### ARTICLE

# A waterproof and breathable nanofibrous membrane with thermal-regulated property for multifunctional textile application

Liqiang Yi<sup>1</sup> | Shuoshuo Wang<sup>1</sup> | Lina Wang<sup>1</sup> | Juming Yao<sup>1</sup> | Jaromir Marek<sup>2</sup> | Ming Zhang<sup>1</sup>

<sup>1</sup>School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou, China

<sup>2</sup>Institute for Nanomaterials, Advanced Technologies and Innovations, Technical University of Liberec, Liberec, Czech Republic

#### Correspondence

Ming Zhang, School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China. Email: zhangming@zstu.edu.cn

Funding information International Cooperation, Grant/Award Number: 2016YFE0131400

### Abstract

In this work, a waterproof and breathable nanofibrous membrane with thermal-regulated performance and exhibits excellent mechanical property is fabricated by coaxial electrospinning. The fiber shell is consisted of polyvinylidene fluoride (PVDF) and polyvinyl butyral (PVB), and the core is octadecane. First, well-performed waterproof and breathable membranes are obtained by optimizing its morphology and pore structure. Then octadecane is loaded into the fibers in the form of core by coaxial electrospinning, though it gives the membranes a thermal regulating function, but the drawback is the sacrifice of overall properties. Thus, carbon nanotubes are loaded into the shell and studied, finally, the best membrane has a comprehensive performance with hydrostatic pressure of 59.2 kPa, water vapor transmission rate (WVTR) of 7.846 kg m<sup>-2</sup> d<sup>-1</sup>, latent heat of 50.1 J g<sup>-1</sup>, as well as excellent tensile strength of 20.2 MPa, which shows its certain reference significance to the synthesis of multifunctional membrane.

#### K E Y W O R D S

electrospinning, composites, membranes

## **1** | INTRODUCTION

Waterproof-breathable (W&B) fabric, act as "second skin", is a kind of high technology and unique functional fabric, which means that the water does not penetrate the fabric under certain pressure, but the sweat of the human body can be transferred to outside through the fabric in the form of moisture, so as to avoid the accumulation and condensation of sweat between the body surface and to maintain human comfort.<sup>1-4</sup> Therefore, it has been widely applied in protective clothing, building materials, separation membranes, and aviation equipment.<sup>5-8</sup> So far, there are many available techniques to fabricate W&B membranes, including mechanical stretching, melt blown, and

phase separation. However, these methods suffer serious drawbacks, such as, complex preparation process and bad performance efficiency.<sup>5,9</sup> Electrospinning is a convenient technique to get ultrafine fibers with light weight and high specific surface area.<sup>10–12</sup> Until now, many different polymer fibers have been studied as substrates for W&B membranes, such as polyacrylonitrile (PAN), PVDF, polyurethane (PU), and so on.<sup>13</sup> PU is first used as W&B membranes in 2007, but it has very low hydrostatic pressure of 3.7 kPa.<sup>14</sup> And hydrophilic PAN fibers can also be used as W&B membranes by coating of polydimethylsiloxane (PDMS).<sup>15</sup> Unfortunately, due to the complex post-process, PDMS cannot be evenly distributed within the membranes.<sup>16</sup> PU and PAN, subjecting to the

# <sup>2 of 10</sup> WILEY\_Applied Polymer

poor hydrophobicity of these raw polymers, the obtained membranes exhibit inferior waterproof performance,<sup>17</sup> thus, it is necessary to use hydrophobic substances, such as, particles and waterproofing agents to modify the surface.<sup>18–20</sup> However, the following problem is that particles and other materials are very likely to fall off under conditions, such as, membrane deformation, resulting in a decrease in performance. PVDF has many favorable properties, such as, low surface energy and good chemical inertness, and has been intensively investigated to use as W&B membranes.<sup>21</sup> Zhang et al.<sup>22</sup> fabricated a PVDF/PVB W&B membrane and possessed good performance. PVB was heated to the softening temperature to connect the fibers, forming a 3D porous nonwoven geometry with bonded networks, adjusted the pore size of the fiber membrane, and improved its mechanical property.

Phase change material (PCM) is a substance able to releases and absorbs heat during phase transition.<sup>23,24</sup> And it has been widely applied in solar energy storage, textile garment, food packaging, buildings, industrial waste heat recovery, and other fields.<sup>25-29</sup> Commercial temperature-regulating textiles are usually made by loading phase change microcapsules onto the substrates, which may cause the pores between the fibers to be blocked, resulting in a decrease in air and moisture permeability. Membranes obtained by electrospinning possess good moisture permeability due to its high porosity, specially, core-sheath structured phase change fibers can be obtained by coaxial electrospinning in one step. Although it also has some disadvantages, such as, poor mechanical properties, which should be improved by effective methods. Adding nanofiller enhancer, such as, CNTs is a widely used method to improve mechanical property.30

Nowadays, people attitude about comfort and versatility are breaking down traditional textiles, multifunctional textiles have attracted more and more attentions.<sup>31</sup> In this study, we combine the PCM and W&B membrane to develop a multi-functional composite membrane with both of the above function. The mixture of PVDF and PVB is selected as the composite membrane substrate, though, PVB is not heated to the softening temperature as Zhang<sup>22</sup> did to prevent the leakage of PCM, but it still plays an important role. When PVB is not applied, the PVDF fibers have much beaded structure at any experimental condition even in the case of NaCl (Figure S1), the addition of PVB greatly improves its morphology, and the mechanical properties and pore size are changed to some extent. The effects of various experimental conditions on the product performance are discussed, and the result of comprehensive performance degradation caused by

combining two functions is improved. The final material has a certain application prospect in comfort protective clothing, and so forth.

### 2 | EXPERIMENTAL SECTION

### 2.1 | Materials

Kerosene, polyvinyl butyral (PVB, B-72,  $M_w = 170,000-250,000$ ), N-N-Dimethylacetamide (DMAC, AR), poly (vinylidene fluoride) (PVDF,  $M_w = 400,000$ ), and hydroxylated multiwall carbon nanotubes (CNTs, length = 10-30 µm, internal diameter 5–10 nm, and outer diameter 10–30 nm, purity >90%) are purchased form Aladdin Chemistry Co., Ltd. Sodium chloride (NaCl, AR) is purchased form Hangzhou Gaojing Fine Chemical Industry Co., Ltd. Octadecane (99%, melting point is about 28.2°C) is purchased from Macklin Biochemical Technology Co., Ltd. Acetone (AR) is purchased from Hangzhou Shuanglin Chemical Reagent Co., Ltd.

### 2.2 | Preparation of solutions

The core solution is obtained by simply dissolving octadecane in kerosene with a mass fraction of 60%. All polymer solutions contain 0.015% NaCl to reduce the beaded structure, and the mass ratio of PVDF and PVB is 8/2. PVDF. PVB. and NaCl are dissolved in mixture of DMAC and acetone and then stirs for 12 h at 50°C to achieve uniform solutions. First, the polymer concentration of PVDF/PVB blending solution is 23%, and the mass ratio of DMAC and acetone is adjusted to 10/0, 9/1, 8/2, 7/3, 6:4, and 5/5. We find that when the mass ratio of DMAC and acetone is 5/5, the membrane possesses best mechanical property and waterproofness and moderate WVTR, the solvent ratio has a great influence on mechanical property and shows obvious regularity, but as for W&B performance, there is no distinct regularity, and the relevant W&B data are provided in Table S1. The ratio of the following polymer solutions is all controlled at 5/5. To obtain membranes with good waterproof and breathable properties, we varies PVDF/PVB blending solution concentration at 17%, 19%, 21%, 23%, 25%, and comprehensive performance is found at concentration of 19%. To obtain PVDF/PVB/CNTs solution, CNTs with different mass ratio of 0.25%, 0.5%, 0.75% are added into the mixture solvent of DMAC and acetone with ultrasonic treatment for 2 h, then PVDF and PVB with mass fraction of 19% are added into the mixture solution and stirs for 12 h at 50°C.

### 2.3 | Fabrication of the membranes

PVDF/PVB W&B membranes are prepared by ordinary electrospinning technology. The polymer solutions are poured into a 10 ml syringe and injected at a rate of 1.5 ml/h, when the positive voltage of 35 kV is applied to the syringe needle, the droplet formed by the advance of the syringe will form a Taylor cone under the pressure of the charge and then form a thin stream, later, undergoing vigorous whipping motions because of the bending instabilities. Finally, the solvent evaporates and the solidified fibers could be received to the roller collector. PVDF/ PVB/octadecane W&B membranes are fabricated by coaxial electrospinning technique. The concentric stainless-steel needles are consisted of an outer needle and an inner needle. For the outer needle, outer/inner diameters are 1.49/1.01 mm and for the inner needle, outer/inner diameters are 0.72/0.41 mm. The sheath feed rate is 1.5 ml/h, and the core feed rate is 0.2, 0.25, 0.3 mL/h, respectively. PVDF/PVB/octadecane/CNTs membranes are also prepared by coaxial electrospinning, the sheath feed rate is 1.5 ml/h, and the core feed rate is 0.25 ml/h. All the prepared samples are dried in a 60°Cblast air oven for 2 h to remove the remaining solvent. The thickness of the membranes is about 70 µm, and the temperature of all experimental environments is controlled at 40°C, the receiving distance is 26 cm, and the rotating speed of the roller collector is fixed at a certain value.

### 2.4 | Characterization of the membranes

The morphology of the prepared membranes is observed by field emission scanning electron microscope (FE-SEM, ULTRA55, Zessi), the acceleration voltage is 3 kV. The samples are all coated with a thin layer of gold, for the samples loaded with octadecane, they are pre-soaked in petroleum ether for 24 h before observation. The diameters of 50 random fibers are measured by the imageJ software, and their mean values are calculated. Transmission electron microscope (TEM, JEM-2100, JOEL) is used to investigate the interior structure of the nanofibers and the acceleration voltage is 200 kV. All TEM samples are prepared by directly depositing the electrospun nanofibers onto 400-mesh carbon-coated Cu grids, and then immerse the grids in petroleum ether for 24 h to remove octadecane. The AFM was performed into this sample using a Nanoscope V Multimode 8 scanning probe microscope from Bruker Corporation. All experiments were carried out with the same AFM probe under ambient conditions (temperature of 25°C,

## Applied Polymer\_WILEY 3 of 10

relative humidity of 25%). Tensile property is measured by multifunctional mechanical tester (KES-G1) with extension rate of 0.1 cm/s at 25°C. The samples are cut into  $0.5 \times 2$  cm pieces, and the thickness of the samples is all measured and accurate to 1 µm, each sample is tested in triplicate. Differential scanning calorimetry (DSC, Q2000) is implemented in nitrogen flow with heating and cooling rate of 10 K/min, the samples are heated from 0 to 50°C and cooled from 50 to 0°C. The pore size is characterized by bubble point method using a capillary flow porometer (CFP-1500AE, Porous Materials Inc., China). Porosity of the fibrous membranes are calculated as the follow equation.

$$Porosity = \frac{D_1 - D_2}{D_1} \times 100\%$$
(1)

where  $D_1$  is the density of the raw materials and  $D_2$  is the density of the obtained fibrous membranes.

# 2.5 | Measurements of waterproof and breathable performance

According to AATCC 127 standard test method, the waterproofness of the membranes is investigated by measuring hydrostatic pressure of water penetration by using a hydrostatic pressure tester (FX 3000-IV, Switzerland). The pressure rise rate is 6 kPa/min. Polyester woven is used to cover the surface of the membrane to prevent it from bursting. According to ASTM E96-CaCl<sub>2</sub> standards desiccant method, the breathable performance is measured by testing the WVTR by using fabric moisture permeability testing apparatus (YG601-1, Ningbo Textile Instrument Factory) at 38°C and relative humidity of 90%. First, put a circular sample with an area of  $26 \text{ cm}^2$  on the moisture vapor transmission cup contains 33 g CaCl2. Then completely seal the perimeter, making sure that water vapor can only enter the cup from the top membrane. Put it in the test environment for 30 min. Later, take out and put it into a silica gel dryer for 30 min, weighing and record for m<sub>0</sub>, then put it into the experimental condition for 1 h, take out again and put into the silica gel dryer balance for 30 min, weighing and record for  $m_1$ . WVTR is calculated by the following formula.

$$WVTR = \frac{m_1 - m_0}{A} \times 24 \tag{2}$$

where  $m_0$  is the initial quality of the whole cup, and  $m_1$  is the final quality of the cup absorbing water vapor. *A* is the area of tested membrane.

## 4 of 10 WILEY\_Applied Polymer\_

### **3** | **RESULTS AND DISCUSSIONS**

# 3.1 | Morphology analysis of W&B membranes

First, we found that a single solvent system of mixture polymer solution is difficult to synthesize a wellperformed W&B membrane at any polymer concentration in this work, so acetone was introduced into the sheath solution and the effect of different solvent mass ratios on membrane morphology was studied. The polymer concentration was controlled at 23%. The FE-SEM images of PVDF/PVB fibrous membranes obtained by varying solvents ratio are presented in Figure 1. When the shell solvent is pure DMAC, there are much polymer solution that are not stretched effectively and show up as clumps as shown in Figure 1(a). After added with acetone and the mass ratio of DMAC and acetone is 9/1, the unstretched bulk polymer still exists, though the situation is much improved. With the decrease of mass ratio to 8/2, the unstretched bulk polymer disappears and the inefficiently stretch phenomenon shows up as spindle like structure as demonstrated in Figure 1(c). And the spindle like structure decreases with the increase of acetone content. When the mass ratio of DMAC and acetone is 5/5, the spindle like structure vanishes and the fibers have good morphology of cylindric. We think that there are two main reasons for this. First, the jet stability section of PVDF solution is very long, and the effective stretching distance of the fiber is short due to its own characteristics, which results in the appearance of spindle like structured fibers and unstretched bulk polymer. Second, acetone is more volatile than DMAC, when there is more acetone content in the mixture solution, the solvents can evaporate more quickly and so that the fibers could be stretched more efficiently, otherwise, the thin solution stream may directly ejects onto the collector and results in the polymer clumps as shown in Figure 1(a)-(b).<sup>32–35</sup> But when there is too much acetone in the mixture solution, the needle would be clogged because of the rapid evaporation of the solvent.

To obtain membranes with good W&B properties, we fabricated membranes by using PVDF and PVB mixture solutions with different concentrations, and the mass ratio of DMAC and acetone was controlled at 5/5. Their FE-SEM images are presented in Figure 2. The fibers have spindle like structure when polymer concentration is 17% as shown in Figure 2(a), which is caused by the low viscosity of the solution, and this kind of structure fades away when the concentration increases to 19%, 21%, and 23%. But as the concentration ascend to 25%, the polymer clumps appear, this is because when the concentration increases, the jet stability section becomes longer, and the molecular chains become more entangled, making it more difficult for the jet to break. Consequently, some jets directly reach the collector without stretching, resulting in the appearance of bulk polymer.<sup>35–37</sup> As expectedly, the fiber diameter increases



**FIGURE 1** FE-SEM images of fibrous membrane from 23% fabricated by different mass ratio of DMAC and acetone (a) 10/0; (b) 9/1; (c) 8/2; (d) 7/3; (e) 6/4; (f) 5/5

## Applied Polymer\_WILEY 5 of 10



**FIGURE 2** FE-SEM images of fibers fabricated by different polymer concentration (a) 17%; (b) 19%; (c) 21%; (d) 23%; (e) 25%, and (f) their analysis of mean diameter

FIGURE 3 (a) Stress-strain curves of membranes from different solvent ratio, the polymer concentration is controlled at 23%; (b) stress-strain curves of membranes from different polymer concentration, the mass ratio of mixture solvents is 5/5 [Color figure can be viewed at wileyonlinelibrary.com]



with the augment of polymer concentration, the mean diameter of 50 fibers from 17% is 105 nm, and 130 nm from 19%, and it rises up to 432 nm when the concentration is 25% as shown in Figure 2(f).

# 3.2 | Mechanical performance of W&B membranes

The mechanical properties of the fibrous membranes would be affected distinctly by the solvent ratio owing to the structure transformation of the fibers. As presented in Figure 3(a), the tensile strength of the fibrous membrane is 15.3 MPa when the solvent ratio is 5/5, and the strength decreases regularly with the decrease of acetone content. When acetone is not added into the polymer solution, the tensile strength of the fibrous membrane is just 0.7 MPa, which is a full 22-fold decrease from the best one. The results demonstrate that the mechanical properties could be improved by adding more acetone. This is attribute to that spindle like structured fibers and unstretched bulk polymer appears when acetone content is low, which is more likely to cause stress concentration and make the membranes brittle. The mechanical property is also influenced greatly by polymer concentration as shown in Figure 3(b). The membrane from 17% has a low tensile strength of 7.9 MPa because of its beaded structure, which is easy to cause stress concentration. When the concentration increases to 19%, the membrane strength experiences a sizable increase to 13 MPa. Subsequently, the strength increases with polymer concentration increase until 23% of 15.3 MPa. However, as the concentration continues to rise to 25%, it has a huge drop to 7.4 MPa, which is ascribing to the appearance of polymer clumps.

### 3.3 | Waterproof and breathable performance analysis of W&B membranes

The porous structure of the membranes changes greatly with the transformation of fiber diameter and morphology. As presented in Figure 4(a), with the polymer concentration increases from 17% to 25%, the porosity of membranes goes down from 75.2% to 47.1%. This is ascribing to that pores piled up by thicker fibers are much smaller in amount. Due to the changes in the porosity of fibrous membrane, its breathable performance is affected distinctly, and the breathable performance is judged by measuring WVTR. As shown in Figure 4(c), the WVTR decreases from 8.575 to 7.532 kg m<sup>-2</sup> d<sup>-1</sup> with the increase of polymer concentration from 17% to 25%, this would be attributed to that low porosity reduces the passageway, which water vapor could pass through.<sup>30</sup> Maximum pore size (d<sub>max</sub>) is also greatly influenced by polymer concentration and shows obvious regularity, Figure 4(b) shows that  $d_{max}$  increases from 0.95 to 2.48 µm with polymer concentration rises from 17% to 25%. As presented in Figure 4(d), the membrane obtained from 17% possesses best hydrostatic pressure of 62.8 kPa, and the hydrostatic pressure decreases a little to 60.5 kPa with the increase of concentration to 19%, then a sharp

decline occurs as the concentration continues to rise, which is because that the water droplet is easier to get through the pore with higher size, resulting in lower hydrostatic pressure.<sup>30</sup> The original pore size distribution diagram of membranes from different polymer concentration is provided in Figure S2. And the water contact angle of the membrane from 19% is 131.4° as shown in Figure 4(d), which proves its hydrophobic property, the water contact angle from other concentration is provided in Figure S3. The membrane fabricated from 19% is carried for later study in consideration of its comprehensive performance. To summarize the above paragraph, pure W&B membranes with good performance are synthesized by tuning its morphology and pore structure.

# 3.4 | DSC and mechanical analysis of thermal-regulated W&B membranes

In order to obtain the W&B membranes with thermalregulated ability and show good comprehensive performance, herein, PVDF/PVB/octadecane fibrous membranes containing various octadecane contents were prepared by coaxial electrospinning and investigated, which was carried out by regulating the core feed rate from 0.2 to 0.3 mL/h. The polymer concentration was controlled at 19%, and the solvent ratio was 5/5. Inevitably, with the core feed rate increases, the result is an increase in enthalpy. As shown in Figure 5(a), when the core feed rate goes up from 0.2 to 0.25 mL/h, the



FIGURE 4 Pore structure (a) porosity; (b) maximum pore size, and (c) water vapor transmission rate; (d) hydrostatic pressure of the pure W&B membranes from different polymer concentration

## Applied Polymer\_WILEY 7 of 10



enthalpy has a big rise from 34.5 to 56.3 J g<sup>-1</sup>, though, with the core feed rate continues to increase to 0.3 ml/h, the latent heat just has a little improvement from 56.3 to 62.7 J g<sup>-1</sup>, which perhaps the limited capacity of octadecane under this experimental condition. Otherwise, octadecane as a small molecule PCM, has a negative effect on the mechanical properties of the fibrous membranes. As shown in Figure 5 (b), the PVDF/PVB/octadecane membranes obtained from 0.2 ml/h has a big drop in tensile strength from 13 to 8.9 MPa compares with the membrane without octadecane, and it shows obvious regularity of strength degradation with the increase of core feed rate.

### 3.5 | Waterproof and breathable performance analysis of PVDF/PVB/ octadecane membranes

Not only mechanical properties, but also the pore structure and waterproof and breathable performances are affected by the load of octadecane. The original pore size distribution diagram of membranes from different core feed rate is provided in Figure S4. As presented in Figure 6(a), after loading the octadecane, the porosity of the membranes decreases, and it becomes worse as loading more octadecane. Consequently, the WVTR of the membranes decreases with the rise of octadecane content as shown in Figure 6(c). Otherwise, Figure 6(b) shows

# <sup>8 of 10</sup> WILEY\_Applied Polymer

that  $d_{max}$  increases with the rise of core feed rate, which may be caused by the increase of fiber diameter. And it follows that the hydrostatic pressure of fibrous membranes with 0.2 ml/h core feed rate drops from 60.5 to 49.3 kPa compares that without octadecane, as the core feed rate increases further, its hydrostatic pressure shows a little bit decline. And for the composite fibrous membrane with comprehensive performance from 0.25 ml/h, its hydrophobic property shows a decline compared the one without octadecane, which is proved by the water contact angle as shown in Figure 6(d). Consequently, the results indicate that the load of octadecane though gives the membranes a new function, but the load capacity must be regulated, and the accompanied defects also should be improved.

### 3.6 | Morphology of PVDF/PVB/ octadecane membranes loaded with CNTs

We chose 0.25 ml/h as the core feed rate after evaluating the comprehensive performances of the membrane, then different proportions of CNTs were doped into the membranes and studied, hoping to mitigate the performance degradation. As shown in Figure 7(a)-(c), the general morphology of the fibers containing different proportions of CNTs are almost the same, the fibers are cylindrical, and some collapses on the fibers as shown in Figure 7(b) indicate its hollow structure. The optimized sample from 0.75% has a declined mean diameter compared with PVDF/PVB/octadecane/0.25 without CNTs, the detailed FE-SEM images and histograms of diameter of optimized nanofibers are provided in Figure S5, and the explanation may be that the addition of CNTs further increases the electrical conductivity of the spinning solution, thus, the fibers could be stretched more effectively and possess finer diameter.<sup>30</sup> When CNTs are loaded, the fiber surface becomes rougher, and the high-magnification FE-SEM images show this (Figure S6), in addition, the AFM 3D images provided in Figure S7 clearly proves its roughness after loading CNTs (the size of these protuberances are almost the same with the CNTs, 10-30 nm), which is good for the improvement of hydrophobic property.<sup>30</sup> According to the TEM diagrams as shown in Figure 7(d) and Figure S8, some CNTs are inside the fibers, some are exposed to the surface of the fibers, improving the surface roughness of the fiber, some are loaded in the coresheath structured fibers, and some are loaded in the solid fiber.

### 3.7 | Performance analysis of PVDF/ PVB/octadecane membranes loaded with CNTs

Unfortunately, we find that CNTs almost has no improve in its WVTR, and the latent heat of the best membrane from 0.75% CNTs has a little bit decline to 50.1 J g<sup>-1</sup>, the detail W&B performances are all listed in Table S2. And the original pore size distribution diagram of membranes from different CNTs concentration is provided in Figure S9. The load of CNTs has a great improvement in



**FIGURE 7** FE-SEM images of thermal-regulated W&B membranes obtained from different CNTs concentration (a) 0.25%; (b) 0.5%; (c) 0.75%, and (d) TEM image

## Applied Polymer\_WILEY 9 of 10

FIGURE 8 (a) Stress-strain curves and (b) differential scanning calorimetry curve of the membrane from 0.75% CNTs and its performance data [Color figure can be viewed at wileyonlinelibrary.com]



its hydrostatic pressure and mechanical performance, the water contact angle of the membrane from 0.75% CNTs increases from 127.3° to 133.6° compared the one without CNTs, the deep explanation for this is as follows: for hydrophobic materials, the roughness of the fibers actually increases the contact area between water and the fibers. If the contact angle is constant, the surface area of water will be larger than the original one, since the surface tension of water always drives water to reduce its surface area, so water droplets reduce their surface area by increasing their contact Angle. Its hydrostatic pressure also has an increase from 45.9 to 59.2 kPa as shown in Figure 8(b). In addition, after loading CNTs, the tensile strength has a huge increase, the reasons may be as follows: CNTs itself have high modulus and strength, according to "Crack Filling" theory, when an external force is applied to the fiber, the cracks in the fiber gradually increase. When the CNTs are in contact with these cracks, the load can be effectively transferred to CNTs due to the van der Waals force, which inhibits the stress concentration at the fiber defects and thus improves the strength of the materials.<sup>38</sup> And its strength improves with the increase of CNTs content, when the mass ratio of CNTs is 0.75%, its tensile strength could be as high as 20.2 MPa, which demonstrates the excellent ability of CNTs to improve mechanical properties.

### 4 | CONCLUSIONS

In this work, we synthesize a series of thermal-regulated PVDF/PVB/Octadecane membranes with good waterproof and breathable properties. Octadecane is loaded into the fibers in the form of core by coaxial electrospinning, thus, has minimum influence on the surface properties of the membranes. In the meantime, the regulation of polymer concentration and solvents proportion optimizes the morphology and pore structure of the membranes, thereby, improves the W&B and mechanical performances. Finally, the degradation of overall performance caused by octadecane is mitigated by adjusting its capacity and adding moderate amount of CNTs. Consequently, the composite fibrous membrane exhibits good waterproofness of 59.2 kPa, high WVTR of 7.846 kg m<sup>-2</sup> d<sup>-1</sup>, moderate latent heat of 50.1 J g<sup>-1</sup>, as well as excelent tensile strength of 20.2 MPa. These properties suggest the composite fibrous membrane has potential applications in field, such as, multifunctional protective clothing, and so forth.

#### ACKNOWLEDGMENTS

The authors acknowledge financial support from Key Program for International Cooperation Projects of China (2016YFE0131400).

#### **CONFLICT OF INTEREST**

The authors declare no potential conflict of interest.

### ORCID

Ming Zhang D https://orcid.org/0000-0002-2916-8128

#### REFERENCES

- Y. Y. Liang, J. G. Ju, N. P. Deng, X. H. Zhou, J. Yan, W. M. Kang, B. Cheng, *Appl. Surf. Sci.* 2018, 442, 54.
- [2] J. L. Sheng, Y. Li, X. F. Wang, Y. Si, J. Y. Yu, B. Ding, Sep. Purif. Technol. 2016, 158, 53.
- [3] J. Zhao, W. X. Zhu, X. F. Wang, L. F. Liu, J. Y. Yu, B. Ding, Nanoscale Horiz. 2019, 4, 867.
- [4] W. Zhou, X. Yu, L. T. Cao, M. Yang, Y. Li, Y. Si, J. Y. Yu, B. Ding, Adv. Sustainable Syst. 2020, 4, 2000105.
- [5] J. T. Gu, H. H. Gu, J. Cao, S. J. Chen, N. Li, J. Xiong, Appl. Surf. Sci. 2018, 439, 589.
- [6] J. Zhao, Y. Li, J. L. Sheng, X. F. Wang, L. F. Liu, J. Y. Yu, B. Ding, ACS Appl. Mater. Interfaces 2017, 9, 29302.
- [7] J. L. Sheng, M. Zhang, W. J. Luo, J. Y. Yu, B. Ding, *RSC Adv.* 2016, 6, 29629.
- [8] J. W. Li, H. A. Tsai, H. T. Lee, Y. H. Cheng, C. W. Chiu, M. C. Suen, Prog. Org. Coat. 2020, 145, 105702.

## <sup>10 of 10</sup> WILEY\_Applied Polymer

- [9] J. Zhao, W. X. Zhu, W. A. Yan, X. F. Wang, L. F. Liu, J. Y. Yu, B. Ding, *Compos Commun.* 2019, 15, 40.
- [10] N. Zhang, Y. P. Yuan, X. L. Cao, Y. X. Du, Z. L. Zhang, Y. W. Gui, Adv. Eng. Mater. 2018, 20, 1700753.
- [11] J. J. Xue, T. Wu, Y. Q. Dai, Y. N. Xia, Chem. Rev. 2019, 119, 5298.
- [12] P. P. Li, Q. Zhang, T. T. Chadyagondo, G. Q. Li, H. H. Gu, N. Li, Fibers Polym. 2020, 21, 1444.
- [13] J. Zhao, X. F. Wang, L. F. Liu, J. Y. Yu, B. Ding, ACS Appl. Mater. Interfaces 2018, 10, 30887.
- [14] L. W. Zhang, Y. Li, J. Y. Yu, B. Ding, RSC Adv. 2015, 5, 79807.
- [15] W. Yang, R. Li, C. P. Fang, W. T. Hao, Prog Org Coat. 2019, 131, 67.
- [16] H. M. Cui, Y. Y. Li, X. L. Zhao, X. Yin, J. Y. Yu, B. Ding, Compos Commun. 2017, 6, 63.
- [17] F. F. Yang, Y. Li, X. Yu, G. N. Wu, J. Y. Yu, B. Ding, RSC Adv. 2016, 6, 87820.
- [18] K. Liu, L. Deng, T. H. Zhang, K. Shen, X. F. Wang, Ind. Eng. Chem. Res. 2020, 59, 4447.
- [19] Y. G. Yu, Y. Liu, F. L. Zhang, S. X. Jin, Y. Q. Xiao, B. J. Xin, Y. S. Zheng, *Fibers Polym.* **2020**, *21*, 954.
- [20] H. H. Gu, G. Q. Li, P. P. Li, H. L. Liu, T. T. Chadyagondo, N. Li, J. Xiong, *Appl. Surf. Sci.* **2020**, *512*, 144837.
- [21] J. T. Gu, H. H. Gu, Q. Zhang, Y. H. Zhao, N. Li, J. Xiong, J. Colloid Interface Sci. 2018, 514, 386.
- [22] M. Zhang, J. L. Sheng, X. Yin, J. Y. Yu, B. Ding, Macromol. Mater. Eng. 2017, 302, 8.
- [23] B. Rezaei, M. Ghani, M. Askari, A. M. Shoushtari, R. M. A. Malek, Adv. Polym. Technol. 2016, 35, 1.
- [24] J. Q. Xu, T. T. Yang, X. Xu, X. Guo, J. Z. Cao, Part A. 2020, 139, 106098.
- [25] M. Kenisarin, K. Mahkamov, Renewable Sustainable Energy Rev. 2007, 11, 1913.
- [26] G. Y. Li, G. Hong, D. P. Dong, W. H. Song, X. T. Zhang, Adv. Mater. 2018, 30, 1801754.
- [27] W. Chalco-Sandoval, M. J. Fabra, A. López-Rubio, J. M. Lagaron, Eur. Polym. J. 2015, 72, 23.

- [28] A. K. Pandey, M. S. Hossain, V. V. Tyagi, N. Abd Rahim, J. A. L. Selvaraj, A. Sari, *Renewable Sustainable Energy Rev.* 2018, 82, 281.
- [29] S. K. Song, F. Qiu, W. T. Zhu, Y. Guo, Y. Zhang, Y. Y. Ju, R. Feng, Y. Liu, Z. Chen, J. Zhou, C. X. Xiong, L. J. Dong, *Sol. Energy Mater. Sol. Cells* **2019**, *193*, 237.
- [30] Y. Li, Z. G. Zhu, J. Y. Yu, B. Ding, ACS Appl. Mater. Interfaces 2015, 7, 13538.
- [31] T. Zhang, Z. B. Xu, J. C. Zhao, L. P. Huang, *Macromol. Mater. Eng.* 2020, 305, 2000370.
- [32] L. M. M. Costa, R. E. S. Bretas, R. G, Mater. Sci. Appl. 2010, 1, 247.
- [33] X. J. Zhao, J. Cheng, S. J. Chen, J. Zhang, X. L. Wang, J. Polym, Sci., Part B: Polym. Phys. 2010, 48, 575.
- [34] D. A. Holmes, J. Ind. Text. 2000, 29, 306.
- [35] J. Y. Lin, B. Ding, J. Y. Yu, Y. Hsieh, ACS Appl. Mater. Interfaces 2010, 2, 521.
- [36] D. Zhang, J. Chang, Adv. Mater. 2007, 19, 3664.
- [37] J. Q. Wang, Y. Yang, H. Y. Tian, J. L. Sheng, J. Y. Yu, B. Ding, *RSC Adv.* 2014, 4, 61068.
- [38] L. S. Schadler, S. C. Giannaris, P. M. Ajayan, Appl. Phys. Lett. 1998, 73, 3842.

#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Yi L, Wang S, Wang L, Yao J, Marek J, Zhang M. A waterproof and breathable nanofibrous membrane with thermalregulated property for multifunctional textile application. *J Appl Polym Sci.* 2021;138:e50391. https://doi.org/10.1002/app.50391