Abstract
Carboxymethyl celulose (CMC) is an interesting polymer produced by an easy reaction with chloracetic acid with cellulose. CMC is a hydrophylic polymer soluble in water with huge potential in medical applications in which we can use an extreme high sorption of water, swelling or senzitivity to pH and temperature – for example as a protection of damaged skin. In this study is presented a method of preparation of porouse nanostructured material based on CMC. This special structure is prepared by following production steps: preparation of film of CMC - basic stabilization of CMC film – formation of gel by sorption of water – freezes dryeing of stucture – final stabilization. The stabilization of film is based on changes in CMC based on thermal treatment. The prepared material was evaluated by scanning electron microscopy and infrared spectroscopy. The bahavior in water was tested as well. By the setting of parametres of stabilization of CMC we can obtain structures with different water solubility or different swelling in water. Prepared microporous structures are interesting with large internal surface, high wettability and biodegradability. The product of presented technology is nontoxic with high potential in biological applications.

Key words:
Carboxymethyl celulose, nanostructure, swelling, thermal treatment

1. INTRODUCTION
CMC is prepared by activation of cellulose with an aqueous NaOH in the slurry of an organic solvent which reacts with the cellulose and monochloroacetic acid as an etherifying agent. The first step in the carboxymethylation process is an alkalization where the hydroxyl groups of the cellulose chains are stimulated and altered into more reactive alkaline form. This is followed by an etherification to obtain CMC and a side reaction, which results in sodium glycolate.[1] Carboxymethyl celulose has many desirable applications such as coating, formation of emulsions and suspensions, water retention. Therefore it is used in many applications such as medicine, food, paper making, printing and dyeing. [2]

Carboxymethyl celulose is a biocompatible macromolecule that has been used for drug delivery systems in many investigations with the aim of controlled drug release with various ways: it has been used for a microgel matrix for a new type of sticking plaster; due to its adhesive characteristic it has been used as bioadhesive material, especially as mucoadhesive polymer for nasal and buccal drug delivery systems. [3]

CMC is also used in oil drilling fluids as a component, which adjusts the viscosity and retains water. Insoluble microgranuled carboxymethylcelulose is used as a cation exchange resin in the ion-exchange chromatography for purification of proteins. CMC can also be used in cooling inserts which allows a eutectic mixture and to reduce the melting temperature and thus better cooling in comparison with ordinary ice. Aqueous solutions of CMC can be used to disperse carbon nanotubes. The molecular structure of carboxymethyl celulose is shown in figure 1. [4] [5]

Na-CMC as an amylose with many hydroxy and carboxylic groups can absorb water and moisture, so the hydrogel made of it has many excellent properties, such as high water content, good biodegradation and
wide source for its low cost. Therefore, it can be widely applied in agriculture and forestry with a good foreground. [6]

Crosslinking of macromolecular substances leads to deterioration of solubility and fusibility, increased dimensional stability under heat and chemical resistance and reduce permeability. It also leads to decrease of swelling, moisture absorption and extractable share. There are more ways of crosslinking of CMC, such as thermal (thermal crosslinking has a effect on solubility and absorption properties of CMC), chemical, radiological (interaction between polymer with eneretical rich radiation and radicals are created, they react with each other, thus creating cross links between chains), etc. [7] [8] [9] [10]

Polyester fibre has a highly compact and crystalline structure, and is markedly hydrophobic. CMC absorbs moisture from the atmosphere. The amount of absorbed moisture depends on the initial moisture content and on the relative humidity and temperature of the surrounding air. [11]

![Fig. 1: The molecular structure of carboxymethyl cellulose](image)

2. EXPERIMENTAL

2.1. Materials
- Description of used CMC
  Sodium salt of Carboxymethyl cellulose was used in the powder form (CMC-\(\text{Na}^+\)). The salt was dissolved in water to achieve the concentration of 30 g.L\(^{-1}\). The solution was stirred by the electronic overhead stirrer RZR 2051 control 1 gear stage stirrer for about 15 minutes and left for a day so that the solution gets homogenised and CMC was completely dissolved.
- Description of polyester fabrics
  - PES non-voven thin fabric (area density 32 g.m\(^{-2}\))
  - PES non-voven thick fabric (area density 94 g.m\(^{-2}\))

2.2. Procedure of preparation
CMC solution was applied by on textile materials. It was also made a thin film from the same solution by pouring the solution into the petri dish. All samples were placed into the heated box where they were dried at 105 °C and then fixed at 180 °C for 5-30 minutes. After this prefixation samples were immersed in distilled water for 3 minutes. In this study was not used a vacuum freeze drying, which is described in many studies. It was used a drying of wet CMC gel in dry air at the standard pressure and low temperature (-20°C).

After swelling samples were placed in sealable containers containing 25 g of dried silica gel. All containers with samples were freeze-dried until samples were dry. After that all samples were post-fixed at 200°C for 10 minutes to stabilize the structure. Throughout the preparation of samples were weighed by using an analytical balance.
- Preparation of thin CMC film
  The thin films were prepared with area density 88,5 g.m\(^{-2}\). The CMC solution was put in patty dishes by calculating the required volume. The dishes were kept in open air on a levelled surface so that thickness of the produced film is uniform. Then the patty dishes are transferred into the heaters at 105°C and left for about 50 minutes so that the solution gets converted into thin dried film.
- Preparation of CMC coated polyester non-vowen fabrics
  The polyester fabrics were coated with the 30 g.L\(^{-1}\) CMC solution by padding technique. After this samples were dried at 105°C for 15-40 minutes until it has completely dried.

- Description of the cross linking process
  The CMC film and the CMC coated Polyester fabrics were heated at two different temperatures and variable time durations. Heating the samples leads to polymerisation and cross linking in CMC. The temperatures employed were 180°C for pre-fixation and 200°C for post-fixation. The time duration of polymerisation at 180°C was 5, 10, 15, 20, 30 minutes for all samples and 10 minutes for 200°C.

Fig. 2: The scheme of procedure of preparation of CMC on PES fibros using freezer (dry air)

2.3. Methods of testing

- Water absorption testing
- Scanning electron microscopy

Used formula:

\[
\text{Absorption [\%]} = \frac{(m_2 - m_1)}{m_1} \times 100
\]

\(m_2\) – wet mass after insertion in water and following short remove of surface water by filter paper
\(m_1\) – weight after drying

2.4. Procedure of preparation of samples

The whole process of preparation is shown in figure 3.

Fig. 3: Illustration of preparation of CMC on polyester thick nonwoven fabric (a) using freezer (b) using vacuum freeze-dryer
For comparison was realized one experiment in vacuum freeze dryer. The process of drying is visualized in figure 3. We can see that the process in laboratory vacuum freeze dryer is quicker (48 hours) in comparison with dry air drying (360 hours), which is used in this study.

3. RESULTS

3.1. Scanning electron microscopy
Images from electron microscopy shows that the CMC during freeze drying produces a highly porous structures as a form of a homogeneous film as in the case of composite structures PES fiber / CMC. In the case of fibrous substrates is CMC deployed in the form of small compact film between fibers and on fibers in the fabric structure. This arrangement leads to a reduction in permeability, but not to zero value and also the stiffness of the structure increases within acceptable limits.

Fig. 4: Sample of CMC film (a) after prefixation (180°C 15 min.), (b) after freeze drying and post-fixation (200°C 15 min.)

Fig. 5: Sample of CMC on PES thin fabric (a) after prefixation (180°C 15 min.), (b) after freeze drying and post-fixation (200°C 15 min.)

Fig. 6: Sample of CMC on PES thick fabric (a) after prefixation (180°C 15 min.), (b) after freeze drying and post-fixation (200°C 15 min.)
3.2. Absorption of water

Absorption of water in all forms of CMC is high. Pure CMC film can absorb up to 6000% of water from the original mass of CMC. This value was obtained at conditions of pre-fixation – 180°C and 15 minutes. After post-fixation, which stabilized the structure against the liquid water is the absorption reduced. If the CMC is placed in fibre structure than the water absorption is not so high – the maximum values of absorption are around 2000%.

Fig. 7: Sample of CMC film (a) after pre-fixation (180°C 15 min.), (b) after freeze drying and post-fixation (200°C 15 min.)

Fig. 8: Sample of CMC on PES thin fabric (a) after pre-fixation (180°C 15 min.), (b) after freeze drying and post-fixation (200°C 15 min.)

Fig. 9: Sample of CMC on PES thick fabric (a) after pre-fixation (180°C 15 min.), (b) after freeze drying and post-fixation (200°C 15 min.)
4. CONCLUSION

In this study was prepared composite structures based on polyester fibers and CMC. In a standard fiber structure was placed a solution of CMC, which was thermally fixed in two steps before and after freeze drying. By distributing temperatures of stabilization in two steps was achieve a high variability of possible products.

For example: if sample was little fixed before freeze drying it would absorb large amounts of water and during freeze drying more open structure will be created. If sample is applied an intense postfixation, open structure will be stabilized and becomes almost non-swellable.

By selecting appropriate conditions it can be controlled porosity and absorption properties of final products. Prepared materials can be used as an absorber of water, catalyst carrier, materials for cell growth and so on.

ACKNOWLEDGEMENT

This paper is supported by SGS 4871/115.

REFERENCES


