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Adjusting the interfacial adhesion via surface modification to prepare high-performance fibers

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ABSTRACT

Ultra-high molecular weight polyethylene (UHMWPE) fiber is a new kind of high-performance fiber. Due to its excellent physical and chemical characteristics, it is widely used in various fields. However, the surface UHMWPE fiber is smooth and demonstrates no-polar groups. The weak interfacial adhesion between fiber and resin seriously restricts the applications of UHMWPE fiber. Therefore, the surface modification treatments of UHMWPE fiber are used to improve the interfacial adhesion strength. The modified method by adding nanomaterials elucidates the easy fabrication, advanced equipment and proper technology. Thus, the progress of UHMWPE nanocomposite fibers prepared via adding various nanofillers are reviewed. Meanwhile, the effects of other various methods on surface modification are also reviewed. This work advances the various design strategies about nano technologies on improving interfacial adhesion performance via treatment methodologies.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) fiber, also known as high-strength high-modulus polyethylene fiber or linear polyethylene fiber, is a new generation of high-performance fiber following carbon fiber and aramid fiber [1–4]. It is usually a linear polymer with an average molecular weight of more than 1.5 million. The fiber has the low density of only 0.97 g/m³, which is only two-thirds of aramid fiber and one-half of high-modulus carbon fiber [1]. The UHMWPE fiber has excellent chemical resistance, moisture resistance, good abrasion resistance, bending performance, high specific strength and specific modulus, excellent energy absorption characteristics, light resistance, superior electrical properties and sound performance, superior electrical and acoustic performance, low temperature resistance, biological performance and so on [5–8]. The preparation process of UHMWPE fiber is simple, which is synthesized by drawing and spinning through techniques such as gel spinning and super-stretching. Due to the unique properties of UHMWPE fiber, it is widely used in various fields such as national defense and military industry, security protection, marine industry, aerospace, and functional clothing [1–3].

However, the molecular chain of UHMWPE fiber exhibits a linear structure with only two elements (carbon and hydrogen) on the molecular chain, the surface lacks polar groups and the molecular structure with high crystallinity and high orientation is very compact, resulting in low surface energy and the high chemical inertness, which make it difficult to combine with the resin matrix and poor interfacial bonding performance [1,9]. It limits the promotion and application of UHMWPE fiber in the field of materials. The interfacial bonding performance is crucial because it transfers stress from matrix to UHMWPE fiber. Therefore, how to effectively improve the bonding strength between the fiber and the matrix is extremely significant in related fields [10–12]. The surface modification treatments of the fiber are the most direct and effective method to improve the interfacial adhesion, which have attracted the attention of the researchers [13,14]. The traditional surface modification methods have irradiation surface treatment [5,15,16], corona-discharge treatment [14,17,18], plasma treatment [19,20], matrix modification [21], etc. However, the most methods are limited by low mechanical properties, high-cost instruments, impossibility of Industrialization, specific reaction conditions, and so on [22–24].

In addition, with the development of nanocomposite technology, many researchers report the modified UHMWPE fibers with the nanofiller during gel-spinning process. The UHMWPE nanocomposite fibers are obtained by adding the nanofiller into UHMWPE solutions. The
nano filler, such as carbon nanotubes (CNT) [25], and nano-SiO$_2$ [1,26], etc., is incorporated in the UHMWPE fiber to improve the interfacial bonding performance. The modified method by adding nanomaterials elucidates the easy fabrication, advanced equipment and proper technology. More researches focus on the method. This paper summarizes the research progress of the surface modification in recent years, and prospects its development.

Fig. 1. (a) Tensile stress-strain curves of neat and nanophase UHMWPE filament; (b) SEM micrographs of oriented UHMWPE fibers, partially aligned array of nanotubes, and nanotube coated with thick polymer. a-b reproduced from Ref. [33]. (c) Stress-strain curves of UHMWPE fibers; (d) SEM micrographs of fractured surfaces. c-d reproduced from Ref. [34]. (e) Schematic diagram of treating SiO$_2$ nanoparticle by coupling agent KH-570; (f) SEM images of the UHMWPE fiber surface with SiO$_2$ nanoparticles; (g) The interfacial adhesion strength of the UHMWPE fibers; (h) The mechanical properties of the UHMWPE fibers; (i) SEM images of the UHMWPE fibers and resins after pull-out test. e-i reproduced from Ref. [1].

2. Modification before fiber forming

With the development of nanocomposite technology, the researchers begin to achieve higher performance through the preparation of UHMWPE/nanofiller composite fibers, they no longer simply depend on perfecting the preparation technology of fiber to improve the performance of UHMWPE fibers. Because the high surface energy and nano-
sized properties of nano-particles make them to have great potential to fill in the micro-flaws on the fiber surface, and improve the interfacial adhesion of the fiber/matrix interphase. Modification of the UHMWPE fiber before forming refers to the purpose of fiber modification by adding modified nanomaterials to the spinning solution or extractant during the fiber forming process. The added nanomaterials mainly include carbon nanotubes (CNT) [25], nano-SiO2 [1,26], small molecule coupling agent, high-density polyethylene [27], nylon, magnesium hydroxide nanoparticles [28], nano tungsten disulfide [29], bacterial nanocellulose, etc. The modified fibers enhance interfacial adhesion and mechanical properties, which are attributed to many micro-size and nano-size holes occurred in UHMWPE gel fibers. The modified results are from the synergistic effects of the nanofiller and UHMWPE fibers, due to the mechanical interlocking effect of the fiber and resin. The main advantage of this method is that fiber forming and modification are carried out together without post-treatment process, and the selection range of modified materials is very wide, which can be organic or inorganic materials. Its main problem is that the addition of modified nanomaterials may affect the rheology and spinnability of the spinning solution. The physical and mechanical properties of the fiber are also influenced [1].

Due to the different categories of the nanofillers, the present review article is the summary of previous studies, which is mainly divided into two main sections: carbonaceous nanofillers and non-carbonaceous nanofillers in improving the interfacial adhesion of UHMWPE fiber and resin [26,30].

2.1. Carbonaceous nanofillers

Yeh and his coworkers [25] studied the influence of the addition of CNT on the ultra-tensile properties of UHMWPE primary yarn. It was found that the contents of CNT, the concentration and temperature of the spinning solution had significant effects on the rheological properties, spinnability and draftability of the spinning solution. When the temperature of spinning solution reached 140 °C, the shear viscosities of spinning solution reached the maximum value. With the increase of CNT, the shear strength of the spinning solution increased until it reached the critical value. The influence of the contents of CNT added on drafting ratio also followed a similar rule. In order to explain the above rules, they also studied the birefringence, thermal properties, surface morphology and tensile properties of the gel yarn. Furthermore, they also successfully prepared modified UHMWPE fibers by spinning of adding nano silica and maleic anhydride modified nano silica gel solutions, respectively [31]. The results showed that UHMWPE fibers with a certain degree of orientation, tensile strength and initial modulus could be obtained and the addition of nanoparticles can achieve the expected drafting multiple under certain conditions. Compared with unmodified fibers, the melting temperature and wafer thickness of modified fibers decreased, while the crystallinity of modified fibers increased significantly.

Hao X et al. [32] considered that the uniform dispersion of CNTs in the spinning solution was a research hotspot, and it was the first step to obtain CNT/UHMWPE composite fibers with excellent properties. In order to solve this problem, CNT was coated on UHMWPE powder to obtain composite powder, and then dissolved in decalin, and finally a CNT/UHMWPE composite with higher tensile strength was prepared by gel spinning-ultra-high stretching method.

In the study on the modification of spinning solution, Khan and his coworkers reported the UHMWPE fibers were treated by adding the 2 wt % of single-walled carbon nanotubes (SWCNTs) [33]. It was also noticed that the ultimate tensile strength and Young's modulus of neat UHMWPE were increased with the addition of SWCNTs (Fig. 1a). Fig. 1b showed that significant polymer wetting around the nanotube, which CNTs acted as strong nucleation agents/sites. CNTs could share part of the tensile load, resulting in the increase of fiber tensile strength and modulus in the process of fiber stretching. Subsequently, they also systematically studied adding Nylon 6 and SWCNTs in spinning solution to modify the UHMWPE fibers [34]. The modulus, yield strength and ultimate tensile strength increased with the addition of Nylon 6 and SWCNTs (Fig. 1c). The fractured surfaces of UHMWPE-SWCNT-Nylon 6 demonstrated that multiple shear bands generated at various sites inside the material, which propagated along the filament length (Fig. 1d). The shear bands were formed due to highly localized shearing strain. Another research elucidated adding the Multi-walled carbon nanotubes (MWCNTs) to modify the UHMWPE fibers [35]. The results showed that the mechanical interlocking effect along with the covalent bonding at interface were synergistically playing a major role in such significant improvements in composite properties.

2.2. Non-carbonaceous nanofillers

Subsequently, Zhao and partners systematically designed to modify the surface of UHMWPE fibers by adding two kinds nano-SiO2 through gel spinning process [1]. Modified effect of treated SiO2 nanoparticles by coupling agent was superior to original SiO2 nanoparticles. Fig. 1e showed schematic diagram of treating SiO2 nanoparticle by coupling agent KH-570. SEM demonstrated the modified surface had a few asperities and deep grooves along axial orientation after filling with SiO2 nanoparticles (Fig. 1f). The pull-out tests of modified UHMWPE/treated SiO2 fiber revealed that interfacial adhesion strength increased (Fig. 1g). However, the axial crack also appeared if the content of SiO2 reached a certain extent, which effected the breaking strength of the fiber itself, corresponding breaking strength decreased (Fig. 1h). SEM images of the UHMWPE fibers and resins after pull-out test elucidated that the surface of the treated UHMWPE fiber remained resin, while the corresponding resin also remained a lot of fibers (Fig. 1i). The result indicated the interfacial bonding strength between the fiber and the resin matrix enhanced.

Besides, the Mg(OH)2 nanoparticles modified with oleic acid as the nanofiller also was used to treat the UHMWPE fiber [28]. The addition of Mg(OH)2 would affect the mechanical performance of the fiber. The obtained rough of the surface benefited its applications as reinforcement to other composites. Tian et al. [29] reported a synthetic method to add the Inorganic fullerene WS2 (IF-WS2) to modify the fiber, and the modulus of the fiber increased from 1203 to 1326 GPa. Furthermore, UHMWPE/WS2 fibers showed an improved thermal stability. Furthermore, Halloysite nanotubes (HNTs) were incorporated in the UHMWPE fiber by the drawing process in order to improve the mechanical property of the UHMWPE fiber, due to the high aspect ratio and rigidity [30]. HNTs has a rigid tubular structure with a high aspect ratio, which have the potential to align during the extended flow process. Compared with the HNT fiber with low filler loading, the surfaces of the 4 wt% and 8 wt % HNT fibers were more coarse. This implied that the roughness can improve the mechanical interlocking effect of the fiber and resin. Subsequently, Chitin nanocrystal (CNC) as the nanofiller also was introduced into gel solutions of the UHMWPE fiber [36]. CNCs have the shape like CNFs, which is conducive to the research on the actual mechanism of fibrous nanofillers reinforced UHMWPE fibers.

In addition, the researcher also prepared modified UHMWPE fiber by bacterial cellulose and other one modified by bacterial cellulose, and studied the effect of the addition amount of bacterial cellulose on the draft ratio [37].

3. Modification after fiber forming

Modification of UHMWPE fiber after forming refers to a method adopting to modify the fiber or matrix after the fiber has been molded. After surface modification, the UHMWPE fibers are usually given more functionalities because of the active fiber surfaces (the active functional layer in nanometer thickness). At present, the main methods of UHMWPE fiber modification after molding include irradiation surface treatment [5, 15,16], corona-discharge treatment [14,17,18], surface coating modification [7], chemical oxidation treatment [11], plasma treatment [19,20], matrix modification [21], swelling method, etc. From the molecular
level, UHMWPE surface modification is essentially to modify the UHMWPE macromolecules on the microscopic size of the fiber surface, including the oxidative cutting of macromolecular chains, grafting treatment and physical compounding [10,21]. The main idea of surface modification is to improve the surface polarity and roughness of the fiber through a specific modification method to achieve the purpose of improving the interface performance between the fiber and the resin matrix.

3.1. Irradiation surface treatment

Irradiation surface treatment usually refers to the second monomer graft polymerization initiated by radiating to produce a nano-size covering layer that can be tightly combined with the matrix, thereby improving the interfacial adhesion between the fiber and the matrix [38]. The radiation sources include electron beams, ultraviolet rays, lasers, gamma rays, etc. [5] The second monomers include acrylics, acrylic acid and their derivatives, etc. [5,16] This method has the characteristics of high efficiency, low energy consumption and low pollution, but the process of radiation crosslinking is complicated and requires high equipment and test conditions [39], which need research to find more proper theories and methods to improve the interfacial adhesion. The nanometer-depth of the grafted chains is about several hundred nm after treatment. High-dose irradiation can lead to a decrease in the mechanical properties of the fiber, and the types of radiation used in the cross-linking treatment have a certain degree of danger. Previously, Amornsakchai et al. [40] placed UHMWPE fiber in the atmosphere of vinyl monomer steam, then radiated the fiber with gamma ray to achieve the purpose of fiber graft modification. The changes of compressive strength of fiber after surface modification with two types of vinyl monomers (methyl methacrylate and vinyl acetate) were studied. The results showed that the compressive strength of the modified fiber was significantly improved, and the graft modification effect of vinyl acetate was better than that of methyl methacrylate on surface treatment. The existence of monomer had a certain impact on the irradiation effect in the process of heat treatment and irradiation.

In order to verify the factors influencing the grafting effect, Wang et al. [41] successfully grafted acrylamide monomer onto the surface of UHMWPE fiber under ultraviolet irradiation, and studied the reaction mechanism of radiation grafting modification (Fig. 2a). The treated surface with medicated functional layer in nanometer thickness would directly affect the properties of UHMWPE fiber. It was found that the crystallinity of the fiber, the concentration of the initiating reagent, grafting time and the concentration of grafting monomer (acrylamide) were important factors affecting the grafting efficiency. Fig. 2b exhibited that the interface adhesion strength between the fiber and the resin matrix has been greatly improved after the graft modification treatment. However, the strengths of UHMWPE fiber decreased, indicating the harmfulness of irradiation to fiber with extended irradiation time. SEM showed that acrylamide has been successfully grafted onto the fiber.
surface (Fig. 2c), and AM monomer was also easy to be grafted onto UHMWPE under UV. In a novel work by Kondo et al. [42], the UHMWPE fibers was modified by a special technique using electron beam (EB) irradiation-induced graft-polymerization. The test showed that the shear strength of the modified fiber and rubber composite material increased by 2 times, which proved that the adhesion between the modified fiber and the matrix. Thus, the decorated surface with functional layers in nanometer thickness would give rise to adjusting the adhesion between fiber surface and matrix.

Furthermore, UHMWPE fibers were treated with electron beam and gamma ray irradiation [43], which would also could active the surface layer in tens of nanometers thickness. It was found that many hydrophilic groups on the polymer surface by the oxidation polar groups (such as carboxyl, carbonyl, etc.) appeared on the surface of the modified fibers, which increased the polymer surface polarity. Thus, the surface energy and wettability were increased. Xin et al. [44] grafted methyl acrylate (MA) onto UHMWPE fiber, which effectively increased the surface area of the fiber. However, the tensile strength of UHMWPE fiber with high grafting rate was poor. In order to obtain high-performance fiber/rubber composites, Sakurai et al. [45] used electron beam to induce grafting of styrene or N-vinylformamide onto the surface of UHMWPE fiber to improve the interfacial adhesion through the treatment surface functional layer with tens of nanometers thickness.

As shown in Fig. 3, a continuous light induced graft polymerization modification method to solve the problem of poor interfacial adhesion of UHMWPE fiber through the modification on surface with nanometer thickness [49]. Fig. 3a showed the schematic procedure and chemistry for the sequential photoinduced graft polymerization of UHMWPE fibers under different atmospheres (air, vacuum and acetylene) [46]. The grafting reaction was initiated by semi-isopropanol (SP) group, and then methacrylic acid (MAA) and acrylamide (AM) were gradually grafted onto the surface of UHMWPE fibers. The grafting reaction was initiated by semi-isopropanol (SP) group, and then methacrylic acid (MAA) and acrylamide (AM) were gradually grafted onto the surface of UHMWPE fibers. The grafting reaction was initiated by semi-isopropanol (SP) group, and then methacrylic acid (MAA) and acrylamide (AM) were gradually grafted onto the surface of UHMWPE fibers. SEM images and AFM images revealed the apparent morphology changing, and the grafted layers were observed with nano-scale thickness (Fig. 3c and d). The pull-out test also
Fig. 4. (a) AFM images show UHMWPE fibers; (b) Fracture surface of composite made of UHMWPE fiber; (c) Mechanical properties of the FRCs corona exposure time. a-c reproduced from Ref. [51].

Fig. 5. (a) Mechanism of the UHMWPE fiber treated by Corona-PG-2S; (b) Peel Strength of the composite with different polyvinyl alcohol (PVA) concentration of the six methods; (c) Typical stress–strain curve of the composite of surface treatment methods. a-c reproduced from Ref. [18]. Illustration of procedure for preparing UHMWPE–(PDA + EGDE) fibers, possible mechanism, and chemical reactions of dopamine and EGDE in “one-step” method (d), and “two-step” method. (e); (f) The pull-out force of pristine and modified fibers; (g) The SEM images of interlaminar fracture surface. d-g reproduced from Ref. [7].
indicated that an extensively improved interfacial bonding property (Fig. 3b). The active groups grafted onto the fiber surface can provide sufficient anchor points for chemical bonding or further reaction with various resins. Broujerdi et al. grafted glycidyl methacrylate onto the surface of UHMWPE fibers to improve the interfacial properties of fiber composites [50]. The optimal design method was adopted to obtain the best graft modification treatment conditions. It was found that the grafting rate increased with the increase of monomer concentration and reaction time, and the reaction time had a greater effect on the grafting rate than the former. The bonding strength of composites made of fibers with grafting rates of 11% and 25% increased by 1.26 times and 1.95 times, respectively. With the development of technology, the reduced prices of radioactive sources and accelerators, the improvement of radiation technology, radiation-induced grafting has gradually become an efficient and low-cost UHMWPE fiber surface modification method. However, due to the many influencing factors in the radiation grafting process, the fiber modification effect is likely to be inconsistent under the same conditions.

3.2. Corona-discharge treatment

The corona discharge method was originally used to treat polymer films and had been used for surface treatment of non-polar fibers since the 1980s [51]. The gas medium near the electrode is broken down by high-frequency voltage to produce corona discharge. Due to the applied high-frequency and high-voltage electricity, the electric field near the electrode becomes very strong, the gas adjacent to the electrode is partially broken down and produced many particles. The particles interact with the molecules on the fiber surface, which affect the physical and chemical properties of the surface of the fibers [14,51]. The average surface roughness usually was the nanometer-depth.

The main change of modified UHMWPE fiber by corona-discharge treatment is that the content of oxygen on the surface of the fiber greatly increase. Further analysis of the modified UHMWPE fiber by far-infrared spectroscopy showed that there were characteristic peaks of active groups. The max average surface roughness was up to 171 nm upon corona discharge duration (Fig. 4a), a good interfacial adhesion (Fig. 4b) and higher flexural strength, flexural modulus, and fracture toughness than other groups (Fig. 4c) in 5s corona exposure times. The treatment of the UHMWPE fibers provided micro-pits on the surface of fibers and changed the surface chemistry through introducing polar oxygen-containing groups. The former provided micro mechanical interlocking between matrix resin and fibers; the latter enhanced the wetting of the fibers by resin matrix [51].

Besides, Zheng’s team [17] also treated UHMWPE fibers by corona-discharge treatment. It was found that microscopic grooves appeared on the fiber surface after treatment. With the increase of treatment power, the number and size of grooves increased significantly. Many oxygen-containing active groups also appeared on the fiber surface. Due to active groups, the interface strength of the composite increased. However, when the power increased to a certain extent, the fiber crystal structure was damaged. The best process condition was 0.075% at 6 kW. Furthermore, the contact angle between the UHMWPE fibers and epoxy resin changed little before and after modified by the corona discharge method, which were 40.18° and 38.2° respectively [32]. Therefore, the bond strength between oxygen resins was improved. The improvement of bonding strength was due to the immersion of fiber surface caused by corona discharge. For the past few years, Ogawa and his coworkers reported that the interfacial shear strength and tensile strength of UHMWPE fiber were improved by 30% after the treated fiber was combined with epoxy resin matrix through corona discharge treatment in air [53]. However, the tensile strength could only reach half of the predicted value, which was caused by the degradation of macro molecules during the treatment process. The same result was found from Zhang’s group [54]. They modified the UHMWPE fibers by combining corona discharge with UV radiography. The interfacial properties between fiber and matrix were improved via the modification on surface with nanometer thickness, but the tensile strength of fiber itself was significantly reduced. Therefore, they improved the mechanical properties by ultraviolet irradiation for a certain time after corona discharge treatment.

In a novel work by Han et al. [18], the two-step PVA-glutaraldehyde condensation (Corona-PG-2S) strategy was used to form an interface membrane on the surface of the UHMWPE fiber (Fig. 5a). Fig. 5b,c showed that the modified UHMWPE fiber by Corona-PG-2S had the highest peel strength and the best tensile strength. XPS and EDS results of the modified UHMWPE fiber demonstrated that oxygen content of the surface was up to 25.0 wt %, which indicated that the surface polarity was greatly enhanced. The adhesive properties were improved by improving the polarity of the surface. Table 1 listed the mass fraction of carbon and oxygen on the UHMWPE fiber surface. Corona-discharge treatment can obtain excellent infiltration and surface adhesion properties by strictly controlling the operating conditions. However, the surface of fiber established microporosity by excessive treatment. Uncontrolled and nonuniform the treatment effect, continuous the fiber treatment restricts the improving the interfacial adhesion of fibers.

3.3. Surface coating modification

The surface coating modification of UHMWPE fiber refers to the treated body such as fiber, yarn and fabric with a certain coating method and a coating agent with special properties, forming a nanometer thickness layer of coating with specific functions on the surface to achieve the purpose of the fiber modification [7,55]. The emphasis of this method mainly focuses on the parameter of coating wear resistance. Hu [56] et al. used the self-polymerization of dopamine to coat the surface of UHMWPE fiber, and then coated the metal silver ion layer on the fiber surface to improve the electrical conductivity of the fiber.

In order to improve the surface properties of UHMWPE fiber, SA R et al. [7] first coated the fiber with dopamine (PDA), and then grafted ethylene glycol glycidyl ether (EGDE) on the dopamine coating. EGDE was grafted through the reactions with amide and amino groups of polys (dopamine) surface via a “two-step” or “one-step” method (Fig. 5d&e). The SEM images demonstrated the significant amount of rubber left on the UHMWPE-PDA-EGDE and UHMWPE-PDA + EGDE fiber surface, contributing to the epoxy groups grafted onto the fibers which supplied enough anchor points for chemical bond (Fig. 5f). The single-fiber pull-out force of the composites filled with UHMWPE-(PDA + EGDE) fibers achieved 67.5% improvement (Fig. 5g). This novel modification method was also suitable for the surface modification of polyimide fibers [55]. Previously, Lu and his coworkers synthesized a water-based coating agent with the emulsion polymerization of methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), and hydroxyethyl acrylate (HEA) to modify the UHMWPE fiber [57]. The effects of the amount of emulsifier, reaction time and monomer ratio on the properties of emulsion and its membrane were studied. The chemical structure and glass transition temperature of the microemulsion film were characterized by FTIR and DSC. The results showed that the microemulsion was an ideal coating agent for fibers. Furthermore, a new patent pending technique was proposed to improve the mechanical and biological performance of the UHMWPE fibers by uniformly coating nylon onto the UHMWPE fiber [58]. They dissolved Nylon 6,6 and Nylon 6,12 pellets in 99% anhydrous methyl or ethyl alcohol, respectively, in the presence of anhydrous CaCl$_2$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Unmodified (wt%)</th>
<th>Corona (wt%)</th>
<th>Corona-PG-2S (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>92.31</td>
<td>81.82</td>
<td>74.93</td>
</tr>
<tr>
<td>Oxygen</td>
<td>7.69</td>
<td>18.18</td>
<td>25.07</td>
</tr>
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and obtained the best dissolution conditions. Subsequently, UHMWPE bundle fibers were coated with solution. It was found that the maximum creep time, maximum fracture strength and toughness of the fiber have been greatly improved after coating treatment. Moreover, the osteolysis results of the three incubation times (24, 48, and 72 h) after exposing the U-97 human macrophage cells to Nylon 6,6 coated UHMWPE material showed that the survival rate of cells was greatly improved. In addition, they also used nylon to coat UHMWPE fabric to improve the puncture resistance of the fabric [59]. The puncture resistance of the fabric has been significantly improved, and the static test value was increased by more than 75%. Moreover, there was no phenomenon of fiber pulling out after the puncture damage of the coated fabric.

To improve the adhesion between UHMWPE fiber and polymer matrix, pyrrole was oxidatively polymerized on the UHMWPE fiber surface continuously (Fig. 6a) [60]. Fig. 6b exhibited the schematic of the fiber pull-out test. Compared with the as-received UHMWPE fiber, the IFSS between PPy-coated UHMWPE and epoxy increased from 1.06 MPa to 5.72 MPa. As given in Fig. 6c, the high magnitude optical microscope was used to observe the geometrical characteristics of micro-droplets and fibers. The PPy-coated UHMWPE fiber surface showed large amounts particles attached and roughened surface (Fig. 6d). The surface coating modification can effectively enhance interfacial adhesion by environmentally friendly reagents, but it still suffers from long modification time and high cost of expensive reagents. Therefore, there are limitations for its industrial application.

### 3.4. Chemical oxidation treatment

The chemical oxidation treatment mainly refers to the use of strong oxidizing chemical reagents to treat the surface layer with nanometer thickness of the fiber, the surface of the fiber is oxidized and the oxygen-containing active functional groups are introduced [61]. The fiber is etched in the process of strong oxidant treatment, making the surface of the fiber appear irregular etched grooves and become rough, the specific surface area of the fiber increases, and other properties (such as wetting performance, bonding performance, friction, mechanical properties, dyeing properties, etc.) also change [13,62]. The commonly using strong oxidizing chemical reagents for treating UHMWPE fiber mainly include chromic acid, hydrogen peroxide, potassium permanganate, potassium dichromate and so on. The chemical oxidation treatment is relatively mild and can realize continuous industrial production, but the degree of oxidation needs to be well controlled, otherwise, it will have a great

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**Fig. 6.** (a) Illustration of procedure for preparing the polypyrrole (PPy)-coated UHMWPE fibers, and the photo of UHMWPE fiber as received (white) and PPy-coated UHMWPE fiber (black); (b) Schematic of fiber/epoxy micro-drop; (c) Photos of fiber/epoxy micro-drop; (d) SEM of fibers surface: (a) UHMWPE fiber as received; (b) PPy-coated UHMWPE fiber. a-d reproduced from Ref. [60].
impacted on the strength of the fiber. Kalteh et al. studied to modify UHMWPE fibers by preirradiation method in air in the presence of Mohr salt and sulfuric acid. The results showed that the grafting and acid etching had a synergetic effect. The polar groups on the fiber surface increased after the two methods, and the wettability and adhesion of the interface also improved significantly.

Furthermore, a specific concentration of chromic acid solution was performed to modify the UHMWPE fibers [11]. The reaction mechanism of PU was shown in Fig. 7a. Fig. 7b showed the reaction schematics of the treated ultrahigh molecular weight polyethylene (UHMWPE) fibers and polymeric diphenyl-methane-diisocyanate (polymeric-MDI); (c) Scanning electron microscopy micrographs; (d) Tensile properties of UHMWPE fibers/polyurethane (PU) composites; (e) Bending properties of ultrahigh molecular weight polyethylene (UHMWPE) fibers/polyurethane (PU) composites; (f) Scanning electron microscopy micrographs of UHMWPE fibers/polyurethane (PU) composites a-f reproduced from Ref. [11].

More recently, the UHMWPE fiber were also treated with chromic acid oxidation to generate hydroxyl groups on the surface with nanometer thickness, and combined the treated UHMWPE fiber with PU to prepare composite materials (Fig. 8a) [12]. Tensile and impact tests of the composites were studied, and the results showed that the modified UHMWPE fibers had a more positive effect on the mechanical properties of the composites than those of original UHMWPE fibers (Fig. 8b & c). SEM showed a rough surface and many micron-sized crack lines for modified fibers, which was form effective surface cross-linking (Fig. 8d). Li et al. [10] studied the surface treatment of UHMWPE fibers by potassium permanganate and the mechanical properties of epoxy composites after modification. The surface of the fiber produced oxygen-containing groups and formed cracks, which sharply decreased the contact angle of the fiber surface with water and ethylene glycol. It was found that the tensile strength of the modified fiber composite...
Fig. 8. (a) Schematic illustration of click reaction of the modified UHMWPE fibers with isocyanate component; (b) Stress-strain curves of Neat RPU and 1 wt% UHMWPE fibers reinforced RPU composites; (c) The specimens after the Izod impact test; (d) SEM images of the fractured surface. a-d reproduced from Ref. [12].

Fig. 9. (a) Schematic representation of composite design; (b) Schematic representation of the composites production process; (c) Optical micrographs of PE fibers; (d) Cross-section of composites and their magnified parts showing the interfacial adhesion. a-d reproduced from Ref. [21].
decreased, while the bending and interlaminar shear strength increased. The main reason for this phenomenon was that the weak boundary layer with nanometer thickness on the fiber surface was removed by the strong oxidizing agent, the internal microfiber structure was exposed, and the surface area and roughness were increased, which was more conducive to the resin infiltration and mechanical meshing between the interfaces.

Furthermore, Zec et al. [21] used chromic acid to treat UHMWPE fibers to obtain oxidized polyethylene fibers, and different alumina particles (nanoparticles, whiskers, synthesized), and the one doped with iron oxide (Fe–Al2O3), were used as reinforcing fillers and UHMWPE fibers were used as a reinforcement in prepared composites (Fig. 9a). Therefore, Hydrolysis of EVA and oxidation of PE produce EVAOH and ox-PE polymers, respectively. Fig. 9b showed the schematic representation of the composites production process. The optical micrographs of PE fibers displayed that the roughed surface and diameter reduction after etching process (Fig. 9c). The cross-section of 3Fe–Al2O3/S/ox-PE/EVAOH demonstrated the fibers represented a cohesive failure of the matrix, while the interface layer remained on the fiber surface (Fig. 9d). In general, the bonding strength of UHMWPE fiber/resin interface was improved after oxidation treatment, but the breaking strength of UHMWPE fiber itself was significantly reduced.
3.5. Plasma treatment

Plasma refers to the nanometer-depth of high-energy substances such as molecules, ions, atoms and other high-energy substances formed by specific gases at high temperature [64,65]. The depth on the surface of the fiber only involves tens of nanometers by plasma irradiation. After plasma irradiation, the fiber only has an impact on the fiber surface, does not affect the internal structure of the fiber, and has little impact on the strength of the fiber. At present, the plasma method is one of the most effective methods to modify UHMWPE fibers. The fibers form a good bonding ability with the resin matrix after plasma irradiation, which can reach a crosslinking depth of 30 nm. Since plasma treatment does little damage to the fiber body (nano-level), the physical and mechanical properties of the fiber will not change much [23]. In addition, it also has the advantages of no pollution and fast speed. The plasma treatment technology is energy-saving and environmentally friendly, and has good uniformity of fiber surface treatment [8].

In order to improve the wettability, dyeability and adhesion properties, Ren et al. modified different nanometer-depths of the surface of the UHMWPE fibers by the combination treatment of dielectric barrier discharge (DBD) plasma and chitosan coatings (Fig. 10a) [8]. Fig. 10b exhibited the introduction of the hydroxyl, carbonyl, and carboxyl groups onto the UHMWPE fiber surfaces after the combined treatment. The contact angle of UHMWPE fibers became smaller and the interfacial shear strength (IFSS) between the fiber and the epoxy resin also enhanced with the plasma treatment time (Fig. 10c&d). SEM showed a homogeneous layer of chitosan polymers were observed on the surfaces of the UHMWPE fibers after the DBD chitosan combined treatment (Fig. 10e).

Struszczyk et al. [19] used plasma-assisted chemical vapor deposition to modify UHMWPE fiber and aramid fiber materials by improving the cross-linking of the nanometer-depth on the surface layer. The effect of this combined modification on the properties of fiber materials was studied, and the mechanical strength and water resistance of the materials before and after the modification were tested and evaluated. Kusano Y et al. [59] optimized the interface adhesion between the resin matrix and UHMWPE fiber, so that the stress can be transferred evenly and smoothly at the resin matrix/fiber interface. The oxygen content on the fiber surface functional layer with nanometer thickness increased significantly after plasma treatment. There were two different types of the surfaces on the fibers before and after treatment, one was a typical polyethylene polymer, and the other was a modified polyethylene with a higher solubility parameter value (HSP). The polarity and hydrogen bond parameters of the fiber were improved. Their research also showed that it was feasible to predict whether the interfacial bonding strength was enhanced through the HSP method. A new type of polyvinyl alcohol (PVA) grafting technology was successfully developed to modify the UHMWPE fibers (Fig. 10f&g) [66]. The fibers were treated by oxygen plasma treatment to activate the surface (Fig. 10h), then soaked in a glutaraldehyde solution and catalyzed them for 18 h. After washing, the aldehyde-functionalized fiber was immersed in 10% PVA. PVA was grafted onto the fiber surface through aldehyde catalysis (Fig. 10i&j). The interfacial adhesion was improved by forming a covalent bond at the UHMWPE-PVA composite interface. The interface shear strength of the composite material increased from 11.5 ± 2.9 kPa to 228.6 ± 77.1 kPa (Fig. 10h).

Besides, a combination of oxygen plasma and coated polypyrrole
Besides, Wu and his coworkers also modified the UHMWPE fiber by plasma treatment on the bonding properties of the UHMWPE textile [23]. SEM showed the surface of the PPy-P-treated UHMWPE fibers coated with SiO2 nanoparticles on the surface by low-temperature plasma under low pressure has a good effect on adhesion between the fiber and the matrix. The nanoparticles as fillers would contribute to the generation of many micro-size and nano-size holes in UHMWPE gel fibers, which enhances the mechanical interlocking effect of the fiber and resin to improve the interfacial adhesion. The nanofiller elucidate the easy fabrication, advanced equipment and proper technology to modify the UHMWPE fiber.

According to the existing research results, it can be found that the surface modification methods of UHMWPE fiber can be summarized into two categories: chemical bond cooperation and physical microstructure engagement, and the synergistic action of the two methods will produce better modification effects. In the future, the development direction of fiber surface modification mainly includes several aspects: 1) Improving the dispersibility of nanofillers. 2) Exploring the synergistic effects of different modification methods. 3) Optimizing the process conditions of plasma, corona discharge and radiation methods to ensure the stability of their processes and results.

Declaration of competing interest

The authors declare that they have no conflict of interest.

References
