CHANGES IN SELECTED PROPERTIES OF CARBOXYMETHYL CELLULOSE MATERIALS AFTER LYOPHILIZATION

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Abstract

This study deals with the change of selected properties of samples of modified carboxymethyl cellulose after freeze drying. The investigated properties are changes in thickness; permeability; water sorption; thermal resistance and thermal absorption capacity. Thermal insulation properties under the simulated outdoor conditions will be monitored. The prepared materials were evaluated by scanning electron microscopy and computer tomography. The product of presented technology has a large internal surface, high wettability and biodegradability. It is nontoxic with high potential in biological aplications.

Key words:

Carboxymethyl cellulose, lyophilization, sorption, thermal insulation properties, permeability

1. INTRODUCTION

Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups attached to any of the hydroxyl groups of the glucopyranose monomers forming the backbone of the cellulose. Functional properties of CMC depends on the degree of substitution of the cellulose structure. [1, 2]

Optimum water solubility and other desirable physical properties of CMC are obtained at a much lower degree of substitution than 3. The most widely used types of CMC have a DS of 0.7, or an average of 7 carboxymethyl groups per 10 anhydroglucose units. Higher degrees of substitution result in CMC products having improved compatibility with other soluble components. The viscosity of CMC solutions increases rapidly with concentration. Many hydroxyl groups are available to participate in substitution reactions. The polar character of the carboxymethyl groups makes CMC water soluble and chemically reactive. [3, 4]

It is used primarily because it has high viscosity, is non-toxic, and is non-allergenic. CMC is an important industrial polymer with a wide range of applications in flocculation; drag reduction; detergents; textiles; paper; foods; drugs; and oil well drilling operation. Due to its good viscosity building; high shear stability; biocompatibility; easy availability and low cost compared to other polysaccharides it is most preffered. [5, 6]

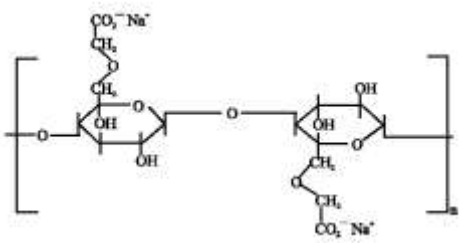

Fig. 1 Structure of carboxymethyl cellulose

Freeze drying, also known as lyophilization, is widely used for pharmaceuticals to improve the stability and longterm storage stability of labile drugs, especially protein drugs. Lyophilization is the process we use to remove water from a formulation at low temperatures (prevents thermal degradation) through a process of sublimation.

A typical freeze-drying process consists of three stages; that is, freezing, primary drying, and secondary drying. Freezing is an efficient dessication step where most of the solvent, typically water, is separated from the solutes to form ice. As freezing progresses, the solute phase becomes highly concentrated and is termed the “freeze concentrate.” By the end of freezing, the freeze concentrate usually contains only about 20% of water (w/w), or less than 1% of total water in the solution before ice formation. The freezing stage typically takes several hours to finish. Primary drying, or ice sublimation, begins whenever the chamber pressure is reduced and the shelf temperature is raised to supply the heat removed by ice sublimation. During primary drying, the chamber pressure is well below the vapor pressure of ice, and ice is transferred from the product to the condenser by sublimation and crystallization onto the cold coils/plates (<−50°C) in the condenser. Typically, the primary drying stage is the longest stage of freeze drying and optimization of this stage has a large impact on process economics. Secondary drying is the stage where water is desorbed from the freeze concentrate, usually at elevated temperature and low pressure. [7, 8]

The aim of this study is to compare how the lyophilization changed the thermo-insulating and sorption properties of CMC materials, compared to those samples which were dried in air.

2. EXPERIMENTAL PART

2.1 Materials

Description of used CMC

- Sodium salt of Carboxymethyl cellulose was used in the powder form (CMC-Na^+). The salt was dissolved in water to achieve the concentration of 30 g/l[1]. The solution was stirred by the eletronic 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.

- CMC nonvowen fabric - areal density 60 $g.m^{-2}$, DS 0.345, pH 6.6 – this type of CMC was used in textile form and it was also dissolved in water to achieve the solution with concentration of 25 g/l[1].

2.2 Lyophlization

For this study a laboratory freeze dryer Christ, type Epsilon 2- 6D freezer shelves with a total area of 0.27 m^2 was used. The best freeze-drying process consisted of: 4 hours of freezing (-80°C), 15 hours of vacuum (1.0 mbar) and 1hour of heating shelves (0.5 mbar).

2.3 Evaluating methods

- Electron microscopy - Electron microscopy was performed on the device Tescan-Vega. All samples were covered with a layer of gold before scanning.

- Computer tomography - Desk micro-tomograph device SkyScan 1272 is able to non-destructively analyze and visualize the structure of materials. (Image Pixel Size (μm)=1.28; Exposure (ms)=530; Source Voltage (kV)= 40)

- Permeability – Permeability was performed by FX 3300 Air Permeability Tester III from TexTest company. The entire test procedure was in accordance with EN/ISO 9.237 (used pressure 100 Pa).

- Water sorption - Measurements consisted in immersing samples of approx. 0.2 g in water. Samples were immersed in water over a defined time. Samples were weighed dry before soaking and then after soaking. The weighing was done on analytical balances.

- Measurement of thickness - Measurement was performed on device Uni-thickenss-meter (Computex) with area of jaw 20 mm^2 and pressure of 1 kPa.

- Measurement of thermal absorbing capacity and thermal resistance - Measurement was performed on device Alambeta with pressure of 200 Pa.

- Innovative device for measuring the thermal insulation properties, which uses the air-conditioning chamber (CTS) was used. Within the air-conditioning chamber a steel cylinder is placed which is heated to 35 °C. The cylinder simulates the surface of human skin. Temperature of the material which is placed on the cylinder is measured using a digital infrared thermometer. The temperature in the chamber was set to – 20 °C (+/ - 0.1°C) with 80 % of humidity.

3. RESULTS AND DISCUSSION

3.1 Vizualization using SEM and CT

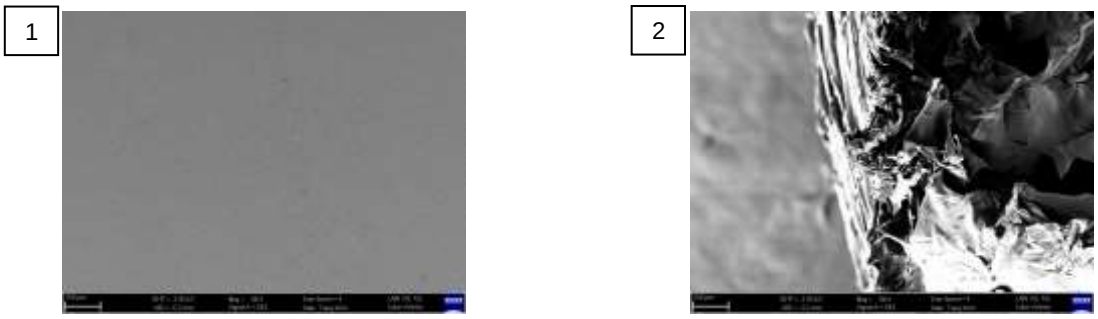

Fig. 2 Stucture of CMC film before (left) and after (right) lyophilization

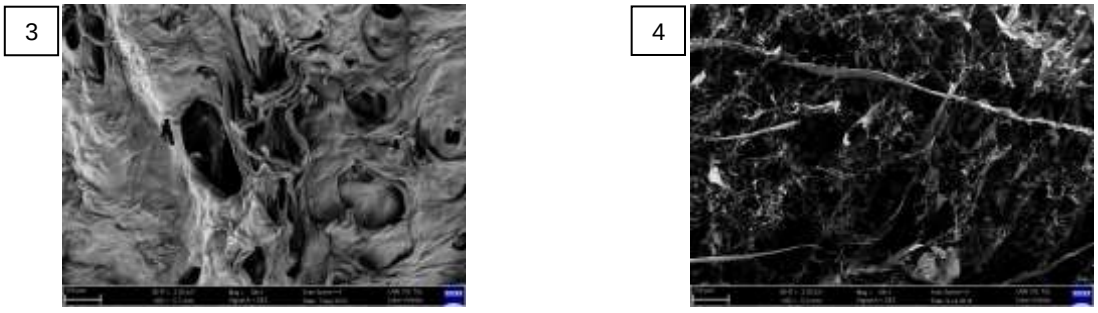

Fig. 3 Stucture of CMC nonvowen fabric mixed with water before (left) and after (right) lyophilization

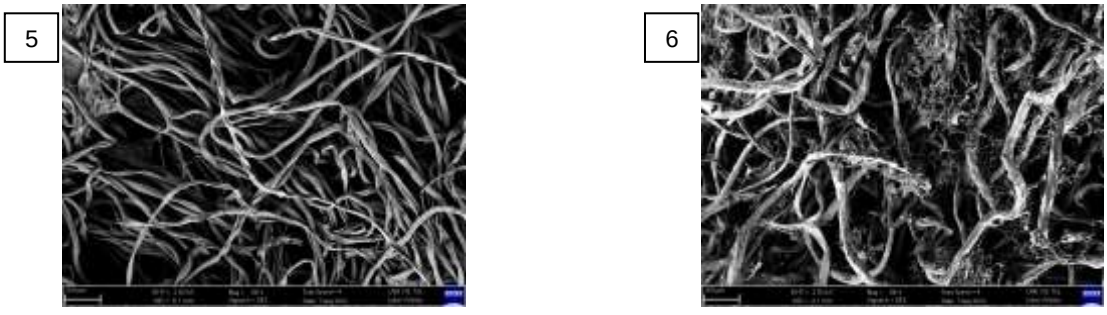

Fig. 4 Stucture of CMC nonwonen fabric before (left) and after (right) lyophilization

From figure 2 it is evident that in the case of CMC film after lyophilization there was a significant change in structure. All three tested materials have a gelling character. Gelling parts in materials created a „nanostructure“ under the low pressure which is shown in figure 3 and 4. The resulting structure was fixed by drying at low temperature.

Fig. 5 Pictures of tested samples - CMC film (left) nonwoven fabric mixed with water (middle) nonwoven fabric (right)

From figure 5 it can be seen that the samples of films after lyophilization formed a foam structure.

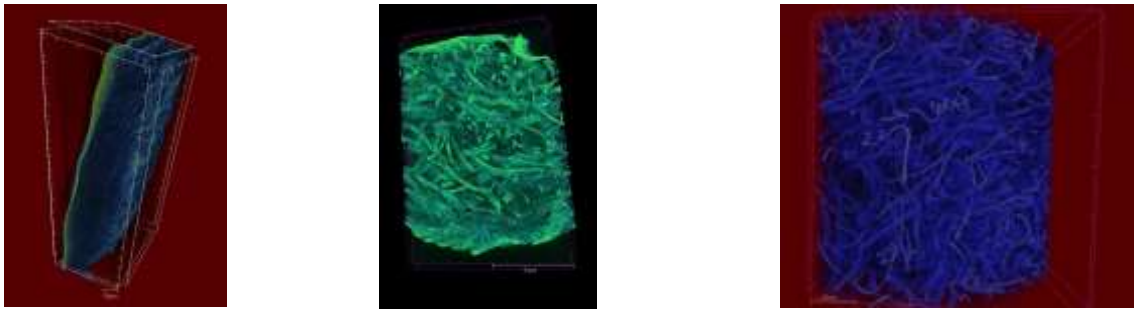

Fig. 6 Pictures of lyophilized samples taken by CT (left) CMC film (middle) nonwoven fabric mixed with water (right) nonwoven fabric

The images of cross-sections of samples taken by CT (see figure 6) shows that the sample of film made from nonwoven fabric and nonwoven fabric itself after lyophilization kept the fiber structure.

3.2 Thermal insulation properties and permeability

Table 1 Thermal insulation propertiesμ

	Thermal conductivity	Thermal absorbtivity	Thermal resistivity	Sample thickness	CTS (-20°C)
	λ (.10^{-3})	b (.1)	r (.10^{-3})	h	
sample	[W.m^{-1}.K^{-1}]	[W.s$^{1/2}$.m^{-2}.K^{-1}]	[W^{-1}.K.m^{2}]	[mm]	[°C]
1	32.40	94.53	40.43	1.15	22.50
2	48.03	40.16	192.00	9.20	-2.40
3	102.57	305.33	29.87	1.45	15.90
4	83.27	86.00	102.30	14.19	-6.90
5	34.06	78.23	36.00	1.21	18.90
6	41.66	56.63	112.00	3.37	-0.40

In the case of high value of thermal absorbing capacity the material has a cold feel touch and conversely if this value is low, the material has a warm feel. The higher value of the resistance of the textile means that the material is less able to dissipate heat. That shows a good ability of material to keep the warmth. Higher temperature measured by digital infrared thermometer means worse thermal insulation properties.

The results of both tested methods for evaluation of thermal insulation properties shows that samples after lyophilization obtained an excellent thermal insulation properties

Table 2 Permeability

sample	1	2	3	4	5	6
[l/m²/s]	0.00	62.40	0.00	137.60	1660.00	29.60

Permeability of samples after lyophilization slightly increases in case of CMC film and solution of nonwoven fabric dissolved in water.

3.3 Sorption properties

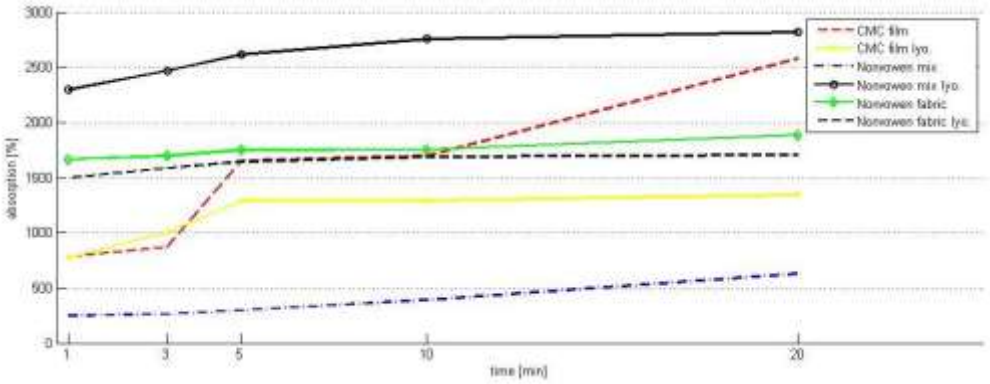

Fig. 7 Absorption of tested samples

Sample of CMC film after lyophilization reached two times higher values of absorption of water than sample before lyophilization. Sample of film made from nonvowen fabric mixed with water after lyophilization reached 4 times higher values of absorption compare to sample before lyophilization. Lyophilization does not significantly affect the sorption in case of nonvowen fabric.

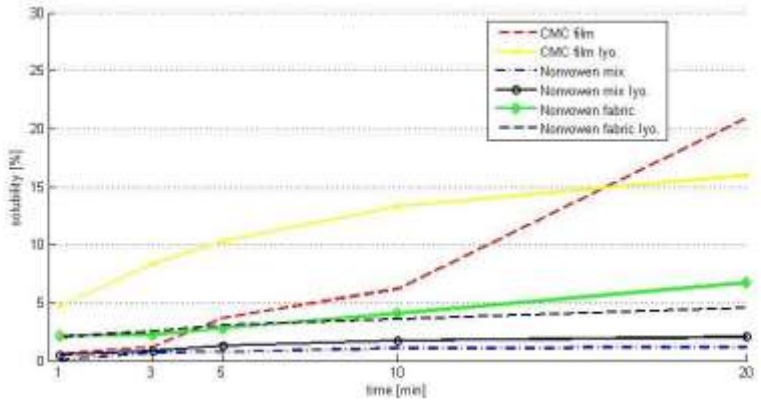

Fig. 8 Solubility of tested samples

In case of CMC film after lyophilization the solubility decreased by about 5% compared with the sample which was not lyophilized. Lyophilization does not significantly affect the solubility of the sample of film formed by dissolving the nonwoven fabric in water and sample of nonvowen fabric itself (see figure 8).

CONCLUSION

This work dealt with the preparation and testing of samples of modified CMC, which were subsequently lyophilized. Lyophilization led to increase in thikness of samples up to ten times higher values and all tested materials showed a soft and warm feel. Absorption of all tested samples is high. All tested samples after lyofilization have lower value of thermal absorption capacity and higher value of thermal resistance to retain the heat as compared to samples which were not freeze dried. It means that samples after lyofilization have a warm feel and they are more efficient to keep the warmth.

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