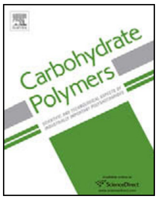
Carbohydrate Polymers 110 (2014) 309–319

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Influence of plasticiser on the barrier, mechanical and grease resistance properties of alginate cast films

Verena Jost[a,b,*], Karin Kobsik[a], Markus Schmid[a,b], Klaus Noller[a]

[a] *Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Strasse 35, 85354 Freising, Germany*
[b] *Chair of Food Packaging Technology, Technische Universität München, Weihenstephaner Steig 22, 85354 Freising, Germany*

ARTICLE INFO

Article history:
Received 6 September 2013
Received in revised form 5 March 2014
Accepted 31 March 2014
Available online 8 April 2014

Keywords:
Alginate
Plasticiser
Mechanical properties
Barrier
Oxygen permeability
Water vapour transmission rate

ABSTRACT

Alginate cast films were plasticised by two plasticisers – glycerol and sorbitol – in different concentrations. As a function of the plasticiser type and concentration, the following parameters were investigated: equilibrium moisture content (EMC), colour measurement, microscopic analysis by SEM, grease resistance, oxygen permeability (OP), water vapour transmission rate (WVTR) and the mechanical properties. Both plasticisers have a positive influence on the mechanical properties but differ in their effect on the barrier properties. Whilst an increasing concentration of glycerol increases the permeability of alginate films to oxygen and water vapour, sorbitol did not influence the barrier properties to oxygen or water vapour. The behaviour of glycerol is in accordance with the free volume theory. The effect of sorbitol is assumed to be due to the good steric fit of sorbitol into the alginate network. The good embedding of sorbitol between the alginate polymer chains means it can lower the intermolecular bonding while still offering bonding possibilities. Therefore the flexibility of the cast films is increased while maintaining the barrier properties.

1. Introduction

With the aim of creating a sustainable packaging material for sensitive products, efforts have been made to develop materials based on renewable resources rather than petrochemical-based materials. The requirements of packaging materials depend on the packed goods. The packaging materials need to fulfil different needs in terms of moisture and grease resistance as well as the water vapour and gas barriers. In order to create a packaging concept for optimal preservation of the packed goods, for example foods, different parameters such as the barrier and mechanical properties, packing atmosphere and the transpiration and respiration rate of the food must be taken into account in order to avoid loss of nutritional content, off-flavours, colour changes, oxidation processes and spoilage. In order to meet these requirements, multilayer structures based on polymer or paper substrates are widely used in the packaging industry. These structures consist of materials with the requisite functional properties combined by co-extrusion or lamination (Mueller, Schoenweitz, & Langowski, 2012; Petersen et al., 1999). Within these structures, ethylene vinyl alcohol copolymers (EVOH) are commonly employed to create an adequate barrier against oxygen. Besides EVOH, the polymers used for this application are almost always petrochemical-based. Another aspect is the recyclability, which is often not possible for these multilayer structures because separation into the pure materials is difficult (Bugnicourt et al., 2013; Endres & Siebert-Raths, 2011; Schmid, Hinz, Wild, & Noller, 2013). By using bio-based and biodegradable materials in such a system, the dependence on petrochemical-based materials can be reduced and a solution for the recycling process can be provided. Thus research on biopolymer packaging materials has recently intensified.

To accelerate the development of bio-based and biodegradable polymers, various attempts have been made to improve the properties of carbohydrates, proteins and even natural waxes (Chiumarelli & Hubinger, 2014; Janjarasskul, Rauch, McCarthy, & Krochta, 2014; Mekonnen, Mussone, Khalil, & Bressler, 2013; Rodrigues et al., 2013; Schmid et al., 2013). The present article focuses on alginate, a

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* Corresponding author. Tel.: +49 8161 491 227; fax: +49 8161 491 555.
E-mail address: Verena.Jost@ivv.fraunhofer.de (V. Jost).

http://dx.doi.org/10.1016/j.carbpol.2014.03.096
0144-8617/

carbohydrate. Other carbohydrate-based materials are widely used and are still being optimised for packaging purposes: cellulose, starch, chitosan and xylan. Cellulose – one of the first biopolymers used – has been studied with regards to modification of its surface (Rodionova, Lenes, Eriksen, & Gregersen, 2011) and size (Aulin, Gallstedt, & Lindstrom, 2010; Siro & Plackett, 2010). The properties of amylose and amylopectin coatings have been analysed in detail (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). It was shown that an increase in relative humidity (rh) leads to plastification of the films (Stading, Rindlav-Westling, & Gatenholm, 2001). The resulting increased mobility in the network results in swelling which reduces the oxygen barrier. In contrast to starch, chitosan films show extremely low oxygen permeability values at low relative humidity, but high water vapour permeabilities (Aider, 2010; Kurek, Galus, & Debeaufort, 2014). Over storage time the oxygen permeability stays constant while the water vapour permeability decreases (Butler, Vergano, Testin, Bunn, & Wiles, 1996). Kjellgren, Gallstedt, Engstrom, and Jarnstrom (2006) studied greaseproof paper and reported that chitosan coatings on cellulose show good adhesion probably because of the different ionic character (chitosan – cationic, cellulose – anionic), which is important for further packaging applications.

Alginate is one of the most promising carbohydrates for packaging applications, especially for foods sensitive to gas permeation. Most research on alginate has concerned edible coatings, for example to improve the quality of pork patties by coating with calcium alginate (Wanstedt, Seideman, Donnelly, & Quenzer, 1981) or to improve the colour and flavour of frozen shrimps (Earle & Snyder, 1966). Some types are already used as approved food additives (E 400). Applications of alginates can additionally be found in the area of release drug delivery systems and for the encapsulation of herbicides, microorganisms and cells (Chandra & Rustgi, 1998).

With respect to functional coatings, alginates have shown much promise for application in packaging systems. Work has been published on the development of alginate-based coatings with high oxygen barrier properties (Cao, Yang, & Fu, 2009; Earle & McKee, 1985, Rhim, Lee, & Hong, 2006; Hambleton, Debeaufort, Bonnotte, & Voilley, 2009; Olivas & Barbosa-Cánovas, 2008). The addition of antimicrobial substances to an alginate matrix for smart packaging applications has also been reported (Concha-Meyer, Schobitz, Brito, & Fuentes, 2011; Jang, Lim, & Song, 2010).

Alginate is a carbohydrate, a salt of alginic acid, which is found in the cell membrane of brown algae and some bacteria. The molecular structure of alginates is a binary linear heteropolymer consisting of two uronic acids: β-D-mannuronic acid (M) and α-L-guluronic acid (G) (see Fig. 1) (Hirst, Jones, & Jones, 1939). These acids are joined by a β-1,4-glycosidic linkage (Moen & Ostgaard, 1997). Depending on the functional group at C2 or C3, the source of the alginate can be determined: Alginates derived from bacteria have an acetyl group while algae-derived acids have a hydroxyl group (Smidsrod & Draget, 1997). The polymer chain is divided into alternating segments of M-blocks, G-blocks or MG-blocks. There is no ordered sequence of the blocks, and for this reason the structure of the alginate is not determined by the order of the monomers (Smidsrod & Draget, 1997). The distribution and the proportion of the blocks vary with the brown algae species, geographic origin and the degree of maturity and harvesting time (Marburger, 2003). This different composition is the reason why the molecular weight (M_w) can range from 32 to 400 kDa (Lee & Mooney, 2012; Mergenthaler, 1984).

Due to the different bonding of the monomers, various kinds of chain conformation are possible. M-blocks form even structures while G-blocks build an 'egg-box-type' structure (Hänsel & Sticher, 2010; Straatmann, 2003). The properties of the alginate are essentially influenced by the bonding type and the structure: MG-chains are the most flexible form in the alginates due to the equatorial-axial bonding (Ertesvåg & Valla, 1998). Also, the M-blocks can be very flexible due to their conformation (Draget, Moe, Skjak-Braek, & Smidsrod, 2006; Draget, Skjåk-Bræk, & Stokke, 2006) while the G-blocks are stiffer and less flexible due to steric hindrance (Fasihuddin, Wedlock, Omar, & Phillips, 1988). Viscosity measurements reveal that the molecular strength increase in the following order: MG < MM < GG (Steinbüchel & Rhee, 2005).

In the presence of monovalent cations, alginates are soluble in water. The addition of polyvalent cations such as Ca^{2+}, Cu^{2+}, Al^{3+} and Fe^{3+} results in insolubility in water due to gel formation via crosslinking reactions (Chandra & Rustgi, 1998). Alginate films have very low moisture barriers but very high oxygen barriers

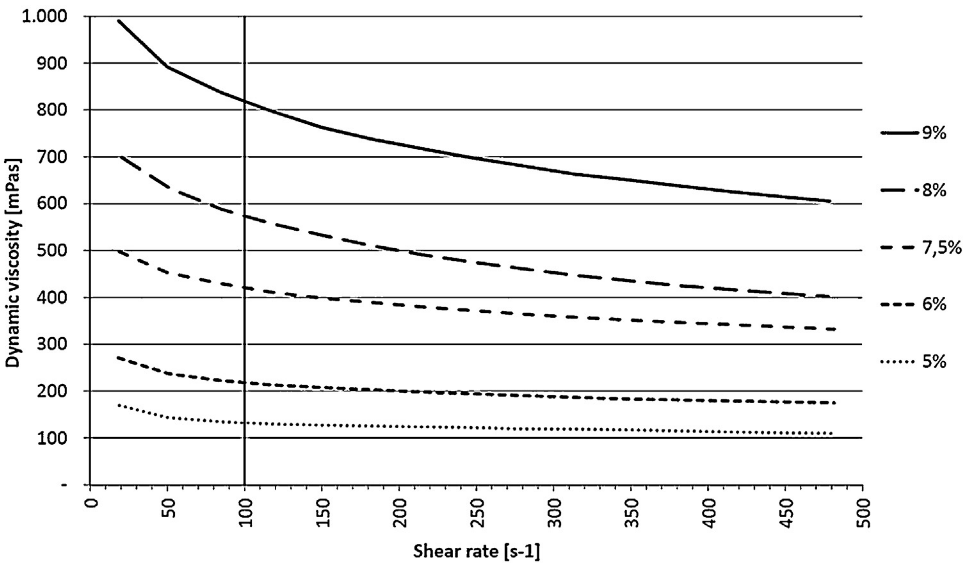

Fig. 1. Dynamic viscosity of pure alginate solutions with different dry matter contents.