygen plasma durations of C & D) 0 s, E) 15 s, F) 30 s, G) 60 s, and H) 90 s.

between ZnO NWs and ketone functional groups have also been demonstrated in previous work [36–38,40,43]. Therefore, the C=O% obtained using XPS was correlated to the IFSS measurements of ZnO NW coated UHMWPE with various oxygen plasma treatment durations. Fig. 6C shows that the trend of IFSS is in agreement with the C=O% as a result of the plasma treatment, which confirms that the performance of the ZnO NW interphase is significantly dependent on its adhesion and chemical interaction with the fiber surface. It can be concluded that, to

produce the strongest adhesion between ZnO NWs and the UHMWPE fiber surface, the C=O functional group should be maximized on the surface of the fiber.

To fully understand the reinforcing mechanism of the ZnO NW interphase in UHMWPE composites, SEM images of the fiber surface were taken following pullout. The ZnO NWs act as a hierarchically micro-structured interphase that bridges the discontinuities fiber-matrix interface and introduces a functional gradient that reduced interfacial

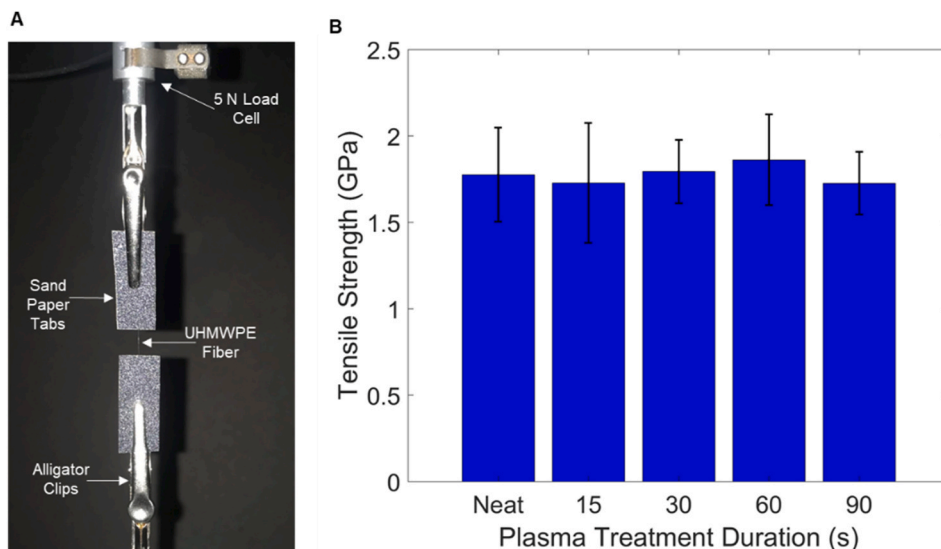


Fig. 5. A) UHMWPE single fiber tensile test setup. B) Tensile strength of untreated and ZnO NW coated UHMWPE fiber with varying oxygen plasma treatment durations.

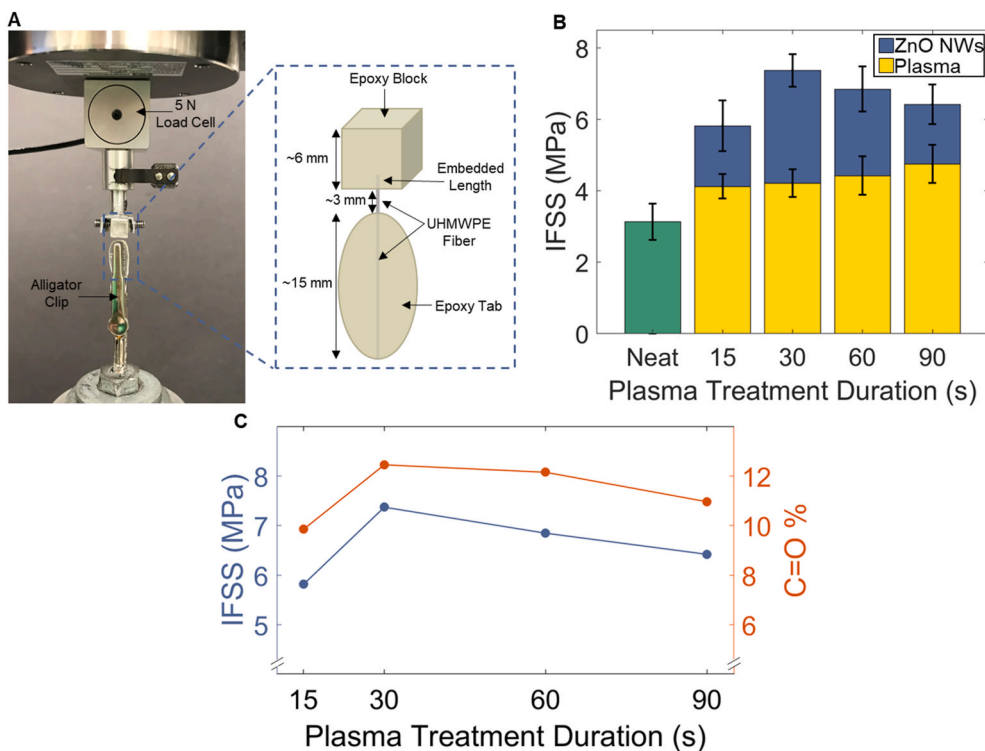


Fig. 6. A) Single fiber test setup and schematic of a single fiber pullout test specimen. B) IFSS of UHMWPE fiber with varying oxygen plasma treatment durations with and without ZnO NWs. C) Correlation between the IFSS of ZnO NW coated UHMWPE fibers and C=O% for varying oxygen plasma treatment durations.

stress concentrations. This functional gradient reduces shear strain concentrations and transition them away from the weaker fiber-matrix interface and into the tougher, more crack resistant matrix [44]. Furthermore, the nanowire interphase further increases the distance between the fiber and the matrix, which reduces the overall shear stress experienced by the matrix according to the shear lag theory [54]. Initially, the ZnO NWs are chemically bonded to the UHMWPE fiber surface through oxygen functional groups and then embedded in an epoxy matrix once introduced in a composite, thus introducing a large bonding area between the fiber and the matrix and providing a mechanical interlocking mechanism. During fiber pullout, the sample fails

at the weaker interface, which is between the ZnO NWs and the UHMWPE fiber, causing the ZnO NWs to detach from the UHMWPE fiber surface and remain embedded inside the epoxy matrix. This can be confirmed through SEM imaging shown in Fig. 7, where all fibers, regardless of oxygen plasma treatment duration, display a ZnO NW-free, clean surface post pullout. This can be attributed to the interaction area between the ZnO NWs and the fiber surface being significantly smaller than that between ZnO NW and epoxy matrix, causing for interfacial failure to occur in the form of ZnO NWs debonding from the fiber surface. This failure mechanism is consistent with previous studies reported in the literature that study the interfacial properties of ZnO NW coated

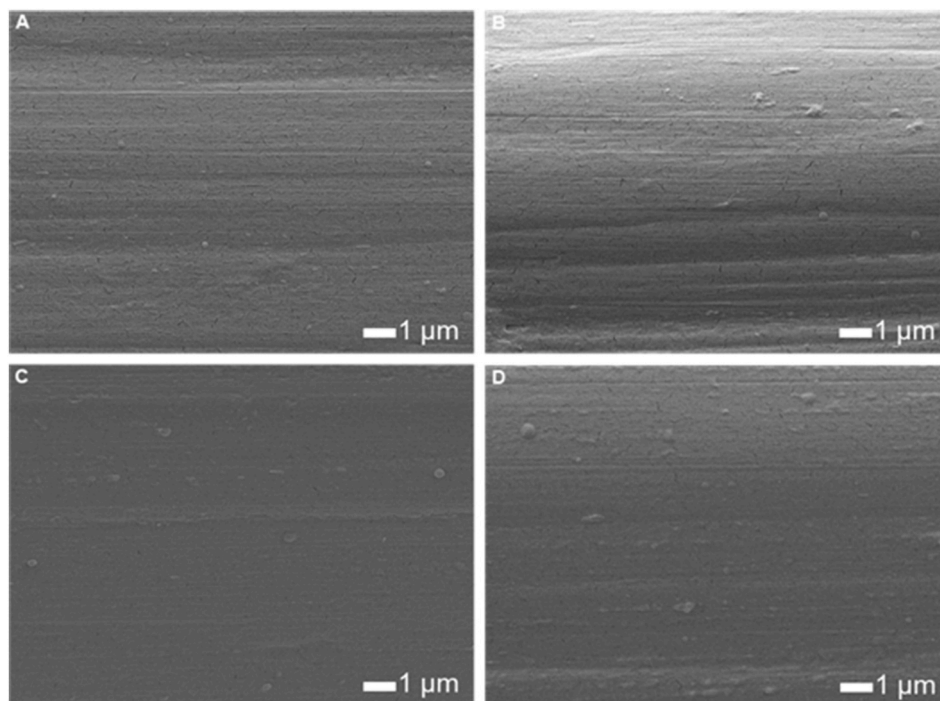


Fig. 7. SEM images of the UHMWPE fiber surface following single fiber pullout after a A) 15 s plasma treatment, B) 30 s plasma treatment, C) 60 s plasma treatment and D) 90 s plasma treatment.

fibers [36–38,40,43].

To improve the IFSS of the UHMWPE composites, further improvements in the bonding strength between the ZnO NWs and the UHMWPE fiber can be explored. For example, different surface functionalization can be developed to enhance the ketone concentration on the surface of the UHMWPE fiber to improve bonding with the ZnO NWs. Additionally, the morphology of the ZnO NWs can be optimized to study the effect of bonding with the fiber and mechanical interlocking between the nanowires and the matrix [39]. For example, larger diameter ZnO NWs would result in an increased surface area interaction between individual nanowires and the UHMWPE fiber which can potentially improve ZnO NW-fiber surface bonding. Additionally, changing the aspect ratio of the ZnO NWs would provide further study into the interlocking mechanism and ZnO NW-epoxy interface interaction to further optimize the IFSS of UHMWPE composites.

4. Conclusion

This study demonstrates an improved IFSS of oxygen plasma functionalized and ZnO NW coated UHMWPE fiber-reinforced composites. The ZnO NWs grown on untreated UHMWPE fibers were shown to have poor adhesion to the fiber, therefore oxygen plasma functionalization was applied to the UHMWPE fiber surface to overcome this weak interface. The UHMWPE fibers were oxygen plasma treated to populate the fiber surface with oxygen functional groups; more specifically the ketone functional group which have been proven to provide enhanced ZnO NW adhesion. XPS showed that the ketone functional group had a maximum concentration of 12.45% after a 30 s plasma treatment duration. Single fiber tensile tests showed that the tensile strength of the UHMWPE fiber was preserved, regardless of oxygen plasma treatment duration and ZnO NW growth. Through single fiber pullout testing, the IFSS of UHMWPE composites was shown to improve by over 86% for all oxygen plasma treatment durations with ZnO NWs and exhibited a maximum increase of 135% with a 30 s plasma treatment prior to the ZnO NW growth. This increase in IFSS can be attributed to the enhanced surface area and mechanical interlocking between the ZnO NWs and the

matrix. The IFSS results correlate with the XPS data, where the 30 s plasma treatment had the highest ketone functional group concentration, which resulted in the strongest adhesion between the UHMWPE fiber and the ZnO NWs. The process of a simple oxygen plasma functionalization and grafting of a ZnO NW interphase on the surface of UHMWPE fibers has demonstrated to significantly increase the IFSS of UHMWPE fiber-reinforced composites and therefore has the potential to be implemented into industrial composite manufacturing and expand the use of UHMWPE fiber-reinforced composites as a whole.

CRediT authorship contribution statement

Kelsey Steinke: Conceptualization, Investigation, Methodology, Writing – original draft. **Henry A. Sodano:** Conceptualization, Project administration, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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