Wet-driven shape-memory behaviors and thermal adaptability of cotton knitted fabrics containing crosslinked poly(ethylene glycol) moieties

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ABSTRACT: Cotton knitted fabrics were treated with poly(ethylene glycol) (PEG) in the presence of polyhydric alcohol etherified dimethylol dihydroxy ethylene urea as the crosslinker and magnesium chloride hexahydrate as the catalyst. In wet–dry cycles, the fabrics treated with 30% PEG1500 in the presence of 15% crosslinker and 3% catalyst showed obvious wet-driven shape-memory behaviors in terms of a 12% shrinkage rate in the wet state and a 80% shrinkage-recovery rate in the dry state. The results of weight gain, morphological structures, Fourier transform infrared spectra, and X-ray diffraction pattern tests confirmed PEG deposits on the surface of the treated fabrics, demonstrated the crosslinking of cotton cellulose with PEG and crosslinker, and also explained the wet-driven shape-memory mechanism. The results from differential scanning calorimetry show that the treated fabrics with wet-driven shape-memory behaviors had a phase-change enthalpy and heat-storage capacity. The crosslinking of cotton cellulose with PEG had a strong influence on the mechanical performance and air permeability of the cotton knitted fabrics. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43473.

INTRODUCTION

Shape-memory polymers (SMPs) are stimuli-sensitive polymeric materials that can respond to an external stimulus (e.g., temperature, light, pH, water) and rapidly change their shapes with respect to their dimensions.[1–5] In the past decade, many researches have focused on stimulus-active polymers. However, most SMPs only show one-way shape-memory behavior. Some kinds of polymers were investigated for potential two-way shape-memory properties.[6,7]

Recently, the shape-memory behavior of water-driven SMPs was observed after immersion in water. The shape recovery of the deformed SMPs were triggered by water or moisture because of the plasticizing effect of water molecules.[8,9] Some investigations have shown that the hydrogen bonding formed between water and polymers is the key player behind the water-driven SMPs and water or moisture absorbed in the polymer plays a dominant role in the wet-driven shape-recovery process.[10] Fabrics/textiles can be prepared to show shape-memory functionality through the application of these wet-driven SMPs onto fabrics through specific finishing processes. In comparison with wet-driven SMPs, wet-driven composites need less time for recovery;

this is much faster, and therefore, they can be more suitable for self-tightening sutures and self-retractable and removable stents in the biomedical field.[11]

Poly(ethylene glycol) (PEG) as a functional polymer material has been widely investigated in thermally induced shape-memory materials[6,12] and in smart-phase-change materials,[13–15] and its applications in wet-driven shape-memory materials have rarely been reported.

In this article, we present an investigation of the wet-driven shape-memory behaviors and thermal adaptability of fabrics treated with PEG in the presence of polyhydric alcohol etherified dimethylol dihydroxy ethylene urea (DMDHEU) as the crosslinker and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) as the catalyst. Figure 1(a) shows the molecular structure of the treated cotton fabric. The wet-driven shape-memory behaviors of the cotton knitted fabric was due to the shape change of the PEG molecular structure in the wet–dry cycles, as shown in Figure 1(b).[16] While immersed in water, the fabrics treated with PEG showed shrinkage behavior because of the flexibility of the $1 + 1$ rib knitted structure and the hydrogen bonds formed between the water and —C—O—C— structure of the PEG molecular chain. While being dried by airing, the treated fabrics
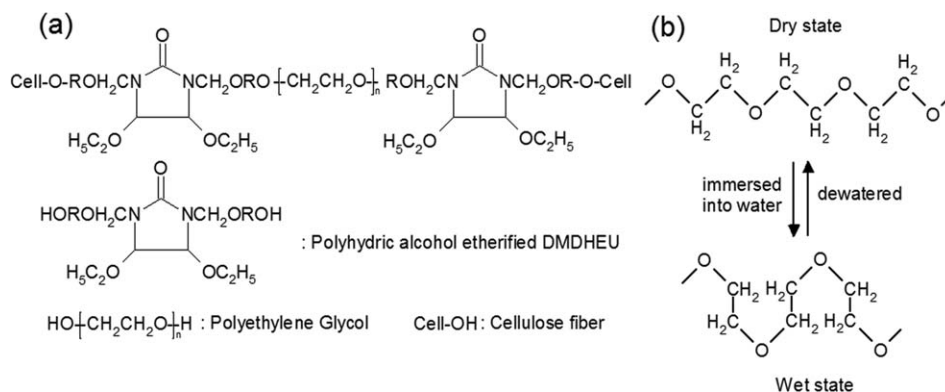
Figure 1. (a) Molecular structures of wet-driven shape-memory cotton knitted fabric and (b) illustration of the wet-driven shape-memory behaviors for the cotton knitted fabric based on PEG.

showed shrinkage-recovery behavior because of the recovery of the —C—O—C— structure of the PEG molecular chain. In the wet–dry cycles, the cotton knitted fabrics showed wet-driven shape-memory behaviors in two-way actuation. In addition, the treated fabrics showed thermal adaptability because of the phase change of PEG after the heating and cooling cycles. The wet-driven shape-memory behaviors of the treated fabrics were studied through the shrinkage rate measurement and the shrinkage-recovery rate testing. The treated fabrics' surface morphological structure, molecular structure, crystalline structure, and thermal adaptability were investigated with scanning electron microscopy (SEM), Fourier transform infrared (FTIR) analysis, X-ray diffraction (XRD) analysis, and differential scanning calorimetry (DSC). These wet-driven shape-memory cotton knitted fabrics with thermal adaptability may find more applications in the near future.

EXPERIMENTAL

Materials
PEG polymers with average molecular weights of 600, 1000, 1500, 2000, and 3000 were supplied by Sinopharm Chemical Reagent Co. Ltd. (China). Polyhydric alcohol etherified DMDHEU used as a crosslinker was supplied by Guangzhou Fengran Chemical Reagent Co. Ltd. (China). $MgCl_2 \cdot 6H_2O$ supplied by Tianjin Bodi Chemical Reagent Co. Ltd. (China) was an analytically pure reagent and was used as a catalyst without further purification. In this study, scoured and bleached $1 + 1$ rib knitted fabrics (weft density = 15 loops/cm, warp density = 17 loops/cm) from Tianran Textile Industrial Co., Ltd. (China) were used.

Preparation of the Wet-Driven Shape-Memory Cotton Knitted Fabrics
The fabrics were treated with the pad–dry–cure process. Padding was performed in a rapid padding machine manufactured by Labortex Co., Ltd. PEGs with different average molecular weights of 600, 1000, 1500, 2000, and 3000 were prepared with aqueous solutions with concentrations of 0, 5, 10, 20, 40, and 50% w/v. In each solution mentioned previously, 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$ were added. The cotton fabrics were padded with each solution with 100% wet pickup. The samples were dried at 100 °C for 5 min

and then cured at 160 °C for 3 min. The cured fabrics were washed with purified water at 60 °C for 10 min, dried, and then conditioned at 21 ± 1 °C and 65 ± 2% relative humidity for 24 h before the measurements of the fabric lengths.

Test of the Wet-Driven Shape-Memory Behaviors
As shown in Figure 1, the treated cotton knitted fabrics showed shrinkage behavior when swollen by water (wet state) and shrinkage-recovery behavior when dried by airing (partially dry state) both at 24 ± 1 °C. In wet–dry cycles, the length of the fabric in the wet state (L_i') and the length of the fabric in the dry state (L_i) were tested to calculate the shrinkage rate and shrinkage-recovery rate with the following equations:

$$\text{shrinkage rate (\%)} = [(L_{i-1} - L_i')/L_{i-1}] \times 100 (i \geq 1) \quad (1)$$

$$\text{shrinkage recovery rate (\%)} = [(L_i - L_i')/L_{i-1} - L_i'] \times 100 (i \geq 1) \quad (2)$$

where the L_0 is the original length of treated fabric and i is the number of the wet-dry cycle.

Weight Gain
The weight gain of the fabric was calculated through the measurement of the weight of the dried fabrics before and after the treatments. The percentage weight gain was calculated with the formula as follows:

$$\text{Weight gain (\%)} = [(W - W_0)/W_0] \times 100 \quad (3)$$

where W_0 is the weight of the untreated cotton fabric and W is the weight of the treated cotton fabric. Table I presents the weight gain of the different fabric samples.

Examination of the Morphological Structures
After it was sputtered with gold *in vacuo*, the surface morphological structures of the wet-driven shape-memory fabrics were examined with a KYKY2008B scanning electron microscope (Zhongke Scientific Instruments, Beijing) with an accelerating voltage of 20 kV and a current of 10 μA at a high-magnification power up to 2000×.

FTIR Analysis
The FTIR spectra of different fabric samples were measured with a Nicolet 6700 FTIR instrument (Thermo Fisher Scientific) in the range 4000–600 cm^{-1}.

Table I. Weight Gains of the Different Samples Treated with PEG

PEG molecular weight	PEG concentration (%)	Polyhydric alcohol etherified DMDHEU concentration (%)	MgCl$_2$·6H$_2$O concentration (%)	Weight gain (%)
600	30	15	3	36.51
1000	30	15	3	37.42
1500	30	15	3	39.42
2000	30	15	3	37.27
3000	30	15	3	37.32
1500	0	15	3	5.18
1500	5	15	3	10.01
1500	10	15	3	14.89
1500	20	15	3	25.41
1500	40	15	3	42.35
1500	50	15	3	46.07

XRD

XRD patterns of the samples were obtained on a Rapid II X-ray diffractometer (Rigaku). The goniometer scanned with a scan rate of 1°/min.

Determination of the Thermal Properties

The thermal properties of the pure PEG and the treated fabrics, such as the melting and crystallizing temperatures and enthal-

pies, were measured with a DSC1 STARe system (Mettler-Toledo). The analyses were conducted with heating and subsequent cooling at a rate of 10 °C/min under a nitrogen flow rate of 60 mL/min from −40 to 130 °C.

Determination of the Bursting Strength and Air Permeability

The bursting strengths of the different samples were measured with an HD026C electronic fabric strength tester (Nantong
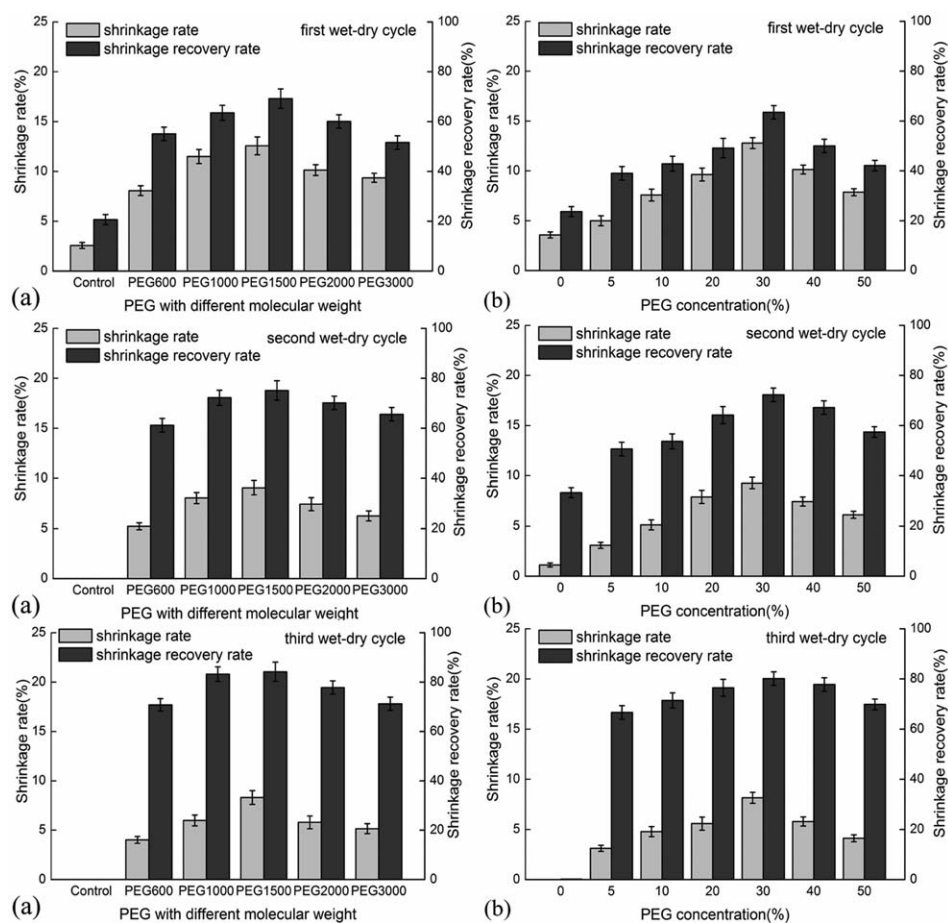

Figure 2. Wet-driven shape-memory effects of different fabrics treated with (a) PEGs with different molecular weights and (b) different PEG1500 concentrations (all in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% MgCl$_2$·6H$_2$O).
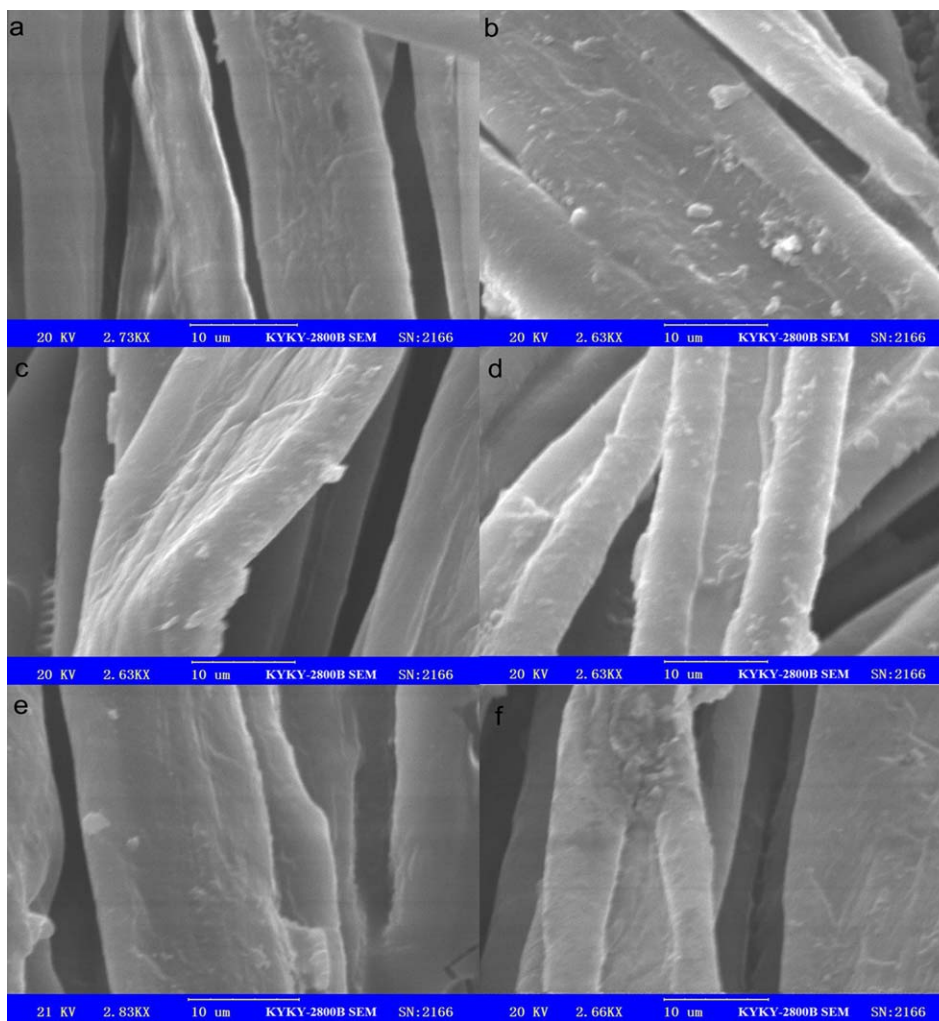
Figure 3. SEM images of (a) the control cotton sample; fabrics treated with (b) PEG600, (c)PEG1000, (d) PEG1500, (e) PEG2000, and (f) PEG3000 (all at a concentration of 30%); and fabrics treated with PEG1500 at concentrations of (I) 0, (II) 5, (III) 10, (IV) 20, (V) 40, and (VI) 50%. All of the treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hongda Experiment Instruments Co., Ltd.) according to the Chinese standard GB/T 19976-2005 ("The Bursting Strength Test of Textiles with Steel Ball Method").

The air permeability of different samples was measured with a YG461H automatic air permeability tester (Ningbo Textile Instrument Factory) according to the Chinese standard GB/T 5453-1997 test.

RESULTS AND DISCUSSION

Wet-Driven Shape-Memory Behaviors of Cotton Knitted Fabrics

The wet-driven shape-memory behaviors of the cotton knitted fabrics were measured in terms of the shrinkage rate and shrinkage-recovery rate, respectively, in three wet–dry cycles. Figure 2(a) presents the wet-driven shape-memory behaviors of the control sample and fabrics treated with a homologous series of PEGs (with various molecular weights) in three wet–dry cycles. The wet-driven shape-memory behaviors of the fabrics

treated with different PEG concentrations are shown in Figure 2(b). The results indicate that the fabrics treated with PEG showed both shrinkage and shrinkage-recovery behaviors in the wet–dry cycles. This was due to the crosslinking degree of the cotton fabrics treated with PEG, as shown in Figure 1(a), and the deformability of the PEG molecular chain in the wet–dry cycles, as shown in Figure 1(b).

Because of the construction and hygroscopicity of the cotton fibers, the control sample also showed shrinkage and shrinkage-recovery behaviors in the first wet–dry cycle and then showed no shape-memory behavior in the second and third wet–dry cycles, as shown in Figure 2(a). The weight gains of the treated fabrics are given in Table I. It is evident from Table I that the weight gains of the treated fabrics reached the highest point when PEG1500 was used.

In the aforementioned three wet–dry cycles, the fabric treated with PEG1500 showed an increase in the shrinkage and shrinkage-recovery rates when compared with the fabrics treated with PEG600 and PEG1000, as shown in Figure 2(a).
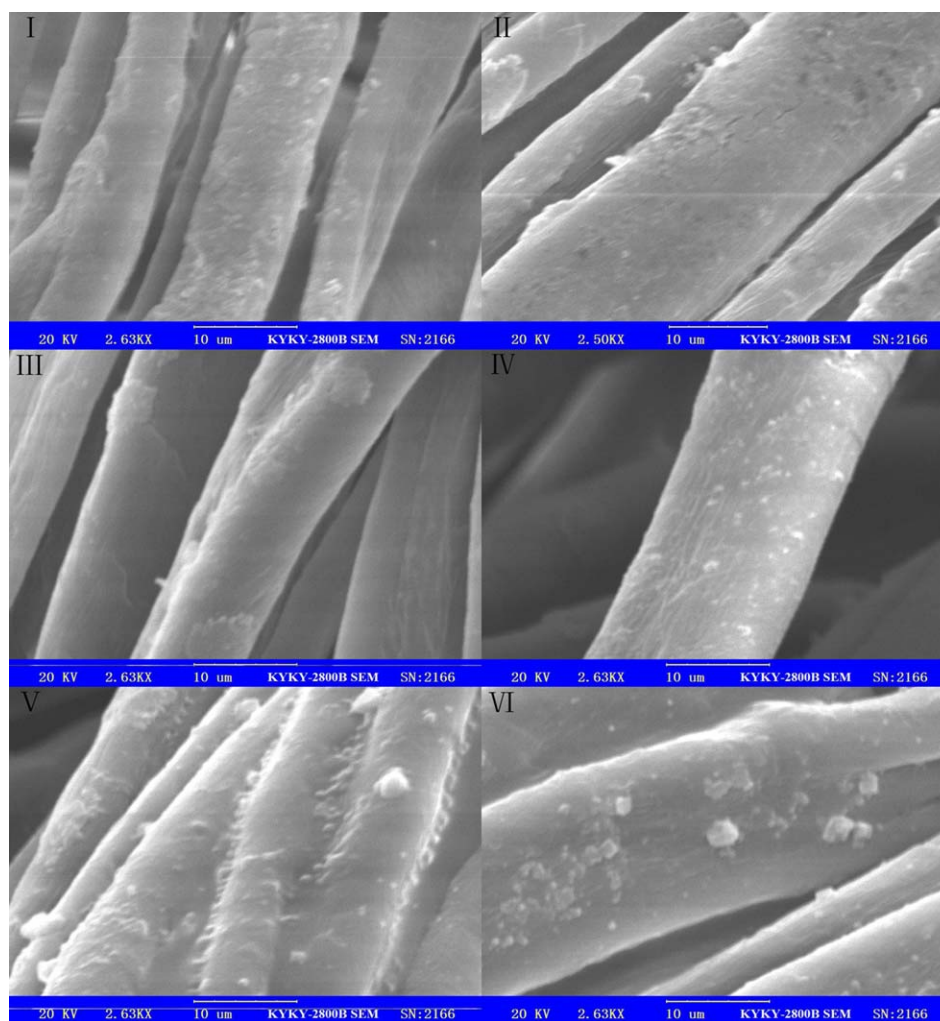
Figure 3. *Continued.*

The increase in the shrinkage and shrinkage-recovery rates were caused both by the increase in the crosslinking degree between the cotton fabrics and PEG and the different transition temperature of PEG. The deformability of the fabrics was enhanced by the increased crosslinking, and the deformation of the PEG molecular chain in the wet–dry cycle made it easier for the shrinkage and shrinkage recovery of the fabrics from the deformation. The fabrics treated with PEG2000 and PEG3000 showed decreases in the shrinkage and shrinkage-recovery rates because of the decrease in the reactivity of the hydroxyl groups on PEG, and thus, the decreased crosslinking degree between the cotton fabrics, PEG, and polyhydric alcohol etherified DMDHEU was obtained. It is evident from Table I that the weight gains of the treated fabrics reached the highest point when the fabric was treated with PEG1500.

The treated fabrics showed a remarkable increase in the shrinkage and shrinkage-recovery rates because of the increase in the PEG concentration and showed the highest values of shrinkage and shrinkage-recovery rate when the fabric was treated with 30% PEG1500, as shown in Figure 2(b). In terms of the weight gains of the treated fabrics, the fabrics treated with less than 30% PEG1500 showed a decrease in the shape-memory effect because of the decrease in the crosslinking degrees of the PEG and fabrics; this decreased the deformability of the treated fabrics. When concentrations of PEG1500 higher than 30% were used, there was no corresponding increase in the shape-memory effect. Figure 2 confirms that the fabrics treated with PEG showed remarkable wet-driven shape-memory behavior with two actuations because of the adequate PEG molecular weight and concentration.[16]

Morphological Structures of the Fabrics

Figure 3(a) presents the SEM image of the untreated (control) fabric, which showed the spiral and surface structure of cotton fibers clearly.

The SEM images of the fabrics treated with PEG with different molecular weights of PEG600, PEG1000, PEG1500, PEG2000, and PEG3000 are shown in Figure 3(b–f), respectively. Compared with the control sample, Figure 3(b–d) shows the formation of the coating layers on the surface of the treated fibers, and this confirmed that the wet-driven shape-memory behaviors of the fabrics in the wet–dry cycles were caused by the
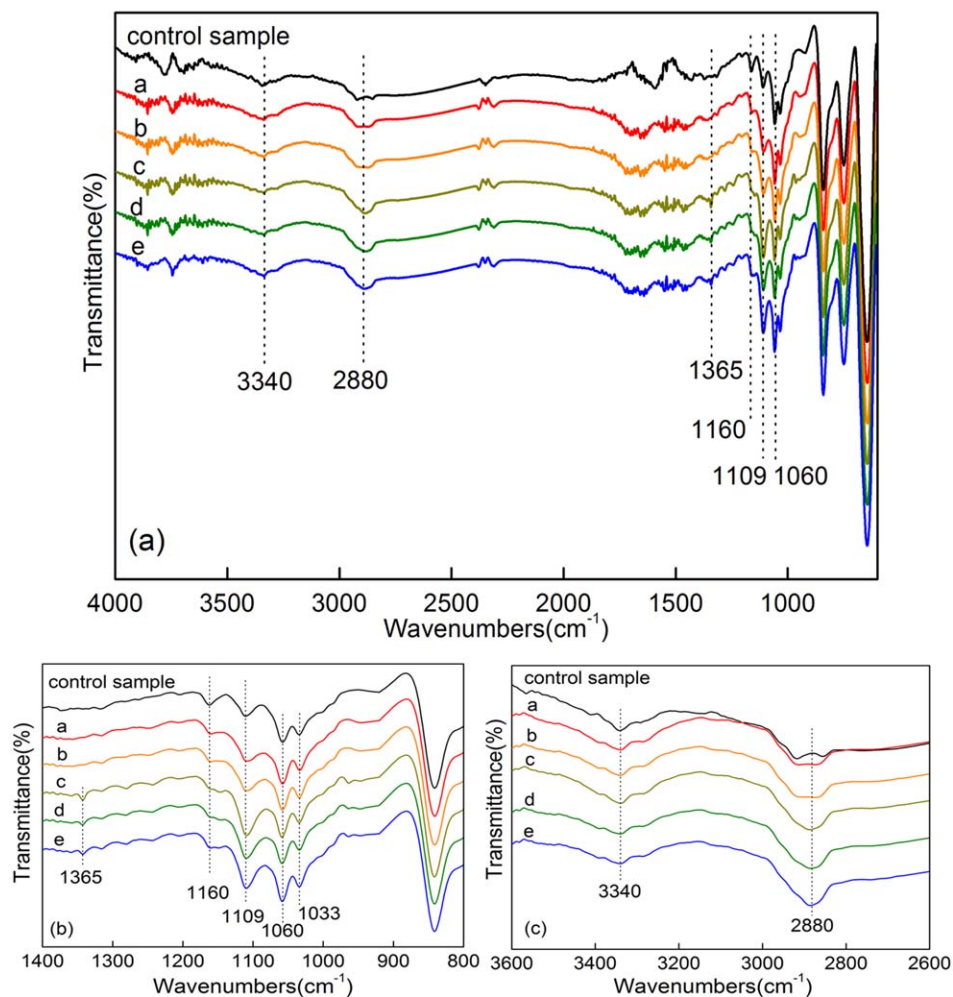
Figure 4. FTIR spectra of the control sample and the fabrics treated with PEGs with different molecular weights: (a) PEG600, (b) PEG1000, (c) PEG1500, (d) PEG2000, and (e) PEG3000. All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslinking between the fabrics, PEG, and the crosslinking agent.[18] As shown in Figure 3(e,f) when PEG with a molecular weight higher than 1500 was used, there was no further increase in the depositions of PEG and the crosslinking agent. It is evident from Table I that the increase in the weight gain of the treated fabrics was due to the increase in the crosslinking degree.

The SEM images of the fabrics treated with PEG1500 with different concentrations of 0, 5, 10, 20, 40, and 50% are shown in Figure 3(I–VI), respectively. Figure 3(I) presents the rough surfaces of the fabrics treated without PEG in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. Figure 3(II,III) shows the SEM images of the fabrics treated with 5 and 10% PEG1500, respectively, and the nonuniform depositions of PEG on the surface of the fibers were observed. Figure 3(IV,d) shows the SEM images of the fabrics treated with 20 and 30% PEG1500, respectively.

The images show that higher depositions of PEG and crosslinking agent were found on the fiber surface of the fabrics because of the increase in the PEG concentration. The polyhydric alco-

hol etherified DMDHEU was able to effectively crosslink the hydroxyl groups on both the cellulose molecules and PEG molecules. In addition, the coating layers on the surface of the treated fibers were smoother, thicker, and more uniform compared with the fabrics treated with 5 and 10% PEG1500. Figure 3(V,VI) demonstrates the SEM images of the fabrics treated with 40 and 50% PEG1500, respectively. The images show an increase in the thickness of the coating layers because of the increase in the crosslinking degree. In addition, an increase in the deposition of PEG1500 was found on the treated fabrics because of the increase in the crosslink degree. The thickness, uniformity, and smoothness of the coating layers on the treated fabrics depended on the crosslinking degree; this was related to the PEG molecular weights and the concentrations.

FTIR Spectroscopy Analysis

Figures 4(a) and 5(a) show the FTIR spectra of the control sample and fabrics treated with the PEG with different molecular weights and PEG1500 with different concentrations. The spectra reveal the presence of all of the peaks corresponding to various
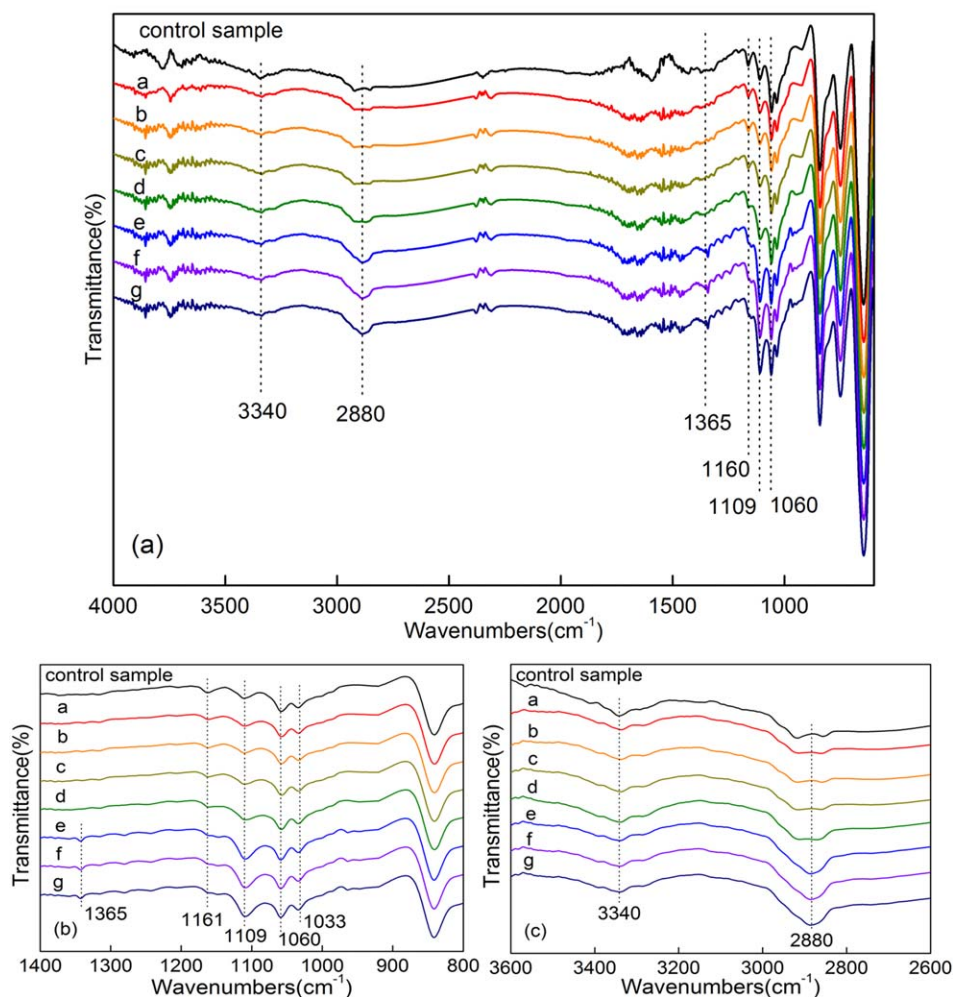
Figure 5. FTIR spectra of the control sample and fabrics treated with PEG1500 at different concentrations: (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, and (g) 50%. All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

functional groups both in the control sample and the treated fabrics.

The characteristic cellulose peaks were found in the spectra according to the literature[19] in that the peak at 3340 cm^{-1} corresponded to H-bonded OH stretching, the peak at 2880 cm^{-1} corresponded to C—H stretching, the peak at 1160 cm^{-1} at corresponded to asymmetrical bridge —C—O—C—, and the peaks at both 1060 and 1033 cm^{-1} corresponded to asymmetrical in-plane ring stretching. The intensity of the corresponding absorption peaks was in proportion to the concentration of the functional groups according to Beer's law.

Figures 4(b) and 5(b) show the changes in the peak at 1109 cm^{-1} corresponding to —C—O—C— stretching vibrations.[20,21] The intensity of the peak at 1109 cm^{-1} was increased for the fabrics treated with PEG with different molecular weights in the order Control < PEG600 < PEG1000 < PEG1500 ≈ PEG2000 = PEG3000 for the fabrics treated with PEG1500 at different concentrations in the order 0 < 10 < 20 < 30 < 40 < 50%; this indicated that the concentrations of the —C—O—C— groups forming between PEG, the crosslink agent, and the fiber increased for the samples treated with

PEG. The increase in the ether bonds enhanced the wet-driven shape-memory behaviors of the fabrics. As shown in Figures 4(b) and 5(b), the weak peak at 1365 cm^{-1} corresponding to —CH$_2$— deformation stretching of PEG confirmed the deposition of PEG on the surface of the treated fibers.[14,22,23]

As shown in Figures 4(c) and 5(c), the peak at 3340 cm^{-1} corresponding to H-bonded OH stretching in the spectra of the untreated cotton fibers decreased after treatment. This indicated that the number of terminal OH groups of cellulose decreased after treatment; this confirmed the chemical crosslinking of cellulose with the crosslinking agent and PEG. The increased intensity in the peak at 2880 cm^{-1} corresponding to the —CH$_2$— deformation stretching of PEG[20,24,25] also confirmed the deposition of PEG on the surface of the fibers treated with PEG.

Figure 6 shows the FTIR spectra of the fabrics treated with PEG1500 in the dry state, and under different water-soaking contents, that is, 100 ± 5, 60 ± 5, and 30 ± 5%. It seemed that water had a significant effect on the absorptions according to the states. Compared to the dry state, the wet-state-treated fabric had a much more intensive peak located at 3440 cm^{-1}
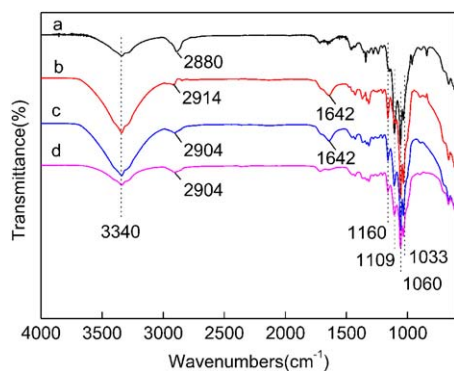
Figure 6. FTIR spectra of the fabrics treated with PEG1500 (a) in the dry state and (b–d) with different water-soaking contents [(b) 100 ± 5, (c) 60 ± 5, and (d) 30 ± 5%]. All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% MgCl$_2$·6H$_2$O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
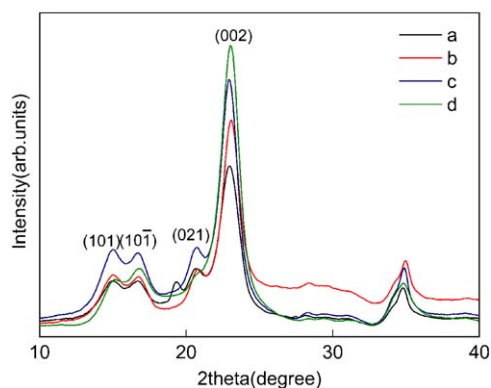

Figure 8. XRD spectra of the fabrics treated with PEG1500 (a) in the dry state and (b–d) with different water-soaking contents [(b) 100 ± 5, (c) 60 ± 5, and (d) 30 ± 5%]. All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% MgCl$_2$·6H$_2$O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

because of absorbed free-water molecules. The wet-state-treated fabric also had less intensive peaks, both located at 2880 and 1109 cm^{-1} because of the association of water molecules and ether bonds; this caused an orientation change of the hydrocarbon chain and a rearrangement of the carbon chain structure.[26] The effect of water molecules on the carbon chain structure increased with increasing water-soaking contents. The change in the intensive peak of the treated fabric combined with the shrinkage and shrinkage-recovery rate in the wet and dry states gave a clear explanation of the wet-driven phenomenon.

XRD Analysis

Figure 7 illustrates the XRD diagrams of the control fabric and the fabrics treated with PEG with different molecular weights and at different concentrations. The presence of the peaks along the (002), (021), (101), and (10$\bar{1}$) directions of the native cellulose are shown in Figure 7 according to the reported results.[27]
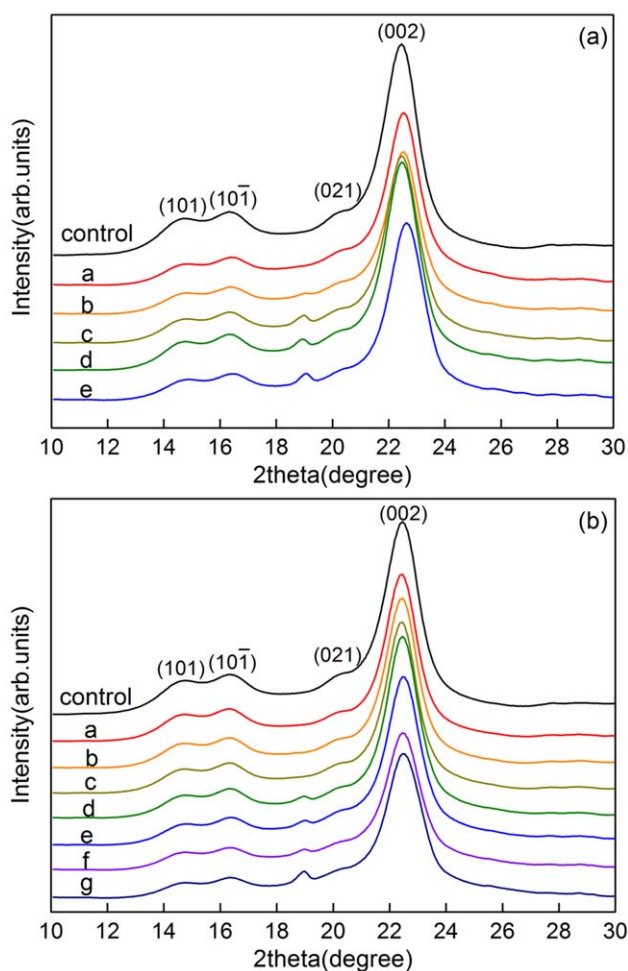

Figure 7. (a) XRD spectra of the control sample and fabrics treated with (a) PEG600, (b) PEG1000, (c) PEG1500, (d) PEG2000, and (e) PEG3000 (all at the concentration of 30%). (b) XRD spectra of the control sample and fabrics treated with PEG1500 at concentrations of (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, and (g) 50%. All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% MgCl$_2$·6H$_2$O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The diffraction intensity of the control fabric was higher at all lattice planes than those of the fabrics treated with PEG with different molecular weights and at different concentrations. Figure 7 shows a decrease in the amorphous regions of the treated fibers along the (101) and (10$\bar{1}$) directions because of the increase in the crosslinking degree of the cotton fibers.[28] The diffraction peak at 19.24° was observed for the PEG; this indicated that the PEG on the surface of the treated fibers was present in the crystalline state.[29]

Figure 8 illustrates the XRD spectra of the fabrics treated with PEG1500 in the dry state, and under different water-soaking contents, that is, 100 ± 5, 60 ± 5, and 30 ± 5%. Compared to the dry state, although sharp peaks due to the crystalline and amorphous structures of the treated fabrics in the wet state became much sharper, the treated fabric in the wet state showed a more crystalline structure because of the orientation change of the hydrocarbon chain and the rearrangement of the carbon chain structure caused by water soaking, as shown in Figure 1. With decreasing water-soaking content, the intensity of the amorphous structure increased because of the relaxation
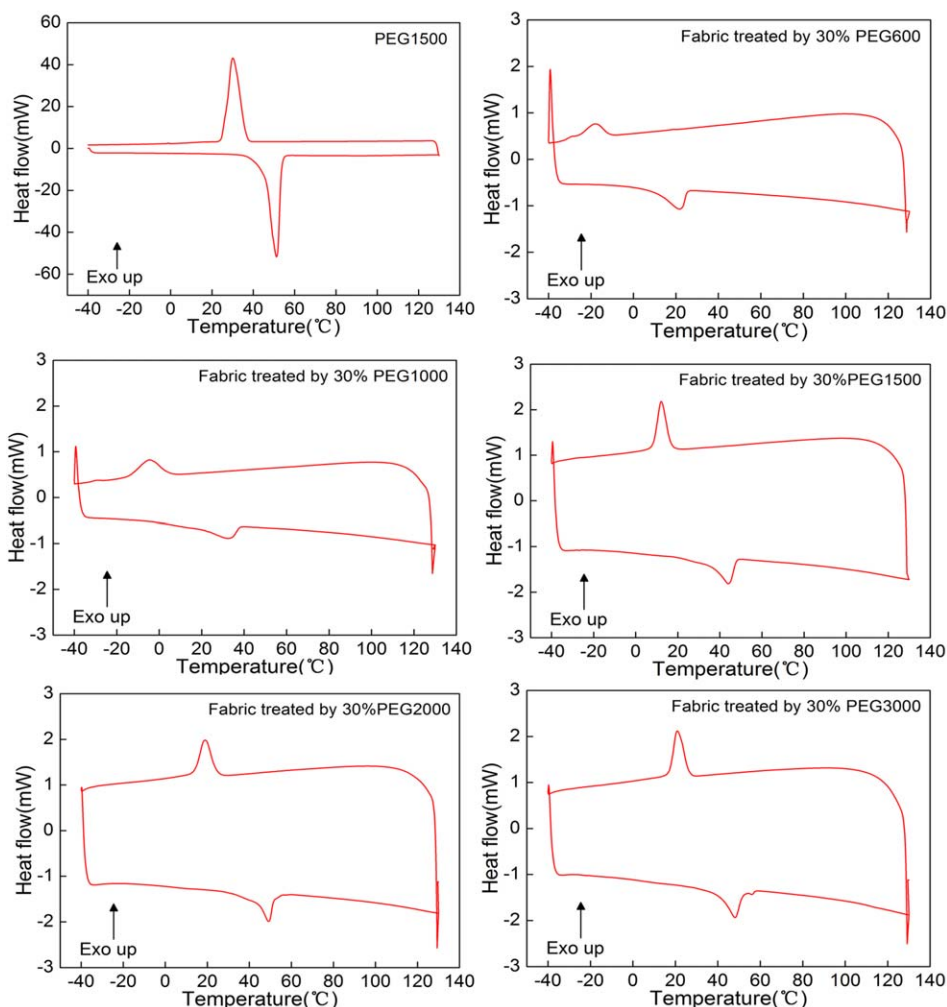
Figure 9. DSC curves of the pure PEG1500 and fabrics treated with PEG in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

behavior of cellulose chains caused by the mobility of the water content[30] and then decreased because of the amorphous region transferred into a much more compact architecture accompanied with the water loss.[31] The intensity of the crystalline structure also increased with the decrease in the water-soaking content because of the rearrangement of the carbon chain structure. The aforementioned results from the XRD and FTIR measurements were predicted to support the assumption.

DSC Analysis

The thermal characteristics of the pure PEG1500 and fabrics treated with PEG in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$ are presented in Figure 9 with heating and cooling between temperatures of -40 and $130\,^\circ C$ at a rate of $10\,^\circ C/min$. Table II shows the endothermic and exothermic enthalpy values of the different samples from the DSC curves. The endothermic and exothermic enthalpy values of the fabrics treated with PEG were 3.37–24.84 and 3.15–24.52 J/g, respectively; this indicated the remarkable phase-change enthalpy and heat-storage capacity.

As shown in Figure 9 and Tables II and III, the endothermic and exothermic enthalpy values of the treated fabrics were much lower than those of the pure PEG because they took the total weight of the pure PEG for analysis. The results indicate that there were no melting and crystallization peaks for the fabrics treated with 0 and 5% PEG1500 in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$.

However, according to the weight gain results and SEM images, there was no PEG deposition on the fibers. The results show an increase in the endothermic and exothermic enthalpy values of the treated fabrics because of the increase in the PEG molecular weights and concentrations; this confirmed the crosslinking structure. In addition, the transition temperature of different samples also demonstrated the change in the shrinkage and shrinkage-recovery rates, as mentioned before in the results of the wet-driven shape-memory behaviors and FTIR spectra.

The effects of the temperature on the differences in the shrinkage and shrinkage-recovery rates were examined, as shown in Tables IV and V. Table IV indicates that the shrinkage rate of

Table II. Thermal Adaptability of the Fabrics Treated with PEG1500 at Different Concentrations

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
Fabric treated with 0% PEG1500	None	0	None	0
Fabric treated with 5% PEG1500	None	0	None	0
Fabric treated with 10% PEG1500	42.8	3.37	11.9	3.15
Fabric treated with 20% PEG1500	43.1	5.68	12.0	5.45
Fabric treated with 30% PEG1500	43.9	8.94	12.2	8.81
Fabric treated with 40% PEG1500	45.3	16.60	13.8	16.30
Fabric treated with 50% PEG1500	46.5	24.84	14.3	24.52

All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. Tm: melting temperature; Tc: crystallization temperature; Hm: endothermic enthalpy; Hc: exothermic enthalpy.

Table III. Thermal Adaptability of the Pure PEG and Fabrics Treated with 30% PEG of Different Molecular Weights

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PEG600	33.1	130. 88	8.2	122.18
Fabric treated with 30% PEG600	21.5	4.81	−18.5	4.51
PEG1000	41.2	161.70	20.67	156.48
Fabric treated with 30% PEG1000	32.1	6.96	−4.82	6.83
PEG1500	49.7	171.65	31.1	169.96
Fabric treated with 30% PEG1500	43.9	8.94	12.2	8.81
PEG2000	63.0	180.08	34.7	174.46
Fabric treated with 30% PEG2000	49.1	8.62	19.1	8.60
PEG3000	60.0	179.79	36.3	167.14
Fabric treated with 30% PEG3000	48.1	9.58	21.1	9.57

All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. Tm: melting temperature; Tc: crystallization temperature; Hm: endothermic enthalpy; Hc: exothermic enthalpy.

different treated fabrics all decreased with increasing soaking temperature. The movement of water molecules was enhanced because of the increasing temperature; this probably decreased the hydrogen bonds formed between the water molecules and —C—O—C— structure of the PEG chain. This demonstrated the relationship between the shrinkage rate and the different deformability of the PEG molecular chain on the fabrics from the dry state to the wet state. Table V shows that the shrinkage-recovery rate of the different treated fabrics all increased with increasing drying temperature. The extension of the different PEG chains on the treated fabrics increased because of the increasing drying temperature with the loss of

water molecules. The fabrics treated by different PEG chains showed a significantly decreasing shrinkage rate and increasing shrinkage-recovery rate when the soaking or drying temperature was higher than the corresponding glass-transition temperature of the PEG molecules. This demonstrated the relationship between the different transition temperatures of PEG and the shrinkage and shrinkage-recovery rates.[31]

Bursting Strength and Air Permeability of the Fabrics
The bursting strength and air permeability of the untreated cotton knitted fabric and the treated cotton fabrics are demonstrated in Table VI.

Table IV. Effect of the Soaking Temperature on the Difference in the Shrinkage Rates

Sample	Soaking temperature (°C)			
	25	50	75	100
Fabric treated with 30% PEG600	8.07	7.85	7.47	7.30
Fabric treated with 30% PEG1000	11.50	10.70	10.20	10.15
Fabric treated with 30% PEG1500	12.57	11.89	11.23	11.10
Fabric treated with 30% PEG2000	9.23	8.78	8.60	8.22
Fabric treated with 30% PEG3000	8.47	8.13	7.98	7.44

All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$.

Table V. Effect of the Drying Temperature on the Difference in the Shrinkage-Recovery Rates

Sample	Drying temperature (°C)			
	25	50	75	100
Fabric treated with 30% PEG600	55.06	56.22	60.79	61.40
Fabric treated with 30% PEG1000	63.53	68.70	72.23	73.18
Fabric treated with 30% PEG1500	69.25	75.13	78.80	78.68
Fabric treated with 30% PEG2000	60.07	65.18	67.47	68.26
Fabric treated with 30% PEG3000	51.62	60.52	66.49	66.82

All treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$.

Table VI. Bursting Strength and Air Permeability of Different Fabrics

PEG molecular weight	PEG concentration (%)	Polyhydric alcohol etherified DMDHEU concentration (%)	$MgCl_2 \cdot 6H_2O$ concentration (%)	Bursting strength (N)	Air permeability (mm/s)
Untreated fabric				136.4	626.75
600	30	15	3	110.0	714.50
1000	30	15	3	108.3	678.93
1500	30	15	3	109.1	670.34
2000	30	15	3	107.4	657.70
3000	30	15	3	111.5.	660.49
1500	0	15	3	91.5	565.93
1500	5	15	3	101.7	599.96
1500	10	15	3	106.2	642.92
1500	20	15	3	108.7	689.97
1500	40	15	3	103.2	711.41
1500	50	15	3	104.8	772.63

Table VI indicates that the bursting strength of the treated cotton fabrics all decreased compared with the untreated fabric. The crosslinking treatment had a severe effect on the reduction of the bursting strength of the treated fabrics because of the constraint of sliding between fibers. This was because of the fact that polyhydric alcohol etherified DMDHEU depolymerized cellulose and increased the brittleness of the cotton fibers at high-temperature curing. In addition, the bursting strength loss was enhanced with increasing degree of crosslinking of cellulose molecules; this caused a stiffening of the cellulosic macromolecular network and fiber embrittlement.[32]

Table VI also show that the air permeability of the treated fabrics increased compared with that of the untreated fabric, expect the samples treated with no PEG1500 and 5% PEG1500. This was probably because of the result of PEG deposition on the surface of fibers; this could have helped the water molecule transfer in the fibers. The reduction in crevices on the fiber surface resulted in increased changes with respect to the ventilation. When PEG1500 was added at less than 10% in the treatment, an uneven PEG deposition on the surface of the fibers and the lower fibrous porosity caused by increased crosslinking both resulted in a decreased air permeability in the treated fabrics;[33] this was also demonstrated in the morphological structures of the fabrics, as shown in Figure 3.

The air permeability of the untreated fabric and fabrics treated by 30% PEG1500 under different water-soaking contents are demonstrated in Table VII. With decreasing water-soaking content, the air permeability of the untreated fabric increased and then decreased; this was consistent with statements in the literature.[34] The air permeability of the treated fabrics in the wet

Table VII. Air Permeability of the Fabrics Treated with 30% PEG1500 with Different Water-Soaking Contents

Sample	Water-soaking content (%)	Air permeability (mm/s)
Untreated fabric	Dry state	626.75
	30 ± 5	679.54
	60 ± 5	701.66
	100 ± 5	612.22
Treated fabric	Dry state	670.34
	30 ± 5	603.67
	60 ± 5	611.41
	100 ± 5	582.16

All of the treatments were performed in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$.

state was decreased compared to the dry state because of the tightening of the fabric structure; this was also demonstrated in the aforementioned results from the XRD and FTIR measurements. The reversible transition of the treated fabric structure provided a possible mechanism for the wet-driven shape-memory behaviors.

CONCLUSIONS

PEG was used on the cotton knitted fabrics with polyhydric alcohol etherified DMDHEU as the crosslinker and with $MgCl_2 \cdot 6H_2O$ as the catalyst to impart the properties of wet-driven shape memory to the treated fabrics. The wet-driven shape-memory behaviors varied with the molecular weights and the amounts of PEG and reached the highest point when the fabric was treated with 30% PEG1500 in the presence of 15% polyhydric alcohol etherified DMDHEU and 3% $MgCl_2 \cdot 6H_2O$. Both the weight gains and SEM images of the treated fabrics indicated the formation of the coating layers on the fibers due to the crosslinking of cotton with PEG and crosslinker. The FTIR spectroscopy and XRD results demonstrate the crosslinking of the cotton fiber with PEG and crosslinker and also support the assumption of wet-driven shape-memory behavior. The results of DSC analysis indicate that the treated fabrics with wet-driven shape-memory behaviors also possessed phase-change enthalpy and heat-storage capacity. The bursting strength loss of the treated fabrics was enhanced with increasing degree of crosslinking of the cellulose molecules. The air permeabilities of the treated fabrics in the wet and dry states were due to the wet-driven shape-memory structural changes caused by the absorbance and removal of water molecules.

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