



Stability of methylcellulose-based films after being subjected to different conservation and processing temperatures

M.J. Tavera Quiroz, J. Lecot, N. Bertola, A. Pinotti *

Centro de Investigación y Desarrollo en Criotecología de Alimentos (CIDCA), CONICET La Plata, Facultad de Ciencias Exactas, Argentina

ARTICLE INFO

Article history:

Received 14 December 2012

Received in revised form 20 February 2013

Accepted 12 March 2013

Available online 21 March 2013

Keywords:

Methylcellulose
Biodegradable films
Sorbitol
Frozen films
Stored films

ABSTRACT

Methylcellulose films with and without sorbitol addition were developed. The major objective of this study was to attempt insights into the stability of the methylcellulose-based film properties after having been subjected to freezing, storage or a combination of both procedures. The importance of the sorbitol concentration and process temperature was also to be elucidated. As-prepared film solubility decreased at 100 °C, as a result of the methylcellulose thermogelation property when the samples were exposed to high temperatures. By analyzing the film pattern behavior and its properties 0.25% w/v sorbitol concentration turned out to be an inflexion point. The moisture content as well as the mechanical and thermal properties made this fact evident. Moreover the elastic modulus (E_c) and glass transition temperature (T_g) did not undergo significant changes for higher plasticizer concentrations. The methylcellulose film properties remained more stable in the presence of sorbitol, which would act as a protective agent due to its hydrogen bonding capacity. This stability is crucial for film and coating applications in the food industry.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Cellulose is the most abundant polysaccharide, which occurs mainly within the cell wall of higher plants as a structural material [1,2]. Modification of cellulose with hydrophobic side groups disrupts the rigid crystalline structure stabilized by strong intermolecular hydrogen bonding and improves the polysaccharide's water affinity [3,4]. An optimum level of substitution is required for an appropriate water solubility, which is usually between 1.4 and 2.0 [5]. The simplest derivative of cellulose, methylcellulose (MC), which has methyl groups substituted for hydrogen, forms a clear viscous polymer in an aqueous environment [3]. Methylcellulose is useful for a variety of applications because of its low cost and its unique ability to gel at elevated temperatures [5]; it is also used in the pharmaceutical and food industry as a thickener, water binder and film forming agent [6–8]. According to their physico-chemical properties, MCs can be also employed as emulsifiers, medicine constituents, colloidal stabilizers, viscosity and flow controllers.

Even though water is a ubiquitous natural plasticizer, the effects of water on molecular mobility including plasticization are poorly understood mainly because molecular and structural analyses are scarce. Kilburn et al. [9] concluded that the plasticization effect of water in carbohydrates is via a complex mechanism involving both hydrogen bond formations and disruption and changes in the matrix free volume. In the

dry state, the hydrogen bonding between carbohydrate molecules leads to the formation of large molecular entities. When water is absorbed, it disrupts the hydrogen bonds between the carbohydrate chains [10]. Plasticizers, which are low molecular weight components, increase the free volume of the material or the macromolecular mobility of the polymer, and consequently the polymeric network becomes less dense due to the decrease in intermolecular forces, thus improving the extensibility and flexibility of the films [11–13]. The most effective plasticizers will more closely resemble the structure of the polymer they plasticize. Thus, the plasticizers most commonly used in starch and cellulose-based films are polyols, such as sorbitol [14,15]. Sorbitol is a common pharmaceutical excipient used to improve the stability of proteins and other drug molecules during freezing, drying and storage [16].

In order to avoid food deterioration, different methods are used. One of them is freezing, which is one of the most widespread preservation techniques. The use of edible coatings could have a beneficial effect on the quality of frozen food, since they act as a barrier against moisture transfer and oxygen uptake [17]. Several studies have shown that edible coatings help to control quality deterioration during frozen fish storage and to prolong its shelf life [18,19].

Although several researches have been conducted on methylcellulose films and films plasticized with sorbitol, their combination in the same system is not frequent [11,20,21]. To the best of our knowledge, studies on the properties of MC films after being submitted to freezing and storage have hardly been reported. Thus, the major objective of this study was to attempt insights into the stability of the methylcellulose-based film properties after having been subjected to freezing, storage or a combination of both procedures. The importance of the processing

* Corresponding author at: Facultad de Ingeniería, UNLP, 47 y 116, La Plata (1900) Argentina. Tel.: +54 2216221294.

E-mail address: acaimpronta@hotmail.com (A. Pinotti).

and conservation temperature and the sorbitol concentration was also to be elucidated.

2. Materials and methods

2.1. Hydrocolloid solutions

Methylcellulose (A4M, Methocel) was provided by COLORCON S.A. (Argentina). According to specifications of the supplier, the molecular weight was 65.10^3 Da. To prepare the hydrocolloid solution, 1.5 g methylcellulose (MC) was slowly dispersed in 50 mL of hot distilled water (80 °C) under constant stirring for 1 h. Once a homogeneous system was obtained, a total volume of 100 mL was made up with cold distilled water and the solution was kept under stirring until it attained room temperature.

Sorbitol (Merck, USA) was added as a plasticizer after MC was completely dissolved at different concentrations (0.25, 0.5, 0.75 and 1.0% w/v). Each experiment was made in triplicate.

2.2. Film preparation

The film-forming solution weight (about 20 g) with and without plasticizer casted onto Petri dishes (9 cm diameter) was controlled in order to guarantee a constant film thickness and dried at 37 °C in an oven until reaching a constant weight. The obtained films were removed from the dish and afterwards they were stored at 20 °C and 65% RH in a controlled room.

Film thickness was determined by using a coating thickness gauge Check Line DCN-900 (New York, USA) for non-conductive materials on non-ferrous substrates. The informed values correspond to the average of at least fifteen measurements at different positions for each specimen.

Samples were divided in different groups for the assays.

A: unplasticized and plasticized as-prepared samples.

B: unplasticized and plasticized samples stored at room temperature for 3 months.

C: unplasticized and plasticized samples frozen and stored for 3 months, to study both effects jointly.

D: unplasticized and plasticized samples frozen and immediately thawed to study the effect of the freezing process separately from the storage process.

Film will be named as-prepared, stored, frozen-thawed and frozen-stored or groups A, B, C and D from here onwards, interchangeably. Within every group, film nomenclature used will be: MC for methylcellulose films and MC-0.25S, MC-0.5S, MC-0.75S and MC-1S for films containing 0.25, 0.5, 0.75 and 1% sorbitol, respectively. In addition, as-prepared MC was used as a principal control, whereas films of group A were used as secondary controls (as-prepared MC-0.25S, MC-0.5S, MC-0.75S and MC-1S).

2.3. Physicochemical characterization

2.3.1. Moisture content

As-prepared film moisture contents were determined by measuring their weight loss, upon drying in an oven at 105 ± 1 °C until reaching constant weight (dry sample weight). Samples were analyzed at least in triplicate and results were expressed as grams of water per 100 g of dry sample.

2.3.2. Film solubility and water uptake

As-prepared MC-based films were cut in 30×30 mm pieces to determine both water uptake and film solubility. To determine the solubility, the samples were weighed, immersed into distilled water at 20 and 100 °C, and maintained under constant agitation for 1 h.

After soaking, the remaining pieces of the films were dried again in an oven at 105 ± 1 °C until reaching constant weight. Film solubility (%) was calculated as it was described by Rivero et al. [22].

Water uptake was measured by immersion of previously weighted film pieces in 80 mL distilled water. One hour after, samples were recovered and dried with filter paper to remove the excess of surface water and weighted again (film wet weight). The water uptake of the films was calculated as follows,

$$\% \text{ Water uptake} = \left[\frac{(W_t - W_i)}{W_i} \right] \times 100 \quad (1)$$

where: W_t is the weight of the swollen sample at time t and W_i is the weight of the film before immersion. Samples were analyzed at least in triplicate.

2.3.3. Water activity

Water activity of as-prepared samples was evaluated by using an AquaLab Water Activity Meter (Decagon Devices, Inc., Washington, USA) equipment. The measurements were performed in triplicate.

2.3.4. Water vapor barrier properties

Water vapor permeability (WVP, $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$) tests were performed on groups A, B, C and D, by using a modified ASTM method E96 [23] as it was described in previous work [21].

Each sample was sealed over a permeation cell which was maintained at 20 °C. A driving force of 1753.55 Pa, corresponding to a 75% RH gradient across the film was used. After steady state conditions were reached, the permeation cells were weighed (0.0001 g) at a 1 h interval for 8 h. The reported values correspond to the average of at least three determinations.

2.3.5. Differential scanning calorimetry (DSC)

Film thermal properties were determined by using a DSC model Q100 controlled by a TA 5000 module (TA Instruments, New Castle, USA), with a quench-cooling accessory, under a N_2 atmosphere (20 mL min^{-1}).

Film samples of 6–7 mg were weighed in aluminum pans and were hermetically sealed; an empty pan was used as reference. Samples were analyzed at a heating rate of 10 °C min^{-1} . The first scan was performed from -100 °C up to 250 °C to limit possible methylcellulose degradation. After the first scan was completed, the sample was cooled until -100 °C and then a second scan was recorded between -100 and 350 °C . The pans were punctured and dried until reaching constant weight at 105 °C to obtain the dry weight of the samples.

From the thermograms, glass transition temperature T_g was obtained using the Universal Analysis V1.7F software (TA Instruments).

2.3.6. Dynamic mechanical analysis (DMA)

DMA assays were conducted in a dynamic-mechanical thermal equipment Q800 (TA Instruments, New Castle, USA) using a tension clamp with a liquid N_2 cooling system. Film probes with a rectangular geometry (6 mm width and 30 mm length) were assayed. Amplitude sweep from 1 to 50 μm at a fixed frequency (5 Hz) was performed. Multi-frequency sweeps (1, 5, 10 and 15 Hz) at fixed amplitude from -100 to 250 °C at 5 °C/min were carried out, with an isotherm of 10 min at -100 °C . Storage (E'), loss (E'') modulus and $\tan \delta$ (E''/E') curves as a function of temperature were recorded and analyzed using the software Universal Analysis 2000. Temperatures of the relaxation processes associated to glass transition temperatures were determined through the inflexion point of the maximum peak in the $\tan \delta$ curves.

2.3.7. Film stress–strain behavior

Probes of 6×30 mm were used to analyze the tensile stress–strain behavior of the MC films with and without plasticizer through the DMA TA Instruments-Q 800, using the tension clamp as was described in previous work [21]. Tests were conducted on samples from groups A

Download English Version:

<https://daneshyari.com/en/article/10614683>

Download Persian Version:

<https://daneshyari.com/article/10614683>

[Daneshyari.com](https://daneshyari.com)