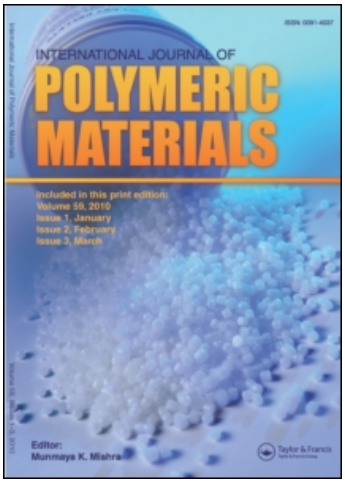

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Preparation and Characterization of Hydrocolloid Biopolymer-Based Films for Dressing Applications

K. Zaher[a]; M. El Kolli[a]; F. Riahi[a]; R. Doufnoune[b]
[a] Laboratoire des Matériaux Polymériques Multiphasiques (LMPMP), Département de Génie des Procédés, Faculté des Sciences de L'Ingénieur, Université Ferhat-ABBAS, Sétif, Algérie [b] Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Département de Génie des Procédés, Faculté des Sciences de L'Ingénieur, Université Ferhat-ABBAS, Sétif, Algérie

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Preparation and Characterization of Hydrocolloid Biopolymer-Based Films for Dressing Applications

K. Zaher,[1] M. El Kolli,[1] F. Riahi,[1] and R. Doufnoune[2]
[1]Laboratoire des Matériaux Polymériques Multiphasiques (LMPMP), Département de Génie des Procédés, Faculté des Sciences de L'Ingénieur, Université Ferhat-ABBAS, Sétif, Algérie
[2]Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Département de Génie des Procédés, Faculté des Sciences de L'Ingénieur, Université Ferhat-ABBAS, Sétif, Algérie

In this study three types of dressings in the form of thin films were prepared from a mixture of two natural biopolymers, namely gelatin and pectin. The protein and the polysaccharide were chosen because of their hydrosolubility and interactivity, respectively. Glutaraldehyde was also used to crosslink the films.

The physical properties of the resulting films were evaluated through measurements of absorption capacity and water vapor permeability. FTIR and UV spectroscopy were also used to characterize the films.

It was found that crosslinking much increased the absorption capacity, reflecting the strong interactions that developed between gelatin and pectin. It was also found that the water vapor permeability depends greatly on the film thickness and evolves linearly with time.

The FTIR analysis also allowed us to identify the different functional groups through which gelatin and pectin chemically interacted. The quantitative analysis of the residue by means of UV spectroscopy indicated that the films were biodegradable and therefore can be used for biomedical applications.

Keywords: absorption capacity, dressing, gelatin, pectin, permeability

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Address correspondence to F. Riahi, Laboratoire des Matériaux Polymériques Multiphasiques (LMPMP), Département de Génie des Procédés, Faculté des Sciences de L'Ingénieur, Université Ferhat-ABBAS, Sétif, Algérie. E-mail: faridriahi@yahoo.com

INTRODUCTION

To take care of wounds is an art as old as the medical profession itself. However, chronic wounds such as those of knee ulcers and those of the diabetic foot represent, in terms of cost and quality of life, a real public health problem. Over recent years the treatment of such wounds has improved and many innovations in the use of dressings have been employed on a large scale. Most studies [1–3] agree that any wound evolves through three phases before healing. First is a cleansing phase (necrosis and fibrin); then, if the wound is correctly treated, it evolves to the budding phase, which is necessary but which must not be excessive so as not to hinder the third phase, which is epidermization. The three phases, which can sometimes be associated at different zones, are necessary for the healing process.

On the other hand, preliminary studies [4,5] about cicatrization have confirmed that this phenomenon involves interactions between the different tissue constituents, particularly between the wound cells and those of the extra cellular matrix. The rate of the cicatrization and its quality depend much on the nature of the wound but depend also on medicine and the appropriate choice of the dressing. Dressings are therefore tools which must enable cicatrization to take place under the best physical and chemical conditions. In fact, owing to the characteristics of some of their constituents, they contribute to an efficient and rapid healing of the wound.

Depending on its state, a wound can be treated by means of dressings that are passive or hydroactive. Passive dressings are used for the treatment of acute wounds, for they absorb the exudates and insure a good protection. Hydroactive dressings are used for the treatment of chronic wounds because they perfectly adapt to the different stages of the cicatrization process and create the appropriate conditions necessary for optimal therapeutic efficiency. In this case, the treatment maintains a hot and humid medium rich in carbon dioxide and poor in oxygen in order to stimulate healing. Generally, the dressing is composed of a self-adhesive matrix that contains hydroabsorbing particles. These particles are composed of cellulose derivatives, calcium alginates, pectin or gelatin. Hydrocellular dressings are widely used and often prescribed for chronic wounds. Those based on carboxymethylcellulose (CMC) have a high absorbing capacity.

The performance of hydrocolloid dressings depends greatly on their composition and form. They can be in a paste form, bordered, thin or thick and adapted to every type of a wound. They are simple to use and last longer than traditional dressings. One of their drawbacks is that upon contacting the wound they turn to a bad-smelling gel which

can ooze out, therefore irritating the surrounding skin. They induce maceration and cause hyperbudding, but rarely contact eczema [6].

Gelatin and pectin are two natural polymers that make up the composition of certain dressings. Their great absorbing capacity offers a useful local therapy for the treatment of exuding wounds. Most studies that dealt with gelatin-based dressing focused on attempting to improve the thermal resistance, particularly when the temperature exceeds 37°C, the human body temperature. In order to impart a good thermal resistance it is necessary to chemically modify the gelatin. Crosslinking by means of glutaraldehyde has proven to provide better heat resistance, a decrease in hydrosolubility and an important improvement in the mechanical properties [7–9].

However, hydrocolloid dressings cannot be used alone but in association with polyurethane films which are semipermeable and transparent so that the different phases of the cicatrization process can be visually controlled [7].

The objective of this work is to prepare hydrocolloid dressings based on a mixture of two biopolymers, which are pectin and gelatin. The physical properties of these dressings are compared with those of two commercial dressings, namely Algoplaque HP and Duoderm, which are made from gelatin and carboxymethyl sodium cellulose (NaCMC). The study focuses on swelling measurements in order to assess the absorbing capacity of the different films. Particular attention is paid to the qualitative characterization of the residue formed before and after crosslinking. This analysis is made by UV spectroscopy and FTIR spectroscopy.

EXPERIMENTAL

Materials

The pectin used in this study, which is obtained from highly esterified fruits, is manufactured under the reference code Genu and was supplied from CP Kelco (Grossenbrode, Germany). It is of type A and appears in a form of a whiteish and insipid powder.

The gelatin used is of the animal type and was supplied from Melin Company (France) under the code name A-ph-type B. It is insoluble in cold water but soluble in hot water. Its isoelectric point is 5.2 and has a bloom of 250.

The crosslinking agent used is glutaraldehyde ($C_5H_2O_2$) and was purchased from Aldrich Chemical Company in a liquid form and a purity of 50%(v/v). Sodium azide (NaN_3), used to avoid bacterian contamination, was obtained from Sigma Chemical Company.

The two commercial dressings used were Algoplaque HP which was obtained from URGO Laboratories, and Duoderm from Convatec Company.

Preparation of Hydrocolloid Films

The biopolymer-based films were prepared from a mixture of pectin and gelatin by casting using the following procedure. Five (5) grams of pectin/gelatin mixture at a ratio of 60/40 were dissolved in 100 ml distilled water and a small amount of sodium azide, which was added to each solution to prevent bacterial contamination. After allowing the grains to swell for 30 min, the mixture was placed in a water bath heated at 70°C under slow agitation for 35 min. Once the resulting solution became clear, three different samples (5 ml, 10 ml and 15 ml) were withdrawn from the mixture and poured separately into 8.5 cm diameter polystyrene boxes in order to obtain films with different thicknesses. These samples were then allowed to dry in free air at room temperature for 3 to 4 days. The resulting films were crosslinked by means of glutaraldehyde (GTA). Crosslinking was carried out by pouring 20 ml of the GTA solution onto the dry films and allowing the reaction to take place for 24 h. Finally, the crosslinked films were washed with distilled water and dried in free air at room temperature.

Measurement of Film Thickness

The film thickness were measured by means of a digital micrometer to the nearest 0.01 μm and the measurements were taken at five different positions. The average thickness of the films before crosslinking designated F1, F2, and F3, was 42 μm, 83 μm and 97 μm, respectively. After crosslinking and because the glutaraldehyde used was diluted, the resulting crosslinked films absorbed water and got swollen and consequently their thicknesses changed slightly. So the crosslinked films, which are designated as F1C, F2C, and F3C, have thicknesses of 51 μm, 85 μm and 100 μm corresponding to a thin, medium, and thick film, respectively.

Films Characterization

Swelling Measurements

2 cm^2 specimens were immersed in beakers each containing 100 ml distilled water at two different temperatures: room temperature and 37°C, and samples were taken at regular intervals of time ranging from 0 to 120 h. The swollen samples were withdrawn from the

medium and weighed again after removal of excess surface water by using a filter paper. The swelling index, Is (%), was determined using the following equation [10]:

$$\mathrm{Is} = \frac{\mathrm{Ws} - \mathrm{Wd}}{\mathrm{Ws}} \times 100 \quad (1)$$

where Ws is the weight of the swollen film immersed for time t, and Wd is the initial weight of the film.

Analysis of the Residue

After film swelling, the remaining residue, which represents the amount of gelatin and pectin liberated in distilled water, was analyzed by means of a UNICAM–UV Spectrophotometer and a Perkin-Elmer Fourier Transform Infrared (FTIR) Spectrophotometer.

Water Vapor Permeability Measurement (WVP)

The permeability to water vapor test enables the study of the kinetics of the passage of water vapor through isolated films. It gives an indication about the potential protection of the active substance on a film in an aqueous medium.

The test is based on the weight difference measurement as a function of time. It consists of introducing 10 ml of distilled water into a Payne permeability cup having a diameter of 3.5 cm. Then the isolated film is placed and firmly attached between two rubber gaskets. The ring and flange of the cup are accurately tightened to give exposure to exactly 10 cm^2 of the film. A sample of the same film was fixed on another cup without water as a reference. Both sample and reference were accurately weighed (± 0.001 g) and then placed inside a desiccating apparatus containing phosphorus pentoxide (P_2O_5) and silica gel (0% relative humidity). Samples were withdrawn from this set-up at regular intervals of time in order to be weighed and to determine the weight difference with respect to the reference. The water vapor permeability was calculated using the following equation:

$$\mathrm{WVP} = \frac{\mathrm{P} \cdot \mathrm{x}}{\mathrm{t} \cdot \mathrm{A} \cdot \mathrm{P}_0(\mathrm{RH}_1 - \mathrm{RH}_2)} \quad (2)$$

where P/t is the change in the film weight (g/h) which was determined as the slope of the plot of weight loss as a function of time, x the film thickness (mm), A the film cross-sectional area (m^2), P_0 is the pressure of pure water vapor (KPa), and ($RH_1 - RH_2$) is the relative humidity gradient. The value of P_0 at 25°C is 3.159 KPa [10].

RESULTS AND DISCUSSION

Swelling Measurements

These tests were carried out at variable film thickness and temperatures. It was noted that certain films have a higher capacity to absorb water than others, liberating protein and polysaccharide until saturation.

As shown in Figure 1, the variation of the swelling index as a function of time at 37°C is characterized by the presence of three zones that correspond to three steps which are: absorption, protein and polysaccharide liberation, and saturation.

It is observed that the crosslinked samples get saturated after 96 h which means that maximum absorption is achieved after the crosslinking reaction took place. It is also observed that during the first 6 h absorption increases progressively, especially during the first 2 h. It was also found that for F3C film absorption reaches 900% within 2 h before starting to decrease. This shows that the liberation of gelatin and/or pectin occurs during 24 h. Then, the absorption increases again indicating that the film is still absorbing. The state of saturation is reached within 96 h. F2C film absorbs much more than F3C film during the first 24 h. However, after 48 h the absorption of F3C film

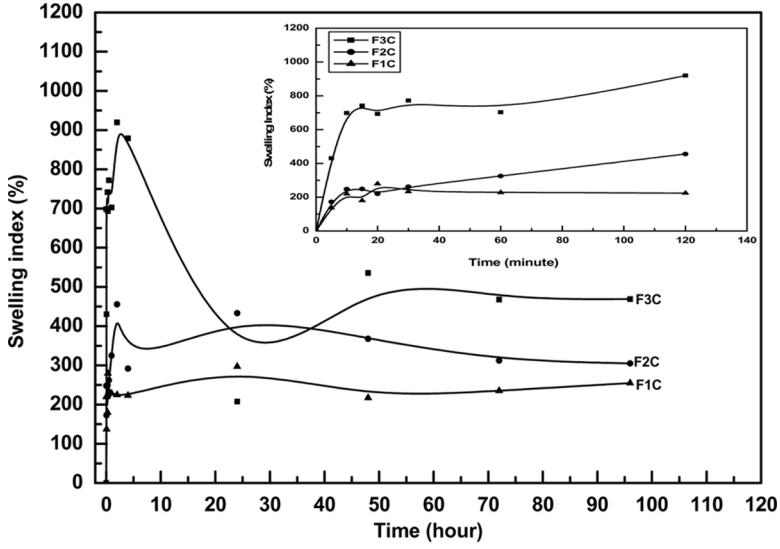

FIGURE 1 Variation of the swelling index for the different crosslinked films as a function of time at 37°C.

becomes clearly higher than that of F2C and F1C. This means that the thickest film absorbs the most and the fastest before getting saturated.

Figure 2 presents the variation of the swelling index with time for the non crosslinked films. It is shown that for the first 30 min the curves have the same general trend, which is characterized by a rapid increase in absorption up to a maximum before decreasing and eventually reaching a state of equilibrium.

As shown in Figure 3, the variation of the swelling index as a function of time (in hours) at room temperature shows that the maximum absorption for the first 24 h for F1C film is 400% but that of F3C film is 700% and that of F2C is 650%. After 48 h F3C film absorbs more than the other films. Figure 3, which presents the evolution of the swelling index with time (in min), shows that the absorption of the crosslinked films at room temperature is as important as was observed at $T = 37°C$ and can even reach 750% for F3C film.

Figures 4 and 5 respectively present the variation of the swelling index with time at 22°C and 37°C for two commercial dressings, Algoplaque HP and Duoderm, which were investigated for a comparison purpose. It was found that these dressings as well as the prepared films get saturated within 96 h at 37°C. The maximum absorption at room temperature for Duoderm and Algoplaque HP hydrocolloids is reached within 24 h and 48 h, respectively. The hydrocolloids have a tendency to absorb more at room temperature because of the polysaccharide phase which is rich in sodium carboxymethylcellulose (NaCMC).

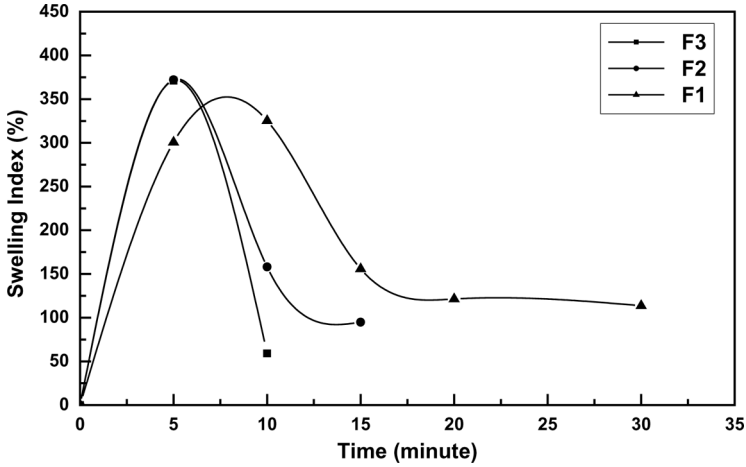

FIGURE 2 Variation of the swelling index for the different noncrosslinked films as a function of time at 37°C.

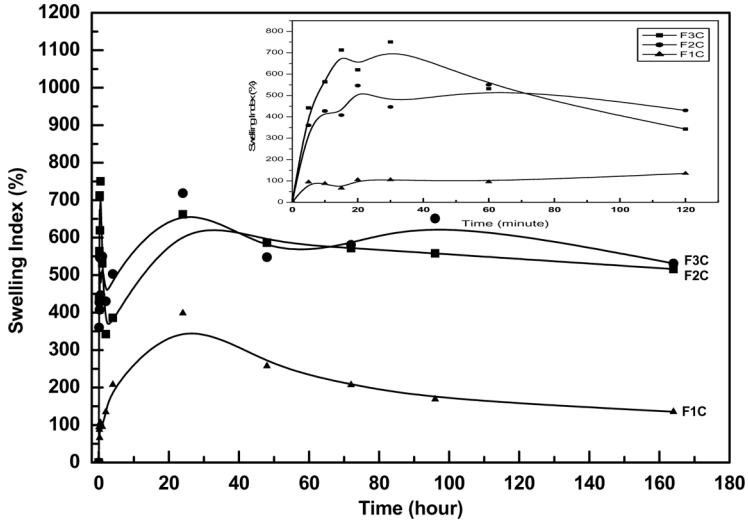

FIGURE 3 Variation of the swelling index for the different crosslinked films as a function of time at room temperature.

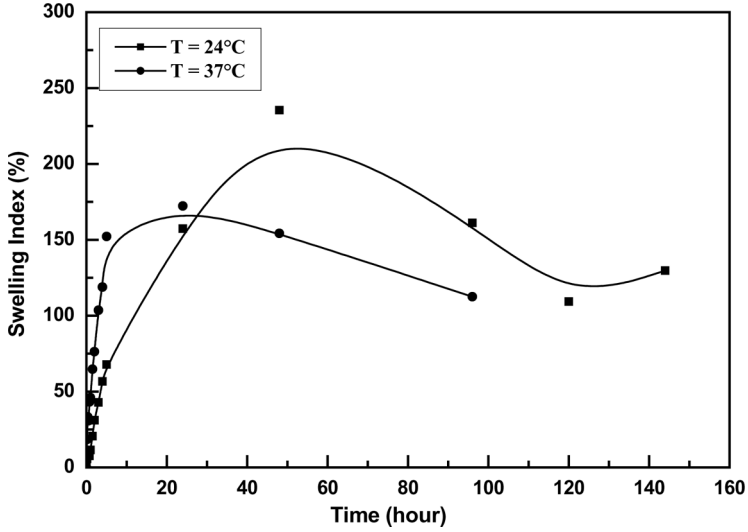

FIGURE 4 Variation of the swelling index of Algoplaque HP dressing at 24°C and 37°C as a function of time.

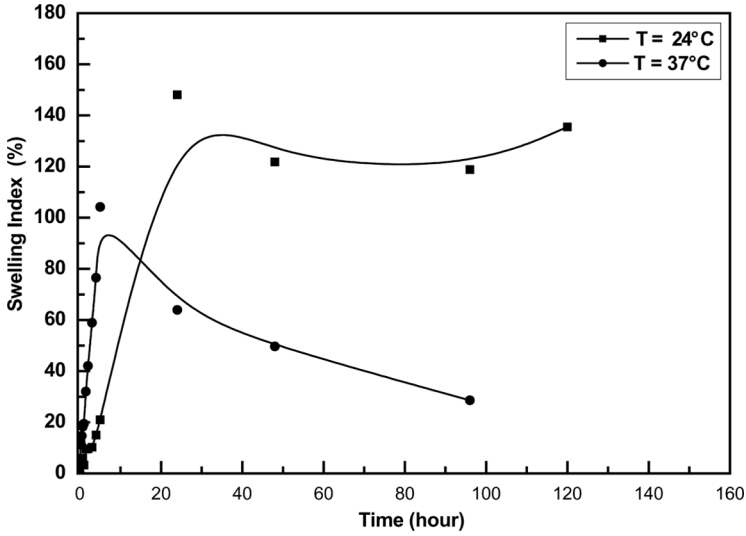

FIGURE 5 Variation of the swelling index for Duoderm dressing at room temperature and at 37°C as a function of time.

The decrease observed in the swelling index is attributed to the liberation of gelatin, which is composed of peptidic bonds that hydrolyze easily.

FTIR Analysis

The infrared spectra for noncrosslinked films are shown in Figure 6. For the pure pectin film, a large band appears at 3390 cm^{-1} and is attributed to the OH group. The band at 1725 cm^{-1} corresponds to the vibration of the C–O bond. The absorption bands occurring at 1194 cm^{-1} and 1000 cm^{-1} can be attributed to the C–O–C group. Concerning the pure gelatin film, many main bands appear among which the absorption band at 3380 cm^{-1} which is characteristic of the OH group and the one at 3330 cm^{-1} which is attributed to the N–H group. The absorption band at 1328 cm^{-1}confirms the elongational vibration of the C–N bond.

The infrared spectrum for the film prepared from a 40/60 gelatin/pectin ratio is characterized by a band at 3375 cm^{-1} which corresponds to the vibration of the O–H group. The band at 3330 cm^{-1} corresponds to the vibration of the N–H bond, but that of the C=O group of the acid functional group appears at 1752 cm^{-1} while that of the C=O of the amide functional group appears at 1652 cm^{-1}.

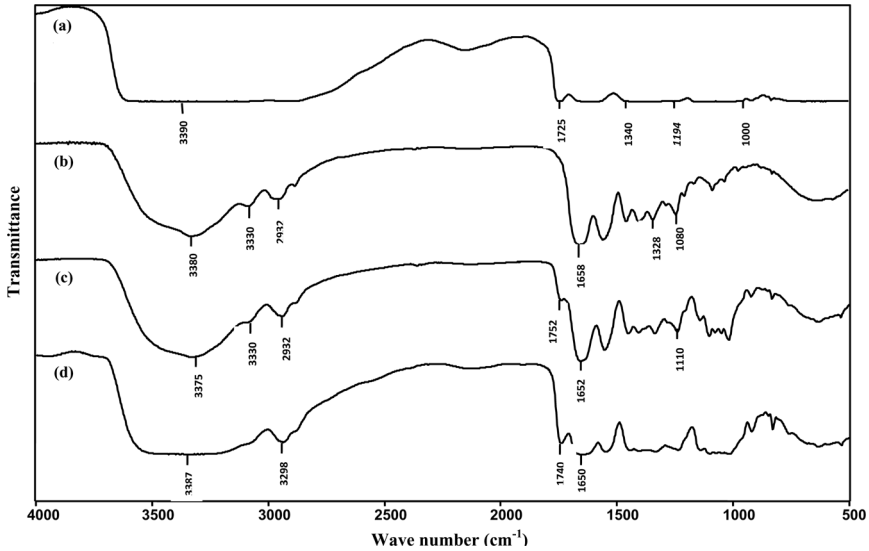

FIGURE 6 FTIR spectra of the noncrosslinked films: (a) pectin; (b) gelatin; (c) pectin/gelatin 40/60; (d) pectin/gelatin 60/40.

The infrared spectrum for the film prepared from a 60/40 gelatin/pectin ratio shows a band at 3387 cm^{-1} which corresponds to the vibration of the O−H group. The band at 3298 cm^{-1} corresponds to the vibration of the N-H bond but the band at 1740 cm^{-1} is attributed to the vibration of the C=O bond of the acid functional group. The absorption band at 1652 cm^{-1} confirms the presence of the C=O bond of the amide functional group.

The infrared spectra for the crosslinked films which are shown in Figure 7 show a new absorption band at 2133 cm^{-1} which is attributed to the CH_2 groups confirming hence the crosslinking. Figure 8 presents the FTIR spectra for the noncrosslinked film residue. The spectrum of the pectin/gelatin mixture points out the main bands resulting from the interactions that developed between the different functional groups. The band at 1740 cm^{-1} reflects a possible complexation between gelatin and pectin.

UV Analysis

The UV analysis of the residue of the prepared film is illustrated in Figures 9 and 10. A shoulder can be seen at 276 nm and 278 nm respectively for 37°C and 24°C corresponding to the $n \rightarrow n^*$ transition

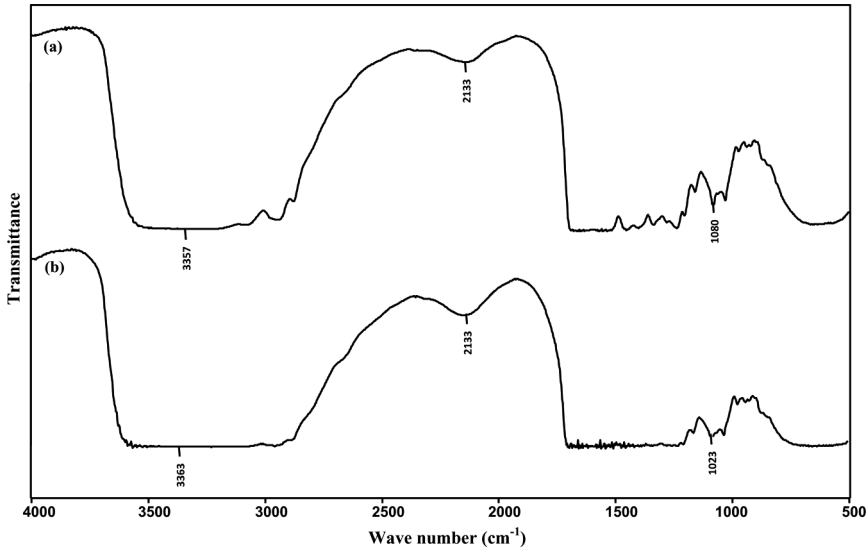

FIGURE 7 FTIR spectra of the crosslinked films: (a) pectin/gelatin (60/40); and (b) gelatin.

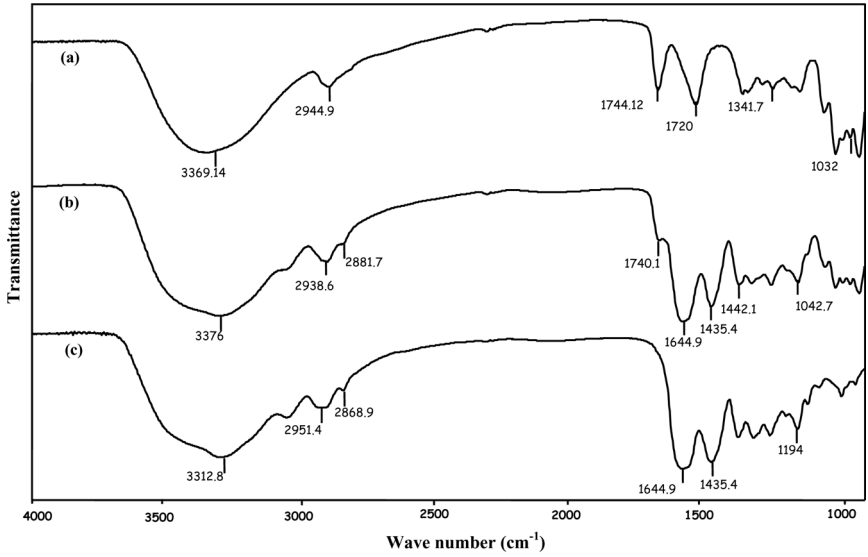

FIGURE 8 FTIR spectra of the noncrosslinked films residue: (a) pectin; (b) pectin/gelatin (40/60); and (c) gelatin.

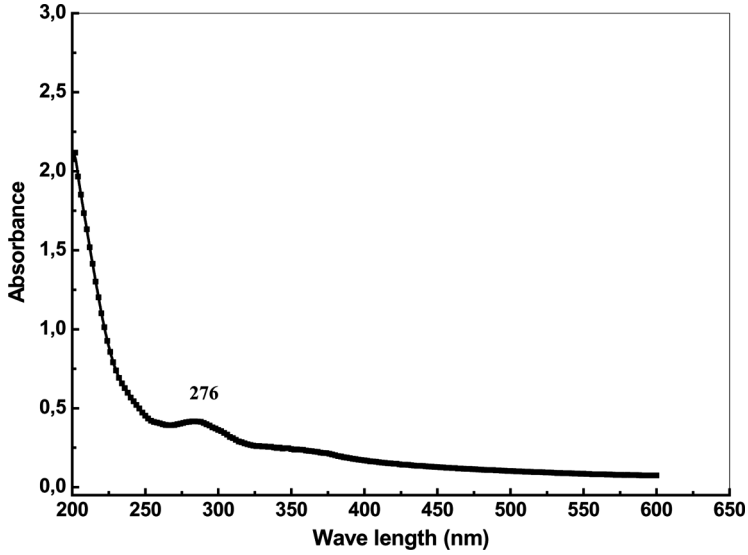

FIGURE 9 UV spectrum of the crosslinked film residue at 37°C.

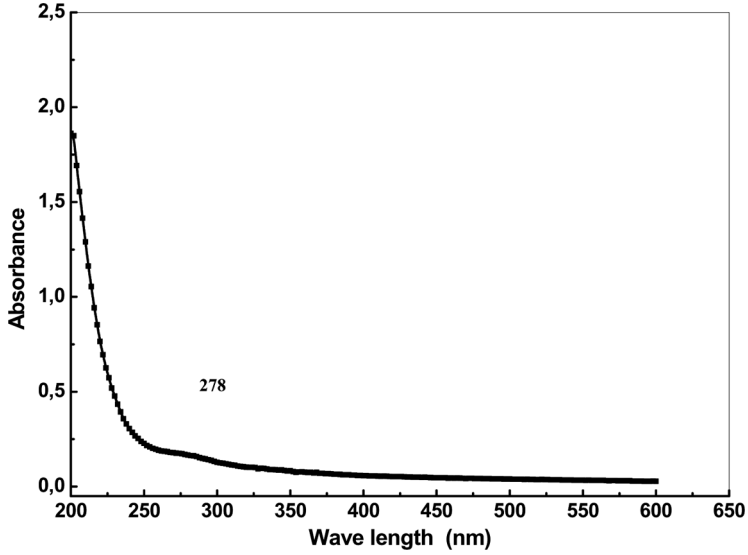

FIGURE 10 UV spectrum of the crosslinked film residue at room temperature.

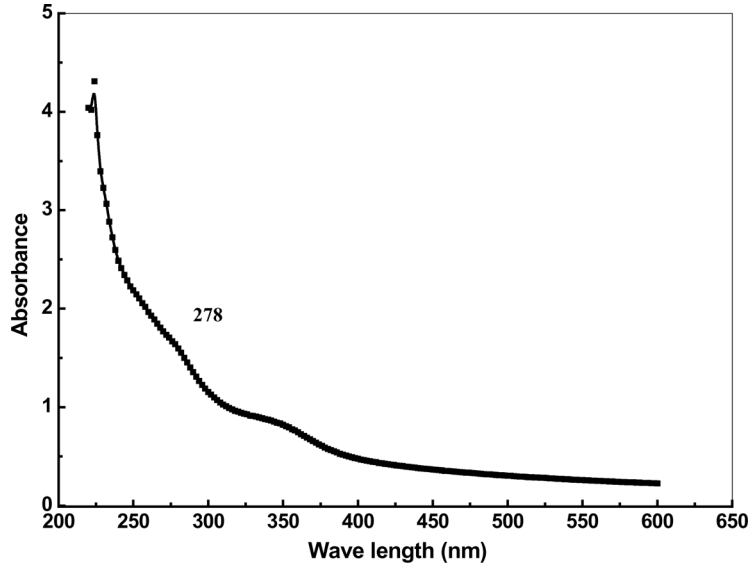

FIGURE 11 UV spectrum of Algoplaque HP film residue.

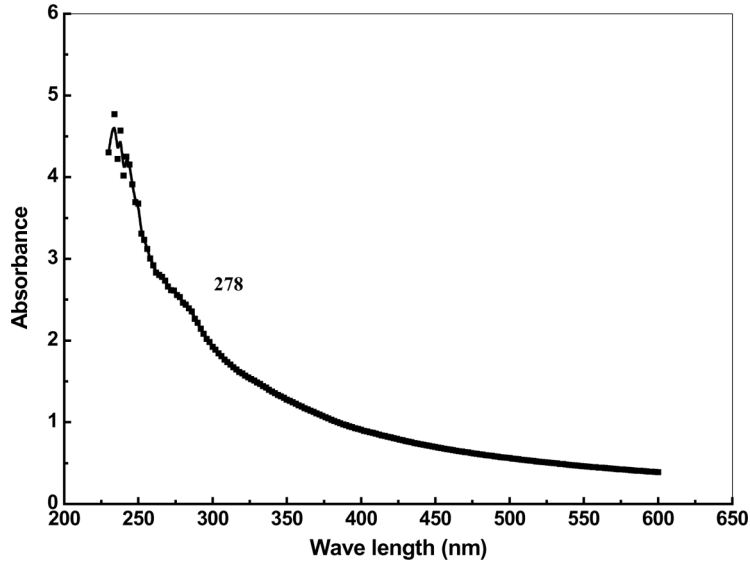

FIGURE 12 UV spectrum of Duoderm film residue.

of the C=O group. Figures 11 and 12 show the UV spectra of the residues formed after the saturation of the commercial dressings. Algoplaque HP and Duoderm are hydrocolloid polymers composed of a mixture of gelatin, pectin, and carboxymethylcellulose and therefore the two samples give up, upon degradation, amino acids which absorb at around 280 nm. In fact, the liberation of the amino acids that was evidenced in the UV spectra is related to the presence of gelatin which is a protein constituted of peptidic bonds that are easy to hydrolyze [11].

Water Vapor Permeability

Figure 13 and Table 1 present the evolution of the water vapor permeability (WVP) of the prepared films in comparison to the commercial ones. The results point out a linear evolution of the amount of the vapor transmitted. The water vapor permeability is much dependent on the film thickness. The thinner the film, the greater is the permeability. It was also found that the commercial dressings were less permeable than the prepared films. This is due to the fact that these hydrocolloid films are associated with a polyurethane layer which reduced their permeability.

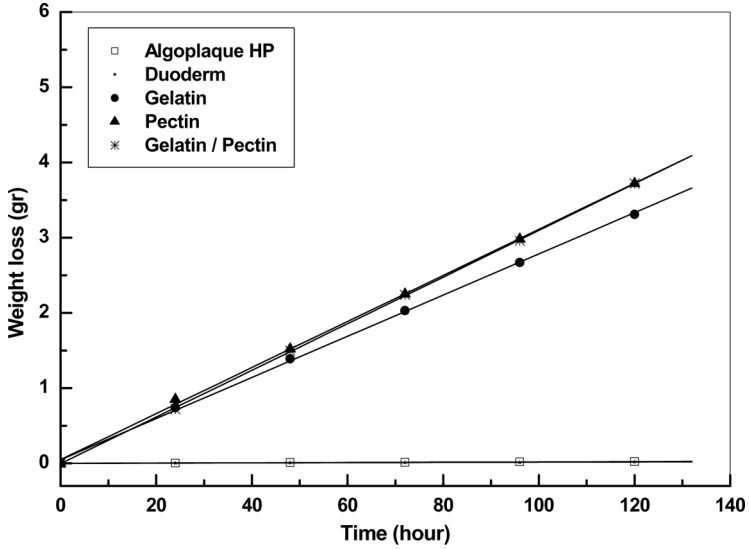

FIGURE 13 Variation of weight loss with time for the prepared films compared to the two commercial dressings.

TABLE 1 Water Vapor Permeability (WVP) of the Prepared Films and that of the Commercial Dressings Algoplaque HP and Duoderm

Specimen	Film thickness (mm)	Mass change (gr./h)	WVP (gr./mm/m^2 h KPa) $\cdot 10^{-5}$
Algoplaque HP	0.87	0.03	0.71
Duoderm	0.58	0.02	0.31
Gelatin	0.1012	3.31	9.204
Pectin	0.039	3.72	3.9824
Gelatin/Pectin	0.0646	3.72	6.587

CONCLUSION

The objective of this work was to study the physicochemical properties of different hydrocolloid films prepared from two natural biopolymers, which were gelatin of an animal origin and pectin of a vegetable origin. In order to enhance the interactions between the protein and the polysaccharide, the prepared films were crosslinked by glutaraldehyde. Flexible and transparent films having different thicknesses were obtained.

The physicochemical properties of the different films were evaluated through the measurement of the absorption capacity and permeability to water vapor. FTIR and UV spectroscopy were also used to characterize the films. The results showed that the crosslinked films have a higher absorption capacity. The water vapor permeability exhibited a great dependency on the film thickness. A linear correlation of the amount of water transmitted with time was observed, indicating an eventual application of the films as dressings that would enable skin transpiration during the cicatrization of the wound.

The results of the UV spectroscopy of the film residue resulting from the immersion of samples in water showed that the films degrade.

In brief, the whole characteristics of the synthetized films were comparable to those of the commercial ones suggesting, therefore, that they can be used as biomedical dressings.

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