

## Preparation and Characterization of a Temperature-Sensitive Nonwoven Poly(propylene) with Increased Affinity for Guest Molecules

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**ABSTRACT:** A temperature-sensitive hydrogel with the capability of inclusion complex formation with guest molecules was successfully grafted onto the surface of nonwoven polypropylene (nonwoven PP). This was carried out by the use of *N*-isopropylacrylamide monomer and a modified cyclodextrin (acrylamidomethyl- $\beta$ -cyclodextrin ( $\beta$ -CD-NMA)). Fourier-transform infra red (FT-IR) and elemental analyses confirmed the presence of poly(*N*-isopropylacrylamide) (PNIPAAm) and  $\beta$ -CD-NMA components on the surface of the textile. Equilibrium swelling ratio measurements showed that the grafted hydrogel maintained its temperature-sensitive property compared to a nongrafted hydrogel. The effect of  $\beta$ -CD-NMA and crosslink agent concentrations on the grafting yield was studied. The  $\beta$ -CD-NMA content into the PNIPAAm- $\beta$ -CD-NMA grafted nonwoven PP (PNIPAAm- $\beta$ -CD-NMA-PP) was estimated by FT-IR through a new procedure. The estimated amounts of  $\beta$ -CD-NMA in PNIPAAm- $\beta$ -CD-NMA-PP were determined to be 0.9, 1.9 mg g<sup>-1</sup> for 0.019M and 0.049M concentrations of  $\beta$ -CD-NMA in monomer solution, respectively. The PNIPAAm- $\beta$ -CD-NMA-PP showed a remarkable increase in absorbance affinity of 8-anilino-1-naphthalenesulfonic acid ammonium salt at 20°C from 0.93 to 3.33  $\mu$ mol g<sup>-1</sup> compared to PNIPAAm-PP. Furthermore, the results showed a temperature-sensitive loading affinity for PNIPAAm- $\beta$ -CD-NMA-PP in absorbance of guest molecules due to the presence of  $\beta$ -CD-NMA. The use of hydrophobic guest molecules such as fragrance oils and antibiotics in modified fabrics can provide new applications in textile and pharmaceutical industry. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40497.

**KEYWORDS:** grafting; polyolefins; stimuli-sensitive polymers; textiles; swelling

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### INTRODUCTION

During the last decades, smart functional textiles have been developing rapidly.<sup>1,2</sup> Smart or intelligent textiles comprise a highly diverse group of materials with a wealth of functions. Prominent examples include, wound dressing products,<sup>3</sup> deodorant fabrics,<sup>4</sup> photochromic textiles,<sup>5</sup> and selective permeability for heat or moisture management.<sup>6</sup> To introduce multiple functionalities into smart textiles, combinations of different functionalities may be considered. The combination of the thermo sensitivity of poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels with the controlled release properties of cyclodextrins (CDs) may be an interesting route toward thermo-sensitive textiles with a high loading/release capacity toward functional molecules.

Temperature sensitive polymers that become insoluble below or above a particular temperature, lower or upper critical solution temperature (LCST), respectively, are often referred to as intelligent hydrogels.<sup>7-9</sup> PNIPAAm hydrogels are thermo-sensitive smart gels that can be used in separation systems<sup>10</sup> and in drug delivery<sup>11,12</sup> because of their LCST in the physiological temperature

range. Unmodified PNIPAAm hydrogels are swollen and deswollen below and above 32°C, respectively. However, PNIPAAm has some disadvantages such as weak mechanical strength, slow response rate, and low loading capacity toward hydrophobic molecules such as drugs, fragrances, and other functional molecules, which limit their applications.<sup>13</sup>

CDs are a family of cyclic oligosaccharides derived from starch. Among these, only  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs and a range of their chemical derivatives are commercially available.<sup>14,15</sup> CDs possess a relatively hydrophobic cavity and a hydrophilic outer shell. This structure results in a remarkable general ability of CDs to form inclusion complexes with hydrophobic guest molecules and enables applications in drug delivery systems, controlled release of fragrances, and antibacterial compounds for textile applications.<sup>16-22</sup> One study has further indicated that CDs improve some properties of the formed hydrogels such as their low response rate.<sup>23,24</sup> In addition, the combinations of PNIPAAm and modified CDs result in novel multifunctional hydrogels with new application potentials such as enhanced loading of selected active compounds, controlled and sustained release

capabilities, which can be used in new drug delivery systems and pharmaceuticals.<sup>25–31</sup> Furthermore, studies have indicated that a temperature controlled molecular recognition function with potential applications in separation systems can be achieved when a molecular recognition host (CD) and a stimuli-responsive polymer (PNIPAAm) are integrated into the same material.<sup>32–34</sup> Although many studies have been carried out for grafting temperature sensitive hydrogel based on PNIPAAm into fabrics surface,<sup>35–38</sup> the amount of work published on the preparation a temperature-sensitive fabric by graft polymerization of PNIPAAm and CDs into fabric surface for textile applications is very limited. Thermo-responsive membranes based on PNIPAAm and CDs have been prepared for chemical valves, separation purposes, sensors<sup>32,39</sup> as well as drug delivery applications.<sup>40</sup> In our last study, we successfully grafted PNIPAAm and unmodified  $\beta$ -CD onto the surface of nonwoven poly(propylene) (PP) materials showing the presence of  $\beta$ -CD in samples after grafting and washing.<sup>41</sup> In this study, we prepared a temperature-sensitive fabric by graft polymerization of PNIPAAm and functionalized  $\beta$ -CD aiming at the construction of a fabric with a high temperature-sensitive affinity for guest molecules. This modified textile could be used as a temperature-sensitive fragrant textile with high durability due to the combination of high load and release capacity and temperature sensitivity.

## EXPERIMENTAL

### Materials

*N*-isopropylacrylamide (NIPAAm, Aldrich Chemical Co., NS), was purified by recrystallization from *n*-hexane.  $\beta$ -CD was provided by Wacker Chemie (Burghausen, Germany). Formic acid 85%, *N*-(hydroxymethyl)acrylamide (NMA) solution, 48 wt % in H<sub>2</sub>O, *N,N'*-methylene-bis-acrylamide (NMBA), ammonium persulfate (APS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), 8-anilino-1-naphthalenesulfonic acid ammonium salt (ANS) were purchased from Sigma Aldrich (Steinheim, Germany) and were used as received. Corona-treated nonwoven PP was supplied by Fibertex A/S, (Aalborg, Denmark). In all studies, corona-treated nonwoven PP with a thickness of 0.14 mm and weight of 40 g m<sup>-2</sup> was used.

### Synthesis of Acrylamidomethyl $\beta$ -cyclodextrin

Acrylamidomethyl  $\beta$ -cyclodextrin ( $\beta$ -CD-NMA) was synthesized according to literature.<sup>42</sup> In short,  $\beta$ -CD (68.5 g, 60 mmol) and NMA solution (53.4 g, 253 mmol) were added to 500 mL of 1% formic acid solution. The reaction was performed at 80°C for 30 min. The product was precipitated in 5 L of acetone and the mixture was stored at 5°C to allow complete precipitation of the product. The product was filtered, washed several times with acetone and dried at 40°C *in vacuo* overnight. The crude product (50.1 g) contained 20%  $\beta$ -CD-NMA and 80% unmodified  $\beta$ -CD based on <sup>1</sup>H-NMR analysis and was used directly without further purification.

### Modification of Fabric Surface by Graft Polymerization

Corona treatment of the nonwoven PP was carried out by a corona discharge generator Model HV3020 (Tantec A/S, Lunderskov, Denmark) at Fibertex A/S, Aalborg, Denmark. Corona

treatment was carried out with an energy density of 10 kJ m<sup>-2</sup> for the modification of nonwoven PP.

Graft polymerization on the corona-treated nonwoven PP was conducted in five replicates for both PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP according to a previously published method.<sup>31</sup> Samples were cut into circles (9 cm diameter). About 110 mL aqueous solution of NIPAAm (0.798M),  $\beta$ -CD-NMA (0.018 and 0.049M, the content of native  $\beta$ -CD taken into account), and NMBA (8 mM) were prepared and stirred for 8 h to allow the chemicals to dissolve and to mix completely. Thereafter, APS (13.67 mM) and TEMED (30  $\mu$ L) were added to initiate free radical polymerization, and, finally, the corona-treated nonwoven PP was swiftly transferred to this solution. The process was repeated for the preparation of PNIPAAm-PP, which was made without  $\beta$ -CD-NMA. The mixtures were allowed to react for 24 h at room temperature. Thereafter, during a period of 1 week the samples were rinsed daily by several portions of distilled water in order to remove unreacted homopolymers and nonattached material. The grafting yield of nonwovens was determined through the gravimetric method by using (1):

$$\text{GY (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where GY is the grafting yield,  $W_g$  and  $W_0$  are the mass weights of the grafted and initial samples, respectively.

### Water Uptake

To assess the temperature response of the samples, their water uptake (WU) behavior was studied. Five samples of PNIPAAm-PP and five samples of PNIPAAm-CD-NMA-PP were soaked in a temperature-controlled water bath at different temperatures (25, 30, 32, 40, 45, and 50°C). After 4 h of soaking, the samples were removed from the water bath and gently blotted with filter paper to remove surface water, followed by immediate weighing. WU% was calculated by using (2):

$$\text{WU \%} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where  $W_d$  and  $W_s$  are the weights of dried and swollen samples after graft polymerization, respectively. Finally, an average WU was constructed from the WU data of the five samples.

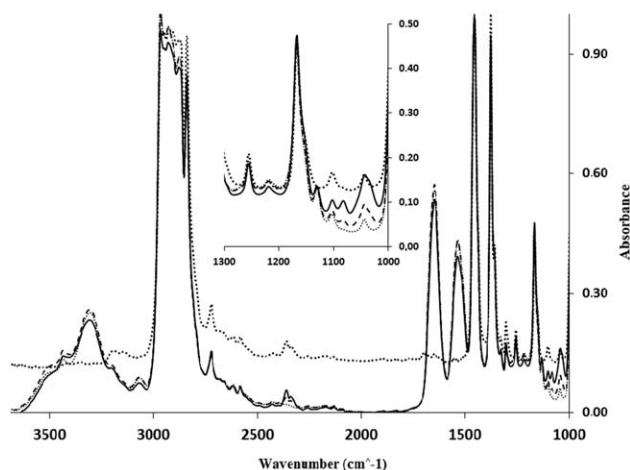
### Influence of NMBA and $\beta$ -CD-NMA Concentration on the Grafting Yield

The effect of NMBA and  $\beta$ -CD-NMA concentrations on grafting yield was examined using different concentrations of NMBA and  $\beta$ -CD-NMA in the polymerization solution.

### Instrumental Analyses

The grafted nonwoven PP surfaces were characterized by Fourier-transform Infrared (FT-IR) (Varian 610-IR). FT-IR examinations were measured on a spatial holder in ten spots of each sample of PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP. Thereafter, an average FT-IR spectrum was constructed from the FT-IR data of the 10 spots. Surface morphologies of the samples were examined by scanning electron microscopy (SEM, Philips-XLC, Mulgrave Victoria, Australia) after coating with gold using SEM coating equipment.

The grafting yield was calculated by gravimetric method and by the use of elemental analysis instrument (Perkin Elmer 2400



**Figure 1.** FT-IR spectra for corona-treated nonwoven PP (...), PNIPAAm-PP (...), and PNIPAAm- $\beta$ -CD-NMA-PP (broken line and solid line) for 0.019 and 0.049 *M* concentrations of  $\beta$ -CD-NMA in monomer solution).

series II, CHNS Analyzer, Okehampton, UK) as well. We used a Cary Eclipse Fluorescence Spectrophotometer (Varian, Australia) to confirm the presence of  $\beta$ -CD in hydrogel grafted on the surface of nonwoven PP and the determination of temperature sensitive capacity of samples by the changes in the fluorescence intensity of ANS. The content of  $\beta$ -CD in PNIPAAm- $\beta$ -CD-NMA-PP was determined by the use of FT-IR analysis.

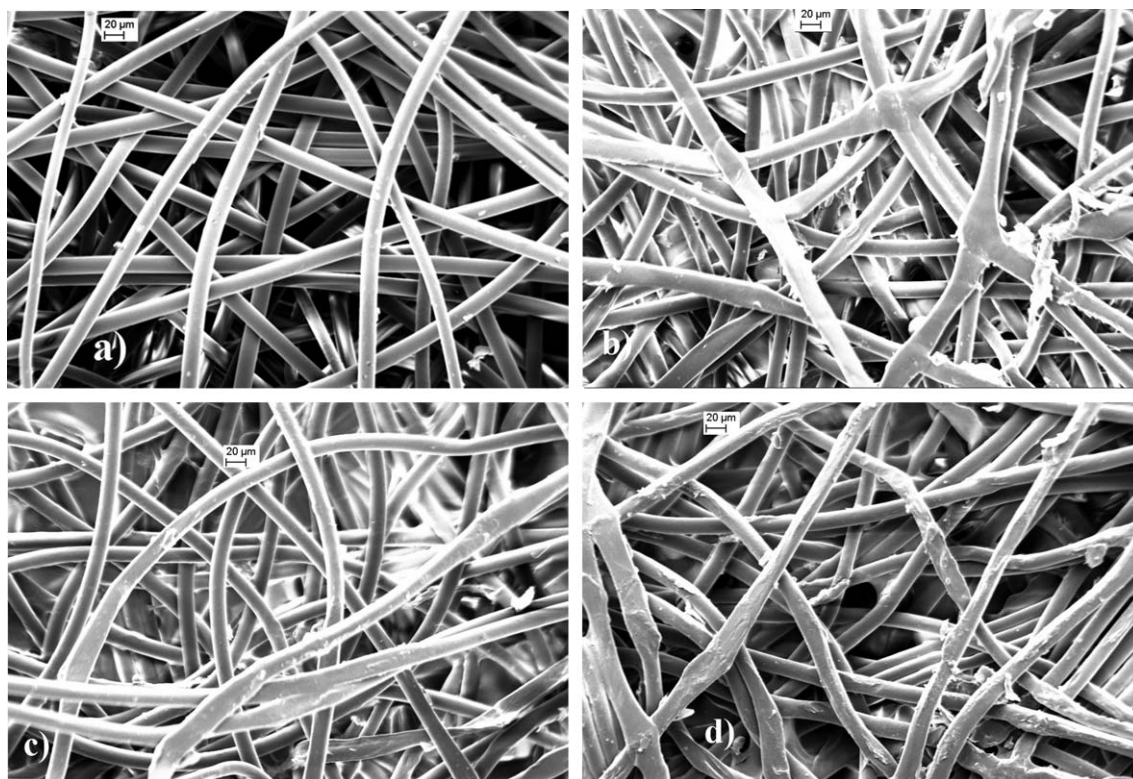
#### Investigation of the Effect of Temperature on Loading Affinity.

To investigate the effect of temperature on the loading affinity

of modified fabrics, PNIPAAm- $\beta$ -CD-NMA-PP and PNIPAAm-PP were separately immersed in ANS solution (1 *mM*) as a guest molecule at 20°C and 45°C for 24 h. Thereafter, the samples were gently blotted with filter paper to remove surface ANS and were placed at a 45° angle on the incident light path of Fluorescence Spectrophotometer. Then, fluorescence intensity was measured in three different spots of each sample with an excitation wavelength of 350 nm, and the emission rate was measured in the range of 400–600 nm. The experiment was replicated five times and an average fluorescence intensity spectrum was constructed from the fluorescence intensity data. A fluorescence calibration curve was made to calculate the ANS content in the prepared samples. A sample of PNIPAAm- $\beta$ -CD-NMA-PP with a weight of 0.035 g was consecutively added by 200  $\mu$ L of the ANS solution (1 *mM*) so that a higher amount of ANS was dispensed on the sample surface with each incremental addition. Fluorescence intensity was measured for PNIPAAm- $\beta$ -CD-NMA-PP added with different concentrations of ANS.

#### Calculation of $\beta$ -CD-NMA Content by FT-IR Spectroscopy.

To make a FT-IR calibration curve for the calculation of  $\beta$ -CD content in PNIPAAm- $\beta$ -CD-NMA-PP, 200  $\mu$ L of the  $\beta$ -CD-NMA solution (1.4  $\mu$ M L<sup>-1</sup>) was consecutively added to the surface of a sample of PNIPAAm-PP with a diameter of 2.5 cm and with a weight of 0.035 g so that a higher amount of  $\beta$ -CD-NMA (0.0, 0.208, 0.416, 0.624, 0.832, 1.08, 1.25, 1.87, 2.5, 3.12, 3.74, 4.37% wt/wt) was dispensed on the sample surface each time. FT-IR analysis was measured on ten independent spots distributed across the dried sample and after each incremental



**Figure 2.** SEM images for (a) corona-treated nonwoven PP, (b) PNIPAAm-PP, (c) PNIPAAm- $\beta$ -CD-NMA-PP ( $\beta$ -CD-NMA = 0.019*M*), (d) PNIPAAm- $\beta$ -CD-NMA-PP ( $\beta$ -CD-NMA = 0.049*M*). Magnification =  $\times 200$ .



**Table I.** Grafting Yield Calculated by Elemental Analysis and Gravimetric Method

Samples	Elemental analysis (wt %)				Grafting percentage (wt %)	
	$\beta$ -CD-NAM (M)	C	H	N	Elemental analysis	Gravimetric method
Corona-treated nonwoven PP		85.75	13.34			
PNIPAAm-PP		80.01	11.07	2.17	17.53	19.4
PNIPAAm-CD-NMA-PP	0.019	79.48	11.28	2.373	19.22	22.14
PNIPAAm-CD-NMA-PP	0.049	78.92	10.50	2.606	21.05	22.64

addition of  $\beta$ -CD-NMA. Thereafter, an average FT-IR spectrum was constructed from the FT-IR data of the 10 spots. The  $\beta$ -CD-NMA content in PNIPAAm- $\beta$ -CD-NMA-PP was calculated by the use of the obtained calibration curve.

## RESULTS AND DISCUSSION

### FT-IR Results

FT-IR analysis was carried out to prove the presence of PNIPAAm and  $\beta$ -CD-NMA in PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP (Figure 1). Several peaks at 1648, 1521, and 3400  $\text{cm}^{-1}$  can be attributed to the characteristic peaks of C=O stretching, N-H deformation (amide I, amide II), and -NH stretching in NIPAAm polymer, respectively. The presence of  $\beta$ -CD-NMA becomes evident in the synthesized hydrogel on the surface of nonwoven PP by a new peak at 1082  $\text{cm}^{-1}$  and by an increase in the absorption band at 1041  $\text{cm}^{-1}$  in the FT-IR spectra of PNIPAAm- $\beta$ -CD-NMA-PP (Figure 1) which can be assigned to characteristic stretching vibrations of the C-O-C and C-OH of  $\beta$ -CD, respectively.<sup>28</sup> As it can be seen, the absorption bands around 1041 and 1082  $\text{cm}^{-1}$  increase with an increase of the  $\beta$ -CD-NMA concentration in the hydrogel.

### Morphological Analysis by SEM

The morphology of nonwoven PP before and after grafting with PNIPAAm and PNIPAAm- $\beta$ -CD-NMA was observed by SEM [Figure 2(a-d)]. The distance between nonwoven PP fibres is clearly seen in Figure 2(a). The grafting layers of PNIPAAm and PNIPAAm- $\beta$ -CD-NMA can be seen on the surface of fibres and between the pores of nonwoven PP in Figure 2(b-d). However, no morphological differences could be recognized by SEM analysis for the samples grafted with PNIPAAm and PNIPAAm- $\beta$ -CD-NMA, respectively.

### Calculation of Grafting Yield by Gravimetric Method and Elemental Analysis

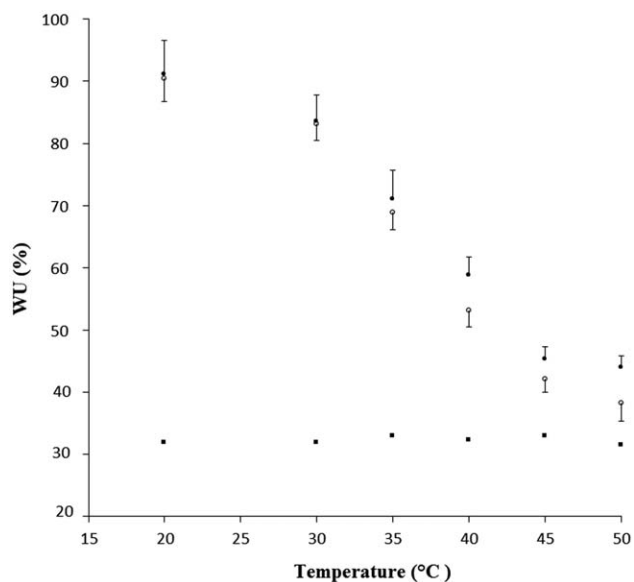
For the evaluation of the accuracy of estimated grafting yield by gravimetric method for PNIPAAm-PP and PNIPAAm- $\beta$ -CD-PP, grafting yield was estimated by the content of C, N, and H measured by elemental analysis as well (Table I). Elemental analysis results confirmed the presence of C and H in corona-treated nonwoven PP and C, H, N in the PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP, respectively. For the calculation of grafting yield in PNIPAAm- $\beta$ -CD-NMA-PP by elemental analysis, it was supposed that the content of determined N belonged to PNIPAAm grafted onto the nonwoven surface and the N amount originating from grafted  $\beta$ -CD-NMA was ignored in the calculations. The lower weight percentage of nitrogen in  $\beta$ -CD-NMA ( $14.007/1217.4 \times 100 = 1.15\%$ ) compared to that of

PNIPAAm ( $14.007/113.16 \times 100 = 12.38\%$ ) and the higher grafting yield of PNIPAAm compared to that of  $\beta$ -CD-NMA into the nonwoven PP surface were the reasons for this assumption. The results of elemental analysis and gravimetric confirmed that the grafting yield increased with the increasing of CD-NMA concentration in the monomer solution (Table I).

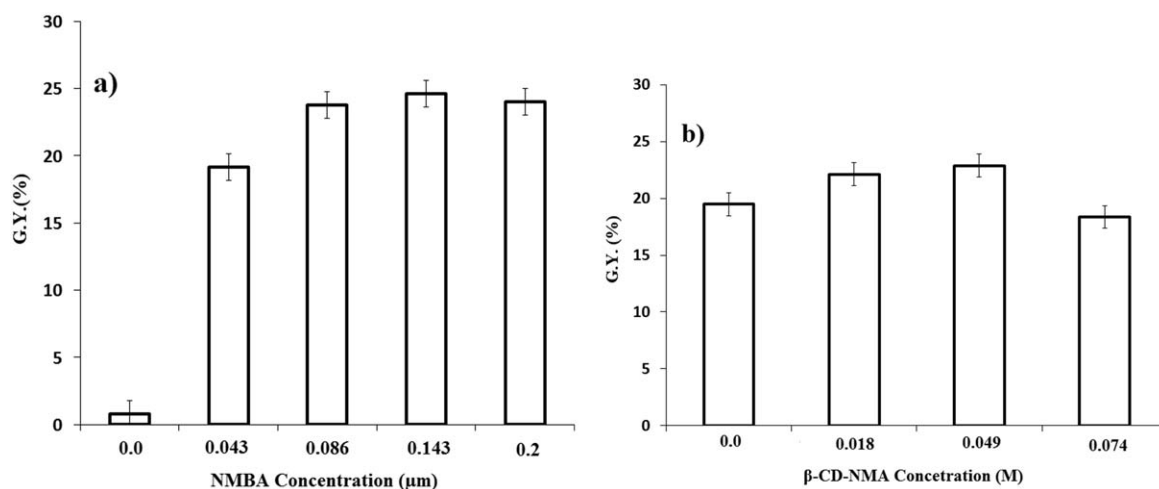
### Water Uptake

Figure 3 depicts WU% of corona-treated nonwoven PP, PNIPAAm-PP, and PNIPAAm- $\beta$ -CD-NMA-PP. As expected, no change in WU% was observed for corona-treated nonwoven PP. However, for PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP, WU% decreased with increasing temperature. This indicates that PNIPAAm-PP as well as PNIPAAm- $\beta$ -CD-NMA-PP still possesses the intrinsic properties of PNIPAAm. In other words, both of them are temperature sensitive.

PNIPAAm- $\beta$ -CD-NMA-PP exhibited thermo-sensitive response similar to PNIPAAm-PP with almost identical LCST. Both of these hydrogels are swollen below their LCST and shrunken above their LCST. However, the WU% of PNIPAAm- $\beta$ -CD-NMA-PP is higher than that of PNIPAAm-PP at the temperatures above the LCST. For instance, WU% at 50°C is 44% and 38% for PNIPAAm- $\beta$ -CD-NMA-PP and PNIPAAm-PP, respectively. It may be attributed to the presence of the  $\beta$ -CD-NMA



**Figure 3.** WU for corona-treatment nonwoven PP (solid square), PNIPAAm-PP (solid circle) and PNIPAAm- $\beta$ -CD-NMA-PP (hollow circle).



**Figure 4.** The effect of the concentration variation of a) NMBA, (NIPAAm = 0.79M and  $\beta$ -CD-NMA = 0.049M) and (b)  $\beta$ -CD-NMA (NMBA = 0.086  $\mu\text{M}$  and NIPAAm = 0.79M).

component which can effectively prevent the PNIPAAm component from forming a more compact structure.<sup>28</sup>

#### Reproducibility of the Coating Process

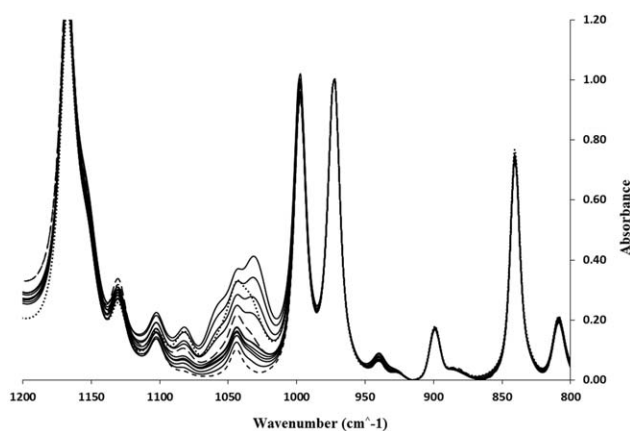
The modification of nonwoven PP was repeated five times to investigate the reproducibility of the graft polymerization onto the surface of the textile. The results indicated that grafting process is reproducible with a slight variation in yields. The average grafting yield and relative standard deviation for five samples grafted with PNIPAAm and PNIPAAm- $\beta$ -CD-NMA-PP were  $21.92 \pm 3.2\%$  and  $21.72 \pm 2.9\%$ , respectively.

#### Effect of NMBA and $\beta$ -CD-NMA Concentration on the Grafting Yield

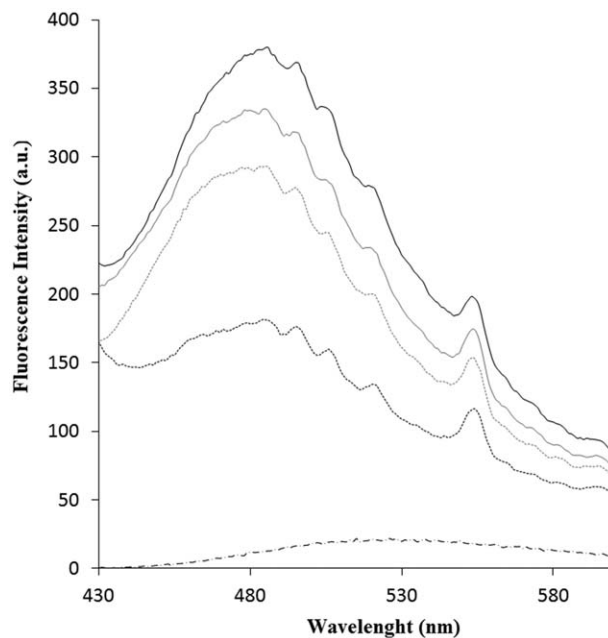
The effect of the concentration variation of crosslinking agent (NMBA) on the grafting yield showed that the grafting yield increased significantly as the concentration of crosslinking agent increased to 0.143  $\mu\text{M}$ . However, there was no noticeable effect on grafting yield at higher concentrations of the crosslinking agent. Besides, graft polymerization onto the surface of

the fabrics is not noticeable in the absence of crosslinking agent [Figure 4(a)]. This is corroborated by Chen and coworkers who showed that graft polymerisation of PNIPAAm onto the surface of fabrics did not occur in the absence of a crosslinker and in low concentrations of NIPAAm in the monomer solution.<sup>31</sup>

The results for the effect of concentration changes of  $\beta$ -CD-NMA on the grafting yield indicated that with increasing  $\beta$ -CD-NMA concentration in the monomer solution the grafting yield increased slightly and then decreased nearly to the grafting yield in the absence of  $\beta$ -CD-NMA [Figure 4(b)].



**Figure 5.** FT-IR spectra for corona-treated nonwoven PP (---), PNIPAAm-PP added with different concentrations of  $\beta$ -CD-NMA (solid lines) and PNIPAAm- $\beta$ -CD-NMA-PP ( $\beta$ -CD-NMA = 0.019M (—) and 0.049M (···)).



**Figure 6.** The fluorescence intensity of free ANS solution, 1 mM (---), ANS molecules for PNIPAAm-PP (black dotted line) and PNIPAAm- $\beta$ -CD-NMA-PP (black solid line) at 20°C, for PNIPAAm-PP (gray dotted line) and PNIPAAm- $\beta$ -CD-NMA-PP (gray solid line) at 40°C.

**Table II.** ANS Content in PNIPAAm-PP and PNIPAAm-CD-NMA-PP Measured by Fluorescence Spectroscopy at 20 and 40°C

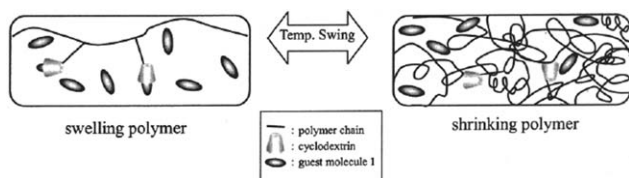
	20°C		40°C	
	PNIPAAm-PP	PNIPAAm-CD-NMA-PP	PNIPAAm-PP	PNIPAAm-CD-NMA-PP
Fluorescence intensity (a.u.)	181.44	379.78	293.10	334.9
ANS content ( $\mu\text{mol g}^{-1}$ )	0.93	3.33	2.28	2.79

### Calculation of $\beta$ -CD-NMA Content in PNIPAAm- $\beta$ -CD-NMA-PP by FT-IR Spectroscopy

The  $\beta$ -CD-NMA content was analyzed for PNIPAAm- $\beta$ -CD-NMA-PP with two different concentrations of  $\beta$ -CD-NMA in the monomer solution. FT-IR spectra for corona-treated nonwoven PP, PNIPAAm- $\beta$ -CD-NMA-PP with two different concentrations of  $\beta$ -CD-NMA in monomer solution and PNIPAAm-PP added with different concentrations of  $\beta$ -CD-NMA can be seen in Figure 5. The FT-IR spectra show that there is a close similarity between  $\beta$ -CD-NMA added to the PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP. Hence, these FT-IR spectra were applied for the estimation of  $\beta$ -CD-NMA contents in PNIPAAm- $\beta$ -CD-NMA-PP and accordingly, a FT-IR calibration curve was made on the basis of the absorption changes at  $1030\text{ cm}^{-1}$  with increasing concentrations of free  $\beta$ -CD-NMA added to the PNIPAAm-PP. Based on this procedure,  $\beta$ -CD-NMA contents in PNIPAAm- $\beta$ -CD-NMA-PP were estimated to be increased from  $0.9\text{ mg g}^{-1}$  to  $1.9\text{ mg g}^{-1}$  with the increase of  $\beta$ -CD-NMA concentrations from  $0.019\text{ M}$  to  $0.049\text{ M}$  in monomer solution, respectively.

### Investigation of Thermo-Responsive Loading Affinity of Modified Fabrics

Fluorescence spectroscopy gives significant information about loading affinity of the samples. ANS was used as a probe to assess the loading affinity of the fabrics toward guest molecules. As represented in Figure 6, the fluorescence intensity of free ANS solution ( $1\text{ mM}$ ) is negligible. However, the fluorescence intensity of ANS for PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP is remarkable at different temperatures. Moreover, the results show that the fluorescence intensity of ANS for PNIPAAm-PP is higher at  $40^\circ\text{C}$  compared to that at  $20^\circ\text{C}$ . The higher fluorescence intensity indicates that ANS is situated in a hydrophobic environment,<sup>43</sup> as a significant increase in fluorescence intensity of ANS for PNIPAAm-PP at high temperature may be attributed to the well-known increase in hydrophobicity of PNIPAAm at high temperature (Figure 6). Interestingly, the fluorescence intensity for PNIPAAm- $\beta$ -CD-NMA-PP immersed in ANS is much higher than that of PNIPAAm-PP at both  $20$  and  $40^\circ\text{C}$



**Figure 7.** Proposed mechanism of the collapse of NIPAAm polymer chains in the CD cavities at higher temperature and a decrease in association constant of  $\beta$ -CD-NMA with guest molecular.<sup>32</sup>

(below and above the LCST of NIPAAm). This is highly likely due to complex formation of ANS molecules with the present  $\beta$ -CD-NMA in PNIPAAm- $\beta$ -CD-NMA-PP. In addition, it can be seen that the fluorescence intensity for PNIPAAm- $\beta$ -CD-NMA-PP immersed in ANS is higher at  $20^\circ\text{C}$  compared to that at  $40^\circ\text{C}$ . This may be due to the collapse of NIPAAm polymer chains in the CD cavities at higher temperature and a decrease in association constant of  $\beta$ -CD-NMA with ANS (Figure 7).<sup>32</sup> Moreover, as Yanagioka and coworkers<sup>26</sup> showed, a large guest molecule such as ANS can be partly included in the CD cavity, and the molecules placed outside of the cavity will have a steric hindrance effect on the PNIPAAm chains.<sup>33</sup> When temperature goes up to  $40^\circ\text{C}$ , the shrunken polymer chains show a larger steric hindrance for the guest molecule ANS. Conversely, NIPAAm polymer chains swell at  $20^\circ\text{C}$  and there is no steric hindrance on the hydrophobic cavity of  $\beta$ -CD-NMA, leading to a considerable increase in fluorescence intensity for PNIPAAm- $\beta$ -CD-NMA-PP. The results in Table II show the calculated ANS content in PNIPAAm-PP and PNIPAAm- $\beta$ -CD-NMA-PP. The results indicated that PNIPAAm- $\beta$ -CD-NMA-PP not only possess a higher affinity than PNIPAAm-PP of absorbing guest molecules but also that this affinity can change with a change of temperature and thus confirmed the temperature-sensitive property of the modified textiles.

### CONCLUSIONS

In this study, a  $\beta$ -CD-NMA-incorporated PNIPAAm hydrogel was grafted onto the surface of corona-treated nonwoven PP fabrics through a graft polymerization technique. A new procedure for the estimation of  $\beta$ -CD-NMA content into PNIPAAm- $\beta$ -CD-NMA-PP by FT-IR was developed. The FT-IR spectra revealed a relatively good correlation between PNIPAAm-PP added with  $\beta$ -CD-NMA and PNIPAAm- $\beta$ -CD-NMA-PP so that the estimation of  $\beta$ -CD-NMA content in samples by this procedure seems to be accurate. Furthermore, fluorescence results showed that PNIPAAm- $\beta$ -CD-NMA-PP possess a higher loading affinity for absorption of guest molecules compared to PNIPAAm-PP. The loading affinity of samples was temperature dependent as well. Due to the temperature-sensitive properties and the high loading affinity, new applications such as temperature-sensitive fragrance textiles and temperature-sensitive antibacterial wound dressings may result from the combination of the PNIPAAm and  $\beta$ -CD functionalities.

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