Carbohydrate Polymers 97 (2013) 217–225

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Carvacrol affects interfacial, structural and transfer properties of chitosan coatings applied onto polyethylene

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ARTICLE INFO

Article history:
Received 8 March 2012
Received in revised form 16 April 2013
Accepted 17 April 2013
Available online xxx

Keywords:
Bio-based polymer
Coating
Chitosan
Wettability
Surface energy
Permeability

ABSTRACT

Different chitosan coating solutions were tested with the aim of investigating their adhesion and wettability onto polyethylene film to improve packaging performance and provide antimicrobial properties. Surface wetting kinetics was monitored by contact angle measurements. Addition of ethanol and carvacrol improved wettability and adhesion of the thin chitosan layer. Structure, water vapour, O_2, CO_2 and air permeabilities of self supported chitosan films and coated polyethylene were determined. The formation of a thin chitosan layer on polyethylene improved gas barrier properties decreasing the Permeability Coefficient for oxygen and carbon dioxide (P_{O_2}, P_{CO_2}) from 100 to 10,000 times. Presence of carvacrol in the chitosan coating layer increased P_{O_2}, P_{CO_2} and P_{air} by a factor of ten. Moreover, it influenced film microstructure. However chitosan was shown to be good gas barrier film in the dry state.

1. Introduction

The combination of bio-based polymers with common synthetic materials is a novel approach in material engineering that has significantly increased over the past few years (Farris et al., 2011). Derived from various natural sources bio-based polymers can be formed as either coatings or self standing films (Hong & Krochta, 2006). Still, the replacement of plastics with a self standing bio-based polymer is a difficult task to achieve. Therefore development of new bio-based coatings or internal layers to improve barrier, thermal and mechanical properties has been proposed (Farris et al., 2011; Hong, Lee, & Krochta, 2005).

The wettability of a solid surface is one of the crucial parameters in the production of composite coated materials. Moreover it is of a great importance for industrial application. Surface layer properties, wettability, surface free energy and phenomena that occur at the interfaces are important criteria for the efficiency of the adhesion properties of the coatings onto polymers (Zenkiewicz, 2007). The similarity between the coating solution and the surface to be coated in values of dispersive and polar components influences the spreadability of the coating solutions. A better compatibility between the coated surface and the coating film forming solutions can be achieved by incorporating surface-active agents within the casting solution. Chitosan is a functional bio-based polymer with a great potential in food applications. It is due to its biodegradability, biocompatibility, antimicrobial activity, nontoxicity and film forming capacity (Arvanitoyannis, 1999; Tharanathan & Kittur, 2003). Chitosan based films are good oxygen and carbon dioxide barriers. Still, due to its hydrophilic nature, they are highly permeable to water vapour (Suyatma, Copinet, Tighzert, & Coma, 2004).

Due to the health concerns and environmental problems, the current research on active packaging has focused on natural preservatives or natural active compounds introduced into biodegradable/biosourced packaging materials (Siripatrawan & Harte, 2010; Suppakul, Miltz, Sonneveld, & Bigger, 2003). Therefore, the incorporation of carvacrol as the main component from oregano essential oil can improve both the antimicrobial and the functional film properties (Vargas, Albors, Chiralt, & González-Martínez, 2009).

When designing the most suitable film for a determined use, it is important to understand the influence of physico-chemical factors on the functional properties of the film forming solutions

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http://dx.doi.org/10.1016/j.carbpol.2013.04.059

and obtained films. The application target of this research was the development of the environmentally friendly carvacrol activated chitosan-coated polyethylene film. Carvacrol was incorporated in the coating layer with the purpose of creating an active antimicrobial film for further application. Furthermore, it is aimed to assess the ability of the deposition of different compositions of chitosan coatings on the low density polyethylene. Therefore, surface modifications and barrier property changes after the coating process have been studied as a function of the coating composition. To better understand the possible changes in the chitosan coatings and in the chitosan self standing films have also been studied.

2. Materials and methods

2.1. Materials and reagents

Commercial grade chitosan (CS) (France Chitine, Marseille, France, powder 652, having a molecular mass of 165 kDa, degree of deacetylation of >85%) was used as the film forming matrix. A commercial, low density polyethylene film (LDPE) (Wipak, Lille, LDPE45 UFP; thickness of 45 μm) was used as a polyolefin material. Carvacrol (CVC) (purity >97%, Fluka) was used as the aroma compound in order to improve the functional film properties. Acetic acid (glacial 100%, Merck, Darmstadt, Germany) and pure ethanol (absolute, Sigma–Aldrich) were used as solvents in the preparation of the film forming solutions (FFS). Magnesium chloride ($MgCl_2$, Sigma) was used to prepare saturated salt solutions to fix the relative humidity for water vapour permeability measurements. Deionised water, diodomethane (purity >99%, Sigma–Aldrich), glycerol (Fluka Chemical, 98% purity, Germany) and tetradecane (purity >99%, Sigma–Aldrich) were used for surface analysis. No further purification of chemicals has been done and freshly prepared solutions were always used.

2.2. Film preparation

2.2.1. Self standing chitosan films

A chitosan solution was prepared by dissolving the chitosan powder in a 1% (v/v) aqueous acetic acid, to obtain 2% (w/v) film forming solutions (FFS). To achieve a complete dispersion of chitosan, the solution was stirred for 2 h at room temperature. To prepare aqueous hydroalcoholic acid media, ethanol was mixed in a ratio ethanol:aqueous acetic acid of 30:70. To obtain film forming solutions with incorporated aroma compound, carvacrol (0.5%, w/v) was homogenised either in aqueous acid CS solution or hydroalcoholic acid CS solution at 24,000 rpm for 10 min with an Ultra Turrax (T25 IKA). In order to obtain films, solvents were removed by drying in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 20 °C and 30% RH. After drying, the films were peeled off and stored in the same ventilated climatic chamber at 25 °C and 30% RH before measurements. The films prepared in the acetic acid solution were coded as CSA, those in hydroalcoholic acid solution as CSE and those containing carvacrol as CVC.

2.2.2. Chitosan coated polyethylene films

The hydroalcoholic acid chitosan solution with/or without carvacrol was prepared as described in Section 2.2.1. Chitosan coated PE were prepared according to Sollogoub et al. (2009). The coating was carried out at room temperature, using a Nordson slot die (ChameleonTM), appropriate to fluids of viscosity ranging between 0.5 and 2 Pa/s. Films were dried in a flow of a dry air at 50 °C and RH < 10%. After drying, they were stored in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) before measurements at 25 °C and 30% RH.

2.3. Contact angle, surface tension, critical surface tension, surface free energy and wettability measurements

2.3.1. Determination of a contact angle

Contact angle (θ) is described as a relationship between the surface tension at a point of the three phase contact line between a solid phase S, a liquid L and its vapour V given by:

$$\gamma_{LV} \times \cos\theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

where γ_{LV}, γ_{SV} and γ_{SL} are the surface tensions of the liquid–vapour, solid–vapour and solid–liquid, respectively (Young, 1805).

The contact angle was measured by the sessile drop method, in which a droplet of the tested liquid was placed on a horizontal film surface. Measurement was done using a DGD-DX goniometer (GBX, Romans-sur-Isere, France), equipped with the DIGIDROP image analysis software (GBX, Romans-sur-Isere, France) according to Karbowiak, Debeaufort, and Voilley (2006). A droplet of a testing solution (~1.5 μL) was deposited on the film surface with a precision syringe. The contact angles were measured on both sides of the drop and averaged. The measurement was carried on over 120 s. The effect of evapouration was assessed on the aluminium foil considered as an impermeable reference surface. All measurements were done on both sides of the films. For chitosan self supported films, the surface in contact with the glass support during drying will be referred to as the "support side" and the other surface in contact with the air during drying will be referred to as the "air side".

2.3.2. Surface tension and critical surface tension determination

The surface tension of the film forming (coating) solutions (γ_L) was measured by the sessile drop method and Laplace–Young approximation (Song & Springer, 1996a,b). In order to determine the drop shape, using the image analysing software, solutions were taken with a 1 mL syringe (Hamilton, Switzerland). The estimation of the critical surface tension (γ_C) of the PE, the coated PE and the self standing chitosan films was obtained by extrapolation from the Zisman plot (Zisman, 1964). Zisman plots were obtained by plotting the cosine of the contact angles ($\cos\theta$) of a series of standard liquids (Table 1) on the film surface versus the surface tension of the same liquids. The critical surface tension values of films are the mean of the extrapolation of $\cos\theta$ for the liquids that form approximately a straight line. Extrapolation of this line to the point of $\cos\theta = 1$, yields the value of the critical surface energy equal to liquid surface tension (γ_L) at this point.

2.3.3. Surface free energy and wettability

The surface free energy (SFE) and its polar (γ_S^P) and dispersive (γ_S^D) components were calculated by the Owens–Wendt method (Owens & Wendt, 1969), according to Eqs. (2) and (3):

$$\gamma_S = \gamma_S^D + \gamma_S^P \quad (2)$$

$$\gamma_L(1 + \cos\theta) = 2\left((\gamma_S^D\gamma_L^D)^{0.5} + (\gamma_S^P\gamma_L^P)^{0.5}\right) \quad (3)$$

Because two unknowns, γ_S^D and γ_S^P appear in Eq. (3), it is insufficient to determine the SFE of a polymer. Thus, the contact angle has to be measured using two measuring liquids of known surface tension and their polar (γ_L^P) and dispersive (γ_L^D) component (deionised water as the liquid with the dominant polar component and diodomethane with the dominant dispersive component). That yields to the two equations in the form of Eq. (2), with different