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Bilayer films composed of wheat gluten and functionalized polyethylene: Permeability and other physical properties

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Summary

Bilayer films composed of a wheat gluten layer and a functionalized polyolefin film were performed by hot press process with the aim to improve the moisture barrier property of hydrophilic gluten films. An ethylene/acrylic ester/maleic anhydride terpolymer (Lotader 3410) and an ethylene/glycidyl methacrylate copolymer (Lotader GMA) were used. The use of both Lotader products had no incidence on film opacity, and was effective to reduce dispersion in water and water vapor permeability. In the presence of the terpolymer, the mechanical properties were enhanced and the wide range selectivity of gluten films was preserved.

Introduction

Fresh fruits and vegetables, being living commodities, maintain a respiratory and metabolic activity after harvest. The postharvest respiration and transpiration cause their progressive deterioration which occurs mainly through physiological changes and moisture loss (1, 2). The storage at low temperature and the modification of the atmosphere surrounding horticultural produces are generally used in order to extend their shelf-life and maintain their quality (3). In the « modified atmosphere packaging » (MAP), the decrease of O_2 and the increase of CO_2 involved by the natural respiration of the product, is promoted by adequate gas-exchange properties of the package material. The low O_2 and higher CO_2 concentrations slow down respiration and thus ripening and senescence (4, 5). MAP is an attractive alternative to low temperature storage for preserving many tropical and subtropical fruits and vegetables, which possess a high respiration rate and are sensitive to chilling injury (6).

The polymeric materials semi-permeable to gases are the most suitable for MAP (7, 8). However, the common plastic films (low density polyethylene, poly(vinylchloride), polystyrene, and polypropylene) can not be used to this aim, especially for fruits and vegetables, which are actively respiring and/or sensitive to a lack of O_2 or an excess of CO_2. Microperforation of common packaging films is generally used to obtain the required permeability of oxygen or carbon dioxide (9). Furthermore, the key parameter of MAP is its selectivity which refers to the ratio of CO_2 permeability to O_2 permeability of the packaging materials and determines the possible combination of oxygen and carbone dioxide concentrations inside the package (10). Microperforated films are obviously not selective (CO_2/O_2 permeability ratio close to one).

To overcome this problem, the potential of edible films to generate a favorable MAP has been considered (11, 12). Film-forming capacities of wheat gluten have been largely studied (11, 13) to make films or coatings with remarkable functional properties related to the heterogeneous complex structure of the plant proteins (14, 15). Films based on wheat gluten proved to have suitable optical, mechanical and water solubility properties. Moreover, they are biodegradable and made of inexpensive, abundant, and renewable raw material. The best original advantage offered by wheat gluten films compared to usual plastic films is their gas permeability and selectivity which are sensitive to temperature and more particularly to relative humidity (16). Wheat gluten films have impressive gas barrier properties when they are not moist, specially versus O_2. Furthermore, they exhibit a wide range of selectivity values (from 3 to 28), unlike the selectivity of most synthetic films which is usually between 4 and 6 (16, 17). The high selectivity value of wheat gluten film (28 at 24°C, 100% RH) could be very promising for fresh or minimally processed fruits and vegetables preservation under modified atmosphere (18). However, wheat gluten films are highly sensitive to moisture and show poor water vapor barrier properties. This behaviour is attributed to the hydrophilic character of proteins. Thus, in moist conditions, the use of wheat gluten films is limitated because they tend to swell or even dissolve (12, 19).

Therefore, the improvement of moisture barrier properties is of first importance for the development of these « biopackagings ». The chemical modification of proteins and the use of specific additives (crooslinking and tanning agents) have been checked to this aim (14, 20). Lipid compounds incorporation was also largely experimented to enhance moisture barrier of wheat gluten films (14, 19). For example, the combination of beeswax and DATEM (« diacetyl tartaric ester of monoglyceride ») reduced the water vapor permeability of composite films (21) or beeswax/(gluten + DATEM) bilayer structure (22). But some lipid compounds have brought disadvantages such as opacity, brittleness, unstability (rancidity), and organoleptic drawbacks (waxy taste) to the film materials. Attempts to improve mechanical and barrier properties of wheat gluten films by coating them with polylactic acid were also carried out by Ghorpade et al. (23). Gennadios et al. have tested the addition of mineral oil to a gluten/keratine mixture (24) and the preparation of films from proteins mixtures (gluten/zein, gluten/soy proteins) (25).

In the present study, we describe the improvement of moisture-resistance of wheat gluten films by using original synthetic hydrophobic films in bilayer structures in order to take advantage of complementary functional properties of both constituents and to overcome their respective drawbacks. Two types of modified polyethylene films with different reactive groups were chosen according to their potential ability to enhance the adhesion capacities between the natural and the synthetic films. Wheat gluten films were initially prepared following a casting procedure. Bilayers with the hydrophilic film and each one of the modified polyethylene film were preformed by hot press process. Satisfactory conditions limitating the degree of degradation by heat and pressure were determined. A comparative study of bilayer materials and a standard gluten film was then carried out, including physical (tensile strength, percentage elongation at break, opacity, dispersion in water), water vapor barrier and gas permeability properties. The adhesion between gluten film and modified polyolefin film was evaluated by manual peeling test and by means of scanning electron spectroscopy.

Experimental

Materials and methods

Materials

The following materials were used to prepare wheat gluten films : gluten (7.9% water content, Ogilvie Aquitaine, Bordeaux, France), distilled water, sodium sulfite, ethanol, glycerol, acetic acid, and formaldehyde (Aldrich Chemie, Steinheim, Germany). The used modified polyethylene films : ethylene/acrylic ester/maleic anhydride terpolymer (Lotader 3410), and ethylene/glycidyl methacrylate copolymer (Lotader GMA) were kindly provided by ATOCHEM.

Wheat gluten and bilayer films preparation

Wheat gluten based films (around 50 μm thick, and plasticized by 0.2 g of glycerol per g of dry material) were prepared according to Gontard procedure (13) which consists in casting in thin layer and then drying of 100 ml film-forming solution.

Hot press process was used to perform the bilayer materials following three steps :

-- melting of the natural and synthetic films in hot press without any pressure, and during the « melting time »,

-- hot press process at 200 bars, at the « pressing temperature », and during the « pressing time »,

-- cooling of the bilayer films outside the press (for 40 minutes).

All the hot press parameters were determined for each bilayer in order to decrease as much as possible the degree of their degradation (color, odor, and deformation).

Characterization

Physical and barrier properties of a control gluten film and the new bilayer materials were measured.

Film opacity was determined using a spectrophotometer cell, and following a modified standard procedure BSI (26). It was calculated from the recorded spectrum and expressed as absorbance value wavelength product (VA.nm).

The percentage of dry material which dispersed in water after 24h immersion at 25°C was obtained according to Gontard (21).

Water vapor permeability of films was determined gravimetrically at 20°C and 100-0 % relative humidity (RH) using a modified ASTM 96-80 procedure (27).

Tensile tests were carried out using a stable microsystem TAXT2 texture analyser (model Champlan, France) and in accordance with ASTM standard method D882-88 (28). Samples were previously prepared using the NFT 54-102 norm and conditioned at 58% and 98% RH. Strength and elongation at break measurements of a total of 12 specimens were determined at 0.5 $mm.s^{-1}$ and were used to calculate tensile strength and the percentage of elongation.

To study the structure and adhesion in the bilayers, the samples were fractured in liquid nitrogen. The fracture surfaces were examined by scanning electron microscopy (SEM, Cambridge Stereoscan 260) after they have been coated with a thin conductive layer of gold and platine alloy. The enlargements are specified in the legends.

Oxygen and carbon dioxide permeability were carried out in dried and high moisture conditions at 23°C by using a sweeping method. The permeation equipment was Lyssy GMP 500 coupled with the gas chromatograph CPG (MP Series 2). The standard testing gas was a $O_2/CO_2/C_2H_4$ mixture, whose molar percent proportions were 79/20/1. Helium was the carrier gas.

Results and discussion

Parameters of hot press process

The retained conditions to prepare the gluten / modified polyethylene bilayers were : « pressing temperature » of 90°C for terpolymer and 110°C for copolymer (around the melting point of both Lotader), « melting, and pressing time » equal to 2 minutes. Under these conditions, a low degradation of the bilayers was observed. Furthermore, thermolgravimetric analyses showed that the weigth loss at these defined pressing temperatures was mainly due to water evaporation.

Influence of the modified polyethylene films on functional properties of bilayer films

Opacity

Transparency is of prime importance for film packaging. Opacity measurements (Figure 1) of a control gluten film and both types of bilayers showed that the synthetic films have no incidence on the transparency quality of proteic film. The sligth differences can be related to the cristallinity degree of each polymer. The consequences of the hot press process such as yellowing must be also taken into account.

Dispersion in water

The water resistance of gluten/polyolefin bilayer is an important property in some applications such as fresh food packaging when water content is high. The weigth loss of the prepared films by dipping into water is expressed as g of dispersed dry material per 100 g of initial dry material and represented in Figure 1. The low solubility in water of wheat gluten films was previously demonstrated and was attributed to low content of ionized polar aminoacids (≈14%), to numerous hydrophobic interactions between non polar aminoacids (39.6%), and to the presence of covalent disulfide bonds (15). Compared with the control gluten film, the weigth losses for bilayer structures were 34% and 40% lower for the terpolymer and the copolymer respectively. In conclusion, the hydrophobic polyolefin films increased the water resistance of wheat gluten film, as expected.

Water vapor permeability

The presence of polyolefin films with high moisture barrier property decreased the water vapor permeability of gluten film in bilayer structures. The results listed in Figure 1 are expressed as water vapor permeance, which does not take the film thickness into account. The hydrophobicity of the synthetic polymers should have reduced the water molecule sorption and the water vapor transfer through the bilayer films. In addition, it is interesting to compare this water vapor permeance values with those obtained from other methods. It was demonstrated that combining wheat gluten proteins with beeswax using the emulsion technique led to a maximum of fourfold reduction of water vapor permeability of gluten

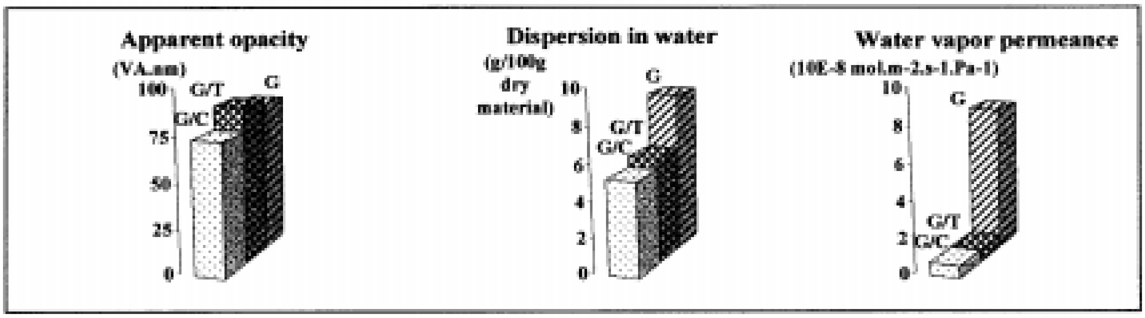

Fig.1. Apparent opacity, dispersion in water (20°C, 24h) and water vapor permeance (30°C, 100-0% RH) of control gluten film (G) and bilayer films, T : terpolymer film, C : copolymer film.

based films, but the films became highly opaque and brittle (21). Furthermore, the coating technique for combining wheat gluten proteins with lipid compounds (which forms a bilayer) was more efficient to decrease water vapor permeability (22). Both tested Lotader films which enhance highly, and in the same way the water vapor barrier property of wheat gluten film, were less efficient than beeswax layer (16). The Lotader films permitted to reduce the water vapor permeance (about 0.70 10^{-8} $mol.m^{-2}.s^{-1}.Pa^{-1}$) by 91% whereas the lipid compound reduced it by 99.8% (permeance of bilayer : $0.014.10^{-8}$ $mol.m^{-2}.s^{-1}.Pa^{-1}$). However, the other properties must be considered, especially the organoleptic and mechanical properties.

Mechanical properties

To maintain their integrity and barrier properties, the bilayer materials must be able to withstand the normal stress encountered during their application, subsequent shipping and food handling. High mechanical strength is required, but deformation values must be adjusted according to the intented application of the film (21). Tensile strength represents the maximum stress developed in a film during a tensile test and offers the measurement of integrity and heavy-duty use potential for films. The elongation percentage at break is the quantitative representation of a film ability to stretch (24). These properties were measured at 20°C and for 58% and 98% RH, and the experimental results are shown in Figure 2.

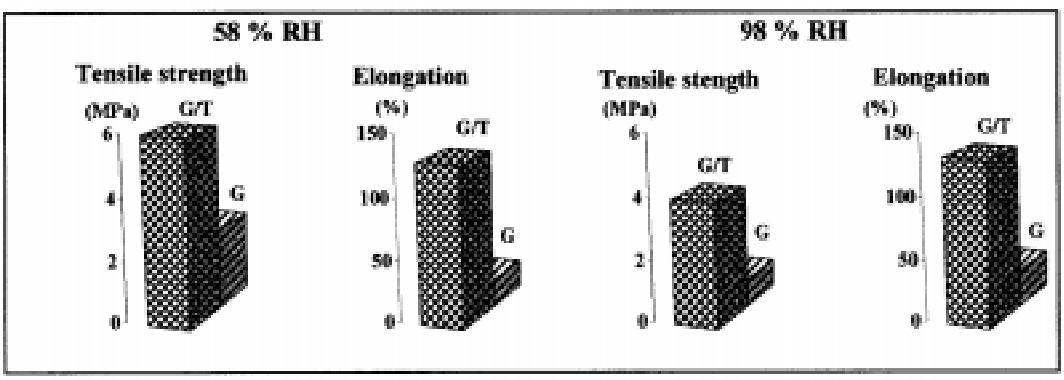

Fig.2. Tensile strength and percentage elongation of standard gluten film (G) and gluten/terpolymer bilayer film (G/T) at 20°C and 58%, and 98% RH, but not measured for gluten/copolymer bilayer because of the adhesion breaking between the two layers.

The plasticizing effect of water on the gluten film was obvious : its elongation values increased with relative humidity whereas tensile strength decreased. In the case of gluten/terpolymer bilayer, the elevated humidity had few or no consequence on the mechanical properties. However, its elongation percentage and tensile strength values were much higher than those of wheat gluten film. The gluten/Lotader GMA bilayer exhibits poor mechanical properties because of the low adhesion between both films. This insufficient adhesion was firstly demonstrated by manual peeling test and then confirmed by a peeling of the synthetic film during the tensile test.

Bilayer microstructure

A key requirement for a bilayer film is a good adhesion between both different layers. The study by scanning electron spectroscopy of the fractured sample surface showed different results depending on the comonomer nature of the modified polyethylene (Figure 3). In the case of acrylic ester and maleic anhydride functionalized polyethylene (Lotader 3410), two entirely jointed layers were observed (figure 3a), whereas a continuous space existed between the gluten film and the ethylene/glycidyl methacrylate copolymer film (Figure 3b). According to the literature, adhesion could be explained following different mechanisms. Mechanical, thermomechanical, chemical theories, and also theories of electrostatic diffusion, of adsorption or of low cohesion layer are generally proposed (29, 30). The fact that no difference was observed between the bilayers prepared by the hot press process on the rough or smooth surface of the gluten film, makes the mechanical theory unlikely. Furthermore, the suspected interdiffusion phenomena between both constituents of bilayers were not confirmed by scanning electron spectroscopy. The expected covalent bonds between the epoxide groups of glycidyl methacrylate comonomer (Lotader GMA) and amino or acido groups of gluten proteins could not be observed. But the water in gluten film can make easier the hydrolysis and then the opening of the maleic anhydride cycle.

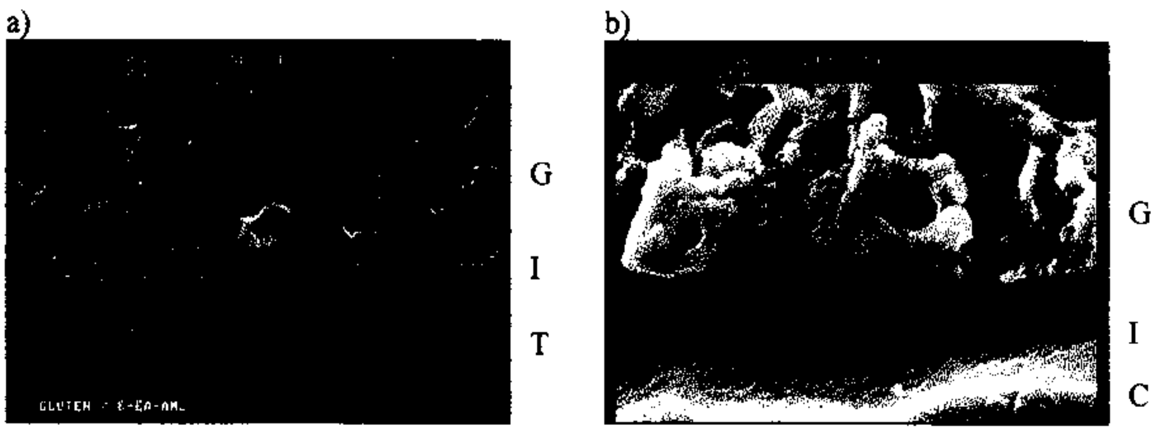

Fig.3. Photomicrographs of gluten/Lotader bilayers, a) gluten/terpolymer (x 2800), b) gluten/copolymer (x 2700), G : gluten film, T : terpolymer film, C : copolymer film, and I : interface.

Considering the results, we thought that the most likely explanation is the existence of Van der Waals or hydrogen bonds between the wheat gluten based film and the terpolymer film.

O_2 and CO_2 permeability - Selectivity

O_2 and CO_2 permeability measurements were carried out on the most interesting bilayer prepared with the acrylic ester and maleic anhydride functionalized polyethylene. First, the permeation device was tested with a polyethylene terephtalate control film (PET Lyssy). The values are given in the table. The O_2 and CO_2 permeabilities and the selectivities of bilayer material increased with humidity in the same way as those of gluten film. Even though the O_2 and CO_2 permeability values of gluten/Lotader 3410 bilayer were lower than those of gluten film, the selectivity values remained very high in moist conditions. The gluten film kept its very interesting wide range of selectivity in a bilayer structure with the terpolymer.

Material	thickness (µm)	HR (%)	PO_2	PCO_2	β
PET ref	25	0	9	31	3.4
PETmes	25	0	10	42	4.1
gluten/	97	0	7	20	3.0
terpolymer	93	92	67	2803	41.9
gluten	-	0	77	140	1.8
	-	95	1290	36700	28.4

Table. O_2 and CO_2 permeability measurements (respectively PO_2, and PCO_2) expressed as $amol.m^{-1}.s^{-1}.Pa^{-1}$ ($amol = 10^{-18}$ mol) of PET control film (PET mes), and of gluten/terpolymer bilayer at 23°C. PET ref : permeability values of literature, β : selectivity.

Conclusions

Attempts to improve wheat gluten film properties using a functionalized polyethylene layer were successfully achieved. Actually, the use of hot press process allowed us to obtain bilayer films with minimal degradation. Between both tested synthetic hydrophobic films (Lotader), ethylene/acrylic ester/maleic anhydride terpolymer and ethylene/glycidyl methacrylate copolymer, the terpolymer was the most effective. Both prepared gluten/Lotader bilayers showed good transparency, reduced dispersion in water and water vapor permeability, compared with a control wheat gluten film. However, the nature of the functionalized polyolefin comonomer seemed to have a direct incidence on the adhesion degree with the proteins based film and thus influence the mechanical properties. Ethylene/glycidyl methacrylate copolymer had no adhesion with gluten film whereas the terpolymer had good adhesion, improved the mechanical properties in moist conditions, and maintained the high selectivity value of gluten film at high humidity. But the technology can probably be improved. Casting film-forming solutions is not an easily and economically transferable process on an industrial scale. The bilayer gluten/terpolymer could be carried out by a co-extrusion process since the thermoplastic properties of wheat gluten have been demonstrated. Finally, the use of ethylene/acrylic ester/maleic anhydride terpolymer is very promising for the development of wheat gluten based films as selective packaging for fresh fruits and vegetables preservation under modified atmosphere.

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