Arabinoxylan-Lipids-Based Edible Films and Coatings. 2. Influence of Sucroester Nature on the Emulsion Structure and Film Properties

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This work is a contribution to better knowledge of the influence of the structure of films on their functional properties obtained from emulsions based on arabinoxylans, hydrogenated palm kernel oil (HPKO), and emulsifiers. The sucroesters (emulsifiers) have a great effect on the stabilization of the emulsified film structure containing arabinoxylans and hydrogenated palm kernel oil. They improve the moisture barrier properties. Several sucroesters having different esterification degrees were tested. Both lipophilic (90% of di and tri-ester) and hydrophilic (70% of mono-ester) sucrose esters can ensure the stability of the emulsion used to form the film, especially during preparation and drying. These emulsifiers confer good moisture barrier properties to emulsified films.

KEYWORDS: Water vapor permeability; water absorption rate; surface hydrophobicity; barrier layer

INTRODUCTION

Arabinoxylans from maize bran are polyosidic chains included in the hemicellulosic chemical group. These are nonsoluble fibers when in their native form, and they are characterized by a very high moisture retention capacity. However, after alkaline extraction, arabinoxylans become totally soluble in water and are responsible for a high viscosity (*1, 2*). Solubility of arabinoxylans, their ability to form a continuous and cohesive matrix, and their neutral taste and odor led to their use as film formers (*3*). A preliminary study of their properties as edible films was done by Chanliaud (*3*). Their mechanical and barrier properties are of the same order of magnitude as those of gluten films (*4*), whey protein films (*5*), hydroxypropyl methylcellulose films (*6*), methylcellulose films (*7*), and starch films (*8*). These films exhibit very good performance against oxygen and carbon dioxide transfer when dry, but they lose their barrier properties when exposed to high water activities (*3*). Péroval et al. (*9*) added some lipids, such as fatty acids, triglycerides, or hydrogenated oils, as emulsion or bilayer structures to decrease the moisture sensitivity of arabinoxylans-based films. Hydrogenated palm kernel oil tends to give the best results, but the

barrier performances seems to depend strongly on the film structure. Indeed, bilayer films exhibit much better moisture barrier properties than films obtained from emulsions (*4, 10−13*). However, bilayer films are obtained from lamination of the melted lipid onto a hydrocolloid-based film previously formed on a support. So, this technique requires at least three manufacturing steps instead of only two in the case of edible films prepared from emulsions. Therefore, emulsion-based edible barriers are of greater interest for the food industry.

The moisture permeability of the emulsion-based films depends mainly on the distribution of the lipid globules within the film. Park et al. (*14*) and Debeaufort and Voilley (*15*) showed that the smaller the lipid globule size is, and the more homogeneously distributed they are, the lower the water vapor permeability is. Then, the emulsion structure has to be controlled and stabilized during the preparation and formation (drying) of the film. However, heat and solvent evaporation during the drying of the film-forming-emulsion induces changes in the emulsion characteristics, particularly destabilization phenomena such as creaming, aggregation, and/or coalescence. So, the use of emulsifiers is often recommended. Several works have been done on edible films prepared from emulsions containing monoglycerides or esterified monoglycerides (*10, 15−17*). These authors showed that the diameter and distribution of fat globules in the film depend on the nature of the emulsifier but very little on its hydrophilic−lipophilic balance (HLB). Moreover, their efficiency strongly depends on their concentration which is optimal when the diameter is the smallest and the size distribution is monomodal (*15*).

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Table 1. Physico-Chemical Characteristics of Sucroesters

characteristic	SP 10	SP 30	SP 40	SP 70
HLB[a]	2	6	8	15
melting point (°C)	58	55	52	50
% of monoesters	10	30	40	70
fully soluble in:	oils	−	ethanol	water, ethanol, glycerol
partially soluble in:	−	water, oils, glycerol, ethanol	water, glycerol, oils	−
not soluble in:	water, glycerol	−	−	oils

[a] HLB, Hydrophilic–lipophilic balance.

The objective of this work was to better understand the influence of the concentration and nature of some lipid sucroesters on the structure of the film-forming emulsion and on the structure and functional properties of edible films after drying.

MATERIALS AND METHODS

Materials. Arabinoxylans (AX, qualité D, Ulice, France) were used as the film-forming component of the hydrophilic continuous phase of emulsion-based edible films. Arabinoxylans are the soluble fraction of maize bran fibers and are usually used for their nutritional and water retention properties (*3*). Arabinoxylans are linear chains composed of D-xylopyranose residues linked by $\beta 1-4$ bonds and mainly branched by L-arabinose residues. Anhydrous glycerol (98% purity, Fluka Chemical, Germany) was added to arabinoxylans to improve their mechanical properties. Indeed, glycerol is one of the most efficient plasticizers for polysaccharide-based or protein-based edible films and coatings. The hydrophobic dispersed phase was hydrogenated palm kernel oil (HPKO, OK 35, S. I. O., France) with a melting point of 34.5−36.5 °C. To improve the stability of film-forming emulsions, four sucroesters (Sisterna-Unipex, France) were tested. Their physico-chemical characteristics are given in Table 1.

Homogeneous edible films were also composed of either pure hydroxypropylmethylcellulose (HPMC, E15 LV Premium, Dow Chemical, France) or of HPMC and anhydrous glycerol. They were used as references for comparison of the film properties.

Two synthetic films were also used as standards: a cellophane film (300P, Courtauld's, U.K.), hydrophilic but not soluble in water, 20 μm thickness, and a low-density polyethylene film (LDPE, Riblène FF30, EniChem, France) with a crystallinity of 37% and thickness of 25 μm.

Preparation of Homogeneous Edible Films. Arabinoxylan films were obtained after solubilization of 16 g of AX in 100 mL of osmosed water at 75 °C for 40 min under a 600-rpm magnetic stirring. Then, glycerol was added at a concentration of 15% of the total dry basis. The film-forming solution was kept for 10 min under the same conditions of temperature and stirring prior to being spread onto a glass plate that had been previously covered with a poly(vinyl chloride) adhesive sheet to prevent the sticking of dried films. A continuous thickness of 1000 μm was obtained for the cast solution using a thin-layer chromatography spreader. All the films were then dried for 4 h in a ventilated cupboard (KBF 240 Binder, ODIL, France) with temperature and relative humidity fixed at 30 ± 1 °C and 40 ± 2% RH, respectively. The temperature was chosen so as to be lower than the melting point of lipids to prevent lipid globule aggregation and coalescence during drying of emulsion-based films.

The HPMC films were prepared with the same procedure except that the film-forming solution was composed of 9 g of HPMC dissolved in 100 mL of a water/ethyl alcohol mixture (75:25, w/w). Thickness of the spread solution was 1000 μm, and drying conditions were the same as those for the homogeneous AX films.

After drying, the thickness of all homogeneous edible films from either arabinoxylan or HPMC ranged between 65 and 75 μm.

Preparation of Emulsion-Based Films. Emulsion-based films were obtained from a process very similar to that used for homogeneous films. The addition of lipid (OK 35) and emulsifier (SP 10 to SP 70) differed according to the HLB of the emulsifier. For SP 70 (hydrophilic), the lipid and the sucroester were successively added to the arabinoxylan/glycerol solution. For SP 10 (hydrophobic), the sucroester was first solubilized in the molten lipid prior to being added to the arabinoxylan/

glycerol solution. For SP 30 and SP 40 (intermediate HLB), the sucroester was first dissolved in ethyl alcohol prior to being mixed in the molten HPKO and then added to the arabinoxylan/glycerol solution.

After the addition of lipid and sucroester, the mixture was predispersed under magnetic stirring for 5 min at 600 rpm and 75 °C before being homogenized using an Ultra-Turrax homogenizer (T25-IKA, Labortechnik, ODIL, France) for 2 min at 24000 rpm.

Film-forming emulsions were then spread at a 625-μm thickness prior to being dried at 30 °C and 40% RH. After drying, film thickness ranged between 65 and 75 μm.

Characterization of Film-Forming Emulsions and Dried Films. *Film and emulsion structure* were characterized by laser light scattering granulometry. Globule size distribution profiles were determined using both a Malvern Mastersizer M20 for emulsions and a Malvern Mastersizer Hydro 2000G (Malvern Instruments, U.K.) for films. The mean diameter of lipid globules and specific surface area were calculated from an optical model involving the absorbance of a 633-nm laser light by the lipid phase and the ratio of refractive indices of dispersed phase (lipid) and water which equals to 1.11. The emulsion structure of dried films was determined using the same methodology, but 5 g of film were previously solubilized in 45 mL of osmosed water at a temperature lower than the melting point of lipid in order to prevent aggregation or coalescence of fat droplets during sample preparation. Aggregates were disrupted by adding a solution of sodium dodecyl sulfate (SDS) in order to get a final concentration of 0.1% prior to analysis.

Film microstructure was also observed by environmental scanning electron microscopy (ESEM, Phillips XL 30 ESEM, Japan). A 5 × 10 mm² film was fixed on the support using double-sided adhesive tape, with an angle of 90° to the surface which allowed observation of the film section.

Film thickness was measured with an electronic gauge (Multicheck FE, SODEXIM, France) of which precision ranged between 0.1 and 1% as a function of the thickness value (0−100 μm or 0−1000 μm). Twenty replicates were done on each film-making.

Surface hydrophobicity and wettability of films were estimated from the contact angle measurement of a 20-μL water droplet deposited on the film surface using a G1 Kruss goniometer (KRUSS GmbH, Germany) equipped with an image analysis software (Drop Shape Analysis, Kruss GmbH, Germany). Kinetics of contact angle and liquid moisture absorption rate were determined at 25 °C.

Water vapor permeability (WVP) at a relative humidity differential of 84−22% was measured using a modified French standard method (*18*), homologous to the ASTM E96-80 method (*19*) and adapted to edible materials by Debeaufort et al (*7*) and McHugh et al (*5*). Films were fixed between two Teflon rings on the top of a glass cell containing a saturated salt solution of potassium chloride (KCl, Merck, Germany) of which the water activity is 0.84 at 25 °C. Test cells were placed in a stirred air cupboard (KBF 240, Binder, ODIL, France), the temperature and relative humidity of which were fixed at 25° and 22% RH, respectively. Test cells were periodically weighted up to a constant weight variation rate. Prior to measuring water vapor permeability (WVP), all films were stored at 25 °C for 48 h in a desiccator over potassium acetate saturated solution (CH₃COOK, Merck, Germany) which fixes the RH at 22%. WVP (g·m⁻¹·s⁻¹·Pa¹⁻) was calculated using the following equation:

$$\text{WVP} = \frac{\Delta m \cdot x}{A \cdot \Delta t \cdot \Delta p}$$

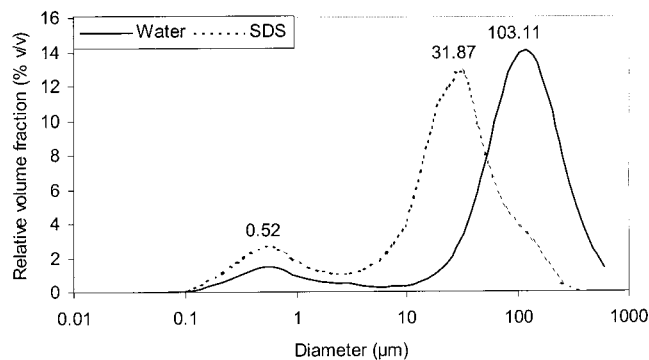**Figure 1.** Granulogram of film-forming emulsions prepared without emulsifier after dispersion in cold water or in cold SDS solution.

where Δm is the weight loss of the permeation cell (g), x is the film thickness (m) with A exposed area (9.11×10^{-4} m^2) during Δt duration (s) under a Δp partial water vapor pressure differential (Pa).

Significance. Each film attribute was measured at least in triplicate, and differences between means were tested at the $p < 0.05$ level using the Student's–Newman's–Keul's t-test of SAS-ANOVA (Statistical Analysis System, Ver 6.02). No repetition of the film preparation was done in this work because Peroval et al. (9) showed that the standard deviation on the film properties (according to the same type of recipe of arabinoxylan-based films from emulsions) is lower than 6%.

RESULTS AND DISCUSSION

Effect of the Nature and Concentration of Sucroester on the Granularity of the Film-Forming Emulsion. Film-forming emulsions prepared from lipids dispersed in arabinoxylans solutions are water-in-oil type and contain 7% (w/v) dry matter. They are stabilized by sucroesters differing by their esterification degree, and, consequently, their hydrophobicity. Emulsifier content was always expressed as regards the lipid phase and not the whole composition, because when films are dried, the emulsifier concentration remains constant when expressed as gram of emulsifier per 100 g of lipid phase. Emulsions were diluted either in an aqueous solution of SDS (0.1%) used as a dissociating medium or in water (nondissociating medium), and comparison of the particle sizes measured in these two media allows display of lipid globule aggregation. The analysis of granulograms shows that all emulsions present 2 populations of lipid globules with respect to diameter. One has an average diameter ranging between 0.5 and 0.9 μm, and the other one varies widely depending on the nature and content of the emulsifier. Without sucroester, granulograms determined in water and in SDS solution greatly differ, which means that aggregation may occur. Indeed, Figure 1 shows a shift of the mean particle size from 103 μm in water down to 31 μm in the presence of SDS. Moreover, the 0.5-μm diameter population increases when SDS is used. This result confirms that lipid globules tend to aggregate when no emulsifier is used.

When SP30, SP40, or SP70 were used to stabilize the film-forming emulsion, we found an optimal concentration for which emulsion is the most stable (i.e., absence of aggregates) because granulograms obtained without SDS and with SDS are super-imposable. For instance, Figure 2 displays that there are no aggregates when 6.25% of SP30 is used, whereas aggregation does occur with 10% of SP30 as shown in Figure 2b. However, SP10 has a particular behavior because whatever its concentration (from 2.5 to 12.5%), the emulsion presents the same granulograms either in water or in SDS solution.

Figures 2b and 3 display the cases of SP30 and SP10 at a 10% concentration in the lipid phase. Very different behaviors were observed according to the nature of the emulsifier. In an
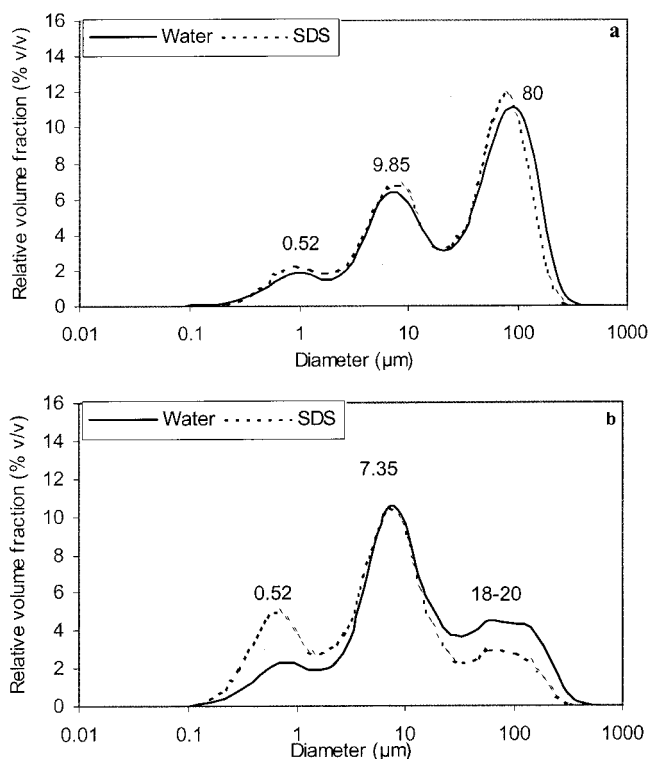

Figure 2. Granulogram of film-forming emulsions containing (a) 6.25% or (b) 10% SP30 in the lipid phase (HPKO + SP3) after dispersion in cold water or in cold SDS solution.
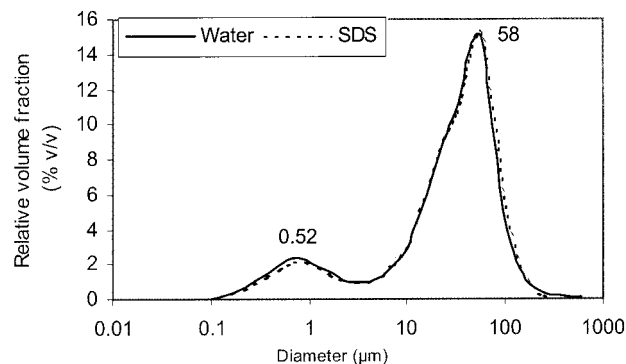

Figure 3. Granulogram of film-forming emulsions containing 10% SP10 in the lipid phase (HPKO + SP) after dispersion in cold water or in cold SDS solution.

emulsion containing SP30, particle-size distribution is trimodal and aggregates are present, whereas distribution is bimodal with no aggregates in emulsions containing SP 10. Indeed, the efficiency of an emulsifier mainly depends on its solubility in each phase of the emulsion. Usually, the emulsifier has to be greatly soluble in the continuous phase (20). So in our case, sucroester should be hydrophilic to stabilize HPKO–arabinoxylans emulsions. Among the tested sucroesters, only SP70 is fully soluble in water; and it should be the most effective, whereas SP10 would be the worst because it is not soluble in the aqueous phase. However, our results show that emulsion stability depends on the sucroester solubility in the aqueous phase, but also, and mainly, on its concentration. Indeed, the sucroester concentration has a tremendous influence when the emulsifier is fully or partially soluble in the aqueous phase such as SP70, SP40, and SP30. So the mean diameter is the smallest and there is no aggregation for a specific concentration of SP70, SP40, or SP30 in the emulsion.

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Table 2. Mean Diameter[a] (D[3,2], μm) of HPKO Globules of Film-Forming Emulsions Dispersed Either in Water or in 0.1% SDS Solution as a Function of Both Nature and Content of Sucroesters

emulsifier	dispersant	sucroester content of the lipid phase					
		1.25%	2.5%	6.25%	10%	12.5%	25%
SP70	water	3.10 c	**1.29 a**	1.28 a	1.88 a,b	2.03 b	n.d.
	SDS	1.64 a	**1.28 a**	1.94 b	1.70 a	1.97 b	n.d.
SP40	water	n.d.	1.94 b	1.72 a	1.51 a	**1.36 a**	2.36 c
	SDS	n.d.	1.65 a	1.40 a	2.37 c	**1.50 a**	4.41 d
SP30	water	n.d.	2.87 c	**1.72 a,b**	2.87 c	2.52 c	n.d.
	SDS	n.d.	1.65 a	**1.83 b**	1.53 a	2.80 c	n.d.
SP10	water	n.d.	**2.77 c**	**2.90 c**	**2.95 c**	**3.00 c**	n.d.
	SDS	n.d.	**2.48 c**	**2.94 c**	**3.32 c**	**3.09 c**	n.d.
without emulsifier	water			4.37 d			
	SDS			2.1 b			

[a] n.d., Not determined. Values having the same letter are not significantly different at *p* < 0.05 level.

Table 3. Mean Diameter[a] (D[3,2], μm) of HPKO Globules in Films after Drying

film composition	mean diameter D[3,2] (μm)	
	in water	in SDS solution
without emulsifier	8.74 ± 1.81 a	10.01 ± 1.64 a
2.5% SP70	9.38 ± 0.36 a	0.95 ± 0.03 c
12.5% SP40	6.72 ± 0.20 b	0.72 ± 0.06 c
6.25% SP30	6.30 ± 0.20 b	0.84 ± 0.02 c
2.5% SP10	0.67 ± 0.03 c	0.55 ± 0.01 c
6.25% SP10	0.67 ± 0.02 c	0.56 ± 0.02 c
10% SP10	0.50 ± 0.04 c	0.55 ± 0.02 c
12.5% SP10	0.47 ± 0.01 c	0.54 ± 0.02 c

[a] Values having the same letter are not significantly different at *p* < 0.05 level.

Determination of the Optimal Formulations of Film-Forming Emulsions. Mean diameters (D[3,2]) of HPKO globules in the film-forming emulsion are given in Table 2 as a function of both the nature and concentration of the sucroester. In our conditions of homogenization−emulsification, emulsions prepared without emulsifier display the highest mean diameter. The presence of an emulsifier contributes to formation of smaller globules, but diameters differ and depend on the sucroester used. When emulsions are dispersed in water, data show bigger lipid particles are obtained with SP30 and SP10 than with the more hydrophilic emulsifiers, SP70 and SP40. However, in SDS solution in which aggregates are dissociated for SP70, SP 40, and SP 30, mean diameters are not significantly different. So we have determined an optimal sucroester concentration in terms of smallest globule size and highest stability of emulsion. These concentrations are printed in bold in Table 2. They are 2.5% SP70, 12.5% SP40, 6.25% SP30, and for SP10, from 2.5 to 12.5%. These concentrations of emulsifier are considered to be optimal because no aggregation or coalescence occur. These formulations were selected for the study of the film properties.

Effect of the Sucroesters on the Structure of Emulsion-Dried Films. All film-forming emulsions were dried under the same temperature (30 °C) and relative humidity (40%) for approximately 8 h (i.e., the time corresponding to a constant mass of the sample). The structure of dried films was characterized by both laser light scattering granulometry and ESEM. As was done for the emulsions, films were dissolved in cold water or cold SDS solutions for the granulometry analysis. Mean diameters of HPKO globules as a function of the sucroester nature are given in Table 3. As observed for the emulsion prior to drying, when no emulsifier is used, lipid globules are much bigger but no aggregation is displayed because globule size is the same in both water and SDS solution. Hydrophilic (SP70 and SP40) and intermediate (SP30) sucroesters do not improve
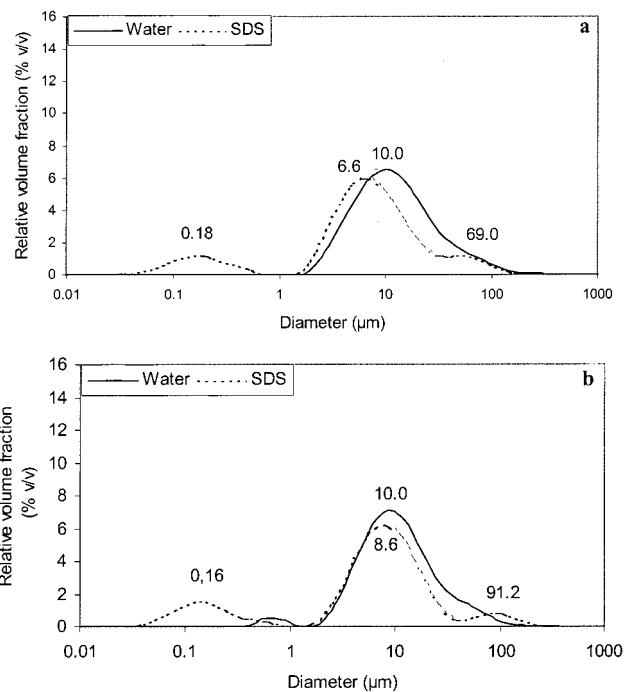
Figure 4. Granulograms of arabinoxylan films containing (a) 2.5% SP70 or (b) 12.5% SP40 in the lipid phase (HPKO + SP) after dissolution in cold water or in cold SDS solution.

very much the dispersion of lipid in the film during drying because the mean diameter measured in water always remains higher than that obtained with SP10 (Figures 4 and 5). Moreover, Table 3 shows evidence for a great aggregation of lipid globules during drying of films made with SP70, SP40, and SP30. This is also proved by the granulograms in which the population of globules having the biggest diameter is shifted toward a population of smaller diameters when SDS is used. If coalescence should occur, no shift should be observed. Moreover, this was also displayed by the ESEM micrographs. On the contrary, SP10 prevents HPKO globules aggregation during drying of the film-forming emulsions. We have to note that the much lower diameters obtained for films compared to those obtained in emulsions (prior to drying) are explained by the use of a more sensitive laser light granulometer for the films. Indeed, films were analyzed using the Hydro 2000G granulometer instead of the 20M.

These results can be explained by the granulogram profiles. Indeed, as observed in Figure 4 for hydrophilic and intermediate sucroesters, films display 3 globule-diameter populations when dispersed in 0.1% SDS solution, although they only had one
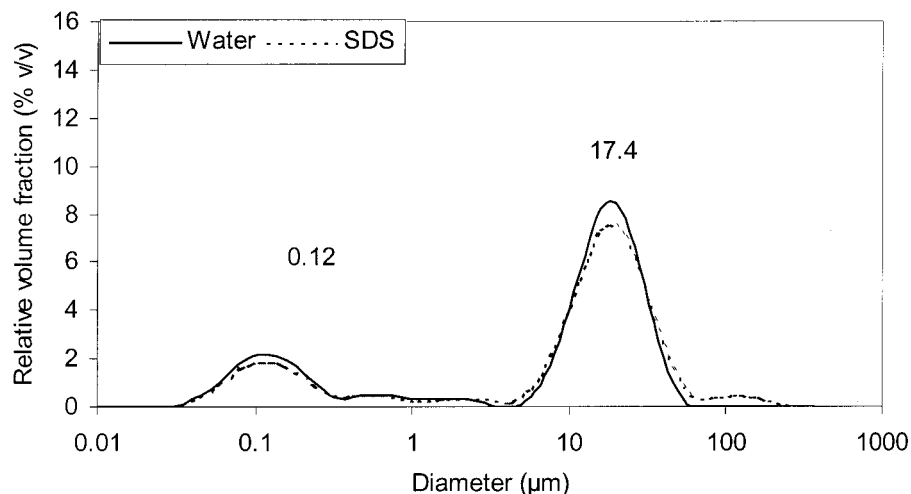
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Figure 5. Granulogram of arabinoxylan films containing 12.5% SP10 in the lipid phase (HPKO + SP10) after dissolution in cold water or in cold SDS solution.

Table 4. Structure of Emulsions Before and After Drying (Emulsified Films)

composition of film	emulsion before drying	dried films
without emulsifier	aggregation	agregation + coalescence
2.5% SP70	stable	aggregation
12.5% SP40	stable	aggregation + coalescence
6.25% SP30	stable	aggregation
2.5% SP10	stable	stable
6.25% SP10	stable	stable
10% SP10	stable	stable
12.5% SP10	stable	stable

diameter population when dispersed in water. In SDS, a 0.2-μm population appears and the proportion of big globules (>10 μm) decreases, which confirms the aggregation phenomena occurring during drying. This behavior was also observed for films composed of paraffin wax dispersed in methylcellulose solution containing acetylated monoglycerides as emulsifier (*15*). From Tables 3 and 4, it seems that aggregation and coalescence was favored by the hydrophilicity of the emulsifier and the drying temperature. Increasing temperature induces more motion in emulsions, so the probability of collision between lipid globules is increased, which makes aggregation easier. Temperature rise favors the merging of molten fat globules in aggregates, i.e., coalescence occurs. On the contrary, whatever the SP10 concentration, granularity of the dried film is the same in both water and SDS, and two globule diameter populations (0.2 and 20 μm) were always observed (Figure 5).

Comparison of granulograms of emulsions and dried films dispersed in water or SDS solution allows display of all phenomena of structure destabilization occurring during drying. These are summarized in Table 4. In the case of SP10, emulsions and dried films have exactly the same granularity. So there is neither aggregation nor coalescence. However, for the other sucroesters, differences in granulograms reveal either aggregation (SP70 and SP30) or both aggregation and coalescence (SP40).

When only aggregation occurs, granulograms of emulsions and films in SDS are the same, though they are different in water. Coalescence is confirmed when the granularities of emulsions and films are different in SDS solution.

ESEM observations of cross-sections of films allows better understanding of the structure of dried films. Without emulsifier, the creaming of big HPKO globules (i.e., migration of fat to the evaporation surface) occurs and aggregates can be observed on micrographs (Figure 6). Oppositely, in the case of SP70, granulometry analysis showed big globules, but very small globules can be seen on the micrograph, but with a great level of aggregation, though HPKO globules seem to be homogeneously distributed. The micrograph of SP30-based films displays small globules, aggregated or not, and also big globules. SP10 is solubilized in HPKO prior to being dispersed, and it slightly increases the melting point of HPKO. This favors a more rapid crystallization, which could explain the more heterogeneous distribution of the lipid phase. Small oil droplets and the high melting temperature of sucroesters increases the crystallization rate of the HPKO. The more rapid crystallization can also explain why globules are not spherical and why emulsions are less creamed at the evaporation surface.

The structure of dried films strongly depends on the nature of the sucroester. Hydrophilic sucroester SP70 contributes to a more homogeneous distribution of small globules in the arabinoxylans matrix; nevertheless, it allows a great aggregation of HPKO globules. Intermediate sucroesters (SP40 and SP30) give heterogeneous structures because of creaming, aggregation, and coalescence during drying. Lipophilic SP10 gives the best stability to the emulsion during drying, regardless of its concentration.

Water Vapor Permeability of Films. Water vapor permeability of film was measured at 25 °C for a 22−84% RH differential; values are given in Table 5. It is well-known that thickness influences the transfer rate, and thus the permeability, of moisture through edible films and is of an inverse exponential shape. But a previous work (*9*) and unpublished works showed that water vapor permeability is not significantly affected by the thickness in a range of 50 to 110 μm. Then, all arabinoxylans-based films can be compared, and their water vapor permeabilities can be discussed. Films based on SP10 and SP70 at a 2.5% concentration have a lower water vapor permeability than those made with SP30 and SP40. Moreover, the less stable system corresponding to the film prepared without emulsifier leads also to a low permeability value. From Kester and Fennema (*21*), lipids having low melting points and possessing hydrophilic groups have poor barrier properties. So, the presence of SP10 in emulsion improves the moisture resistance of films. This property could be due to both the increase of lipid (HPKO + SP10) melting point and the lipophilic character of the sucroester used. From our results, we cannot directly correlate the water vapor permeability and
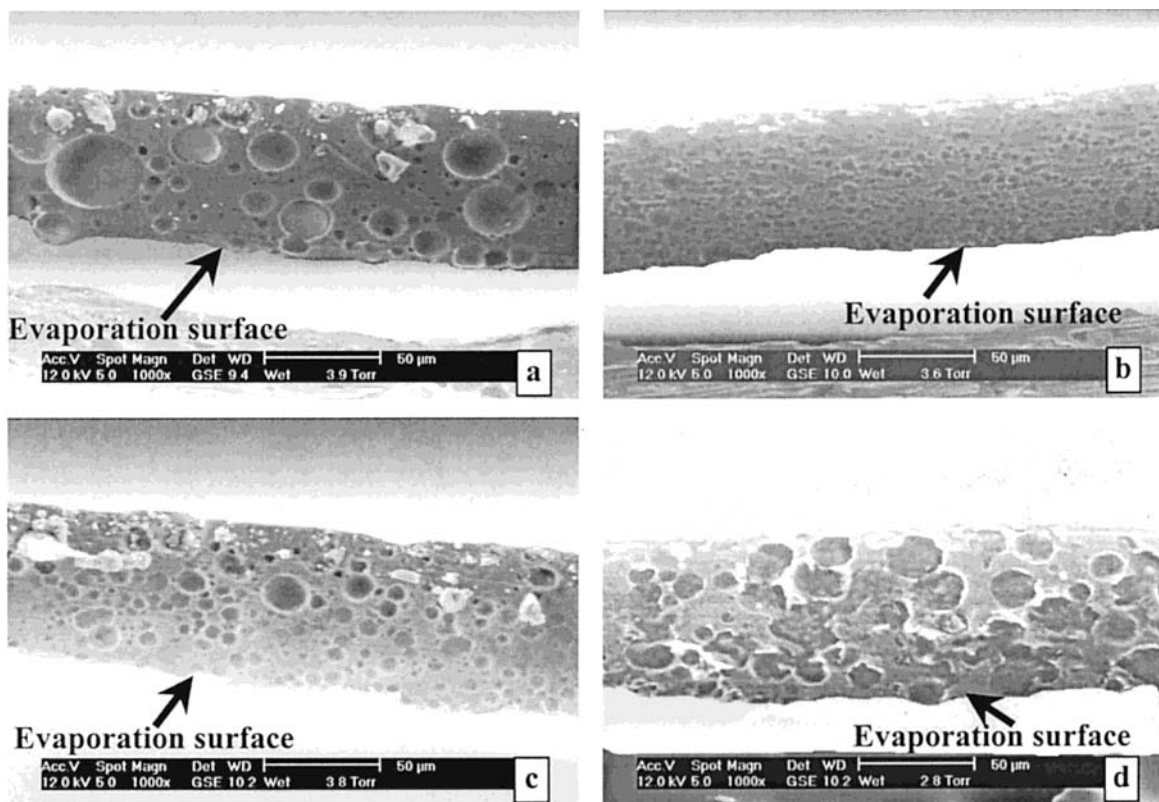
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Figure 6. ESEM micrographs (×1000) of the cross section of arabinoxylan-based films (a) without sucroester, or containing (b) 2.5% SP70, (c) 6.25% SP30, or (d) 12.5% SP10 in the lipid phase (HPKO + SP) (magnification ×1000).

Table 5. Water Vapor Permeability ($\Delta RH = 22-84\%$; 25 °C) of Arabinoxylan-Based Edible Films and of Cellophane and Low-Density Polyethylene Films

film composition	thickness (μm)^a	water vapor permeability (10^{-11} g·m^{-1}· s^{-1}·Pa^{1-})^a
AX + 15% glycerol	57.8 ± 2.1 d	13.82 ± 0.72 b
AX + 15% glycerol + 25% HPKO	70.0 ± 9.4 e,f	9.31 ± 0.46 d
AX + 15% glycerol + 25% (HPKO + 2.5% SP70)	68.7 ± 2.5 e	11.12 ± 0.55 c
AX + 15% glycerol + 25% (HPKO + 12.5% SP40)	78.0 ± 2.3 f	13.15 ± 0.37 b
AX + 15% glycerol + 25% (HPKO + 6.5% SP30)	78.7 ± 7.5 f	13.38 ± 0.56 b
AX + 15% glycerol + 25% (HPKO + 2.5% SP10)	69.0 ± 1.0 e	9.51 ± 0.79 d
AX + 15% glycerol + 25% (HPKO + 6.5% SP10)	75.5 ± 0.6 e,f	11.32 ± 0.36 c
AX + 15% glycerol + 25% (HPKO + 10% SP10)	61 ± 1.1 d	11.17 ± 0.84 d
AX + 15% glycerol + 25% (HPKO + 12.5% SP10)	84.5 ± 2.5 f	13.32 ± 0.69 b
hydroxypropylmethylcellulose (HPMC)	35.5 ± 0.6 b	9.97 ± 0.76 d
HPMC + 15% glycerol	43.5 ± 1.3 c	20.01 ± 0.55 a
cellophane	22 ± 0.4 a	6.92 ± 0.06 e
low-density polyethylene	30 ± 0.2 b	0.20 ± 0.01 f

^{a} Values having the same letter are not significantly different at $p < 0.05$ level. Mean ± standard deviation.

mean globule diameter of the different films because both nature (hydrophobicity) of emulsifiers and film structures (lipid distribution across the section) change. So water vapor permeability cannot be explained by emulsion characteristics alone.

Absence of emulsifier, as shown on the micrograph (Figure 6), favors the creaming of lipid toward the evaporation surface which contributes to decreasing the permeability because the structure tends to be like a bilayer film. Moreover, McHugh and Krochta (*22*) observed a linear correlation between water vapor permeability and beeswax globule size of whey protein-based films. In this case, moisture transfer occurs preferentially

in the continuous protein matrix, whereas the dispersed lipid phase just increases the tortuosity and thus the way of water molecules. Then SP70 leads to a relatively good barrier efficiency of films because it provides a small size of HPKO globules homogeneously distributed within the arabinoxylan matrix.

From our results, the lowest water vapor permeability was obtained for free emulsifier films and films prepared with 2.5% SP10. These values are 30% lower than that of lipid-free arabinoxylan films, but they remain 45 times greater than the permeability of low-density polyethylene films. SP30 and SP40 do not improve the barrier efficiency of films which do not contain lipids.

Surface Hydrophobicity and Wettability. To estimate the resistance of films to liquid moisture, contact angle (surface hydrophobicity) and water absorption rate (wettability) were determined, and the values are given in Table 6.

Film obtained without emulsifier exhibits the highest contact angle, which is explained by the higher lipid concentration at the surface because of the creaming phenomenon. This is confirmed by the water absorption rate which is the lowest (0.17 μL·sec^{-1}), and lower than that measured on the opposite surface (0.31 μL·sec^{-1}). As observed for the water vapor permeability, sucroester-free films and films containing 2.5% SP10 have the same surface hydrophobicity and wettability.

SP30, SP40, and SP70 do not affect significantly the contact angles nor the water absorption rates of arabinoxylan-based films. These tend to confirm that the structure of films obtained from emulsion and the stability of the latter during drying strongly influence their barrier efficiency.

CONCLUSION

In summary, the moisture barrier performances of emulsion-based films composed of arabinoxylans and HPKO are improved

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Table 6. Contact Angle and Water Absorption Rate of Arabinoxylan-Based Edible Films and of Cellophane and Low Density Polyethylene Films (25 °C)

film composition	contact angle (°)[a]	water absorption rate (×1000 μg·s^{-1})[a]
AX + 15% glycerol	65 ± 4 b	193 ± 9 b
AX + 15% glycerol + 25% HPKO	79 ± 1 c	174 ± 65 b
AX + 15% glycerol + 25% (HPKO + 2.5% SP70)	57 ± 2 b	237 ± 25 c
AX + 15% glycerol + 25% (HPKO + 12.5% SP40)	55 ± 2 b	250 ± 50 c
AX + 15% glycerol + 25% (HPKO + 6.5% SP30)	62 ± 2 b	272 ± 59 c
AX + 15% glycerol + 25% (HPKO + 2.5% SP10)	61 ± 5 b	194 ± 40 b
AX + 15% glycerol + 25% (HPKO + 6.5% SP10)	63 ± 9 b	284 ± 45 c
AX + 15% glycerol + 25% (HPKO + 10% SP10)	59 ± 4 b	287 ± 20 c
AX + 15% glycerol + 25% (HPKO + 12.5% SP10)	54 ± 4 b	313 ± 41 c,d
hydroxypropylmethylcellulose (HPMC)	75 ± 6 c	166 ± 20 a
HPMC + 15% glycerol	64 ± 1 b	444 ± 36 e
cellophane	7 ± 0.5 a	n.d.
low-density polyethylene	105 ± 1 d	n.d.

[a] Values having the same letter are not significantly different at $p < 0.05$ level. Mean ± standard deviation. n.d., Not determined.

by either (a) the great structure stability of the emulsion during drying when the hydrophobic SP10 sucroester is used; or (b) the homogeneous distribution of very small lipid globules within the film cross section; or (c) the great destabilization of the emulsion by creaming, aggregation, and/or coalescence of the HPKO at the evaporating surface which leads to an apparent bilayer film structure.

Then, two ways can be proposed for future work to further improve film barrier ability: either improve the stability of the emulsion by using a more efficient emulsifier, or increase the emulsion destabilization during drying.

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LITERATURE CITED

(1) Watson, S. A. Corn Hull Gum. In *Industrial Gums, Polysaccharides And Their Derivatives*; Whistler, R. L., BeMiller, J. N., Eds.; Academic Press: New York, 1959.

(2) Sugawara, M.; Benno, Y.; Koyasu, E.; Takeuchi, M.; Mitsuoka, T. Digestion and Fermentation by Human Intestinal Bacteria of Corn Fiber and its Hemicellulose *in vitro. Agric. Biol. Chem.* **1991**, *55*, 565−567.

(3) Chanliaud, E. Extraction, Caractérisation et Propriétés Fonctionnelles des Hétéroxylanes de Son de Maïs, Ph.D. Dissertation, University of Paris VII and ENSIA, 1995.

(4) Gennadios, A.; Weller, C. L.; Testin, R. F. Modification of Physical and Barrier Properties of Edible Wheat Gluten-based Films. *Cereal Chem.* **1993**, *70*, 426−429.

(5) McHugh, T. H.; Avena-Bustillos, R.; Krochta, J. M. Hydrophilic Edible Films: Modified Procedure for Water Vapor Permeability and Explanation of Thickness Effects. *J. Food Sci.* **1993**, *58*, 889−903.

(6) Kester, J. J.; Fennema, O. An Edible Film of Lipids and Cellulose Ethers: Barrier Properties to Moisture Vapor Transmission and Structural Evaluation. *J. Food Sci.* **1989**, *54*, 1383−1389.

(7) Debeaufort, F.; Martin-Polo, M.; Voilley, A. Polarity, Homogeneity and Structure affect Water Vapor Permeability of Model Edible Films. *J. Food Sci.* **1993**, *58*, 426−434.

(8) Arvanitoyannis, I.; Psomiadou, E.; Nakayama, A.; Aiba, S.; Yamamoto, N. Edible Films Made from Gelatin, Soluble Starch and Polyols, Part 3. *Food Chem.* **1997**, *60*, 593−604.

(9) Peroval, C.; Debeaufort, F.; Despre, D.; Voilley, A. Arabinoxylan-lipid-based edible films. 1, Water vapor permeance and other physical properties. *J. Agric. Food Chem.,* submitted for publication, 2001.

(10) Martin-Polo, M.; Mauguin, C.; Voilley, A. Hydrophobic Films and Their Efficiency against Moisture Transfer. I. Influence of the Film Preparation Technique. *J. Agric. Food Chem.* **1992**, *40*, 407−412.

(11) McHugh, T. H.; Krochta, J. M. Water vapor permeability properties of edible whey protein−lipid emulsions films. *J. Am. Oil Chem. Soc.* **1994**, *71*, 307−311.

(12) Debeaufort, F.; Quezada-Gallo, J. A.; Delporte, B.; Voilley, A. Lipid hydrophobicity and physical state effects on the properties of bilayer edible films. *J. Membr. Sci.* **2000**, *4679*, 1−8.

(13) Quezada-Gallo, J. A.; Debeaufort, F.; Callegarin, F.; Voilley, A. Lipid hydrophobicity, physical state and distribution effects on the properties of emulsion-based edible films. *J. Membr. Sci.* **2000**, *4678*, 1−10.

(14) Park, H. J.; Bunn, J. M.; Vergano, P. J.; Testin, R. F. Gas permeation and thickness of the sucrose polyesters, Semperfresh coatings on apples. *J. Process. Preserv.* **1994**, *18*, 349−358.

(15) Debeaufort, F.; Voilley, A. Effect of Surfactant and Drying Rate on Barrier Properties of Emulsified Edible Films. *Int. J. Food Sci.* **1995**, *30*, 183−190.

(16) Krochta, J. M. Emulsion Films on Food Products to Control Mass Transfer. *JAIChE* **1990**, *86*, 57−61.

(17) Gontard, N.; Duchez, C.; Cuq, J. L.; Guilbert, S. Edible Composite Films of Gluten and Lipids: Water Vapour Permeability and other Physical Properties. *Int. J. Food Sci. Technol.* **1994**, *29*, 39−50.

(18) AFNOR H-00-030 Matières en Feuille. Détermination du Coefficient de Transmission de la Vapeur d'Eau. In Recueil des Normes Françaises, Association Française de Normalisation, 1974.

(19) ASTM E96-80. Standard test method for water vapor transmission of materials. In *ASTM Book of Standards*; American Society for Testing and Materials: West Conshohocken, PA, 1980.

(20) Marion, D.; Doublier, J. L. Agents Emulsifiants. In *Additifs & Auxiliaires De Fabrication Dans Les Industries Agro-Alimentaires*; Multon, J. L., Ed.; Tec&Doc, Lavoisier: Paris, France, 1992.

(21) Kester, J. J.; Fennema, O. Edible Films and Coatings: A Review. *J. Food Technol.* **1986**, *12*, 47−59.

(22) McHugh, T. H.; Krochta, J. M. Dispersed Phase Particle Size Effects on Water Vapour Permeability of Wey Protein-Beeswax Edible Emulsion Films. *J. Food Process. Preserv.* **1994**, *18*, 173−188.

(23) Dickinson, E.; Stainsby, G. *Advances in Food Emulsions and Foams*; Elsevier Applied Sci.: London, U.K., 1988.

(24) Gennadios, A.; Brandenbourg, A. H.; Weller, C. L.; Testin, R. Effect of pH on Properties of Wheat Gluten and Soy Protein Isolate Films. *J. Agric. Food Chem.* **1993**, *41*, 1835−1839.

(25) Kamper, S. L.; Fennema, O. Water Vapour Permeability of an Edible, Fatty acid, Bilayer Film. *J. Food. Sci.* **1984**, *49*, 1482−1485.