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

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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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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

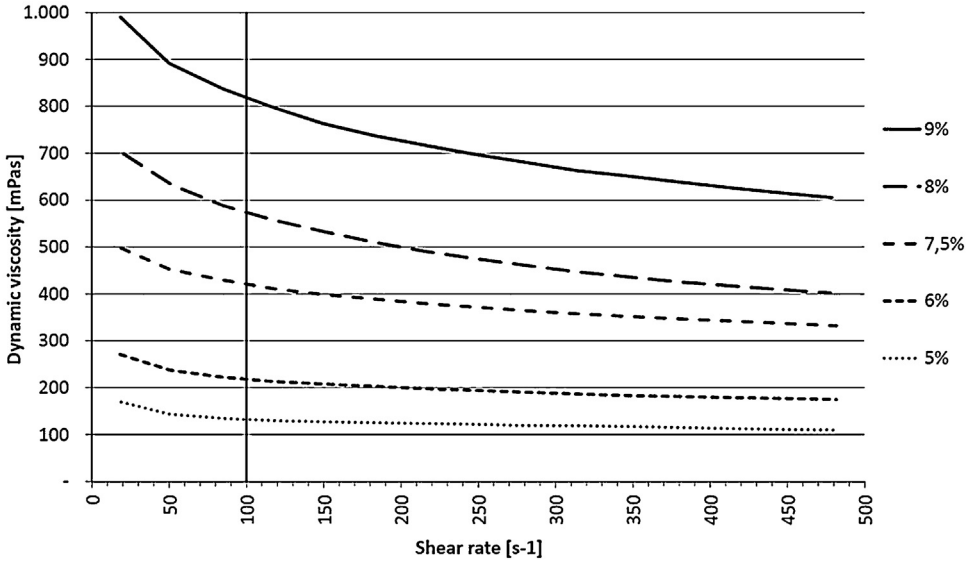

Fig. 1. Dynamic viscosity of pure alginate solutions with different dry matter contents.

and high grease resistance (Andersson, 2008). The low moisture barrier is caused by the absorption and swelling behaviour of alginates which accelerates the water uptake and the water vapour transmission (Rhim et al., 2006). However, alginates have good water-holding properties and runability in conventional coating techniques.

In order to benefit from the excellent barrier properties to oxygen, alginate coatings must be further optimised before they can be used in packaging systems. One big obstacle to overcome is the brittleness of the alginate coatings. One way to increase the strength of alginate films is to increase the length of the G-blocks or to increase the molecular weight (Lee & Mooney, 2012). An increase in the M-blocks results in greater flexibility and elasticity of the films (Draget, Moe et al., 2006; Draget, Skjåk-Bræk, et al., 2006). Another approach for improving the flexibility is to add plasticisers. Plasticisers are added to polymers to improve their processing behaviour and their flexibility by decreasing the melt viscosity, the glass transition temperature (T_g), the melting temperature (T_m) and Young's Modulus (YM). There are two ways of plasticisation: external plasticisation (addition of physical materials, usually low-molecular weight additives such as propylene glycol, glycerol and sorbitol) or internal plasticisation (copolymerisation of molecular groups which increase the chain dynamics) (Elias, 2009). Suitable mechanical properties are essential requirements of packaging materials for the packaging process. Depending on the packaging application, high mechanical loads may be necessary to form the packaging. Knowledge about the influence of plasticisers on the mechanical properties of packaging materials is very important in order to develop customised packaging materials. The objective of this study was therefore to investigate how and to what extent the addition of two external plasticisers, namely glycerol and sorbitol, influence the mechanical properties, grease resistance and oxygen and water vapour barriers of alginate cast films.

2. Materials and methods

2.1. Materials

Sodium alginate powder (GRINSTED® Alginate LFD 1205) was obtained from Danisco Gums & Systems Division, Kreuzlingen, Switzerland. This product is laid down in the Food Chemical Codex and is covered by EU reference number E401 and CRF 184.1724. The ratio of guluronic acid/mannuronic acid is approx. 40/60, the molecular weight (M_w) is approx. 55 kDa and the residual water content is 10–12%. The information was provided by Danisco.

Glycerol was obtained from Merck Millipore KGaA, Darmstadt, Germany (CAS-no. 56-81-5, order no.8.18709.1000). No purity was stated on the data sheet. The residual water content was ≤0.5%. According to the material data sheet the density varies from 1.259 to 1.263 g/cm^3 and the M_w is 92 Da. Neosorb 70/70 from Roquette GmbH, Frankfurt, Germany, was used as the sorbitol additive. This food grade sorbitol has a dry matter content of at least 70% and a density of 1.49 g/cm^3. The M_w is 182 Da. The information was taken from the product data sheets.

2.2. Methods

2.2.1. Preparation of coating formulation

Aqueous alginate solutions (pH 7) were prepared by mixing 7.5 wt.% alginate powder and the respective amount of plasticiser (the residual water content of alginate and plasticiser were taken into account) with distilled water. No further additives were used. The solution was continuously stirred (300 rpm) in an electric stirrer (Thermomix 31-1, Vorwerk Elektrowerk GmbH & Co. KG, Wuppertal, Germany) while heating to 90 °C and holding at this temperature for 15 min. Thereafter the solution was treated for 15 min in an ultrasonic bath (Digitec DT 514 H, Zefa-Laborservice GmbH, Harthausen, Germany) at a frequency of 37 kHz and at 80 °C. Foam and bubbles were removed after the ultrasonic treatment using a pipette.

2.2.2. Film casting

The formulations were filled into petri dishes (120 mm × 120 mm × 17 mm) made of polystyrene (PS) in order to form films with a dry film thickness of approximately 100 μm. The original sample weight depended on the type and amount of plasticiser. To achieve a homogenous distribution of film thicknesses, the filled dishes were moved in a figure eight. For drying, the dishes were placed on level ground under conditions of 23 °C and 50% rh. They were considered to be at their equilibrium moisture content (EMC) when the weight changes were less than 0.01 g per day.

2.2.3. Conditioning

All the cast films were conditioned at a constant temperature and humidity of 23 °C and 50% rh for at least 48 h in order to adjust the moisture content before further analysis.

2.2.4. Thickness measurements

The thickness of the cast films were measured after they reached their respective equilibrium moisture content using a Precision Thickness Gauge FT3 (Rhopoint Instruments, Bexhill on Sea, UK) which provided 0.4 μm repetition accuracy. Five different positions on each sample were measured; the measurement conditions were 23 °C and 50% rh. To determine the oxygen permeability (OP), water vapour transmission rate (WVTR) and mechanical properties, each specimen was measured and then the values were normalised to a constant thickness.

2.2.5. Viscosity

The viscosity of the solution was measured by a cone-plate rheometer CVO50 of Bohlin Instruments (Malvern Instruments Ltd, Malvern, GB). The solution was analysed with a linear increasing shear rate of 10–1000 s^{-1} over a time period of 100 s at a constant 40 °C (processing temperature). One measurement on each sample was performed.

2.2.6. Equilibrium moisture content

To measure the equilibrium moisture content (EMC), an MA30 balance (Sartorius AG, Göttingen, Germany) was used. A specimen of the cast film of weight between 0.8 and 1.1 g was placed flat on a tarred aluminium sample dish. The specimens were dried at a temperature of 105 °C until mass constancy had been reached for at least 5 min. The water content is given in wt.%. Duplicate determinations were performed. Average values and standard deviations were calculated.

2.2.7. Colour measurement

The colour of the films was measured using a spectrophotometer (CM-700d manufactured by Konica Minolta Sensing, Tokyo, Japan). After calibration of the spectrophotometer with a white and black calibration device, a white ceramic plate was measured as the reference by applying an illuminant D65 with a wavelength range from 400 to 700 nm. The colour was measured using a MAV-measuring lens (measuring field 8 mm) in the CIE-$L^*a^*b^*$-colour space at four

positions on each sample. Only the values of the SCI (Specular Component Included) mode were interpreted.

2.2.8. Microscopic analysis

The cross-sections of selected samples were analysed in a Scanning Electron Microscope (SEM) manufactured by Hitachi, Chiyoda, Tokyo, Japan (S-4000, cold-cathode field emission electron gun) at different magnitudes (1000 and 5000) and at a working distance of 18–20 mm. The vacuum in the sample chamber was 7×10^{-4} Pa, the voltage was 20 kV and the voltage accelerated in 1 kV steps; the emission extracting voltage was 5.1–5.7 kV. The cross-sections were prepared at a thickness of 20 μm under ambient conditions. No cryofracture was applied. Subsequently the cross-sections were subjected to a sputtering process with gold on a Hummer JR system (Argon inert gas, voltage 5 kV).

2.2.9. Grease resistance

The grease resistance of the cast films was measured using an internal Fraunhofer IVV method. The test area of the film surface (50 cm^2) was covered with fleece – for constant and sufficient covering – and saturated with a solution of coloured peanut oil. As colouring agent Sudan red III from Merck Millipore KGaA, Darmstadt, Germany (CAS-no. 85-86-9, order no. 111747) was used in a concentration of 1 ppt. No further weight was applied. After 24 hours under the defined conditions of 23 °C and 50% rh the fleece and oil residues were removed and the stained area was evaluated by graphic software. For this test at least four specimens were characterised. The final result is the arithmetic mean value of the stained area as a percentage of the whole test area of all tested samples.

2.2.10. Tensile strength and elongation at break (E_b)

The tensile strength and elongation at break of the cast films were measured according to DIN EN ISO 527 using a device of Schenck Trebel Corporation, New York, USA, with a load cell of 1 kN. The samples were cut into strips with a width of 15 mm and had an effective length of 50 mm between the clamps at the beginning of the measurement. In order to measure the tensile properties as a function of the thickness, the thicknesses of each specimen was measured. For each specimen, five-fold determination was performed and the arithmetic mean and standard deviation were calculated. The samples were tested under monoaxial tensile stress at a velocity of 100 mm/min.

2.2.11. Oxygen permeability

The oxygen permeability (OP) was measured by a carrier gas (N_2) method (according to DIN 53 380 Part 3) in Oxtran Twin devices from Mocon Inc. The amount of oxygen which permeates through a packaging material under constant conditions (23 °C, 50% rh) is detected by an electrochemical sensor. A two-fold determination was performed in all cases and from these measurements the standard deviation was calculated.

The OP values, Q, are given in cm^3 (STP) m^{-2} d^{-1} bar^{-1} and were converted to a normalised constant thickness, d, of 100 μm (Q_{100}) using the following equation in order to allow direct comparison of different materials independent of the film thickness. Therefore the unit of Q_{100} is cm^3 (STP) 100 μm m^{-2} d^{-1} bar^{-1}.

$$Q_{100} = Q \cdot \frac{d}{100} \quad (1)$$

2.2.12. Water vapour transmission rate

The water vapour transmission rate (WVTR) was determined by a gravimetric measurement (according to DIN 53 122-1). This involved measuring the amount of water vapour which permeates through a sample under constant conditions (23 °C, 85 → 0% rh). A four-fold determination was performed on each sample and for statistical analysis the standard deviation was calculated. The equipment used for this measurement was aluminium cups with ring-shaped lids containing a joint ring for tight closure. Closing was ensured by a torque spanner. The measuring area of the samples was 9.6 cm^2. The humidity inside the cups (0% rh) was fixed by silica gel and the external conditions (85% rh) by a climate chamber of Binder GmbH.

The WVTR values, Q, are given in g m^{-2} d^{-1} and were converted to the normalised thickness d of 100 μm (Q_{100} (g 100 μm m^{-2} d^{-1})) using Eq. (1).

3. Results and discussion

Glycerol and sorbitol were selected as plasticisers in this work. After a literature study (Olivas & Barbosa-Cánovas, 2008; Rhim, 2004; Rodriguez, Oses, Ziani, & Mate, 2006) and some preliminary trials to determine the most suitable concentration of the respective plasticiser, samples were prepared with the mixing ratios given in Table 1 and these were characterised in further detail. The most decisive factors for the selected mixing ratios were processability (development of bubbles in the formulation, castability of the formulation, drying behaviour, corrugation of the films, ability to be removed from the petri dishes), transparency and sufficient flexibility for further handling/processing. The most suitable concentration (glycerol: 20–40%, sorbitol: 30–50%) was determined as being the lowest amount for sufficient film flexibility without brittle fracture. The plasticiser concentration refers to the dry alginate content.

Table 1
Prepared alginate cast films with their respective moisture content and colour values (Lab).

Base material	Plasticiser	Plasticiser concentration (wt.%)	EMC (%)	L^* (D65)	a^* (D65)	b^* (D65)
Alginate pure	–	–	18.8 ± 0.1	83.29 ± 0.49	0.06 ± 0.01	17.33 ± 0.92
Alginate	Glycerol	20%	17.1 ± 0.04	85.58 ± 0.56	−0.22 ± 0.01	14.07 ± 1.11
Alginate	Glycerol	25%	–	–	–	–
Alginate	Glycerol	30%	16.6 ± 0.4	85.42 ± 0.42	−0.14 ± 0.02	14.06 ± 0.67
Alginate	Glycerol	40%	18.1 ± 0.4	86.39 ± 0.56	−0.22 ± 0.01	12.29 ± 0.90
Alginate	Sorbitol	30%	14.6 ± 0.8	86.24 ± 0.52	−0.33 ± 0.03	12.54 ± 0.94
Alginate	Sorbitol	40%	15.5 ± 0.1	86.43 ± 0.36	−0.34 ± 0.03	12.14 ± 0.70
Alginate	Sorbitol	45%	–	–	–	–
Alginate	Sorbitol	50%	15.3 ± 1.0	88.34 ± 0.53	−0.37 ± 0.04	8.68 ± 0.75

The samples with 25% glycerol and 45% sorbitol were exclusively characterised for their mechanical properties.

3.1. Dynamic viscosity

For application using conventional coating techniques, the dry matter content has to be carefully adjusted because of its influence on the coating weight and dynamic viscosity, which also influence the drying process. The higher the dry matter content, the higher the coating weight (necessary for paper substrates) but also the higher the viscosity which is often the limiting factor for processability. In order to allow application by casting, gravure roll or blade, a viscosity below 600 mPa s was favoured for this study. A further effect of a higher dry matter content is the lower required drying capacity. Also, parameters such as the solubility of the alginate and flowability influence the choice of the dry matter content.

For the above-mentioned reasons, the dynamic viscosity of the alginate-based cast films as a function of the shear rate was investigated. These measurements were performed in order to determine the most suitable alginate concentration for processing and therefore only the reference solution without plasticiser was analysed. The influence of the plasticiser on the viscosity of the solution was not measured separately because the plasticiser did not show an obvious impact. The impact was dominated by the dry matter content of the alginate. The results indicate that a 10 wt.% alginate concentration is the maximum dry matter content because of the limited solubility. Concentrations of 8 and 9 wt.% gave a viscosity that was too high for further processing, so the optimal dry matter content was found to be at 7.5 wt.% having a viscosity of <450 mPa s at a shear rate of 100 1/s. All samples in this study were thus prepared with a dry matter content of 7.5 wt.%. Additionally, the flow properties of alginate solutions can be classified by their shear-thinning behaviour which is comparable to starch solutions. This behaviour is preferred in many industrial applications for better processability because the dynamic viscosity decreases on increasing the shear rate (Barnes, Hutton, & Walters, 1989).

3.2. Equilibrium moisture content

The equilibrium moisture content (EMC) was analysed in order to characterise the water holding influence of the respective plasticiser. Water can cause similar effects to glycerol on the mechanical and other physical properties of bio-based films since water can easily penetrate into the film matrix to interact with polar groups (di Gioia & Guilbert, 1999).

The solubility of alginate in water is dependent on the pH and ionic concentration of the solvent as well as the concentration of ions in the solution (Pawar & Edgar, 2012). Since the cast film solutions were prepared using distilled water, the pH and ionic concentration do not influence the solubility and therefore nor the structure of the cast films. The concentration of ions in the solution is largely dependent on the alginate base material. This was the same for all samples, but the amount of alginate and plasticiser did change. Therefore, the decreasing EMC of the films on adding the respective plasticiser (as illustrated in Table 1) can be interpreted as being due to the lower water binding capability of the glycerol and sorbitol, which means these additives are less hydrophilic than alginate. This agrees with the results published by Talja, Helén, Roos, and Jouppila (2007). They observed decreasing EMC values for potato-starch based films when sorbitol or glycerol was added as plasticiser. However, the concentration of the plasticiser (at least the concentrations used in the study) did not affect the EMC. In addition to this, literature was found describing an increase in the moisture content on increasing the glycerol content of starch films (maize, rice and wheat starch) (Enrione, Hill, & Mitchell, 2007) or carboxymethyl cellulose (CMC) films (Rachtanapun & Tongdeesoontorn, 2009). This can be explained by the lower hydrophilicity of these biopolymers (maize starch, CMC) compared to alginates and potato-starch.

3.3. Colour measurement

The lightness values (L^*) reveal only small differences (see results listed in Table 1): the pure alginate film has a slightly lower L^* value than the films with plasticiser. Alginates create low transparency films (L^*: 83.3). The addition of the highly transparent plasticisers glycerol or sorbitol leads to a dilution of the alginate material and therefore increases the transparency of the plasticised cast films (sorbitol more so than glycerol). The a^* values are negative and very low but only differ slightly which means the green colour is not a significant factor in the colour of the films. However, also for the a^* values (green colour) the influence increases in the following order: pure alginate < alginate + glycerol < alginate + sorbitol. The pure alginate films reveal a significant influence of the b^* value which refers to their yellow colour. A strong impact on the b^* value was observed for all films: On addition of plasticiser the yellow component decreases. The higher the concentration of plasticiser the greater the decrease of the b^* value, with sorbitol having a greater effect than glycerol. The decrease in the b^* component can also be explained by a diluting effect of the almost colourless plasticisers. The greater influence of sorbitol might be due to the better fit to the mannuronic and guluronic acids than low molecular weight glycerol.

3.4. Microscopic analysis

In order to evaluate the structure of the samples, SEM micrographs of a pure alginate film (Figs. 2 and 3) as well as film samples with 30% glycerol (Figs. 4 and 5) and 50% sorbitol (Fig. 6) were taken.

The reference material has a lamellar structure. The higher magnification reveals a slightly porous network. This porosity could also

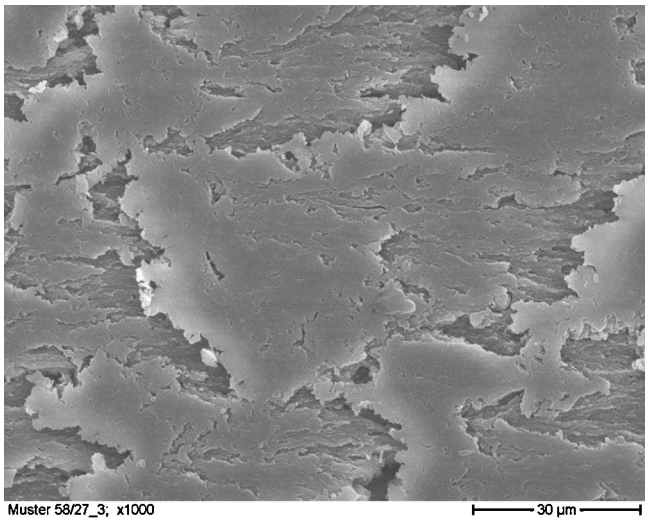

Fig. 2. SEM micrograph of pure alginate cast film (1000×).

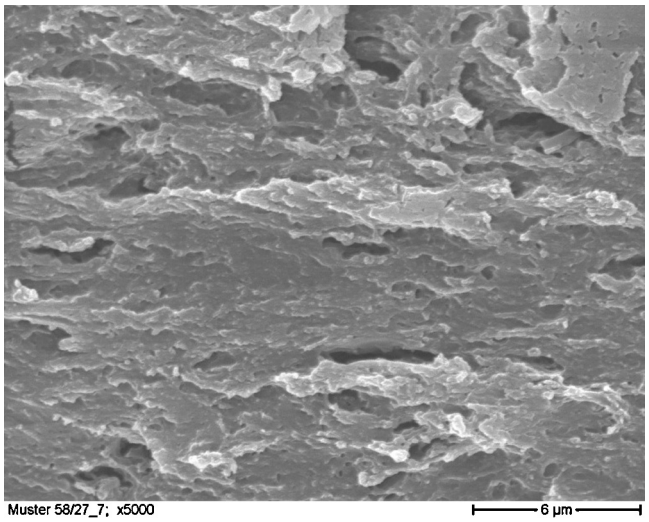

Fig. 3. SEM micrograph of pure alginate cast film (5000×).

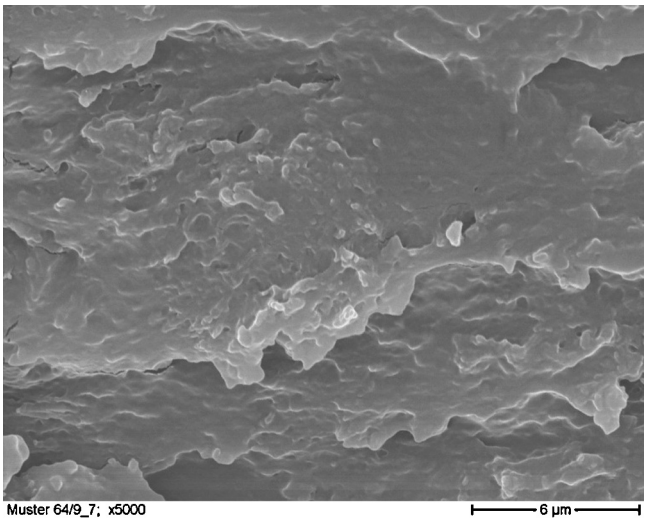

Fig. 5. SEM micrograph of alginate + 30% glycerol cast film (5000×).

be affected by partial evaporation of water molecules bound in the alginate network.

The film with glycerol also shows a lamellar structure but the network is smoother and not so porous (see Fig. 5) as the reference without a plasticiser. However, these structures could also be affected by partial evaporation of water and/or glycerol molecules during the SEM analysis (Fig. 6).

Compared to the other films, the sample with sorbitol shows a smoother surface and a more homogenous network. Interestingly the sample with sorbitol is more heat sensitive than the other films. This behaviour could also be explained by a too high sorbitol concentration which results in interactions under the measuring conditions. For this reason a higher magnification image could not be taken.

3.5. Grease resistance properties

All samples were tested for their resistance to grease. All samples reveal a staining of 0%. This confirms the excellent barrier properties of alginate films against grease published in the literature (Khwaldia, Arab-Tehrany, & Desobry, 2010; Robertson, 2005). Since alginate-based films are highly hygroscopic, lipophilic materials such as oil do not dissolve in the alginate films to a high extent, leading to excellent grease barrier properties. The colouring agent Sudan red has a relatively high molecular weight (352 g mol^{-1}) and three ring structures. Our tests confirm the high grease barrier for relatively non-polar, large molecules. They gave no information about the grease barrier against polar, small molecules.

3.6. Tensile strength and elongation at break (E_b)

The results of the mechanical characterisation are listed in Table 2. Since the mechanical properties are dependent of the relative humidity (Hambleton, Perpiñan-Saiz, Fabra, Voilley, & Debeaufort, 2012), the samples were conditioned and tested under defined conditions (23 °C/50% rh). The results reveal a correlation between plasticiser concentration and the strength of the film. An

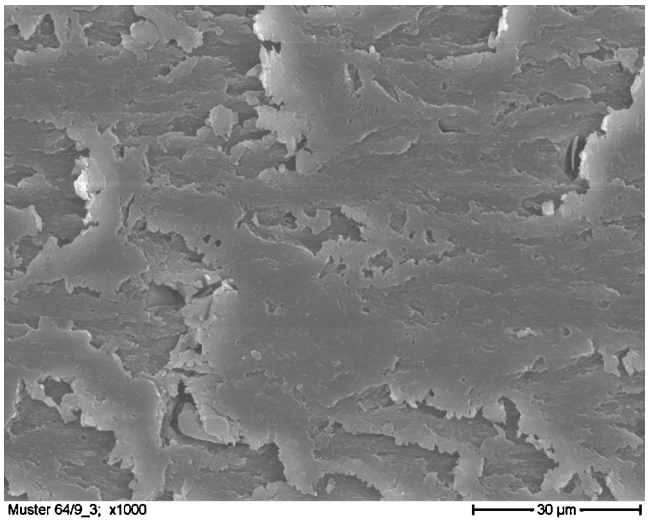

Fig. 4. SEM micrograph of alginate + 30% glycerol cast film (1000×).

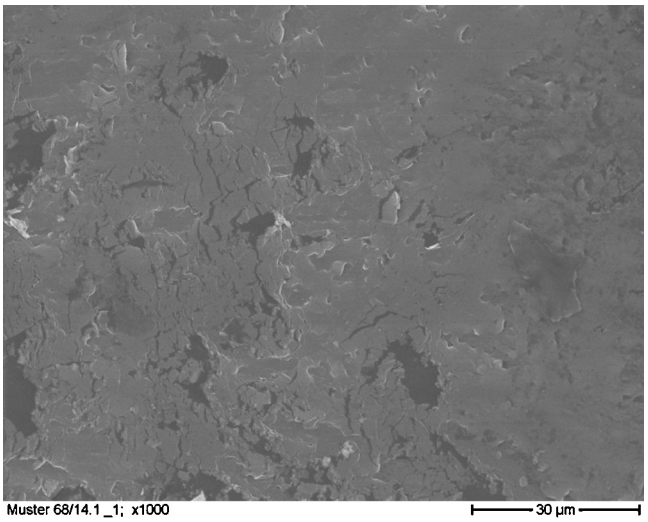

Fig. 6. SEM micrograph of alginate + 50% sorbitol cast film (1000×).

Table 2
Mechanical properties of alginate cast films.

Sample	Tensile strength (N/mm²)	Elongation at break (E_b) ⟨br⟩ (%)
Alginate pure	59.9 ± 5.7	10.3 ± 7.5
Alginate (G 20)	71.0 ± 15.5	7.3 ± 1.3
Alginate (G 25)	63.5 ± 2.8	7.8 ± 1.4
Alginate (G 30)	15.6 ± 2.9	29.1 ± 5.6
Alginate (G 40)	5.3 ± 0.5	34.9 ± 3.8
Alginate (S 30)	50.7 ± 3.5	5.6 ± 1.4
Alginate (S 40)	23.2 ± 3.6	6.6 ± 2.0
Alginate (S 45)	13.6 ± 1.0	15.9 ± 3.6
Alginate (S 50)	11.3 ± 0.8	27.0 ± 2.1

increase in plasticiser leads to a decrease in tensile strength and to an increase in elongation at break (E_b). This influence is more pronounced for glycerol than sorbitol, even though glycerol was added in lower concentrations.

The E_b values of the pure alginate films approximate the values obtained in other studies ((Bierhalz, da Silva, & Kieckbusch, 2012) (6.6%) and (Rhim, 2004) (14.0%)) but the tensile strength differs significantly ((Bierhalz et al., 2012) (122.5 MPa) and (Rhim, 2004) (33.6 MPa)). This leads to the conclusion that the way of preparation of the cast films (e.g. G/M ratio, M_w distribution, dry matter content, composition, handling, mixing time, drying parameters, final thickness, etc.) has a major effect on the final properties of the films.

The correlation between glycerol concentration and the mechanical properties is in accordance with other publications: For alginate-poly(vinyl alcohol) blend films according to Russo, Malinconico, Petti, and Romano (2005), for alginate-magnesium aluminium silicate films according to Pongjanyakul and Puttipipatkhachorn (2007), for pullulan-alginate carboxymethyl cellulose blend films according to Tong, Xiao, and Lim (2008) and for crosslinked alginate-pectin composite films according to Silva, Bierhalz, and Kieckbusch (2009). Pongjanyakul and Puttipipatkhachorn (2007) already described the decreasing tensile strength with increasing amount of glycerol even though the measured values were higher than those in our study. Also, for the elongation at break the same tendencies were shown: A significant increase in E_b was correlated with increasing the glycerol concentration, but the increase measured in our study is more significant. Pongjanyakul and Puttipipatkhachorn (2007) explain the effectiveness of glycerol on the mechanical properties as being due to the low M_w of glycerol which favours the reduction of intermolecular and intramolecular hydrogen bonding in the alginate network.

For addition of glycerol, the same tendencies were found for another carbohydrate – corn starch. Qiao, Tang, and Sun (2011) showed a correlation between increasing glycerol content and decreasing tensile strength. Their results for sorbitol were not corroborated by our study: With increasing concentration of sorbitol the tensile strength of alginate films decreased, unlike the findings of Qiao et al., 2011. For a further carbohydrate – chitosan – the same trend was found by Thakhiew, Devahastin, and Soponronnarit (2010) and Epure, Griffon, Pollet, and Averous (2011). Studies on other biopolymers such as whey protein isolate by McHugh and Krochta (1994) reveal a greater influence of glycerol than sorbitol on E_b, which differs from our findings with alginate.

The mechanical properties of the samples reveal that both glycerol and sorbitol have a plasticising effect on the alginate films. The effectiveness of glycerol seems to be higher – the sample with 30% glycerol has almost the same mechanical properties as the sample with 50% sorbitol. Even though glycerol has a M_w of 92 Da that is approximately half the M_w of sorbitol (M_w 182 Da), more than half of the mass (30%) is needed – compared to sorbitol (50%) – to attain the same mechanical properties. It appears that sorbitol is the more effective plasticiser based on the number of molecules, but that glycerol is more effective based on the actual mass content.

3.7. Oxygen permeability (OP)

The results illustrated in Fig. 7 indicate that an increasing glycerol concentration leads to increased OP values of the films. In contrast, the incorporation of sorbitol shows no significant influence on the OP values. Neither the addition itself nor the increase in concentration of sorbitol changed the OP significantly.

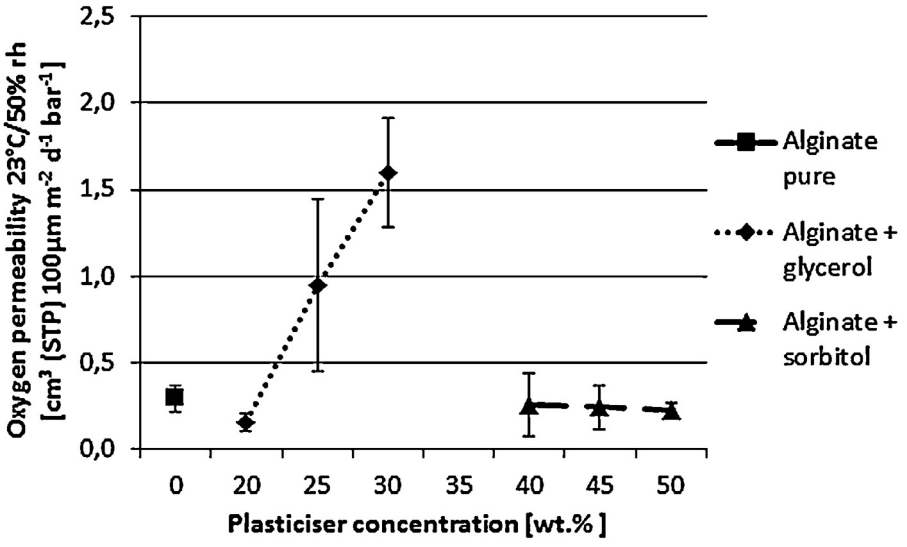

Fig. 7. OP of alginate cast films.

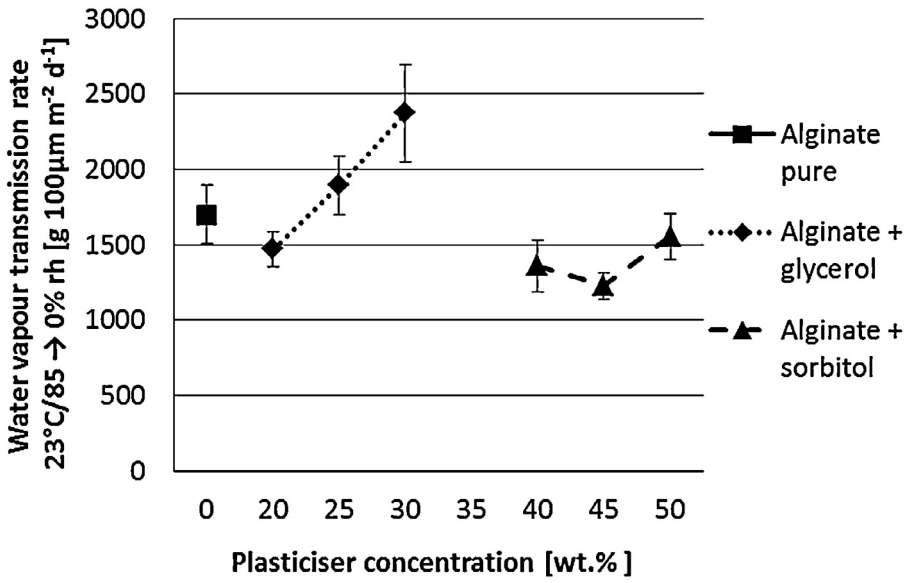

Fig. 8. WVTR of alginate cast films.

Interestingly for glycerol, one concentration (20 wt.%) showed an OP lower than those of pure alginate films. However, this influence was not observed for sorbitol-plasticised films. This contradicts the commonly known behaviour of low molecular weight additives acting as plasticisers in such polymer networks, increasing the permeabilities of the base material as described by Wypych (2004).

The observation that an increasing sorbitol concentration does not lead to an increase in OP but that an increasing glycerol concentration does was also reported by McHugh and Krochta (1994) for whey protein isolate (WPI) based films. McHugh and Krochta (1994) as well as the authors of the present study were not able to explain this observation since polyol plasticisers are believed to act in the same way. Therefore, they suggested measuring the temperature dependence of oxygen permeability and tensile properties to aid interpretation of the observed results. Compared to other biopolymers, sodium alginate films show the highest barrier properties against oxygen according to Wang, Liu, Holmes, Kerry, and Kerry (2007), who measured a value of <30 cm^3 µm m^{-2} d^{-1} kPa^{-1}, and Yoo and Krochta (2011), who measured a value of 6.9 cm^3 µm m^{-2} day^{-1} kPa^{-1}. They explained this behaviour as being due to the high polarity of the sodium alginate films.

3.8. Water vapour transmission rate (WVTR)

The results of the WVTR measurements Fig. 8 show the same tendencies as the OP measurements. Glycerol significantly influences the WVTR of alginate films-increasing glycerol concentration leads to a higher transmission rate. As already stated in the OP results, the sample with 20 wt.% glycerol showed a lower WVTR than the no-additive sample. This behaviour was also found by Farahnaky, Saberi and Majzoobi (2013) for wheat starch films and was explained by microcracks in the pure material. In contrast, films with sorbitol almost have the same WVTR as the pure alginate films. Olivas and Barbosa-Cánovas (2008) also observed that the WVTR of glycerol-plasticised samples was higher than sorbitol-plasticised samples, but they only analysed one concentration of plasticiser.

This behaviour can be explained by the size of the plasticiser. Glycerol with a molecular weight of 92.1 Da is a smaller molecule with only three hydroxyl groups compared to sorbitol with a molecular weight of 182.2 Da and five functional hydroxyl groups. Glycerol can therefore effectively hinder intermolecular and intramolecular bonding in the network, increasing the free volume and thereby increasing the permeability of oxygen and water vapour. This was described by Qiao et al. (2011). Sorbitol, in contrast, is more similar to the structure of the monomers of the alginate acids M and G, which results in good embedding of sorbitol in the alginate network and good possibilities for hydrogen bonding to ensure a stable, dense network. Therefore, the changes in the barrier properties are supposedly due to the changed diffusion and not a changed solubility effect. Plasticisers can be categorised according their working mechanism (Zhang & Han, 2006a, 2006b): Plasticisers of the first group interact directly with the base polymer. Subsequently hydrogen bonds are formed which give distance between the polymer chains. Plasticisers from the second group attract water molecules and store them in the polymer network which leads to a plasticisation effect. According to the same authors, sorbitol belongs to the first group while glycerol belongs to the second group. In conclusion, the films plasticised with glycerol have a higher moisture content (EMC) than sorbitol-plasticised films. This also applies to the films characterised in this study and thus may be an additional explanation for the higher WVTR of glycerol-plasticised films.

Some sources confirm the effect of increasing concentration of glycerol leading to an increase in WVTR for bio-based films such as wheat gluten (Gontard, Guilbert, & Cuq, 1993) and whey protein (Sothornvit & Krochta, 2000). However, there are also sources which do not agree on that point for alginate-based films (Pongjanyakul & Puttipipatkhachorn, 2007) and gelantin-based films (Vanin, Sobral, Menegalli, Carvalho, & Habitante, 2005).

In conclusion, our results show that a higher amount of glycerol leads to an increase in the free volume and EMC of the films which results in a significant increase in the permeabilities to oxygen and water vapour (see Table 2). Sorbitol, on the contrary, has a better steric fit in the alginate network which ensures maintenance of

the barrier properties. Another point is the better networking of the hydroxyl groups which lead to less bonding points for water vapour (see Table 1). The reduced moisture content is another explanation for the better barrier properties of the sorbitol-plasticised films. In order to produce a flexible, high oxygen barrier coating material, the incorporation of sorbitol into alginate films is recommended.

4. Conclusion

In order to develop and tailor alginate formulations for packaging applications, knowledge of how plasticisers affect the mechanical properties of packaging materials is very important. To enhance the flexibility and to increase the resistance to mechanical stress, alginate cast films were formulated with plasticiser and subsequently characterised to evaluate the influence on the films' properties. It can be concluded that films with glycerol have a higher EMC than films with sorbitol. However, both plasticisers tend to lower the EMC compared to pure alginate films, which typically leads to more brittle films since water acts as an effective plasticiser in biopolymer films. Despite the lower EMC values, the structure of the plasticised films showed less porosity with both plasticisers. The excellent grease resistance properties were not affected either by the type of plasticiser nor by its concentration. However, the influence on the barrier properties was dependent on both the type and concentration of the plasticiser. While the addition of glycerol led to an increase in the permeability of oxygen and water vapour, the addition of sorbitol did not affect these barrier properties. Besides the dependency on the type of plasticiser, the concentration of plasticiser also had an effect: increasing the concentration of glycerol resulted in a significant increase in the OP and WVTR, but this was not observed on increasing the concentration of sorbitol. Interestingly, the mechanical properties were improved by both plasticisers. Films with 30% glycerol had almost the same tensile strength and E_b as films with 50% sorbitol. This different effectiveness may be explained by the molecular weight of the plasticisers: with approximately half the M_w of sorbitol (M_w 182 Da), glycerol (M_w 92 Da) more effectively embeds in the alginate network. However, it can be concluded that slightly more glycerol molecules are necessary (30% glycerol sample) to attain equal mechanical properties (50% sorbitol sample), and thus sorbitol has a higher molecular effectiveness.

According to the free volume theory postulated by Fox and Flory (1950), an effective plasticiser embeds in the polymer matrix between the chains, especially in the amorphous regions due to the lower packing density. As a consequence of this embedding, the free volume between the polymer chains increases which leads to films with a higher flexibility and also with a higher diffusion coefficient (Sears & Darby, 1982; Wypych, 2004). According to this theory, the films with glycerol have an increased diffusion coefficient (D) for water vapour and oxygen. The solubility coefficient (S) of water vapour in the glycerol films is slightly decreased compared to pure alginate films (see results of EMC measurements), while the solubility coefficient (S) of oxygen is not significantly influenced. According to the permeability coefficient (P) with $P = D \times S$, P should increase (due to the increased D) which was shown by the results presented here. To be in accordance with this theory, the sorbitol films would also have an increased D. Sorbitol films also showed a lower hydrophilicity than pure alginate films (confirmed by EMC measurements) and therefore a decreased S of water vapour in sorbitol films is assumed. Estimating that these two effects are of the same order of magnitude, P of water vapour in the sorbitol films remains at the same level which was shown by our results. However, this conclusion for water vapour permeability cannot be drawn for the permeability of oxygen: In accordance with the free volume theory, D is increased and S of oxygen is slightly increased due to the reduced hydrophilicity of the sorbitol films (Sothornvit & Krochta, 2005). This would result in a significant increase in P of oxygen which cannot be proven by our results. Therefore the behaviour of sorbitol-plasticised alginate films cannot be explained by the free volume theory. We assume that sorbitol has a good steric fit in the M and G network of alginate. Therefore sorbitol is able to embed between the alginate chains, lower the intermolecular interactions between them but also offer bonding possibilities due to its hydroxyl groups, following the gel theory which is an extension of the lubricity theory (Hernandez-Izquierdo & Krochta, 2008; Mekonnen et al., 2013). Due to the enhanced interactions with sorbitol, the interactions of the alginate chains with water molecules are reduced but the induced interactions with sorbitol lead to increased flexibility of the films with maintained barrier properties. This is even so if the sorbitol concentration is increased.

Based on the improved mechanical properties and the differing influence on the barrier properties, a plasticiser for a packaging system can be chosen depending on the specific requirements of the product. Another advantage of the addition of plasticisers is the reduction in cost to produce a biopolymer based coating material.

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