

## Effect of treatment pressure on structures and properties of PMIA fiber in supercritical carbon dioxide fluid

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**ABSTRACT:** The effects of treatment pressure on the structures and properties of PMIA fiber were investigated by Scanning electron microscopy, Dynamic wetting measurements, Fourier transform infrared spectrometry, X-ray diffraction, thermogravimetric analysis, and mechanical properties test technology in supercritical carbon dioxide. The results indicated that the surface morphology, the water contact angle, the interaction of macromolecules, the crystal structure, the thermal property, and tensile strength of PMIA fibers were changed during supercritical carbon dioxide treatment, particularly the surface morphology and the wettability of fiber changed the most obviously with the increase of treatment pressure. Furthermore, the thermal property and tensile strength of treated PMIA fiber sample were improved in comparison with those of untreated sample. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41756.

**KEYWORDS:** fibers; morphology; properties and characterization; surfaces and interfaces; thermal properties

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### INTRODUCTION

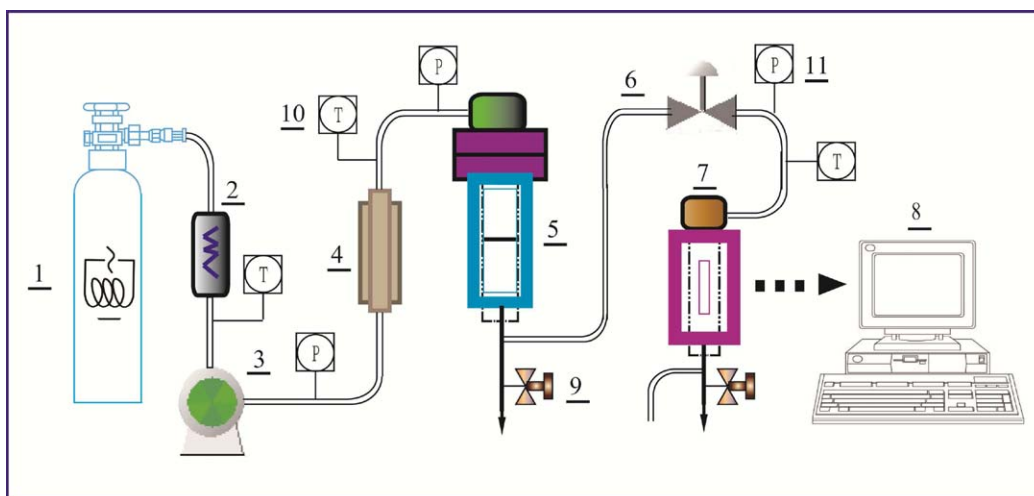
Poly-m-phenylene isophthalamide (PMIA) is a manufactured fiber which is a long-chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings.<sup>1</sup> This fiber, which was first created in 1960, has been used widely in the field of protective apparatus, filtration, and aerospace because of its high strength, good thermal stability, high fracture strain, and low density.<sup>2,3</sup>

However, PMIA fiber has also some drawbacks in the industrial-scale production. On the one hand, the highly hydrophobic surface of PMIA fiber increases the difficulty to interact with dyes in the textile industry because of the intermolecular hydrogen bonds of the amide groups.<sup>4</sup> On the other hand, owing to high crystallinity and lack of the polar functional groups in the polymer molecule chain, the surface of PMIA fiber is so chemically inert and smooth, resulting in the poor adhesion between aramid fiber and the resin matrix.<sup>5,6</sup> Therefore, it is important to improve the wetting behavior of PMIA fiber.

At present, various approaches of the modification for PMIA fiber have been adopted to change relatively inert polymer surfaces, including chemical treatment, plasma discharge, and even ultrasonic treatment.<sup>7–12</sup> Nevertheless, some of these meth-

ods have constrained the practical use, and frequently lead to the decrease of the mechanical strength, elevated production cost, and complicated work procedures.<sup>13</sup> Thus, there is an increasing demand for a novel modification method which can be applied easily and efficiently to PMIA fiber.

As a green, safe, and environmentally friendly solvent, supercritical carbon dioxide (critical temperature: 31.1°C, critical pressure: 7.4 MPa) which was first introduced into textile dyeing field by Schollmeyer in 1988 has been developed rapidly in recent years.<sup>14</sup> Using supercritical carbon dioxide as solvent to replace water presents the advantages of water free, nonpollution, as well as energy preserving and is used for numerous applications such as polymer processing, environment, food, cosmetics, and pharmaceuticals.<sup>15–18</sup> Recently, employing supercritical carbon dioxide fluid has been shown to be effective and is replacing traditional chemical method for the surface modification of some fibers since supercritical carbon dioxide fluid shows properties of both liquid and gas phases and has a density similar to liquids.<sup>19</sup> Katayama investigated the modification of the cotton in supercritical carbon dioxide fluid, and proved that large pleat-like wrinkles could be formed on the cotton surface with supercritical carbon dioxide fluid at 40°C, and 20 MPa for 60 min.<sup>20</sup> Long examined the effects of supercritical carbon dioxide on the structure and properties of wool fiber,



**Figure 1.** Schematic diagram of the supercritical carbon dioxide fluid apparatus used for the treatment of PMIA samples: (1) CO<sub>2</sub> cylinder, (2) refrigerator, (3) high-pressure pump, (4) heat exchanger, (5) treatment vessel, (6) back pressure valve, (7) separator, (8) personal computer, (9) relief valve, (10) temperature gauge, (11) pressure gauge. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and revealed that a notable etching effect or dilapidation on the scales was observed.<sup>21</sup> Hirogaki proved that the PET yarns had different morphologies depending on the draw ratio in different supercritical carbon dioxide conditions.<sup>22</sup>

However, up to now no information has been available on the PMIA fiber modification in the supercritical carbon dioxide fluid and its influence on the wetting, thermal and mechanical behavior of PMIA fiber. In this study, the wetting and thermal properties together with the mechanical performance of PMIA were investigated using characteristic techniques, including Scanning electron microscopy (SEM), Dynamic wetting measurements (DWM), Fourier transform infrared spectrometry (FT-IR), X-ray diffraction (XRD), as well as thermogravimetric analysis (TG). In addition, mechanical properties of PMIA fiber were also measured.

## EXPERIMENTAL

### Instruments and Equipments

A supercritical carbon dioxide fluid apparatus (SFE-500-2-C10, TharSFC, USA) was used to treat PMIA fiber. SEM (JSM-6380LA, JEOL, Japan) was employed to observe the morphological change of the treated fiber. Wettability of PMIA fiber surface was determined by a dynamic contact angle analysis device (K100, KRUSS, Germany). FT-IR (Nicolet 8700, Thermo Fisher Scientific, USA) and XRD (XRD-6100, SHIMADZU, Japan) were employed to evaluate the surface characteristics of PMIA fiber. Thermal property of PMIA fiber was measured on a thermal analysis machine (STA PT 1600, LINSEIS, Germany). Mechanical properties of PMIA fiber were tested using a universal materials test machine (TH-8102S, TopHung, China).

### Materials

PMIA fabrics (weft and warp 32s/2 with a fabric weight of 217.0 g m<sup>-2</sup>) were supplied by Yantai Tayho Advanced Materials and the fabric sample with a dimension of about 105 × 200 mm was used in the treatment procedure. The analytical reagent grade acetone was purchased from Tianjin Kemiou Chemical Reagent. The car-

bon dioxide gas used in all of the experiments was purchased from the Guangming (99.99% pure).

### Desizing

The PMIA samples were scoured with acetone for 20 minutes at room temperature before the supercritical carbon dioxide fluid treatment in order to remove spinning and knitting waxes and oils. Then the samples were dried in an air oven at 100°C for 30 minutes before being used as the control sample.

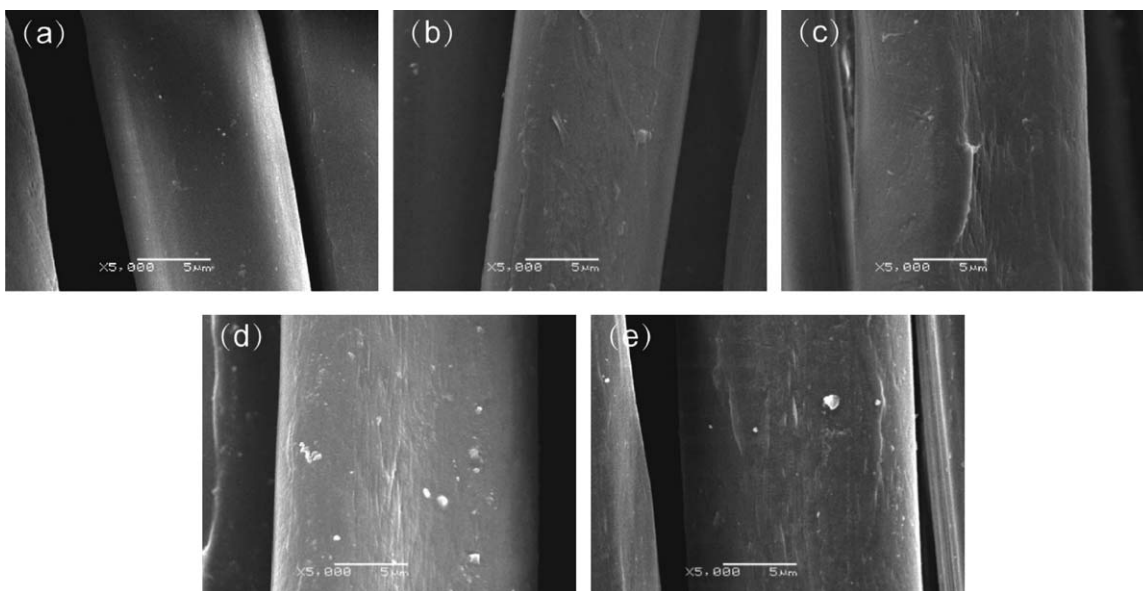
### Supercritical Carbon Dioxide Treatment

A schematic diagram of the apparatus used for the supercritical carbon dioxide fluid treatment of the PMIA fiber was shown in Figure 1. In this apparatus, PMIA fabric was positioned inside the treatment vessel (500 mL). CO<sub>2</sub> in a gas cylinder was liquefied through a refrigerator. The liquefied CO<sub>2</sub> was heated to above critical temperature with a heat exchanger and was pressurized to above critical pressure using a high-pressure pump. Carbon dioxide that was in the supercritical state was then injected to the treatment vessel in which PMIA fabric would be modified. The treatment experiments were conducted at a system temperature of 120°C with different pressures (18, 22, 26, and 30 MPa). After a requested treatment period of 60 min, the system was decompressed by controlling the relief valves and the PMIA fabric was removed and used for further analysis. In the whole treatment procedure, system pressure was regulated by the back pressure valve, and system parameters were displayed on a computer.

### Characterizations

**SEM Analysis.** SEM was performed to observe the morphology of the PMIA fiber. The fiber samples were fixed on the aluminum plate via a conducting adhesive and degassed sputter coated with the gold for 80 s to provide the conductivity for the impinging electrons. Subsequently, a thin layer of gold (about 10 nm) was coated at the fibers' surface. The typical values of the voltage and operation distance were 10 kV and 9 mm, respectively.

**Water Contact Angle Measurements.** A surface tension instrument equipped with a high speed video camera was used to



**Figure 2.** SEM images of the PMIA: fiber surface of the untreated sample (a) and treated at system pressures of 18 MPa (b), 22 MPa (c), 26 MPa (d) and 30 MPa (e) in the supercritical carbon dioxide fluid by employing a treatment temperature at 120°C and a treatment time of 60 min.

analyze the surface wetting behavior of the PMIA fiber by measuring the water contact angle and the absorption time. The instrument was located in a temperature and humidity controlled laboratory ( $20 \pm 1^\circ\text{C}$ ,  $65 \pm 2\%$ ). The data shown for each sample were averages of five single measurements.

**FT-IR Analysis.** Infrared spectra of the PMIA fiber were recorded using an FT-IR spectrophotometer with attenuated total reflection (ATR) method at room temperature in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Thirty-two scans with  $4.0\text{ cm}^{-1}$  resolution were carried out for each case under the reflection mode.

**XRD Analysis.** The crystalline states of PMIA fiber were conducted with an XRD instrument at room temperature. The test condition was that wavelength  $1.5406 \times 10^{-10}\text{ m}$ , tube voltage 40 kV, current 25 mA, sequential scanning counting mode and

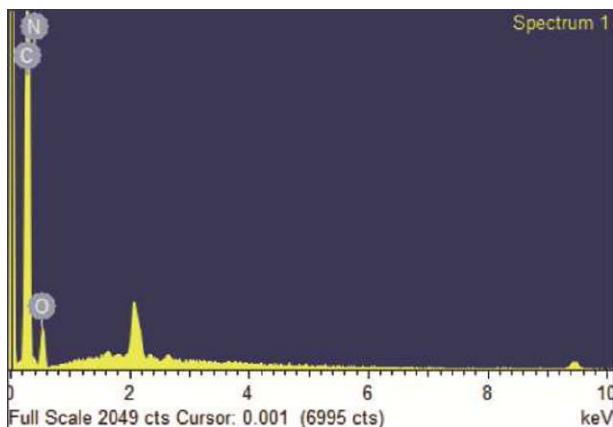
scanning speed  $4^\circ\text{ min}^{-1}$ . The standards employed were DS 1°, SS 1° and RS 0.3 mm.

**Thermogravimetric Analysis.** The thermal property analysis of PMIA before and after the supercritical carbon dioxide fluid treatment was carried out on a thermal analysis machine in the temperature range of  $30\text{--}800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ , and the mass of each sample was approximately 2–4 mg.

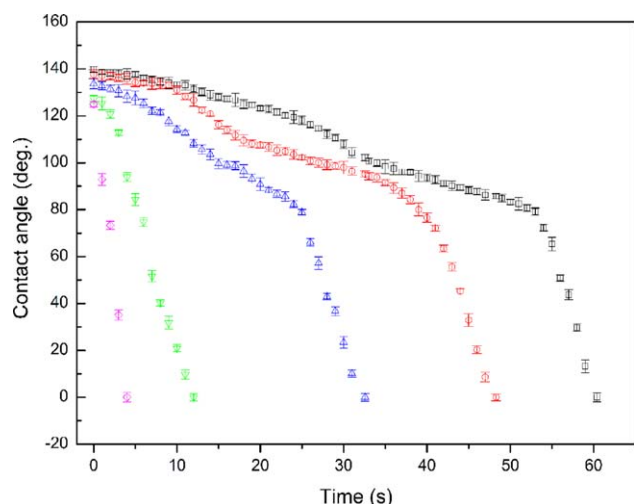
**Mechanical Properties.** The tensile strength of the PMIA samples were carried out on a universal material testing machine with the gauge length 100 mm, test speed  $100\text{ mm min}^{-1}$  and preliminary tension 2 N. The strength value ( $\sigma_t/\text{MPa}$ ) was calculated according to the following equation:

**Table I.** Energy-Dispersive X-ray Results of Different Pressure Treated PMIA Fibers in the Supercritical Carbon Dioxide Fluid

Samples	Elements	Weight (%)	Atomic (%)
Untreated	C	$69.64 \pm 2.03$	$74.11 \pm 2.25$
	N	$14.41 \pm 0.31$	$13.15 \pm 0.36$
	O	$15.95 \pm 0.52$	$12.74 \pm 0.32$
18 MPa	C	$65.92 \pm 2.15$	$70.67 \pm 2.10$
	N	$16.54 \pm 0.53$	$15.21 \pm 0.41$
	O	$17.54 \pm 0.46$	$14.12 \pm 0.26$
22 MPa	C	$68.13 \pm 2.10$	$72.86 \pm 2.12$
	N	$13.59 \pm 0.28$	$12.46 \pm 0.29$
	O	$18.28 \pm 0.53$	$14.68 \pm 0.23$
26 MPa	C	$66.96 \pm 1.95$	$71.77 \pm 2.17$
	N	$14.34 \pm 0.30$	$13.18 \pm 0.31$
	O	$18.70 \pm 0.42$	$15.04 \pm 0.38$
30 MPa	C	$64.91 \pm 2.00$	$69.84 \pm 1.90$
	N	$15.82 \pm 0.31$	$14.59 \pm 0.32$
	O	$19.28 \pm 0.49$	$15.57 \pm 0.42$



**Figure 3.** Energy-dispersive X-ray analysis of the untreated PMIA fiber. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Dynamic contact angle of water and absorption time for untreated sample (-□-) and treated at treatment pressures of 18 MPa (-○-), 22 MPa (-△-), 26 MPa (-▽-) and 30 MPa (-◇-) in the supercritical carbon dioxide fluid by employing a treatment temperature at 120°C and a treatment time of 60 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$\sigma_b = \frac{4F_p}{\pi D^2} \quad (1)$$

where  $F_p$  is the maximal tensile fracture force in kilogram;  $D$  is the mean diameter of the PMIA fiber in centimeter. Each experiment was carried out five times, and each data entry was the average of five samples.

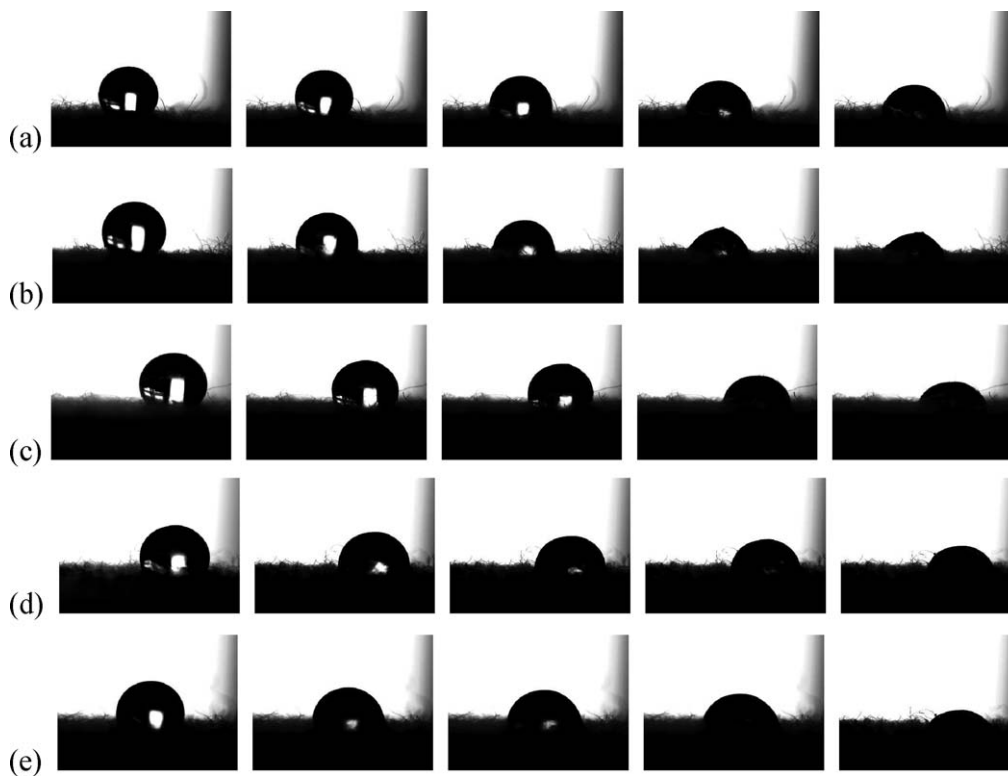
## RESULT AND DISCUSSION

### Effect of Treatment Pressure on the Surface Morphology of PMIA Fiber in the Supercritical Carbon Dioxide Fluid

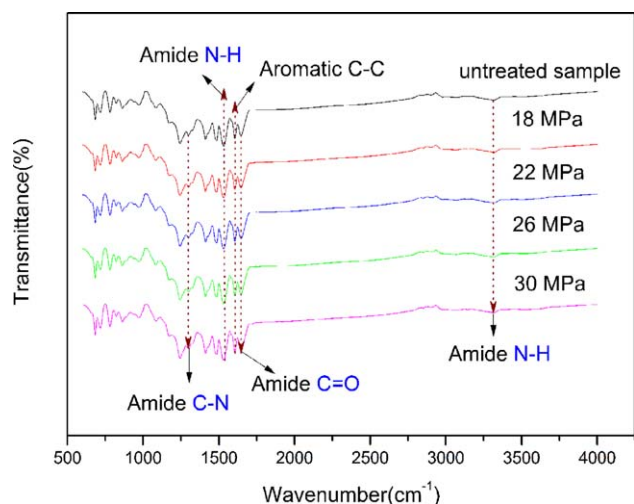
SEM was used to investigate the surface morphology changes of PMIA fiber before and after the supercritical carbon dioxide fluid treatment. Figure 2 shows a comparison of the SEM images of the untreated fiber and the fibers treated in the supercritical carbon dioxide fluid for 18, 22, 26, and 30 MPa. It can be seen from Figure 2 that the surfaces of the treated fiber samples were uneven and clearly different from that of the untreated one [Figure 2(a)], which was clean and smooth.

When the PMIA fiber was treated for 18 MPa in the supercritical carbon dioxide fluid, the irregular surface with apparent bulges and ruts can be observed in Figure 2(b). However, when the treatment pressure was further increased to 30 MPa, more grooves and bulges appeared on the surface of the PMIA fibers as shown in Figure 2(c–e). The results showed that surface roughness of PMIA fiber was increased with the increase of treatment pressure. The changes of PMIA fiber surface features before and after the treatment were probably because of the excellent mass transfer ability and low surface tension of the supercritical carbon dioxide fluid, which could enhance the fiber surface roughness.<sup>23,24</sup>

Moreover, EDX was utilized to measure the chemical composition of PMIA fiber in volume with 1  $\mu\text{m}$  dimension. The EDX analysis result (Figure 3) shows that three elements, carbon (C), nitrogen (N), and oxygen (O), exist on the untreated sample's surface. Table I presents the percentages of the elements on

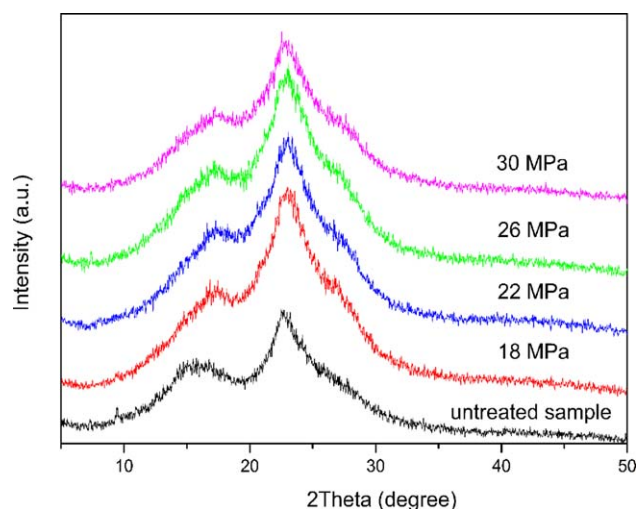


**Figure 5.** High-speed image sequences of water drops applying to the untreated sample (a) and treated at system pressures of 18 MPa (b), 22 MPa (c), 26 MPa (d) and 30 MPa (e) in the supercritical carbon dioxide fluid by employing a treatment temperature at 120°C and a treatment time of 60 min.

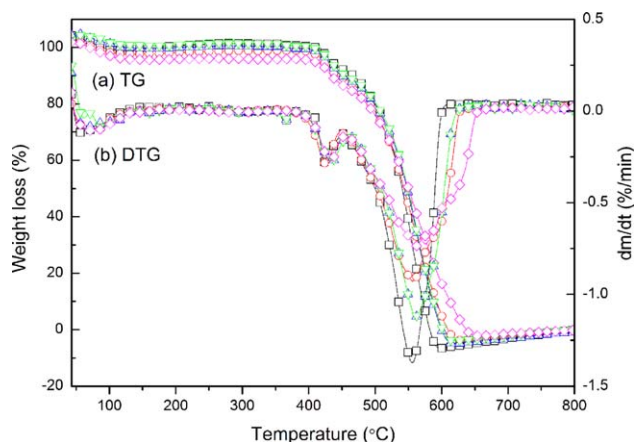


**Figure 6.** FT-IR spectra of the PMIA fibers treated at different pressures in the supercritical carbon dioxide fluid. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

PMIA surfaces. It can be seen from the EDX results that the carbon (C) concentration, nitrogen (N) concentration, and oxygen (O) concentration of the untreated PMIA fibers were 74.11%, 13.15%, and 12.74%, respectively. After 18 MPa supercritical carbon dioxide fluid treatment on PMIA fiber, it was observed that the C concentration was decreased to 70.67% while the N concentration was increased to 15.21% and the O concentration was increased to 14.12%. When the treatment pressure was increased further, it was noticed that the C concentration was decreased from 72.86% to 69.84%, and the O concentration was increased from 14.68% to 15.57%, but the change of N concentration was not significant. In general, these changes of fiber surface chemical compositions may be caused by the introduction of oxygen-containing polar groups onto the fiber surface in the supercritical carbon dioxide fluid processing.



**Figure 7.** XRD spectra of the PMIA fibers treated at different pressures in the supercritical carbon dioxide fluid. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** TG-DTG curves of untreated sample ( $-\square-$ ) and treated at treatment pressures of 18 MPa ( $-\circ-$ ), 22 MPa ( $-\Delta-$ ), 26 MPa ( $-\nabla-$ ) and 30 MPa ( $-\diamond-$ ) in the supercritical carbon dioxide fluid by employing a treatment temperature at 120°C and a treatment time of 60 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Effect of Treatment Pressure on the Wettability of PMIA Fiber in the Supercritical Carbon Dioxide Fluid

The water contact angle is a good indicator of the relative hydrophobicity or hydrophilicity of a substrate.<sup>25</sup> Therefore, the contact angle of water and absorption time were used to study the effect of different pressures on the fiber surface wettability. The dynamic contact angle of water and absorption time of the untreated fiber and the supercritical carbon dioxide fluid treated fiber samples were given in Figure 4. As shown in Figure 4, the water contact angle and absorption time for the untreated sample were 139.8° and 60.4 s, respectively. And for the treated PMIA samples, the contact angle against water and absorption time were reduced significantly from 137.6° to 124.9° and 48.3 to 4 s, respectively. Evidently, the water absorptivity was enhanced greatly by the supercritical carbon dioxide fluid treatment. Furthermore, lower contact angles meant higher amounts of hydrophilic groups were formed on the surface of the PMIA fiber and improved the wetting properties. Figure 5 illustrates the images of sequences of water drops applied to the surface of untreated and treated PMIA samples. Therefore, the wettability of the PMIA fiber could be improved notably with the increase of treatment pressure in the supercritical carbon dioxide fluid.

#### Effect of Treatment Pressure on the Chemical Structure of PMIA Fiber in the Supercritical Carbon Dioxide Fluid

Figure 6 depicts the FT-IR spectra of the PMIA samples treated at different pressures in the supercritical carbon dioxide fluid. As shown in Figure 6, the characteristic bands of the PMIA fiber, aromatic ring stretching vibration, N-H stretching, N-H bending, C=O stretching, C-N stretching, were observed in FT-IR spectra of all samples.<sup>6</sup> The infrared spectra of the untreated PMIA fiber indicated that band at 3315.36  $\text{cm}^{-1}$  was attributed to N-H stretching vibrations ( $\nu_{\text{N-H}}$ ) of the amide linkage. The strong peak with absorption band at 1647.32  $\text{cm}^{-1}$  was because of the stretching vibration of C=O ( $\nu_{\text{C=O}}$ ) from amide I. And the peaks with absorption bands at 1531.66 and 1299.63  $\text{cm}^{-1}$  corresponded to the bending vibration of N-H ( $\delta_{\text{N-H}}$ ) from amide II and the

**Table II.** Tensile Properties of PMIA Fibers Treated at Different Pressures in the Supercritical Carbon Dioxide Fluid

Samples	Breaking force (N)	Tensile strength (MPa)	Elongation at break (%)
Untreated	1187.978 ± 5.021	47.519 ± 3.055	56.146 ± 2.436
18 MPa	1206.708 ± 3.227	48.268 ± 2.272	58.262 ± 1.251
22 MPa	1217.692 ± 3.102	48.708 ± 2.317	58.442 ± 1.320
26 MPa	1239.757 ± 3.432	49.590 ± 3.104	56.450 ± 2.117
30 MPa	1224.654 ± 4.164	48.986 ± 2.238	52.400 ± 2.325

stretching vibration of C-N ( $\nu_{C-N}$ ) from amide III, respectively. In addition, band at  $1605.58\text{ cm}^{-1}$  was emerged because of stretching vibration of aromatic C=C ( $\nu_{C=C}$ ). After the supercritical carbon dioxide fluid treatment, slight shifts could be observed for the characteristic bands of amide and aromatic ring. Moreover, the difference in the intensities of the characteristic bands of the PMIA samples was relatively small when the untreated PMIA fibers and the treated ones were compared. This observation can be explained by the chemical stability and highly crystalline nature of the aramid polymer, which was hard to result in the change of the macromolecular structure.<sup>19</sup>

#### Effect of Treatment Pressure on the Crystal Structure of PMIA Fiber in the Supercritical Carbon Dioxide Fluid

Figure 7 shows the XRD curves of the untreated PMIA fiber and the supercritical carbon dioxide fluid treated fibers. The crystalline peaks around  $2\theta = 17^\circ$  and  $2\theta = 23^\circ$  were observed in all the fiber samples.<sup>26</sup> In comparison with the untreated one, the crystallinity of the PMIA samples treated with the supercritical carbon dioxide fluid was gradually increased from 18 to 26 MPa, then slowly decreased at 30 MPa. Theoretically, carbon dioxide could swell and plasticize polymer in the supercritical state, which contributed to the interactions and movements of the macromolecular chains of PMIA fiber, thereby leading to the rearrangement of macromolecular chains under high pressure conditions. However, the decrease of the diffraction intensity at 30 MPa was probably because the defects of the macromolecular chains were destroyed in the rearrangement process in the supercritical carbon dioxide fluid.

#### Effect of Treatment Pressure on the Thermal Property of PMIA Fiber in the Supercritical Carbon Dioxide Fluid

TG and DTG curves of the PMIA samples are illustrated in Figure 8. The TG curves showed that weight loss of the PMIA fiber could be divided into two steps. The first weight loss step was appeared from  $30^\circ\text{C}$  to  $125^\circ\text{C}$  accompanied by the lowest point at  $60.7^\circ\text{C}$  in DTG curves because of the release of the adsorbed water. The prominent step of weight loss was observed from  $380^\circ\text{C}$  to  $600^\circ\text{C}$  corresponding to the endothermic peaks from  $380^\circ\text{C}$  to  $460^\circ\text{C}$  and  $460^\circ\text{C}$  to  $600^\circ\text{C}$  in DTG curves. In general, the hydrogen bonding between molecular chains were damaged and led to the hydrolysis of molecular chain when the temperature was increased to  $380^\circ\text{C}$ . After the decomposition temperature was increased to  $460^\circ\text{C}$ , besides the hydrolysis reaction, the homolysis among the amide linkage and the bonding between the amide group and aromatic ring was occurred. Moreover, DTG curves revealed that the water vaporization temperature and the thermal decomposition temperatures of PMIA samples

were shifted to a higher temperature with treatment pressure increasing because of the re-arrangements and re-crystallizations of the polymer chains in the supercritical carbon dioxide fluid.

#### Effect of Treatment Pressure on the Mechanical Properties of PMIA Fiber in the Supercritical Carbon Dioxide Fluid

The test data of mechanical properties of different supercritical carbon dioxide fluid treated PMIA fiber are summarized in Table II. It can be seen from Table II that the tensile strength of the treated PMIA samples was increase from 47.519 to 49.590 MPa. Although the tensile strength was reduced slowly to 48.986 MPa when the treatment pressure was increased to 30 MPa, its strength data was higher than the untreated PMIA fiber. Thus, the improvement in tensile strength for treated fiber samples suggested that the supercritical carbon dioxide fluid had excellent mass transfer and penetration effect on PMIA fibers, which could significantly neat the macromolecular structure of polymer, and resulted in the tensile strength increasing.<sup>14,27</sup> This indicated that supercritical carbon dioxide fluid treatment was a novel modification method without weaken the tensile strength of the PMIA fiber.

#### CONCLUSIONS

The experimental results of this study proved that the supercritical carbon dioxide fluid can effectively modify the surface of PMIA fiber. SEM, DWM, FT-IR, XRD, and TG-DTG results gave distinctive differences in morphology, wettability, thermal and mechanical properties of the untreated and the supercritical carbon dioxide-treated PMIA samples. After the supercritical carbon dioxide treatment, surface roughness of the PMIA fiber was increased with the rising of treatment pressure, which was illustrated by SEM evaluation. The water contact angle and absorption time were significantly reduced from  $139.8^\circ$  to  $124.9^\circ$  and from 60.4 to 4 s. FT-IR analysis showed that the slight shifts could be observed for the characteristic bands of PMIA fiber with the pressure increasing. XRD analysis revealed that the crystallinity of the PMIA samples treated with supercritical carbon dioxide fluid was increased gradually from 18 to 26 MPa because of the re-arrangements and re-crystallizations of the molecule chains generated. Moreover, TG-DTG analysis indicated that the thermal property of PMIA fiber was improved with the increase of treatment pressure. The tensile strength for treated PMIA samples was also enhanced in comparison with that for the untreated samples.

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