SciVerse ScienceDirect

Procedia Food Science 1 (2011) 240 – 245

Procedia Food Science

11th International Congress on Engineering and Food (ICEF11)

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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2211 601X

doi:10.1016/j.profoo.2011.09.038

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 dihidroxyethyl 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-700IF). 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, CH_3COOK, K_2CO3, $Mg(NO_3)_2$, $NaNO_2$, $(NH_4)_2SO_4$,$BaCl_2$ and K_2SO_4, which have a_w 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].