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Effect of surface modifications on the properties of UHMWPE fibres and their composites

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Abstract: In this study, ultrahigh-molecular-weight polyethylene (UHMWPE) fibres, modified by acetic acid, sulfuric acid and water at a ratio of 20:25:2 for different time periods and modified UHMWPE/EP composites were prepared. The micromorphology, chemical composition, contact angle, H sample extraction, tensile properties and bending performance of the composite material of the UHMWPE fibres before and after modification were tested and analysed. The results show that, after the UHMWPE fibres were treated with the modified liquid, the surface roughness of the fibre increased, the contact angle decreased, and the surface chemical composition and species significantly changed; the mechanical properties of the composites are best when the fibres were treated for 9 min. For the same fibre content, the specific strength, specific modulus and bending load of UHMWPE composites treated for 9 min were increased by 16.7%, 82.9% and 55.3%, respectively, compared with untreated samples.

Keywords: composite materials; liquid oxidation treatment; mechanical properties; UHMWPE fibres; H sample extraction test

1 Introduction

Ultrahigh-molecular-weight polyethylene (UHMWPE) fibres, carbon fibres and aramid fibres are three high-performance fibres used in the world today. These fibres have excellent properties such as a high specific strength, a high specific modulus, light weight, and fatigue resistance. Since entering the market, UHMWPE fibres have been used in composites such as reinforced resins, rubber, ropes, and cables (1-5). Fibre-reinforced composites are high-performance materials that are considerably superior to single-phase materials in terms of their mechanical, physical, and chemical properties. Therefore, they are important for the development of composite materials.

UHMWPE fibres consist of a hydrocarbon linear molecular structure without polar molecular groups on the surface and have a low surface energy. Therefore, these fibres demonstrate a strong chemical inertness, leading to very weak interfacial adhesion between the fibre reinforcement and the matrix material, which has greatly limited their development in the field of composite materials (6). Therefore, it is particularly important to modify the UHMWPE fibres. By improving the surface roughness of the fibres or increasing the number of polar groups on the fibre surface, the interfacial adhesion between the fibre and the matrix can be improved, which eventually enhances the mechanical properties of the composites (7-9).

At present, the modification methods of the UHMWPE fibres are divided into physical methods, surface coating methods and chemical methods.

The physical methods include high-energy X-ray radiation (10), plasma modification (11), and ultrasonic immersion (12,13), among others. Although the fibres may be subjected to a certain degree of damage, these methods are relatively environmentally friendly, and their processing is also simple, safe and effective. Alternatively, the surface coating method increases the binding force of the fibre to the matrix by using a coated organic material as a bond, and its process is simple and feasible, but the coating and fibre are only a physical combination, and there are certain limitations when blending with the material (14,15). Chemical methods introduce more polar functional groups by chemical grafting or chemical etching (16-18). Therefore, this method can improve the interfacial properties of the fibre/ matrix. Although the intermolecular bond is stronger, the reaction rate and reaction time must be strictly controlled.

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X Jin et al. (19) used plasma technology to pretreat the surface of the UHMWPE fibres and then bond them with a polypyrrole (PPy) coating. The results showed that plasma modification can increase the interfacial adhesion by 84.8% and the compression strength by 54%. In addition, the increased adhesion and compressive strength are mainly caused by hydrogen bonding interactions.

L Zhang et al. (20) used a concentrated sulfuric acid oxidation method to modify the polypropylene (PP) coarse fibres and fibre dispersion in a cement mortar matrix, and the influence of the early-age crack resistance of the cement mortar matrix before and after PP coarse fibre modification was studied via experimentation. The results showed that this method significantly enhanced the early-age cracking resistance of the cement-based composite materials, but the reaction rate was difficult to control.

This research proposed using organic acids to modify the UHMWPE fibres. This method overcomes the disadvantage of a sharp drop in fibre strength after traditional strong acid treatment. On one hand, the fibre increases the active groups on the surface by treatment with the modified liquid, which effectively improves the activity of the fibre surface. On the other hand, this method increases the roughness and specific area of the fibre surface. The UHMWPE fibres are modified with a liquid composed of a certain proportion of deionized water, acetic acid and sulfuric acid. We study the effect of modification time on the tensile and bending properties of UHMWPE/EP composite materials to determine the optimal treatment time of the modified liquid.

2 Experimental materials and methods

2.1 Experimental materials

The following materials were used in the experiments: ultrahigh-molecular-weight polyethylene fibres (UHMWPE, 400 den), acetone (99.5%, Jinan Chunlufu Trading Co., Ltd.), acetic acid (36%–38%, Jinan Chunlufu Trading Co., Ltd.), sulfuric acid (75%), deionized water, GCC-135 epoxy resin (Kunshan Greenson Electronic Material Co., Ltd.), and GCC-137 curing agent (Kunshan Lvsun Electronic Materials Co., Ltd.).

2.2 Modification of the UHMWPE fibres

(1) UHMWPE fibre pre-treatment: First, the UHMWPE fibres were soaked in acetone for 3 h to remove impurities from the fibre surface. Then, the fibres were placed into an oven set at 60°C.
(2) Preparation of the modified liquid (water, acetic acid, sulfuric acid; WAS): The modified liquid consisted of acetic acid, sulfuric acid and deionized water at a mass ratio of 20:25:2.
(3) Fibre modification treatment: The pre-treated yarn was placed in a modified solution and treated at 25°C for 0 min, 3 min, 9 min, 15 min, and 30 min. Then, the yarn was washed with deionized water 3 times and placed into a constant-temperature drying oven at 60°C.

2.3 Preparation of the samples

(1) H pull-out sample: The UHMWPE yarn was passed through a device with an approximately 1-mm hole at the bottom. The height of the device was 2 mm. The epoxy resin and curing agent were uniformly mixed at a weight ratio of 100:30, and the resulting mixture was injected into the perforated device. According to the curing process of the composite material, the adhesive strength test specimen was prepared as shown in Figure 1.
(2) Composite test specimen: The modified UHMWPE fibre was knitted using a computerized flat knitting machine (Figure 2) to form a weft-knitted structure as a reinforcement. A GCC-135 epoxy resin and a GCC-137 curing agent were utilized at a weight ratio of 100:30 as the matrix, and the weft-knitted composite was prepared by combining vacuum-assisted resin

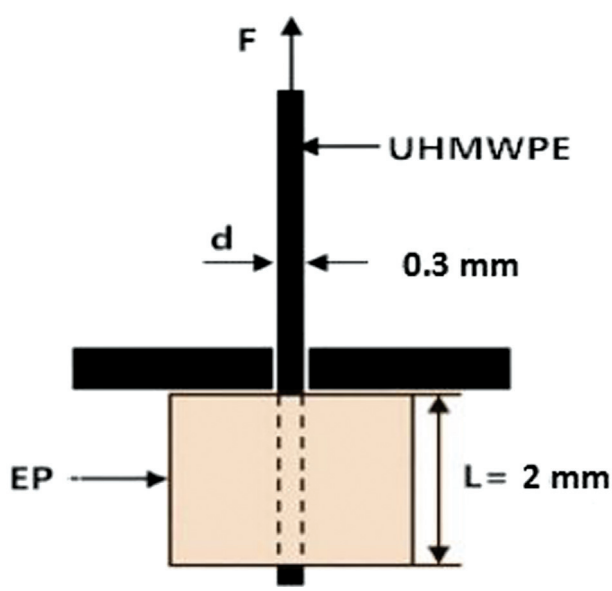

Figure 1: H pull-out sample.

transfer moulding (VARTM) and moulding techniques. The tensile and bending test specimens were cut according to the standard, as shown in Figure 3.

Figure 2: Computerized flat knitting machine.

2.4 Performance characterization

Scanning electron microscopy (SEM) was used (Table 1) to characterize both the UHMWPE fibre properties before and after modification and the fibre and the resin surface conditions after the H sample extraction test. The strength of the yarn before and after modification, the tensile strength and bending strength of the modified UHMWPE epoxy resin matrix composites were tested using a universal strength machine. The effects of the treatment on the strength of the yarn and the composite material were analysed using Fourier transform infrared spectroscopy (FTIR) to characterize the surface functional groups before and after UHMWPE fibre modification. The change in the contact angle before and after modification was measured by using an SCA20 fibre contact angle tester to measure the change in the surface roughness of the fibre.

Table 1: Experimental instruments and specifications.

Laboratory apparatus	Instrument specifications
TM3030	Hitachi TM3030
Fourier transform infrared spectroscopy	Nicolet iS50 (Thermo Scientific)
Contact angle tester	SCA20 fibre contact angle tester
Universal strength meter	INSRTRON 399 electronic universal testing machine
Computerized flat knitting machine	SES 122-S SFJ 20 Shima Seiki computerized flat knitting machine

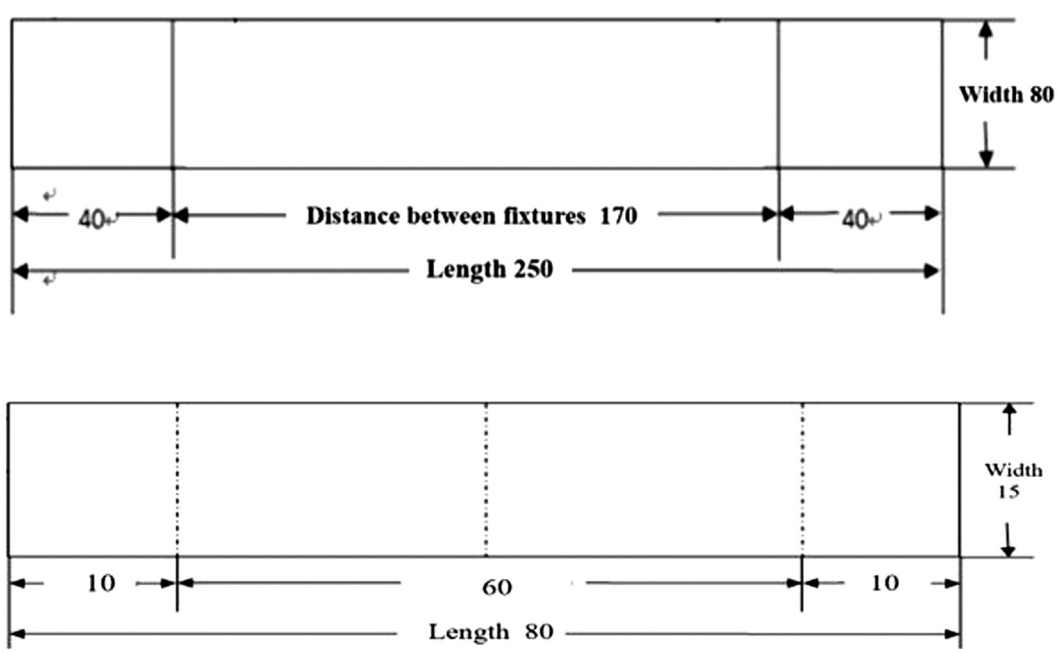

Figure 3: Dimensional drawing of tensile and bending specimens of composite materials (unit: mm).

3 Results and discussion

3.1 Surface morphology

The surface morphology of the UHMWPE fibres was examined by SEM before and after treatment. As expected, compared to the treated fibres, the untreated fibres exhibited a smooth surface with small transverse cracks, as shown in Figure 4a. After treatment with the modified liquid, these small transverse cracks disappeared, and as time increased, the axial cracks gradually appeared. In Figure 4b, the fibres were treated with the modifying solution for 3 min. The fibre surface was etched to a lesser degree, and the surface cracks were less pronounced. In Figure 4c, the fibres were treated for 9 min. The surface cracks were more obvious, and "traps" began to appear, accompanied by a shedding of a small part of the UHMWPE fibre surface. In Figure 4d, after 15 min of fibre modification, the cracks on the surface of the fibre continued to deepen. The "traps" also deepened and increased with a shedding of most of the fibre surface. In Figure 4e, the fibres were treated for 30 min. At this time, the "ditching" behaviour is the most obvious. The fibre etching damage is more serious, and the effect on the strength of the fibre is relatively large.

The change in the fibre surface is based on chemical etching via the modifying liquid; this process causes the surface of the fibre to "trap". However, these "trenches" can increase the contact area between the fibre and the resin and the mechanical meshing of the fibre and the resin, but can also reduce the strength of the fibre itself by etching and breaking the fibre molecular chain structure. Therefore, the modification time plays a crucial role in the modification effect.

3.2 Surface chemical elemental composition

To identify the functional groups on the fibre surface, the FTIR spectra of the modified and unmodified UHMWPE fibres are illustrated in Figure 5. These spectra exhibit characteristic peaks at 2920 cm^{-1}, 2841 cm^{-1}, 1465 cm^{-1} and 720 cm^{-1}. There are many new absorption peaks in the modified fibres, namely, the -OH- peak at 3430 cm^{-1}, the -C=O- peak at 1633 cm^{-1}, the -CH-peak at 877 cm^{-1}, the -C-O- peak at 1038 cm^{-1}-1078 cm^{-1}, and the free -C=O- expansion vibration at 1760 cm^{-1}. The absorption peak of the two dimers is exhibited at 930 cm^{-1}, and the other absorption peak at 1710 cm^{-1} is characteristic of the non-planar rocking vibration of -OH-. The change of -CH2- at S1, S2 and S3 is due to the strong stretching vibration of the long molecular chains, and the cross-linking of the

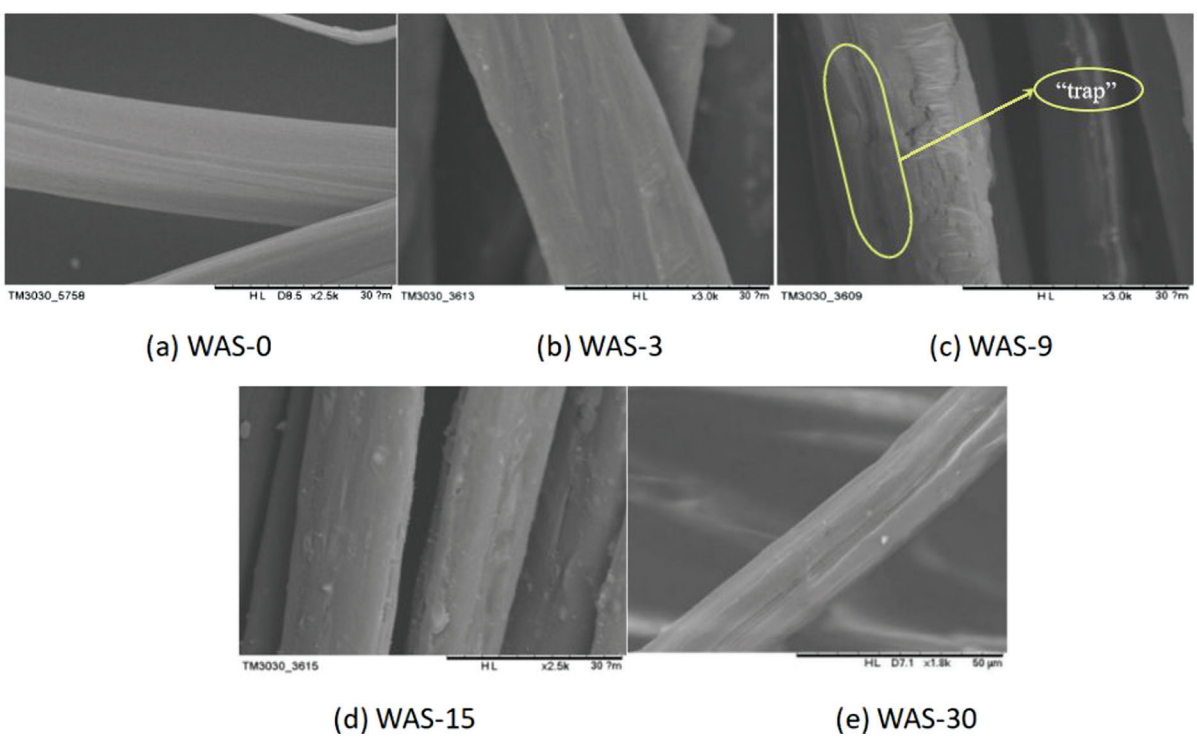

Figure 4: SEM diagram of the UHMWPE fibres before and after modification: (a) untreated fibres, (b) the fibres were treated for 3 min (c) the fibres were treated for 9 min, (d) the fibres were treated for 15 min, (e) the fibres were treated for 30 min.

molecular chains hinders the stretching vibration. The decrease in amplitude of the -CH_2- stretching vibration is due to the existence of oxygen, which results in chain breaking, cross-linking and the formation of oxygen containing groups.

3.3 Contact angle test

Figure 6 shows the contact angle of the fibre surface after modification. The contact angles of the UHMWPE fibres treated for 0 min, 3 min, 9 min, 15 min and 30 min were 76 degrees, 70 degrees, 54 degrees, 47 degrees and 38 degrees, respectively. The surface contact angle of the fibres decreases with an increase in the treatment time. This finding indicates that the wettability of the fibres improved after modification. From a physics viewpoint, this behaviour is due to an increase in the fibre surface roughness, an increase in the fibre surface porosity, and an increase in the contact area between the fibre and liquid. From a chemistry viewpoint, after modification, the polar groups, such as hydroxyl groups, introduced into the fibre improve the hydrophilicity of the fibres, resulting in a change in the contact angles of the materials. A decrease in the contact angle of the yarn will help to increase the bond between the fibre and resin, thereby improving the mechanical properties of the composites.

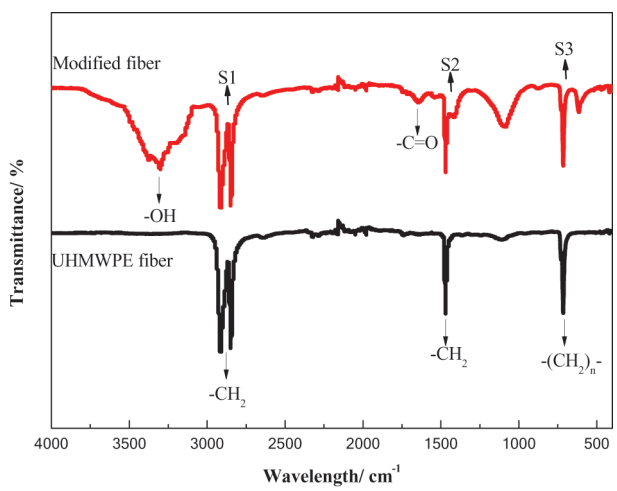

Figure 5: FTIR spectra of the UHMWPE fibre.

3.4 Strength test of the UHMWPE fibre

Figure 7 shows the test results for the tensile strength of the fibre before and after modification. According to the graph, the fibre strength is 101.46 N before treatment, and the strength of the fibres decreased after modification and gradually decreased with increasing modification time. This behaviour is due to the etching effect of the modified liquid. After treatment, the surface of the fibre is etched, the cross-section of the fibre stress is reduced, and the pressure of the unit area increases, which leads

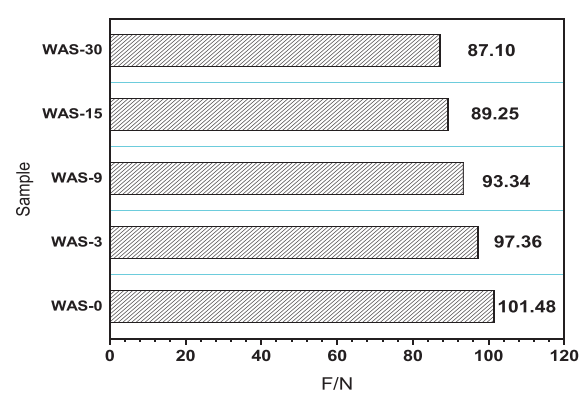

Figure 7: Tensile strength of the fibres before and after modification.

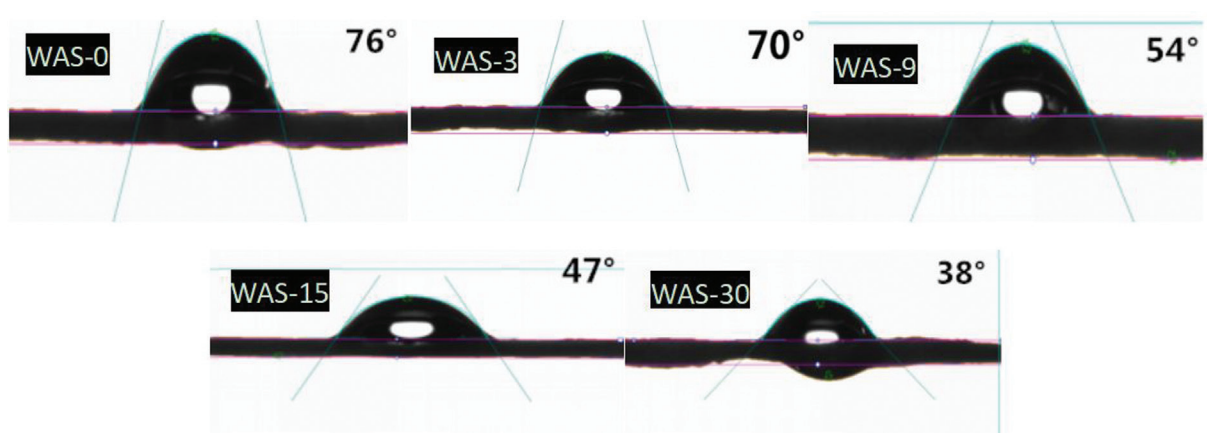

Figure 6: The contact angle testing of the UHMWPE fibre.

to a reduction in the strength of the fibre. However, the strength of WAS-30 is only 14.12% lower than that of the untreated fibre, which is a small drop in strength. Therefore, in a suitable timeframe, the modified liquid has little effect on the yarn strength.

3.5 The H sample extraction test

Figure 8a shows the displacement-load curves of the adhesive force between the fibre and resin after different WAS treatments, At the same embedment depth, the curve presents a "bimodal value" or "multipeak value" phenomenon. The fibre bundle demonstrates a small amount of kinking in the resin, and during the drawing process, the part is stretched by force, and a "multipeak value" appears. The comparison of the fibre strength and pull-out force of the fibre resin before and after modification is shown in Figure 8b. The black square represents the strength of the fibre, and the histogram represents the bond strength between the fibre and the resin. With a growth in the modification time, the strength of the fibres decreases because the degree of etching on the fibre surface increases with time. The bond strength between the fibre and the resin is gradually enhanced. This enhancement is due to the oxidation treatment of the fibre surface. From a physical standpoint, the roughness of the fibre surface increases, the contact area between the fibre and the resin increased, and the physical meshing of the fibre and resin is closer; thus, the bonding force between the fibre and resin is increased. From a chemistry standpoint, after solution modification, the active groups on the surface of the fibres increase, and the chemical bonding between the fibres and resin increase. Thus, the bond force increases.

For the WAS-30 sample, the fibre bundle was not extracted from the resin. As shown in Figure 9, the bonding force at this time is actually equal to the strength of the yarns. This effect is due to the extended amount of time that the fibre is treated with the modified liquid. Therefore, the fibre surface is too rough, and the strength is reduced, resulting in a yarn and resin bonding force that is greater than the strength of the yarn itself, so the yarn breaks. During the drawing process, the fibre is mainly subjected to three forces (Figure 9): the bonding force F1, the pressing force P of the surrounding resin matrix, and the frictional force F2.

The residual resin on the surface of the fibre and the roughness of the surface of the resin can further explain the adhesion between the fibre and resin. The pulled fibre and resin were analysed via SEM (no analysis was conducted because the WAS-30 sample was not extracted).

As shown in Figure 10, the surfaces of the fibres are smooth after the unmodified UHMWPE is extracted. After the drawing test, only a small amount of resin particles is left on the surface of the fibre, and the surface of fibre of is smooth. This finding is due to the smooth surface of the unmodified UHMWPE fibre and the lack of meshing point with the resin; therefore, the binding capacity of the resin is weak, which corresponds to the smaller pulling force. With a gradual increase in the treatment time, the resin residue on the surface of the extracted fibre gradually increased, and the roughness of the resin surface gradually increased after the extraction of the fibre. For a treatment of 9 min, the reticular distribution and agglomeration phenomenon appeared on the surface of the extracted resin, which indicate that the interaction between the fibre and the resin was enhanced.

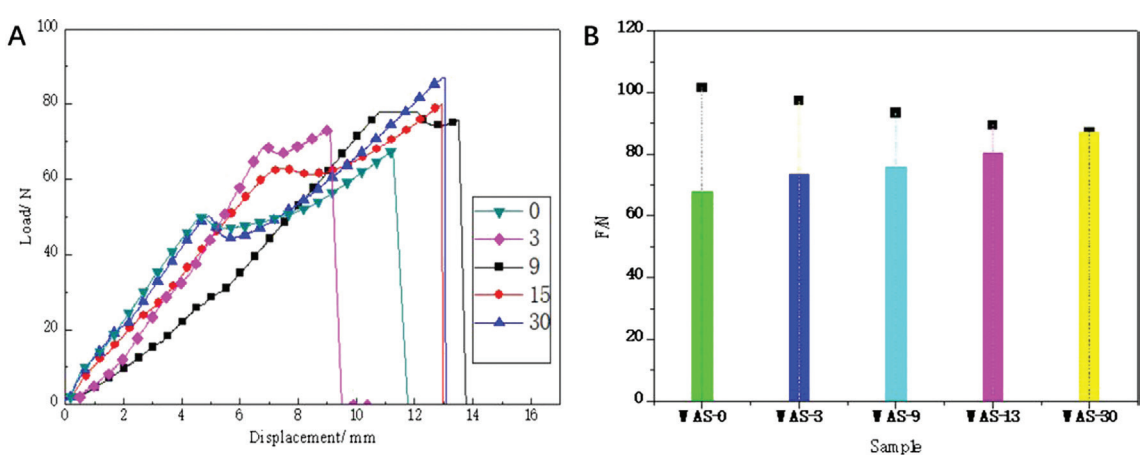

Figure 8: (a) Displacement - load curve H sample drawing. (b) Comparison of the fibre strength and the drawing of force of the H sample before and after modification.

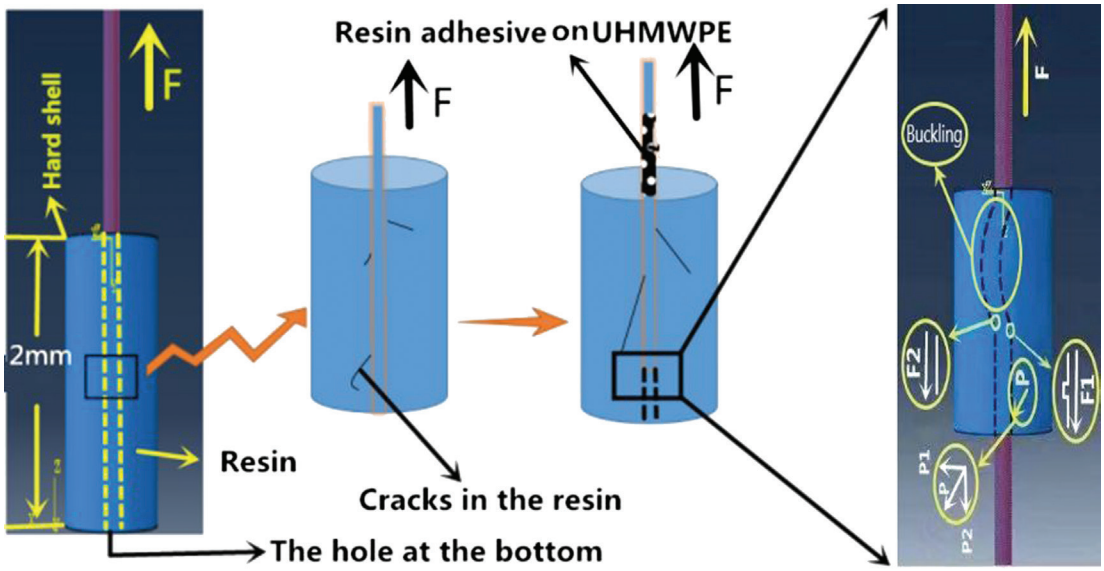

Figure 9: Bond test model and model force diagram.

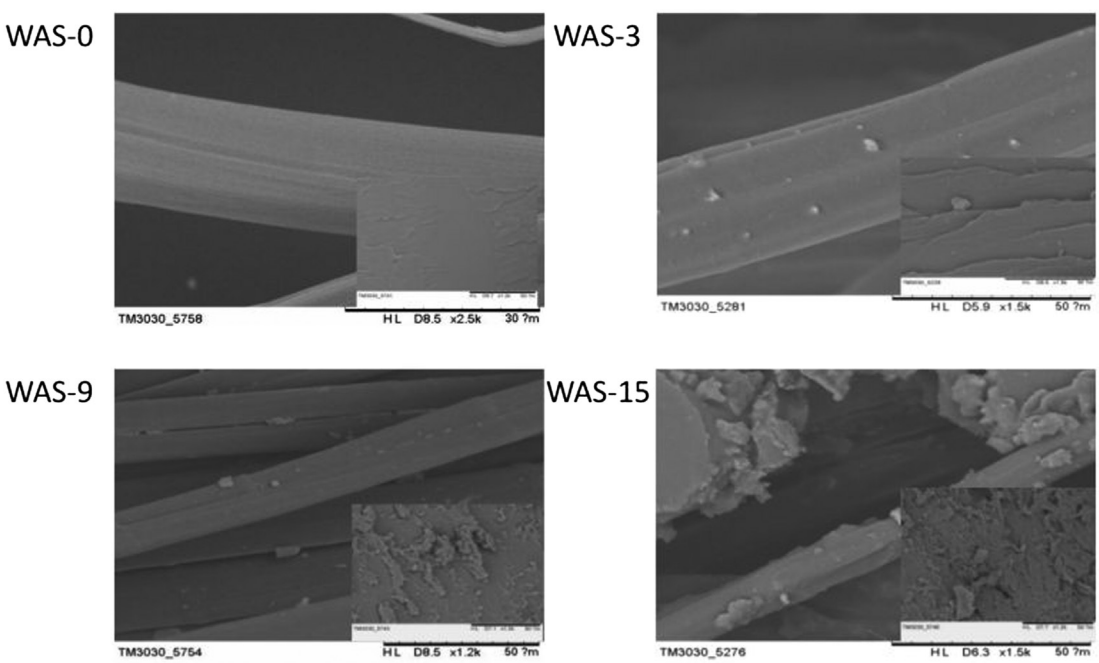

Figure 10: SEM images of the fibre and resin surface after extraction.

3.6 Tensile test of the modified UHMWPE epoxy matrix composites

Figure 11a shows the tensile strength curves of the modified UHMWPE epoxy composites. From the diagram, the maximum tensile strength of the composites increases and then decreases with an increase in the bundle modification time. The maximum stress of the composite materials is exhibited in the following sequence: WAS-9>WAS-15>WAS-30>WAS-3>WAS-0. Compared with the unmodified composites, the tensile stress of the WAS-9 specimen is increased by 16.7%, and the tensile stress of WAS-30 specimen is increased by 11.5%. Tian Y L (21) uses a coating method to deposit polyethylene wax grafted maleic anhydride (PEW, G, MAH) on the surface of UHMWPE fibres to improve adhesion to the epoxy matrix. Tensile testing results showed that the mechanical properties of the fibre did not change significantly, and the tensile strength of 9 wt% PEW-g-MAH-treated fibre-reinforced composite showed enhancement of approximately 10.75%.

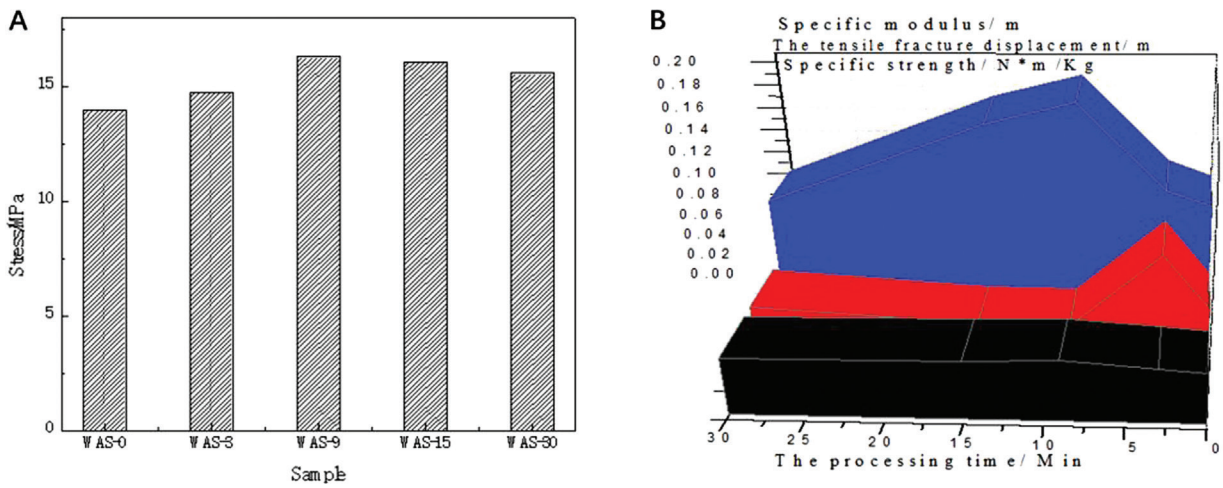

Figure 11: (a) Modified UHMWPE epoxy resin composite tensile strength curve. (b) Modified UHMWPE epoxy resin composite tensile specific strength (bottom), specific modulus (upper) and tensile fracture-displacement (middle) curves.

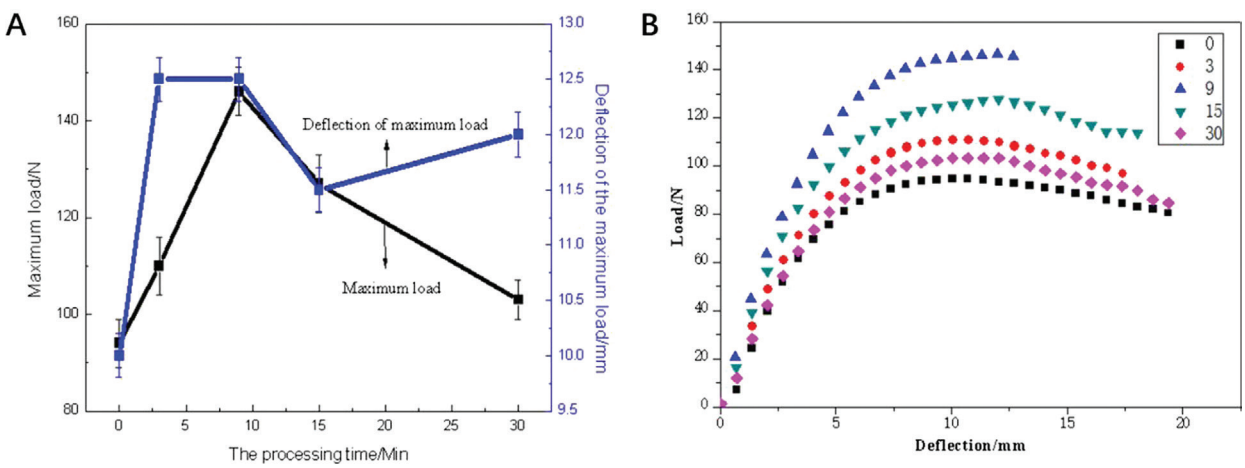

Figure 12: (a) Flexural maximum load and maximum load displacement curves of the modified UHMWPE epoxy composites. (b) Flexural displacement-load curves of the modified UHMWPE epoxy composites.

From Figure 11b, the specific strength and specific modulus were improved to varying degrees after modification. Additionally, the rigidity was enhanced in the composite materials. The performance increase in the WAS-9 sample was the most obvious; the specific strength and specific modulus improved by 16.7% and 82.9%, respectively. The tensile load of WAS-3 increased by only 7.2%, but the tensile fracture displacement clearly increased by approximately 82%. The fracture displacement of the other treatment time was reduced due to the short acid treatment time, which has little influence on the strength of the fibre. The fibre surface exhibited a slight roughness, and the adhesion increased between the fibre and the resin. Long treatment times will increase the roughness of the surface, which seriously affects the strength of the fibre itself. When the composite is subjected to a tensile load, the probability of weakness increases, and the tensile fracture displacement is reduced.

3.7 Bending test of the modified UHMWPE epoxy matrix composites

As seen from Figure 12a, with the increase in the treatment time, the maximum bending load of the composite increases first and then decreases, and the maximum value is obtained at WAS-9. The bending load of the specimen is 55.3% higher than that of the unmodified sample. The displacement curves at the maximum load show that the deflection of the composite was improved after modification, which indicates that the treatment greatly influenced the deflection perpendicular to the surface force, in which WAS-9≈WAS-3>WAS-30>WAS-15>WAS-0, and the maximum increase in the deflection of WAS-3 and WAS-9 is approximately 25%. The increase in the corresponding deflection at the maximum load indicates that the flexural toughness of the composite is enhanced.

Figure 12b depicts the flexural displacement-load curves of the composite material before and after modification. The maximum bending load of the composite is greatly influenced by the drawing. The bending load of the composite material at WAS-3, WAS-9, WAS-15 and WAS-30 is increased by 18.1%, 55.3%, 35.15, and 9.6%, respectively, compared with the sample WAS-0. The bending load at WAS-9 increased the most, which indicates that the bonding force between the fibre and resin can be effectively enhanced after 9 min of oxidation treatment. The reason for this result may be that oxidation first etches the surface of the fibre, thus increasing the surface roughness of the fibre and thereby increasing the contact area between the fibre and the resin. Another reason for this result may be that the modifying liquid increases the reactive groups on the surface of the fibre and promotes the molecular chain between them. The interaction, although negatively affecting the strength of the fibre itself, generally improves the bending properties of the composite.

4 Conclusion

(1) After treatment of UHMWPE fibres by a modified liquid, the surface roughness of the fibre increases, and the content and type of the surface elements change.
(2) The strength of the undrawn WAS-30 sample is only 14.12% lower than that of the untreated fibre, which is not significant. Therefore, the modified liquid has little effect on the strength of the yarn across a suitable time period.
(3) The contact angle of the fibre surface gradually decreases as the modification time increases.
(4) UHMWPE\EP composites were successfully prepared by the chemical modification of fabrics using the VARTM process. The tensile strength of the composites modified for 9 min exhibited the best performance, combined with the unmodified composites. The specific strength, specific modulus and bending load of the material increased by 16.7%, 82.9% and 55.3%, respectively.

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