Research Article

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# Influence of cellulose fibers on physicochemical properties of biodegradable films based on polysaccharide derivatives

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**Abstract:** The article presents a method of obtaining films based on carboxymethyl polysaccharide derivatives cross-linked with citric acid and reinforced with cellulose fibers (CFs). The addition of CFs to a film improves the mechanical properties of the composite. With the increase of filler content, the water solubility drops from 64 to 61%, respectively, for a system without a filler and that containing 7 wt% CFs, whereas Young's modulus increases from 4.8 to 24.8 MPa for a film containing 5 wt% filler.

**Keywords:** carboxymethyl starch, carboxymethyl cellulose, cellulose fibers, natural composite, biodegradable film

## 1 Introduction

The etherification of starch to a carboxymethyl derivative allows obtaining a polymer soluble in cold water. For carboxymethyl starch (CMS), factors such as dissolution rate and viscosity of aqueous solutions primarily determine the degree of substitution (DS, average number of substituted hydroxyl groups in a starch repeating unit) and molecular weight (Spychaj et al. 2013).

Among the carboxymethylated polysaccharides, most often carboxymethyl cellulose (CMC) is used to obtain films (Tharanathan 2003; Ghanbarzadeh and Almasi 2011). CMS and CMC are prepared from biodegradable and biorenewable polymers. CMS is a carboxymethyl derivative cheaper than CMC. This is due to the need for cellulose modification using environmentally noxious organic solvents and higher raw material prices. Therefore, the use of CMS seems to be more favorable in terms of the environment (Wilpiszewska et al. 2015). Starch, which is a renewable, relatively cheap and easily modifiable natural polymer, seems to be a promising raw material for the production of biodegradable films (Arcanitoyannis et al. 1996; Koo et al. 2010; Hassan et al. 2018). There are no reports in the literature on obtaining CMC/CMS-based films by casting (except for the authors' publications). However, such systems are very interesting. Moreover, they exhibit hydrophilic character, which could be beneficial, e.g., in agriculture or the pharmaceutical industry.

Cellulose fibers (CFs) (about 100 μm long) cleaned and separated from other substances (e.g., lignin) exhibit good chemical resistance and good mechanical properties as well as a relatively low price (Ma et al. 2011). Chemical and physical modifications carried out on CFs are aimed at increasing their adhesion to polymer matrices, which allows improving the mechanical properties of the composite (Mohmamed et al. 2010). Unmodified CFs are used in the textile, construction and paper industries (Tharanathan 2003). CFs have been used in the production of membranes for ship water treatment and industrial treatment as well as biodegradable reinforcements in composites. The addition of CFs to cement materials reduces plastic shrinkage, tendency to crack and increases the mechanical strength of concrete (Ma et al. 2011).

In this article, the influence of CF filler content on the physicochemical properties of a CMS/CMC based film has been determined. A natural composite based on two polysaccharides, CMS and CMC (with citric acid [CA] as the crosslinking agent), reinforced with CFs was obtained.

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# 2 Experimental

## 2.1 Materials

CMS was prepared according to the method reported by Spychaj, Zdanowicz, Kujawa and Schmidt (Spychaj et al. 2013). For that purpose, potato starch (Nowamyl S.A., Poland), sodium hydroxide (POCH, Poland), chloroacetic acid (tech.) and 2-propanol (tech.) (Chempur, Poland) were used.

A biodegradable film was prepared by using the obtained CMS, CMC (DS: 0.7, Pollocel AS-2/90) from Pronicel Sp. o.o. (Poland), monohydrate CA (p.a.), plasticizer – glycerol (p.a.) (both from Chempur, Poland) and CFs (tech.) (Arbocel Type UFC 100, Germany) from J. Rettenmaier & Sohne.

## 2.2 CMS preparation

The synthesis using a one-step method was carried out to obtain CMS with a DS of 0.70. According to this method, in a glass reactor, monochloroacetic acid and isopropanol were placed (first, the medium was saturated with nitrogen, and then the acid was neutralized with an aqueous solution of sodium hydroxide in a molar ratio of 1:1). Once the reactor content color turned milky white, the system was stirred for 10 min (200 rpm), and subsequently starch and hydroxide were added. The mixture was stirred for 2.5 h at 50°C, leading to the solution neutralization to pH 6. The product was filtered under reduced pressure and washed five times with 80% methanol solution, and lastly with undiluted methanol (Spychaj et al. 2013).

## 2.3 Preparation of the CMS/CMC film with CFs

To obtain an aqueous dispersion of CFs, 100 g of water and 1, 3, 5 or 7 wt% of CFs based on the dry weight of the mixture of CMS and CMC were added to a reactor; the system was stirred for 30 min. Then 2 g of glycerin and 2 g of CA were added to the system and stirred for dissolution, after which the mixture of CMS and CMC (1:1 by weight) was added and mixed until homogeneity. In the next step, the system was poured into PTFE molds and placed in a dryer for 48 h at 60°C. The film thus obtained (200–300 μm thick) was removed from the mold.

## 2.4 Measurement

### 2.4.1 Water solubility test

Three samples (1.5 cm × 1.5 cm) were cut from the film and placed in a desiccator to remove moisture (to constant mass). The samples were then weighed, placed in vials and filled with 50 mL of distilled water. After 24 h, the samples were removed and dried for about 24 h (60°C) to constant mass. The dry samples were again weighed. The solubility in water values was calculated using the following formula (Almasi et al. 2010; Basch et al. 2011; Wilpiszewska et al. 2015):

$$\mathrm{TSM} = [(M_1 - M_2)/M_1] \times 100\%,$$

where TSM (Total Soluble Matter) – solubility in water (%); $M_1$ – mass of the dry sample (g); $M_2$ – mass of the sample after drying (g).

## 2.5 Moisture sorption test

Three samples (1.5 cm × 1.5 cm) were cut from the film and placed in a desiccator to remove moisture (to constant mass). In the next stage, the samples were weighed and placed in a climate chamber (humidity 55 ± 2%, temperature 25 ± 2°C). The weight was measured after 3, 5, 7, 24, 48 and 72 h in the chamber. The results obtained in this way were substituted in the following formula (Almasi et al. 2010):

$$A_t = [(M_t - M_0)/M_0] \times 100\%,$$

where $A_t$ – sorption of moisture after time $t$ (%); $M_0$ – mass of the dry sample (g); $M_t$ – sample mass after $t$ time: 3, 5, 7, 24, 48 and 72 h (g).

## 2.6 Mechanical property test

An INSTRON testing machine was used to test the tensile strength of the films. Initially, the sample was 50 mm long, 10 mm wide and about 0.2 mm thick. The speed of the mobile clamp was 10 mm/min. The samples were conditioned at room temperature and 55% RH for 24 h before the mechanical test. Seven samples of one material type were tested (Roy et al. 2012).

## 2.7 Dynamic mechanical thermal analysis (DMTA)

Thermal analysis was carried out using a DMTA Q800 (TA Instruments) apparatus in the temperature range

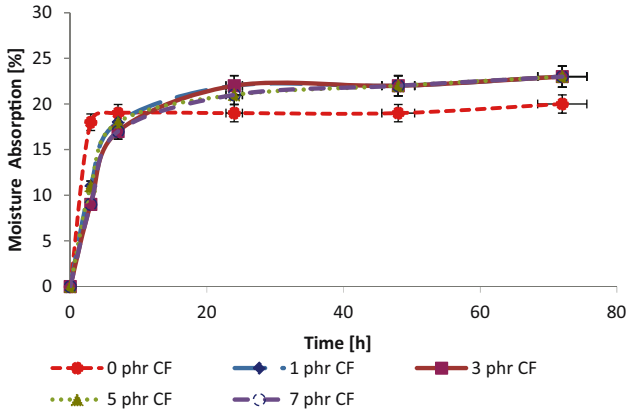


**Figure 1:** Influence of CF content on moisture sorption of CMS/CMC-based composites.

from −30 to 180°C with a heating rate of 3°C/min and an amplitude of 15 nm (Wilpiszewska et al. 2015).

## 3 Results and discussion

In Figure 1, the effect of CF content in the CMS/CMC natural composites on moisture sorption is shown. Introducing CFs resulted in a slight moisture absorption increase when compared to the unfilled system. Interestingly, after 72 h, the value of this parameter was similar for the systems with various filler contents (moisture absorption ca. 23%). The difference between the neat CMS/CMC film and a filled one (~3%) could be the result of intermolecular interaction between polysaccharide derivatives and CF macromolecules giving a more dense structure, which is analogous to microcrystalline cellulose (MCC) filled films (Antosik and Wilpiszewska 2018).

In Figure 2, the solubility in water of CMS/CMC composites with various CF contents is presented. With the CF filler content increase, the solubility of the system in water decreased, from 64% to 61%, respectively, for the unfilled system and that with 7 wt% CFs. Between the carboxylic groups of carboxymethylated starch and cellulose as well as CA, strong hydrogen bonds can be formed. They can interact with the CFs resulting in a structure with increased crosslinking density and, as a result, reduced water solubility of the film. A similar reduction of water solubility was observed for a composite with MCC (Antosik and Wilpiszewska 2018).

In Table 1 and Figure 3, Young's modulus, tensile strength and elongation-at-break properties of natural composites based on CMS/CMC with different CF contents are shown. Along with the increase in the content of the

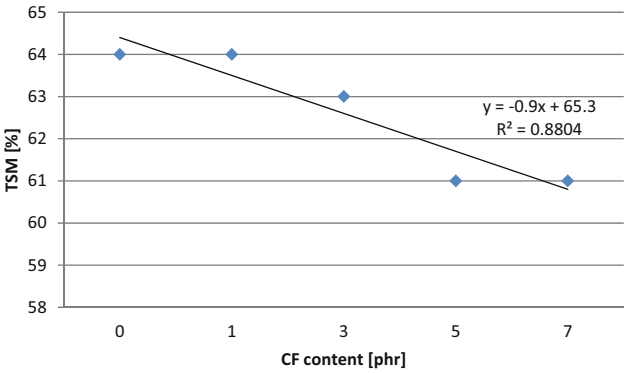


**Figure 2:** Influence of CFs on solubility in water of CMS/CMC-based composites.

**Table 1:** Influence of CF content on elongation at break and Young's modulus of CMS/CMC-based composites

| CF content (phr) | Elongation at break (%) | Young's modulus (MPa) |
|---|---|---|
| 0 | 29 ± 0.5 | 4.8 ± 0.1 |
| 1 | 33 ± 0.5 | 15.9 ± 0.1 |
| 3 | 36 ± 0.5 | 24.1 ± 0.1 |
| 5 | 31 ± 0.5 | 24.8 ± 0.1 |
| 7 | 29 ± 0.5 | 20.0 ± 0.1 |

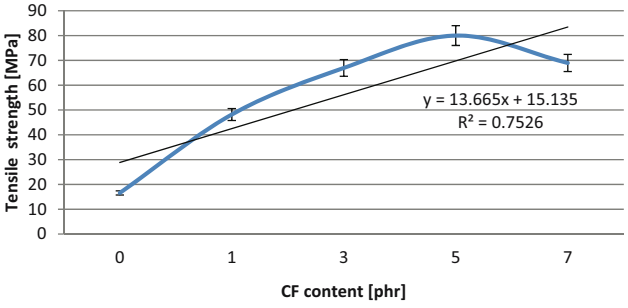


**Figure 3:** Influence of CFs on tensile strength of CMS/CMC-based composites.

cellulose filler in the film, an increase in Young's modulus and tensile strength was observed. The highest values of these parameters were recorded for a system containing 5 wt% CFs, namely 24.8 and 80 MPa, respectively. The observed increase in the strength of composites with an increase in the content of CFs is caused by the formation of hydrogen bonds between carboxymethylated starch and cellulose and cellulose fillers, which resulted in the expansion of the spatial network of the film. The addition of CFs to the composite affected the increase of elongation at break, which suggests inefficient interactions between macromolecules.

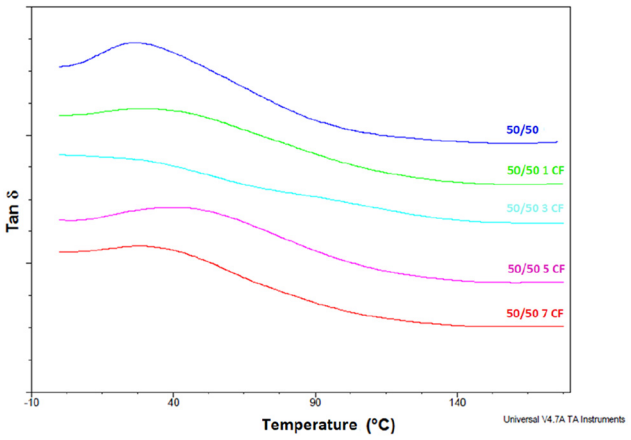


**Figure 4:** DMTA curves of CMS/CMC-based composites with various CF contents.

Comparing the DMTA curves of CMS/CMC films with various CF contents (from 1 to 7 wt% based on the dry weight of the polysaccharide mixture), it can be noted that the glass transition temperature increases from approx. 30°C to approx. 50°C with the filler content increase (for the neat system and that containing 5 wt% CFs, respectively) (Figure 4), indicating the crosslinking density increase.

## 4 Conclusions

The natural composites based on CMS and CMC containing CFs as a filler have been prepared. The addition of CFs positively affects the physicochemical properties of the CMS/CMC film. The filler addition resulted in the reduction of the solubility in water. Moreover, with the increase of filler content in the matrix, an increase in tensile strength and Young's modulus was noted, from 16.5 to 80 MPa and from 4.8 to 24.8 MPa, respectively, for the system without and with 5 wt% CFs. For samples containing 7 wt% filler, a decrease in the mechanical properties of the composite was observed, which could be due to the agglomeration of CFs. An increase in the glass transition temperature of the composite from about 30°C to about 50°C was observed for the system without and with 5 wt% CFs.

The obtained films have good mechanical properties, are hydrophilic, biodegradable and non-toxic. They can be used, e.g., in agriculture (agromembranes), to encapsulate fertilizers (a coating substance that allows controlled release of active compounds), herbicides, bactericides and fungicides as well as related substances; in medicine – as medicine carriers – and in the packaging industry.

**Conflict of interest:** Authors declare no conflict of interest.

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