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# Development of a biobased superabsorbent polymer from recycled cellulose for diapers applications

Clément Lacoste\*, José-Marie Lopez-Cuesta, Anne Bergeret

Centre des Matériaux des Mines d'Alès (C2MA), IMT Mines Ales, Université de Montpellier, France

## 1. Introduction

Superabsorbent polymers (SAPs) are functional materials composed of a crosslinked hydrophilic polymer in a loose three-dimensional network used in many applications such as diapers, cosmetics and absorbent pads [1]. Due to their highly crosslinked structure, SAPs possess an extraordinary capacity to absorb a large quantity of liquid, and can also retain the absorbed liquid during a long time even under compression [2].

The principal superabsorbent polymer commercially used is a crosslinked partially neutralized polyacrylic acid. The polymer is made from acrylic acid and sodium hydroxide (or sodium carbonate), which are inexpensive reagents. Although the SAPs pose no direct threat to human life or health, the disposal of synthetic SAP waste is a source of various environmental pollutants [3].

Bio-based SAPs are attractive due to their renewability and biodegradability. Among them, carboxymethyl cellulose (CMC), a water soluble and biodegradable cellulose derivative (Fig. 1), could be a good precursor for the synthesis of bio-SAP [4]. Nowadays, CMC is manufactured in significant amounts and produced by the 2-step reaction of cellulose with alkali and monochloroacetic acid (MCA), using organic solvents under heterogeneous conditions [5]. In the first step, the cellulose is treated with NaOH in the presence of inert solvent, which acts both as a swelling agent and as a diluent and thus facilitates good penetration of NaOH into the cellulose structure. The alkali cellulose is consequently accessible and reactive toward MCA, which is added to the reaction in the second step. The CMC can be neutralized and dried immediately to give a technical grade or neutralized and washed to give a purified grade and used in many industrial applications (cement, paper and coating industries, adhesives, drug delivery, tissue engineering, wound dressing) [4,6,7].

The properties (viscosity, solubility, biodegradability) of CMC are mainly depending on the degree of substitution (DS). The theoretical maximum DS that can be achieved is 3. CMC is soluble in water when DS is higher than 0.4 and the biodegradability decreased with the increase of the DS. Yeasmean and Mondal [7] have observed the increase of the DS from 0.21 to 2.41 during the carboxymethylation of corn husk cellulose particles when the particles size decreased from 1071  $\mu\text{m}$  to

74  $\mu\text{m}$  respectively. The surface area as well as the availability of the hydroxyl groups are determinant to achieve a high substituted structure. The selection of carboxymethylation conditions (temperature, time, concentration) are also essential to prepare high substituted CMC. For commercial CMC products, the most common DS value is usually between 0.4 and 1.4. Nowadays it exists considerable interest in finding cheaper and environmental-friendly alternative methods and raw materials to produce CMC. Some authors have reported the synthesis of CMC from various cellulosic sources as alternative to virgin softwood pulp. Heydarzadeh et al. [8] successfully synthesized CMC from alkali cotton fibers with DS of 0.15–0.70 and excellent purity of 99.3% recommended for pharmaceutical applications. Unlü [9] has studied the synthesis of CMC from newspaper in aqueous medium and obtained a DS of 0.3–0.7 with 84–94% CMC content. Joshi et al. [10] have pulped and deinked office waste paper with a yield measured at  $80.62 \pm 2.0\%$  to prepared CMC with a maximum DS of 1.07. Haleem et al. [5] have produced CMC from waste cotton ginning and found a maximum DS = 0.874. Mondal et al. [11] have extracted alpha-cellulose from corn husk to prepare high purity CMC with yield 2.4 g/g, DS 2.41, and water holding capacity of 5.11 g/g. Other authors like Bidgoli et al. [12] have produced CMC from cotton and viscose textiles and have obtained a DS between 0.50 and 0.86.

In the first part of this study, the production of CMC from waste cardboards and cellulose fibers was investigated, as precursor for the synthesis of a SAP.

In the recent past, the new class of hydrogels SAP has emerged based on natural derivatives such as CMC having good structure stability and biocompatibility properties [15]. However, chemically crosslinked hydrogels might exhibit cytotoxicity due to the chemical nature of the unreacted crosslinkers (i.e. aldehydes). Therefore, there is a need to promote the use of non-toxic and bio-based crosslinker through the entire process. Citric acid is a cost-effective bio-based monomer that has three carboxylic and one hydroxyl group which provides both hydrophilicity and crosslinking sites and it is also known to be non-toxic [13].

In this work, bio-SAPs were synthesized by crosslinking citric acid with carboxymethyl cellulose, derived either from cellulose fibers as reference source, or from recovered cardboard. Different particle sizes

\* Corresponding author.

E-mail address: [clement.lacoste@mines-ales.fr](mailto:clement.lacoste@mines-ales.fr) (C. Lacoste).

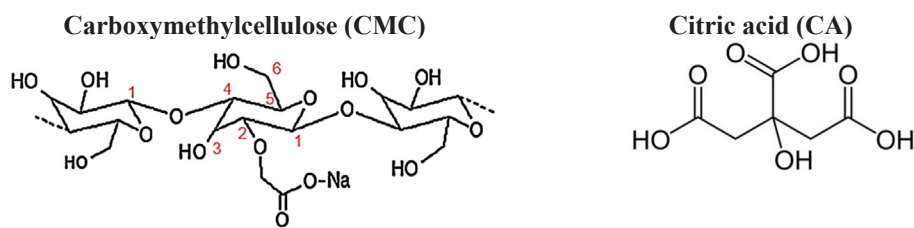


Fig. 1. Carboxymethyl cellulose (CMC) and citric acid chemical structures.

**Table 1**  
Cellulose raw material, CMC, and bio-SAP samples.

Cellulose name	Cellulose origin (median fiber size)	CMC name	Bio-SAP name	Citric acid concentration (%)
ref	Commercial	CMC_ref	SAP_ref	0 – 5 – 10 – 15 – 20
A1	Softwood (300 $\mu\text{m}$ )	CMC_A1	SAP_A1	10
A2	Softwood (23 $\mu\text{m}$ )	CMC_A2	SAP_A2	10
A3	Softwood (8 $\mu\text{m}$ )	CMC_A3	SAP_A3	10
RCC	Waste cardboard (900 $\mu\text{m}$ )	CMC_RCC	SAP_RCC	10

were used and their influence on the final properties of the bio-SAPs is described. The synthesized CMC was characterized in terms of degree of substitution, FTIR and thermal properties. The water absorption capacity of the bio-SAP was measured and the influence of the crosslinker concentration was also discussed.

## 2. Materials and methods

### 2.1. Materials

Waste cardboards were kindly supplied by a local recycling facility, PAPREC, France. All other reagents (glacial acetic acid, sodium hydroxide, monochloroacetic acid, isopropyl alcohol, ethanol, acetone, methanol, acetic acid, sodium silicate) used for cellulose extraction and carboxymethylation were analytical grades, purchased by Merck (Sigma-Aldrich), France.

Some commercial products (cellulose, CMC, and SAP) were used as reference and their properties were compared to the synthesized products of the present study. For cellulose, the fibers Arboce<sup>®</sup> (cellulose content > 99%) were provided by J. RETTENMAIER & SÖHNE, Germany. They are industrially produced from softwood pulp which contain around 45–50% of cellulose extracted through a kraft process and named A1 (fiber length = 300  $\mu\text{m}$ ), A2 (fiber length = 23  $\mu\text{m}$ ) and A3 (fiber length = 8  $\mu\text{m}$ ). Carboxymethyl cellulose (DS = 1.2; molecular weight = 250,000 Da) was provided by Merck, France. A commercial polyacrylate SAP, named HYSORB 9400, was purchased from BASF, Germany.

### 2.2. Isolation of cellulose from waste cardboards

A triple knife mill (Alpine, type 20/10R0, 1500 rpm, and granulator grid of 1 mm) was used to grind the cardboards into particles with average length of 0.9 ( $\pm$  0.2) mm. Purification of cardboards was done using alkaline peroxide treatment. A designed amount of cardboards particles were dispersed in 250 mL aqueous NaOH (20 wt%) and stirred 1 h. Then, addition of NaOH/H<sub>2</sub>O<sub>2</sub>/Na<sub>2</sub>SiO<sub>3</sub> mixture was done and stirred 2 h at room temperature. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), sodium silicate (NaSiO<sub>3</sub>) and alkaline (NaOH) concentrations were kept constant at 1% w/w, 2% w/w, and 2% w/w. The pulp obtained was filtered and washed with distilled water and dried in a fume hood at room temperature overnight. The recovered cardboard cellulose (RCC) was then dried 2 h at 60 °C and weighted.

### 2.3. Synthesis of carboxymethyl cellulose

10 g of cellulose (RCC, A1, A2 or A3) was dispersed in 100 mL

isopropanol. Isopropanol was used as solvent to provide miscibility and accessibility of the etherifying reagent to the reaction center of the cellulose chains [10]. Synthesis of CMC was carried out in a two steps-reaction: (i) alkalization followed by (ii) etherification. Alkalization was done by drop to drop addition of 20 mL aqueous NaOH (20% w/v) under continuous stirring over a period of 1 h at room temperature. Finally, predissolved monochloro acetic acid (MCA) (10 g) in 10 mL isopropanol was added to the alkali treated mass under continuous stirring. The mixture was heated at 50 °C and stirred 2 h. When reaction period was over, the pH was neutralized with glacial acetic acid and the product was filtered and washed three times with ethanol. The remaining material was dried overnight at room temperature and then 8 h at 60 °C in oven.

### 2.4. Synthesis of bio-based superabsorbent polymers

CMC (2 g) was stirred at room temperature in 100 mL distilled water until complete dissolution occurred. Then, the crosslinking agent (i.e. citric acid) was added in different amount (Table 1) and the CMC solutions were stirred continuously for 1 h. The solutions were poured into aluminum molds and were allowed to dry at room temperature for 24 h to remove water. In the sequence, the samples were cured at 80 °C in oven for 24 h for the cross linking reaction. After curing, the samples were cut with a Retsch<sup>®</sup> ZM200 grinder at 8000 rpm using a 1 mm grid.

### 2.5. Determination of CMC yield and DS

The CMC yield was calculated according to the following equation (Eq. (1)):

$$\text{Yield (\%)} = \frac{\text{weight of the dried synthesized CMC (g)}}{\text{weight of the dried initial cellulose (g)}} \times 100 \quad (1)$$

The degree of substitution (DS) is the average number of hydroxyl group in the cellulose structure which was substituted by carboxymethyl groups at C2, C3 and C6 sites. It was determined by the following method. Prepared CMC sample (4 g) was stirred in a beaker with 100 mL acetone for 5 min. 12 mL of chloric acid (6 M) was added to this solution and stirred for 30 min in order to obtain acid CMC (H-CMC). The H-CMC obtained was filtered under vacuum and the residue was washed with methanol. The residue is then stirred in acetone for 5 min, filtered, and dried at 60 °C for 2 h.

Aqueous solution of H-CMC (0.5 g) mixed with 20 mL of 0.2 M NaOH solution and 50 mL of distilled water was titrated with 0.05 M HCl by phenolphthalein indicator. To estimate the degree of substitution, following Eqs. (2) and (3) were used:

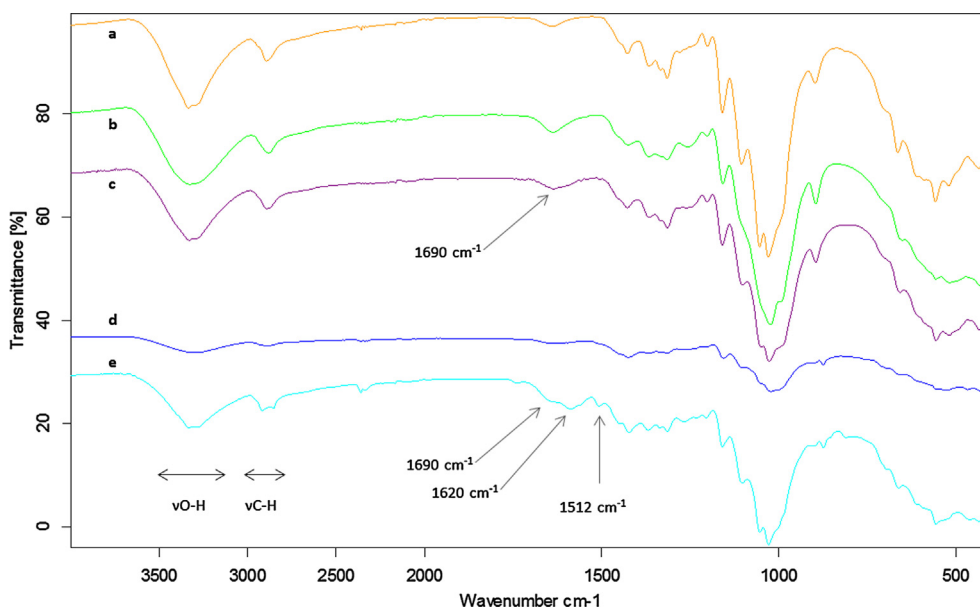


Fig. 2. FTIR spectra of cellulose fibers (a) A1, (b) A2, (c) A3, raw cardboard (d) and recovered cardboard cellulose RCC (e).

$$A = \frac{BC - DE}{F} \quad (2)$$

$$DS = \frac{0.162 \times A}{1 - (0.058 \times A)} \quad (3)$$

where A = milli-equivalents of consumed HCl per gram of specimen; B = volume of NaOH added; C = molarity of NaOH; D = volume of consumed HCl; E = molarity of HCl; F = CMC in grams; 162 Da is the molecular weight of the anhydrous glucose unit and 58 Da is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

## 2.6. Spectral and thermal characterizations

The thermal properties of the products were studied through differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier Transform infrared (FTIR) analysis. Each measurement was done in duplicate.

DSC measurements were performed on a Perkin Elmer Diamond operating under a constant flow of nitrogen ( $30 \text{ mL min}^{-1}$ ). Samples were weighed (around 15 mg) into aluminum crucibles. Analysis in comparison to a blank crucible was performed using a temperature profile (ramp rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ ) from  $0^\circ\text{C}$  to  $250^\circ\text{C}$ . Thermal transitions were calculated from Perkin software through tangent method.

Measurements of mass loss versus temperature were performed using a Perkin Elmer thermogravimetric analyzer (TGA) module Pyris 1, under  $\text{N}_2$  purge (flow rate of  $50 \text{ mL}\cdot\text{min}^{-1}$ ). Typically, 8–10 mg of sample were placed on an aluminum oxide pan, and heated from  $30^\circ\text{C}$  to  $600^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ .

FTIR spectra of sample pellets in potassium bromide (10 wt%) were recorded with a Bruker Vertex 70 spectrometer in transmission mode. The spectra were recorded in the range of  $4000\text{--}400 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$  and 32 scans per sample.

## 2.7. Absorption capacity of the bio-SAPs

SAPs particles (200 mg) were placed in a 50 mL beaker and immersed in excessive amount of distilled water or 0.9% NaCl solution for 1 h. The swollen gels were separated from the water and wiped with a filter paper to remove the excess of liquid and carefully weighted. The absorption capacity was calculated with the following equation (5):

$$Q(\text{g/g}) = \frac{m_s - m_0}{m_0} \quad (5)$$

where  $m_s$  and  $m_0$  are the swollen and dry weight of the SAP respectively.

## 2.8. Environmental scanning electron microscopy

SAPs particles were placed in a Peltier module in an environmental scanning electron microscope (ESEM) (FEI Quanta 200). The working temperature was  $5^\circ\text{C}$  and the pressure was 4.9 Torr in order to obtain a relative humidity of 90% in the working chamber. The samples were left in the chamber for 240 min and pictures were taken every minute.

## 3. Results and discussion

### 3.1. Characterization of cellulose recovered from cardboards (RCC)

In the first step, cellulose was recovered from waste cardboard by alkaline peroxide treatment. This method is used to fractionate crop wastes into cellulose, hemicellulose, and lignin [9]. Hydroperoxide anion radicals and oxygen radicals are generated in the solution from  $\text{H}_2\text{O}_2$  and NaOH. These radicals oxidize cellulose–hemicellulose and hemicellulose–lignin bonds to solubilize cell wall components and obtain recovered cellulose. Recovered cellulose was 88% by weight with respect to the starting material.

FTIR analyses were performed to characterize both cellulose fibers (A1, A2 and A3) and recovered product (RCC) (Fig. 2). The spectrum of the RCC showed typical pattern of cellulose. As a general trend common to cellulosic samples, it can be observed the broad band in the  $3700\text{--}3000 \text{ cm}^{-1}$  region assigned to  $\nu\text{O-H}$  vibrations and the peaks at  $2905 \text{ cm}^{-1}$  related to  $\nu\text{C-H}$  vibrations. The spectrum of RCC shows additional absorption bands located at  $1512 \text{ cm}^{-1}$  and in the  $1620\text{--}1690 \text{ cm}^{-1}$  region compared to cellulose fibers. These bands belong to aromatic ring vibrations of phenylpropane skeleton and non-conjugated and conjugated carbonyl group respectively [6]. The presence of these additional absorbance bands reveal the presence of small amount of lignin fragments bonded to cellulose. Complete removal of lignin was not attended in these mild conditions and could be probably achieved by stronger reaction conditions (higher temperature or alkaline peroxide concentration). As residual lignin will not interfere with carboxymethylation [9], any further purification was done and the

**Table 2**

Cellulose content, yield and degree of substitution of the CMC samples compared to literature.

Name	Cellulose content of the raw material (%)	Carboxymethylation yield (g/g)	DS	Reference
CMC_A1	45–50%	1.602	1.40 (± 0.01)	This study
CMC_A2	45–50%	1.459	1.29 (± 0.01)	This study
CMC_A3	45–50%	1.619	1.35 (± 0.40)	This study
CMC_RCC	65–70%	1.120	1.41 (± 0.14)	This study
Waste of cotton ginning	> 90%	1.437	0.87	[5]
Corn husk	35–45%	1.001–2.406	0.21–2.41	[11]
Office waste papers	75–80%	1.508	1.07	[10]

recovered cellulose was used as it is for carboxymethylation.

### 3.2. Characterization of carboxymethyl cellulose (CMC)

#### 3.2.1. Degree of substitution and yield of the carboxymethylation

The objective of the present study is to use CMC obtained from RCC as precursor for the synthesis of a SAP in water medium. The solubility of the synthesized product is then of major consideration. Mondal et al. [11] have studied the solubility of CMC and found that with DS lower than 0.4, CMC is insoluble. The reaction time (2 h) and the reaction temperature (50 °C) was then chosen in the present study to achieve a DS higher than 0.4.

The DS determination of the samples was performed using the titration method and the results are reported in Table 2. CMC\_A1, CMC\_A2 and CMC\_A3 have a DS of 1.40 (± 0.01), 1.29 (± 0.01), and 1.35 (± 0.40) respectively, whereas CMC\_RCC has a DS of 1.41 (± 0.14). No influence of the particles size on the DS was observed. The DS obtained is quite high considering the mild conditions used in the present study. Haleem et al. [5] have measured a maximum DS of 0.87 for CMC derived from cotton ginning after strong cellulose extraction (10% of H<sub>2</sub>SO<sub>4</sub> at 80 °C) and carboxymethylation with MCA at 40–60 °C for 3 h. Joshi et al. [10] have obtained a maximum DS value of 1.07 for a carboxymethylation at 50 °C for 3 h. It is possible to increase the DS by increasing the reaction temperature, time, or the NaOH concentration [11].

The yield of the carboxymethylation in the present study was measured between 1.459 g/g (A2) and 1.619 g/g (A3) for CMC samples synthesized from cellulose fibers. The yield for cellulose fibers is higher than for CMC derived from office waste papers [10] with similar synthesis conditions. For CMC\_RCC, the yield decrease at 1.120 g/g (Table 2). As the fiber length of RCC is higher (≈ 0.9 mm (± 0.2)), the kinetic of the carboxymethylation was modified. However, the comparison of the carboxymethylation yield with several studies from literature supports the suitability of arbocel fibers and RCC as sustainable sources for CMC production.

#### 3.2.2. FTIR analysis

The infrared spectra of synthesized CMC from A1, A2, A3, and RCC are shown in Fig. 3. The broad absorption band at 3335 cm<sup>-1</sup> belongs to the stretching frequency of the OH group and the band at 2890 cm<sup>-1</sup> is due to C-H stretching vibration. After carboxymethylation, hydroxyl groups of CMC\_A1 are still present in a significant amount compared to the other samples. The high specific surface area of A1 fibers (length = 300 μm) can reduce the accessibility of the reactive sites. For CMC\_RCC, the quantity of hydroxyl groups is clearly reduced after the reaction. However, the presence of a strong absorption band at 1620 cm<sup>-1</sup> confirms the presence of asymmetric elongation of carboxyl groups and the band at 1425 cm<sup>-1</sup> is attributed to carboxyl groups as salt. These bands were also found on the spectra of the other samples but the intensity for CMC\_A1 was lower. As the carboxymethylation took place in basic medium, CMC samples were in sodium salt form (–COO<sup>-</sup>Na<sup>+</sup>) rather than in acid form (–COOH). The acid form was indeed not detected in the sample due to the absence of the characteristic bands usually observed at 1715–1730 cm<sup>-1</sup>. FTIR analyses

proved that carboxymethylation reaction was performed successfully for the samples.

#### 3.2.3. Thermal stability

The results of the TGA analysis are given in Table 3. It can be seen that the degradation temperature of the cellulosic samples are between 349 °C (A3) and 361 °C (RCC). The recovered cellulose from cardboards (RCC) is slightly more stable than the others fibers samples. It can be due to the presence of lignin fragments as seen previously. Lignin is more resistant to thermal degradation than cellulose and its thermal degradation is observed on the curves in Fig. 4. The char content is also higher for this sample resulting also from the lack purity and the presence of mineral charges usually observed in cardboards (≈ 12%) [14].

CMC samples have a lower thermal stability with a decomposition temperature measured between 294 °C (CMC\_A2) and 314 °C (CMC\_RCC). One time more the higher thermal stability of CMC\_RCC could be due to lignin. The pyrolysis of hemicellulose and cellulose occurs quickly with a weight loss from 220 to 315 °C for hemicellulose and from 315 to 400 °C for cellulose. Lignin decomposes over a wider range of temperature (from 160 to 900 °C) and generates a high char yield [15]. However, the quantity of char at 900 °C is huge higher than those of cellulose fibers and similar char content values (≈ 30%) were observed for all CMC samples. The decrease of the decomposition temperature indicates a lower thermal stability of the CMC samples compared to cellulose. But the chemical grafting of carboxyl methyl groups on cellulose backbone induce the formation of a stable char. Many authors have reported a similar phenomenon after the chemical grafting on natural polymers [16].

### 3.3. Characterization of the bio-SAPs

#### 3.3.1. DSC

SAP\_ref were prepared with varying amount of crosslinker from 5% to 20% (Table 1) and DSC curves are presented in Fig. 5. Two glass transition temperatures were observed by DSC. The results are given in Table 4. The addition of citric acid from 5% to 20% slightly increases the T<sub>g1</sub> from 52.8 °C to 64.9 °C respectively. A glass transition temperature was clearly observed for SAP\_ref containing 5% and 10% of CA located at 120.9 °C and 115.1 °C respectively indicating the crosslinking reaction between carboxyl groups of CMC and citric acid. At a concentration of CA 15%, the intensity of the second transition decreases (Table 4) and reaches ΔH = 0.35 J/g.°C, and finally no transition was observed for SAP\_ref with CA 20%. These DSC results indicate that for a concentration of CA of 5%, 10%, and 15%, CMC is partially crosslinked with citric acid but for a concentration of 20% of CA, the network is completely crosslinked. In Fig. 5(b) no transition was observed and all samples are completely crosslinked during the second run. This result also indicates that the curing temperature during the synthesis of the SAP should be selected carefully. The temperature chosen in this work was 80 °C and was convenient.

#### 3.3.2. Gel swelling

Gel swelling characterizations were performed in distilled water as the swelling media. Fig. 6a shows the absorption capacity (Q) of

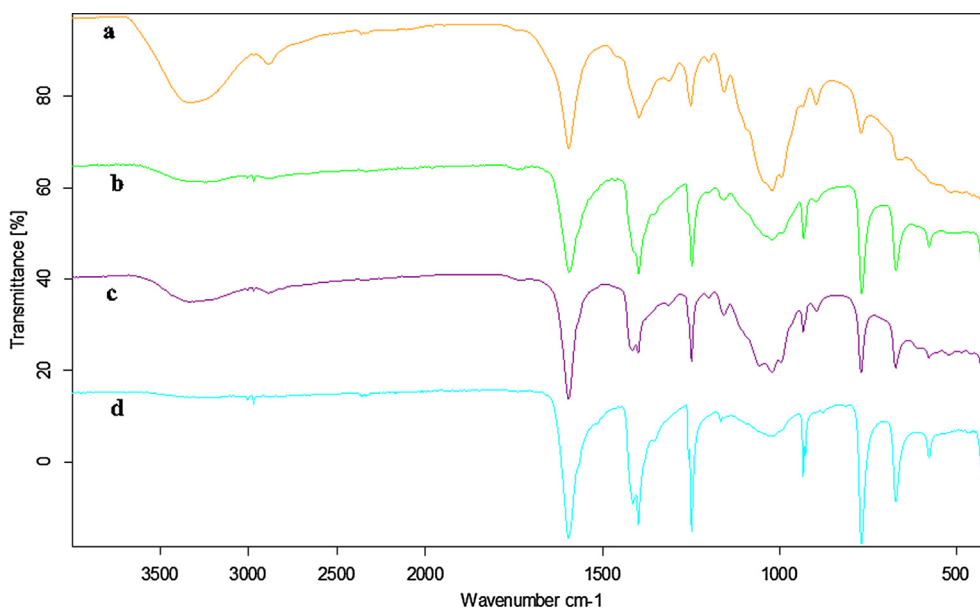


Fig. 3. FTIR spectra of the carboxymethyl cellulose samples (a) CMC\_A1, (b) CMC\_A2, (c) CMC\_A3, (d) CMC\_RCC.

**Table 3**  
Results of the TGA analysis for the cellulose and CMC samples.

	Decomposition Temperature (°C)	Char <sub>900°C</sub> (%)
<i>Cellulose samples</i>		
A1	356 °C	10.2
A2	350 °C	8.8
A3	349 °C	3.2
RCC	361 °C	17.1
<i>Carboxymethylcellulose samples</i>		
CMC_A1	312 °C	29.4
CMC_A2	294 °C	32.9
CMC_A3	298 °C	28.9
CMC_RCC	314 °C	29.5

SAP\_ref as a function of the citric acid (CA) concentration. It can be observed that without crosslinker, the Q was only 2.5 g/g and at low crosslinker concentration (i.e. 5%), the absorption increased up to 32.9 g/g showing the production of a superabsorbent hydrogel. The presence of hydroxylate groups, as negatively charge groups, allowed

the formation of the gel. The polymer is swelling up to a maximum absorption corresponding to a CA concentration of 10%. But the concentration of hydroxylate groups is progressively reduced with the addition of the acid. A decrease of the swelling capacity was observed at higher crosslinker concentrations (> 10%), which evidence the formation of a rigid polymer network with a slow motion. It limits the polymer chains elongation which is a necessary condition of the volume change. The expansion is then limited by the crosslinking density.

It is known that absorption capacities of SAPs depend on the pH and the salt concentration of the solution [13,17,18]. This specificity is due to the presence of ionic charges spaced along the polymer chains (carboxylate groups) that are strongly solvated in the presence of water solution. If ionic components are present in the liquid to be absorbed, ion exchange may occur and alter the absorbancy of the liquid. However, saline absorption is an important characteristic of a SAP considering it simulates urine. The results showing the water and saline absorption capacities of SAP\_ref as a function of the crosslinker concentration is shown in Fig. 6a. The saline absorption capacity is as expected lower than for water, and the mean value was found to be

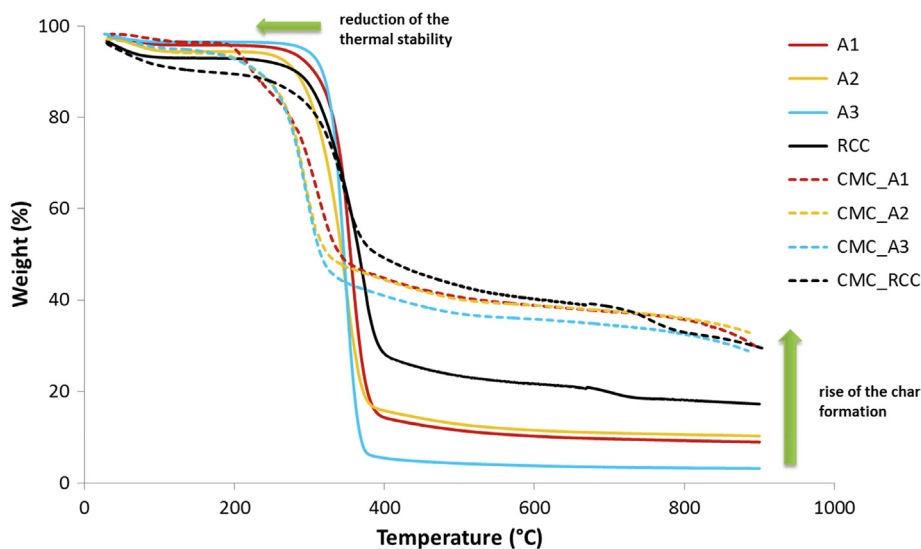


Fig. 4. Evolution of the weight of all cellulose and CMC samples as a function of the temperature.

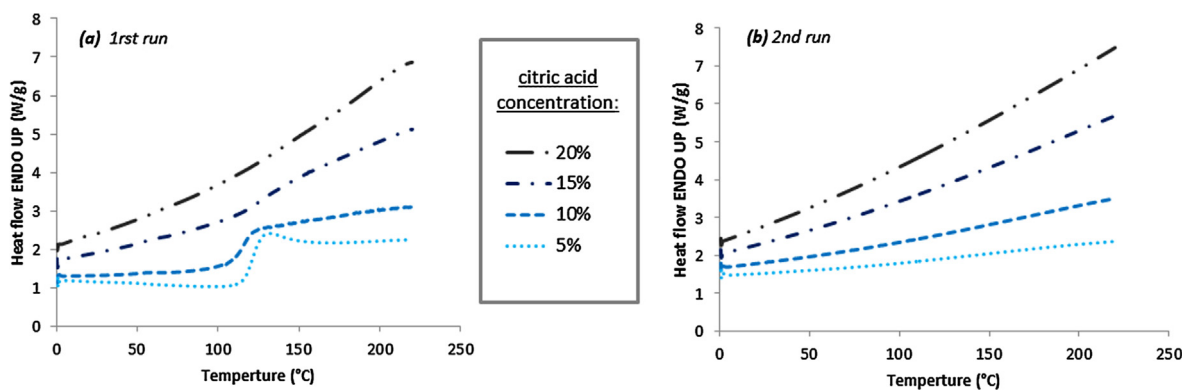


Fig. 5. DSC curves of SAP\_ref containing different quantity of citric acid (a) first and (b) second run.

**Table 4**  
Results of the DSC analysis of SAP\_ref with varying citric acid concentration.

Sample	Citric acid (%)	T <sub>g1</sub> (°C)	ΔH (T <sub>g1</sub> ) (J/g·°C)	T <sub>g2</sub> (°C)	ΔH(T <sub>g2</sub> ) (J/g·°C)
SAP_ref	5	52.8	0.05	120.9	5.64
	10	54.5	0.06	115.1	2.04
	15	63.6	0.10	123.8	0.35
	20	64.9	0.08	–	–

7.45 g/g. The maximum value was 9.03 g/g for CA 5%. No significant influence of the concentration was observed. However, it can be noticed that the saline absorbency value is only 6 times lower than the water absorbency. Such deviation has already been observed in literature for polysaccharides derived hydrogels [17].

In Fig. 6b, the absorption capacity of SAP\_A1, SAP\_A2, SAP\_A3 and SAP\_RCC crosslinked with 10 wt% of citric acid is shown. The absorbency of the SAP\_RCC was 31.5 g/g. The particles size of the raw material seems to influence the absorbency of the final SAP product. Indeed, the water absorption capacities of the SAP\_A1, SAP\_A2, and SAP\_A3 were found to be 33.8 g/g, 36.0 g/g and 38.4 g/g respectively, whereas the particle sizes of these products were 300 μm, 23 μm, and 8 μm respectively. The highest water absorbency was 45.87 g/g measured for SAP\_ref. SAP\_RCC shows a good absorption capacity in comparison with SAP\_ref and confirmed the successful synthesis of a SAP from waste cardboards.

### 3.3.3. ESEM observation

ESEM pictures (Fig. 7) of the SAP\_ref in comparison with a commercial polyacrylate SAP (Hysorb) were taken after 240 min exposition in a Peltier chamber regulated at 90% of relative humidity (RH). In

Fig. 7(A) and (C), both SAP particles have not yet absorb the ambient humidity. The edges of the polyhedron particles were clearly observed as the particle is still dried. After 240 min at 90% RH, the volume enhancement of the particles was perceived corresponding to the penetration of the water molecules into the polymer chains leading to a swollen hydrogel. The phenomenon was more evident on the commercial product which has a water absorption capacity of 300 g/g. The bio-SAP obtained from carboxymethyl cellulose and crosslinked with citric acid appeared as a swelling hydrogel.

## 4. Conclusion

Cellulose was successfully recovered from waste cardboards under mild oxidizing alkaline conditions with a yield of 0.88. FTIR analyses indicate the presence of some residual lignin fragments bonded to the recovered cellulose which slightly increase the thermal stability of the product. However, the presence of residual lignin fragments does not interfere with the carboxymethylation. The degree of substitution was found to be around 1.4 for all samples without any influence of the cellulose source. The carboxymethylation yield was found to be 1.12 g/g and with range 1.46–1.60 g/g for the cellulose recovered from cardboard material and from micrometric cellulose fibers respectively, which confirms the sustainability for industrial production. The results demonstrated that bio-SAPs crosslinked with citric acid were produced. SEM analysis evidenced the formation of the hydrogel. The water absorption capacity was depending on the crosslinker concentration (optimum at 10 wt%) with a maximum measured at 45.87 g/g. The saline solution swelling capacity was 7.45 g/g on average without any significant influence of the crosslinker concentration. The complete production of a bio-SAP was successfully developed from recovered cellulose and could be a promising material for many industrial

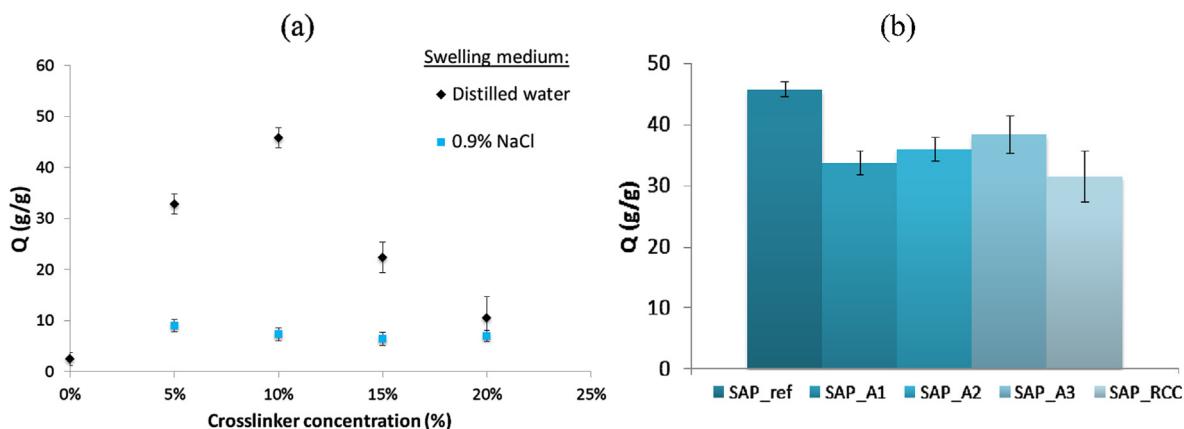


Fig. 6. Water and saline absorption capacity  $Q$  (g/g) of (a) SAP\_ref as a function of the citric acid concentration and (b) water absorption capacity of all SAPs crosslinked with 10% of citric acid.

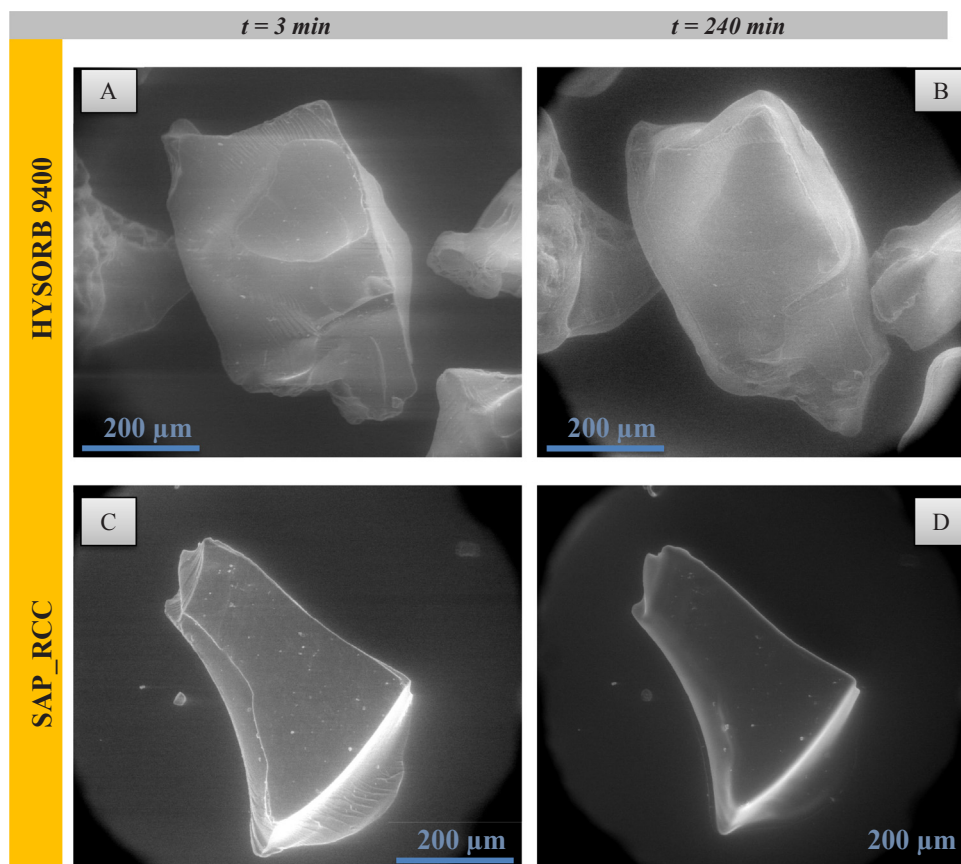


Fig. 7. SEM pictures of Hysob 9400 after (A) 3 min and (B) 240 min; and SAP\_RCC after (C) 3 min and (D) 240 min, at 90% of relative humidity.

applications.

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