



Synthesis and application of new temperature-responsive hydrogels based on carboxymethyl and hydroxyethyl cellulose derivatives for the functional finishing of cotton knitwear

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ABSTRACT

A unique cellulose polymer-based hydrogel with specific dual-responsive absorption properties was prepared from carboxymethyl (CMC) and hydroxyethyl (HEC) cellulose in an aqueous solution employing citric acid (CA) as a crosslinking agent. The effect of preparation conditions, such as the polymer content and the CA amount, on the crosslinking process was investigated by estimating the formation of ester bonds (FTIR), as well as the hydrogel temperature-transition (DSC and optical transparency), weight-swelling ration measurements and morphology (SEM) as a function of time, temperature, and pH medium. The results show that the increment of the HEC content in the polymer solution diminishes the crosslinking degree and, consequently, reduces the pH dependency of the hydrogel. The results also show that the temperature-responsive swelling ability of hydrogel can be formulated based on the hydrogel's composition, and the degree of crosslinking. The swelling profile of knitted cotton fabric treated with a thin surface layer of modifying hydrogels was studied as a function of its fabrication and the conditions of its incubation, showing an opposite effect.

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1. Introduction

As textiles become more functional, stimuli-responsive polymers have also found their application in the creation of intelligent or smart textiles. These environmentally responsive fabrics can be tailored by chemical modification of the textile's surface using polymeric chains, thus being able to respond to a variety of stimuli such as temperature and pH, or can be used in cosmetic and nutrient/drug delivery fabrics. Owing to the above-mentioned attributes, smart textiles may provide us with considerable convenience, support, and even pleasure, in our daily activities. The phenomenon of the polymers that changes the wettability or hydrophobicity, in response to temperature, can be used to fabricate polymer-modified textiles that can when placed near to the skin, render the moisture between the skin and the textile when won, thus reducing or preventing microbes formation, and/or (simultaneously) release a drug onto the skin. In addition, environmentally responsive fabrics can enhance the protective functions of the skin's keratinous layer, reduce skin irritation, and improve the skin's barrier properties, by providing breathable, antistatic and antistain characteristics.

Recently, some attempts have been made to develop dual (pH and temperature) stimuli-responsive textiles by modifying their surface with thermo-responsive synthetic poly(NIPAM) derivatives, in various forms and combinations, showing a reversible phase-change (solution-to-gel) transition at a lower critical solution temperature (LCST) of around 32 °C (Liu & Hu, 2005; Rzaev, Dinçer, & Pişkin, 2007). Above its LCST, poly(NIPAM) is relatively hydrophobic and when grafted to a polymeric surface takes on a globular, packed conformation, whilst below its LCST, the polymer is hydrophilic and hydrated with more extended chains. Different technologies have been used to graft the poly(NIPAM) systems onto textile surfaces as a thin or thick-layer hydrogel: by suitable additives on plasma pre-activated polyethylene terephthalate film and polypropylene nonwoven fabric (Chen, Tsai, Chou, Yang, & Yang, 2002), by radicals of γ -pre-irradiation-induced surfaces of cotton cellulose (Jianqin, Maolin, & Hongfei, 1999), and by the ammonium persulphate-initiated copolymerization of poly(NIPAM) and polyurethane onto the nonwoven cellulose fabrics (Hu, Liu, & Liu, 2006). Similarly, surface modifying systems based on chitosan and poly(NIPAM) were formulated as micro-hydrogels, and incorporated into previously aminized cotton fabric surfaces (Kulkarni, Tourrette, Warmoeskerken, & Jocić, 2010). Taylor and Cerankovski (Manias & Rackaitis, 2004) predicted that the LCST of a water soluble polymer can be varied by controlling the balance of hydrophilic and hydrophobic segments within a polymer-chain. Increasing the length of the hydrophobic side-chains can shift the LCST, whilst, at

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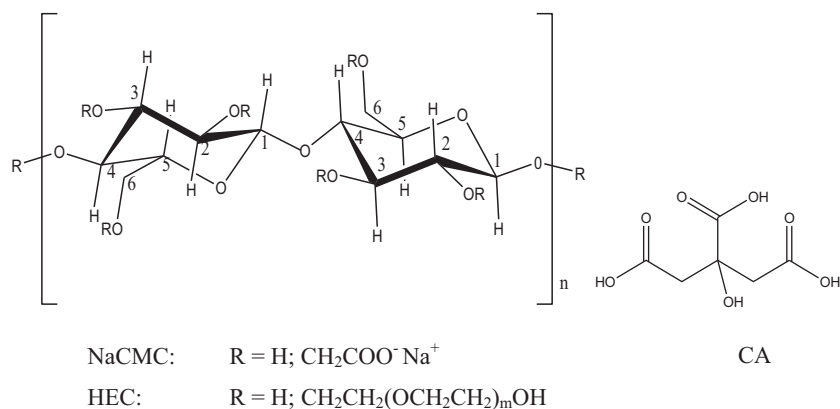


Fig. 1. Chemical structure of NaCMC, HEC and citric acid (CA).

the same time, broadening the phase transition (which occurs over a wide temperature range).

This contribution presents the design and application of cellulose-based hydrogels with temperature-responsive and reversible volume-transition behaviour, as an alternative to those poly(NIPAM) derivatives problematic in terms of toxicity, water-solubility, and biodegradation. Among all cellulose ethers, only carboxymethyl cellulose (CMC), available as the sodium salt NaCMC, is a polyelectrolyte, and thus a smart cellulose derivative which shows sensitivity to pH and ionic-strength variations, plus good swelling capability (Sannino, Demitri, & Madaghiele, 2009). Anionic NaCMC molecules (Fig. 1) are most extended (rod-like) at low concentrations, but at higher concentrations the molecules overlap, coil-up, and then, entangle at high concentrations to become a physically thermoreversible gel (Bochek, Shevchuk, & Kalyuzhnaya, 2008) which responds to external stimuli (i.e. temperature) by shrinkage or water uptake. Hydroxyethyl cellulose (HEC) derivative is thermally stable, having no heating gel phenomenon, but possessing twice the water retention ability of NaCMC.

Results have shown that superabsorbent hydrogels can be synthesized by crosslinking HEC with NaCMC by, e.g. divinylsulphone (Demitri et al., 1996) or water-soluble carbodiimide (Sannino et al., 2005), having an influence on the equilibrium water content and swelling-abilities of products that can be enhanced with an increase in CMC content within the blend. As one of the polymers is pH-sensitive (CMC), the hydrogels show good swelling properties at neutral pH and low swelling ratios at acid pH, although the water sorption capability could be modulated and maximized by adjusting the ratio NaCMC/HEC and the amount of crosslinker used (Sannino et al., 2003, 2009) or by adding molecular spacers to the polymer network (e.g. polyethylene glycol (Esposito et al., 2005).

As the current trend in the design of hydrogels relates to the use of non-toxic crosslinking agents or crosslinking treatments in order to improve the safety of both the final product and the manufacturing process, water soluble citric acid (CA) was selected as a bifunctional crosslinker, which is washed out from the polymer network after syntheses. Having three carboxyl groups (pKs of 3.13, 4.76 and 6.40) the CA crosslinks cellulose macromolecules by esterification of their hydroxyl groups through an anhydride intermediate formation (Fig. 2) (Welch & Andrews, 1994; Zhou, Luner, & Caluwe, 1995). For this purpose NaCMC and HEC cellulose derivatives with different weight ratios were prepared and crosslinked in various CA content in order to investigate CA reactivity with each of the polymers, and to follow the hydrogel temperature-transition, crosslinking density and morphology for limited and controllable absorption properties. A differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy

(FTIR), and weight-swelling ration measurements were performed during the reaction progress. Application of the selected hydrogels as a thin-film onto cotton knitwear in a durable and stable manner (textile pre-treatment, hydrogels deposition, and grafting), was investigated for the production of surface-functionalized textile materials.

2. Experimental

2.1. Materials used

Carboxymethyl cellulose sodium salt (NaCMC) with molecular weight (MW) of 700 kDa, a degree of substitution (D.S.) of 0.65–0.85, a degree of polymerization (DP) of 3200, as well as hydroxyethyl cellulose (HEC) with MW of 250 kDa, a degree of substitution (DS) of 1, and citric acid (CA) in anhydrous form, were purchased from Sigma Aldrich and used for hydrogel formulation, without further purification. A knitted fabric was used with a mass of 260 g/m² and made from 100% organic cotton yarns of 25 tex.

2.2. Synthesis of hydrogels

Firstly, HEC was added into purified water by stirring for around 10 min at room temperature until a clear solution was obtained, with a slight increase in viscosity. Then, CMC was added during the stirring until a clear and highly viscous solution was obtained. Mixing was performed using a IDL RE 10 mixer. The total polymer concentration was 2 wt% or 2.315 wt%, depending on the weight ratios of NaCMC and HEC, that varied from 3:1 to 1:1, respectively, being moderated to a viscosity of 6 Pa s which was then evaluated using an Anton Paar GmbH Reometer at room temperature. 30 ml of hydrogels were prepared from the basic solutions using different concentrations of CA as a crosslinker (1.75%, 2.75%, 3.75%, 5.75%, 10% and 20% (w/w) of polymer). Hydrogel samples were made as a 5 mm thick film in a Petrie dish with diameter of 90 mm, by being pre-dried for 24 h at 30 °C and afterwards crosslinked for another 24 h at 80 °C. In parallel, samples without pre-drying were also prepared in order to indicate the role of CA anhydride formation in the crosslinking reaction. Finally, differently prepared hydrogels were washed with distilled water for 24 h, dried at 45 °C, and kept in a refrigerator before use.

2.3. Hydrogels characterization

2.3.1. Analysis of hydrogels crosslinking by FTIR

FTIR analyses were performed of previously lyophilized non-crosslinked and crosslinked samples. ATR- FTIR spectra were recorded using a Perkin Elmer Spectrum One GX FTIR with a Golden

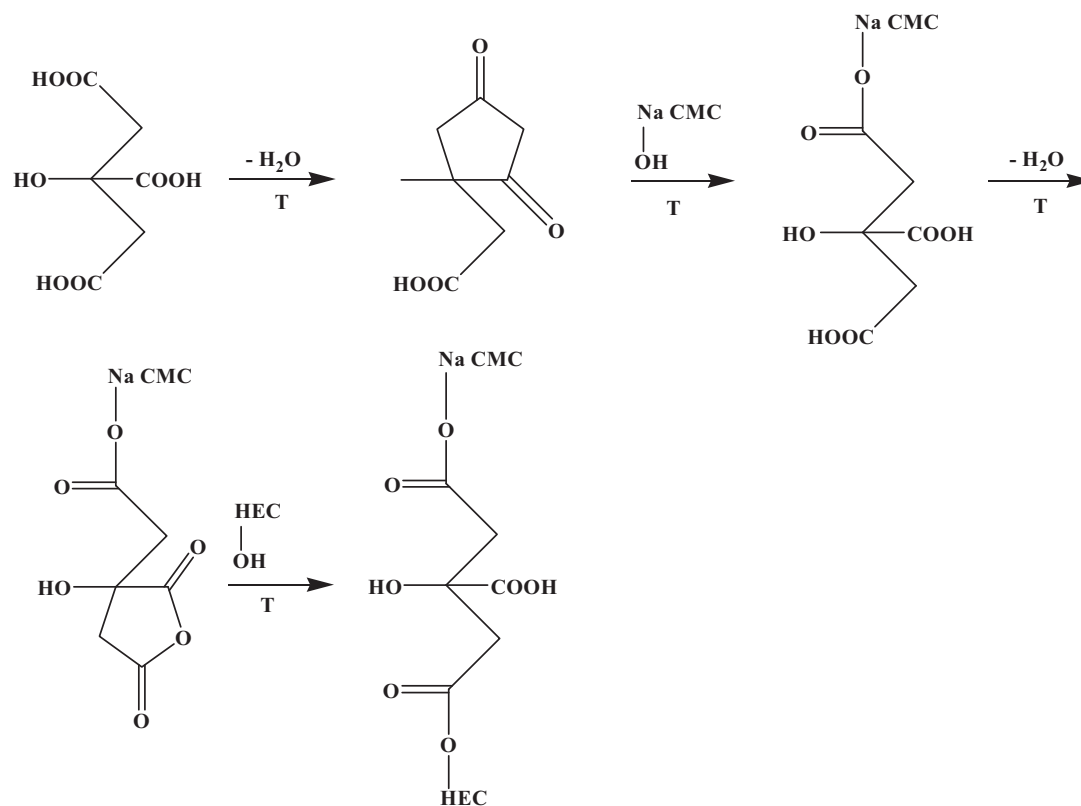


Fig. 2. Proposed mechanism of crosslinking NaCMC and HEC macromolecules by CA.

Gate ATR attachment and diamond crystal. Measurements were carried out within the range of $650\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , interval of 1 cm^{-1} and the number of scans being 16.

2.3.2. Analysis of hydrogel's transition temperature by DSC and optical transparency measurements

A differential scanning calorimeter (Mettler Toledo 851, Mettler DSC 20 standard cell s TC 10 A processor) was used for thermal analysis of the samples within a temperature range between 25 and 600°C . In order to identify the glass-transition temperature (T_g) at which increasing the internal free volume of hydrogel occurs, scanning cycles were performed at the following temperatures and heating rates: heating from 20 to 100°C with a heating rate of $10^\circ\text{C}/\text{min}$ and isotherm at 100°C for 3 min, cooling from 100 to 20°C , isotherm at 20°C for 3 min, heating from 20 to 200°C with a heating rate of $10^\circ\text{C}/\text{min}$ and isotherm at 200°C for 3 min, and cooling from 200 to 20°C ; all measurements were performed against blank (aluminium empty pan). Optical transparency measurements of the gel samples (with thickness of 5 mm) being immersed in distilled water at defined temperatures (22°C , 32°C or 42°C) and for a certain period of time, were also performed in Corning 6 Flat transparent plates by recording the absorbance scan ($230\text{--}1000\text{ nm}$) using a TECAN Infinite M200 UV spectrophotometer. The maximum absorbance values obtained were converted into a transmittance percentage according to the Transmittance absorbance conversion table (Dean, 1973).

2.3.3. Hydrogel's swelling response measurements and morphology

The swelling degrees of all samples in different mediums and under different conditions for defined time periods were evaluated, based on the gravimetric method. The measurements of the hydrogel's swelling as a response to changes in temperature and pH were conducted over two series: (a) by immersing the sam-

ples in purified water and studying the kinetics of their swelling at room temperature (22°C), temperature of human skin (32°C), and higher temperature (42°C); the measurement involved gravimetric determination of the (distilled) water uptake (%) of each sample at certain time intervals, (b) by immersing the samples in pH different (pH 5.5 and pH 8.0) artificial perspiration solutions, and again gravimetrically determining the water uptake (%) at the same time as the intervals and temperatures in the distilled water. The weight measurements were realized with an analytical balance after blotting the samples on filter paper to remove any excess water. The artificial perspiration solutions were prepared according to standard ISO 105-EO4: 1987(E); pH was measured using a Mettler Toledo MA 235 pH/ion analyser. The water/solution uptake (swelling degree, SD) was monitored for 24 h over different time intervals, and calculated from the following formula: $\text{SD} = (W_s - W_d)/W_d \times 100\%$, where W_s and W_d are the weights of the swollen and dried (conditioned at 23°C and relative humidity 65% for 24 h) test samples, respectively. The average of the three samples measurements was given as the final result. The morphology of the freeze-dried and lyophilized hydrogels was observed using scanning electron microscopy (SEM, FEI Quanta 200 3D).

2.4. Surface functionalization of cotton fabric with hydrogels

Prewashed (at 40°C for 30 min according to standards 105-C01: 1987 (E), Labomat W. Mathis), dried (at 50°C until all the water is evaporated) and conditioned (24 h at 22°C and 65% humidity) cotton-knitted fabrics were impregnated with a selected recipe for hydrogels preparation using a defined amount of crosslinker. Impregnation was performed using different technologies: (a) on a W. Mathis AG padder with a pressure of 1 bar and a rotation speed of 2 m/min, and (b) on a printing-table (Johanez Zimmer MDF R-237) with a speed of 3 m/min and magnet 3 ($\varnothing 12\text{ mm}$). After hydrogel impregnation, the samples were dried at 30°C , and crosslinked at

80 °C. In order to study the efficacy of those gel polymers grafting on the cotton's surface, the cotton samples were alternatively pre-impregnated on a padder (W. Mathis AG) with 5% (w/w) CA using substrate: a water volume ratio of 1:20 ensure around 80% wet pickup. One part of the samples was washed in a W. Mathis labomat at 40 °C or 60 °C for 30 min, according to standards 105-CO1:1987 (E) and ISO 105-CO3:1987 (E), respectively. Afterwards, all the samples were washed with distilled water and dried at 50 °C until all the water had evaporated. The deposition of CA (in the case of sample pre-impregnation) and hydrogel on the cotton's surface after the selected type of impregnation (padding or printing) was determined by equation: $(m_{\text{after}} - m_{\text{before}})/m_{\text{before}} \times 100 [\%]$, where m_{before} and m_{after} are the masses of the fabric samples before and after treatment, respectively.

2.5. Characterization of functionalized cotton

2.5.1. Analysis of hydrogels grafting on cotton by FTIR

The FTIR spectra of the samples were performed on each fabric after each treatment step as described under Section 2.3.1.

2.5.2. Swelling response measurements of functionalized cotton

In order to achieve information about the response of the treated fabric under wearable conditions (in the presence of acidic and alkali perspiration), the swelling properties of the cotton material with incorporated hydrogels were assessed by a gravimetric method. Fabric samples of dimension 4 cm × 4 cm were immersed in distilled water, artificial acidic (pH 5.5) and alkali (pH 8.0) perspiration solutions, until the swelling equilibrium was attained (after 3 h) and at different temperatures (22 °C, 32 °C and 42 °C). The weight of the wet sample was determined after removing the surface water by blotting it with filter paper. The swelling percentage was calculated using the equation: $SD = (W_s - W_d)/W_d \times 100 [\%]$, where W_s and W_d are the weights of swollen (or in equilibrium swollen) and dried (conditioned weight) test samples, respectively.

3. Results and discussion

3.1. Hydrogel's preparation and analysis

3.1.1. Assessment of hydrogels crosslinking and physical properties

3.1.1.1. FTIR analysis. FTIR analyses of NaCMC and HEC polymers, as well as hydrogels prepared from them in both weight ratios (3:1 and 1:1), were taken before and after the crosslinking, in order to confirm different substitutions of celluloses as well as the formation of ester bonds. As presented in Fig. 3, FTIR spectra shows the differences in the intensity and the position of absorption picks at specific spectral regions.

Different substitution of cellulose derivatives as well as their crosslinking, being seen as a shifting and broadening of ether C–O–C stretching vibration from ~900 cm⁻¹ (for unsubstituted cellulose) to ~887 cm⁻¹ for HEC and to ~891 cm⁻¹ and ~893 cm⁻¹ for crosslinked NaCMC/HEC samples (A region). At the same time the representative peak of HEC at ~1354 cm⁻¹ (B region) assigned to C–OH in plane stretching disappear in the spectra of the crosslinked samples, explaining the participation of non-substituted hydroxyl groups from HEC at the reactions with NaCMC (Oh, Yo, Shin, & Seo, 2005). In addition, a shifting of the NaCMC peak at ~1412 cm⁻¹ (CH₂ bending vibration) is observed at NaCMC–HEC crosslinked polymers, which overlap with the alkane peak (ethyl group, CH₃ CH₂–) clearly visible at ~1457 cm⁻¹ of HEC.

The differences in absorption peaks between 1500 cm⁻¹ and 1800 cm⁻¹ (C region), especially peak at around 1589 cm⁻¹ (assigned to carboxylate asymmetric stretching of NaCMC) in which the area and intensity are increased and moved towards

~1591 cm⁻¹ in the case of crosslinked samples (Cuba-Chiem, Huynh, Ralston, & Beattie, 2008) are seen. At the same time, the absorption band of HEC at ~1646 cm⁻¹ ascribed to the bending vibration of hydroxyl groups disappeared in the crosslinked samples, which implies that hydroxyl groups of HEC took part during the reaction (Wang, Wang, & Wang, 2010). In parallel, a new peak appears at around 1715–1735 cm⁻¹, being identified only at gels including CA, indicate the formation of ester bonds between the anhydride of CA (formed during 24 h of drying at 30 °C), and non-substituted hydroxyl groups of cellulose derivatives (Coma, Sebt, Pardon, Pichavant, & Deschamps, 2003). Actually, two overlapped peaks are visible within this region: one appeared at ~1715 cm⁻¹ corresponding to the reaction between the anomeric hydroxyl groups of the polymers and the CA's anhydride, and the second one appeared at ~1734 cm⁻¹ corresponding to the reaction of non-substituted secondary hydroxyl groups of both polymers with CA's anhydride (Galgali, Agashe, & Varma, 2007). The spectra also shows that crosslinking does not occur in the case of hydrogels prepared without intermediate drying, and that the degree of crosslinking is lower or does not occur even in the case of pure HEC with 3.75% CA (which is confirmed by the swelling measurements quickly destroying the physical network) compared to pure NaCMC or its blends with HEC using the same CA concentration (spectra not shown) as well as a higher amount of CA, due to an increased intensity of the bands within the ester region (at around 1715–1735 cm⁻¹) and a decrease in the band at ~1590 cm⁻¹. It is well-documented (Capitani, Del Nobile, Mensitieri, Sannino, & Segre, 2000) that the presence of HEC is necessary to promote quantitative intermolecular rather than intramolecular crosslinking. In fact, poor crosslinking efficiency is reported (Anbergen & Oppermann, 1990), if only NaCMC is used, seemingly due to the electrostatic repulsion between charged macromolecules, and to the fact that only a few hydroxyl groups remain available for reaction at C6, the most reactive position (Barbucci, Magnani, & Consumi, 2000).

The absorption peaks between 2500 and 4000 cm⁻¹ (D region) additionally indicate crosslinking reactions between NaCMC and HEC polymers by the increasing and shifting of the peak at around 2883 cm⁻¹ (assigned to aliphatic C–H stretching of HEC) from ~2875 cm⁻¹ to ~2878 cm⁻¹ at NaCMC/HEC crosslinked samples. The broad band in the region between 3600 and 3000 cm⁻¹, which is due to the OH-stretching vibration, gives information concerning the hydrogen bonds. The assignments for intramolecular hydrogen bonds of O(2)H...O(6) and O(3)H...O(5), and intermolecular hydrogen bonds of O(6)H...O(3) in the cellulose structure are generally shown at 3410–3460 cm⁻¹, 3340–3375 cm⁻¹, and 3230–3310 cm⁻¹ (Ciocacu, Kovac, & Kokol, 2010; Heinze, Liebert, & Koschella, 2006; Kondo, 1997), respectively. Since the characteristic absorption peaks of celluloses in the range between 3600 and 3000 cm⁻¹ were broad and overlapped one another, the resolution of the spectra was improved by their deconvolution from background scattering using a Gaussian function curve fitting analysis, which results are presented in Table 1. Two additional bands, at ~3138 cm⁻¹ and ~3074 cm⁻¹ in the case of pure HEC, and at ~3090 cm⁻¹ in the case of pure NaCMC, probably corresponding to the substitution of their hydroxyl groups at the C2 position, disappeared in the case of both crosslinked samples due to their binding (esterification) with hydroxyl groups of the same or other cellulose molecules (NaCMC or HEC). The FTIR spectra of crosslinked celluloses showed a progressive shift in the hydroxyl bonds to higher or lower wave numbers, and a decrease in intensity of these bonds, corresponding to O(6)H...O(3) and O(3)H...O(5), at higher NaCMC concentration, suggesting a breakage of the hydrogen bonds due lower amounts of hydroxyl groups available for esterification and negatively charged carboxymethylate ions, contributing to electrostatic repulsion and bulkiness, respectively.

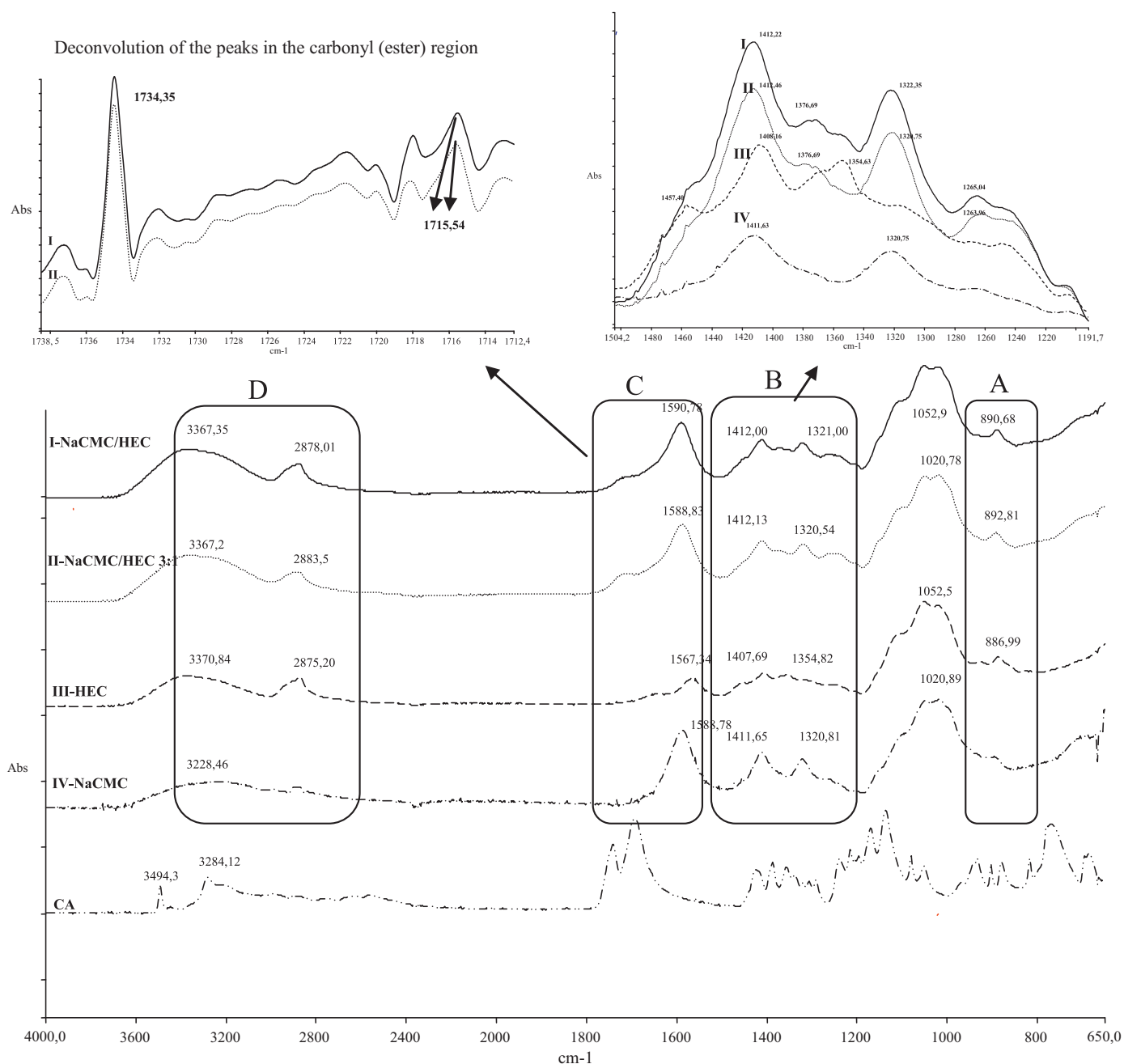


Fig. 3. FTIR spectra of NaCMC and HEC polymers, CA and hydrogels prepared from NaCMC and HEC in different weight ratios (1:1 and 3:1) and 5.75% (w/w) of CA.

3.1.1.2. Differential scanning calorimetry and optical transparency. The swelling behaviour of hydrogels strongly depends of the elasticity of these polymer chains included in the crosslinked network. When this network is immersed in a media with a temperature

higher then glass-rubber transition temperature (T_g) of the polymer network, the mobility of the chains increases and more liquid can be impelled into the hydrogel. The differential scanning calorimetry (DSC) of individual polymers (Fig. 4a) as well as differently

Table 1
FTIR absorption bands assignment to the OH-range (3600–3000 cm^{-1}) of HEC, NaCMC and hydrogels prepared from NaCMC and HEC in different weight ratios (1:1 and 3:1) and 5.75% (w/w) of CA.

Sample designation	Intermolecular hydrogen bonds of O(6)H...O(3)		Intramolecular hydrogen bonds of O(3)H...O(5)		Intramolecular hydrogen bonds of O(2)H...O(6)	
	λ (cm^{-1})	Abs	λ (cm^{-1})	Abs	λ (cm^{-1})	Abs
NaCMC	3205.3	0.065	3386.3	0.080	3543.9	0.031
HEC	3248.8	0.070	3403.1	0.083	3540.6	0.034
NaCMC/HEC 1:1	3245.5	0.125	3386.3	0.140	3550.7	0.058
NaCMC/HEC 3:1	3232.1	0.095	3398.0	0.100	3540.6	0.056

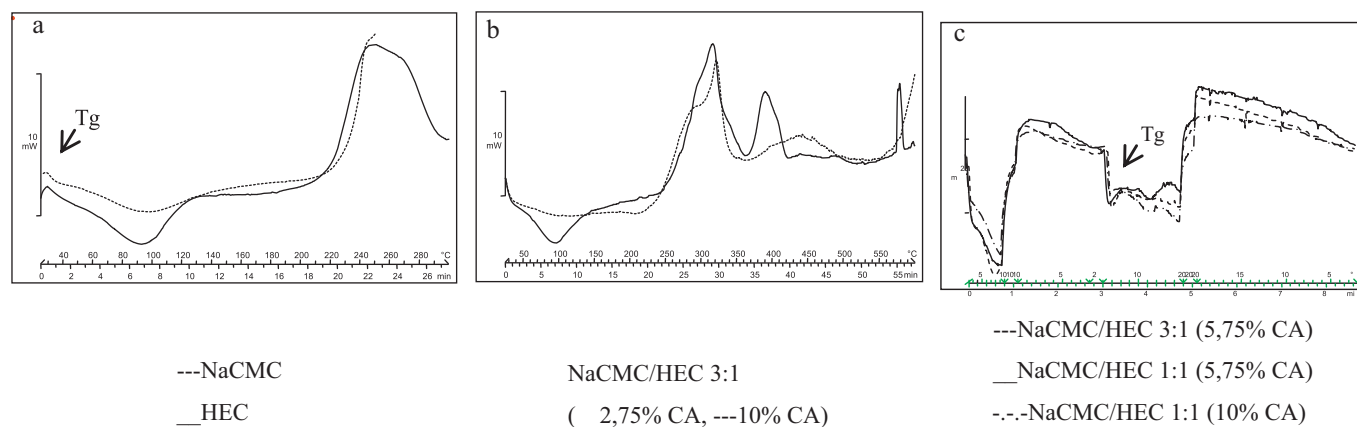


Fig. 4. DSC analysis of NaCMC and HEC and hydrogel prepared from them in different weight ratios and different concentrations of CA (2.75%, 5.75% and 10% (w/w)).

crosslinked samples (Fig. 4b) was thus performed in order to confirm the degree of crosslinking and to define T_g dependence on hydrogel composition, important for the application.

Whilst the first endothermic peak (Fig. 4c) in the region at around 100 °C is due to water evaporation, the second exothermic peak which starts at 210 °C for HEC and at 260 °C for NaCMC, respectively, corresponds to the polymer's thermal decomposition (Han, Shao, Wang, Guo, & Liu, 2010). In the case of crosslinked polymers (i.e. hydrogel samples, middle diagram), the first peak at around 100 °C obviously diminishes at a higher amount of crosslinker (10% (w/w) instead of 2.75% (w/w)) due to the involvement of hydrophilic hydroxyl side-groups into the crosslinking reaction; at the same time this reduces their ability to bind water molecules, consequently a low amount of water can evaporate from the system with the same heating rate. On the other hand, the second peak is no longer observable, indicating that the hydrogel acts as a single network with different transition temperatures than a singular polymer.

Since the broad endothermic peak makes it impossible to observe phase-transitions in the case of crosslinked hydrogel, the measuring procedure was modified, including a second heating cycle. As can be seen from the thermograms presented in Fig. 4c, the T_g (middle-point value) of the hydrogel increases to a higher temperature (from 38 °C for NaCMC/HEC 1:1 (5.75% (w/w) CA) to 42 °C for NaCMC/HEC 1:1 (10% (w/w) CA) and to 44 °C for NaCMC/HEC 3:1 (5.75% (w/w) CA)) with an increase of both the NaCMC content and the degree of crosslinking. The T_g is related to the onset of a certain degree of movement in the main chain and the rotation of side-segments. In the case of cellulose ethers, alkyl side-chains are bound to the hydroxyl groups of the cellulosic chain, causing transition to appear at a slightly lower temperature for HEC than for NaCMC, due to intra- and intermolecular interactions between non-substituted hydroxyl groups, methyl oxygen groups, and hydroxyls introduced by the substituent groups (Gómez-Carracedo, Alvarez-Lorenzo, Gómez-Amoza, & Concheiro, 2003). The lower T_g observed for HEC, where cellulose is substituted with hydroxyethyl groups, should disturb the hydrogen bonding network of cellulose more than the carboxymethyl groups of NaCMC. On the other hand, introducing hydroxyethyl groups may increase the hydrogen bonding formation between substituents, raise T_g , and reduce the interactions of the non-substituted primary hydroxyls of the cellulose chain at the time that the polymer becomes much more amorphous, which lowers T_g . Thus when comparing the DSC thermograms of differently crosslinked samples, it can be seen that the T_g of the NaCMC/HEC 1:1 hydrogel crosslinked with 10% (w/w) CA is higher than that of the crosslinked with 5.75% (w/w) CA. It is obvious that, when the CA amount increases, the T_g value increases because the density of crosslinking is enhanced and therefore the sam-

ple needs more heat-flow (energy) to make the first molecular movement (Lü, Liu, Ni, & Gao, 2010; Xiao & Gao, 2008). In other words, there is insufficient volume necessary to make free movements between pendant groups or crosslinked networks due to the reduced molecular space present in the hydrogel (Rivas-Orta, Antonio-Cruz, Mendoza-Martínez, Morales Cepeda, & Cruz-Gómez, 2006).

However, since the cellulose ethers usually show a glass transition of low intensity and the associated change in heat-capacity is too small to be detected using a conventional DSC (Gómez-Carracedo et al., 2003), the assessment of the hydrogel temperature responsiveness in distilled water has also been realized spectrophotometrically by measuring the transmission. The hydrogels were namely found to undergo a reversible optical transparency transition with the temperature change (Hongjun et al., 2006). It was observed (Fig. 5) that by increasing the temperature of the NaCMC/HEC 1:1 hydrogel from 22 °C to 42 °C, the transmission of the gel remains almost constant until the temperature reaches 32 °C, when it starts to increase. In contrast, the transmission value of the NaCMC/HEC 3:1 hydrogel at the same temperatures is lower and changes oppositely. However, there is only a small difference in the hydrogel structure depending on the transition at middle temperature. Such a change in transmission implies that the thermoresponsive hydrogel changes its morphological structure over a temperature range; i.e. it collapses at the increased transmission value, which can also be seen from the SEM images presented and discussed below.

It is well-known, that both the glass transition temperature and the optical transparency transition of hydrogel, induced by the formation and dissociation of hydrogen bonds, depends on the hydro-

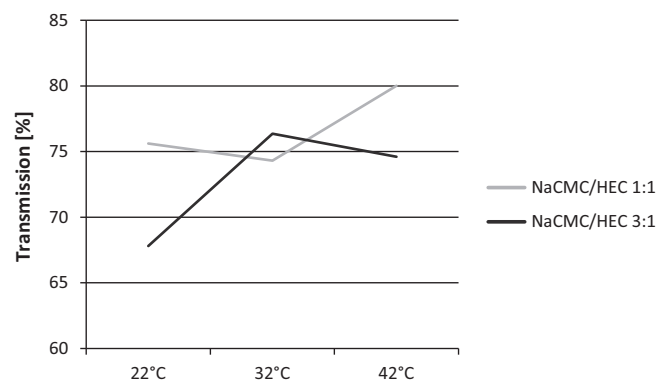


Fig. 5. Transmission transition of NaCMC/HEC hydrogels (crosslinked with 5.75% (w/w) CA) with temperature after their incubation into the distilled water for 3 h.

gen bonds density, network structure (macromolecular-chain concentration and composition ratio, cross-linking degree), and temperature change. The less hydrophilic NaCMC macromolecular-chain content in hydrogel determines the number of hydrogen bonds formed within the limited network space, whilst the presence of a more hydrophilic HEC influences the polymer's hydration, thus shifting the temperature at which gel-volume transition occurs from 22 °C to 32 °C (observed for NaCMC/HEC 3:1) to a higher temperature value (32–42 °C) observed for NaCMC/HEC 1:1. At temperatures above and below of transition temperature, NaCMC/HEC 3:1 hydrogel is more compact and less able to absorb water molecules compared to NaCMC/HEC 1:1 hydrogel possessing the opposite effect. A similar temperature transition effect is obtained by adding salts to the polymer swelling media (data not shown), since salts reduce the hydration level of the polymers by recalling the presence of water molecules around themselves.

3.1.2. Hydrogels swelling properties

The gel's swelling kinetics as a function of composition, crosslinking degree, temperature, pH, and ionic strength was monitored for 24 h. The preliminary results (data not shown) of gels prepared from NaCMC and HEC in the weight ratio 3:1, showed that the lower the percentage of CA used, the higher the value for SD and a longer time is needed to obtain swelling equilibrium. In addition, SD increases over time, but not proportionally, depending on the percentage of CA used for the crosslinking and the solution (pH medium) of incubation. In all cases, the SD is faster and more pronounced at gels prepared with lower concentrations of CA (2.75% (w/w)), where the gel's decomposition was observed after longer time intervals and at higher temperature. In addition, the absorption balance occurred in about 3 h at gels crosslinked with 3.75% and 5.75% (w/w) concentrations of CA in regard to different pH mediums and at lower temperatures (22 °C and 32 °C), but the gels made with 3.75% (w/w) CA again disintegrated at a higher temperature (42 °C) after a longer incubation time. In any case, the differences in SD between samples using different incubation mediums was the most visible during the first 30 min of the gel's incubation and only in the case of hydrogels crosslinked with CA up to 5.75% (w/w).

Based on the preliminary results and in order to achieve the lowest deviation of hydrogel's SD in different perspiration solutions (i.e. to reduce the pH dependence of the gels), new samples made from NaCMC and HEC in weight ratios 3:1 and 1:1, respectively, were prepared using 3.75% and 5.75% (w/w) of CA, and analyzed. In order to get information about the polymers self-crosslinking, only NaCMC and HEC were also immersed in 3.75% (w/w) of CA, incubated for the same time, and analyzed. As can be seen from Figs. 6 and 7, both the NaCMC/HEC weight ratio and the degree of crosslinking significantly affect the hydrogel equilibrium swelling properties.

In fact, as can be seen from Fig. 7, the increasing of NaCMC concentration increases the hydrogel swelling capacity by on average for about 10–20% of hydrogels made from NaCMC/HEC 3:1 compared to the hydrogels made from NaCMC/HEC 1:1. On the other hand, the hydrogels made from higher HEC content were less stable, which can be explained by its low ability for cross-linking as influenced by a higher substitution degree (less available OH groups) compared to NaCMC. However, the SD's of gels immersed in different pH solutions are comparable, whereas its SD is higher and deviates by being immersed in distilled water where the SD was faster and more pronounced, and where the gels decomposed in about 1 h.

At pH 6.25 ± 0.25 (pH of distilled water in which gels were prepared) the carboxylic acid groups should become ionized (COO⁻) since the pK_a of the carboxylic acid in the polysaccharide is ≈4.6 (Taleb, El-Mohdy & El-Rehim, 2009). At that pH the hydrogen bonds would be broken, electrostatic repulsion would arise between

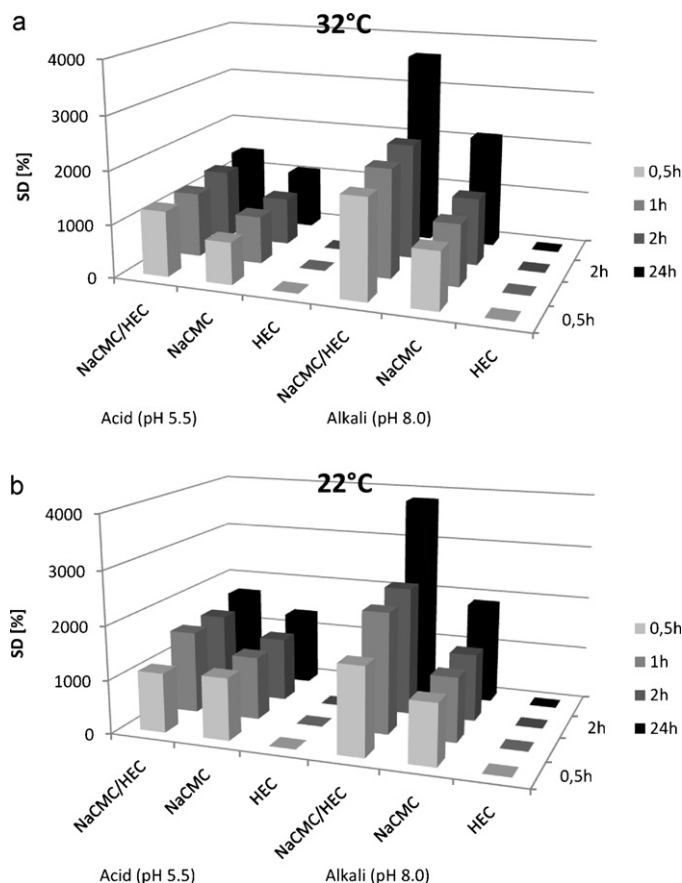


Fig. 6. Swelling degree (SD) of hydrogels prepared from NaCMC and HEC in the weight ratio 3:1 and 3.75% (w/w) CA.

macromolecules, and water would be taken up. The effect is evident in the hydrogel made from NaCMC/HEC 1:1, which has fewer hydrogen bonds than the hydrogel made from NaCMC/HEC 3:1 where larger contents of carboxylic groups determines a higher number of hydrogen bonds and a harder hydrogen-bond network to break, for which higher pH or temperature is needed. Beside, the NaCMC/HEC 3:1 hydrogel crosslinked with higher (5.75%, w/w) CA conc. forms fewer hydrogen bonds compared to the same hydrogels crosslinked with 3.75% (w/w) of CA (Fig. 6), and the response to changes in pH is immediate. Using 3.75% (w/w) of CA (Fig. 6), the SD is higher and more intensive in alkaline than in acidic medium which indicates that the gels, being weakly acidic (ip of NaCMC/HEC gel is at about pH 5.3 determined by titration method), have a higher degree of ionized carboxylic groups in alkaline pH, thus

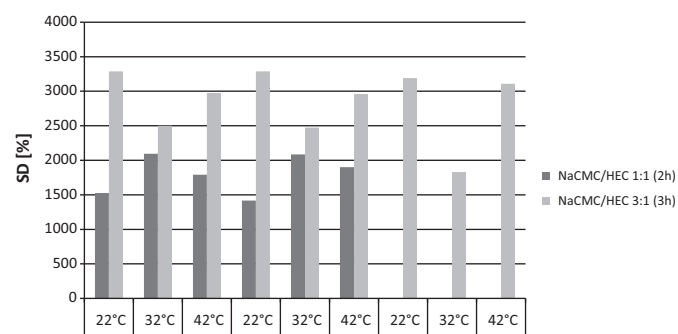


Fig. 7. Swelling degree (SD) of hydrogels prepared from NaCMC and HEC in different weight ratios and 5.75% (w/w) of CA at swelling equilibrium, and at different temperatures.

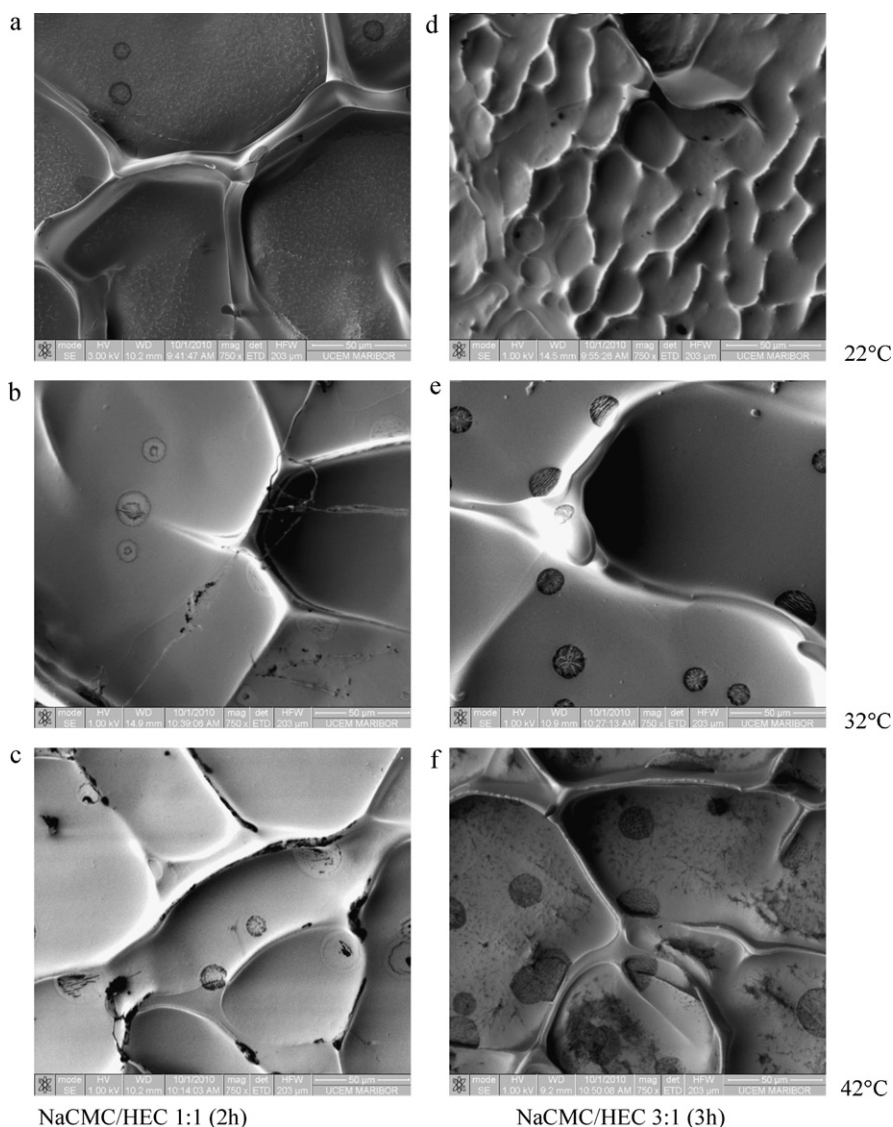


Fig. 8. SEM images of swollen (in distilled water after 3 h and at different temperatures) and lyophilised hydrogels prepared with different weight ratios of NaCMC and HEC and 5.75% (w/w) CA.

more electrostatic repulsion between COO^- groups which opened the network and increased the water uptake of the gels (Barbucci et al., 2000; Sannino, Mensitieri, & Nicolais, 2004). The synergistic effect of negative-charges and hydrogen bonds thus explains water uptake behaviour within the intermediate pH range. On the other hand, as expected, and can be seen nicely from the SD measurements of hydrogels crosslinked with higher concentration (5.75%, w/w) of CA (Fig. 7), equivalent adsorption balance occurred at gels immersed in different pH mediums, at 22 °C and 42 °C, whereas higher and equivalent SD was detected at 32 °C, which indicates the thermo-reversibility of the NaCMC polymer and the gels. The thermo-reversibility of the swelling (transition from 22 °C to 42 °C) after reaching swelling equilibrium is a bit higher in alkali than in acidic medium, and the lowest in distilled water, which again indicates on the ionization effect of the gel polymers.

3.1.3. Hydrogel's morphology

SEM analyses of hydrogel samples, swelled in distilled water at 22 °C, 32 °C and 42 °C for 3 h, was performed to identify the changing of their network morphology. Crosslinking density between polymer chains and the pore-structure formed using different hydrogel compositions are visible in the pictures presented in Fig. 8

where a more-open structure can be observed in the case of the NaCMC/HEC 3:1 sample, in which the pore-areas are the largest at 32 °C, the lowest at 22 °C, and average size at 42 °C. The NaCMC/HEC 1:1 sample also has the largest pore size at 32 °C and with similar shape and distribution, but different when compared with those at 22 °C and 42 °C; as expected, the collapse of pore-structure was obtained at 22 °C, which is due to the rigidity of the polymer chains at this temperature and which is confirmed by swelling-ability studies.

3.2. Functionalization of cotton knitwear surface with hydrogel

The main challenge of developing smart textile materials is confined to techniques for successful attachment of the hydrogel layer to the textile substrate, where coat-thickness is an important issue for preserving the original favourable properties of the substrate (textile material). However, due to the presence of a large fraction of water, hydrogels are typically quite elastic and thus very difficult to attach to the textile material's surface. Accordingly, padding and screen-printing methods were used in this research to create a hydrogel-modified cotton-knitwear surface. In this respect, hydrogel components were applied onto untreated and CA-pretreated

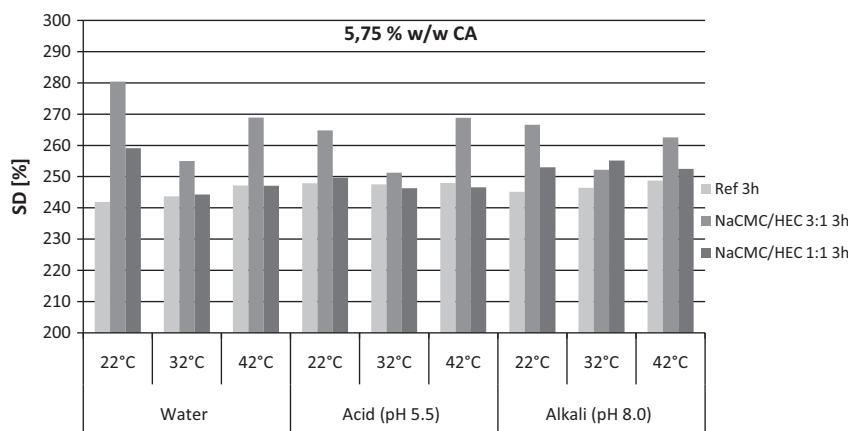


Fig. 9. Swelling degree (SD) of cotton printed three times with hydrogels prepared from NaCMC and HEC in different weight ratios and 5.75% (w/w) CA; SD was determined after 3 h of incubation of cotton samples in different mediums. Quantity of hydrogel applied: $15.49 \pm 0.3 \text{ g/m}^2$ of NaCMC/HEC 1:1 and $30.00 \pm 0.9 \text{ g/m}^2$ NaCMC/HEC 3:1, respectively.

fabrics in order to identify the gel crosslinking and covalent binding with cotton cellulose fibres.

3.2.1. Assessment of the hydrogel grafting

FTIR was used to identify the chemical binding of cotton with hydrogel. CA pretreatment (padding with CA) was also implemented in order to produce more active cities between the fibre surface and the hydrogels, i.e. to increase the number of chemical bonds to be formed between the fibre and the hydrogel, and to check whether CA pretreatment improves (or diminishes) hydrogel grafting to the cotton fibre surface and influences its functional (swelling) properties. The transmission peak at $\sim 1716 \text{ cm}^{-1}$, characteristic for the ester bonds of differently treated cotton samples, indicates a reaction of cotton hydroxyl groups with the anhydride of CA (formed during 24 h of drying at 30°C) and non-substituted hydroxyl groups of cellulose derivatives. Peak at around 1542 cm^{-1} , the characteristic assigned to the carboxylate stretching of cellulose derivate (NaCMC), appears in the case of cotton samples treated with hydrogels; its area and intensity are increased in the case of samples prepared with higher concentrations of CA in the gels. Both peaks were still present after washing, which indicates that the hydrogel is covalently bonded onto the cotton cellulose, and is resistant to washing at 40 and 60°C . In addition, the peak at about 3336 cm^{-1} corresponding to hydrogen bonds is reduced and shifts up to about 3332 cm^{-1} . The spectra also indicates that CA also crosslinks (esterifies) the hydroxyl groups of the cotton cellulose.

3.2.2. Swelling properties of cotton functionalized with hydrogel

The incorporation of hydrogel in a cotton fabric surface causes significant changes in its swelling behaviour depending on the cellulose derivatives ratio and the method used for hydrogel application. Because of the implication of hydroxyl groups for both cotton cellulose and NaCMC/HEC polymers in ester bond, crosslinking of these polymers limits the affinity of the fabric towards water, i.e. untreated cotton without incorporated hydrogel (ref) showed higher SD in water than at the control and all with hydrogel padded samples (data not show). CA pre-treatment contributes to swelling reduction due to CA-esterified cotton hydroxyl groups, and is additionally reduced when the samples are 3-times padded by hydrogels, which is indicated on the limited free volume (pores) between the fibres where the gel is located, using this deposition method. The composition of the hydrogel does not have an important effect on the swelling-degree, but the swelling is reduced at higher temperatures.

On the contrary, when the hydrogel is applied onto the cotton surface by the printing method (Fig. 9), a higher amount of hydro-

gel is applied resulting, in general, to swelling increase (compared to the control, ref) in all mediums, and distilled water, as well as acidic and alkaline environments. Swelling is importantly intensive at samples printed with NaCMC/HEC 3:1 hydrogels which are correlated with the hydrogels swelling properties (not applied on cotton) show that the increasing of NaCMC concentration increases the hydrogel swelling capacity because the greater the number of negative charges in the NaCMC magnifies the polysaccharide-chains repulsion, thus enlarging its meshes and promoting water uptake (Barbucci et al., 2000; Sannino et al., 2004). In addition, when using the NaCMC/HEC 3:1 hydrogels, the swelling of cotton is comparable when being incubated in alkaline and acidic medium, and it increases more intensively at medium temperature (32°C) which is opposite from the results obtained by hydrogels alone (not grafted on the surface). The results indicate that free hydroxyl groups of cotton cellulose and their crosslinking (intra- and/or inter-molecular with cellulose derivatives of hydrogels) importantly contribute to the pH responsiveness of the cotton substrate.

4. Conclusion

Hydrogels, synthesized from NaCMC and HEC, using citric acid (CA) as a crosslinker, were prepared in order to investigate CA reactivity with each of the polymer, using FTIR spectroscopy and to follow their mono/dual (pH and/or temperature) swelling properties in distilled water, and in alkaline and acid solutions. Both the glass-transition temperature and the optical transparency transition of hydrogel confirmed the shifting of temperature at which gel-volume transition occurs to a higher temperature value by increasing the NaCMC content and/or the degree of crosslinking. The equivalent absorption balance occurred at gels immersed at different pH mediums, at 22°C and 42°C , whereas higher or lower, but equivalent SD was detected at 32°C . It was concluded that all the degrees of substitution, molecular weight, weight ratios of both polymers included and the crosslink concentration can be properly adjusted to obtain specific formulations using gelling that will respond at the desired temperature and/or pH medium.

Application of selected stimuli-responsive hydrogels as a thin-film onto cotton knitwear in a durable and stable manner (textile pre-treatment, hydrogel's deposition, and grafting), was investigated for the production of surface-functionalized textile materials. The industrially acceptable pad-dry-cure method was used. The crosslinking of hydrogel to cotton was confirmed by FTIR studies, and the pH and temperature sensitivity of functionalized cotton fabrics was qualitatively and quantitatively investigated by water uptake studies. It has been confirmed that the

stimuli-responsive surface modifying system, imparted pH- and temperature-responsiveness to cotton fabric in terms of regulating its water uptake depending on these two stimuli.

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