SURFACE MODIFICATION OF POLYAMIDE VIA GRAFTED CHITOSAN-BASED RESPONSIVE HYDROGELS

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ABSTRACT

This study focuses on the surface modification of polyamide via chitosan-based hydrogels, which are responsive to pH and temperature changes. SEM and DSC were used for the hydrogels' characterization; Pore Volume Distribution measurements were realized for the polyamide samples' characterization. The hydrogels' response to temperature changes was determined spectrophotometrically and to pH changes gravimetrically. The polyamide samples' response to pH and temperature changes was determined gravimetrically and expressed as the samples' water uptake/loss or moisture regain/loss. The aim of this work was to develop stimuli-responsive polyamide which could serve for controlled substance release and increased wear comfort with a variety of applications in protection clothing and sportswear.

Key Words: Polyamide, chitosan, responsive hydrogels

1. INTRODUCTION

Polyamide (nylon) is a widely used material in the textile industry for outdoor applications (e.g. tents, umbrellas) as well as apparel (e.g. stockings, swim-suits). Some of its attractive properties are elasticity, mechanical strength and abrasion resistance. Although hydrophilic up to an extent owing to their amide (-NHCO-) groups, polyamide fibers and fabric exhibit low moisture absorbance compared to cotton and in the case of clothing, this fact influences the wear comfort properties of a garment. This work attempts to modify the surface of polyamide 6.6 fabric with a hydrogel system based on the biopolymer chitosan. Hydrogels are hydrophilic – although insoluble in water – polymeric networks which contain up to 98 % water in their structure and can absorb even 100 times more water than their initial weight. When they are prepared with stimuli-responsive polymers, such as the pH-sensitive polysaccharide chitosan and the thermo-sensitive poly(N-isopropylacrylamide), hydrogels can expel or take up water depending on the conditions of their environment, which can cause the hydrogels' structure to swell or shrink [1]. The addition of acrylic acid in a chitosan/poly(N-isopropylacrylamide) hydrogel system can impart: a) pH-sensitivity to an extended pH range (chitosan is positively charged in acidic pH (chitosan's pK_a=6.3, [2]), acrylic acid is negatively charged in alkaline pH); b) higher stability to the hydrogel due to chitosan's electrostatic interaction with acrylic acid; c) higher water uptake since acrylic acid is known to be used in superabsorbent polymeric systems. In this work it is attempted to combine bulk hydrogels of genipin-crosslinked chitosan with microparticles prepared from N-isopropylacrylamide and acrylic acid. Embedding microparticles into a bulk hydrogel is expected to give a faster overall response of the system to pH and temperature changes. In this sense, modifying polyamide's surface with such a combinational hydrogel can lead to a new material with increased hydrophilicity, and therefore better moisture management, but also with fast responsiveness to pH and temperature changes for e.g. controlled substance release.

2. MATERIALS

For the preparation of the hydrogels, chitosan (CS, from Primex, Iceland, chitosan source: *Pandalus Borealis*) with deacetylation degree DD=95 % and viscosity η=159 mPa·s was used. Genipin (Gen, from Wako) was used as CS's crosslinker. The rest of the hydrogels' constituents included *N*-isopropylacrylamide (NIPAAm, from Acros Organics), its crosslinker *N*,*N*′-methylenebisacrylamide (BIS, from Sigma) and acrylic acid (AA, from Acros Organics). Ammonium persulfate (APS) was used as initiator. Potassium monobasic phosphate and potassium phthalate were used for the buffers preparation in combination with appropriate amounts of sodium hydroxide 0.1M. Acetic acid glacial (100%) was from Merck and water when used was of analytical grade (0.1μS/cm) purified with the Millipore water-purification system ELIX 3. For the fabric samples, polyamide 6.6 (PA 6.6 standard test fabric-ISO 105 F03, from the Society of Dyers and Colourists) was of plain weave with weight per unit area 130 g·m^{-2} and density 22 threads·cm^{-1} (both warp and weft).

3. PROCEDURES

3.1 Hydrogel preparation and its *in situ* formation on polyamide 6.6

The first step was to prepare P(NIPAAm-AA) microgel particles to be later embedded in the CS bulk hydrogel. The microgel (MG) was synthetized by a surfactant free emulsion polymerization method. NIPAAm was used as received. AA was passed through an inhibitor-remover column (Aldrich) prior to its use. The two monomers (NIPAAm, 2.82 g, and AA, 0.18 g) were dissolved in 300 ml water and placed in a 500-ml flask equipped with a reflux condenser and a mechanical stirrer. 0.06 g of the crosslinker BIS was added. The solution was purged with N_2 for 30 min. 0.3 g of the initiator APS was then added. The reaction took place at 65^{o}C for 6h. The mixture was left overnight at room temperature for the completion of the reaction. To purify the final product dialysis followed (4 spectra/Por, Fisher Scientific, cut-off 12.000-14.000) for 48-72h against water [3-5]. The bulk hydrogels were prepared by dispersing aliquots of the dialysed MG into CS solutions and these pre-gel solutions were subsequently crosslinked with genipin. For this purpose, 0.3 g of CS were dissolved into 30 ml of water (1 % wt. final concentration) where 0.5 ml of acetic acid was added. The solutions were left to stir overnight. Then two batches of bulk hydrogels with embedded microgel (BMG) were prepared, one with 0.2 g and another one with 0.4 g of dialysed MG (0.7 % wt. and 1.4 % wt. in the pre-gel solution, respectively). Each mixture was stirred for 10 min for adequate dispersion of the microparticles into the CS solution and then 0.02 g of genipin were added for the crosslinking reaction. After 10 min of stirring the pre-gel solutions were poured into petri-dishes and left to gelify in an oven at 50^{o}C for 3h. A bulk hydrogel (BG) of only CS crosslinked with genipin was prepared as control.

In the case of PA 6.6, samples of 10 × 10 (cm × cm) were cut and immersed into a genipin solution (2.5 mM) for 10 min (genipin is known to react with primary amine groups [6] and in this case it was used to link CS's to PA's). Then the samples were passed through a laboratory padder and left to dry at room temperature. Subsequently the samples were immersed into a dispersion of MG in CS, prepared as described above, at a liquid-to-goods ratio of 1:30, left to soak for 10 min and passed through the padder. Finally, they were placed in the oven for 3h at 50^{o}C and then washed with water under shaking for 24h. A sample with only CS BG onto PA was prepared as control. A summary of the samples is given in Table 1.

Table 1. PA samples under study.

Sample code	Sample description		
	Fabric	CS	P(NIPAAm-AA) MG
PA	Polyamide 6.6 reference	-	-
PA + BG	Polyamide 6.6 with CS BG	1 % wt solution	-
PA + BMG1	Polyamide 6.6 with CS BG + P(NIPAAm-AA) MG	1 % wt solution	0.7 % wt. in the pre-gel solution
PA + BMG2	Polyamide 6.6 with CS BG + P(NIPAAm-AA) MG	1 % wt solution	1.4 % wt. in the pre-gel solution

3.2 Characterization

Scanning Electron Microscopy (SEM) was used to observe the hydrogels' morphology. An aliquot of P(NIPAAm-AA) MG was diluted 1:500 and a drop of it was placed on a silicon wafer. The sample was air-dried at room temperature. In the case of BMGs, the sample was air-dried at room temperature to form a film and a piece of it was directly attached on the SEM holder. For the analysis a High Resolution Scanning Electron Microscope LEO 1550 (Carl ZEISS, Germany) was used. Differential Scanning Calorimetry (DSC) was used to determine the P(NIPAAm-AA) microgel's LCST. A portion of MG as obtained from the reaction was dried under vacuum with an R200 Rotavapor (BÜCHI, Switzerland) and re-dissolved to form a 5 % (w/v) solution. 8.5 mg of this solution were placed in an aluminium pan. The pan was sealed and placed in the sample holder next to an empty aluminium pan used as a reference. The temperature was raised from 25^{o}C to 45^{o}C at a 5^{o}C/min rate, held at 45^{o}C for 2 min and decreased until 25^{o}C at an 8^{o}C/min rate. Two cycles of heating and cooling were performed with a N_2 gas flow of 30 ml/min using the DSC 822^{e} instrument (Mettler-Toledo, USA). Liquid porosimetry was used to determine the Pore Volume Distribution (PVD) of the polyamide samples. The measurements were conducted with an auto-porosimeter (TRI, USA). The total wetting liquid ($\cos\theta=1$) was 0.1 % solution of Triton X-100 in double distilled water. Measurements were performed in the receding mode in the range of 1–300 μm on 3 swatches of 2.5 cm (weft) × 3.0 cm (warp) cut randomly from each fabric sample. The final PVD was obtained as the average of the three measurements for each sample.

3.3 Response measurements

To establish the thermo-responsiveness of both the P(NIPAAm-AA) MG and the CS/P(NIPAAm-AA) BMGs, a Cary 100 Bis (Varian, USA) spectrophotometer equipped with a temperature controller was used. The changes in the transmittance values (T %) of the samples were monitored and recorded at 480 nm for temperatures between 25°C and 40°C over a period of 30 min. In the case of the microgel, a portion of its solution was diluted 1:10 and used as such for the measurements. In the case of the bulk hydrogels, they were prepared as described above but this time they were left to gelify in disposable cuvettes, and afterwards they were used as such for the measurements. The thermo-responsiveness of the polyamide fabric samples was studied using the bench top test chamber SM-1.0-3800 (Thermotron, USA). From each type of polyamide fabric (reference and surface-modified) three samples of 2.5 × 2.5 (cm × cm) were cut and conditioned for 15h at 20^{o}C and 65% R.H. Afterwards the

samples were weighed and that was considered their initial weight (W_0) for the rest of the measurements. Finally, the samples were conditioned for 4h at 25, 30, 33, 35, 37 and 40°C, and 55 % R.H. The moisture regain (or loss) at each temperature was determined as the average of three values obtained by Eq. (1)

$$R = \frac{W_{4h} - W_0}{W_0} \times 100 \quad (1)$$

where W_{4h} is the weight of the sample after 4h at a certain temperature and 55 % R.H., and W_0 is its initial weight.

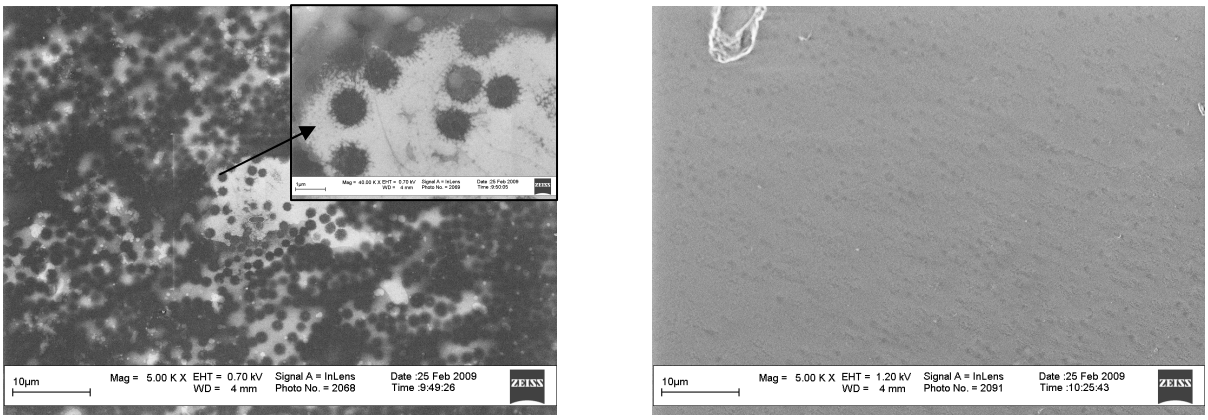
The pH-responsiveness of both the bulk hydrogels and the polyamide samples was tested by immersing each one of them into 10 ml of buffer solutions of pH 4.5, 5.5., 6.5 and 7.5. In the case of the bulk hydrogels, samples in the form of discs with a diameter of 3 cm were prepared and then air-dried at room temperature to form films. For the polyamide fabric samples, pieces of 2.5 × 2.5 (cm × cm) were cut and then conditioned for 15h at 20°C and 65% R.H. In both cases, the immersed samples were thermostated with a water bath at 25°C for 4h and then their water uptake (W_U, %) was calculated by using the Eq. (2)

$$W_U = \frac{W_{4h} - W_0}{W_0} \times 100 \quad (2)$$

where W_{4h} is the weight of the sample after 4h at a certain pH and 25°C, and W_0 is the initial weight. All measurements were done in triplicate.

4. RESULTS AND DISCUSSION

Figure 1 shows the morphology of the P(NIPAAm-AA) MG in dry state and when embedded in CS BG. The microparticles are of uniform shape and they have an estimated size of 1 μm (Figure 1a). Their dispersion in the bulk CS hydrogel seems to be homogeneous as depicted in Figure 1b.



(a) (b)

Figure 1. SEM images of: a) P(NIPAAm-AA) microgel, and b) bulk CS hydrogel with 0.7 % embedded P(NIPAAm-AA) microgel.

Pure PNIPAAm has the intrinsic property of undergoing phase transition when the temperature rises above 33°C (known as Lower Critical Solution Temperature, LCST), and turns hydrophobic and opaque [7]. To determine the LCST of the prepared MG, DSC was used and the obtained graph is shown in Figure 2. The average temperature corresponding to the peak of two cycles was calculated to be 34.4°C.

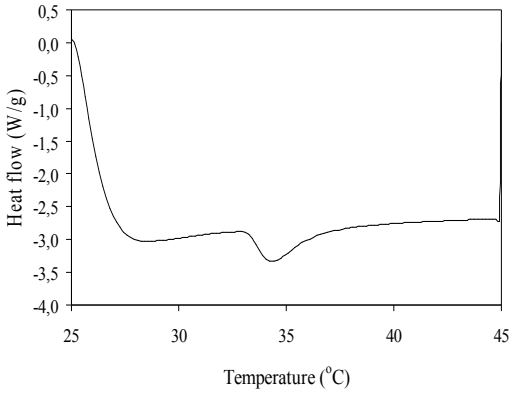


Figure 2. DSC diagram of P(NIPAAm-AA) microgel solution.

This is slightly higher than PNIPAAm's bibliographic LCST because the presence of AA renders the microparticles more hydrophilic and shifts their LCST to higher values [8]. Still, the obtained temperature is somewhat lower than the one mentioned in literature for P(NIPAAm-AA) (35.9°C, [3]) but this is probably due to the use of concentrated microgel solution in this study for the analysis. To compare the thermo-responsiveness of the MG in solution and when embedded in CS BG, the kinetics of the samples' trasmittance changes were studied and the results are shown in Figure 3. At 25 and 30°C the T% values of the MG are stable (Temperature<LCST) but at 35°C a dramatic drop is recorded from about 95 % to almost 5 % (Figure 3a). At 40°C the same drop is observed but at a higher rate (the sample turns opaque in less than 5 min). In the case of the CS BG, the temperature increase has no apparent effect on the T% (Figure 3b). However, when the MG is embedded in it, all T% are shifted to lower values and the higher the temperature, the bigger the T% decrease.

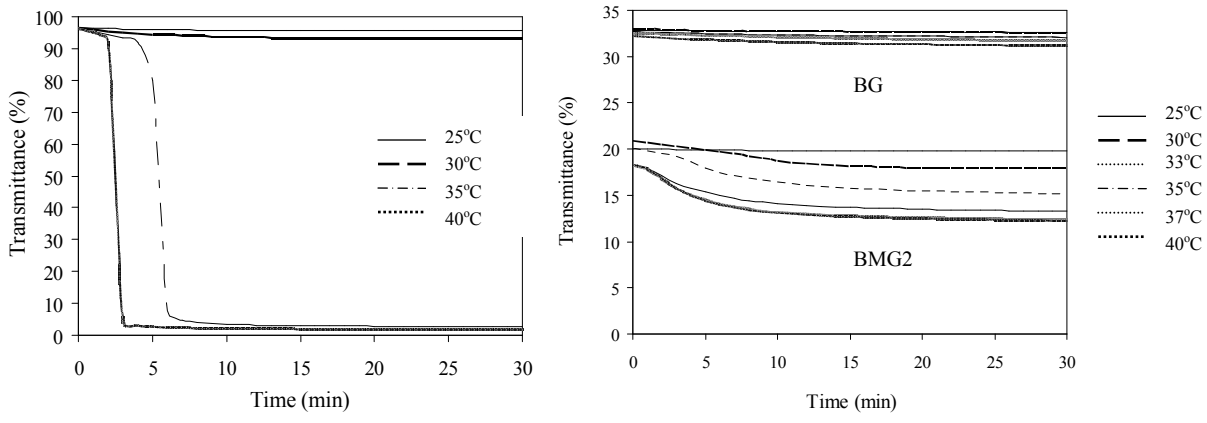


Figure 3. Spectrophotometric evaluation of: a) the MG's thermo-responsiveness, and b) the CS BG's thermo-responsiveness with and without MG, monitored for 30 min at 480 nm and at various temperatures.

With regard to the pH-responsiveness of the BMGs, Figure 4 shows that the hydrogel with the most profound response is BMG2. Although the control CS BG has an increased W_U at pH 4.5, BMG1 exhibits a higher W_U at pH 7.5 due to its AA content (Figure 4a). However at both these pH, BMG2 gives extremely high water uptakes (Figure 4b). This could be attributed to the fact that with increased MG content, the hydrophilic-hydrophobic balance inside the BMG is changed. When CS is at acidic pH (4.5) its amine groups are protonated causing the hydrogel to attract more water.

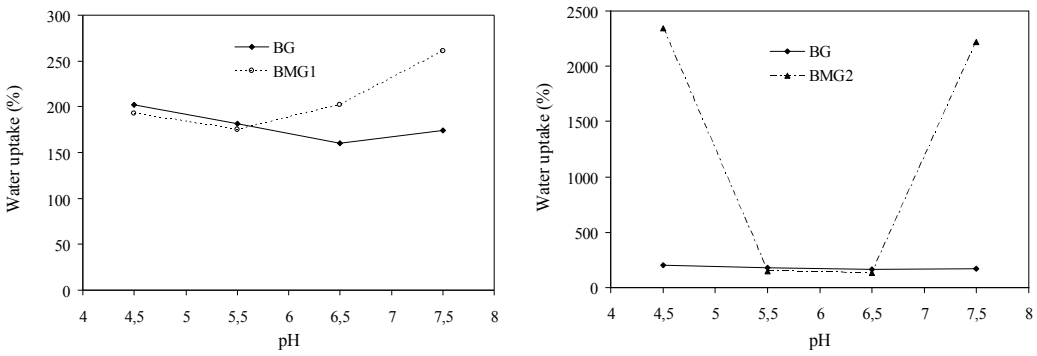


Figure 4. Plot of the water uptake of: a) BMG1, and b) BMG2 at 25°C and various pH. CS BG was used as a control in both cases.

Although, it is the same amount of CS in all bulk hydrogels, BMG2 has a high content of dispersed hydrophilic microparticles which absorb the water from CS's network leaving the amine groups "dehydrated", forcing them to draw more water from their environment to get "re-hydrated". On the other hand, at slightly basic pH (7.5), CS's amine groups are not protonated anymore but AA's carboxylic groups are negatively charged. Since they are highly dispersed into the bulk, they induce a water uptake comparable to CS's at acidic pH.

Regarding the PA samples, the PVD analysis showed that there is a significant 10 μm-increase of the inter-yarn pores (Figure 5a) between the reference fabric and the CS-modified one. However, when MG is also present, the increase is smaller (5 μm) and the pore-size distribution broader. The opposite effect is observed in the area of the intra-yarn pores (Figure 5b). Sample PA+BMG2 with the highest content of microparticles has a maximum of 3.5 μm compared to the 5.5 μm of the reference fabric, indicating the presence of a micro-porous structure inside the yarns.

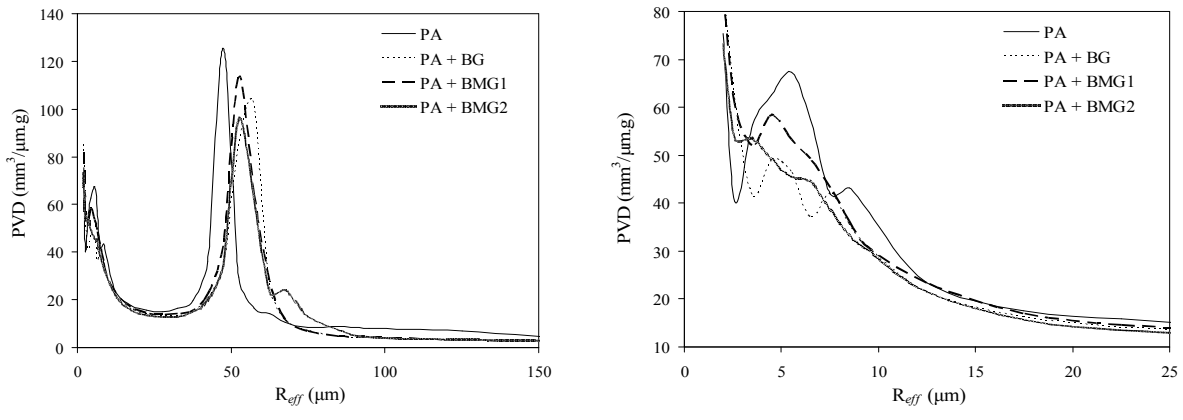
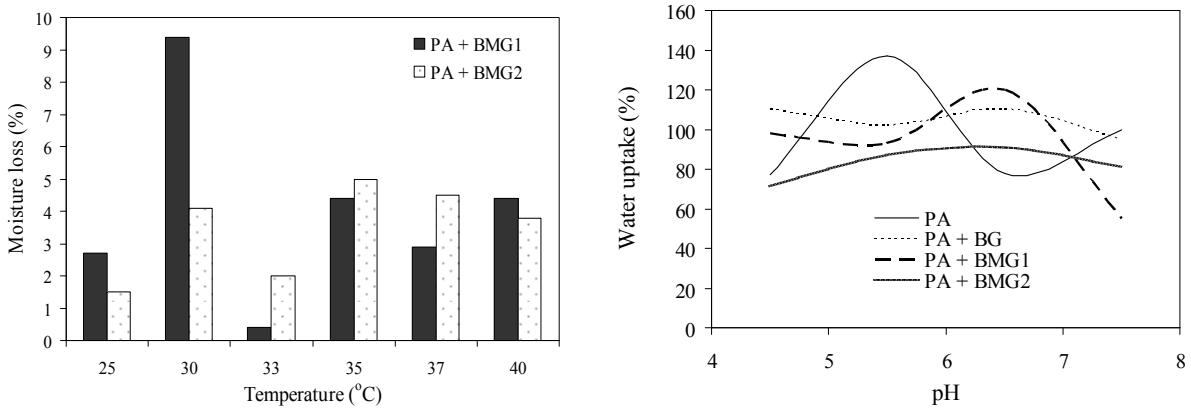


Figure 5. Pore volume distribution of PA samples (reference and surface-modified): a) Depiction of both inter- and intra- yarn pore size distribution. b) Intra-yarn pore size distribution.

Having the above structural differences in mind, and having previously established the bulk hydrogels' thermo- and pH- responsiveness, the PA samples were tested for *their* sensitivity to temperature and pH changes. Since PNIPAAm is the one responsible for the thermal response of the system, only the two samples containing MG are compared here (Figure 6a). The results showed that PA+BMG2 lost more of its moisture at temperatures close to or higher than 34°C (MG's LCST, Figure 2) than PA+BMG1 did, a result which was expected. What is striking though is that at 30°C, the latter one exhibits the highest moisture loss probably due to the crosslinked CS's reduced hydrophilicity. This means that for this sample the hydrophilic MG content is not enough to balance the tendency of the crosslinked CS to repel water (when CS is crosslinked, part of its amine groups are no longer available for water absorption). And although this is not intensely exhibited at 25°C, when the temperature is elevated to 30°C, CS's structure releases water and the moisture loss is presented to be high because the microparticles are not enough to balance this loss with their hydrophilic nature.



(a) (b)

Figure 6. Plot of: a) the moisture loss of PA samples at 55 % R.H. and various temperatures; b) the water uptake of PA samples at 25°C and various pH.

In Figure 6b the response of PA samples to different pH is presented. Since PA has free amine and carboxylic groups that contribute even partly to its hydrophilicity apart from the amide groups, the high water uptake at pH 5.5 and 7.5 could be attributed to this contribution. However, since grafting CS onto PA reduces both CS's and PA's free amine groups, the water uptake at pH 5.5 is reduced for all samples. At higher acidic pH (4.5), it is possible that the effect of the acidic medium overrides CS's intra-molecular hydrogen bonds or inter-molecular with the microparticles' AA and with PA, freeing partly the remaining amine groups and giving a relatively high water uptake [9]. On the other hand, CS BGs form a layer on the fabric's surface, possibly masking the effect of PA's carboxylic groups at pH 7.5. Strangely enough, the sample PA+BMG1 exhibits a complementary or opposite response to pH changes compared to the reference PA, and the most profound differences in water uptake among the different pH, a result which needs further investigation.

5. CONCLUSIONS

The prepared CS bulk hydrogel with embedded P(NIPAAm-AA) microparticles has proven to respond adequately to pH and temperature changes. Attaching it to PA 6.6 fabric by using genipin as a crosslinker gives interesting results. When the MG content is low, the material's

pH sensitivity is higher but when the MG content is high, the thermal sensitivity of the material is higher. This gives the opportunity to modify PA's surface in such a way to achieve the optimum combination of CS and MG content and therefore the optimum pH/temperature responsiveness.

6. REFERENCES

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