Water-Resistant Material from Recovered Fibers and Acrylic Emulsion Terpolymer

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Styrene (SM), methyl methacrylate (MMA), and butyl acrylate (BA) were used to synthesize a polyacrylic emulsion by core-shell emulsion polymerization. The solid content of the emulsion reached 40% using reasonable reactive emulsifier contents and feeding modes. Then, the emulsion and a fiber were dispersed, coated, and dried together. Finally, fiber-based water-resistant material was successfully fabricated. The experimental results showed that under the conditions of a monomer mass ratio of 1:1:1 and a mass ratio of polyacrylic emulsion to fiber of 2:1, the Cobb value of the material reached 5.0 g/m^2. The tensile strength, elongation, and breaking length were 7.4225 kN/m, 1.0%, and 11.706 km, respectively. Using scanning electron microscopy (SEM) to analyze the surface morphology and internal structure of products, the reasons for the high water resistance of fiber-based material was due to the bonding and filling effects of the polyacrylic emulsion on the fibers. For tightly bound fibers, the porous structures formed in fiber-based boards were reduced. On the other hand, the polyacrylic emulsion filled the gaps between fibers. This filling effect led to a continuous structure, and the water resistance of the material was further enhanced.

Keywords: Core-shell emulsion polymerization; Polyacrylic emulsion; Water resistance; Porous structure; Cobb value

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INTRODUCTION

In response to increasing world population and the enhancement of living conditions, people are becoming more concerned about environmental protection. Dust generated from ports, mine fields, and construction sites, *etc*., causes serious environmental pollution, especially in windy conditions (Yin 2009; Sullivan *et al.* 2007; Feng and Chen 2011; Wen 2011; Zhang *et al.* 2004; Cao *et al.* 2003; Yuan *et al.* 2004). Planting canvas covers and spraying water on pollution sources are some management practices used to prevent dust being blown, but this method has high costs for manpower and material resources, as canvas has to be unfolded and water has to be sprayed once again during the hot season. An innovative method is found in the example of sheet forming processes in the paper-making industry, in which spraying water-dispersed pulp on pollution resources results in the pollution resources becoming covered by a fiber-based dustproof layer. However, the pure fiber layer is still lacking in water resistance. Meanwhile, water-resistance agents are usually added to the pulp and coated on the surface of dried paper to enhance its water resistance. However, paper-making agents cannot reach a high level of water resistance, and the surface coating processes of paper may not be satisfactory for open areas (Carvalhol *et al.* 2005; Banerjee 1991; Truong *et al.* 2003).

It is well known that coatings can have high water resistance. Because of the increasing emphasis on environmental protection and health, waterborne coatings with low amounts of volatile organic chemicals (VOCs) have been applied extensively (Yu 2009). Acrylic resin, which is copolymerized by acrylic acid (AA) and MMA, does not contain oxidative and hydrolytic functional groups on its C-C main chain. Additionally, its light absorption peaks are located outside of the solar spectrum region. Otherwise, the polymer absorbs sunlight and would be photo-oxidized easily (Kriwet *et al.* 1998; Marschütz and Bernkop-Schnürch 2002; Zhong and Ha 2011; De *et al.* 2003). Because of their structure stability, inoxidizability, media resistance, and transparency, acrylic polymers are weather resistant (Chen *et al.* 2005; Fan and Zhang 2011; Yi *et al*. 2008; Greindl and Bernkop-Schnürch 2006; Chen *et al.* 2008; Kanou 1996) and can be used as a crude material for preparing a water-resistant material.

Based on pulp and paper-making processing and the properties of polyacrylics, fiber-based materials with high levels of water resistance were prepared by compounding polyacrylic emulsions and plant fibers in this research. Theoretically, dust would not be blown around by the wind after the polluted area was covered by this material. Additionally, the material can withstand rain scouring.

As an important indicator, the Cobb method is generally used on paper sheets for the detection of water resistance properties. Because the material resembles a paper sheet, Cobb value testing for this fiber-based material is reasonable. In addition, the water-resistance mechanism was investigated using scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Bisphenol A ethoxy resin E-44 with epoxide number 0.43 was of reagent grade. The fibers were cardboard tailings obtained from China Sunshine Paper. Other chemicals were of analytical grade.

Preparation of Polyacrylic Emulsion

Polyacrylic emulsion A (m_{SM}:m_{MMA}:m_{BA}=1:1:1): ethenyl benzene (11.25 g), MMA (11.25 g), and BA (11.25 g), was mixed with acrylic acid (1.35 g). OP-10 (0.90 g) and sodium dodecyl sulfate (0.45 g) were used as surfactants. Sodium bicarbonate (0.45 g) was used as a pH buffering agent. Both the surfactant and buffering agents were dissolved as emulsifying agents in distilled water (70 mL). Ammonium persulfate (0.24 g) was dissolved as an initiator in 5 mL of distilled water. A pre-emulsion was made as follows: 1/3 of the emulsifying agent and 1/5 of the mixed monomer were mixed together at high speed for 30 min. At 80 °C, 1/5 of the pre-emulsion and 1/3 of the initiator were stirred in a three-necked round-bottom flask.

After 25 min, 4/5 of the pre-emulsion was added by use of a constant pressure dropping funnel that was fitted to the vice-neck of the flask. Meanwhile, the rest of the initiator was manually added to the reaction system every 10 min. The pre-emulsion and initiator dropping process lasted 60 min. The system was then kept at a fixed temperature for 30 min.

At the same time, epoxy resin E-44 (4.50 g) was dissolved in the 4/5 monomer mixture and emulsified with the rest of the emulsifying agent with high-speed stirring. Then, the new emulsion was placed in the dropping funnel and added at 85 °C.

Ammonium persulfate (0.76 g) was dissolved as a new initiator in 10 mL of distilled water. This initiator was used with the same dropping method as described above. The pre-emulsion and initiator dropping process lasted 90 min. The system was then heated at 85 °C for another 30 min. Finally, the pH of the polyacrylic emulsion was adjusted to 7.0 by ammonia after it was cooled to 40 °C.

Polyacrylic emulsion B (m_{SM}:m_{MMA}:m_{BA}=2:1:1): The dosage of ethenyl benzene was 22.50 g. All other processes were the same as above. Polyacrylic emulsion C (m_{SM}:m_{MMA}:m_{BA}=1:2:1) and polyacrylic emulsion D (m_{SM}:m_{MMA}:m_{BA}=1:1:2) were prepared in a similar manner.

Preparation of Fiber-Based Water-Resistant Material

The fibers were smashed in a high-speed grinder for 3 min. The smashed fibers (100 g) were dispersed together with distilled water (100 g) by a high-speed dispersion machine at the speed of 3000 rpm. After 10 min, a polyacrylic emulsion (solids content, 40%) was added to the dispersion machine. The mixture was dispersed for 30 min at the same speed. Then, fiber-based boards with thicknesses of 0.500 to 0.800 mm were prepared. Fiber-based boards with different polyacrylic emulsion : fiber mass ratios (2:1, 1:1, 1:2, 1:3, 1:4, and 1:5) were prepared by the same process. And all of the mass ratios were calculated by solids content.

Characterization Methods

Particle size and zeta potential analyses of the polyacrylic emulsions were performed using a Malvern Zeta Sizer Nano-Zs900 with deionized water at pH=7.

SEM analysis of the fiber-based water-resistant material was performed using a JEOL JSM-6700F.

To keep the water content in the sample dispersed equally and to avoid test error caused by water balance lag, the fiber-based material was put in an environment as follows for 24 h: temperatures below 40 °C, relative humidity below 35%.

To determine the thickness, a paper thickness gauge was zeroed and placed on a vibration-free horizontal platform. The sample was placed between two measurement planes. The moveable measurement plane was slowly pressed on the sample with a speed of less than 3 mm/s to avoid any impact force. Before the sample was "indented," readings were recorded after the pointer stopped moving. Every sample was tested once.

The fiber-based sample was cut into round slices with diameters of 125 mm using a circular cutter. The water-absorbing capacities of the samples were then measured according to the Cobb method using a Cobb absorption tester. The Cobb values were calculated as follows,

$$C = (G_2\text{-}G_1) \times 100 \quad (1)$$

where G_2 is the mass of the sample after absorbing water and G_1 is the mass of the sample before absorbing water. The lower the Cobb value is, the higher the water resistance is.

Finally, excepting the most important water resistance, other properties of the fiber-based material under the optimum conditions, such as tensile strength, elongation, breaking length, and folding resistance were tested separately.

RESULTS AND DISCUSSION

Particle Size and Zeta Potential of the Polyacrylic Emulsions

The particle size distributions of polyacrylic emulsions synthesized at different monomer ratios are shown in Fig. 1. The resulting quality reports were all good. As seen from the normal distribution curves, the particle size distributions of the emulsions were uniform. Because polyacrylic emulsion A had the best distribution pattern, *i.e.*, a single smooth peak, the particle size distribution of polyacrylic emulsion A was more uniform than the others. The lowest PDI value shown in Table 1 gives additional demonstration of its particle size distribution uniformity.

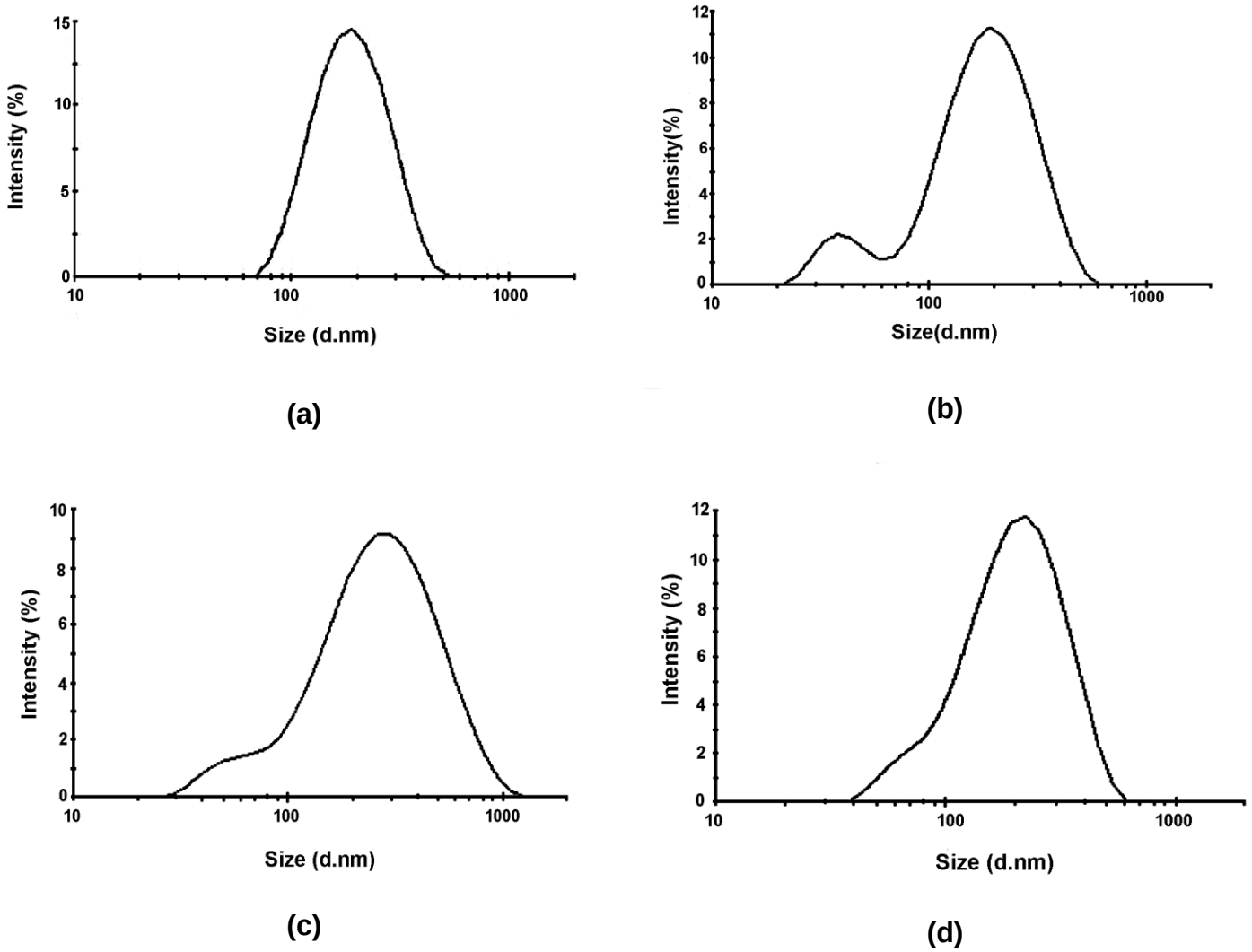

Fig. 1. Particle size distributions of polyacrylic emulsions A (a), B (b), C (c), and D (d)

Table 1. Particle Size Distribution Index (PDI) of the Polyacrylic Emulsions

	Polyacrylic emulsion A	Polyacrylic emulsion B	Polyacrylic emulsion C	Polyacrylic emulsion D
Particle Size(nm)	173.3	138.0	205.9	163.9
PdI	0.119	0.270	0.338	0.193

Note: The lower the PDI value, the more uniform the distribution.

The zeta potentials of the four polyacrylic emulsions were -48.2, -56.0, -59.8, and -61.7 mV, respectively, as shown in Fig. 2. The relationship between zeta potential and emulsion stability is given in Table 2. During testing, the electrophoretic mobility values were respectively recorded as follows: -3.779, -4.390, -4.690, and -4.836 μmcm/Vs. Thus, it can be readily inferred that the polyacrylic emulsions had excellent stabilities.

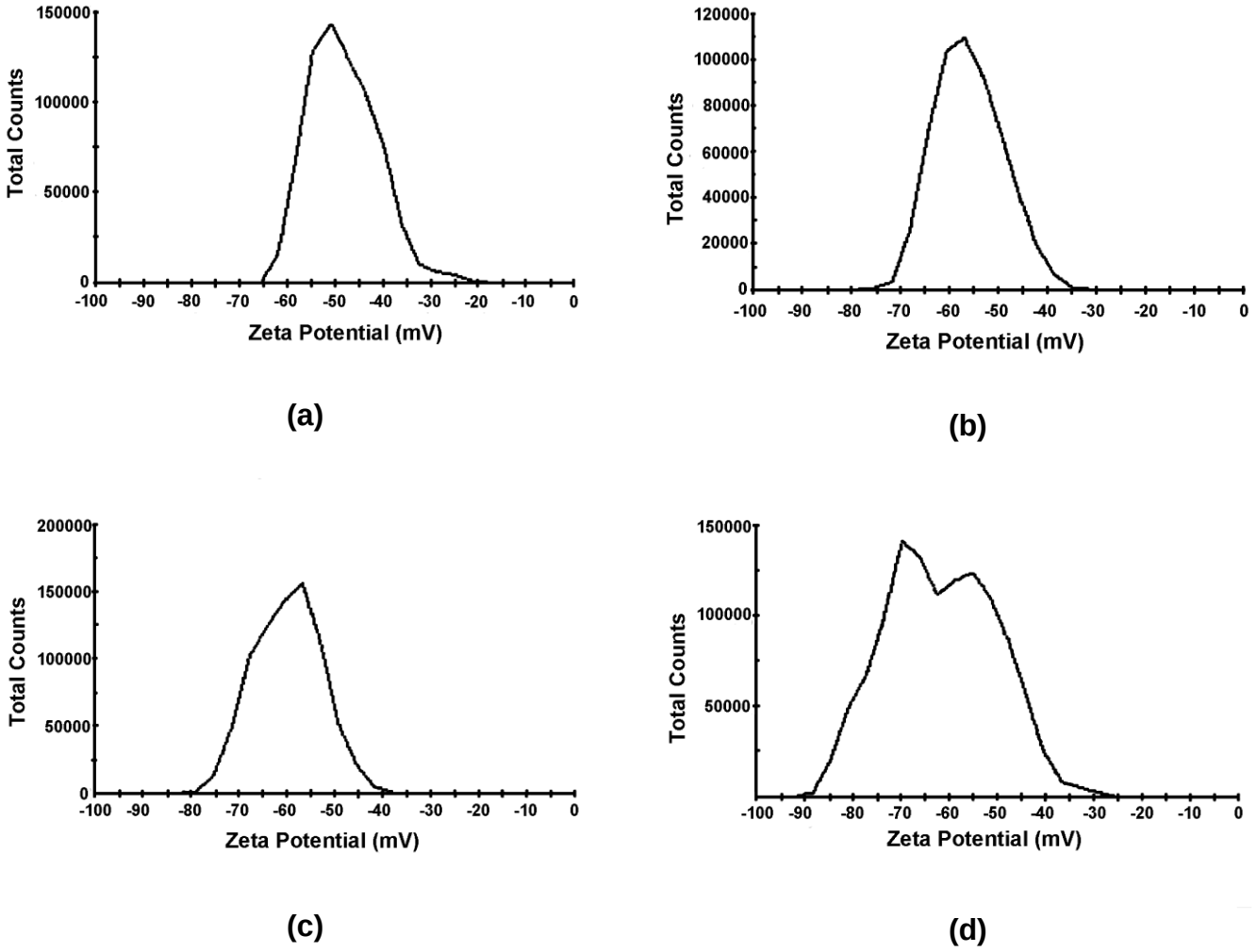

Fig. 2. Zeta potential distributions of polyacrylic emulsions A (a), B (b), C(c), and D (d)

Table 2. Relationship between Zeta Potential and Emulsion Stability

Zeta Potential (mV)	Emulsion Stability
0~±5	Rapid condensation and agglutination
±10~±30	Starting instability
±30~±40	Common stability
±40~±60	Well stability
> ±60	Excellent stability

Water Resistance of the Fiber-Based Materials

Four kinds of fiber-based water-resistant materials were prepared with the same process, varying the mass ratio. The water resistances of materials with different emulsion:fiber mass ratios were tested using a Cobb absorption tester. It is clear from Fig. 3 that, with increasing fiber content, the Cobb value of samples showed a rising trend. It is therefore concluded from Fig. 3 that the best water-resistant material resulted from a polyacrylic emulsion:fiber mass ratio of 2:1. Under these conditions, the Cobb values were 5.0 g/m^2, 9.8 g/m^2, 19.2 g/m^2, and 7.1 g/m^2, respectively. To choose the best emulsion, materials with a mass ratio of 1:1 were also compared, as seen in Fig. 4. Under the condition of a mass ratio of 1:1, the Cobb values were 8.9 g/m^2, 12.0 g/m^2, 21.6 g/m^2, and 22.0 g/m^2, respectively. In addition to the fiber content, the type of emulsion had an important impact on water resistance. To achieve better water resistance, the dosage of polyacrylic emulsion A should be raised.

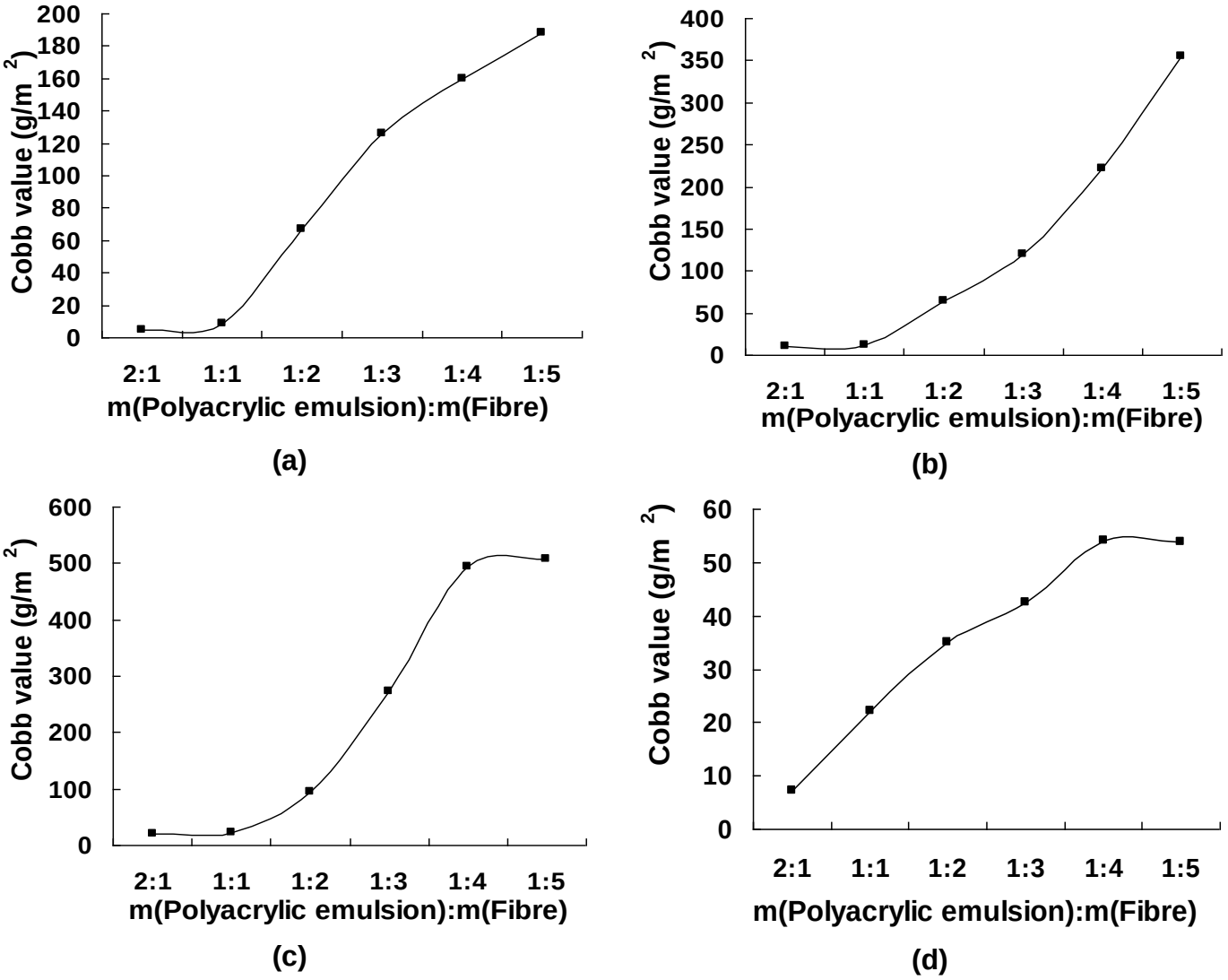

Fig. 3. Cobb values of fiber-based material prepared with various polyacrylic emulsion:fiber mass ratios: polyacrylic emulsions A (a), B (b), C(c), and D (d)

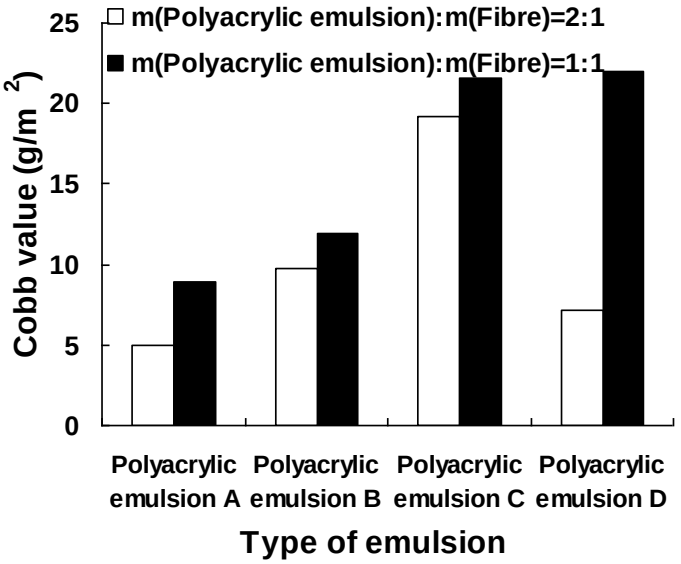

Fig. 4. Cobb value comparison of fiber-based materials prepared with polyacrylic emulsion:fiber mass ratios of 2:1 and 1:1

SEM of Water-Resistant Material

SEM was used to observe the surface features of the water-resistant materials. A series of samples prepared with different emulsion A: fiber mass ratios were chosen for investigation. As shown in Fig. 5, the number of pores increased with increasing fiber contents. This is mainly because the bonding force between fibers was not strong enough, and with low emulsion contents, there was less filler to block the gaps between fibers. Thus, after the water-resistant material was fabricated, many holes were formed in the plate. These holes had a negative effect on water resistance. At the ratio of 1:5 in Fig. 5, the holes can be easily seen, as indicated by the white circles. With increasing polyacrylic emulsion content, fewer pores were formed in the plate. The emulsions filled in the pores and bonded the fiber together during drying. When the emulsion:fiber mass ratio was 2:1, a smooth and continuous surface of the sample can be seen in Fig. 5 (2:1), without any pores. Objectively, interlacing of fibers and the filling and bonding effects of polyacrylic emulsion are two aspects that cause water resistance. Additionally, the dried polyacrylic emulsion itself possessed enhanced water resistance; thus, higher quantities of emulsion resulted in better water resistance.

To further verify the effects of the polyacrylic emulsion used in this process, cross-sectional samples of the water-resistant material were prepared for scanning electron microscopy observation and are displayed in Fig. 6. With low amounts of polyacrylic emulsion (*e.g.*, 1:5), bulky fibers exposed on the cross section can be easily observed (as indicated by the black circle). The phenomenon means that the bonding strength between fibers is not sufficient to prevent fibers from being destroyed while the product was prepared for SEM. The fluffy structure was more porous (as indicated by the white circle) and caused serious water absorption. When the emulsion:fiber mass ratio was 2:1, fibers cohered together because of the polyacrylic emulsion; the pores in the sample had disappeared. This phenomenon demonstrates once again the bonding and filling effects of the polyacrylic emulsion. These aspects are complementary and contribute to the water resistance of the material.

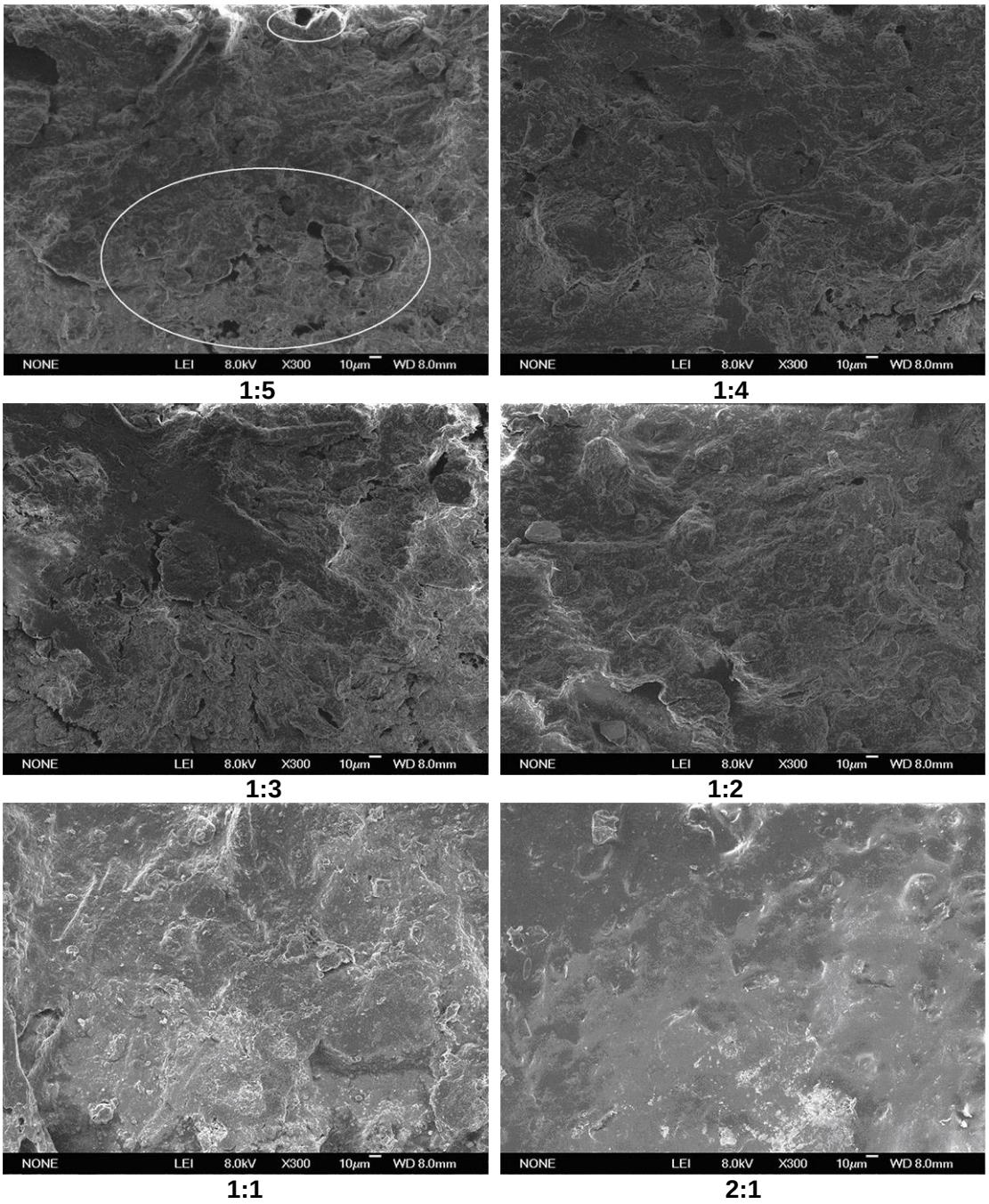

Fig. 5. SEM of surface features of water-resistant material

Other Properties of the Fiber-based Material under the Optimum Conditions

Under the mass ratio of polyacrylic emulsion to fiber of 2:1, the tensile strength, elongation, breaking length, and folding resistance of the fiber-based material prepared by polyacrylic emulsion A were tested. The results were 7.4225 kN/m, 1.0%, and 11.706 km. The material was too brittle to be folded even once, whereas, it was not the main factor for the anticipated application.

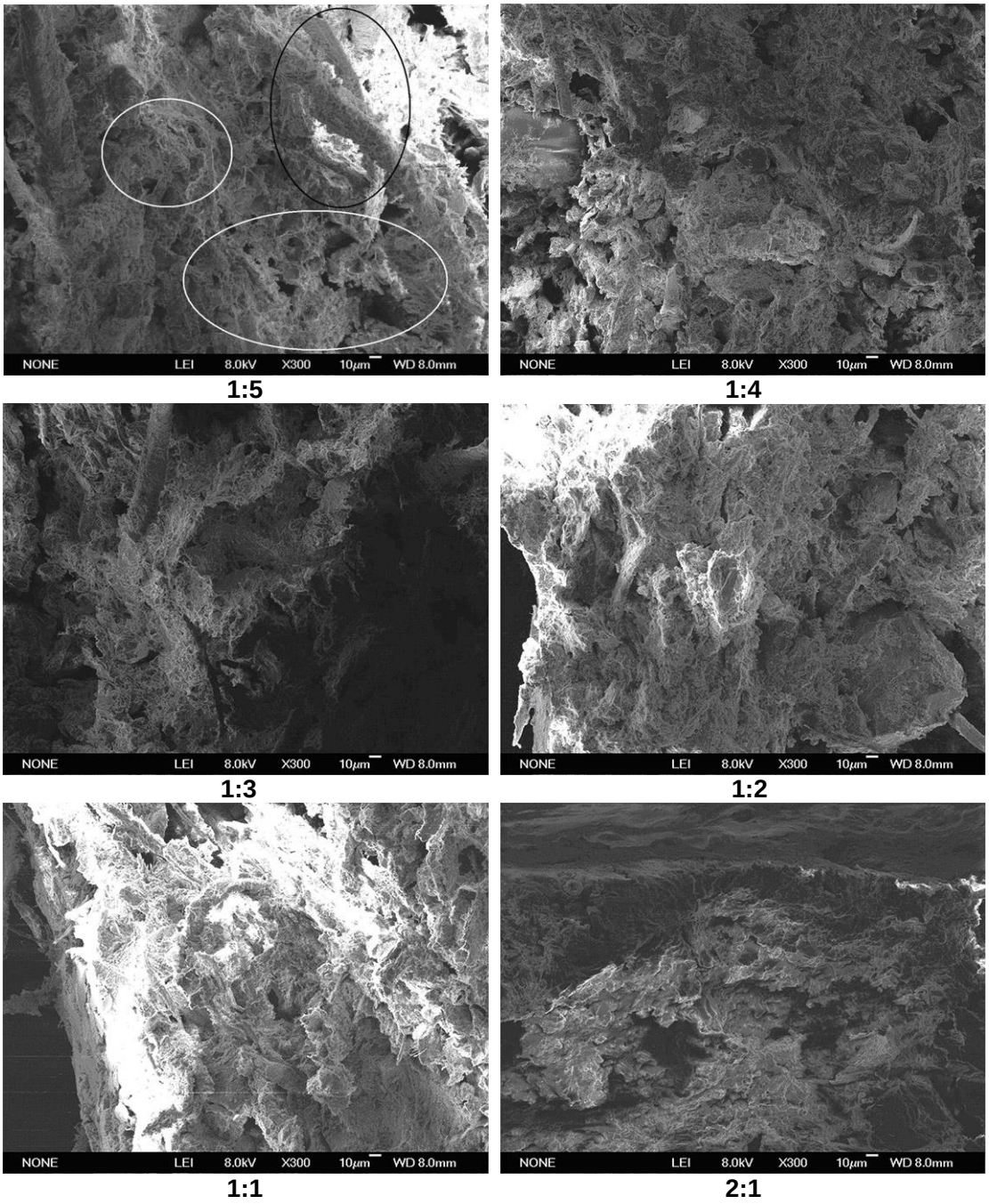

Fig. 6. SEM of cross-sectional features of water-resistant material

As shown by the physical test results, the material formed a sheet-like, adherent layer when sprayed onto a surface and allowed to dry. The system is likely to find application in the covering up of piles of coal fines and fine ores from mining operations. Because such piles are likely to remain in place for long periods, these attributes of strength and adherence, in addition to hydrophobicity of the covering layer, are expected to be important for the minimization of dust entrainment by wind action.

CONCLUSIONS

1. Fiber-based materials were successfully fabricated. To investigate the water resistance of the material, the Cobb value was determined and SEM was used to observe the structure of the material.
2. The monomer ratio of the polyacrylic emulsion and the emulsion usage are key factors in the preparation of highly water-resistant material. The fiber-based material showed the best water resistance at conditions of m_{SM}:m_{MMA}:m_{BA}=1:1:1 and m(polyacrylic emulsion):m(fiber)=2:1.
3. The polyacrylic emulsion played an important role in the water-resistant ability of the material. The bonding and filling effects of the polyacrylic emulsion kept the fibers cohered tightly enough to prevent water being absorbed. The water resistance of the fiber-based material can thus be improved by the addition of a polyacrylic emulsion.
4. Under the condition of conclusion 3, the fiber-based material achieved a tensile strength of 7.4225 kN/m, elongation of 1.0%, and breaking length of 11.706 km.

ACKNOWLEDGEMENTS

This project was supported by the National Natural Science Foundation of China (Grant No. 21176131).

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Article submitted: September 13, 2103; Peer review completed: December 17, 2013; Revised version received and accepted: December 19, 2013; Published: January 9, 2014.