ABSTRACT

The main aims of this work were to determine morphological and thermomechanical properties of films of sodium carboxymethylcellulose (NaCMC). Films prepared with Nikacell (crude grade) present formation of opaque and semi-transparent regions due to a combined effect of NaCl layer formation and entanglement of cellulosic fibers fragments. After elimination of NaCl by precipitation of acid CMC form, the films are slightly opaque when compared to films prepared with Fluka (analytical grade) because of entanglement of fibers fragments not eliminated during precipitation and filtration procedures. NaCMC films show tree step degradation on TGA curves and initial weight loss of 12%. DMA show that NaCl not impacts the Tm of NaCMC at 240ºC. However, NaCl has a remarkable impact on relaxations closed to Tg. CMC films prepared from analytical and purified grades present Tg values at 40ºC and CMC films from crude grade show a remarkable broadening and displacement of this transition.

KEYWORDS: CMC, by-products, Tm, Tg, thermo mechanical properties

INTRODUCTION

Carboxymethylcellulose (CMC) is the most widely used water-soluble cellulose derivative. (1-3) It is prepared from the cellulose macromolecules by the reaction between cellulose and monochloroacetate (or monochloroacetic acid), thus yielding a partial substitution of the hydroxyl groups at the 2, 3 and/or 6 positions in the cellulose structure by carboxymethyl groups. For a long time, NaCMC has been applied such as stabilizer and protective colloids in detergents, in paper coatings and pharmaceuticals,
in cosmetics and food industries. But today, there is an increasing demand for environmentally friendly products, which are renewable and biodegradable. More recently, cellulose derivatives and among them NaCMC are studied to produce new bio-based materials with tailored properties such as composites, films and membranes or fibers obtained by electrospinning process. In this context, the main objective of this work is to provide an accurate characterization of the morphological, thermal and mechanical properties of NaCMC films considering both: i) a crude grade (Niklacell NaCMC), and ii) an analytical grade homologue (Fluka NaCMC) aiming their applications in biomedicine areas. Figure 1 depicts CMC structure. Different degrees of substitution (DS) can be obtained depending of the modification route and the raw materials used, but generally DS values vary between 0.6 and 0.95 from the usual heterogeneous reaction. It is known that during the first step of the carboxymethylation reaction, i.e., formation of alkali cellulose, low molar mass components may be extracted of the cellulosic fibers. These components which are mainly oligosaccharides also undergo carboxymethylation and play a role on the physico-chemical properties of NaCMC. Depending of the NaCMC grade, reaction by-products such as NaCl may be or not removed by further industrial purification steps.

**Fig. 1:** NaCMC molecular structure.

**EXPERIMENTAL**

A) Preparation and optical characterization of Niklacell (crude grade) and Fluka (analytical grade) NaCMC solutions: 1% NaCMC solutions were prepared by dissolving the powder in distilled water at 25°C for 24 h using a magnetic stirrer with Teflon rod. NaCMC solutions were observed with an optical microscope (Axio Imager Min) between
glass thin plates. **B) Purification of Niklacell NaCMC:** A purification of this crude grade was carried out by acidifying 1% Niklacell NaCMC solution with HCl close to a pH of 2 under moderated magnetic stirring. After, 1 L of ethanol was added and the solution left to rest for 30 min. The insoluble acid Niklacell CMC form was then filtered on Whatman paper (grade 4), and washed several times with distilled water until reaching neutral pH. Due to its water insolubility and formation of aggregates not soluble in hot water (at 80°C) and even under vigorous magnetic stirring, the acid CMC form was re-solubilized using an ultra-sound treatment at 80°C for 1 h and at pH of 10 continuously adjusted with NaOH reforming the soluble NaCMC salt form. Finally, purified Niklacell NaCMC form was dried in an oven (at 60°C for 24 h). **C) Preparation of NaCMC films:** 1% NaCMC aqueous solutions were prepared by dissolving analytical and crude NaCMC powders in distilled water at 25°C for 24 h using a magnetic stirrer with a Teflon rod. CMC films were casted in Teflon moulds (diameter 5 cm) under controlled conditions (25°C and 50% RH). **D) Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS):** An environmental scanning electron microscope (Quanta 200) was used to examine representative regions of surface and cross-section of NaCMC films. Samples were conditioned in desiccators and coated with gold under vacuum (Emitech K550x) before analyses. X-ray microanalysis was carried out with X-Flash 5010 detector. **E) Dynamic Mechanical Analyses:** DMA of NaCMC films (10 x 5 mm²) were carried out using a Rheometric System Analyzer III (TA Instruments) on tension mode at 1 Hz scanning frequency and with a 5°C.min⁻¹ heating rate. Nitrogen flow was used during analyses. The glass transition temperature (Tg) was determined as the temperature on the peak of loss tangent curves (Tan δ).

**RESULT AND DISCUSSIONS**

Fluka and Niklacell NaCMC solutions were observed by optical microscopy (see Figure 2). Micrographs show residual fibers apparently partially carboxymethylated and unmodified fibers. Cellulosic fibers differ on terms of their crystalline content, size and orientation, as well as in the amorphous domains, size and shape of voids, and number of inter-fibrillar lateral tie molecules. These properties have influences on the accessibility of monochloroacetate in the cellulose structure during NaCMC synthesis. Monochloroacetate penetrates more easily in the amorphous domains giving rise to the
formation of modified and/or partially modified phases within the cell wall of cellulosic fibers. After contact with water, more and less swollen regions alternate along the main axis of the carboxymethylated fibers. As observed on the micrographs, modified domains of the fibers structure swell on a great extent. Unmodified and/or slightly modified domains do not swell as much, which gives rise to the formation of small rings along remaining fibers. To the best of our knowledge these structures are described for the first time.

**Fig. 2:** Micrographs obtained by optical microscopy for 1% (A) Niklacell and (B) Fluka NaCMC solutions.

Films prepared with Fluka NaCMC solution (analytical grade) are flexible and transparent, and easily removed of Teflon mould without breaking whereas those prepared from Niklacell NaCMC solution (crude grade) are more brittle (although without visual cracks), and visually heterogeneous showing formation of two domains: i.) an opaque and ii.) a semi-transparent region. Samples of NaCMC films were analyzed to explain morphological differences: i.) film of Fluka NaCMC (CMC-fF); ii.) opaque region of Niklacell NaCMC film (CMC-fNo); iii.) semi-transparent region of Niklacell NaCMC film (CMC-fNt); and vi.) film of purified Niklacell NaCMC (CMC-fNp). Figures 3.A and B show micrographs of **CMC-fNo** obtained by SEM analyses of surface and cross-section, respectively. Salts are present on the film surface whereas cross-section displays phase segregation. During films preparation in Teflon moulds by casting we have two surfaces formed, namely: the upper side (on closed contact with atmosphere of environmental chamber) and the bottom side (on closed contact with surface of Teflon mould). The observed upper surface of the film on the cross-section micrograph (Figure 3.A) was in contact with Teflon mould during film preparation (bottom side). Due to water elimination of Niklacell NaCMC solution, salts precipitated and deposited on the mould surface. The observed lower surface of the film on the micrograph (Figure 3.B)
was in contact with the atmosphere of the environmental chamber (upper side). X-ray microanalysis shows that the bottom side is rich in Na and Cl atoms, whereas the upper side of the film contains mostly C, O, Na and Cl atoms. Thus, we can affirm presence of NaCl in Niklacell NaCMC mainly on the film surface on closed contact with the mould surface (bottom side). During casting of the films, there is a segregation of at least two phases: a rich NaCl layer and a mixture Niklacell NaCMC/NaCl layer. CMC-fNt showed closed behavior.

![Fig. 3: Micrographs obtained by SEM analyses of CMC-fNo A and B) surface on close contact with the Teflon mould (bottom side) during film preparation and cross-section, respectively; C and D) surface of CMC-fNp on close contact with the environmental chamber (upper side) and on close contact with the Teflon mould (bottom side), respectively, and E) cross-section of CMC-fNp; F) cross-section of films prepared with Fluka NaCMC (CMC-fF).](image)

Figures 3.C, D and E present micrographs obtained by SEM of CMC-fNp (film of purified Niklacell NaCMC) of both surfaces (upper and bottom sides), and cross-section, respectively. The surface which was in contact with the Teflon mould (bottom side: Figure 3.D) shows a network of entangled fibers which is not present at the surface in contact with the atmosphere of the environmental chamber (upper side: Figure 3.C). Cross-section micrograph (Figure 3.E) also shows fibers, but not clearly formation of
salt layers. X-ray microanalyses confirm presence of C, O and Na atoms as the major components on both sides (upper and bottom). These micrographs and EDS analyses demonstrate that purification procedure used in this work allowed to remove NaCl but did not allow remove cellulosic fibers residues. Figure 3.F presents cross-section micrograph of CMC-fF (analytical grade). As expected, Fluka NaCMC films appear to be homogeneous and it is not possible to observe presence of salt layers and/or segregation of phases. X-ray microanalysis shows that C, O and Na are the major elements forming NaCMC structure and confirms the degree of purity of this chemical.

In order to determine the effects of by-products on thermal mechanical properties of NaCMC films we used dynamic mechanical analyses (DMA). Figure 4.A and B shows storage modulus ($E'$) and loss tangent (Tan δ) curves for CMC-fF and CMC-fNp, respectively.

**Fig. 4:** Storage modulus ($E'$) and loss tangent (Tan δ) curves obtained by DMA analyses of: A) CMC-fF, B) CMC-fNp, C) CMC-fNt and D) CMC-fNo.
CMC-fF shows a higher E’ in the temperature range studied when compared with CMC-fNp probably because of its analytical grade. CMC-fF presents two relaxations on Tan δ curve: i) at ca. 38°C attributed to $T_g$ (10); and ii) at 260°C attributed to $T_m$. An endothermic transition observed on DSC curves at this temperature range supports this assignment even if the films break down under stress during DMA after $T_m$ because of its degradation. CMC-fNp presents three relaxations: i) at ca. 40°C attributed to $T_g$; ii) at 240°C attributed to $T_m$; and iii) between 90 and 120°C attributed to the effects of water elimination on the thermo mechanical properties of the film. When observing E’ curve of CMC-fNp there is an increase of E’ between 90 and 120°C. Generally, the E’ decreases when the temperature increases. Probably, because of water elimination, there is a cooperative segmental mobility in the amorphous phase of neighboring regions and the polymer chains can be on more closed contact increasing interactions between the chains (hydrogen bonds and Van der Waals forces) which restrict polymer chain motions and increasing E’. Here again, the effects of water elimination was not observed for CMC-fF probably because of the high purity of this chemical (low content in NaCl) and its low moisture content. CMC-fNt and CMC-fNo (Figure 4.C and D, respectively) present two relaxations on Tan δ curves: i.) a relaxation between 50 and 100°C and between 50 and 170°C for CMC-fNt and CMC-fNo, respectively. These transitions are attributed to $T_g$ and water elimination effects. The broadening of $T_g$ of CMC-fNt and CMC-fNo when compared to CMC-fF and CMC-fNp is probably due to the highest amount of NaCl (and consequently a higher amount of moisture content) which forms a layer as observed by SEM analyses restricting NaCMC chain motions in amorphous regions; and ii.) a relaxation at around 240 and 250°C for CMC-fNt and CMC-fNo samples, respectively, attributed to $T_m$ of the crystalline regions of NaCMC structure. Based on the results, we can conclude that the presence of NaCl or a NaCl layer in the morphology of NaCMC films has a considerable impact only on $T_g$ and thermodynamic transitions closed to $T_g$.

**CONCLUSIONS**

In this work we studied the impacts of by-products, as NaCl and partially carboxymethylated cellulosic fibers, on morphological and thermal (data not showed), and thermomechanical properties of NaCMC films. The combined effect of NaCl layer
formation and entanglement of cellulosic fibers fragments in the crude NaCMC grade films is responsible by its semi-transparence. For Niklacell NaCMC samples, there was segregation of NaCl and NaCMC phases during film preparation as observed by SEM and EDS. NaCl and residual cellulosic fibres did not impact the relaxations closed to Tm. However, these by-products impact remarkably the Tg values and the thermomechanical properties and relaxations closed to Tg.

ACKNOWLEDGEMENTS

We would like to thanks to ANR (French National Research Agency) and CNPq (Process 200626/2013-2).

REFERENCES


