Journal of Cleaner Production 91 (2015) 36–42

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Valorisation of fishery industry wastes to manufacture sustainable packaging films: modelling moisture-sorption behaviour

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ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form
2 December 2014
Accepted 3 December 2014
Available online 11 December 2014

Keywords:
Valorization
Chitosan
Sustainable films
Moisture sorption
Modelling

ABSTRACT

The waste production from the food processing industry causes serious environmental, economic and social problems. However, this waste streams can be used and transformed into added value products for food packaging applications. With this aim, this work is focused on the manufacture of sustainable films by using chitosan derived from wastes of fishery industry. Since chitosan is a hydrophilic polymer, moisture sorption behaviour was analysed in order to provide novel knowledge related to the best use conditions for chitosans as packaging films. Chitosan films were prepared using different contents of glycerol as plasticizer to improve functional properties. Water sorption isotherms were determined in the range of 0.1–0.9 water activity using a gravimetric method. The experimental data were fitted to several sorption models and the Guggenheim-Anderson-de Boer equation was found to best represent the experimental data through the entire range of water activity in order to predict the moisture sorption behaviour of the films prepared in this study. The results revealed that chitosan films show a great potential to be used as packaging films for food products with intermediate moisture sorption. These findings are expected to aid in the suitable design of chitosan-based sustainable food packaging films that contribute to improve consumer perception of food products, valorise a waste product, maintain food quality and thus, reduce food waste and environmental impact caused by conventional packaging systems.

1. Introduction

Plastics are unique materials that fulfil a huge range of functions in society, but contribute to environmental impacts related to the consumption of resources and the end of life (Dormer et al., 2013). Concerns over the availability of petroleum-derived polymers, together with the waste-disposal problems caused by the use of these non-biodegradable materials, are reviving the interest in renewable polymers (Álvarez-Chávez et al., 2012; Leceta et al., 2013; Soroudi and Jakubowicz, 2013). The end of life aspects constitute the most negative aspect of plastic materials from the consumer point of view, since packaging waste highly impacts on urban, rural and marine environments (Iles and Martin, 2013). Hence, approaches to reduce the environmental impact of the packaging systems have been extended (Kang et al., 2013). In recent years, there has been an increasing pressure from legislation on the packaging industry to reduce the environmental impact of its products. Consumers are also being increasingly informed on the damages to the environment (Laroche et al., 2001; Bertoluci et al., 2014), and future consumers will take ecological and ethical criteria in even greater consideration when selecting food products (Manfredi and Vignali, 2014). In this regard, the introduction of renewable and biodegradable plastics into the market could be a suitable approach to face such a problem (Peelman et al., 2013; Philp et al., 2013; Rhim et al., 2013).

The primary function of packaging, an essential component of the supply chain, is to protect the content and, in the specific context of food packaging, to maintain food quality until it is consumed (Heydari et al., 2013). Therefore, packaging attributes influence food losses, although this fact is usually neglected (Wikström et al., 2014). However, food waste is increasingly recognised as being central to a more sustainable resolution of the global waste challenge (EPA, 2012; Papargyropoulou et al., 2014). Food requires large amounts of energy and other resources during production and distribution (Williams et al., 2012). If food is lost, the resources associated with food are also lost, leading to an unnecessary environmental impact and thus, the suitable choice of

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http://dx.doi.org/10.1016/j.jclepro.2014.12.009
0959-6526/

food packaging materials can contribute to reduce food waste and environmental impacts (Barlow and Morgan, 2013). Sustainable packaging can be developed to reduce the environmental impact of the packaging itself and extend the shelf-life of foodstuff, which makes the product supply chain much more sustainable, decreasing the total environmental impact of the food-packaging system (Svanes et al., 2010; Wikström and Williams, 2010). The most widely used renewable food packaging materials are paper and board, which are based on cellulose, but major efforts are under way to find alternative polymers (Nur Hanani et al., 2012).

Waste valorisation practises have attracted a significant amount of attention in recent years, with the aim of managing waste in the most sustainable way (Oliveira et al., 2013). Since waste can be used as raw material for new products and applications, valorisation of industrial and marine wastes and by-products is regarded as an attractive alternative (Garrido et al., 2014; Mirabella et al., 2014). Among them, chitosan is the most abundant amino-polysaccharide existing in the environment (Elwakeel and Atia, 2014) and it is derived from chitin obtained as solid waste from fish and shellfish (Anh et al., 2011; Shaheen et al., 2013). Therefore, chitosan has a great potential due to its abundance and biodegradable characteristics (Leceta et al., 2014; Portes et al., 2009). The richest source of chitin, and the most available to support the commercial production of chitosan, is crustacean shell waste (Weska et al., 2007).

Chitosan is a well-known film-forming biopolymer (Li et al., 2013), but pure chitosan films are brittle, thus plasticizers are needed in order to improve their mechanical behaviour (De Moura et al., 2012; Meng et al., 2014). Among a vast array of possible plasticizers, glycerol has been widely used to plasticize films (Kammoun et al., 2013; Rodriguez-Núñez et al., 2014). In addition to mechanical properties, barrier properties play an important role for food preservation (Kurek et al., 2012). Since environmental conditions, such as humidity, can affect food quality, the knowledge of moisture sorption behaviour is of vital importance when intending to develop packaging films and reduce food losses (Esse and Saari, 2008; Valenzuela et al., 2013). In this context, the determination of moisture sorption isotherms is a way of characterizing the water vapour sorption capacity of the film to predict its stability during service (Jagadish et al., 2010). The relation between the equilibrium moisture content of the film and the water activity at a constant temperature is described by sorption isotherms and several equations are available in literature to determine them (Suppakul et al., 2013). Although the prediction of water transport through hydrophilic films like chitosan films is complex (Wiles et al., 2000), the determination of sorption isotherms is of great interest for food packaging industry since they provide information for processes like drying, storage and transport, which affect the quality of both films and food. However, there is no study about the moisture sorption behaviour of chitosan films as a function of plasticizer content. Since moisture sorption isotherms provide very useful information to determine the ideal water activity range without sensitive changes for food products, the aim of this work was to obtain reliable data for moisture sorption modelling in order to provide novel and useful information for the processing of chitosan films, as well as for the determination of their proper storage conditions to avoid deterioration effects caused by moisture sorption. In this way, with the appropriate knowledge of the moisture behaviour of chitosan films, an innovative food packaging material obtained by waste valorisation could be developed.

2. Materials and methods

The materials used in the present work were high molecular weight (HMw) and low molecular weight (LMw) chitosans, provided by Sigma–Aldrich (Spain), with a degree of deacetylation higher than 75%. Acetic acid was purchased from Panreac (Spain) and was used to control solution pH. Glycerol (GLY), food grade, was used as plasticizer and was also obtained from Panreac (Spain).

2.1. Film preparation

Chitosan films were prepared by casting. A 1% by weight chitosan solution was prepared in a 1% acetic acid solution. After 15 min under continuous stirring, glycerol was added. Stirring was continued for 30 min until total homogenization of the mixture. After that, solutions were filtered, poured into Petri dishes and allowed to dry at room temperature. HMw and LMw chitosan films with different glycerol contents (0, 15 and 30 wt %) were prepared and designed as 0HMw, 15HMw, 30HMw, 0LMw, 15LMw, and 30LMw. All films were conditioned in a climatic chamber (ACS SU700V) at 25 °C and 50% relative humidity for 48 h prior to testing.

Film thickness (L) was measured to the nearest 0.001 mm with a hand-held digimatic micrometer (QuantuMike Mitutoyo). The values obtained for each sample at five different locations were averaged.

2.2. Water contact angle

A contact angle equipment (model Oca20, dataphysics instruments) was used to measure the water contact angle on the surface of chitosan films. A film sample (20 mm × 80 mm) was put on a movable sample stage and levelled horizontally; then, a drop of about 3 μL of distilled water was placed on the surface of the film using a microsyringe. The contact angle was measured in a conditioned room by recording contact angle values and image analyses were carried out using SCA20 software.

2.3. Water vapour permeability (WVP)

WVP measurements were carried out into a controlled humidity environment chamber (PERME™ W3/0120, Labthink). Films were cut into a circle of 7.40 cm diameter and the test area was 33 cm^2. The setup was subjected to a temperature of 38 °C and relative humidity of 90%, according to ASTM E96-00 (ASTM, 2000). Water vapour transmission rate (WVTR) was calculated by Eq. (1):

$$WVTR = \frac{G}{t \times A} \quad (1)$$

where G is the change in weight (g), t is time (h), and A is the test area (m^2). WVP was calculated by Eq. (2):

$$WVP = \frac{WVTR \times L}{\Delta P} \quad (2)$$

where L is the thickness of the test specimen (mm) and ΔP is the partial pressure difference of the water vapour across the film.

2.4. Moisture sorption isotherms

Moisture sorption isotherms of chitosan films were determined by exposing films to different water activities (a_w) into a controlled humidity environment chamber (PERME™ W3/0120, Labthink) at a constant temperature until equilibrium was obtained. All films were dried in a vacuum desiccator at 25 °C for 72 h. Dried films were placed into the environmental chamber and weighted to the nearest 0.00001 g using an electronic scale installed within the environmental chamber. The setup was subjected to a temperature of 25 °C and a range of relative humidity from 10 to 90%. Equilibrium was considered to be achieved when the difference between