Barrier properties of carrageenan/pectin biodegradable composite films

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Abstract

In this work the barrier properties of biodegradable films for food packaging using commercial pectin and k-carrageenan and nanoclays organically modified were studied. Films (67\% k-carrageenan) and different amounts of nanoclays (1, 5 and 10\%) were prepared by casting. A pronounced decrease in the water vapour permeability with the higher driving force used (RH 92\% - 65\%) is observed. It reduces about 35\% of its initial value at 10\% nanoclay content. The films permeability to carbon dioxide also reduces 50\% for 1\% nanoclay content. Films barrier properties may be further improved by enhancing the particles dispersion and exfoliation degree.

Keywords: biodegradable pectin-carrageenan films; nanocomposites; barrier properties; water vapour and gas permeability

1. Introduction

The environmental pollution caused by the massive use of plastics, has greatly increased the research on biodegradable polymers as potential packaging materials. Utilization of waste materials would seem to be ecologically sound and economically advantageous, as they have low or even no costs. Therefore, a variety of renewable biopolymers have been investigated for the development of biodegradable materials to substitute or complement their non-biodegradable petrochemical-based counterparts [1]. Biopolymers obtained from food processing industry wastes (pectins from citrus fruit) and low cost natural resources (carrageenan from seaweeds) have a particular interest, since they provide new markets for low valued by-products [2]. These films are expected to be good oxygen and carbon dioxide barriers, but they have

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poor vapour barrier properties, limiting their application in food packaging. In addition, the gas permeability increases significantly with the increase of the films water content. Thus, in order to enhance the vapour barrier properties, inert impermeable barriers can be incorporated in the polymer matrix.

It was already stated that blends of kappa-carrageenan and pectin are able to form cohesive and transparent films [3]. Their hydrophilic character has shown to increase with increasing kappa-carrageenan content in the polymer matrix. As such, the water vapour permeability also increased, but reached a plateau at about 67% (dry basis) of kappa-carrageenan. A further increase in the kappa-carrageenan content had not a significant influence on the films water vapour permeability.

In order to enhance the water resistance and barrier properties of these films, inorganic impermeable particles (mica flakes) were included in the polymer matrix [4]. The permeability to water vapour and to gases was reduced with the addition of mica particles. It was observed that, the composition of 10% of mica flakes in the polymer matrix represented a critical fraction of inorganic particles, above which there was a decrease of the films barrier properties, for all components tested.

This high quantity of particles in the films makes them less transparent and not suitable for packaging applications. This drawback can be overcome reducing the size and the amount of the particles to be included in the films. Polymer-clay nanocomposites have received significant attention, because they present also a large improvement in the mechanical and physical properties compared with pure polymer or conventional composites [5].

The objective of this work is to develop model composite films based on commercial pectin and k-carrageenan, containing nanoclays organically modified, and to characterize them in terms of their hygroscopic properties and permeability to water vapour and gases.

2. Materials & Methods

Composite films using commercial pectin (33%), k-carrageenan (67%) organically modified nanoclays (1, 5 and 10%) were prepared by wet casting. Commercial kappa-carrageenan and pectin from citrus fruit and nanoclay, Nanomer 1.34 TCN montmorillonite clay surface modified with 25-35 wt % methyl dihydroxyethyl hydrogenate tallow ammonium were obtained from Sigma Aldrich. The experimental details for film preparation were described previously [4]. Films thickness was measured at different points using a manual micrometer (Braive Instruments, Belgium).

The morphological and chemical composition of the films and the dispersion of the nanoclays were obtained by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDXS), using a field emission scanning electron microscope (Jeol JSM-7001F). A gold coating, which is a few nanometers thick, was made on samples surfaces before they were observed.

Water sorption isotherms were determined by placing the samples in desiccators with different relative humidity, imposed by the use of saturated saline solutions, and weighed periodically until a constant weight was reached. Experiments were carried out at 30 ± 2 ºC using LiCl, CH3COOK, K2CO3, Mg(NO3)2, NaNO2, (NH4)2SO4 ,BaCl2 and K2SO4, which have \( a_0 \) 0.115, 0.225, 0.447, 0.52, 0.649, 0.806 , 0.92 and 0.977, respectively .

The water vapour permeability was measured gravimetrically, based on the ASTM E-96-80. Two different driving forces were imposed in order to have different degrees of hydration, 92-64.9 (%RH) and 64.9-22.5 (% RH).

For the measurement of the films permeability to carbon dioxide a pressure decay method was used. The films were previously equilibrated at a constant relative humidity in order to possess a water content of 25% (dry basis) in the beginning of each experiment. The experimental setup was described previously [4].
3. Results & Discussion

The films prepared were flexible and transparent with a thickness of 50±5 μm. The morphological and chemical composition of the films and the dispersion of the nanoclays were obtained by SEM/EDXS. It was observed that the OMMT is homogeneously dispersed in the matrix in the samples for lower OMMT content (1%), but when the OMMT loading is higher, apparent aggregation of OMMT is observed, indicating an heterogeneous dispersion of the clay particles for high amounts of nanoclay. Figure 1 shows a SEM picture of a film with 10% nanoclay, along with the EDX frames for Si, Al, K and S. The aggregates detected on the SEM picture are located where there is a higher concentration of Al and Si atoms (white spots), which means that those aggregates correspond to non-exfoliated nanoclay particles.

Fig. 1. SEM for films with 10% nanoclay and EDXS for some of its elements (K, S, Al, Si)
The water sorption isotherms of the film samples obtained for the carrageenan/pectin mixture (67% carrageenan), varying the content of the organically modified nanoclays (1, 5 and 10%) are independent of the amount of nanoclay and the equilibrium moisture content increases slowly with increasing environmental $a_w$ up to 0.6, beyond which a steep rise in moisture content is observed. On the contrary, the water adsorption capacity of the films with nanoclays for $a_w$ higher than 0.8, decreases with the amount of particles added. This behaviour is expected for hydrophobic particles indicating that they are repelling water, especially for high water activities (Fig. 2).

The Guggenheim-Anderson-de Boer (GAB) model (Eq. 1) was used to fit the experimental sorption data.

$$X = \frac{CkX_0a_w}{(1-ka_w)(1-ka_w + Ck a_w)}$$  \hspace{1cm} (1)

where $X$ is the equilibrium moisture content at the water activity $a_w$, $X_0$ is the monolayer moisture content and represents the water content corresponding to saturation of all primary energy difference between the water molecules attached to primary sorption sites and those adsorption sites by one water molecule, $C$ is the Guggenheim constant and represents the absorbed to successive sorption layers, and $k$ is the corrective constant taking into account properties of multilayer molecules with respect to the bulk liquid. GAB equation parameters were calculated by non-linear fitting using the software package Scientist™, from MicroMath®.

![Fig. 2. Experimental moisture sorption isotherms of kappa-carrageenan/pectin films with different amounts of nanoclay: (○) 0%, (Δ) 1%, (□) 5% and (•) 10% (mass of nanoclay per mass of dry polymer); the respective fitted GAB curves (lines) and GAB parameters (inserted table).](image-url)

Water vapor permeability values varied between $2 \times 10^{-11}$ and $9 \times 10^{-11}$ mol/m² s Pa, depending on the driving force used and on the particles content (Figure 3). As can be observed, the water vapour permeability is higher when the driving force is 92-64.9 (%RH), this fact is associated to the more
homogenously hydrated films throughout their thickness. For a driving force of 64.9-22.5 (% RH), the WVP is lower, because there is less water in the polymeric matrix and the plasticizing effect is lower.

The water entering the films is acting as a diffusion species and also as a plasticizer. In this way, it loosens the polymeric matrix and, consequently, water transport is facilitated [4].

A pronounced decrease in permeability with the higher driving force is observed. It reduces about 35% of its initial value at 10% nanoclay content. For a driving force of 64.9-22.5 (% RH) the permeability increases for 1% nanoclay content and then remains constant.

Regarding the barrier properties to gases, the permeability was calculated using the following equation:

\[
\frac{1}{\beta} \ln \left( \frac{P_f - P_p}{P_f - P_p} \right) = \frac{1}{\beta} \ln \left( \frac{\Delta p_0}{\Delta p} \right) = P \frac{t}{\delta}
\]

where \(P_f\) and \(P_p\) are the pressures in the feed and permeate compartments, respectively; \(P\) is the gas permeability; \(t\) is the time; and \(\delta\) is the film thickness. The geometric parameter \(\beta\) is \(A (1/V_f + 1/V_p)\), where \(V_f\) and \(V_p\) are the volumes of the feed and permeate compartments, respectively, and \(A\) is the membrane area.

A much lower permeability to oxygen than to carbon dioxide was obtained for the films without particles, \(4.0 \times 10^{-17}\) and \(3.9 \times 10^{-15}\) mol. m/m² s Pa, respectively [4]. Furthermore, a significant decrease of the permeability was observed for CO₂ (73%), for films containing 10% of mica flakes. For the films with nanoclays the permeability to CO₂ reduces 50% for the lower amount of nanoclay (1%) and then slightly increases with nanoclay content (Fig. 4).

These results are interesting, since it was possible to increase the barrier properties to CO₂ of hydrated films (with 25% of water, dry basis), in conditions for which the polysaccharide films start to lose the good gas barrier properties that they possess when dried.
Fig. 4. Carbon dioxide permeability as function of nanoclay content

4. Conclusion

In this work, the enhancement of the barrier properties to water vapour and CO2 of a polymeric matrix composed by kappa-carrageenan and pectin (66.7% kappa-carrageenan), with the inclusion of nanoclays, was studied. The effect of the films particle content on the water vapour permeability (WVP) was dependent on the driving force applied.

A higher WVP reduction (of about 35% for nanoclay content of 10 %), was observed when the films were more homogenously hydrated throughout their thickness. A significant decrease was also observed for CO2 permeability (50%), when the films were plasticized with water for which there is a depletion of the good barrier properties characteristic of dry polysaccharide films.

The results indicate that, the addition of organically modified nanoclay particles to the polymer matrix has a positive impact on the films barrier properties, which may be further improved by enhancing the particles dispersion and exfoliation degree.

References


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