



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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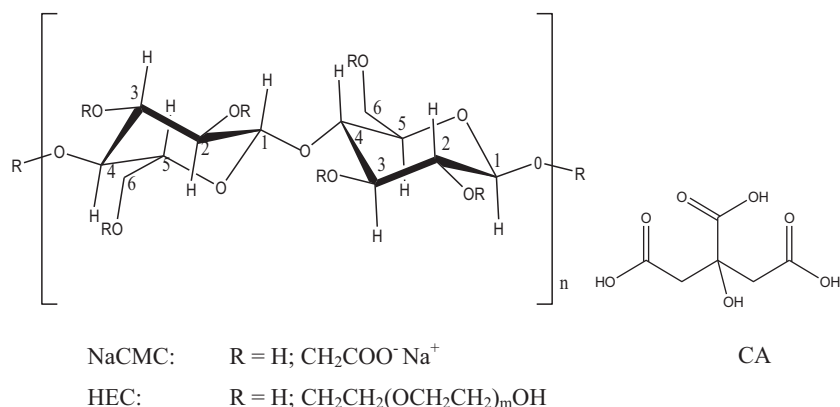


Fig. 1. Chemical structure of NaCMC, HEC and citric acid (CA).

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

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