

Synthesis and Performance Characteristics of a Water-Based Polyacrylate Microemulsion for UHMWPE Fiber Adhesive Coating

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ABSTRACT: The water-based polyacrylate microemulsion for ultrahigh molecular weight polyethylene (UHMWPE) fibers adhesive coating was synthesized by the emulsion polymerization of methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), and hydroxyethyl acrylate (HEA) in the presence of a composite of sodium lauryl sulfate (SLS), OP-10, and *n*-octyl alcohol (NOA) as the emulsifier. The effects of the mass fraction of emulsifier and the reaction time on the properties of emulsion and its membrane were investigated. When $m(\text{BA}) : m(\text{MMA}) : m(\text{AA}) : m(\text{HEA})$ was 50 : 50 : 3 : 10 (wt ratio) and the mass fraction of emulsifier was 13 wt % and the reaction time was 3 h at

80°C, the latex particle diameter was 30 nm tested by transmission electron microscope (TEM). The Fourier transform infrared (FTIR) spectrometer and differential scanning calorimeter (DSC) were used to characterize the chemical structure and the glass transition temperature (T_g) of microemulsion membrane. The application results showed that this microemulsion was an ideal adhesive coating for UHMWPE fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3195–3202, 2006

Key words: adhesives; coatings; emulsion polymerization; polyethylene fibers

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) fibers were the third generation with high strength and high modulus one after the carbon fiber and the aramid fiber.¹ Due to its high molecular weight, high orientation, and high crystallization, this fiber had the highest strength among all the fibers.² Its specific strength was 15 times as much as the high-quality steel fiber and was two times larger than the carbon fiber and 40% larger than the aramid fiber. It also had many advantages, such as excellent chemical erosion resistance, seawater resistance, wear resistance, high shear strength, and low density.³ Therefore, UHMWPE fibers were the ideal material for making soft armored garments, stabproof dress, bulletproof helmets, shellproof armored vehicles, and the anchor dropping ropes, harbor rigging, and wind resistance snub for naval vessels and ships.^{4–6} In the course of making these products, a kind of adhesive coating was needed to adhere a bundle of UHMWPE fibers together as a whole, with good adhesiveness, waterproof, wear resistance, softness and certain protective

properties formed on the surface of this adhesive bundle of UHMWPE fibers.⁷ The common fibers adhesive coating belong to are rubber, polyurethane, and polyacrylate. The rubber adhesive coating has good elasticity, but its membrane easily ages changes color and produces atmospheric pollution because toxic benzene or toluene and xylene are used as solvents. Polyurethane adhesive coating has excellent strength and wear resistance, but it must also use poisonous solvents such as *N,N*-dimethyl formamide (DMF). Water-based polyacrylate microemulsion adhesive coating is ecofriendly and has many excellent properties such as quick permeability, good adhesiveness, and formation of smooth and tight membranes, without producing pollution and using simple technology.^{8–11} In this article, we report the preparation and characterization of the water-based polyacrylate microemulsion and its membrane for UHMWPE fibers adhesive coating. The microemulsion was synthesized by emulsion copolymerization using methyl methacrylate (MMA), butylacetate (BA), acrylic acid (AA), and hydroxyethylacrylate (HEA) as the main monomers and the composite of sodium lauryl sulfate (SLS), OP-10, and NOA as emulsifier. The microemulsion copolymerization conditions and the properties of microemulsion and its membrane were investigated. The technology provided efficient and easy processing in

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TABLE I
Relationship between the Monomer Composition and Properties of Coating^a

	Monomer weight ratio $m(\text{BA}) : m(\text{MMA}) : m(\text{AA}) :$ $m(\text{HEA})$ (g)	Membrane properties				Elasticity and flexibility
		Tensile strength (MPa)	Tensile elongation (%)	T_g (°C)	Wear loss (%)	
1	50 : 50 : 3 : 5	2.33	1147.42	-19	0.17	Adhesive
2	50 : 50 : 3 : 10	3.10	1013.13	-28	0.10	Good
3	50 : 50 : 3 : 15	3.13	869.13	-20	0.11	Good
4	50 : 50 : 3 : 17	3.13	845.24	-14	0.13	Better
5	50 : 50 : 3 : 20	3.12	813.15	-8	0.11	Harder
6	50 : 50 : 3 : 25	3.13	798.81	5	0.10	Hard

^a The emulsifier mass fraction was 13 wt %, the emulsion concentration was 30 wt %, the emulsion polymerization was processed at 80°C for 3 h.

preparing the adhesive coating for UHMWPE fibers, with low cost and without pollution. The results show that this polyacrylate microemulsion is an ideal adhesive coating for UHMWPE fibers and reinforces the industrialization of application of UHMWPE fibers.

EXPERIMENTAL

Materials

The UHMWPE fibers studied here were DC88 supplied by Ningbo Dacheng Advanced Material Co. Ltd., China, (specifications 1480 denier/500 number filaments). The fibers were used for our experiments after being washed with ethanol and water. These are the earliest and simplest surface treatments to improve adhesion of polymer and matrix.¹²⁻¹⁴ MMA, BA, HEA, and AA are all analytical reagents and were supplied by Tianjing Bodi Chemical Co. Ltd., China. Sodium lauryl sulfate (SLS) OP-10, and n-octyl alcohol (NOA) were chemical reagents and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ was an analytical reagent supplied by Xi'an Chemical Reagent Plant, China. All of the above reagents were used as received.

Instruments

Measurements of tensile properties of the polyacrylate microemulsion membrane, such as tensile strength

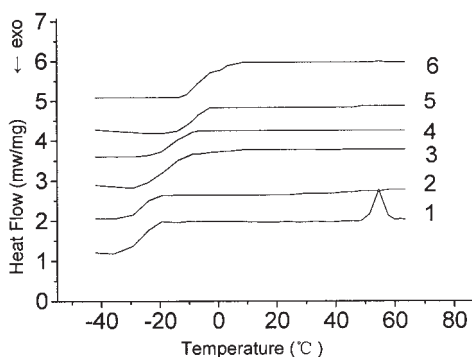


Figure 1 DSC thermograph of polyacrylate emulsion membranes (1, 2, 3, 4, 5, and 6 are described in Table I).

and elongation at break, were performed on a TS2000-S Universal Electronic Tensile testing machine (made by Gaotie Science and Technology Co. Ltd., China). The wear loss of coating film and the adhesion strength between coating and UHMWPE fibers were measured on a Fiber Dynamic Wear Loss Tester (made by Changzhou Textile Instrument Factory, China). The structure of the membrane was verified on a WQF-310 Fourier transform infrared (FTIR) spectrometer (made by Beijing No.2 Optical Instrument Factory, China). The glass transition temperature (T_g) of the membrane was examined by using a DSC-200PC differential scanning calorimeter (DSC) (made by NETZSCH Instrument Co. Ltd., Germany). The TEM images of the polyacrylate (PMA) microemulsion were characterized on a S-600 Transmission Electron Microscope (made by HITACHI Instrument, Japan).

Synthesis of polyacrylate microemulsion

Polyacrylate microemulsion was synthesized with the monomer-drop feeding method by the emulsion copolymerization. In the process of synthesis, the mixture of SLS, OP-10, and NOA was used as emulsifier

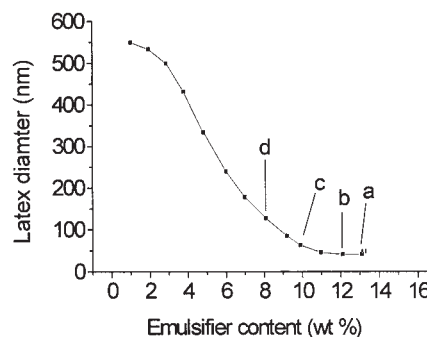


Figure 2 Relationship between emulsifier mass fraction and latex particle diameter (a, b, c, and d were the latex diameter when the emulsifier mass fractions were, respectively, 13, 11, 10, and 8 wt %). The emulsion polymerization was processed at 80°C for 3 h when $m(\text{BA}) : m(\text{MMA}) : m(\text{AA}) : m(\text{HEA}) = 50 : 50 : 3 : 10$ (wt).

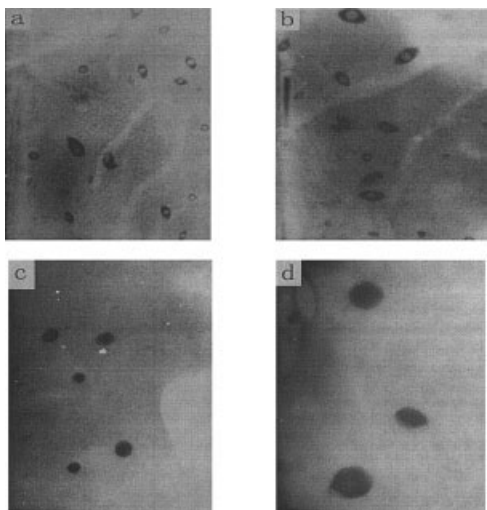


Figure 3 TEM photos of latex particles (a, b, c, and d emulsion were same as in Figure 2, latex diameter: (a) 30 nm, (b) 40 nm, (c) 52 nm, (d) 146 nm; original magnification: X50,000).

and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as initiator. Out 250-ml distilled water, 1.2 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and emulsifier (see Figure 2 for the amount of emulsifier) were added to a clear 500-ml four-neck round-bottom flask with a stirrer, a condenser and a thermometer. The premixed monomer (see Table I for the composition of monomers) was put into a 250-ml dropping funnel. When the liquid in the flask was heated to design temperature 70°C (or 80 or 90°C), the mixed monomers were added to the flask over 0.5 to 1.5 h. After the drop feeding was ended, the thermal insulation reaction was completed for 1.5 h at the design temperature. The product then was cooled to room temperature and the pH value adjusted to 7.0 with 10 wt % NaOH solution. The obtained emulsion was spread evenly on the polytetrafluoroethylene plastic plate and the emulsion membrane was obtained at room temperature.

Testing the stability of the polyacrylate microemulsion

The stabilities of the polyacrylate microemulsion, such as the centrifugal stability, high temperature stability, the freeze-thaw stability, the pH stability, and the dilute stability were tested according to Hu.¹⁵

Characterization of microemulsion membrane and adhesive performances

The uniform and clean membranes obtained from microemulsion were used to test the water resistance, the tensile strength, and the elongation at break of the membrane. The tensile strength and elongation at break of the membrane were performed according to the People's Republic of China National Standard

Methods (GB/T1040-1992). The clean and vacuum-dried microemulsion membrane added to the distilled water for 96 h. After a certain time, the water uptake of coating was tested and calculated by the following equation:

$$\text{Water uptake} = [(W_1 - W_0)/W_0] \times 100$$

where W_0 and W_1 were the preuptake membrane weight and the postuptake membrane weight, respectively.¹⁶ Five replicates were tested for each membrane specimen, and average values of the water uptake were determined.

The adhesion strength of polyacrylate membrane on UHMWPE fibers was measured by using a Fiber Dynamic Wear Loss Tester. The testing conditions were as follows: The initial tension was 9.8 N, the length of the UHMWPE fibers treated by adhesive coating were 33 cm. When wear frequency was 1,000 times, wear loss was determined, which characterized the coating strength. The maximum wear frequency was determined when the coating on the fiber surface was fully abraded, which was used to evaluate the adhesion strength of adhesive coating and UHMWPE fibers. The wear loss was calculated by the following equation:

$$\text{Coating Wear Loss (\%)} = [(G_0 - G_1)/G_0] \times 100$$

where G_0 and G_1 were the prewear and postwear samples weight, respectively. Ten replicates were tested for each specimen.

The diameter of latex particles was determined by TEM. The diameters could be calculated according to the amplification factor. FTIR spectra of the microemulsion membrane were used to characterize its chemical structure of polyacrylate copolymer. The

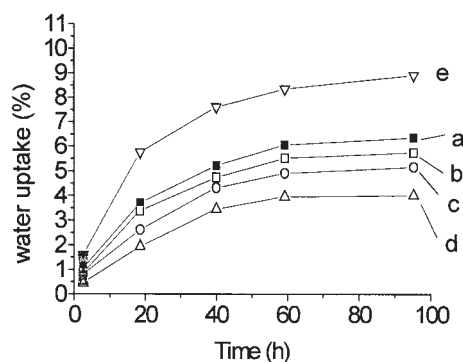


Figure 4 Relationship between water uptake of emulsion membranes and time (a, b, c, and d were the water uptake of relevant membranes of emulsion, which were same as in Figures 2 and 3, e was the water uptake of ordinary polyacrylate emulsion membrane and its latex diameter was $50\ \mu\text{m}$).

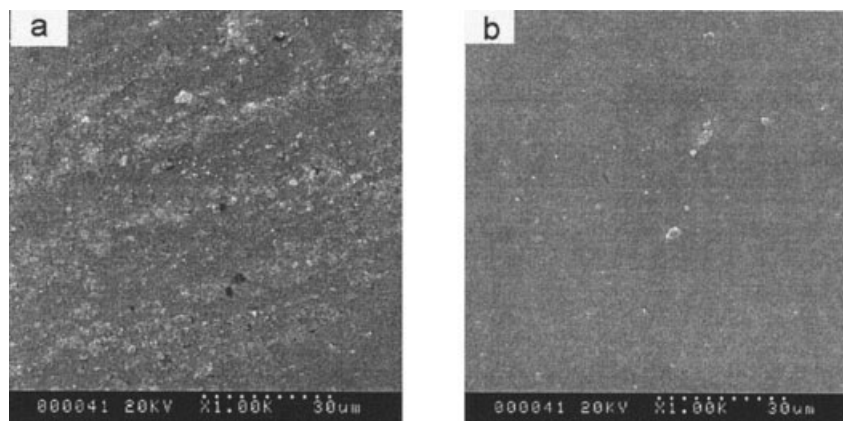


Figure 5 SEM surface photograph of (a) ordinary microemulsion membrane and (b) polyacrylate microemulsion membrane.

spectrometer is designed to record the IR spectra of samples in the frequency range $400\text{--}4000\text{ cm}^{-1}$. T_g was used to evaluate the elasticity and flexibility of polyacrylate microemulsion membrane, which was tested by putting an approximate 5-mg sample into an aluminum pan and sealing it. Under the condition of nitrogen atmosphere and liquid nitrogen cooling, T_g was tested at heated rate of $10^\circ\text{C}/\text{min}$ from -60 to 120°C .

RESULTS AND DISCUSSION

Effects of monomers composition on adhesive coating properties

Polyacrylate microemulsion for the UHMWPE fibers adhesive coating should have excellent adhesive, wear resistance, water proof, elasticity, and flexibility properties. These characteristics can be obtained by controlling the composition of copolymerization monomers. Because the HEA is a determining monomer in controlling wear resistance, elasticity, and flexibility of polyacrylate adhesive coating, the effects of

HEA on the properties of the adhesive coating must be mainly considered.¹⁷ The relationship between the HEA content and the membrane properties is shown in Table 1 and Figure 1. The tensile strength and T_g increased with the increase in HEA content while the membrane wear loss decreased with the increase in HEA content. The results show that the content of HEA had great influence on the tensile strength and membrane wear loss; the maximum tensile strength occurred at 15 g HEA and minimum wear loss occurred at 10 g HEA because the HEA acts as a crosslinker in the polyacrylate membrane. After the formation of membrane, the linear polymer was transformed into the network polymer by the crosslinking reaction of HEA (see Figure 9), which led to the increase of tensile strength and lower wear loss. The T_g of emulsion membrane was tested by DSC and used to evaluate the freezing resistance of the polyacrylate microemulsion membrane. Generally speaking, a lower T_g was favorable for UHMWPE fibers adhesive coating. Considering the comprehensive properties of samples from comprehensive, the optimum composition of monomers was $m(\text{BA}) : m(\text{MMA}) : m(\text{AA}) : m(\text{HEA}) = 50 : 50 : 10$ (wt, g).

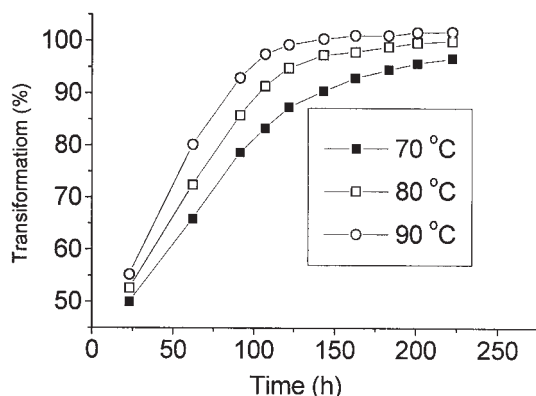


Figure 6 Effects of the reaction temperature and time on monomer conversions (other reaction conditions were the same as in Fig. 2).

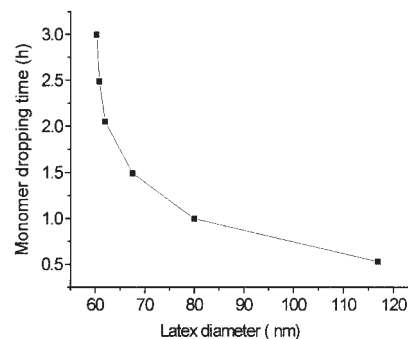


Figure 7 Effects of feeding time on latex particle diameter (other reaction conditions were the same as in Fig. 2).

TABLE II
Stabilities of the Polyacrylate Microemulsion

pH value of stable emulsion	Centrifugal stability	High temperature stability	Freeze-thaw stability	Dilution stability
3-10	Stable	Stable	Stable	Stable

Effects of emulsifier on the latex particles diameter

The emulsifier composed by SLS, OP-10, and *n*-octyl alcohol was used to synthesize the water-based polyacrylate microemulsion. The relationship between the mass fraction of emulsifier and latex particle diameter is shown in Figure 2. The latex diameter was characterized by TEM and the results are shown in Figure 3. With the increase of emulsifier, the latex particle diameter decreased. When the emulsifier concentrations were, respectively, 8, 10, 11, and 13 wt %, the latex particle diameters were, respectively, 146 nm [Fig. 3(d)], 52 nm [Fig. 3(c)], 40 nm [Fig. 3(b)], and 30 nm [Fig. 3(a)]. The water uptake of emulsion membrane increased with the increasing amount of emulsifier. The results are shown in Figure 4. It shows that the larger the mass fraction of emulsifier, the larger the water take of membrane. From Figure 4 it is found that the water uptake of membrane increased successively. Compared with the ordinary polyacrylate emulsion membrane, the water absorption of the microemulsion membranes was smaller (the ordinary polyacrylate latex particle diameter was 50 μm) because the latex particle diameter of microemulsion was small and its membrane was dense and smooth and molecular arrangement was intense (Fig. 5). As a consequence, the polyacrylate microemulsion could form the dense and smooth coating surface. At the same time, proper crosslinking removes a part of hydrophile so as to make the coating have better water resistance com-

pared with the ordinary emulsion membrane. The minimum film forming temperature of the polyacrylate microemulsion is 10°C. Its optimum temperature of forming membrane is 60°C when it is used as coating on UHMWPE fibers.

Effects of reaction temperature and time on the conversion and latex particle diameter

The effects of the reaction temperature and time of emulsion polymerization on the monomers conversion and latex particle diameter are shown in Figure 6. From Figure 6 it can be seen that the monomers conversion rapidly increased with increasing reaction time up to 2 h, after which the conversion started to level off when the reaction temperature was at 80 or 90°C. The monomer conversion was obviously lower

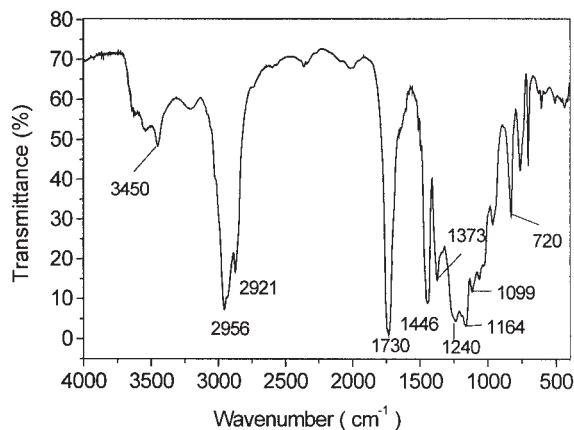


Figure 8 FTIR of the polyacrylate microemulsion membrane.

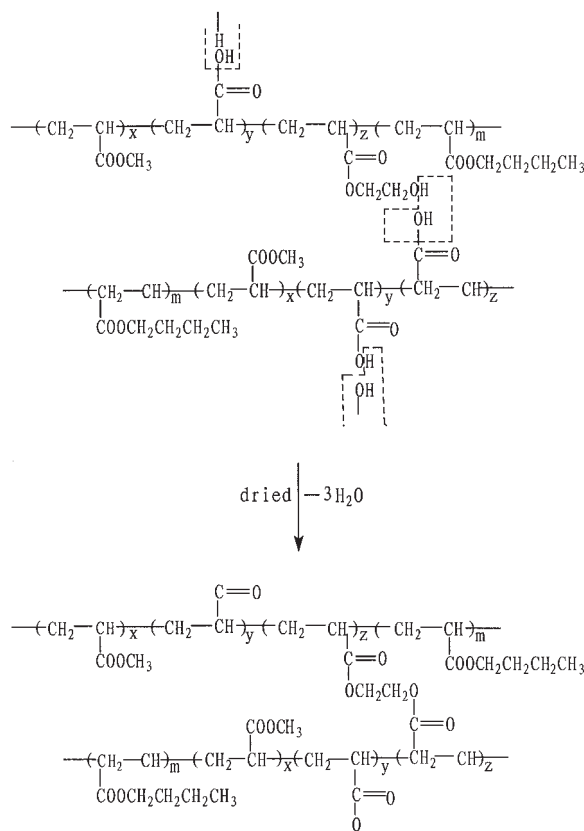


Figure 9 The schematic of chemical structure of the polyacrylate microemulsion membrane.

TABLE III
Properties of UHMWPE Fiber Treated with Different Adhesive Coating

Adhesive coating agent ^a	Solvent	Tensile strength (GPa)	Elongation at break (%)	Wear loss (%)	Maximum wear frequency
Untreated		2.80	4.4	—	—
Polyurethane	<i>N,N</i> -Dimethyl formamide	2.95	4.5	0.16	5364
Rubber	Benzene,toluene,xylene	3.04	4.6	0.15	4980
Polyacrylate	Water	3.16	4.5	0.10	6721

^a PU used in this research is T1180, an elastic polyurethane adhesive made by Tanjing Polyurethane Factory in China. Rubber used in this research is a modified neoprene made by ourself.

Polyacrylate used in this research is polyacrylate microemulsion adhesive coating. The mass concentration of polyacrylate micromembrane is 30 wt%.

at 70°C. When the polymerization was processed, respectively, at 90, 80, and 70°C for 3 h, the monomer conversions were 99.5, 96.7, and 89.1%, respectively. This result shows that the reaction temperature and time are important factors controlling the monomer conversion. Due to the increase of reaction temperature, initiation rate increases and the polymerization rate increases. So the monomer conversions increase. The polymerization time was composed of the feeding time and thermal insulation time. The relationship between feeding time and latex particle diameter is shown in Figure 7; the longer the feeding time, the smaller the latex particle diameter, and the shorter the feeding time, the larger the latex particle diameter. The results shows that monomer penetration and distribution in the latex particles were even.

Testing results of emulsion stability

The stability of polyacrylate microemulsion not only reflected the degree of copolymerization and the rationality of every monomer proportion in the polymeric system, but greatly influenced the storage and

application of emulsion and the properties of the membrane as well. The testing results of the above-mentioned microemulsion stability with less than 100 nm of latex particle diameter are shown in Table II. The table showed that this polyacrylate microemulsion had very good stability, which is better suited for storing and applying to the UHMWPE fibers coating.

Structure characteristics of polyacrylate microemulsion membrane

FTIR spectra of polyacrylate microemulsion membrane are shown in Figure 8, where 3450 cm^{-1} is the $-\text{OH}$ absorbing peak, and 2956 and 2921 cm^{-1} are the C-H tensile vibrating absorbing peaks of $-\text{CH}_3$ and $-\text{CH}_2$ in the polymer chain. 1730 cm^{-1} is the $-\text{C}=\text{O}$ tensile vibrating peak. 1446 and 1373 cm^{-1} are the C-H flexural vibrating peaks of $-\text{CH}_3$, $-\text{CH}_2$. 1240, 1164, and 1099 cm^{-1} are C-O-C tensile vibrating absorbing peaks of methyl ester and butyl ester in the side chain of the polymer. FTIR illustrated that all the monomers had done the polymerization. Figure 9 shows the structure of the polyacrylate membrane.

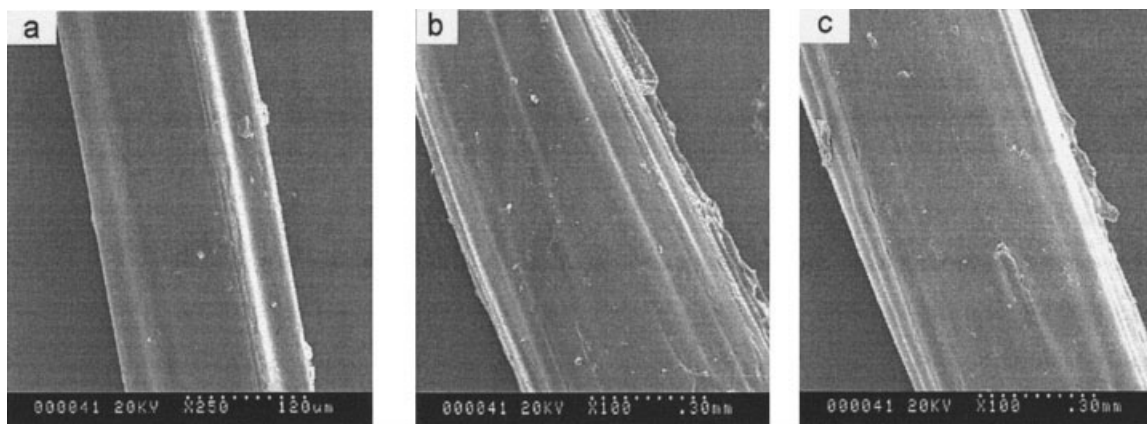


Figure 10 SEM photographs of fibers surface treated by the microemulsion adhesive coating: (a) polyacrylate microemulsion; (b) polyurethane; (c) modified neoprene.

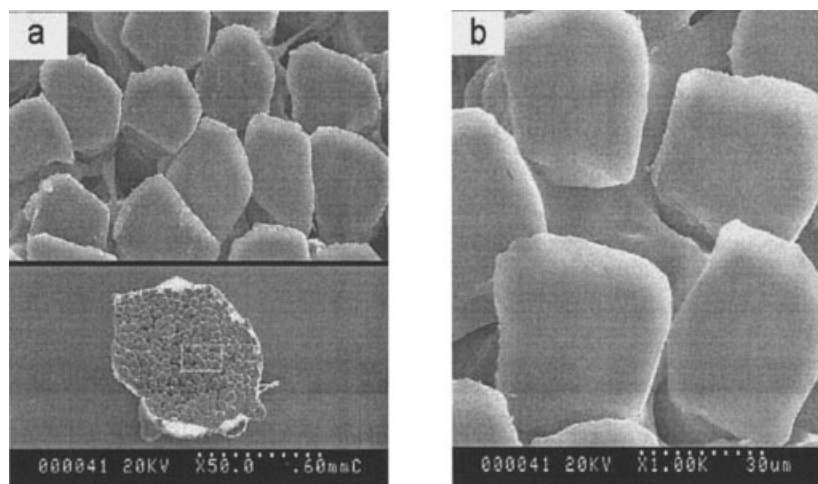


Figure 11 SEM photographs of fiber fractures treated by the microemulsion adhesive coating in the cross-sectional direction: (a) whole cross section; (b) part of a cross section.

Application results of polyacrylate microemulsion adhesive coating

The application results of polyacrylate microemulsion adhesive coating are shown in Table III. From Table III it can be seen the tensile strength of UHMWPE fibers treated with polyacrylate adhesive coating is the greatest compared with UHMWPE fibers treated by polyurethane and modified neoprene adhesive coating. The wear loss and maximum wear frequency of UHMWPE fibers treated by polyacrylate microemulsion are also the best in the three treatments of UHMWPE fibers. Figure 10(a,b) indicate that the coating on the fibers surface is very smooth and tight. Figure 11(a,b) show better compatibility between adhesive and fibers, meaning that the microemulsion adhesive coating has good wetting of the UHMWPE fibers surface, which is usually the first demand for good adhesion. This is because there are many side groups of butyl acrylate and methyl acrylate in the molecular chain of adhesive coating, and the butyl and methyl have the same molecular structure as UHMWPE fibers, so they have good compatibility and interdiffusion of adhesive and fibers,^{18,19} as shown in Figure 12. On the other hand, the water-based poly-

acrylate microemulsion adhesive coating emits no harmful gas into air to pollute the environment in the application because it used water as the solvent. Therefore, it is an ideal adhesive coating for UHMWPE fibers and reinforces the industrialization of high property rope with UHMWPE fibers.

CONCLUSIONS

In this study, we synthesized polyacrylate microemulsion for UHMWPE fibers adhesive coating. The microemulsion adhesive coating agent had many excellent characteristics, such as softness, elasticity, flexibility, weather resistance, good adhesion, and wear resistance when it was used as the adhesive coating for high strength ropes made by UHMWPE fiber. It was very convenient to use this emulsion and there was no pollution. Therefore, it is an ideal adhesive coating for UHMWPE fibers

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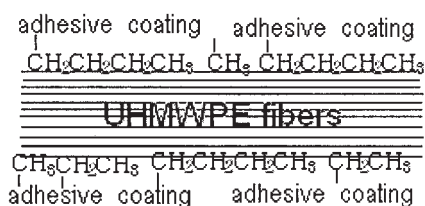


Figure 12 Schematic illustration of the interface between adhesive and fibers.

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