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Interfacial bond property of UHMWPE composite

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Abstract The ultrahigh molecular weight polyethylene (UHMWPE)/hydrocarbon (PCH) composite was prepared by selecting a PCH resin as the matrix, which has the similar structure to UHMWPE fiber. The interfacial bond property between the PCH resin and UHMWPE fiber was investigated by macromechanics, micromechanics, and contact angle. The results show that the PCH resin has good wettability with the UHMWPE fiber surface. The UHMWPE/PCH composite has excellent transverse tensile strength, interlaminar shear strength, and the pull-out strength together with the outstanding interfacial bond property.

Keywords Ultrahigh molecular weight polyethylene fiber · Composite material · Interfacial bond property

Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) fiber, which is also called ultrahigh modulus polyethylene fiber, is the third generation of high-performance fiber-reinforced materials following the carbon fiber and Kevlar fiber. It is the latest ultralight, high-specific strength and high-specific modulus fiber at present, which has low-dielectric constant, low-dielectric loss tangent, small electrical signal distortion, and good microwave-transparent performance. The UHMWPE fiber possesses excellent properties such as high-impact resistance, low hygroscopicity, good wear resistance, corrosion resistance, UV radiation resistance, and electrical insulation [1, 2]. UHMWPE fiber-reinforced composite has high axial direction

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tensile of specific strength and specific modulus, excellent energy absorption capacity, outstanding humidity resistance and chemical corrosion resistance, good wear-resisting performance, and UV radiation resistance and electrical insulation. However, the UHMWPE fiber molecular chain is the nonpolar pure hydrocarbon structure, there is no reaction activity center on the fiber surface, so the surface energy of the fiber is very low, and it has poor wettability with the resin. The fiber cannot form the chemical bonding with the matrix. The UHMWPE composite material has weak interfacial combination and low interlaminar shear strength (ILSS), which restricts the application of the UHMWPE fiber [3]. As a result, the key problem of the application is the interfacial bond property of the UHMWPE fiber-reinforced composite. Surface treatment to the fiber is now the used methods to solve the problem. There are so many methods for the surface treatment, but the effective online matching processing methods are seldom reported [4]. After the surface treatment of the fiber, ILSS was improved, the tensile strength decreased significantly. Based on the principle of “similarity dissolves mutually theory” and the structural features of fibers, the hydrocarbon (PCH) resin was selected as the matrix, which had similar structure to UHMWPE and good wettability with fiber surface. So a lot of surface treatment which was very complex and not satisfactory in its effect can be left out.

Experiment

Material

UHMWPE fiber filament yarn (Dyneema SK75) was obtained from the DSM high-performance fiber B.V. MFE-2 vinyl ester resin (VE) was received from Huachang polymer Co. Ltd of ECUST (China). E-51 bisphenol A liquid epoxy resin (EP) and styrene were purchased from Shanghai resin factory Co. Ltd (China) and from Shanghai Lingfeng Chemical Reagent Co. Ltd (China), respectively. MEP was chemically modified EP made in the laboratory. The 2,4,6-tri-(dimethylamino-methyl)-phenol (DMP-30) was bought from Sinopharm Chemical Reagent Co. Ltd (China). PCH resin is a kind of thermosetting polymer prepared by anionic polymerization of hydrocarbon monomer in the laboratory. PCH resin was liquid at room temperature. There was no by-product when the resin was cured. The resin was suitable to several molding processes. The cured product of PCH resin was nonpolar crosslinking structure, which had low hygroscopicity, dielectric constant, and loss tangent.

Sample preparation

Preparation of resin liquid cement

Certain proportional styrene and peroxide initiator were put to PCH resin while certain proportional DMP-30 was put to MEP. Then, the resin liquid cement with low viscosity can be obtained.

Preparation of the unidirectional UHMWPE fiber-reinforced composite laminate and samples

The UHMWPE fiber filament yarn was dipped in the uniformly stirred resin liquid cement for some time, and unidirectional prepregs were prepared by the winding method. Then, the prepregs were put in the 100 °C oven to be dried for 1 h to get the dried prepregs. The dried prepregs were tailored, laid, and spread on the plate, then were hot pressed. The composite laminates with 56 wt% resin content were made by hot press molding under the processing condition (120 °C/3 h, 2 MPa). Finally, the sample was incised according to the related testing standard.

Preparation of the UHMWPE single-fiber microcomposite

The UHMWPE single-fiber was cut into segments at the length of 5 cm which was pasted on the coordinate paper with an opening hole in the middle. A little resin drop was put on the fiber by a fine iron wire and cured by the above laminate curing condition. The cured drop was a little sphere, and the fiber passed through the sphere.

Test method

Transverse tensile test of the unidirectional fiber-reinforced composite

Referring to GB3354-82 Test method for tensile properties of oriented fiber-reinforced plastics, the testing instrument is CMT5105 electronic universal testing machine made in China.

ILSS test of the unidirectional fiber-reinforced composite

Referring to GB3357-82 Test methods for interlaminar shear of unidirectional fiber-reinforced plastics, the testing instrument is also CMT5105 electronic universal testing machine. The test used three-point short-beam loading (the span-to-depth ratio was 5:1 and the loading speed was 2 mm/min). The thickness of the sample was 2 mm, and the width was 12.5 mm.

Single-fiber pull-out test of the microcomposite [5]

The testing instrument is the YG020B electronic single yarn strength machine made in China. The fiber diameter was observed and measured by the optical microscope, and the resin drop diameter was measured by the vernier caliper. The prepared microcomposite was clamped on the electronic single yarn strength machine, then the pull-out test was processed (the loading speed was 0.1 mm/min). The pull-out strength of the UHMWPE single-fiber can be calculated according to formula (1):

$$\tau_{\mathrm{pull-out}} = P/(\pi d l), \tag{1}$$

where P is the maximum pull-out load, l is the fiber diameter, and d is the resin drop diameter.

Contact angle

Liquid drop method The testing instrument was the JC-2000C1 contact angle instrument. All the concentration of solutions of PCH, EP, and VE is 50 wt%, and the solvent is styrene. The PCH, EP, and VE were, respectively, dissolved in styrene to get solutions with the same concentration. A 2 μL aliquot of each sample solution was carefully squeezed out by microinjector, and the aliquots settled on the surface of the polyethylene (PE) film slowly. A series of images were recorded by a video camera when the aliquots were static. An image analyzing software was used to calculate the contact angles between the aliquots and PE film.

Capillarity infiltration way The testing instrument was self-made. All the concentration of solutions of PCH, EP, and VE is 50 wt%, and the solvent is styrene. Different resins were dissolved in styrene at the same concentration. The orderly UHMWPE fiber passed through the PE pipe with the length of 6–7 cm and 3.3 mm in diameter. The fiber voidage was from 0.47 to 0.53. One end of the pipe was connected to the test arm of electronic balance, and the other end of the pipe was contacted to the wetting fluid. The resin solution rose along the void between the fibers because of capillarity, the weight gain of the fiber by absorbing the solution was tracked by electronic balance, and the curve of infiltration was made by the recorder. The contact angle between the fiber and resin solution was calculated by the curve of infiltration.

SEM analysis

JSM-6460 scanning electron microscope made in Japan was used to study the morphology of fracture surface of the laminate samples and the change of surface state of the fiber before and after pulling out. Specimens were surface coated with gold.

Result and discussion

Transverse tensile properties of the unidirectional fiber-reinforced composite

When the unidirectional fiber-reinforced composites are stretched at 90° to the fiber direction, the main load bearing parts are the matrix and interface. Generally, interface is the weak link of the composite and it is damaged before the matrix is damaged. Therefore, the transverse tensile strength is not only far lower than the longitudinal tensile strength, but also much lower than the strength of the pure matrix, thus limiting the performance of the composite system. This strength is an important index of evaluating interface bond characteristics of composites. Table 1

Table 1 Transverse tensile properties of UHMWPE unidirectional fiber-reinforced composites

Sample type	Transverse tensile strength (MPa)	Transverse tensile modulus (GPa)
UHMWPE/PCH	13.2	0.94
UHMWPE/MEP	7.0	0.46

shows the transverse tensile properties of UHMWPE unidirectional fiber-reinforced composites. The transverse tensile strength of UHMWPE/PCH is 13.2 MPa, and the tensile modulus is 0.94 GPa, which are higher than UHMWPE/MEP. It shows the interfacial bond property between UHMWPE fiber and PCH resin is excellent.

Figure 1(a, b) shows the SEM micrographs of the transverse tensile fracture of UHMWPE unidirectional fiber-reinforced PCH composite. Figure 1(a, b) shows that there are many resins pasted on the surface of UHMWPE fiber. The fiber is closed packaged by resin, and there is no clear two-phase interface between fiber and resin, which shows that UHMWPE fiber and resin had good interfacial bond property.

ILSS of the composite

ILSS reflects the interface combination status of the composite in respect of the macromechanical properties. Table 2 shows that the ILSS of UHMWPE unidirectional fiber-reinforced PCH composite is 48.1 MPa which is obviously superior to that of UHMWPE/MEP composite. The UHMWPE fiber is consisted of nonpolar

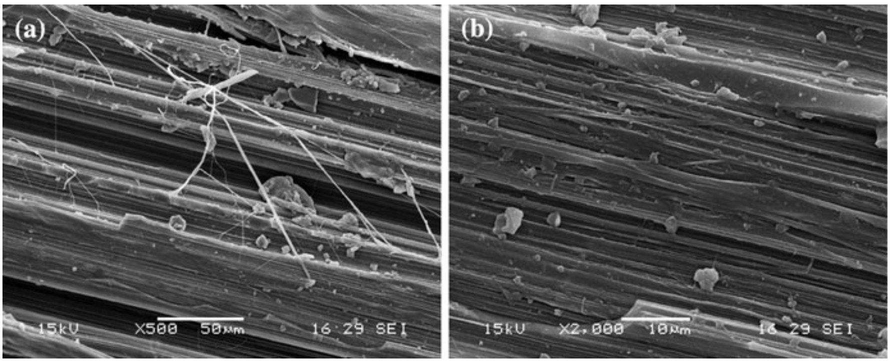

Fig. 1 SEM micrographs of the transverse tensile fracture of UHMWPE unidirectional fiber-reinforced PCH composite

Table 2 ILSS of UHMWPE unidirectional fiber-reinforced composites

Sample type	ILSS (MPa)
UHMWPE/PCH	48.1
UHMWPE/MEP	10.7

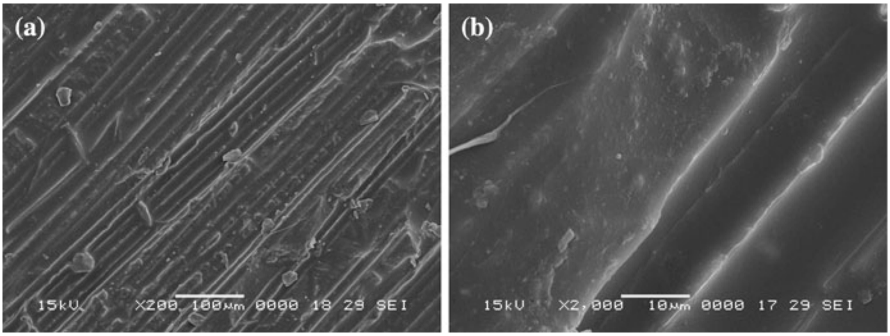

Fig. 2 SEM micrographs of the interlaminar shearing fracture of UHMWPE unidirectional fiber-reinforced PCH composite

C–C bond. The resin is also rich in C–C bond, which is similar to the UHMWPE fiber in structure, so the PCH resin has good wettability with the UHMWPE fiber surface, and the compatibility of resin and the fiber is good and ILSS is high. The SEM micrographs of the interlaminar shearing fracture of UHMWPE/PCH composite are shown in Fig. 2. There is little naked fiber, and the fracture of UHMWPE fiber is surrounded by PCH resin, which fully illustrates UHMWPE fiber and PCH resin have excellent interfacial bond property.

Pull-out strength of the microcomposite

The pull-out strength of the microcomposite reflects the interface combination status of the composite more accurately in respect of the micromechanical properties. The single-fiber pull-out tests are processed on different resin matrix of UHMWPE reinforced microcomposites at indoor temperature condition, and the results are shown in Table 3. The pull-out strength of the UHMWPE/EP and UHMWPE/VE is 5.92 and 6.20 MPa, respectively, while that of UHMWPE/PCH reaches 21.8 MPa. It illustrates that in terms of UHMWPE fiber, the cohesiveness of PCH resin is much better than EP and VE resin.

Figure 3(a) shows the SEM micrograph of the bonding status of PCH resin and UHMWPE fiber before the resin drop is pulled out. Figure 3(b, c) shows the SEM micrographs of the bonding status of resin and fiber after the resin drops was pulled out. It is clear that the state of interface after the resin drop is pulled out was completely different from the state of interface before the resin drop is pulled out. The resin drop is uniformly covered on the fiber surface, and the contact part of the two is a continuum of one integrated mass before the PCH resin drop is pulled out.

Table 3 Pull-out strength of UHMWPE microcomposites

Sample type	Pull-out strength (MPa)
UHMWPE/PCH	21.8
UHMWPE/EP	5.92
UHMWPE/VE	6.20

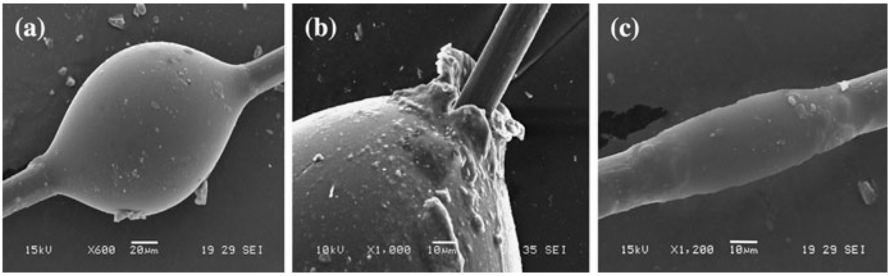

Fig. 3 SEM micrographs of the bonding status of PCH resin and UHMWPE fiber

After the resin drop is pulled out, there is a clear dividing line in the contact part of fiber and resin, which signs that the resin drop and fiber is entirely separated, and there are some resin blocks pasted on the fiber surface. The results show that PCH resin has good wettability with the UHMWPE fiber surface due to the interaction of physical adsorption and chemical bonding between resin and fiber, and the pull-out strength of UHMWPE/PCH microcomposite reaches 21.8 MPa.

Contact angle

The wettability between the reinforcing material and matrix has much influence on the composite properties. The wettability is good, so the interfacial bond strength is high. Good bonding interface can transfer stress well, thus the composite possesses better mechanical properties. The wettability can be weighed by contact angle, which can be measured by many methods such as liquid drop method and capillarity infiltration way.

Liquid drop method

Based on the surface physicochemical principle, the contact angle (θ) is closely related to the wettability between the solution and film. The smaller the contact angle is, the better the wettability. The micrographs of contact angles between resin solutions and PE films are shown in Fig. 4, the contact angles are calculated by the computer software. The results show that the contact angle between the PCH resin

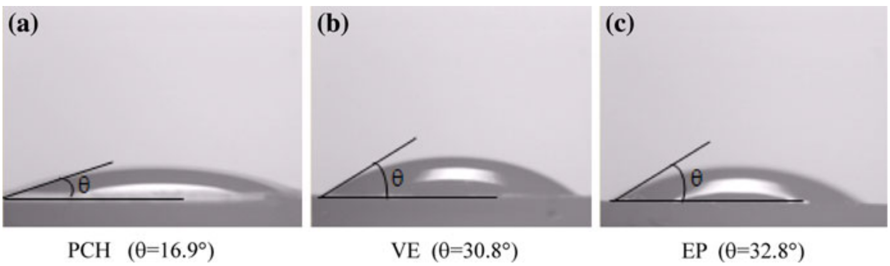

Fig. 4 Contact angle between different resin solutions and PE films

solution and PE film is 16.9° and it is the smallest, the contact angle between the VE resin solution and PE film equals to 30.8°, and the contact angle between the EP resin solution and PE film is 32.6°. Therefore, it is clear that the PCH resin solution had the best wettability with the PE film, and their interfacial compatibility is nice. UHMWPE fiber and PE film have the same structure of repeating unit. Therefore, the wettability between the resin solution and PE film can reflect the wettability between the resin solution and UHMWPE fiber to some extent. We can deduce that the wettability between the PCH resin solution and UHMWPE fiber is better than others.

Capillarity infiltration way [6]

According to the fluid mechanics principle of capillarity, when the fiber voidage is from 0.47 to 0.53, the relationship between weight gain (*m*) and infiltrating time (*t*) in normal infiltration is as follows [7]:

$$m^2 = w_1^3 \Delta r/(H^2 \eta_1 w_f A_f \rho_1)t, \tag{2}$$

where Δr is the change of the surface energy of fiber; *H* is the length of the PE pipe; η_1, w_1, and ρ_1 are the viscosity, mass, and density of the wetting fluid, respectively; A_f and w_f are the specific surface area and mass of the fiber, respectively.

According to the formula (2), a figure on $m^2 \sim t$ was drawn, and a linear is fitted on the basis of least square method (Fig. 5). The straight slope (*k*) is

$$k = w_1^3 \Delta r/(H^2 \eta_1 w_f A_f \rho_1) \tag{3}$$

$$\Delta r = kH^2 \eta_1 w_f A_f \rho_1 / w_1^3 \tag{4}$$

where η_1 can be measured by the viscosity instrument, and w_f, ρ_1 can be measured in the experiment. If the fiber is a cylinder, the specific surface area of fiber can be represented as formula (5).

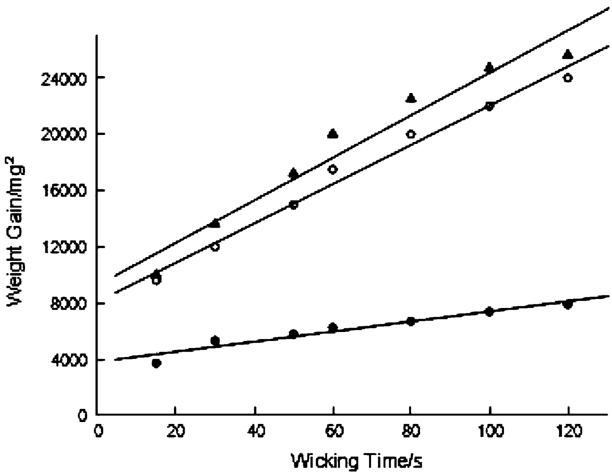

Fig. 5 Curves of UHMWPE fiber infiltration. *Open circle* EP ($Y_{EP} = 8099.4 + 139.35X$); *closed circle* PCH ($Y_{PCH} = 3825.4 + 35.873X$); *closed triangle* VE ($Y_{VE} = 9270.3 + 151.01X$)

$$A_f = 4/d\rho, \tag{5}$$

where d is the diameter of the fiber and ρ is the density of the fiber.

By substitution of the straight slope of fitting straight lines in Fig. 5 into the formula (4), the change of the surface energy of fiber (Δr) is figured out.

$$\cos\theta = \Delta r/\sigma_1, \tag{6}$$

where σ_1 is the surface tension of the wetting fluid, which can be determined by drop volume method and calculated based on formula (7).

$$\sigma_1 = \rho_1 Vg/(2\pi rf), \tag{7}$$

where ρ_1 is the density of the wetting fluid, V is the drop volume, r is capillary radius, and f is the correction factor.

$$f = 0.9045 - 0.7249(r/V^{1/3}) + 0.4293(r/V^{1/3})^2,\ (0.3 < r/V^{1/3} < 1.2) \tag{8}$$

or

$$f = 1.007 - 1.4789(r/V^{1/3}) + 1.829(r/V^{1/3})^2,\ (0.058 < r/V^{1/3} < 0.3). \tag{9}$$

Uniting out formula (6–9), the cosine of contact angle (cos θ) between the wetting fluid and fiber can be obtained, then the contact angle (θ) can be figured out (Table 4).

The fiber bundle is used in the capillarity infiltration way, so the test results have statistical properties, which can reflect the actual situations more accurately. Table 4 shows that during the impregnation process, the change of the surface energy (Δr) between the PCH resin solution and UHWPE fiber is the biggest of three, the surface tension of the PCH wetting fluid (σ_1) is the smallest, and the contact angle (θ) between the PCH wetting fluid and UHWPE fiber is the smallest. Therefore, the interface adhesion between the PCH resin and UHWPE fiber is the best and the ILSS is the highest of three.

Conclusion

(1) The transverse tensile strength of UHMWPE unidirectional fiber-reinforced PCH composite is 13.2 MPa and ILSS is 48.1 MPa (obviously higher than UHMWPE/MEP), which illustrates that the interfacial bond property of UHMWPE/PCH composite is good in respect of the macromechanical properties.

Table 4 Experimental parameters of capillarity infiltration way

Type of wetting fluid	k (mg^2/s)	η_1 (CP)	Δr (mN/m)	σ_1 (N/m)	θ (°)
PCH	35.9	53	27.2	31.9	31.5
EP	139	13	21.3	34.3	51.6
VE	151	17	24.6	35.3	45.8

(2) The pull-out strength of the UHMWPE/PCH microcomposite reaches 21.8 MPa, while the pull-out strength of the UHMWPE/EP microcomposite and UHMWPE/VE microcomposite are 5.92 and 6.20 MPa, respectively, which reflect that the interface combination status of the UHMWPE/PCH composite is excellent in respect of the micromechanical properties.
(3) The contact angle between the PCH resin solution and PE film measured by the liquid drop method is 16.9° and the contact angle between the PCH resin solution and UHMWPE fiber tested by capillarity infiltration way is 31.5°, and both of them are lower than EP and VE resin solutions. Good interface adhesion of UHMWPE/PCH composite can be attributed to the fact that nonpolar PCH resin solution has good wettability with the UHMWPE fiber surface.

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