



# Changes induced by UV radiation in the presence of sodium benzoate in films formulated with polyvinyl alcohol and carboxymethyl cellulose



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## ABSTRACT

This work was focused on: i) developing single and blend films based on carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVOH) studying their properties, ii) analyzing the interactions between CMC and PVOH and their modifications UV-induced in the presence of sodium benzoate (SB), and iii) evaluating the antimicrobial capacity of blend films containing SB with and without UV treatment.

Once the blend films with SB were exposed to UV radiation, they exhibited lower moisture content as well as a greater elongation at break and rougher surfaces compared to those without treatment. Considering oxygen barrier properties, the low values obtained would allow their application as packaging with selective oxygen permeability. Moreover, the characteristics of the amorphous phase of the matrix prevailed with a rearrangement of the structure of the polymer chain, causing a decrease of the crystallinity degree. These results were supported by X-rays and DSC analysis. FT-IR spectra reflected some degree of polymer–polymer interaction at a molecular level in the amorphous regions. The incorporation of sodium benzoate combined with UV treatment in blend films was positive from the microbial point of view because of the growth inhibition of a wide spectrum of microorganisms. From a physicochemical perspective, the UV treatment of films also changed their morphology rendering them more insoluble in water, turning the functionalized blend films into a potential material to be applied as food packaging.

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## 1. Introduction

Among cellulose ethers, the most widely used is carboxymethyl cellulose (CMC) produced in the form of sodium salt. The CMC structure is based on the 1,4-β-D-glucopyranose polymer of cellulose. Cellulose derivatives have been used to develop cellulose-based hydrogels through physical and chemical cross-linking [1–3]

On the other hand, polyvinyl alcohol (PVOH), a semi-crystalline polymer is among the most widely used synthetic water-soluble polymers. This polymer is extensively produced for its excellent chemical resistance, physical properties and complete biodegradability, which has led to broad practical applications [4,5]. PVOH has been used in polymer blends with natural polymeric materials such as cellulose derivative and chitosan. In these systems, good material performance was obtained, which is attributable to the formation of intermolecular hydrogen bonds between the hydroxyl groups of the respective polymers [6]. The blend of two polymers allows the preparation of

polymeric materials with controllable properties differing significantly from those of the individual components [7].

In so doing, blends of CMC and PVOH have been the subject of a number of investigations [8–10,4,11–14]. The mixture of these polymers enables the production of biodegradable materials with physical and functional properties, allowing their application in the emerging field of packaging.

The photo-curing technique has proved to be an important method for cross-linking polymers because their functional groups undergo light induced reactions [15,16], being used to improve the properties of the matrices associated to the chemical reaction [17]. Modifications by using UV radiation of polymer films have been studied in recent years [17–19].

UV radiation requires the presence of substances known as photosensitizers which induce the changes in the substrate after absorbing appropriate radiation.

Chen and Lin [20] found that the modification of PVOH can be carried out by UV radiation in the presence of photosensitizers or by chemical reactions. These processes can lead to the cross-linking of PVOH molecules, making the polymer more insoluble in water. The most efficient photosensitizer is sodium benzoate (SB), known to be photolysed by UV radiation [21,22]. Excitation of photoinitiator

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produces reactive radicals which initiate subsequent reactions in the polymer blend thus facilitating cross-linking between the two polymer chains [16].

Other use of SB is focused on the preservation of food matrices because of its antimicrobial capacity, extending its functionality and its spectrum of application. SB is the most common, safe, food preservative and antimicrobial agent classified in the United States as Generally Recognized as Safe (GRAS) [23].

To the best of our knowledge, the use of UV light to induce the photo-crosslinking of PVOH:CMC blend films in the presence of SB has hardly been reported. Thus, new materials with tailored properties from PVOH and CMC blends were expected to be found.

This work was focused on:

- i) Developing single and blend films based on carboxymethyl cellulose and polyvinyl alcohol analyzing their properties.
- ii) Studying the ultraviolet-induced cross-linking of blend films with SB in order to alter their surface properties and introduce new functionalities, evaluating the changes undergone by the blend because of the addition of the photo-initiator by using SEM and DMA techniques.
- iii) Evaluating the antimicrobial capacity of blend films containing SB with and without UV treatment.

Thus, microstructural, physical, optical and thermal properties were monitored for single, blend films and UV crosslinked matrices.

## 2. Materials and methods

### 2.1. Reagents

Sodium carboxymethyl cellulose of commercial grade was supplied by Parafarm (Buenos Aires, Argentina) with a degree of substitution of 0.95. Polyvinyl alcohol ELVANOL® T25 was purchased from DuPont (Buenos Aires, Argentina) with a hydrolysis degree of 86–89%. Sodium benzoate, supplied by SUPELCO Analytical (USA), was used as a photosensitizer.

### 2.2. Film-forming solution and film preparation

CMC aqueous solution was prepared by dispersing 1.5% (w/w) of the polymer in stirred distilled water at 80 °C, for 12 h approximately. Then, the beaker containing the solution was sonicated for 30 min to remove the air bubbles at room temperature.

PVOH solution of 2% (w/w) was obtained by solubilization in water at 90 °C under continuous agitation for 45 min approximately.

In previous work, solutions with different ratios of CMC:PVOH (25:75, 50:50, 75:25) were tested [24]. The blend 50:50 (w/w) was selected for further studies owing to its better barrier and mechanical properties, bearing in mind that it would be used as a functional active film. Blend films containing SB as a photosensitizer for the crosslinking reaction were also prepared. With the purpose to meet the required amounts for a potential application as packaging where the films are in contact with food products, the concentration of SB was fixed at 0.1% (w/w), according to the current norm [25].

Single CMC, PVOH and their blends were prepared by casting of 25 g of filmogenic solutions onto Petri dishes (9 cm diameter) and drying at 37 °C in an oven until reaching constant weight (approximately 36 h). Film thickness was determined 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.

Films were conditioned in a controlled room at 20 °C and 65% relative humidity (RH) before doing the analyses. From here

onwards, blend films with the addition of SB will be also named CMC:PVOH/SB.

### 2.3. UV-treatment

In this study the matrices underwent a photochemical treatment as a result of UV curing in solid state (film). The blend films with SB were placed in plastic supports under a bank of mercury lamps, which emits light mainly of 254 nm wavelength (TUV G30T8, 30 W, Philips, Bs. As., Argentina). The intensity of radiation was 0.14 J cm<sup>-2</sup> min, obtaining different doses by altering the duration of the exposure at a fixed distance. The dose of incident radiation was 22 J cm<sup>-2</sup> 160 min. Blend films were rotated to expose each side to radiation after 80 min.

The radiation intensity was measured with an UV digital Radiometer (Model WLX3W, Cole-Palmer Instrument Company, Vernon Hills, IL, USA). All measurements were performed in the same conditions of temperature and humidity to avoid any influence on the physicochemical properties of films.

Blend films with the addition of SB exposed to UV radiation and CMC:PVOH/SB UV will be used as synonymous.

## 3. Film properties

### 3.1. Moisture content

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 sample.

### 3.2. Optical properties

Film opacity was determined by using the procedure described by Cho and Rhee [26] and film transparency was determined following the method described by Zhang and Han [27]. Film samples were cut into a rectangle and placed on the internal side of a spectrophotometer cell. The absorption spectra of films were recorded in the wavelength range 200–700 nm by using a UV-visible Spectrophotometer (Hitachi U 1900, Japan).

Film opacity was defined as the area under the recorded curve determined by an integration procedure between 400 and 700 nm. The opacity was expressed as absorbance units per nanometers (AU). Film transparency was calculated by the ratio between the absorbance at 600 nm ( $A_{600}$ ) and film thickness, being expressed as  $A_{600} \text{ mm}^{-1}$ . The measurement was repeated three times for each type of film, and the average value was informed.

### 3.3. Film solubility and swelling

To determine film solubility, the samples were cut in 3 × 3 cm pieces, weighed and placed into test beakers with 80 ml deionized water. The samples were maintained under constant agitation for 1 h at 20 °C. The remained pieces of the films after soaking were dried again in an oven at 105 ± 1 °C to a constant weight. Film solubility (%) was calculated as follows:

$$\% \text{Solubility} = \left[ \frac{(\text{Initial dry weight} - \text{Final dry weight})}{\text{Initial dry weight}} \right] \times 100. \quad (1)$$

Swelling was measured by immersion of previously weighted film pieces in 80 ml distilled water. After 60 min of hydration, the samples were recovered and dried with filter paper to remove the excess of surface water and weighted (weight of swollen sample). The swelling of the films was calculated according to the following equation, where

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