

## Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra  
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

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## Influence of plasticizers on the mechanical and barrier properties of cast biopolymer films

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**ABSTRACT:** The potential of biopolymers for packaging application is often limited due to their poor processability. In this study, the effect of commonly used plasticizers on the properties of different cast biopolymer films is investigated. This enables a valuation of the potential of different biopolymers as packaging materials and an estimation of the effectiveness of plasticizers for certain biopolymer systems. Polysaccharides (corn starch and alginate) and plant proteins (wheat gluten and pea protein) were tested as film materials. To improve the processability by decreasing the brittleness of these cast biopolymer films, glycerol (Gly), sorbitol (Sor), and triethanolamine (TEA) were added as plasticizers. The structural, mechanical, and barrier properties to water vapor and oxygen were characterized in order to study the effectiveness of the plasticizers and their respective influence on the film properties. The mechanical results show there was a plasticizing effect with all the plasticizers, but the influence on the barrier properties depends on the specific plasticizer: While glycerol (Gly) leads to an increase in water vapor and oxygen permeability (OP), Sor leads to almost constant, and TEA even to decreased OP of the biopolymer films. Therefore, careful selection of the plasticizer allows biopolymer films with improved processability and high or low permeabilities to be manufactured. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42513.

**KEYWORDS:** biopolymers and renewable polymers; coatings; mechanical properties; packaging; plasticizer

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### INTRODUCTION

The demand for biopolymers as an alternative to petrochemical based polymers in packaging applications has increased over recent years and there is a need to optimize the processability of these biopolymers for common application techniques. Major drawbacks for applying biopolymer coatings by lacquering are, for example, their foaming behaviour,<sup>1</sup> their increased viscosity, and especially the high brittleness of the final coating layers which can result in inhomogeneities and defects. To overcome these obstacles and meet the requirements for a stable coating process, the biopolymer formulation, and the final properties are commonly optimized by the addition of plasticizers. Using suitable plasticizers the processing, film forming, and mechanical properties of the biopolymers can be improved – but they also affect the barrier properties. In this work, the effects of three commonly used additives on the properties of cast biopolymer films were studied. The selected biopolymers were corn starch and alginate (polysaccharides) and wheat gluten and pea protein (plant proteins). The chosen plasticizers are commonly found in the literature: glycerol (Gly),<sup>2–7</sup> sorbitol (Sor),<sup>5,8,9</sup> and triethanolamine (TEA).<sup>10–12</sup> As TEA was found to be effective for proteins, it was only applied for the two protein samples. Based on the results of pre-trials, the plasticizers were added in the minimum

concentration that led to flexible films without brittle fracture, and subsequent increased to further increase the flexibility. The plasticizers were added to the biopolymers in various concentrations (see Table I). Additionally, pure, unplasticized cast biopolymer films were produced for better valuation of the plasticizers' influence. The characterization of these brittle films was challenging and the preparation sometimes only possible via prior conditioning at 23°C and 85% relative humidity (rh) for maximum 2 h followed by a post-conditioning to 23°C and 50% rh.

### MATERIALS AND METHODS

#### Materials

Esterified corn starch (CLEARGUM<sup>®</sup> MG 85, CAS-no. 9045-28-8), wheat gluten (NUTRALYS<sup>®</sup> W, CAS-no. 100684-25-1), and pea protein (NUTRALYS<sup>®</sup> S85F, NC-no. 35040090) were obtained from Roquette GmbH, Frankfurt, Germany. CLEARGUM<sup>®</sup> MG 85 has a molecular weight ( $M_w$ ) of 480 kDa, a dry matter content (DMC) of 86%, is in conformance with FDA - CFR 21 and listed as food additive E 1420 in EU Regulation No. 1333/2008. NUTRALYS<sup>®</sup> W is a hydrolyzed protein obtained from wheat with an  $M_w$  of 30 kDa and a DMC of 92%. NUTRALYS<sup>®</sup> S85F has an  $M_w$  of 300 kDa and a DMC of 90%. Sodium alginate powder (GRINSTED<sup>®</sup> Alginate LFD

**Table 1.** Mechanical and Barrier Properties of Cast Biopolymer Films

Biopolymer	Polysaccharide	Weight fraction		Tensile strength $\sigma$ (N mm <sup>-2</sup> )	Elongation at break $\epsilon$ (%)	WVP Q <sub>100</sub> H <sub>2</sub> O (g 100 $\mu$ m m <sup>-2</sup> d <sup>-1</sup> mbar <sup>-1</sup> )	OP Q <sub>100</sub> O <sub>2</sub> (cm <sup>3</sup> (STP) 100 $\mu$ m m <sup>-2</sup> d <sup>-1</sup> bar <sup>-1</sup> )	Biopolymer and type of protein	W <sub>Plasticiser</sub> and type of plasticizer	Tensile strength $\sigma$ (N mm <sup>-2</sup> )	Elongation at break $\epsilon$ (%)	WVP Q <sub>100</sub> H <sub>2</sub> O (g 100 $\mu$ m m <sup>-2</sup> d <sup>-1</sup> mbar <sup>-1</sup> )	OP Q <sub>100</sub> O <sub>2</sub> (cm <sup>3</sup> (STP) 100 $\mu$ m m <sup>-2</sup> d <sup>-1</sup> bar <sup>-1</sup> )
		$w_{Plasticiser}$	fraction										
Starch	-	37.7 ± 1.1	1.7 ± 0.1	40.8 ± 5.3	-	Pea protein	-	29.2 ± 6.0	2.2 ± 0.4	16.8 ± 1.3	26.9 ± 2.0		
Starch	0.225 Gly	27.9 ± 6.5	5.2 ± 3.1	55.5 ± 4.4	11.8 ± 0.2	Pea protein	0.15 Gly	7.0 ± 1.7	21.0 ± 9	74.7 ± 5.0	32.2 ± 5.8		
Starch	0.25 Gly	21.6 ± 3.2	8.1 ± 1.2	110 ± 10.0	14.2 ± 1.1	Pea protein	0.20 Gly	4.2 ± 0.7	167 ± 32	75.0 ± 10.6	49.6 ± 5.1		
Starch	0.275 Gly	20.5 ± 5.1	10.9 ± 4.0	98.2 ± 0.7	15.8 ± 0.9	Pea protein	0.25 Gly	5.5 ± 0.3	219 ± 41	130 ± 7.0	53.8 ± 7.5		
Starch	0.30 Gly	16.1 ± 5.3	20.9 ± 7.1	119 ± 2.3	38.3 ± 2.0	Pea protein	0.35 Sor	17.0 ± 1.2	9.8 ± 5	70.1 ± 12.2	38.1 ± 19		
Starch	0.35 Gly	9.3 ± 2.8	28.4 ± 5.5	118 ± 3.4	44.4 ± 10	Pea protein	0.40 Sor	6.3 ± 0.7	48.5 ± 13	70.6 ± 15.9	32.9 ± 11		
Starch	0.30 Sor	16.7 ± 6.6	9.9 ± 5.1	39.0 ± 4.0	1.5 ± 0.4	Pea protein	0.45 Sor	4.4 ± 0.2	163 ± 21	87.2 ± 7.1	35.0 ± 10		
Starch	0.325 Sor	12.0 ± 1.3	14.4 ± 5.9	41.2 ± 1.2	2.4 ± 0.4	Pea protein	0.15 TEA	9.9 ± 2.1	22.2 ± 13	45.3 ± 5.7	76.9 ± 23		
Starch	0.35 Sor	13.6 ± 1.8	23.1 ± 4.3	56.6 ± 5.4	3.7 ± 1.5	Pea protein	0.20 TEA	7.2 ± 2.2	36.4 ± 20	45.4 ± 6.9	68.6 ± 18		
Starch	0.40 Sor	6.5 ± 1.4	30.6 ± 14	67.7 ± 6.4	8.2 ± 0.7	Pea protein	0.25 TEA	6.3 ± 1.3	148 ± 23	87.8 ± 8.8	11.7 <sup>a</sup>		
Alginate	-	55.1 ± 7.3	2.9 ± 0.5	71.1 ± 9.3	0.29 ± 0.1	Gluten	-	3.3 ± 0.5	0.7 ± 0.2	14.7 ± 3.0	7.84 ± 0.4		
Alginate	0.20 Gly	71.0 ± 16	7.3 ± 1.3	61.5 ± 5.7	0.15 ± 0.1	Gluten	0.175 Gly	2.6 ± 0.5	47.6 ± 0.7	96.7 ± 12.6	44.0 ± 9.1		
Alginate	0.25 Gly	63.5 ± 2.8	7.8 ± 1.4	79.2 ± 9.4	0.95 ± 0.5	Gluten	0.20 Gly	2.1 ± 0.2	47.8 ± 10	98.5 ± 10.9	48.5 ± 8.4		
Alginate	0.30 Gly	15.6 ± 1.0	29.1 ± 2.3	99.2 ± 15.6	1.60 ± 0.3	Gluten	0.225 Gly	2.8 ± 0.5	46.0 ± 12	96.0 ± 6.2	73.7 ± 12		
Alginate	0.40 Gly	5.3 ± 0.5	34.9 ± 3.8	79.1 ± 9.3	0.76 ± 0.6	Gluten	0.25 Gly	1.1 ± 0.0	116 ± 15	110 ± 3.1	127 ± 5.4		
Alginate	0.30 Sor	50.7 ± 3.5	5.6 ± 1.4	55.8 ± 7.9	0.13 ± 0.0	Gluten	0.175 TEA	1.6 ± 0.3	68.2 ± 36	47.4 ± 14.6	87.2 ± 3.0		
Alginate	0.40 Sor	23.2 ± 3.6	6.6 ± 2.0	56.7 ± 8.1	0.26 ± 0.2	Gluten	0.20 TEA	2.7 ± 0.3	47.8 ± 12	52.4 ± 12.0	84.0 ± 39		
Alginate	0.45 Sor	13.6 ± 1.0	15.9 ± 3.6	51.3 ± 4.2	0.24 ± 0.1	Gluten	0.225 TEA	1.6 ± 0.4	90.6 ± 6	93.6 ± 1.0	59.5 ± 4.2		
Alginate	0.50 Sor	11.3 ± 0.8	27.0 ± 2.2	65.0 ± 7.4	0.22 ± 0.0	Gluten	0.25 TEA	0.9 ± 0.1	123 ± 18	100 ± 5.8	56.7 ± 19		

<sup>a</sup> Single determination



1205) was provided by Danisco Gums & Systems Division, Kreuzlingen, Switzerland. This product is in the Food Chemicals Codex and is listed as E401 in the EU food additive list. This grade has a ratio of guluronic acid to mannuronic acid of approximately 40/60, the residual water content is 10 – 12%, the density is 0.5 – 0.7 g/cm<sup>3</sup>, and the  $M_w$  is approximately 55 kDa. This information was provided by Danisco.

Glycerol (CAS-no. 56–81-5, order no. 8.18709.1000) was obtained from Merck Millipore KGaA, Darmstadt, Germany. This material has a residual water content of  $\leq 0.5\%$ , a density of 1.26 g/cm<sup>3</sup>, and an  $M_w$  of 92 Da. Sorbitol (NEOSORB<sup>®</sup> 70/70, CAS-no. 50–70-4) from Roquette GmbH, Frankfurt, Germany was used. The DMC of this food grade Sor is at least 70%, the density is 1.49 g/cm<sup>3</sup> and the  $M_w$  is 182 Da. Triethanolamine (CAS-no. 102-71-6, product no. T58300) was obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. The DMC of this substance is 98%, the density is 1.124 g/mL, and the  $M_w$  is 149.2 Da.

If not indicated otherwise, the information was obtained from the product data sheets.

## Methods

**Preparation of Formulation.** Formulations of the different biopolymers were prepared at pH 7 by mixing a defined amount of the respective biopolymer with distilled water as solvent. Additionally, the plasticizer was added, considering the residual water content of the biopolymer and plasticizer. No further additives were used.

The respective dry matter content (DMC) was 7.5 wt % for alginate (due to hygroscopic behavior) and 10 wt % for gluten, pea protein, and starch. While stirring constantly at 300 rpm by an electric stirrer (Thermomix 31-1, Vorwerk Elektrowerk GmbH & Co. KG, Wuppertal, Germany) the formulation was heated to 90°C for 15 min for the alginate and proteins and for 30 min for the starch sample. An ultrasonic bath (Digitec DT 514 H, Zefa-Laborservice GmbH, Harthausen, Germany) was used to separate inhomogeneities for 15 min at a frequency of 37 kHz. The temperature was set at 50°C for the alginate and proteins and at 80°C for the starch sample (to avoid retrogradation). Afterwards resulting foam and bubbles were removed.

**Solvent Casting.** To cast films the formulations were filled into petri dishes. The sample weight depended on the DMC and density of the biopolymer as well as the type and amount of plasticizer and was calculated separately to cast films with a thickness of 100 or 200  $\mu\text{m}$  depending on handling. In order to distribute the formulation homogenous on the surface of the dishes, they were moved in a figure eight. Drying was enabled at conditions of 23°C and 50% relative humidity (rh) for several days. After weight changes of less than 0.01 g per day the films were considered to be at their equilibrium moisture content.

An exception was pure gluten which was not possible to be produced by the described casting method. Therefore the pure gluten formulation (with a DMC of 25 wt %) was coated on Teflon sheets by blade coating and peeled off afterwards.

**Conditioning.** In order to adjust the equilibrium moisture content of the films they were conditioned at 23°C and 50% rh for at least 48 h before further analysis.

**Thickness Measurements.** The thickness of the cast films was measured by a Precision Thickness Gauge FT3 (Rhopoint Instruments, Bexhill on Sea, UK) having a 0.4  $\mu\text{m}$  repetition accuracy. For each sample five different positions were measured.

**Microscopic Analysis.** For the microscopic analysis a Scanning Electron Microscope (SEM) manufactured by Hitachi, Chiyoda, Tokyo, Japan (S-4000, cold-cathode field emission electron gun) was used. The cross-sections (cs) of selected samples were measured at different magnifications (1000 or 5000), the working distance was 18 – 20 mm. For most samples a higher magnification was not possible due to structural changes in the biopolymers induced by the high current density at a lower diameter of the electron beam. The vacuum in the sample chamber was  $7 \times 10^{-4}$  Pa and the voltage was 20 kV. If possible the cross-sections (cs) were prepared at a thickness of 20  $\mu\text{m}$  under ambient conditions. If the samples were too brittle for the preparation of cs, an ambient fracture at 23°C (af) or cryo-fracture (with fluid N<sub>2</sub>) (cf) was applied. Subsequently a sputtering process with gold was applied for the cs and fractures (Hummer JR system, Argon inert gas, voltage 5 kV).

**Mechanical Properties: Tensile Strength and Elongation at Break.** The mechanical properties of the cast films were analyzed by a monoaxial tensile test according to DIN EN ISO 527-1 using equipment of Schenck Trebel Corporation, New York, USA. The parameters tensile strength ( $\sigma$ ) and elongation at break ( $\epsilon$ ) were measured with a load cell of 1 kN and a velocity of 100 mm/min. Strips of 15 mm width were cut of each sample and inserted with an effective length of 50 mm between the clamps at the beginning of the measurement. The thickness of each sample was determined five-fold, the arithmetic mean and standard deviation were calculated.

**Water Vapor Transmission Rate (WVTR), Water Vapor Permeability (WVP).** The water vapor transmission rate (WVTR) was determined according to DIN 53122-1. By this measurement the amount of water vapor permeating through a sample is measured gravimetrically at constant conditions (23°C, 85 ± 0% rh), the conditions were established by dried silica gel (0% rh) and a climate chamber of Binder GmbH, Tuttingen, Germany, equipped with permanent air circulation (85% rh). The samples were put in aluminum cups containing a joint ring for tight closure (ensured by a torque spanner). Four specimens of each sample were tested. The measuring area of the samples was 9.6 cm<sup>2</sup> with the exception of pure starch films. Due to their high brittleness, the measuring area for these films had to be reduced to 2 cm<sup>2</sup>.

The values of the WVTR are obtained in g m<sup>-2</sup> d<sup>-1</sup> at the stated humidity gradient. The values obtained were normalized to a sample thickness of 100  $\mu\text{m}$  and a partial pressure difference of 1 mbar, giving a normalized water vapor permeability (WVP) (similar to a permeation coefficient),  $Q_{100 \text{ H}_2\text{O}}$ , in g 100  $\mu\text{m m}^{-2} \text{ d}^{-1} \text{ mbar}^{-1}$  by using eq. (1).

**Oxygen Transmission Rate (OTR), Oxygen Permeability (OP).** The oxygen transmission rate (OTR) was measured by two different techniques:

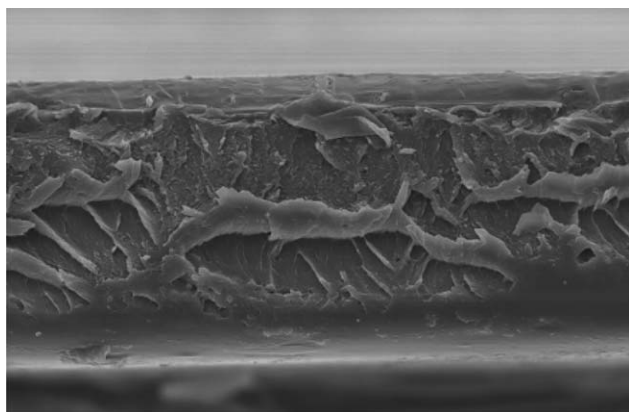


Figure 1. SEM-image of pure starch ( $\times 500$ , cs).

Starch, gluten, and pea protein samples were analyzed with the Presense method according to E DIN 53380-5. The measurement is based on the effect of dynamic luminescence quenching by molecular oxygen.<sup>13,14</sup> To excite the sensor dye, a light source is applied. The method measures the luminescence lifetime of the activated state of the sensor dye. The luminescence lifetime correlates negatively with the oxygen partial pressure. The carrier gas was  $N_2$  and the measuring conditions were  $23^\circ C$  and 70% rh.

Alginate samples were analyzed with the carrier gas ( $N_2$ ) method according to DIN 53380-3 in Oxtran Twin devices from Mocon. An electrochemical sensor detects the amount of oxygen permeating through the sample at constant conditions ( $23^\circ C$ , 50% rh, recorded oxygen pressure difference about 1 bar), thus giving the OTR in  $cm^3$  Standard Temperature and Pressure (STP)  $m^{-2} d^{-1}$ .

The measuring area of the samples was  $9.6\text{ cm}^2$  except for pure starch films. Here, the measuring area had to be reduced to  $2\text{ cm}^2$  because of the high brittleness of pure starch films. For all samples, independent of the applied method, a two-fold determination was performed and the standard deviation was calculated. The normalized OP can be calculated from the OTR values by normalizing them to a thickness of  $100\ \mu m$  and a partial pressure difference of 1 bar by using eq. (1). This enables a direct comparison of different materials independent of the film thickness. The normalized OP,  $Q_{100\ O_2}$ , is given in the unit of  $cm^3$  (STP)  $100\ \mu m\ m^{-2}\ d^{-1}\ bar^{-1}$ .

$$Q_{100\ H_2O} = WVTR \cdot \frac{d}{\Delta p_{100}} \quad \text{and} \quad Q_{100\ O_2} = OTR \cdot \frac{d}{\Delta p_{100}} \quad (1)$$

Here,  $d$  denotes the actual film thickness (in  $\mu m$ ) and  $\Delta p$  the partial pressure difference under the measurement conditions (in mbar for water vapor, in bar for oxygen).

## RESULTS AND DISCUSSION

In this study, low  $M_w$  substances were employed as external plasticizers in the biopolymer network.<sup>15</sup> The low  $M_w$  additives move in the polymer network and widen the distance between the chains by increasing the free volume. Due to this change in the network, the flexibility of the network can be enhanced resulting in changes to the mechanical properties.<sup>16,17</sup> As a fur-

ther effect, the permeability of gases and water vapor often increases. The effect of commonly used additives on the structural, mechanical, and barrier properties of cast biopolymer films was investigated. The structural properties were studied by microscopic analysis, the mechanical properties by a tensile test, and the barrier properties were characterized by the permeabilities to water vapor and oxygen.

### Microscopic Analysis (SEM)

The Figures 1–13 illustrate the cross-sections (cs), ambient fractures (af), and cryo-fractures (cf) of selected cast films analyzed by SEM (the magnification is given in the caption of each figure). Microscopic analysis should show up structural differences between unplasticized and plasticized biopolymer films. For illustrative purposes, the pure biopolymer as well as one sample of each plasticizer is shown. The pure starch sample can be seen to have a rough structure while both plasticized samples are smoother and more even. The unplasticized alginate has an inhomogeneous structure. The addition of Gly makes the structure rougher compared to Sor. The protein samples by comparison show an inherently smoother structure. The structure of gluten is rougher and more inhomogeneous when plasticizer is added, independent of the type of plasticizer. For pea protein the structure is not influenced significantly by Gly or Sor, while the film with TEA shows a smooth, homogenous structure.

### Mechanical Properties: Tensile Strength and Elongation at Break

The pure biopolymer films differ in their mechanical properties (see Table I). Interestingly, alginate shows both the highest tensile strength ( $\sigma$ ) and highest elongation at break ( $\epsilon$ ). The tensile strength ( $\sigma$ ) decreases in the order alginate > starch > pea protein > gluten. The  $\epsilon$  shows almost the same order except that pea protein has a higher  $\epsilon$  than starch. Comparing the pure biopolymers, alginate shows the most promising mechanical properties, being the material with the highest strength and flexibility. For all the plasticizers we can state that on increasing the concentration there is a steady decrease in  $\sigma$  and a steady increase in  $\epsilon$ . This supports the choice of plasticizers as being effective for these biopolymers.

On addition of low amounts of Gly to alginate,  $\sigma$  increases. This might be due to the high brittleness of the pure biopolymer film. On further increasing the Gly or Sor concentration, the  $\sigma$  significantly decreases and  $\epsilon$  significantly increases.



Figure 2. SEM-image of pure alginate ( $\times 500$ , cs).

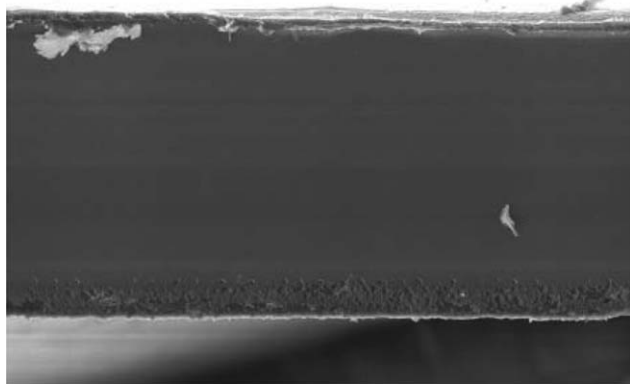


Figure 3. SEM-image of starch + 30 wt % Gly ( $\times 250$ , cs).

However, the changes are more dramatic for Gly samples which are in agreement with the literature.<sup>18–20</sup> This improvement in flexibility correlates with the smoother, more homogenous structure seen by SEM. Even though pure starch films are very brittle, they show the highest  $\sigma$  compared to all plasticized starch films. Comparison with the literature is not always clear: Ortega-Toro, *et al.*<sup>21</sup> state a comparable  $\sigma$  but lower  $\epsilon$  while Jimenez, *et al.*<sup>22</sup> show comparable  $\epsilon$  but lower  $\sigma$  for a 0.25 Gly starch film. Our results for starch also show a significant decrease in  $\sigma$  and increase in  $\epsilon$  on increasing the plasticizer concentration. The effect seems to be more evident for Gly samples than for Sor samples. Assuming  $\sigma > 15 \text{ N mm}^{-2}$  and  $\epsilon > 15\%$  are necessary for stable processing of such films, the most suitable formulation includes 0.3 Gly or 0.35 Sor in starch films and 0.3 Gly or 0.45 Sor in alginate films.

Pea protein and gluten show different results regarding their unplasticized films: While pea protein has a high  $\sigma$  and an  $\epsilon$  comparable to the polysaccharide films, gluten reveals very low mechanical properties. This might be due to the different preparation of pure gluten films (by a coating process). The addition of any selected plasticizer to pea protein significantly decreases  $\sigma$  and increases  $\epsilon$ , with plasticized pea protein films having the highest  $\epsilon$  of all the tested plasticized biopolymer films. This agrees with the SEM analysis and is due to the more homogeneous structure of the plasticized films. Even though pea protein with 0.2 Gly showed a  $\sigma$  comparable to literature data ( $4.9 \text{ N}$

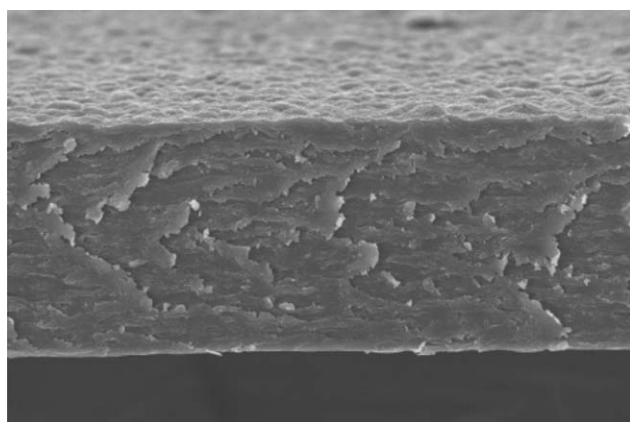


Figure 4. SEM-image of alginate + 30 wt % Gly ( $\times 500$ , af).

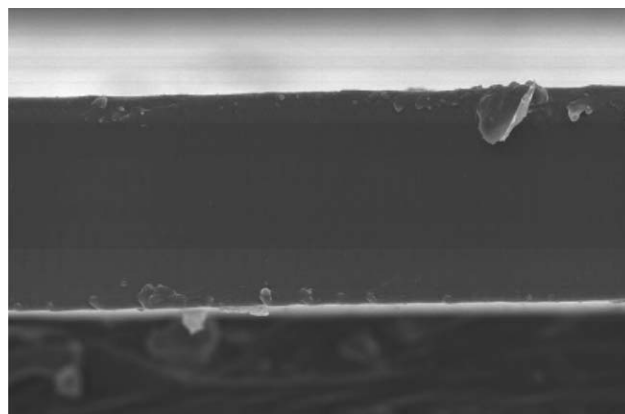


Figure 5. SEM-image of starch + 35 wt % Sor ( $\times 250$ , cs).

$\text{mm}^{-2}$ ),<sup>2</sup> the  $\epsilon$  of our sample is significantly higher compared to the literature (0.6%<sup>2</sup> or 75% for a pea protein film with 0.5 Gly<sup>23</sup>). There seems to be a critical plasticizer concentration for pea protein films which, if exceeded, results in a considerable increase in  $\epsilon$  while not affecting  $\sigma$  to the same extent. This critical concentration for Gly is between 0.15 and 0.2, for Sor is between 0.35 and 0.4 and for TEA is between 0.2 and 0.25. For plasticized gluten films  $\sigma$  also decreases and  $\epsilon$  increases, but the concentration of plasticizer does not seem to have a major impact on the properties. The most significant effect is the addition of the plasticizer itself. Mojumdar, *et al.*<sup>24</sup> measured a  $\sigma$  of  $1.2 \text{ N mm}^{-2}$  for a gluten film plasticized with 0.375 Gly, which is in agreement with our 0.25 Gly sample, but measured an  $\epsilon$  of 397% which is significantly higher than our sample. The plasticization might have a higher impact on  $\epsilon$  than on  $\sigma$ . Since the  $\sigma$  of the protein films is always  $< 10 \text{ N mm}^{-2}$  (except pea protein + 0.35 Sor), the most suitable formulations were selected based on the highest  $\sigma$ : for pea protein 0.15 Gly, 0.35 Sor or 0.15 TEA, and for gluten 0.175 Gly or 0.175 TEA are favored.

Based on the results, it can be stated that the polysaccharides show promising results for single films while the proteins seem to be more suitable as a coating material for a lacquering process.

#### Barrier Properties: Water Vapor Permeability $Q_{100 \text{ H}_2\text{O}}$ and Oxygen Permeability $Q_{100 \text{ O}_2}$

The water vapor permeability (WVP) and oxygen permeability (OP) of all the biopolymer films are listed in Table I.

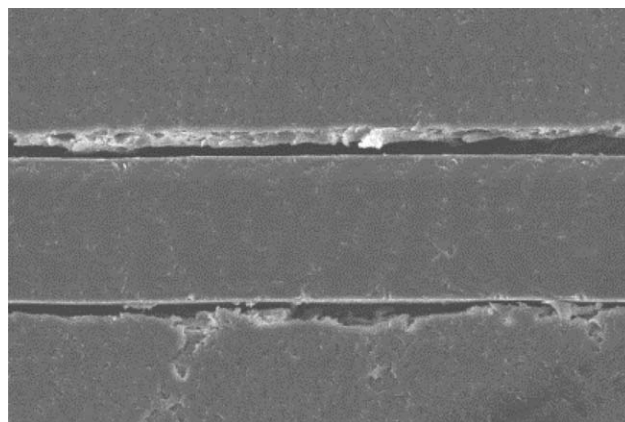


Figure 6. SEM-image of alginate + 50 wt % Sor ( $\times 200$ , cs).



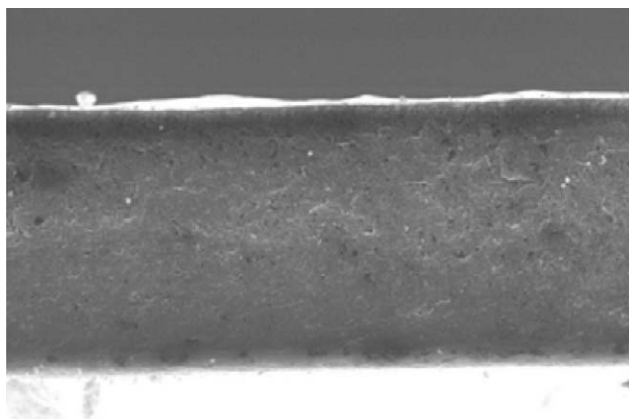


Figure 7. SEM-image of pure pea protein ( $\times 500$ , af).

Comparing the WVP results of the pure cast biopolymer films reveal that polysaccharides have higher permeabilities than proteins. While pure alginate films have the highest WVP, pure starch films show a lower permeability, although the smaller measuring area of these samples could also influence this result. The pure protein films show comparable results but are significantly lower than the pure polysaccharide films. This leads to the conclusion that unplasticized protein films are more suitable than unplasticized polysaccharide films when a low permeable material is favored.

On addition of plasticizer to starch, the WVP is significantly increased which is in agreement with other studies.<sup>25</sup> Interestingly, Gly leads to a greater increase than Sor – namely to an almost threefold increase (0.3 wt % relative to the unplasticized starch film) for Gly compared to not even a twofold increase for Sor (0.4 wt %). These results are in agreement with the literature<sup>21</sup> (or lower<sup>22</sup>) as can be seen for the 0.25 Gly starch sample. As the mechanical properties are affected by Gly and Sor to almost the same extent for the applied concentrations, the following conclusions can be drawn: Gly with a low molecular weight ( $M_w$ ) widens the biopolymer network and facilitates the permeation of water molecules by increasing the diffusion coefficient. Sor with a higher  $M_w$  might be a better steric fit in the starch network due to similarity with the reduced monomer of starch (glucose). The resulting dense network only increases

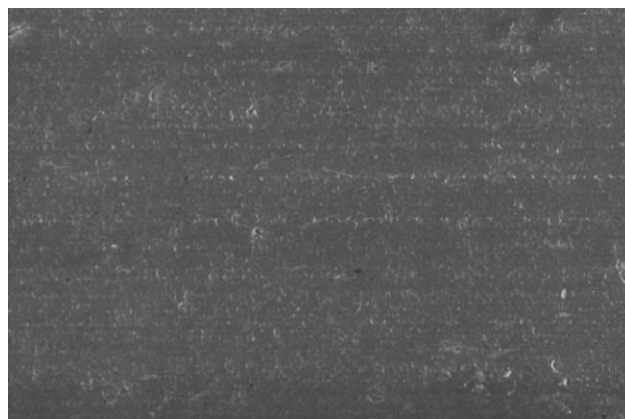


Figure 9. SEM-image of pea protein + 20 wt % Gly ( $\times 500$ , cs).

the permeability to a small extent. Furthermore, water vapor permeation is hampered due to the low hygroscopicity of Sor. The addition of Gly to alginate also shows a slight increasing effect on the WVP, which continues with a further increase in the concentration. For alginate, the effect of Gly is comparable to starch (as described above) but not so pronounced. However the addition of Sor leads to a slight decrease of WVP. It seems that Sor has a good fit in polysaccharide networks probably stabilized by hydrogen bonds with the biopolymer chain. This leads to a denser network which does not increase the permeability in a way that plasticizer with less interaction possibilities do.

The addition of plasticizer to both pea protein and gluten leads to a huge increase in WVP. A further increase in the plasticizer concentration results in a further increase in WVP but not as considerable as the initial addition. However, the WVP of plasticized pea protein films does not differ between the first two concentration steps for all applied plasticizers. The WVP of pea protein with 0.2 Gly is of the same magnitude as literature values ( $103 \text{ g } 100 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ mbar}^{-1}$ )<sup>2</sup> but in contrast to the cited literature our results show a strong increase in WVP even at 0.25 Gly (not only at 0.5 Gly).<sup>2</sup> The highest WVP of plasticized pea protein films was measured with Gly followed by Sor and TEA which is in agreement with the literature.<sup>26</sup> This leads to the conclusion that Sor also has a good fit in the pea protein

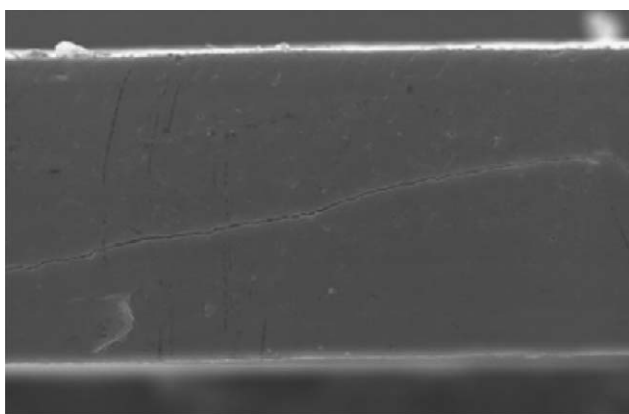


Figure 8. SEM-image of pure gluten ( $\times 500$ , af).

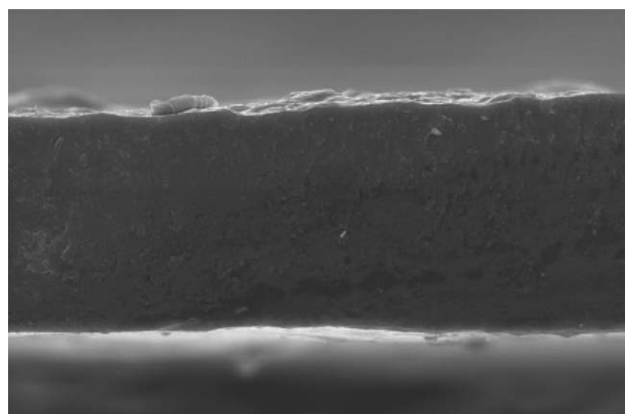


Figure 10. SEM-image of gluten + 20 wt % Gly ( $\times 500$ , cf).

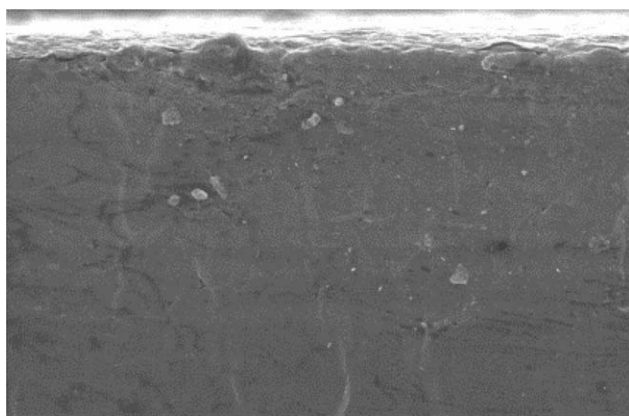


**Figure 11.** SEM-image of pea protein + 40 wt % Sor ( $\times 500$ , cs).

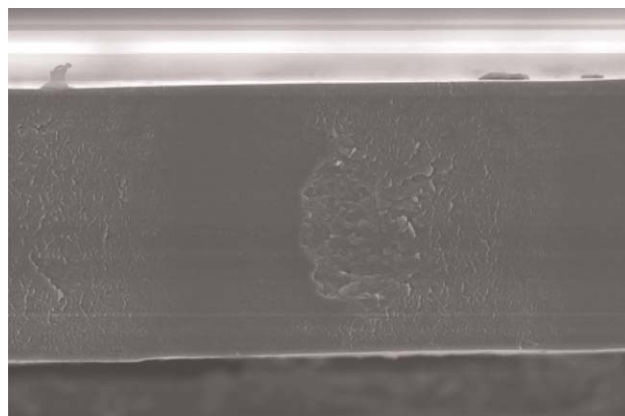
network. Another reason for this behavior is the low hygroscopicity of Sor.<sup>26</sup> Besides the hydrogen bonds which are also formed with Gly and Sor, the plasticizer TEA forms ionic bonds between free carboxyl groups of the protein with its amine group, as stated in the literature.<sup>11</sup> Also, the plasticization of gluten with Gly does not lead to a continuous increase in WVP, while TEA increases the WVP of gluten continuously with increasing concentration, which was also shown for other additives.<sup>11,27</sup> Comparing the same concentrations of Gly and TEA which were applied to pea protein and gluten, the WVP of plasticized pea protein was found to be slightly lower (except the sample with 0.25 Gly).

The addition of plasticizer improves the flexibility of biopolymers and therefore the ability to maintain their properties for further processing. The most suitable formulations named in the previous section show different results for their WVP: The lowest WVP was measured for TEA-plasticized pea protein and gluten followed by Sor-plasticized starch and alginate. A slightly higher permeability was measured for Sor-plasticized and Gly-plasticized pea protein followed by the Gly-plasticized gluten, alginate, and starch. Interestingly, the commonly used Gly leads to the highest permeabilities for all the tested biopolymers while TEA seems to be a working alternative for plasticizing proteins without leading to a highly increased WVP.

The oxygen permeability (OP) of pure starch was not possible to measure because the films always broke in the measuring



**Figure 12.** SEM-image of gluten + 22.5 wt % TEA ( $\times 500$ , cs).



**Figure 13.** SEM-image of pea protein + 20 wt % TEA ( $\times 250$ , cs).

cells. Some literature overcomes this challenge by giving data for coated starch films on a substrate.<sup>28</sup> The oxygen permeabilities of the pure biopolymer films differ in the following order by approximately one order of magnitude: alginate < gluten < pea protein.

Increasing the plasticizer concentration leads to increased permeabilities of starch films, again with significantly higher values for Gly samples (in agreement with recent literature<sup>21</sup>). In contrast, the starch films with Sor show only a slight increase in OP. The plasticized alginate films show interesting results: While the OP is slightly increased by Gly, the samples with Sor show an almost constant or slightly decreasing permeability with increasing concentration.<sup>29</sup> Interestingly, the OP of all the alginate samples is significantly lower than that of the starch samples, indicating alginate is a promising material with low OP.

On addition of plasticizer to both proteins, the OP is increased. Interestingly, the effect on gluten is much more pronounced than on pea protein. With a further increase in the concentration of Gly the OP is further increased for both proteins. By the addition itself of Sor or TEA the OP of pea protein is increased. However, with a further increase in Sor respectively TEA the OP of pea protein is not changed significantly respectively decreased. An increase of TEA leads also to decreased OP for gluten films but less pronounced (compared to TEA-plasticized pea protein films). This decrease in OP agrees with the SEM analysis of a homogenous, dense network of TEA- and also Sor-plasticized films. Again this indicates a good steric fit of Sor also in the protein network and an effective formation of ionic bonds by TEA.

Comparing the influence of the different plasticizers in the most suitable samples (based on their mechanical properties, see Section “Mechanical Properties: Tensile strength and elongation at break”), Sor-plasticized alginate and starch as well as Gly-plasticized alginate have the lowest OP. Significantly, higher OP values were found for Gly-plasticized pea protein and starch as well as Gly-plasticized gluten and Sor-plasticized pea protein. Interestingly, the highest permeabilities were measured on TEA-plasticized gluten and pea protein. These results indicate that the polysaccharide films have lower oxygen permeabilities than the protein films.

**Table II.** Relative Change in the Mechanical ( $\sigma$ ,  $\epsilon$ ) and Barrier (WVP  $Q_{100 H_2O}$ , OP  $Q_{100 O_2}$ ) Properties

Bio-polymer	Weight fraction $W_{Plasticiser}$ & type of plasticizer	Ratio of $\sigma$ to the pure biopolymer	Ratio of $\epsilon$ to the pure biopolymer	Ratio of WVP $Q_{100 H_2O}$ to the pure biopolymer	Ratio of OP $Q_{100 O_2}$ to the pure biopolymer
<i>Polysaccharides</i>					
Starch	0.30 Gly	0.4	12.0	2.9	-
Starch	0.35 Sor	0.4	13.3	1.4	-
Alginate	0.30 Gly	0.3	10.2	1.4	5.5
Alginate	0.45 Sor	0.3	5.6	0.7	0.8
<i>Proteins</i>					
Pea protein	0.25 Gly	0.2	100.6	7.7	2.0
Pea protein	0.40 Sor	0.2	22.2	4.2	1.2
Pea protein	0.25 TEA	0.2	68.0	5.2	0.4
Gluten	0.20 Gly	0.6	65.5	6.7	6.2
Gluten	0.175 TEA	0.5	93.4	3.2	11.1

The results show that the plasticizers have different effects on the mechanical properties and in particular on the barrier properties of the biopolymer films. To analyze these influences, Table II lists the change of the properties of selected samples relative to the unplasticized biopolymer films. The selection of the plasticized samples is based on comparable mechanical properties (especially  $\sigma$ ).

Due to approximately the same effect on the  $\sigma$  of each biopolymer, Table II gives a comparison of the influence of each plasticizer on  $\epsilon$ , WVP, and OP. The effect of both plasticizers on the properties of alginate is less than the effect on the properties of starch. Gly-plasticized and Sor-plasticized starch films have almost the same effect on  $\epsilon$  but there is a higher effect on WVP by Gly. Also, Gly has a higher effect on the permeabilities of alginate films compared to Sor. There is no clear trend here regarding the influence of the plasticizers on the proteins. Concerning  $\sigma$ , the influence on gluten films seems to be higher for all the plasticizers but this is related to the very low  $\sigma$  of pure, unplasticized gluten films. The effect on  $\epsilon$  is varying: While Gly shows the biggest impact on pea protein, it has the lowest impact on gluten. However, TEA leads to lower  $\epsilon$  for pea protein films but to higher  $\epsilon$  for gluten films compared to the respective Gly-sample. Sor leads to the smallest effects in almost all properties. The WVP is influenced most by Gly and significantly less by TEA for both protein films. The strongest effect on OP of pea protein films is measured by Gly, with Sor and TEA having a lower effect. However, the influence of TEA on the OP of gluten films is much higher than of Gly indicating a different effectiveness of TEA in different protein materials.

The results show that the plasticizers have a greater influence on almost all the properties of protein films than they do on the properties of polysaccharide films. The plasticized protein films have higher flexibility but also higher permeabilities. On comparing plasticized biopolymer films with approximately the same  $\sigma$ , Gly has the biggest effect on  $\epsilon$ , WVP, and OP in almost all cases, with Sor having a smaller influence. The effect of TEA-plasticized protein films is especially apparent for the OP which can be reduced compared to the pure unplasticized pea

protein. This effect is also evident for TEA-plasticized gluten films but not so pronounced than with the pea protein films.

## CONCLUSIONS

The effectiveness of a plasticizer depends on its molecular size but also on the interaction with the functional groups of a biopolymer. This study presents an overview of different cast biopolymer films plasticized by different low molecular substances in order to evaluate their effectiveness in the different biopolymer systems. By an equivalent production and characterization a comparison of the potential of different biopolymers as packaging materials and a valuation of plasticizers for certain biopolymer systems is enabled. As a result of an effective plasticizer the flexibility of these films is improved, as found in this study for all plasticized films by the decreasing tensile strength ( $\sigma$ ) and increasing elongation at break ( $\epsilon$ ). External plasticizers often also lead to increased permeabilities. The results presented here show that this correlation is not always given.

The unplasticized polysaccharide films were found to have higher strength than unplasticized protein films. The addition and further increase in concentration, of plasticizers led to a steady decrease in  $\sigma$  and steady increase in  $\epsilon$  for all tested biopolymer films. The plasticized polysaccharide films show higher strength while protein films show higher  $\epsilon$  which lead to the conclusion that polysaccharides might be used as single films while proteins are more suitable as a coating material. The plasticizer Gly seems to be more effective on mechanical properties for both polysaccharides and proteins than Sor because lower concentrations lead to comparable effects. The plasticizer TEA seems to be as effective as Gly for similar concentrations but has different effects on the OP. Furthermore, the addition of plasticizer leads to increasing water vapor (WVP) and oxygen permeability (OP) for all biopolymers independent of the applied plasticizer. A further increase in plasticizer concentration leads to increasing WVP, with the increase most pronounced for Gly. The lowest WVP values were measured for Sor-plasticized polysaccharides and TEA-plasticized proteins. Interestingly, a further increase in Sor does not lead to a

significant change in OP while an increase in Gly results in an increase and in TEA in a decrease of OP.

The different effects of Gly and Sor are mainly due to their different  $M_w$ , since both molecules stabilize the polymer network via the formation of hydrogen bonds, and the lower hygroscopicity of Sor compared to Gly. The bigger, less hygroscopic Sor molecules improve the flexibility for improved processing whilst maintaining the low permeabilities of biopolymers. TEA, however, stabilizes the biopolymer network by forming ionic bonds with its amine group. With increasing TEA concentration these ionic bonds are more numerous and lead to a lower barrier to polar water vapor molecules but a higher barrier to non-polar oxygen molecules. Of all the characterized films, alginate films have the most promising properties, namely they are flexible materials with adequate strength and with low permeability especially to oxygen.

Biopolymers are highly complex systems having different functional groups and conformations to conventional polymers used for packaging applications. This work shows that plasticizers can be used to beneficially influence the properties of certain biopolymers. Biopolymer films with customized permeability properties and sufficient flexibility can be manufactured. Therefore biopolymers have the potential to replace petrochemical based polymers and contribute to sustainable packaging concepts.

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