

Modified Arabinoxylan-Based Films. Part B. Grafting of Omega-3 Fatty Acids by Oxygen Plasma and Electron Beam Irradiation

C. PÉROVAL,[†] F. DEBEAUFORT,^{*,†,‡} A.-M. SEUVRE,^{†,‡} B. CHEVET,[§]
D. DESPRÉ,[#] AND A. VOILLEY[†]

ENSBANA-GPAB, Université de Bourgogne, 1, Esplanade Erasme, F-21000 Dijon, France, IUT-Génie Biologique, Boulevard Dr Petitjean, BP 17867, F-21078 Dijon Cedex, France, IFTH, Avenue Guy de Collongue, F-69134 Ecully Cedex, France, ULICE, ZAC (Les Portes de Riom), BP 173, F-63204 Riom Cedex, France

Arabinoxylans (AXs) are byproducts of the cereal milling industry. To obtain high-value products, AXs have been used as a film-forming agent. Hence, AX-based films are poor water vapor barriers. The objectives of this study were to graft omega-3 (ω 3) fatty acids onto AX polymeric chains by using two new technologies: cold plasma and electron beam (EB) irradiation. Results show that the surface hydrophobicity of the modified films is higher than that of a waxy coating or a low-density polyethylene (LDPE) film. In addition, FTIR spectroscopy analysis reveals vibration bands attributed to new chemical functions. Finally, a decrease in water vapor permeability (WVP) is obtained for the film treated with the α -linolenic acid-rich oil. This result could be explained by a better diffusion of this shorter polyunsaturated fatty acid into the AX network. Linseed oils provide better barrier properties and a higher surface hydrophobicity than oils extract from marine oils. Edible oils were chosen for edible application of these films to retard moisture transfers in stuffed biscuits.

KEYWORDS: Arabinoxylans; oxygen plasma; electron beam irradiation; water vapor permeability; edible film(s) and coating(s)

INTRODUCTION

In recent years, biomaterials from renewable sources (proteins, carbohydrates, and lipids) have gained considerable research interest. Indeed, such substances can be used as a food coating or a stand-alone film wrap to retard unwanted mass transfer in food products (1–3). In general, polysaccharides and proteins have good mechanical properties and are excellent gas, aroma, and lipid barriers, but they are inefficient against water transfer. Lipids, on the other hand, offer high water barrier properties, but they form brittle films.

Arabinoxylans (AXs) constitute a major fraction of cereal cell wall polysaccharides. In previous works, edible AX films were developed (4–6). They have good tensile resistance and are an effective barrier against oxygen or carbon dioxide (4). Nonetheless, AX films are extremely hydrophilic, and their water vapor performances are low (4, 5).

To improve the water vapor barrier properties of edible films, several solutions have been proposed. First, composite films

have been made by adding a lipid as an emulsion (5–8) or by laminating a lipid layer onto a previously formed film (9–11). It results in film water vapor permeability (WVP) increases as the length of lipid hydrocarbon chain decreases and the unsaturation degree increases (5, 12–13). Additionally, a film's water vapor resistance is inversely related to lipid polarity. Second, cross-linking reactions have been reported to decrease the WVP of edible films (14–16). Hence, a decrease of about 36% is observed for WVP of films made of soy protein isolate and carboxymethylcellulose (17). Moreover, γ -irradiation significantly decreases the WVP of films based on soy protein isolate and caseinate from 1.79 to $1.19 \times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ (18–19).

Graft polymerization is a new method to modify the structure of biopolymers films and thus makes them attractive biomaterials in food packaging and pharmaceutical coatings. Indeed, grafting consists of giving new and permanent properties to a polymer. In recent years, two grafting technologies retained attention: gas plasma and electron beam (EB) irradiation. Gas plasma is a neutral and luminous gas composed of ionized species (excited molecules, ions, electrons, free radicals) and UV radiations (20). Plasma treatments for surface modification purposes are generally carried out at low temperatures and gas pressures. For these reasons, there are called “nonthermal”, “nonequilibrium”, or “cold” plasma (20, 21). The application

* To whom correspondence should be addressed. Laboratoire GPAB, ENSBANA, 1, Esplanade Erasme, F-21000 Dijon. Telephone: +33 (0)3 80 39 68 43. Fax: +33 (0)3 80 39 66 11. E-mail: frederic.debeaufort@u-bourgogne.fr.

[†] Université de Bourgogne.

[‡] IUT-Génie Biologique.

[§] IFTH.

[#] ULICE, ZAC.

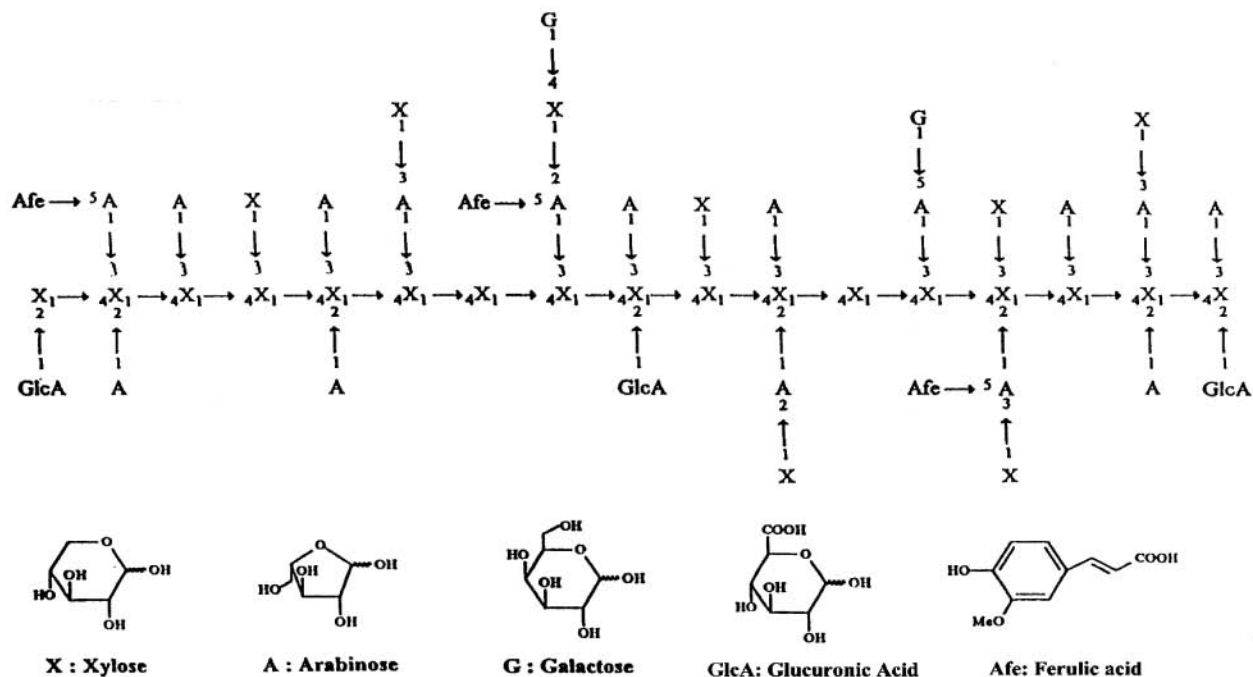


Figure 1. Arabinoxylan structure.

of cold plasma for surface modifications becomes more and more attractive and competitive than conventional technologies. Indeed, the use of gases instead of liquid chemicals as reagents makes it a dry and clean process. Then, the process occurs in one step in the absence or with a minimum of undesirable byproducts. Cold plasmas do not alter or damage bulk properties of polymers (21, 22). In the textile industry as well as in food packaging industry, interests in cold plasma technology have risen in recent years (21, 23–25). EB irradiation is also an excitation process during which a certain amount of radicals is produced by breakage of the H–C bonds in a material (20, 23). The EB irradiation method is easier to employ and to control than conventional chemical methods. This technique has also some advantages over conventional grafting processes such as the absence of catalyst residue and the complete control of temperature; it is a solvent free-system (26). Recently, octadecyl acrylate and stearyl methacrylate have been grafted on the AX polymeric chains (27). It resulted in a decrease in WVP, an increase in film surface hydrophobicity, and vibration bands attributed to new chemical groupings is observed on FTIR spectra.

The major objective of this study was to graft omega-3 fatty acids on AX polymeric chains by oxygen plasma associated with EB irradiation. Afterward, the effects of immobilized fatty acid on WVP, film structure, and surface hydrophobicity was studied. The targeted application is dry biscuit coating to delay moisture absorption from stuffing; it deals with edible films instead of biodegradable ones.

MATERIAL AND METHODS

Materials. Food grade AX powder extracted from maize bran was freely provided from ULICE (Riom, France). AXs contain a backbone structure of D-xylopyranosyl residues linked by $\beta(1 \rightarrow 4)$ bonds to which units such as L-arabinofuranose are attached as branches via $\beta(1 \rightarrow 3)$ and/or $\beta(1 \rightarrow 2)$ linkages (Figure 1). They are extensively substituted with single unit of L-arabinofuranose, D-xylopyranose, or d-glucopyranosic acid and with short side chains composed of two or three units of L-arabinofuranose, D-xylopyranose, and D-galactopyranose.

Phenolic acids, *p*-coumaric acid, and mainly ferulic acid esterify some L-arabinofuranose units (4). Some polyunsaturated fatty acids with long chains have interesting nutritional values and are essential for human health. Indeed, nutritionists recognize α -linolenic acid (ALA – 18:3 *n*-3) as an essential fatty acid because in the body ALA can be desaturated and elongated to form eicosapentaenoic acid (EPA – 20:5 *n*-3) and docosahexaenoic acid (DHA – 22:6 *n*-3). However, this conversion is not always predictable or efficient. For this reason, EPA and DHA must be provided by the human diet (28). In this study, three fish oils (A, B, C oils) and one plant one (D oil) that contain large amounts of omega-3 (ω 3) fatty acids have been chosen. The ω 3 fatty acids composition of these oils is given in Table 1. The anhydrous glycerol (Sigma-Aldrich Chimie, Saint Quentin Fallavier, France, 98% purity) was used to plasticize the film.

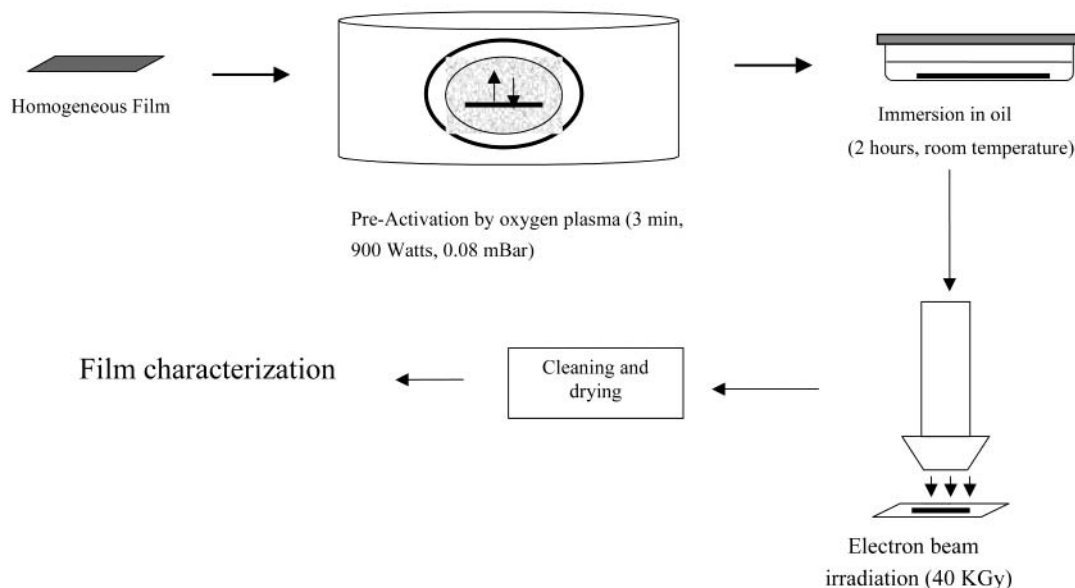
Arabinoxylan Film Preparation. An AX film-forming solution was prepared by dispersing 16 g of AX powder in 100 mL of osmosed water at 75 °C for 40 min while stirring constantly. During the heating and stirring of the sample, anhydrous glycerol was then added at a concentration of 20% (w/w total dry matter). A vacuum was applied with a vacuum pump to remove dissolved air bubbles. Then, the film-forming solution was poured into a thin-layer chromatography spreader and cast onto glass plates previously covered by an adhesive PVC sheet to prevent the sticking of dried films. To evaporate the solvent (water) and thereby form a network, the solution was dried in a ventilated chamber (WTB Binder, Labortechnik, GmbH, Germany) for approximately 4 h at 40% relative humidity and 30 °C. These drying conditions allowed reasonably quick formation of homogeneous AX films, which could be peeled intact from their supports.

Grafted Procedures. The experimental setup is shown in Figure 2 and can be divided into three steps: preactivation by cold plasma, impregnation by immersion in oil, and ionization by electron beam. First, a homogeneous AX-based film previously weighted was introduced into a cylindrical vacuum chamber to be preactivated by oxygen plasma. To provide gas plasma, a gas or gas mixture is submitted to an electromagnetic field in a reactor. The hot electrons generated and accelerated by the applied field collide with gas molecules and thereby transfer energy through ionization, bond breakage, and other forms of excitation. Excited molecules and atoms in the plasma could emit photons in ultraviolet region. The plasma processor was supplied by the Institut Français du Textile et de l'Habillement (IFTH, Lyon, France). The equipment was composed of a microwave oscillator and generator (4.33 GHz, 900 W), a quartz glass tube, a reaction chamber

Table 1. ω 3 Fatty Acid Content of Oils Used as Impregnation Solution in the Grafted Process

content (%)	A oil	B oil	C oil	D oil
trade name	Huile 5/25 SA Sea oil (Beaumont-Hague, France)	Ropufa 30 <i>n</i> -3 Hoffman La Roche (Basel, Switzerland)	EPAX 6000 Gee Lawson Nutritional (London, UK)	flaxseed oil Omega Nutriton (Vancouver, Canada)
origin	mixture of tuna, salmon, herring and pilchard oils	fish oil blend	blend of free fatty acids from marine fish oils	linseed oil
acid value (mg of KOH/g)	0.15	0.32	180.4	
peroxide value (mEq O ₂ /g)	2.7	<0.01	3.8	
ALA				37
EPA	7.7		34	
DHA	23.6	16.9	25	
ω 3 fatty acid total	35.3	31.7	70	

^a ALA: α -linolenic acid [18:3 *n*-3]; EPA: eicosapentaenoic acid [20:5 *n*-3]; DHA: docosahexaenoic acid [22:6 *n*-3].

**Figure 2.** Experimental setup for grafting omega-3 fatty acids on AX polymeric chains.

(capacity 50 L), an oil rotary pump, a diffusion pump, and a mass flow controller. The polymeric film was deposited on a sample holder at 57 cm from the center of the plasma source. Once the pressure of 0.08 mBar was reached and remained constant, oxygen gas was introduced at the desired flow rate into the plasma chamber, and the glow discharge was initiated. The time exposure was about 3 min. During this phase, peroxides were formed on the surface of film. Oxygen plasma-treated films were immediately immersed in oil and were kept 2 h at room temperature. Electrons beam exposure induced the grafted mechanism by producing the energy required for breaking reactive bonds. Hence, a molecule that is in contact with the "activated" material could copolymerize. The first molecule is grafted on the activated polymeric chain by opening of its reactive double bond. At the same time, the activated molecule can therefore react forward with another neighboring molecule. It is the spreading step of the copolymerization. The grafted mechanism is close to lipid oxidation process with an initiation phase following with propagation and termination phases. The film samples were previously sealed into plastic bags, and they were subjected to EB irradiation in air at room temperature. The intensity of electron beam was about 2.5 mA. The irradiation dose used was about 40 kGy. The 40 kGy irradiation dose was used according to the previous experiments done to set up the technology though the food regulations limit the dose at 10 kGy. The time exposure was about 3 s. The final steps consisted of cleaning the grafted films in hexane to

eliminate the excess of molecules and drying them at room conditions. At the end, the modified film was weighed to determine the grafting level in percent as follows:

$$\text{grafting level (\%)} = \left(\frac{m_1 - m_0}{m_0} \right) \times 100 \quad (1)$$

where " m_0 " is the weight of the untreated film and " m_1 " is the weight of grafted film. For each oil, a minimum of three films was treated.

Film Thickness Measurement. The thickness of conditioned (22% relative humidity, 25 °C, and 48 h) films was determined by using an electronic gauge (Multi Check FE List-Magnetik GmbH, Germany) with a precision of 1 μ m. The average values of 30 thickness measurements *per* type of film were used in all WVP calculations.

Water Vapor Transfer Rate (WVTR) and Water Vapor Permeability (WVP) measurement. The WVTR was gravimetrically determined at 25 °C using an AFNOR modified procedure (29). The modifications of the standard deals with the substitution of the stainless steel or aluminum cup by glass cell on which the film is fixed by screw between two Teflon rings instead of being sealed by molten paraffin wax. Moreover, the relative humidity (RH) differential was set up to correspond to that of food application targeted such as a biscuit (15–30% RH) and its stuffing (0.8–0.9% RH). Before WVTR determina-

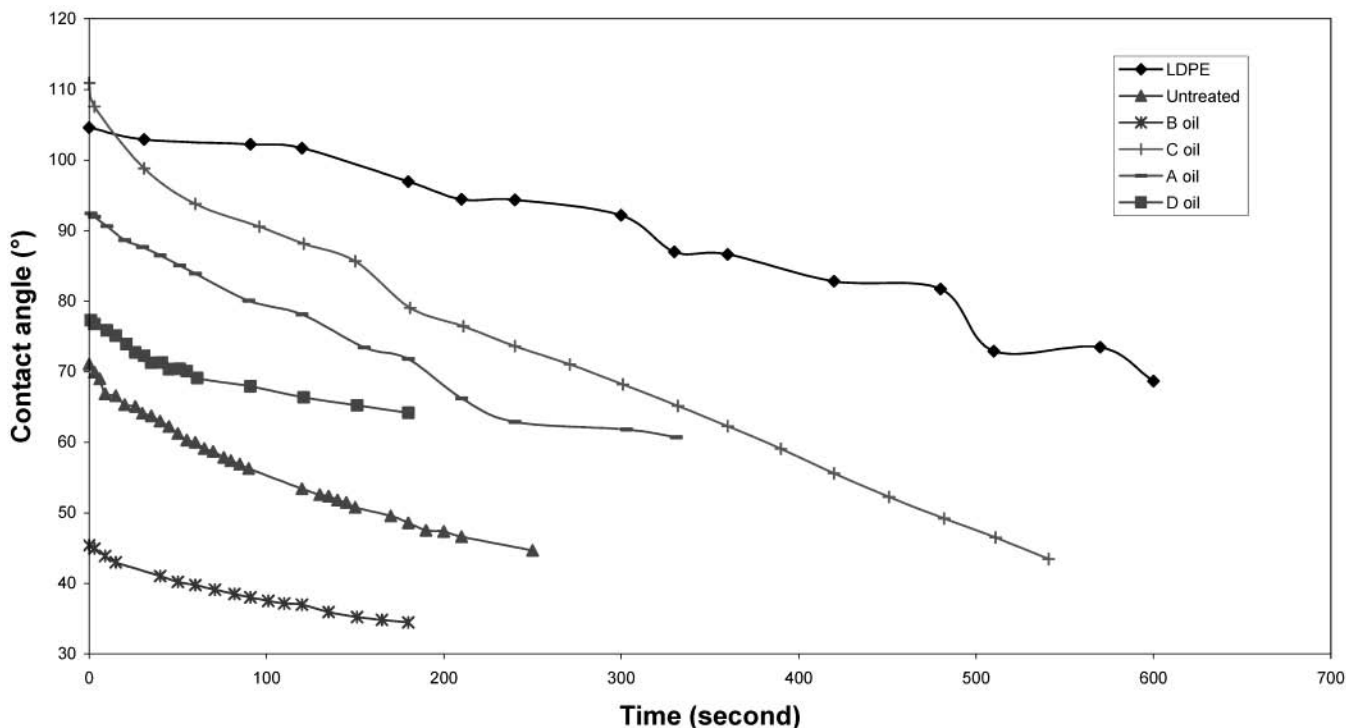


Figure 3. Kinetics of contact angles of AX-based films and a low-density polyethylene (LDPE) film (25 °C).

tion, all films were equilibrated at 22% RH using a saturated salt solution of potassium acetate at 25 °C for 48 h. Four samples, 4.2-cm diameter disks, were cut from each film. Each sample was placed between two Teflon rings on the top of a glass cell containing a saturated salt solution of potassium chloride with a water activity of about 0.84 at 25 °C. Test cells were weighed and introduced into a climate-controlled chamber (WTB Binder Labortechnik GmbH, Germany) regulated at RH of 22% and 25 °C. Cells were weighed three times *per* day for 7 days. At the steady state, the WVTR ($\text{g m}^{-2} \text{s}^{-1}$) and WVP ($\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$) coefficients were defined as follows:

$$\text{WVTR} = \frac{\Delta M}{\Delta t \cdot A} \quad (2)$$

$$\text{WVP} = \frac{(\text{WVTR} \cdot e)}{\Delta p} \quad (3)$$

where $\Delta M/\Delta t$ is the amount of moisture lost *per* unit of time (g/s), A is the film area exposed to moisture transfer ($8 \times 10^{-4} \text{ m}^2$), e is the film thickness (m), and Δp is the water vapor pressure differential (Pa) between the two sides of the film. For each type of film, a minimum of three determinations, each one including the four test cells, was made.

The water vapor barrier efficiency of the modified films can be compared to that of untreated films by the expression:

$$\text{Eff} (\%) = \frac{\text{WVTR}_u - \text{WVTR}_t}{\text{WVTR}_u} \times 100 \quad (4)$$

where "Eff" is the efficiency to retard water vapor transfer in percent, subscript "u" denotes the untreated film support, and subscript "t" refers to treated films.

Surface Hydrophobicity. The surface hydrophobicity or wettability of the films was evaluated from static contact angle measurement using a goniometer (model G1, Krüss GmbH, Germany) equipped with camera and image analysis software (Drop Shape Analysis, Krüss GmbH, Germany). A water droplet of about 20 μL was deposited on the film surface, and the angle of the tangent to the basis of the droplet (contact angle) was measured and expressed in degrees. The kinetic of contact angle was determined in air at room conditions. A minimum of five measurements *per* film was carried out.

Table 2. Grafting Level and Contact Angles of the Untreated Films and Modified Films by Oxygen Plasma and EB Irradiation (40 kGy)

films	grafting level (%)	contact angle (deg)
untreated		66.8 ± 4.6
A	5.7	91.2 ± 6.8
B	6.4	49.1 ± 3.9
C	5.1	115.1 ± 17.5
D	6.1	71.8 ± 9.3

Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectra of AX films were recorded in the region from 3600 to 600 cm^{-1} , with a Spectrum One (PerkinElmer Inc., Shelton, USA) spectrometer equipped with a TGS detector. Four scans with a resolution of about 4 cm^{-1} were collected and averaged to get one spectrum.

Statistical Analysis. All data were analyzed and means were compared by using variance analysis and Student-Newmans-Keuls t-tests ($\alpha = 0.05$) on SAS software (SAS Institute Inc., version 6.02, Cary, NC, 1991).

RESULTS AND DISCUSSION

Grafting Level. According to the oil used for the immersion step, the same letter used for the oil is used in treated films. The grafting level represents the amount of immobilized molecule and is given in the Table 2. The highest grafting levels are obtained for the B (fish oil) and D (linseed oil) films and are close to that of the octadecyl acrylate-grafted films (27). Considering the $\omega 3$ fatty acid composition of the three fish oils (Table 1), we notice that the greatest grafting level corresponds to the lowest DHA content and $\omega 3$ fatty acid total. This could be explained by the fact that $\omega 3$ fatty acids have a long hydrocarbon chain that could interfere with molecule diffusion. Furthermore, this steric hindrance could inhibit the development of an interlocking network within the film (7). Finally, grafting levels determined are lower than those obtained for fabric. Indeed, in textile industry, the grafting level could reach 80% (30). The grafting process should link the fatty acid to the AX string by the breaking of the double bond under the electron

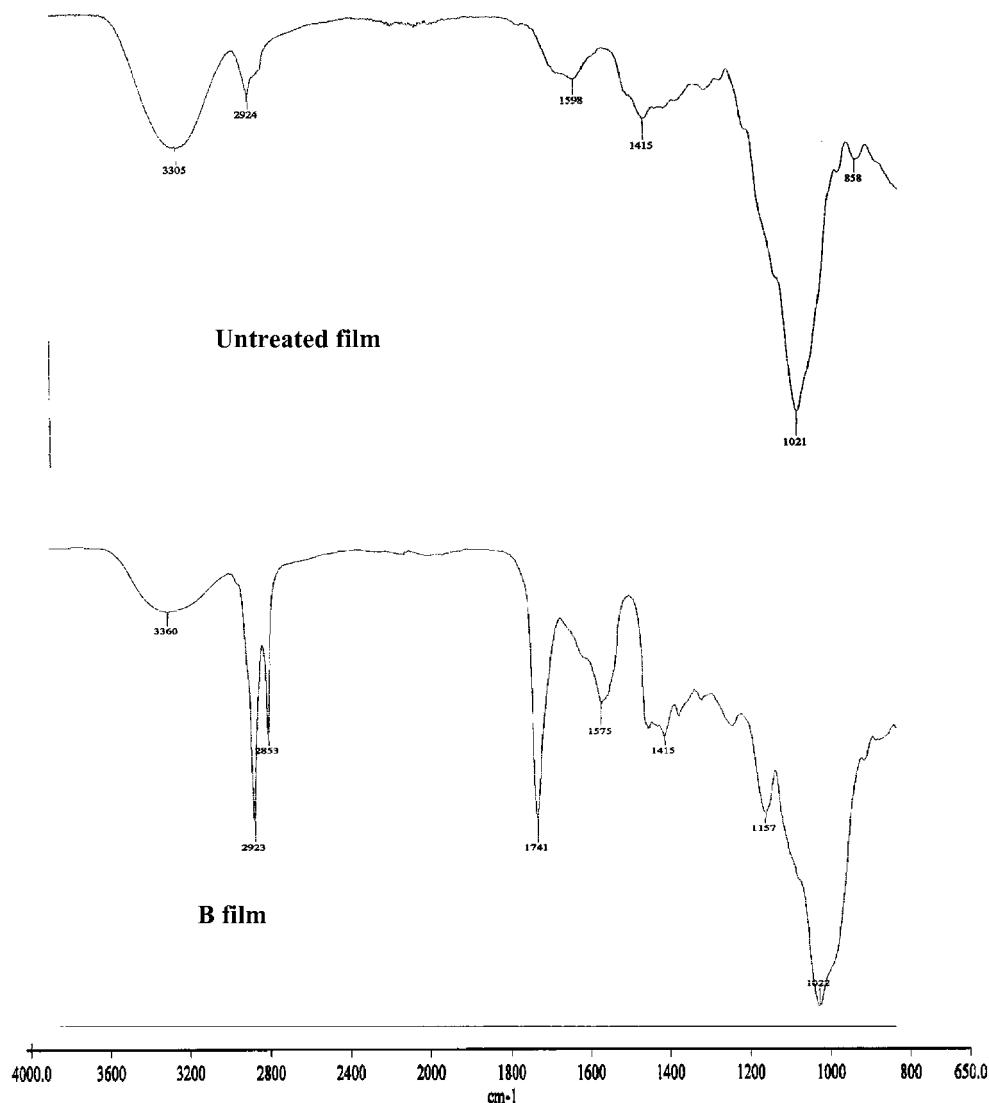


Figure 4. FTIR spectra of the untreated AX film and the B films (oxygen plasma preactivation, immersion in oil B, and EB irradiation at 40 kGy).

beam exposure or by the high oxidative properties of the plasma activation of the film surface. So we could imagine that all the sites of the lipid able to be oxidized have already been reacted during the grafting process. Moreover, any changes in color or odor (even for fish-based oils) have been noticed after the films were treated by electron beam and plasma.

Surface Hydrophobicity. Contact angles measured on the untreated AX films are about 67° (Table 2). This value is similar to those previously observed on AX films (5–6) and is comparable to those regularly obtained for polysaccharide-based films. A (blend of fish oil) and C (fatty acids from marine oil) films have contact angles significantly higher than those of the untreated films. Surface hydrophobicity of these films increases and becomes comparable to those of LDPE films (6), waxy coating (31), and functional acrylate-grafted films (27). B films have contact angles lower than those of untreated films. Such a tendency has already been observed for emulsified triolein–AX-based films and was attributed to the polar character of the lipid that enhances water affinity of the polymer (5). The contact angles of the linseed oil-based films (D films) are not significantly different ($p > 0.05$) from those of untreated films.

The evolution of the contact angle with time was recorded and is presented on the Figure 3. The aging of the contact angles depends on several phenomena, in particular the surface chemical heterogeneity and roughness (32). To reduce the effects

of the surrounding atmosphere, all contact angle measurements were carried out under the same conditions. The initial slope of the curve has been determined and represents the film surface absorption of the water droplet and chemical interactions (32, 33). The contact angle decreases and disappears very quickly on the untreated film surface (slope about -0.153 deg/s). C films wet more quickly (slope about -0.149 deg/s) than D films (slope about -0.135 deg/s) and A films (slope about -0.114 deg/s). The contact angle decrease of the B films (slope about -0.069 deg/s) is the lowest, but this contact angle kinetic is faster than that of a LDPE film (slope about -0.044 deg/s). These different contact angle kinetics shows that the oils used induce surface modifications and polymeric chain rearrangements. The contact angles measured on the C films are the highest but the evolution of these contact angles with time is close to that observed for the untreated films. These results presume that C oil generates only surface chemical modifications. In contrast with the C films, surface hydrophobicity of the B films is the lowest but the contact angle decreases as slow as that of LDPE films. B oil probably produces internal chemical modifications of the AX network.

Infrared Analysis. FTIR spectra of the untreated and grafted films are presented in Figure 4. The assignments proposed for the bands observed are given in Table 3. FTIR spectrum of untreated film shows a medium broad absorption band at 3305

Table 3. Bands Observed on the FTIR Spectra of Untreated and Modified AX Films^a and Assignment Modes Proposed

wavenumbers (cm ⁻¹)					assignments (modes) ^c
untreated	A film	B film	C film	D film	
3305	3298	3360	3315	3317	$\nu_{\text{O-H}}$ (hydrogen bond)
2924	2924	2923 ^b	2922 ^b	2926	$\nu_{\text{C-H}}$ (CH ₂ group)
		2853 ^b	2853 ^b		$\nu_{\text{C=O}}$ (fatty acid)
		1741	1741		$\nu_{\text{C=C}}$ (lateral chain and phenol ring of ferulic acid)
1598	1598	1598	1598	1598	$\nu_{\text{C=C}}$ (aliphatic chain of ω 3 fatty acid)
		1575 ^b	1576 ^b		$\delta_{\text{H-C-H}}$, $\omega_{\text{C-H}}$, $\omega_{\text{H-C-H}}$, $\delta_{\text{O-H}}$
1415	1416	1415	1417	1416	$\nu_{\text{C-O}}$ (fatty acid)
		1157 ^b		1254	$\nu_{\text{C-O}}$ (COH and COC group ring)
1021	1019	1022	1021	1019	$\nu_{\text{C-C}}$
858				858	

^a Oxygen plasma preactivation, EB irradiation at 40 kGy. ^b Immersion in oil. ^c ν : stretching mode, δ : bending mode, ω : wagging mode.

Table 4. Treatment Efficiency and Water Vapor Barrier Properties of AX Films^a

films	thickness (μm)	WVTR ($\times 10^{-3} \text{ g m}^{-2} \text{ s}^{-1}$)	WVP ($\times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$)	efficiency (%)
untreated	93.5 \pm 8.9	4.45 \pm 0.35 ^a	2.05 \pm 0.23 ^a	
A	99.2 \pm 7.2	3.89 \pm 0.35 ^{b,c}	1.91 \pm 0.15 ^{a,b}	12.6
B	92.2 \pm 8.9	3.59 \pm 0.18 ^c	1.63 \pm 0.15 ^{c,b}	19.3
C	92.2 \pm 5.5	3.19 \pm 0.26 ^d	1.45 \pm 0.16 ^c	28.3
D	77.5 \pm 10.8	2.86 \pm 0.17 ^d	1.09 \pm 0.13 ^d	35.7

^a Mean of 20 measurements at least \pm standard deviation for thickness. Mean of three replicates at least \pm standard deviation for WVTR and WVP determination. a–d: values in one column followed by same letter are not significantly different at the probability 5%.

cm⁻¹ attributed to the O–H stretching mode. There also is a medium weak band at 2924 cm⁻¹ that is assignable to C–H stretching mode. Another medium-weak absorption band at 1598 cm⁻¹ characterizes the C=C stretching mode of the phenol ring and the lateral chain of the ferulic acid. The region 1400–1200 cm⁻¹ exhibits several medium bands, probably due to the C–H bending and wagging modes, and O–H bending mode. A strong and composite band with a maximum intensity at 1021 cm⁻¹ involves the stretching mode of the C–O bonds of C–O–H and C–O–C groups. A weak absorption band at 858 cm⁻¹ corresponds to the stretching mode of the glucosidic ring ($\nu_{\text{C-C}}$).

On the FTIR spectra (**Figure 4**), OH vibrations show large absorption bands, with maxima at 3305 and 3360 cm⁻¹ on the untreated and B films, respectively. In this region, different OH groups are involved: OH ring, OH carboxylic function of glucuronic and ferulic acids, and in the case of B film, added ω 3 fatty acids bring new OH groups vibrations. The difference of maxima could arise from ω 3 fatty acids presence. Two intense absorption peaks are observed on the FTIR spectrum of the B film. The IR band at 2923 cm⁻¹ is more intense than that of the untreated film, and the new frequency at 2853 cm⁻¹ was attributed to the C–H stretching mode of the aliphatic chain of the ω 3 fatty acids. Another intense IR band at 1741 cm⁻¹ corresponds to C=O stretching mode of the fatty acid. The peak at 1598 cm⁻¹ was not integrated. A new and intense frequency at 1575 cm⁻¹ is assignable to the C=C stretching mode of the aliphatic chain of the ω 3 fatty acids. At 1157 cm⁻¹, a new medium absorption attributed to the C–O stretching mode of the fatty acid is observed. For the C film, the same IR bands than of B film are observed on the FTIR spectrum (data not shown). No additional new chemical grouping is noticed on the FTIR spectra of the A and D films (spectra not shown). These spectra are identical to that of the untreated films.

Water Vapor Barrier Properties. WVTR and WVP of the untreated AX films were about 4.45 $\times 10^{-3} \text{ g m}^{-2} \text{ s}^{-1}$ and 2.05 $\times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively (**Table 4**). These values are higher than those of previously determined for AX films

(5, 27). These results could be explained by the increase in the glycerol content to reduce the film brittleness resulting from the grafted treatment. In all cases, grafted treatment significantly decreases the film WVTR ($P \leq 0.05$). However, A film WVP is not significantly different ($P > 0.05$) from that of the untreated film. Moreover, the A film presents the lowest efficiency to retard water migrations. Then, FTIR spectrum of this film is identical to that of the untreated film, while the A film has a great grafting level and surface hydrophobicity. All these results presume that the grafted treatment modifies only the film surface.

The WVTR and WVP of the B film (fish oil) are not significantly different ($P > 0.05$) from these of A film (**Table 4**). Meanwhile, the efficiency to retard water migrations is higher. This could be explained by a greater amount of immobilized molecule (grafting level about 6.4%) onto the AX network. Furthermore, FTIR spectrum reveals new frequencies that confirm internal chemical modifications in the film structure.

The Callanish oil-based film (C film) WVP is not significantly different ($P \leq 0.05$) from that of the B film. In comparison with this, the C film has a lower grafting level, a higher surface hydrophobicity, and a faster contact angle kinetic. However, this film presents similar IR bands to B film. These results assume that grafted treatment produces surface modifications more than internal chemical modifications.

The lowest WVTR and WVP and the best efficiency to retard water migrations are obtained for the linseed oil-based edible film (D film). This film offers water vapor barrier performances higher than those of the octadecyl acrylate-grafted films (27). These results are surprising because film surface hydrophobicity and FTIR spectra of this film are similar to those of the untreated films. However, these results could be explained by the composition of the linseed oil that is mainly constituted with α -linolenic acid (18:3 *n-3*). As suggested for the grafting of functional acrylate, small and linear molecules diffuse and graft easier onto the AX polymeric chains. Moreover, previous works

on emulsified films show that the best water vapor barrier properties are obtained when palmitic or stearic acids are dispersed (7, 9).

This study displays that cold plasma associated with EB ionization induces the grafting of molecule onto polymeric chain. For further research, the use of polyunsaturated fatty acid with chain length about 16–18 carbon atoms is proposed.

ACKNOWLEDGMENT

We gratefully acknowledge Jacques Maguin and Patrick Gayrine for their contribution to the realization of cold plasma and EB irradiation treatments. We thank Isabelle Ferreira for her help in FTIR spectroscopy analysis and interpretation.

LITERATURE CITED

- Kester, J. J.; Fennema, O. R. Edible Films and Coatings: A Review. *Food Technol.* **1986**, *48*, 47–59.
- Krochta, J. M.; De Mulder-Johnston, C. Edible and Biodegradable Polymer Films: Challenges and Opportunities. *Food Technol.* **1997**, *51*, 61–74.
- Guilbert, S.; Cuq, B. Les Films et Enrobages Comestibles. In *L'emballage des Denrées Alimentaires de Grande Consommation*; Multon, J.-L., Bureau, G., Eds.; Technique & Documentation, Lavoisier: Paris, France, 1998; pp 472–530.
- Chanliaud, E. Extraction, Caractérisation et Propriétés Fonctionnelles des Hétéroxylyanes de Son de Maïs. Ph.D. Thesis, Université de Paris VII, Paris IX et ENSIA, Paris, France, 1995.
- Péroval, C.; Debeaufort, F.; Despré, D.; Voilley, A. Edible Arabinoxylan-Based Films. 1. Effect of Lipid Type on Water Vapour Permeability, Film Structure and Other Physical Characteristics. *J. Agric. Food Chem.* **2002**, *50* (14), 3377–3383.
- Phan The, D.; Péroval, C.; Debeaufort, F.; Despré, D.; Courthaudon, J.-L.; Voilley, A. Arabinoxylan-Lipids-Based Edible Films and Coatings. 2. Influence of Sucroester Nature on the Emulsion Structure and Film Properties. *J. Agric. Food Chem.* **2002**, *50*, 266–272.
- Koelsch, C. M.; Labuza, T. P. Functional, Physical and Morphological Properties of Methylcellulose and Fatty acid-Based Edible Barriers. *J. Food Sci. Technol.* **1992**, *54*, 1383–1389.
- Gontard, N.; Ducheze, C.; Cuq, J. L.; Guilbert, S. Edible Composite Films of Wheat Gluten and Lipids: Water Vapour Permeability and Other Physical Properties. *Int. J. Food Sci. Technol.* **1994**, *29*, 39–50.
- Kamper, S. L.; Fennema, O. Water Vapor Permeability of an Edible, Fatty Acid, Bilayer Film. *J. Food Sci.* **1984**, *49*, 1482–1485.
- Gontard, N.; Marchesseau, S.; Cuq, J. L.; Guilbert, S. Water vapour permeability of edible bilayer films of wheat gluten and lipids. *Int. J. Food Sci. Technol.* **1995**, *30*, 49–56.
- 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.
- Fennema, O.; Donhowe, I. G.; Kester, J. J. Lipid Type and Location of the Relative Humidity Gradient Influence on the Barrier Properties of Lipids to Water Vapor. *J. Food Eng.* **1994**, *22*, 225–239.
- Morillon, V.; Debeaufort, F.; Blond, G.; Capelle, M.; Voilley, A. Factors Affecting the Moisture Permeability of Lipid-Based Edible Films. *CRC Nutr. Food Sci.* **2002**, *42*, 67–89.
- Pascat, B. Study of Some Factors Affecting Permeability. In *Food Packaging and Preservation, Theory and Practice*; Mathlouthi, M., Ed.; Elsevier Applied Science: London, U.K., 1986; pp 7–24.
- Avena-Bustillos, R. J.; Krochta, J. M. Water Vapor Permeability of Caseinate-Based Edible Films as Affected by pH, Calcium Cross-linking and Lipid Content. *J. Food Sci.* **1993**, *58*, 904–907.
- Parris, N.; Coffin, D. R. Composition Factors Affecting the Water Vapor Permeability and Tensile Properties of Hydrophilic Zein Films. *J. Agric. Food Chem.* **1997**, *45*, 1596–1599.
- Sabato, S. F.; Ouattara, B.; Yu, H.; D'Aprano, G.; Le Tien, C.; Mateescu, M. A.; Lacroix, M. Mechanical and Barrier Properties of Cross-Linked Soy and Whey Protein Based films. *J. Agric. Food Chem.* **2001**, *49*, 1397–1405.
- Ouattara, B.; Canh, L. T.; Vachon, C.; Mateescu, M. A.; Lacroix, M. Use of γ -Irradiation Cross-linking to Improve the Water Vapor Permeability and the Chemical Stability of Milk Protein Films. *Radiat. Phys. Chem.* **2002**, *63*, 821–825.
- Lacroix, M.; Le, T. C.; Ouattara, B.; Yu, H.; Letendre, M.; Sabato, S. F.; Mateescu, M. A.; Patterson, G. Use of γ -Irradiation to Produce Films from Whey, Casein and Soya Proteins: Structure and Functional Characteristics. *Radiat. Phys. Chem.* **2002**, *63*, 827–832.
- Delcroix, J.-L.; Bers, A. *Physique des Plasmas 1*, InterEditions and CNRS Editions; Savoir Actuels: Paris, France, 1994.
- Ozedemir, M.; Yurteri, C.; Sadikoglu, H. Surface Treatment of Food Packaging Polymers by plasma. *Food Technol.* **1999**, *53*, 54–58.
- Wertheimer, M. R.; Fozza, A. C.; Holländer, A. Industrial Processing of Polymers by Low-Pressure Plasma: the Role of VUV radiation. *Nuclear Instrum. Methods Phys. Res. B* **1999**, *151*, 65–75.
- Sotton, M.; Demuth, O.; Chatelin, R. New Fibers Modified by electron Beam and Low-Pressure Plasma Treatment, Princeton, USA, 1994.
- Rossi, A.; Incarnato, L.; Tagliaferri, V.; Aciermo, D. Modification of Barrier Properties of Polymeric Films of LDPE and HDPE by cold plasma treatment. *J. Polym. Eng.* **1995**, *14*, 191–197.
- Friedrich, J. F.; Wigan, L.; Unger, W.; Lippitz, A.; Erdmann, J.; Gorsler, H. V.; Prescher, D.; Wittrich, H. Barrier Properties of Plasma and Chemically Fluorinated Polypropylene and Poly(ethylene terephthalate). *Surf. Coat. Technol.* **1995**, *75*, 910–918.
- Dutta, S. K.; Bhowmick, A. K.; Chaki, T. K. Structure Properties Relationship of Ethylene Vinyl Acetate Copolymer Grafted with Triallyl Cyanurate by Electron Beam Radiation. *Radiat. Phys. Chem.* **1996**, *47*, 913–926.
- Péroval, C.; Debeaufort, F.; Seuvre, A.-M.; Chevet, B.; Despré, D.; Voilley, A. Modified Arabinoxylan-based Films. Part A. Grafting of Functional Acrylates by Oxygen Plasma and Electron Beam irradiation. *J. Membr. Sci.* **2003**, submitted.
- Leonard, E. C. Dietary fatty acids: effect of the n-6/n-3 balance on human nutrition and disease. *Lipid Technol.* **1995**, *5*, 110–114.
- Debeaufort, F.; Martin-Polo, M. O.; Voilley, A. Polarity Homogeneity and Structure Affect Water Vapor Permeability of Model Edible Films. *J. Food Sci.* **1993**, *58*, 426–434.
- Gawish, S. M.; Gavet, L.; Chabert, B.; Nemoz, G. Grafting of 2n-Morpholinoethyl Methacrylate to polyethylene fabrics by electron beam irradiation. *Am. Dyestuff Rep.* **1990**, *4*, 22–32.
- Martin-Polo, M.; Mauguin, C.; Voilley, A. Hydrophobic Films and Their Efficiency against Moisture Transfer. 1. Influence of the Film Preparation Technique. *J. Agric. Food Chem.* **1992**, *40*, 413–418.
- Kwok, D. Y.; Neumann, A. W. Contact Angle Measurement and Contact Angle Interpretation. *Adv. Colloid Interface Sci.* **1999**, *81*, 167–249.
- Bourgès, C.; Shanahan, E. R. L'influence de l'évaporation sur l'angle de contact des gouttes d'eau. *C. R. Acad. Sci.* **1993**, *t. 316*, Série II, 311–316.

Received for review July 23, 2002. Revised manuscript received January 28, 2003. Accepted February 6, 2003. This work was supported by the Ministère de l'Éducation Nationale, de la Recherche et de la Technologie through the REACTIF Program.