

# Preparation and Characterization of Poly(ethylene terephthalate) Fabrics Treated by Blends of Cellulose Nanocrystals and Polyethylene Glycol

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**ABSTRACT:** In this study, the coating based on the blends of low molecular weight polyethylene glycol (PEG) and cellulose nano-crystals (CNC) was introduced to immobilize on the surface of polyethylene terephthalate (PET) fabrics to modify the surface properties of fabrics, and to fabricate comfortable fabrics for formidable climate. Field-emission scanning electron microscope, attenuated total reflectance Fourier transform infrared spectroscopy, and differential scanning calorimetry (DSC) were employed to study the topography, superficial ingredients, and thermal activity of the finished fabrics. The observation of field-emission scanning electron microscope and attenuated total reflectance Fourier transform infrared

spectroscopy confirmed that the surface of PET fabrics was covered by CNC/PEG1000/PEG600 coating. The transition onset temperature and phase change enthalpy of PET fabrics treated with CNC/PEG1000/PEG600 were at 7.06°C and 11.41 kJ/kg, respectively. Dimensional memory measurement demonstrated that the introduction of CNC caused the deformation percent to decrease by about 41% for PET fabrics covered with CNC/PEG1000/PEG600 coating. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 373–378, 2007

**Key words:** surface property; polyethylene glycol; cellulose nano-crystals; thermal activity

## INTRODUCTION

Polyethylene terephthalate (PET) fabric is one of the most widely used polymer materials because of its excellent wash-and-wear, chemical resistance, heat stability, high tenacity, and resistance to wrinkling properties. However, the lack of polar groups, such as —COOH and —OH, on main chains of PET, as well as high crystallinity result in low surface free energy, surface inertia, high hydrophobicity, static electrification, low wettability, and poor adhesion.<sup>1</sup> A number of modifications have been carried out to overcome these disadvantages and to obtain textile materials with the desired performances, such as copolymerization, blending, plasma and irradiation treatments, coating, and so on.<sup>2–4</sup> Among these approaches, surface modification has been proved to be effective in enhancing hosts of properties of PET fabrics, and are extensively investigated.<sup>5</sup>

As one of the most promising PCM, PEG can be durable bonded to many kinds of fabrics (such as cotton, polyester, nylon, and vinylon) through a

crosslinking reaction between PEG and fibers in a pad-dry-cure process, which imparts fabrics thermal activity and adjusting-temperature function in the textile's finishing process.<sup>6</sup> PEG PCMs-containing fabrics have attracted a great deal of attentions owing to their dynamic and actively responsive thermal properties.<sup>7–10</sup> In recent years, three types of practical methods have been utilized to fabricate series PEG PCMs fabrics, including the following: Vigo and Frost impregnated hollow fibers with PEG aqueous solution;<sup>11</sup> Vigo and Frost studied fibers coated with crosslinked PEG;<sup>12</sup> Zhang et al. studied the melt spinnability of PEG mixed with ethylene-vinyl acetate and PET-PEG block copolymer.<sup>13</sup> When the environmental temperature reaches the phase change point of PEG, its physical state will change from one crystal form to another (i.e., solid–solid transition) or from solid to liquid along with the absorption of heat, and the reverse process occurs during the cooling process. PCMs fabrics absorb and emit heat while maintaining a nearly constant temperature at the transition point,<sup>14</sup> thus they can adjust temperature automatically and are suitably used as thermal-regulated material. Besides above-mentioned latent heat storage performance, PEG coating also improve surface energy, static electrification, and wettability and adhesion properties of fabrics.<sup>15</sup>

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Once physical transition or water absorbing occurs, PEG coating exhibits great deformation as a result of volume expansion and can be used as shape memory material.<sup>16</sup> In the present work, CNC bearing a great deal of reactive hydroxyl groups on the surface was used as multifunctional additive for PEG and PET crosslinking system to overcome this drawback. After curing, the CNC-containing coating has many spherical nodes, which provide efficient channels for gases and moisture.

The aim of this article is to study the influence of CNC on PET fabrics treated with PEG/CNC through FE-SEM, ATR-FTIR, DSC, and deformation testing measurements. Because phase transition temperature region of the blends of PEG1000 and PEG600 at crosslinking state covers the range interval 25–35°C at which people feel comfortable, we chose them as experimental materials.

## EXPERIMENTAL

### Materials

The PET fabric (supplied by XiangSheng Group, Zhejiang, China.) had been desized, alkali etched, and scoured before use. Chemical agents including PEG1000, PEG600, toluene-*p*-sulfonic acid, dimethyl sulfoxide (DMSO), sulfuric acid, hydrochloride acid, and dimethyldihydroxyethyleneurea (2D resin, solid content 40 wt %), purchased from GuangZhou Chemical Reagent Company, GuangDong, China. All reagents were AR grade chemicals without further treatment prior to use.

### Preparation of CNC

The short-staple cotton was pretreated before reacting with sulfuric acid and hydrochloride acid (at the *v/v* ratio of 3 : 1) catalysts using sodium hydroxide aqueous solution of 5 mol/L and DMSO as pretreated reagents at a 1 : 1 volume ratio. The reaction of short-staple cotton with catalysts was carried out at 75°C for 4 h, followed by washing using deionized water until its pH value was readjusted to 8 or even lower. The optimal aqueous solution concentration of the mixed acids is 40% (*v/v*), and the ratio of cotton to hydrolyst was determined at 0.025 g/mL.

After the pretreatment, cotton fibers and acids were proportionally mixed and put into ultrasonic instrument (NP-B-66-400 model, NewPower Ultrasonic Company, Guangzhou, China, power of 400 W, frequency of 15 kHz) at 75°C for more than 10 h. The ivory yellow suspension was obtained after the sequential processes of filtering, washing, and centrifugating. The aqueous suspension of CNC used in this experiment was 6.5 wt %, which was pretreated with ultrasonic for 30 min to untie aggregations

prior to use because CNC whiskers have great trend to aggregate to form bigger particles.<sup>17,18</sup>

### Preparation of CNC/PEG1000/PEG600 treated PET fabrics

PEG1000/PEG600/CNC ternary blends were added to alkali etched PET fabrics (aqueous solution containing 3 g/L of sodium hydroxide, at 65°C for 30 min) through pad-dry-cure process in the presence of 2D resin as a bridge and acidic catalyst. Fabric pieces were immersed in a finished bath, which contained containing 50 wt % PEG1000 and PEG600 (mole ratio of PEG1000 to PEG600 = 1 : 2), 1 wt % CNC, 8 wt % 2D resin, 1.5 wt % toluene-*p*-sulfonic acid, and 39.5 wt % deionized water as medium. After immersing-padding, the extra liquid was removed by passing the fabrics through the pad rolls with high pressure, and the wet pickup of fabrics was more than 150%. The prefabricated fabrics was then dried at 85°C for 6–7 min followed by being cured at 140°C for 3 min. Finally, the fabric pieces finished by PEG/CNC ternary blends were washed with deionized water at 70°C repeatedly for 10 min, and subsequently dried in oven at 85°C for 2 h and equilibrated to constant weight (final add-on was 79%).

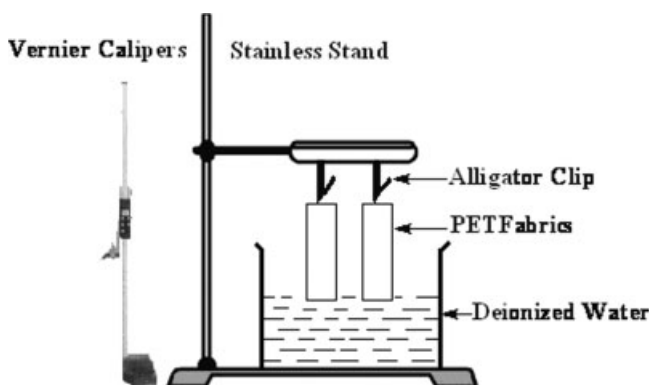
### Measurements

FTIR spectra of pristine PEG and dry CNC were taken in NICOLET-760 (Nicolet, USA) Infrared Spectrophotometer, the samples were mixed with KBr and the mixture was pressed into a pellet. ATR-FTIR spectra of neat, alkali etched, and ternary blends of CNC/PEG1000/PEG600 treated PET fabrics were obtained in a single reflection mode on a Nicolet spectrometer system with an Avatar<sup>TM</sup>OMINI-Sampler<sup>TM</sup> accessory. This device allows the analysis of a thin surface layer of the sample with a 4 μm effective path length.

The morphology of CNC particles was determined by transmission electron microscopy (FEI-Tecnaï 12, FEI, Netherlands) operated at 120 kV. PET fabrics treated with alkali and CNC/PEG1000/PEG600 ternary crosslinking system were observed by FE-SEM at an acceleration voltage of 10 kV under vacuum with a JSM-6700F (JEOL, Japan) instrument.

Thermal behaviors of neat PET fabrics, CNC, pristine PEG1000/PEG600, and alkali-treated and CNC/PEG1000/PEG600 ternary blends-treated PET fabrics were characterized on P-E differential scanning calorimetry (DSC-2C, USA). The specimen was heated from –10°C to 80°C under nitrogen atmosphere at a heating rate of 10°C/min.

The deformation of the PET fabrics covered by CNC particles-containing coating and CNC particles-



**Figure 1** System sketch for deformation measurement.

free coating when absorbing water were measured through self-made equipment. PET fabrics (1 × 16 in.) were clamped by metal alligator clips and suspended from a stainless stand vertically to horizontal plane prior to their underside wetted with deionized water, and the linear shrinkage percentage of all samples were measured using vernier calipers once they were completely wet. The system sketch for deformation measurement is shown in Figure 1.

## RESULTS AND DISCUSSION

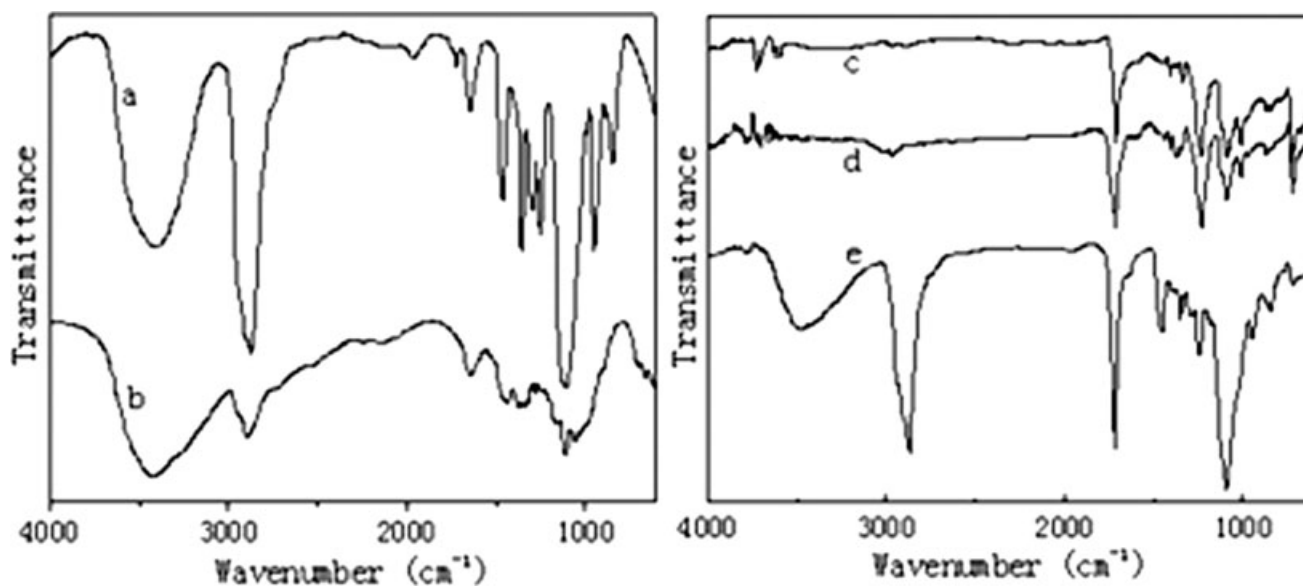
### FTIR study

Figure 2 shows FTIR spectra of pristine PEG (a) and CNC (b), ATR-FTIR spectra of neat (c), alkali etched (d), and ternary blends of CNC/PEG1000/PEG600 (e) treated PET fabrics. Except for the difference in absorption band at 2874  $\text{cm}^{-1}$  attributed to  $-\text{CH}_2-$

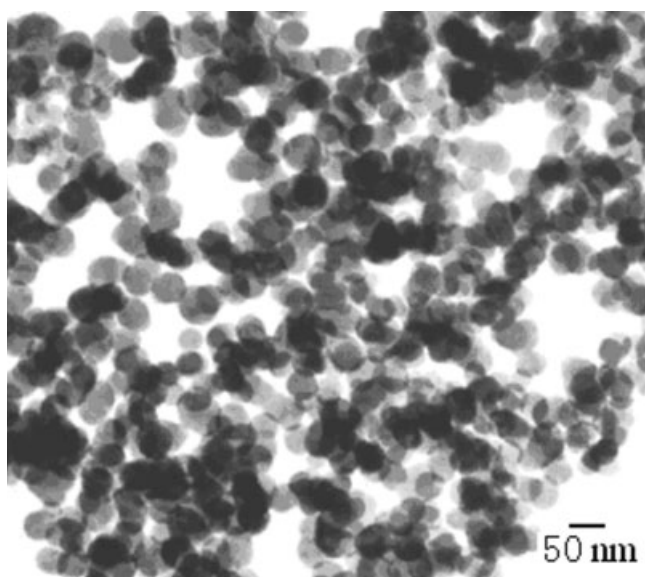
groups, spectra of PET fabrics changed slightly before (c) and after (d) alkali etching. There were pronounced differences between the spectra of PET fabrics treated with alkali (d) and ternary blends of CNC/PEG1000/PEG600 (e) in the range of 600–4000  $\text{cm}^{-1}$ . Compared with alkali etched PET fabric, several new absorption peaks that belonged to CNC and pristine PEG [Fig. 2(a,b)], were obviously observed in Figure 2(e), in which the peak at 1180  $\text{cm}^{-1}$  was attributed to ether bonds existing in CNC and PEG, and the peak at 3345  $\text{cm}^{-1}$  was assigned to the association effect of unreactive  $-\text{OH}$  groups in CNC. In addition, the intensity of the absorption peak at 2874  $\text{cm}^{-1}$  attributed to the stretching vibration of  $-\text{CH}_2-$  groups increased greatly. All these changes verified that CNC and PEG were immobilized on the surface of PET fabrics. As a result of shield produced by the network coating based on crosslink reaction of ternary blends of CNC/PEG1000/PEG600 and the superficial moiety of PET fabric, and the intensity of characteristic peaks of benzene rings absorption band from 650 to 900  $\text{cm}^{-1}$  and ester  $-\text{C}-\text{O}-$  at 1242  $\text{cm}^{-1}$  belonging to PET substrate decreased dramatically, whereas that of carbonyl bond absorption peak at 1717  $\text{cm}^{-1}$  and  $-\text{C}-\text{O}-$  absorption peak at 1096  $\text{cm}^{-1}$  increased greatly.

### Morphological study of CNC and treated fabrics

TEM image, as shown in Figure 3, verified that the dimension of spherical CNC particles available in this work was in the range of 30–50 nm. The number



**Figure 2** FTIR spectra of pristine PEG (a) and CNC (b), ATR-FTIR spectra of neat (c), alkali etched (d) and ternary blends of CNC/PEG1000/PEG600 (e) treated PET fabrics.



**Figure 3** TEM photo of CNC.

average molecular weight of CNC particles was about 5000.

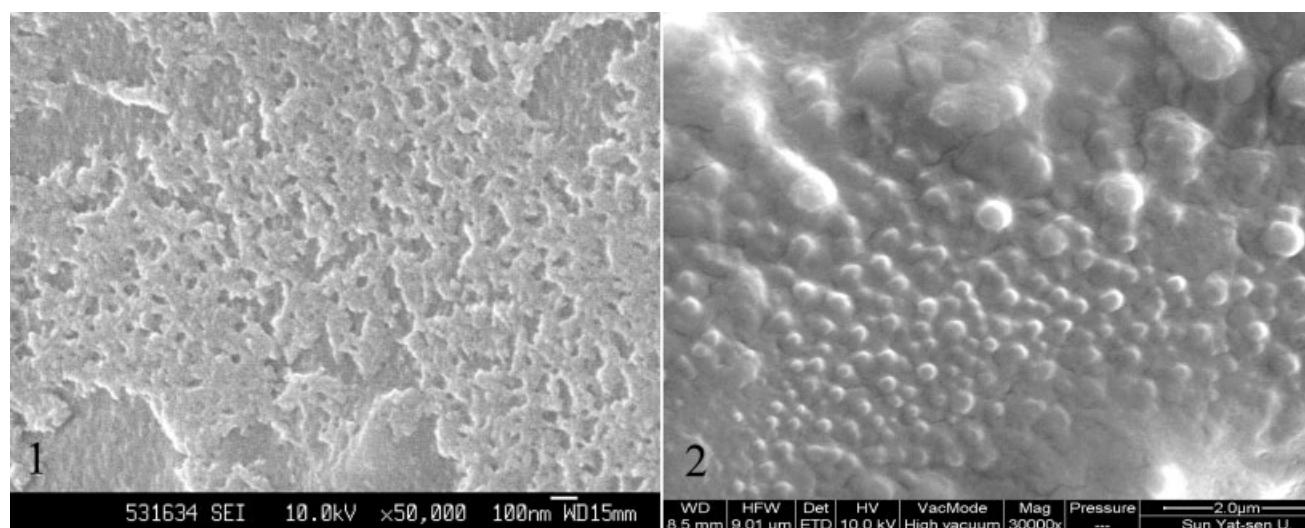
Figure 4 showed FE-SEM photos of surface morphology of PET fabrics treated by alkali etching (1) and ternary blends of CNC, PEG1000, and PEG600 (2), respectively. Alkali etched PET fiber (1) had many pores on its surface, which resulted from the hydrolysis of surface amorphous region of the substrate. Seen from Figure 4(2), spherical and aggregated CNC particles were observed to be randomly immobilized on the surface of PET fabrics, which were covered with the coating based on the crosslink reaction of CNC, PEG1000, and PEG600, and the coating leveled the pores at the surface of PET fab-

rics. After curing, as shown in Figure 4(2), the CNC-containing coating had many spherical nodes that consequentially provided efficient channels for gases and moisture. Compared with virgin CNC particles, the dimension of CNC particles involved in cross-linking coating increased greatly, which was over the range of several hundred nanometers (average diameter was about 220 nm). This might be explained by the fact that CNC particles aggregated and/or CNC particles were covered with continuous PEG wall.

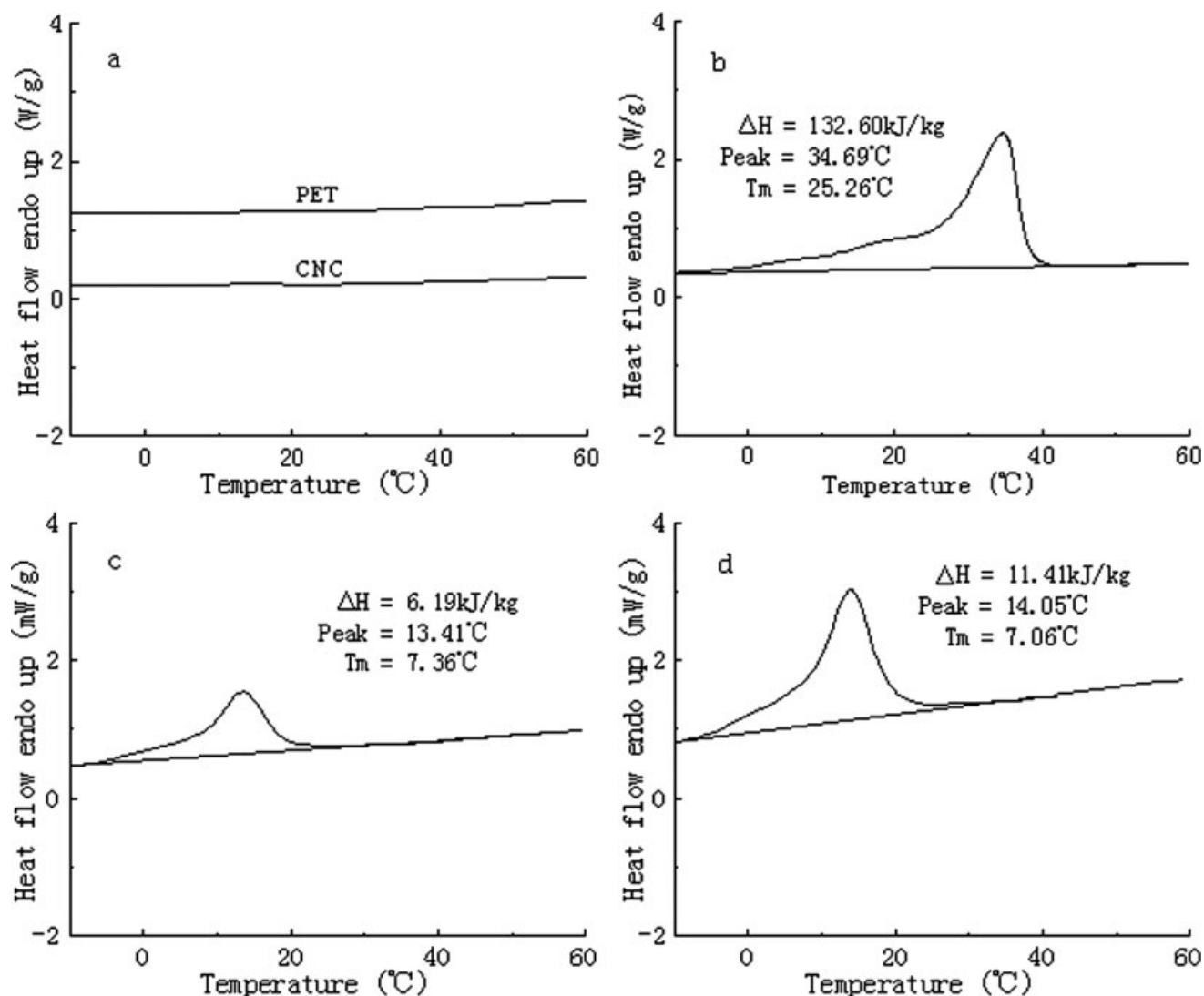
### Thermal properties

All samples were treated to 100°C and kept for 10 min to remove thermal memory prior to DSC measurement. The phase change temperature of samples corresponding to the onset temperature could be obtained by drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating the baseline on the same side as the leading edge of the peak, and the latent heat of transition was evaluated by integration of the peak.

No endothermic and/or exothermic peaks over testing range was observed for neat PET and CNC [as shown in Fig. 5(a)]. Compared with the curve of PET fabrics treated with binary blends of PEG1000/PEG600 [Fig. 5(c)], the temperature range at which phase change occurs for the PET fabrics treated with ternary blends of CNC/PEG1000/PEG600 [Fig. 5(d)] became wider, from -6 to 35°C. One possible reason was that PEG molecules were separated by CNC particles through a condensation using 2D resin as bridge, which caused partly crosslinked PEG1000 and PEG600 to exhibit ther-



**Figure 4** FE-SEM photos of surface morphologies of alkali etched (1) and ternary blends of CNC/PEG1000/PEG600 treated (2) PET fabrics.



**Figure 5** DSC curves of neat PET fabrics and dry CNC (a), pristine PEG1000/PEG600 (b), and PEG1000/PEG600 treated (c) and CNC/PEG1000/PEG600 ternary blends treated (d) PET fabrics.

mal behaviors independently. CNC particles bearing a great deal of reactive hydroxyl groups served as reactive reagent for PEG1000/PEG600 and PET fabrics crosslinking system, consequently impelled crosslinking reaction and made reaction become facile and complete.

In comparison with pristine PEG [Fig. 5(b)], phase change onset of both PEG1000/PEG600 and CNC/PEG1000/PEG600 treated PET fabrics shifted to lower temperature. The  $\text{CH}_2\text{CH}_2\text{O}$  segments near crosslinking sites were confined after the active hydroxyl end-groups of PEG consumed, and consequently the arrangement and orientation of PEG molecules were partially suppressed whereas the resulting crystalline regions turned smaller, which caused the transition point to fall down to a certain extent. Phase change enthalpy of CNC/PEG1000/PEG600 treated PET fabrics was largely higher than

that of PEG1000/PEG600 treated fabrics, reaching 11.41 kJ/kg. A reasonable explanation might be attributed to the fact that the add-on of CNC/PEG1000/PEG600 composite coating was bigger than that of PEG1000/PEG600 (less than 50%) at the same PEG concentration and in identical curing process. CNC particles with a number of hydroxyl groups brought about the increase of synergistic interaction, which improved systematic affinity of ternary blends to fabrics substrate whose surface held many hydroxyl and carboxyl groups created by alkali treatment. Though condensation between 2D molecules hardly happened,<sup>19</sup> the reaction among phase change main bodies i.e., PEG1000 and PEG600, and 2D resin became complicated and facile for the introduction of CNC particles which served as host node in crosslinking system. Two-end anchored and one-end linked PEG molecules coexisted in

the resulting coating, which might be another reason for wider phase change temperature range.

### Dimensional memory study

When absorbing deionized water completely, the deformation percent of the PET fabrics covered with coating containing CNC particles and CNC particles-free coating equaled to 6.5 and 11%, respectively, in other words, the presence of CNC caused the deformation to decrease by about 41%, so it could be concluded that the former exhibited better shape-stability than the latter. This result demonstrated that CNC particles served as not only multifunctional reactant but also reinforcing filler that made easier the formation of crosslinking network and therefore improved the shape-stability of PET fabrics.

### CONCLUSIONS

CNC aqueous suspension was prepared by hydrolyzing small squares cotton filter paper with the blends of sulfuric acid and hydrochloric acid through sequential processes of filtering, washing, and centrifugating. The dimension of spherical CNC particles was in the range of 30–50 nm. The introduction of CNC particles bearing a great number of reactive hydroxyl groups into PEG1000/PEG600 and PET fabrics crosslinking system via pad-dry-cure process brought about the increase of hydrogen bond and synergistic interaction, thus promoted their systematic affinity to fabrics substrate. CNC particles acting as reinforcing filler and reactive rea-

gent could impel crosslinking reaction, and make phase change temperature range become wider and phase change enthalpy become higher. In addition, the presence of CNC lift shape-stability of PET fabrics covered by PEG coating, and the deformation after absorbing water declined from 11% for the PET fabrics covered by CNC-free coating to 6.5% for the PET fabrics with CNC-containing coating. As a whole, the CNC was an efficient additive for PEG crosslinking coating to modify PET fabrics.

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