

Bilayer films composed of wheat gluten film and UV-cured coating: water vapor permeability and other functional properties

Josiane Irissin-Mangata, Gérard Bauduin, Bernard Boutevin

Laboratoire de Chimie Macromoléculaire, UMR CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue de l'École Normale, 34296 Montpellier Cedex 5, France

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Summary

Two types of UV-cured coating were deposited on wheat gluten film to improve the water vapor barrier properties of this highly interesting natural film in such application as fresh produces packaging. The use of an epoxy acrylate and an urethane acrylate coating allowed to reduce by half the water solubility and the water vapor permeance of the gluten film. Concerning the mechanical properties, the new bilayer films were more resistant but less resilient and flexible than the control gluten film. But the good adhesion between each UV coating and the gluten film increased the interest for these original materials.

Introduction

The improvement of the safety and quality of fresh or little processed food is of major interest for both consumer and food industry. The storage at low temperature and modification of the atmosphere surrounding living horticultural commodities are the usual methods to extend shelf-life (1). In modified atmosphere packaging (MAP), the natural product respiration involves a decrease of O₂ and an increase of CO₂ in conjunction with adequate gas exchange through the package material. The low O₂ and higher CO₂ concentrations slow down respiration and subsequently ripening and senescence (2).

The most suitable films to create MAP are materials semi-permeable to gases (3). Thus, an increase of the use of plastic film packaging such as low density polyethylene, poly(vinylchloride), and polypropylene occurred in the last few years. The potential of edible films to generate MAP has been recently considered (4, 5) since these natural films are biodegradable and made of inexpensive, abundant, and renewable raw material. Among agricultural macromolecules, proteins have been long and empirically used as packaging materials (e.g. traditional lipoprotein skins in Asia, and collagen sausage casings) (6). In addition, agro-packaging based on proteins are generally characterized by remarkable functional properties because of their heterogeneous specific structure (6, 7).

Film-forming capacities of wheat gluten, water insoluble proteins of wheat flour, have been largely studied, and wheat gluten homogeneous films with suitable optical, mechanical and water vapor solubility properties, have been developed (8, 9). Their gas permeability and

selectivity (CO_2 to O_2 permeability ratio) are sensitive to temperature and more strongly to relative humidity (10). Wheat gluten based films have impressive O_2 barrier properties when they are not moist and then exhibit a wide range of selectivity values (between 3 and 28) compared with the selectivity of most synthetic films which is usually between 4 and 6 (10, 11). Selectivity is the key parameter of MAP because it determines the concentrations of O_2 and CO_2 inside the package (12). Its very high selectivity value could make gluten film more convenient than usual synthetic film packaging, especially for the preservation under modified atmosphere of very much respiring and/or anoxic and CO_2 sensitive fresh fruit and vegetables (13).

Unfortunately, the hydrophilic wheat gluten films are so highly moisture sensitive that they tend to swell or even dissolve in moist conditions (5, 14). Moreover, they show poor water vapor barrier properties whereas it is important to retard moisture-exchange (gain or loss) between a fresh produce and its surrounding environment to maintain or improve its quality, stability, and shelf life (15).

Attempts to improve moisture resistance and water vapor barrier properties of wheat gluten films have been carried out in different ways. Chemical modification of proteins and use of additives (crosslinking and tanning agents) have been studied (7, 15). Wheat gluten proteins have been combined with various lipidic materials using an emulsion technique (composite films) (16) or a coating technique (bilayer films) (17) in order to improve the water vapor barrier properties of gluten films. Beeswax and DATEM (tartaric ester of diacetyl monoglyceride) were been proved to be more efficient. Ghorpe et al. (18) have coated wheat gluten films with polylactic acid layer. Gennadios et al. have tested the addition of mineral oil to a gluten/keratine mixture (19) and the preparation of films with proteins mixtures (gluten/zein, gluten/soy proteins) (20). In a previous paper, we already presented the protection of a gluten film with modified polyolefins (21).

This paper deals with the improvement of moisture resistance and water vapor barrier properties of wheat gluten films by coating with a hydrophobic crosslinked photopolymer layer. Radiation curing (ultra-violet and electron beam curing) is known to be a very efficient method for producing quasi-instantly highly crosslinked polymeric materials (22, 23). Owing to its distinct advantages such as absence of solvent, rapid cure and energy saving, this technology is widely used in the coatings, graphic arts, electronic and adhesive industries (24, 25), and has found a variety of medical and dental applications (26, 27). For packaging applications, UV curing is sometimes used for inks (decoration) or adhesives. In the particular case of flexible packaging, flexographic printing of various film or foil substrates are current (22).

We intended to develop a new application of the UV-curing technology. To this aim, two UV coating formulations, both composed of three basic components, i.e., an oligomer, a monomer, and a photoinitiator, were directly cured via a free radical process on wheat gluten film substrates. The oligomers belong to urethane acrylates and epoxy acrylates, both largely experimented because of their ability to create hard coating, their chemical and water resistance, strong adhesion to a large variety of substrates, good abrasion resistance, and fast cure rate (22, 23, 28). While urethane acrylates possess the characteristics of the urethane resins, especially flexibility, epoxy acrylates lead to too tough film materials (29). For this reason, a flexible epoxy acrylate was selected to provide the flexibility required by film packaging. A comparative study of bilayer materials (gluten film/UV-cured coating)

and a control gluten film was carried out in order to determine physical properties (tensile strength, percentage of elongation at break, modulus, opacity, dispersion in water, water vapor barrier properties), and morphology.

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).

All the components of both UV-curing formulations were kindly provided by the UCB Society. Their trade names and parts by weight are given in the following Table 1.

	% Oligomer	% Monomer	% Photoinitiator
Epoxy acrylate Resin (EA)	70 Ebecryl 3703 (amino modified epoxy acrylate)	22 TPGDA (tripropylene glycol diacrylate)	8 Irgacure 261 (acrylated benzophenone)
Urethane acrylate Resin (UA)	70 Ebecryl 210 (urethane acrylate)	25 HDDA (hexane diol diacrylate)	5 Irgacure 369 (benzophenone)

Table.1. Composition of used UV-curing formulations (parts by weight).

The photoinitiator Irgacure 261 was selected for its capacity to copolymerize and enter the network, thus avoiding the problem of its migration.

Wheat gluten film preparation and UV-curing

Wheat gluten films (about 50 μm thick, and plasticized by 0.2 g of glycerol per g of dry material) were prepared according to slightly modified Gontard procedure (8) which refers to the casting in thin layer and then drying of 100 ml film-forming solution.

The UV-curable resins were applied on the smooth gluten film surface as a uniform layer of 10 μm thickness by means of a calibrated wire-wound applicator. Samples were exposed, in the presence of air and at room temperature, to the radiation of a medium pressure mercury lamp (80 W/cm). This type of light source, which is the most widely used in UV-curing applications, has its strongest UV emission lines at 254 and 303 nm. The maximum cure-speed of each resin on white paper was previously determined neglecting the possible absorption of UV light by the gluten film substrate. The selected cure-speeds, respectively 15 and 10 m/min for the epoxyacrylate and the urethane acrylate resin, were sufficient to achieve the curing of the coating.

Characterization

Film opacity was determined using a spectrophotometer cell, and following a modified standard BSI procedure (30). It was defined as the area under the recorded absorbance-wavelength curve and expressed as the absorbance-wavelength product (VA.nm).

The percentage of dry material of the films which was dispersed in water after 24h immersion at 25°C was calculated according to Gontard method (16).

Water vapor permeability of films was determined three times gravimetrically at 20°C and 100/0 % relative humidity (RH) using a modified ASTM 96-80 procedure (31).

Tensile tests were carried out using a stable microsystem TAXT2 texture analyser (model Champlan, France) and in accordance with ASTM standard method D882-88 (32). Samples were previously prepared using the ISO 527-2 standard : 1993 F and conditioned at 58 and 98% RH respectively. Strength and elongation at break measurements of a total of 10 specimens were determined at 0.3 mm.s^{-1} and were used to calculate tensile strength and elongation. The Young modulus was calculated using the slope of the stress-deformation curves at the origin.

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.

Results and discussion

Opacity

Generally, wheat gluten films proved to be optically clear in good adequacy with the transparency requirement for film packaging (8). The opacity measurements of a standard gluten film and both bilayers showed quite similar results (Figure 1).

Cuq (33), Cheesman and Davies (34) assumed that the opacity of proteins based films were not related to their thickness since their absorbance was essentially that of the two film-atmosphere interfaces. According to this theory, interchanging a gluten-atmosphere interface with an UV coating-atmosphere interface seemed to have very little incidence on the film transparency in the case of urethane acrylate coating, whereas the opacity was 19% reduced with the epoxy acrylate layer.

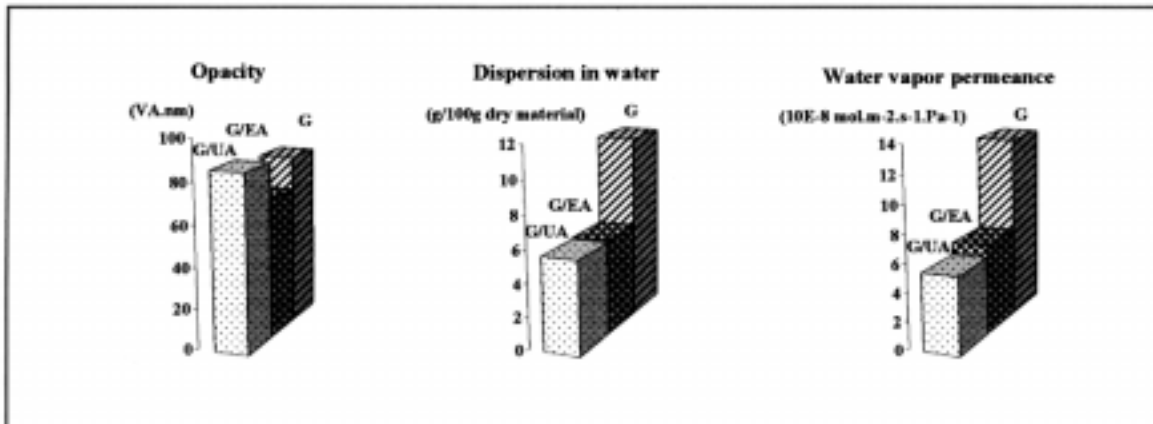


Fig.1. Average values of optical, water resistance, and water vapor permeability properties of a control gluten film (G) and the bilayer materials G/EA, G/UA where EA : epoxy acrylate coating, UA : urethane acrylate coating.

Dispersion in water

The water resistance of gluten/photopolymer bilayers is necessary for packaging of high moisture fresh produces. The solubility of control gluten film and bilayers was defined as the percentage of the dry material which entered the aqueous phase per 100g of initial dry material, since the UV-cured films were assumed not to be soluble in water. The results are shown in Figure 1. The gluten film in bilayer structures was twice less soluble than the standard gluten film, though the low water solubility of the latter was previously demonstrated and attributed to its low content of ionized or polar aminoacids, to numerous hydrophobic interactions between its non polar aminoacids, and to the presence of covalent bonds (6). The presence of epoxy or urethane acrylate function seemed to improve the structure cohesion of gluten film through water resistant bonds with the protein based film.

Water vapor permeability

The coating of wheat gluten film by a photopolymer layer reduced its water vapor permeability. The results represented in Figure 1, are expressed as water vapor permeance, which does not take into account film thickness. The water vapor permeance of the hydrophilic natural film was thus reduced by 51% and 57% respectively for the epoxy acrylate and urethane acrylate UV-cured layers. This improvement of water vapor barrier is supposed to be related to the reduction of the water molecule sorption owing to the reduction of free volume in the crosslinked photopolymer film. The higher is the crosslink density inside the cured layer, the better is the water vapor barrier effect.

Mechanical properties

As packaging films, our bilayer materials were expected to withstand stress and food handling. So, samples of gluten/photopolymer bilayers and of a control gluten film were submitted to a tensile test to characterize their mechanical properties at 20°C and for 58% and 98% relative humidity (RH). The results are summarized in Figure 2. A decrease of tensile strength and Young modulus at 98% RH attested the plasticizing effect of water. This effect was a little less important for bilayer materials than for the control gluten film. In other respects, whatever the humidity the bilayer structures had higher tensile strength, poorer elongation percentage, and higher modulus than the gluten film. Consequently, they are more resistant but less resilient and flexible. The exception to this tendency was the higher tensile strength of standard gluten film compared with urethane acrylate coating/gluten film bilayer, at 58% RH.

Moreover, a comparative study of mechanical properties between both bilayers showed that urethane acrylate coating yielded lower modulus but poorer tensile strength and elongation than epoxy acrylate coating/gluten film bilayer at medium humidity, whereas the opposite behaviour could be observed at high humidity. The discrepancies between the epoxy acrylate and polyurethane acrylate coating influences on mechanical properties must be related to their crosslink density which depends on the functionalities, the chemical structures, and the quantities of the monomers and oligomers used (24, 28).

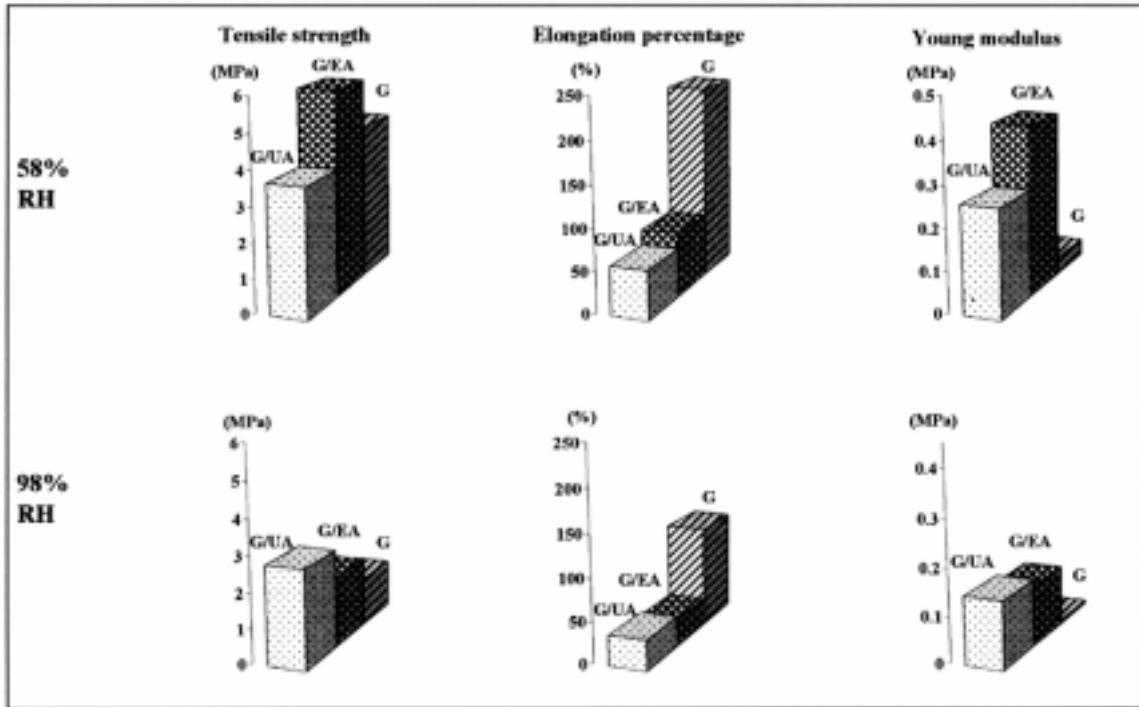


Fig.2. Tensile mechanical characteristics (average values) of a control gluten film (G) and bilayer materials gluten film/epoxy acrylate photopolymer layer (EA) and gluten film/urethane acrylate photopolymer layer (UA) at 20°C, 58 and 98 % RH.

Microstructure

A key requirement for success when preparing a bilayer film is good adhesion between the different layers. During the tensile test of the bilayer materials, no peeling of the UV-cured coating was observed. The supposed good adhesion between both films was confirmed by scanning electron spectroscopy of fractural sample surface of bilayers. The pictures (Figure 3) showed a gluten film layer (up) and a UV coating layer (down), both entirely joined, whatever the formulation used.

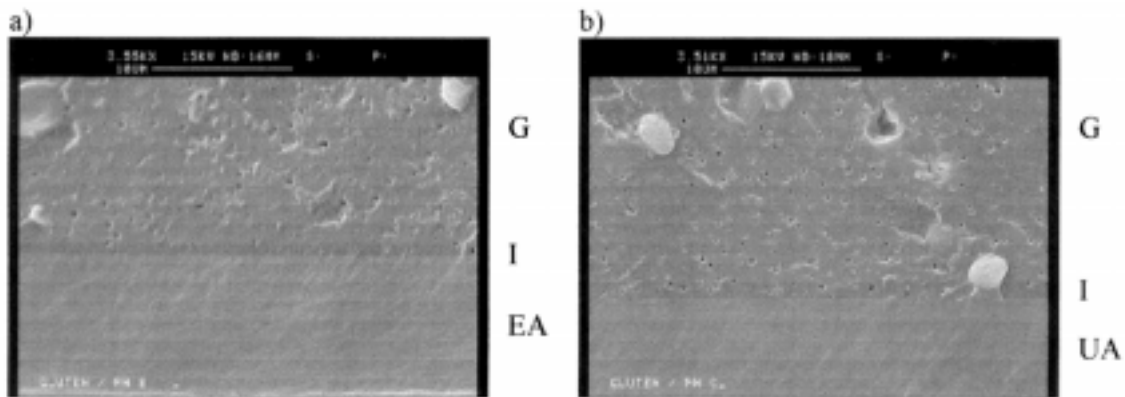


Fig.3. Photomicrographs of gluten film/UV coating bilayer materials. G : gluten film, EA : epoxy acrylate coating, UA : urethane acrylate coating, I : interface. a) G/EA (x3000), b) G/UA (x3000).

The observations were in accordance with the known excellent adhesion property of acrylics to various types of substrates. Consequently, an adhesion agent seemed not to be useful.

Conclusions

The coating of a gluten film with a UV crosslinked film improved its water resistance and water vapor barrier property. Nevertheless, the properties required for a packaging film could not be obtained altogether, since the mechanical properties of the bilayers were poorer than those of the standard gluten film. Thus, the bilayer films were more resistant but stiffer than gluten film according to the elongation and modulus values. These results could be explained by the high crosslink density of the UV coatings.

On other respects, a comparative study between both the tested UV formulations showed that the epoxy acrylate was a little more efficient than urethane acrylate resin concerning the transparency and the water vapor barrier property. Both coatings yielded similar water resistance. Since their modulus and tensile strength evolved in an opposite way according to the relative humidity, it could be interesting to combine both resins in a same coating.

The coating structures characterized by current techniques such as real-time infrared and ultraviolet spectroscopies, dynamic mechanical thermal analysis, leaching and swelling tests, could be correlated with the observed properties.

Finally, more investigations should be carried out to develop this promising UV coating technology.

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