The study of UHMWPEF surface modification with plasma-induced polymerization

Yu-Fang Zhang, Qing-Xiu Jia, Xin Wang and Pei-Ran Zhang
Beijing Key Laboratory of Clothing Materials R&D and Assessment School of Material Science and Engineering Beijing Institute of Fashion Technology Beijing 100029, China

E-mail: zhang-y-f@163.com

Abstract. In order to improve the surface activity levels of the ultrahigh molecular weight polyethylene fiber (UHMWPEF), as well as enhancing the interface strength of the UHMWPEF based composite materials, the method of plasma-induced polymerization was applied to modify the UHMWPEF surface. In this study, the plasma’s power, time, pressure and the grafting monomer concentration were introduced. Also, through a well-conducted comparison and analysis of the grafting rate, fabric surface functional groups and the microcosmic morphology, the most suitable plasma modification process was discovered and determined. The mechanics performance of hybrid composites with the modified UHMWPEF and unidirectional carbon fiber cloth (CF) was tested to reveal that, compared with the unmodified composites, the tensile strength and the laminar shear strength could be improved.

1. Introduction
The wettability performance of UHMWPEF surface is generally poor because of its chemical inert behavior, non-polarity, highly orientation and crystallinity of the surface. Thus, when producing the UHMWPEF based composite materials, the bond strength between fiber and matrix resin is small, which would affect the mechanical properties of the UHMWPEF composites, especially the laminar shear strength, transverse tensile strength and fracture toughness etc. This disadvantage of the UHMWPEF hindered the progress in application of structural materials [1]. In order to increase the interface adhesion of UHMWPEF, as well as taking full advantages of its mechanical properties, many modification methods have been researched in terms of improving the wettability performance. For instance the chemical etching method, the radiation induced grafting method and plasma-induced polymerization, etc. In this paper, low temperature plasma treatment method was applied to modify the properties of UHMWPEF, the variation of the percentage of the grafting polymer of UHMWPEF surface with plasma treatment parameters have been explored and the surfaces’ functional groups and the microcosmic morphology is also investigated. In the experiment, the hand-made UHMWPEF/CF composite board was prepared for testing the tensile and shear properties of composite materials, and

1 Address for correspondence: Yu-Fang Zhang, Beijing Key Laboratory of Clothing Materials R&D and Assessment School of Material Science and Engineering Beijing Institute of Fashion Technology Beijing 100029, China. E-mail: zhang-y-f@163.com.
the relationship between the mechanical properties and the grafting monomer concentration is discussed in detail.

2. Experimental section

2.1. Experimental materials and equipment
In this experiment, the fabric of UHMWPE we used was provided by the Beijing Tongyizhong Specialty Fiber Company. The fabric is of 300 g/m², and the density of warp and weft is 20 beam/in. The unidirectional carbon fiber sheet and ANKO-300s two-component epoxy adhesive was sourced from Mitsubishi Co, the carbon fiber is also of 300 g/m². Other materials are the analytical reagents (AR).

HD-2 the plasma surface-treatment apparatus was manufactured by Changzhoushitai plasma Co. The Soxhlet Extractor was self-produced.

2.2. Specimen preparation

2.2.1. Fiber cloth pretreatment. The UHMWPE fiber cloth was cut into 50mm×50mm samples, firstly they were dipped into the n-heptane for the period of 24 hours, then soaked in a Soxhlet Extractor with acetone extraction for 4 hours, to remove the impurities from the surface of the fiber. After extraction, the fabrics were dried up at 60°C in vacuo, until the weight remained constant.

2.2.2. Plasma treatment. The pre-treated UHMWPEF samples were immersed in acrylamide monomer solvent which was dissolved in N, N - dimethyl formamide (DMF). After soaking entirely, the samples were taken out to dry up. Then the samples were placed into the low temperature plasma processing chamber, where the carrier gas was oxygen. Thorough selection of plasma processing power, time, pressure and the grafting monomer concentration was made, then, the plasma equipment was shut down after achieving processing conditions, and samples were taken out. The homopolymer and impurities on the fabric surface were removed, as described in section 2.2.2, to dehydrate the samples until constant weight was reached at 60°C in the vacuum oven.

2.2.3. UHMWPEF/CF composite material preparation. According to (CF)₀(UHMWPE)(CF)₀ layering method, the Plasma-induced polymerization treated UHMWPE fabrics and carbon fiber sheets were coated with ANKO-300s two-component epoxy adhesive by roller coating. Then the resin-impregnated composite product solidified at room temperature. The dosage of ANKO-300s adhesive is 500 g/m².

2.3. The performance tests and method

2.3.1. The calculation of grafting rate. The grafting rate of monomer on UHMWPEF surface is defined as:

\[
\text{Grafting rate} = \frac{(W_1 - W_0)}{W_0} \times 100\%
\]

Where \(W_0\) is the weight of UHMWPEF before processing, and \(W_1\) is the weight of UHMWPEF after plasma treatment.

2.3.2. Tensile properties tests. The tensile property of UHMWPEF/CF composite was measured by the directional fiber reinforced plastic tensile performance test method (GB/T1447-2005) [2]. The width of the test specimen was 12.5 mm and the length was 230 mm. The sample length direction is the same as carbon cloth direction of composite surface.
2.3.3. Shear properties tests. The interlaminar shear property was measured by the fiber reinforced plastic interlayer shear strength test method (GB/T1450.1-2005) [3]. The length of the test specimen was 25 mm and the width was 6.5 mm.

2.3.4. Surface analysis. The functional groups spectra of the plasma-treated and untreated UHMPEF surface were analysed by Nicolet 670 type FT-IR. The microstructure of the plasma-treated and untreated UHMPEF surface was investigated by JEOL JMS – 6360 LV scanning electron microscopy (SEM).

3. Results and discussion

3.1. The influence factors of plasma modified UHMWPEF fabric

3.1.1. The effects of grafting monomer concentration. In the experiment, the plasma processing power was 140 W; the pressure was 40 Pa; the processing time was 3 min, and the concentration of grafting acrylamide monomer was 0-2 mol/l. Figure 1 presents the variation of the grafting rates of UHMPEF surface with monomer concentration, which shows that the grafting rates increase gradually with further increase in monomer concentration. This is because in the plasma processing chamber, monomers vapour by glow discharging process which generated free radicals mixture of small molecules. These active free radicals reached the surface of the fabric, and reacted fast with monomer on the fabric surface to the generated active free radical macromolecules [4, 5]. As the monomer concentration increases, the more the chances of active free radicals were generated by monomer vapour, and the higher the probability that monomer polymerization was induced. Therefore, the grafting rate increases accordingly. In addition, at the interface of gaseous phase and liquid monomer of the plasma, high-energy electrons were mixed with organic solvent DMF, which produced ionic active free radicals, which would induce monomer polymerization. When this kind of ionic active free radical diffused and contacted with the liquid monomer, it would cause further polymerization of acrylamide monomer. That is the reason of the existence of solvent effect in the plasma induced polymerization [6, 7].

![Figure 1](image1.png)  
**Figure 1.** The variation of grafting rate with monomer concentration.

![Figure 2](image2.png)  
**Figure 2.** The variation of grafting rate with plasma processing power.

3.1.2. The influence of plasma processing power. In the use of plasma to the modified materials, the degree of the carrier gas ionization is different as the plasma output power changes, thus the plasma concentration inside the chamber is different. In the experiment, the concentration of grafting acrylamide monomer was 1.0 mol/l; the pressure was 40 Pa; the processing time was 3 min, and the plasma processing power was 120-160 W. The variation of the grafting rates of UHMPEF surface with processing power was displayed in figure 2. It is evident that the change of the power largely influenced the result of fabric modification. On one hand, if the processing power was too large, the high energy particles in plasma were increased in number, which would cause strikes to the material...
surface, neutralising some of the active groups on the material surface, and blocking the insertion of polar groups, thus not leading to graft polymerization [8]. On the other hand, when the processing power was insufficient, the carrier gas was not stimulated to produce plasma, so it was impossible to form active free radicals and to trigger reaction.

3.1.3. The influence of the plasma processing time. In the plasma modification, the processing time is a very important parameter. In this study, monomer concentration was 1.0 mol/l; processing power was 140 W; the pressure was 40 Pa. The variation of the grafting rate of UHMPEF surface together with processing time was displayed in figure 3. The UHMWPEF grafting rates show a maximum value at a plasma treatment time of 3 min and then gradually decrease with further increase in plasma-treatment time. This is mainly because at the beginning of the treatment, the active free radicals concentration increases sharply with the increase in processing time. After a certain period of time, the amount of monomer vapour decreases, making it difficult to form active free radicals [9]. Thus, the grafting rate of the fabric surface initially increases and as the processing time continues, active free radicals cause monomers to polymerize. Then, polymerization results in a decrease of free radical concentration, so the grafting rate declines. Therefore, when conducting the plasma optimization process, it is necessary to determine the appropriate processing time.

![Figure 3](image_url). The variation of grafting rate with plasma treatment time.

3.1.4. The influence of plasma processing pressure. The conditions were changed to: monomer concentration was 1.0 mol/l; the processing power was 140 W; the processing time for 3 min and pressure was 20-60 Pa. The variation of the grafting rate of UHMPEF surface with processing pressure was displayed in figure 4. The grafting rates show a maximum value at a plasma treatment pressure of 40 Pa and then gradually decrease with further increase in pressure. This is mainly because the pressure directly affects the gas density in the reaction chamber. As the pressure increases, the plasma density in the chamber increases. The number of active free radicals increases too, and so does the grafting rate. When the pressure is too large, part of the particles carrying the energy of the plasma will collide with the other particles, resulting in energy transfer and lower plasma flight speed, and thus the plasma impact on the fabric surface will be slower. In addition, in the high-frequency AC field, heat quantity by gas molecules vibration poses a great influence on the UHMWPE fiber. Because of the UHMWPE fiber with low glass transition temperature and melting point, in plasma treatment high pressure would likely cause fiber fracture or contraction. Therefore the optimal pressure range is 20-40 Pa.

To sum up, using low temperature oxygen plasma treatment UHMWPE fabric, the most suitable process conditions are: the plasma power is 140 W, the pressure is 40 Pa together with the processing time set to 3 min.

3.2. Surface analysis
3.2.1. Infrared spectroscopy test results and analysis. Figure 5 presents FT-IR spectra of the UHMPE fabric surface. Figure 5(a) is the spectrum from an untreated fiber surface and figure 5(b) is for a surface plasma-treated where the monomer concentration is 1.0 mol/l. There was a difference in these two spectra. It is known that amide groups are formed on the UHMPE fiber surface by oxygen-plasma induced polymerization treatment. Although it is difficult to analyze each chemical group quantitatively from these spectra, it is possible to understand the surface grafting polymerization state from the ratio of carbonyl peak and NH\textsubscript{2}- peak area against the internal standard peak area. As showed in figure 5, the peak at 2916 cm\textsuperscript{-1}, 2849 cm\textsuperscript{-1}, 1471 cm\textsuperscript{-1}, 717 cm\textsuperscript{-1} is thought to be characteristics of the UHMWPE fiber -CH\textsubscript{2}- peak, and the peak at 3359 cm\textsuperscript{-1} is assigned to the -NH\textsubscript{2} of acrylamide, the peak at 1658 cm\textsuperscript{-1} is assigned to the C=O vibration peak. It is shown that acrylamide has been grafted to the UHMWPEF surface.

![Figure 5](image)

**Figure 5.** The FT-IR spectra of UHMWPEF surface: (a) in red, the spectrum of an untreated UHMPEF surface and (b) in blue, the spectrum of plasma treated UHMPEF surface (plasma output power: 140 W, pressure: 40 Pa, treatment time: 3min, monomer concentration: 1.0 mol/l).

3.2.2. The SEM test results and analysis. Figure 6 shows the scanning electron micrographs of fiber surfaces. The uniform bamboo-like cracks on the untreated fiber surface are shown in figure 6(a). After plasma processing, the UHMWPE fiber surface became coarse, and the uniform bamboo-like cracks appear covered by an additional coating layer (see figure 6(b)). It is shown that monomer was grafted onto the fiber surface.

![Figure 6](image)

**Figure 6.** SEM of UHMWPEF surface: (a) the spectrum of an untreated UHMPEF surface and (b) the spectrum of plasma treated UHMPEF surface (plasma output power: 140 W, pressure: 40 Pa, treatment time: 3min, monomer concentration: 1.0 mol/l).

3.3. The mechanical performances of UHMWPEF/CF composites
3.3.1. Tensile property. Figure 7 shows the variation of the tensile strength of modified UHMWPEF/CF composites with grafting monomer concentration. It is clear that with the increase of grafting monomer concentration, the tensile strengths of the composites on (CF)₀(UHMWPE)(CF)₀ layers increased. It is because the plasma induced chemical modification can obviously improve the wettability of UHMWPEF surface, increasing the adhesion between the fiber and resin matrix.

Figure 7. The variation of the tensile strengths with grafting monomer concentration.

3.3.2. Interlayer shear strengths. Figure 8 shows the variation of the interlayer shear strengths of modifying-UHMWPEF/CF composites with grafting monomer concentration. Same as the grafting rate of UHMWPEF surface, the interlayer shear strengths increase with the increase in grafting monomer concentration. As we know that the breakdown of the interlayer shear of the composite material mainly depends on the adhesion between the fiber and resin matrix, fiber and fiber, and different fiber layers. The plasma-induced grafting polymerization introduces active polymer mixture on the fiber surface by reaction, and this active mixture improves the adhesion between the UHMPE fiber and the epoxy adhesive by chemical bonding. This chemical bonding plays an important role in improving the interfacial adhesion between the UHMWPEF and the epoxy adhesive. On the other side, the oxygen plasma also brings micro-pitting on the fiber surface by etching, and this micro-pitting by mechanical interlocking improves the interfacial adhesion. Therefore the interlayer shear strengths of the composites would increase accordingly.

Figure 8. The variation of the Interlayer shear strengths with grafting monomer concentration.

4. Conclusion

(1) Using low-temperature oxygen plasma induced acrylamide monomer polymerization on the UHMWPE fabric surface, the grafting rates of fabric surface with different processing parameters state that, the most apt condition for plasma treatment is the power 140 W, the time 3 min, and the pressure 40 Pa. As the grafting monomer concentrations increase, the grafting rates of fabric surface increase accordingly.

(2) Using SEM and FT-IR analysis the UHMWPEF surface, it is shown that the low temperature plasma treatment can induce acrylamide-DMF solvent polymerization on the UHMWPEF surface.

(3) The wettability of UHMWPEF surface enhanced largely by low temperature plasma treating. When it recombines with the unidirectional carbon fiber cloth on (CF)₀(UHMWPE)(CF)₀ layering, where the grafting monomer concentration is 2.0 mol/l, which compared with the untreated UHMWPEF, the tensile strength of the composite could be increased by 38.2%, and the interlayer shear strength can be increased by 22.7%.
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