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Study of Graft Copolymerization of Soy Protein-Methyl Methacrylate: Preparation and Characterization of Grafted Films

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Abstract Hybrid materials represent the family of compounds comprising mixtures of natural and synthetic materials. The study of this field is in a marked expansion since their preparation represents a valid methodology for optimizing the insufficient properties exhibited by materials integrally formed from naturally-occurring sources. In the present work, we describe soy protein modification by grafting reaction with methyl methacrylate. The reaction was confirmed by Fourier Transform Infrared Analysis and Carbon Nuclear Magnetic Resonance. In addition, films were prepared with the material by heat compression. Films were physically and mechanically characterized by determining contact angle with water, total soluble matter, moisture content, swelling in water, water vapor permeability, tensile strength, elongation at break and Young's modulus. These measurements suggest that the material increased its hydrophobic character as compared with that of the control film since marked reductions in water vapor permeability, swelling and water solubility were determined. Moreover, their mechanical properties were improved by obtaining a more rigid material. These results

represent an interesting advance in the preparation of hybrid biocomposites.

Keywords Proteins · Grafting · Copolymers · Films · Packaging

Introduction

The development of biodegradable polymer coatings from natural materials (renewable sources) reduces the need for synthesizing petroleum-based polymers, eliminating the negative effects produced on the environment. In particular, packaging represents a potential new market for such materials. At present, natural materials are not usually used for coating due to their poor barrier and mechanical properties, especially in wet state [1]. Despite this, soy protein-based edible films have received considerable attention due to their excellent film-forming ability, low cost and barrier properties against oxygen, lipid and aroma permeation under low to intermediate humidity conditions [2]. Soy proteins' ready availability, biodegradability, renewable character, functional properties, environmental friendliness, low cost, no health risk and ability to provide unique properties through structural modification open up a wide range of applications for soy [3, 4]. Hybrid materials represent the family of compounds comprising mixtures of natural and synthetic materials. At present, the study of this field is in a marked expansion as the preparation represents a valid methodology for optimizing the insufficient properties exhibited by materials integrally formed from naturally-occurring sources [5, 6]. This fact is based on the synergistic effect produced among the advantageous properties of both components upon the formation of hybrid materials, thus solving the deficiencies found in

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each material [7]. Several hybrid systems have been developed in order to reinforce films formed from natural polymers. As an example, we can mention the use of inorganic nanofibers [8–13], clay nano-reinforcements [14, 15] and blends with synthetic polymers [16–19]. Particularly, the reaction of graft copolymers between naturally-occurring materials and different synthetic monomers represents, these days, a strategy for preparing hybrid materials [4, 20–23]. The grafting of synthetic polymers is a convenient method for improving properties in natural polymers with minimal loss of the beneficial properties of the initial substrate. Thus, desired properties are added to the natural base material using particularly low amounts of synthetic monomers.

Isolated soy proteins (SPI) have useful properties that make this product an interesting starting material for the synthesis of graft copolymers. Nesteresko et al. reported several works where graft reactions were performed in order to improve microencapsulation capacity. They found that the grafting of fatty acid chains to soy protein by acylation improved its amphiphilic character and affinity with hydrophobic substances [4].

The graft polymerization of polyvinyl compounds on natural materials is mainly achieved by radical polymerization. The properties of the resulting graft copolymers can be widely controlled according to the characteristics of the grafted side chains. Poly(methyl methacrylate) (PMMA) is a vinyl polymer formed by radical polymerization of the methyl methacrylate (MMA) monomer. This material is a thermoplastic, hard and clear polymer having excellent optical properties with high-refractive index and good resistance to aging and weathering. Its breaking strength is seven times higher than that of glass, making it more resistant to impacts; yet, its main drawback is cost.

The grafting reaction of a naturally-occurring material, chitosan (Ch) with PMMA, was reported in the literature. The authors showed the biodegradation of Ch-g-PMMA composites, where 45 % of biodegradation rate occurred after 25 days in contact with an aerobic culture of *Aspergillus flavus* fungus. A study on the graft copolymerization of Ch with acrylonitrile (AN) is also reported, where a description of the optimal reaction conditions is found [20]. Here, the solubility of the prepared copolymer was investigated by using several solvents, confirming that composites had good film-forming properties. In addition, AN was also used in grafting reactions onto soy flour (SOY) via free radical-induced graft copolymerization to develop novel materials for multifunctional applications [24]. Then, SOY/AN-g-SOY composites were used as a reinforcement of PMMA matrix. Results of dynamic mechanical analysis showed that AN-grafted SOY exhibited marked reinforcement effects on PMMA composites. A further example of grafting reaction onto natural materials is related

with the research reported by Liu et al. In the work, the authors developed a novel adhesive based on undecylenic acid-modified soy protein composites. This development was carried out in order to improve the water resistance of the original material [25]. In the present research work, the use of MMA as monomer to be grafted on SPI is developed in order to obtain films with enhanced properties to be used in different applications as packaging. It is expected that this modification improves the mechanical properties of the initial material since MMA forms materials with rigid structures having a relatively low glass transition temperature (T_g). Furthermore, due to its structure, this component will contribute to the matrix hydrophobicity, enhancing properties where the role played by water is central.

In this research, physicochemical properties that have not been properly reported in the literature for SPI-g-PMMA films (contact angle, moisture content, total soluble matter, swelling, water vapor permeability and tensile assays) were assayed since they have major importance considering the potential application that these films could have.

Materials and Methods

Materials

The following chemicals were used: soy protein isolate (SPI) (SUPRO E with 90 % protein on a fat-free, dry-weight basis, donated by The Solae Company, Argentina), methyl methacrylate (MMA) (Sigma), ammonium persulfate (APS) (Anedra), urea (Taurus), sodium bisulfate (Cicarelli), sodium azide (Anedra) and KBr (Cicarelli).

SPI/MMA Grafting Reaction

An aqueous dispersion of 20 g of SPI in 400 mL of distilled water was prepared and 3.2 g of urea and 0.5 g of sodium bisulfite (protein unfolding agents) were added. The oxygen was evacuated from the system by a nitrogen stream and 0.75 g of radical initiator (APS) and 7.5 mL of the MMA were added dropwise. The reaction occurred for 4 h at 70 °C. Once the reaction proceeded at the specified time, the product was precipitated with 100 mL of ethanol for 24 h and successively washed with ethanol and acetone in order to remove the unlinked PMMA. The product obtained was freeze-dried and finely milled before being characterized by ^{13}C -NMR and FTIR.

FTIR Analysis

FTIR spectra were recorded in KBr discs on a FTIR Nicolet 5-SXC spectrometer under transmittance mode at

room temperature. Approximately 2 mg of dried sample was blended with 40 mg of potassium bromide (IR grade) and used to prepare a pellet.

¹³C-NMR Analysis

¹³C-NMR spectra were obtained on a Bruker Advance II spectrometer Ultra Shield 400 400.16 MHz equipped with tricanal inverse detection probe (BBI), and described in parts per million (ppm) relative to tetramethylsilane.

Determination of Grafting Yield and Efficiency

The achieved grafting yield (%G) and grafting efficiency (%E) were calculated in order to know the reaction results. These values were calculated on the basis of the increase in product weight after grafting reaction, as indicated by Eqs. 1 and 2. W_{gp} , W_{spi} and W_m represent the grafted SPI weight, SPI initial weight and weight of the monomer used, respectively.

$$\%G = (W_{gp} - W_{spi}) \times W_{spi}^{-1} \times 100 \quad (1)$$

$$\%E = (W_{gp} - W_{spi}) \times W_m^{-1} \times 100 \quad (2)$$

SPI and SPI-g-PMMA Film Preparation

After the synthesis and characterization of the grafted material, the preparation of films was performed according to compression molding with temperature.

A hydraulic press (CARVER, USA) was used. 1.5 g of SPI or SPI-PMMA powders were placed between two aluminum foils and compression molded to form films. Various experimental compression conditions were assayed. Those that yielded the best results were: initial temperature of 150 °C and pressure of 150 kg/cm² for 5 min with subsequent cooling at 80 °C while maintaining the pressure. After their preparation, SPI and SPI-g-PMMA films were stored at 25 °C and 50 % relative humidity (RH) for further characterization.

Film Characterization

Macroscopic Aspect and Thickness

The films were photographed with a digital camera (Nikon, Japan) in order to show their macroscopic aspect. Thickness was determined as the average of 10 measurements for each sample with a hand-held micrometer (Schwyz model ESP1-0001PLA, Schwyz, Swiss). The average of the films thickness was used for assessing mechanical properties and water vapor permeability.

Contact Angle Determinations

The contact angle (θ) measurements performed on the samples were carried out by sessile drop method using a homemade contact angle goniometer [26]. Contact angles were measured carefully from the left and right sides of the drop and subsequently averaged. The experiments were performed at room temperature using distilled water.

Moisture Content and Total Soluble Matter

Moisture content (MC) was determined according to a described method [27, 28]. Film samples were weighted (W_o) into glass dishes, dried in an air-circulating oven at 105 °C for 24 h and weighted again (W_i). MC for each film was determined in quadruplicate according to Eq. (3).

$$MC = (W_o - W_i) \times W_o^{-1} \times 100 \quad (3)$$

Total soluble matter (TSM) was determined according to a described method [27]. Dry and soluble matters were measured on different portions from each cast film trying to avoid cross-linking by heating the samples prior to incubation in water. For this, two portions of equal masses of each film were used, one was dried at 105 °C for 24 h and the other was directly immersed in beakers containing 30 mL of distilled water. Traces of sodium azide were also added to inhibit microbial growth. The beakers were covered and stored in an environmental chamber at 25 °C for 24 h with occasional stirring. The insoluble matter was then separated and dried in an oven at 105 °C for 24 h (W_f) to determine the solubilized dry matter according to Eq. (4). Initial dry matter values (W_i) required were extracted from the masses of the film portion that was dried. Different film specimens were used to measure initial and soluble dry film matter since proteins are susceptible to heat-induced cross-linking and this effect would decrease the TSM of the films [29]. The drying of the film at 105 °C for 24 h may result in the formation of new crosslinks (in addition of those produced in the compression molding procedure) which should not interfere with the measurement of TSM of the films since these crosslinks are not present in the original films. The measurements for each type of film were obtained in quadruplicate.

$$TSM = (W_i - W_f) \times W_i^{-1} \times 100 \quad (4)$$

Swelling Analysis

The swelling characteristics of the different specimens were studied in triplicate at different times. All the films were weighted (W_d) and immersed in 30 mL of deionized water for specific time intervals at room temperature. The

samples were removed from the swelling medium, wiped with a piece of tissue paper to absorb excess of water on the surfaces and reweighted (Ws). The swelling ratios (S) of the samples were calculated from Eq. (5).

$$S = (W_s - W_d) \times W_d^{-1} \times 100 \quad (5)$$

Determination of Mechanical Properties

In these analyses, each sample was cut into 25 × 100 mm pieces and stress–strain curves were performed. Tensile strength (TS), elongation at break (EB) and Young's modulus (E) were determined according to a standard method [30]. An Instron Texturometer (model 3342, Norwood, MA, USA) equipped with a 500 N cell was used at a 0.5 mm/s speed. For each sample, five measurements were made and averaged.

Determination of Water Vapor Permeability

The water vapor permeability (WVP) was determined in triplicate for all films according to the desiccant method described in the ASTM standard method [31]. Each film of 38.5 cm² (without physical defects such as cracks, bubbles or pinholes) was sealed onto an aluminum permeation cup containing dry CaCl₂. Once the films were held, the test cells were then placed in a humidity chamber at (75 ± 3) %RH and 25 °C. The permeability cups with the films were weighted at intervals of 1 h during 12 h. Linear regression was used to calculate the slope of a fitted straight line in a graph of variation of mass versus time. The water vapor transmission rate (WVTR) (kg s⁻¹m⁻²) and the WVP (kg m Pa⁻¹ s⁻¹ m⁻²) were calculated from Eqs. (6) and (7) respectively:

$$WVTR = F/A \quad (6)$$

$$WVP = (WVTR \times e)/[S_p \times (RH1 - RH2)] \quad (7)$$

where F is the slope of the graph of variation of mass versus time (kg s⁻¹), A is the test area (cup mouth area), e is the film thickness (m), S_p is the saturation pressure (Pa) at the test temperature, RH1 is the relative humidity in the humidity chamber, and RH2 is the relative humidity inside the cell test (0 %).

Statistical Analysis

Data for each test were statistically analyzed. The analysis of variance (ANOVA) was used to evaluate the significance in the difference between means. Tukey test was used for comparing mean values. Differences between means were considered significant when $P \leq 0.05$.

Results and Discussion

Synthesis and Characterization of SPI-g-PMMA Copolymer

The grafting reaction of PMMA onto SPI was assayed by proceeding, in a first step, to achieve PMMA graft on soy protein, and in a second step, to prepare the films. Hence, an aqueous dispersion of SPI was prepared and two agents promoting unfolding of protein chains such as urea and sodium bisulfite (reducing agent that breaks disulfide linkages) were added. Then, all the oxygen was evacuated out of the reaction system with a nitrogen flow and an aqueous solution containing the radical initiator (APS) and the monomer (MMA) was added. During the reaction, a foamy white solid was observed. Once the reaction proceeded for the specified time, the product was precipitated in ethanol for 24 h and washed successively with ethanol and acetone to remove the unbounded PMMA until verifying by FT-IR the absence of the synthetic polymer in the solvent. The solid obtained was dried and finely ground. The grafting reaction conditions can be extracted from the literature since many studies reported similar procedures [32–34]. The copolymerization mechanism of SPI and MMA was well described by Yang and co-workers for SPI and methacrylic acid, except that in the present work sodium bisulfite was used instead of β-mercaptoethanol as unfolding agent [33]. Sodium bisulfite was added since this compound cleaves disulfide bonds of SPI performing protein unfolding and exposing more carboxyl, sulfhydryl and amine groups of SPI. These groups were easily attacked by APS initiator to form the radicals to initiate graft copolymerization. Thus, the reaction mechanism was described by the following reactions:

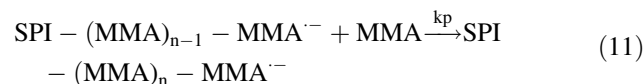
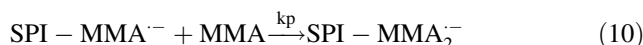
Radical formation:



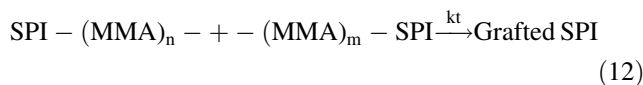
Initiation:



Propagation:



Termination:



where k_r , k_i , k_p and k_t are the constants of the radical formation, initiation, propagation and termination reactions.

The graft reaction was evidenced by FTIR and ^{13}C -NMR. Figure 1 shows the FTIR spectrum of the grafted protein, where we can see the appearance of the band at 1736 cm^{-1} corresponding to the C=O stretching of the ester carbonyl and at 1152 cm^{-1} to the C–O stretching of the corresponding ester. These bands correlate to the presence of PMMA. A well-characterized absorption peak at 1663 cm^{-1} corresponds to the carbonyl group of SPI [33]. Furthermore, a relative decrease in the intensity of the band at 1534 cm^{-1} corresponding to the N–H deformation of the primary amine was observed. It would indicate that the growing of PMMA chains could be initiated from radicals consigned from those functional groups [24]. A relative increase in the band at 1460 cm^{-1} corresponding to the deformation of methyl and methylene groups of the PMMA was also observed.

Moreover, by analyzing the ^{13}C -NMR spectrum of SPI, a single peak can be observed at 173.8 ppm corresponding to the carbon of the amide linkages. In contrast, in the spectrum of the grafted protein, two peaks which correspond to the carbonyls of amide (173.4 ppm) and ester (179.02 ppm), corresponding to the presence of PMMA, are observed. The appearance of the peak at 48 ppm corresponding to the carbon of OCH_3 in the PMMA can also be seen. Furthermore, the appearance of peaks at 56, 18 and 48 ppm corresponds to the presence of CH_2 , CH_3 and C carbons of PMMA, respectively. These data are in agreement with the ^{13}C -NMR spectra reported by Yang and co-workers for methacrylic acid grafted SPI [33]. In addition, a peak at 52 ppm observed corresponds to the presence of residual ethanol from the grafted polymer precipitation. Figure 2 shows the ^{13}C -NMR spectra of the protein and the grafted protein. By verifying the presence of PMMA in the grafted material by the two techniques mentioned above, and considering that the unbound PMMA was eliminated, it can be stated that the grafting reaction was successful [35].

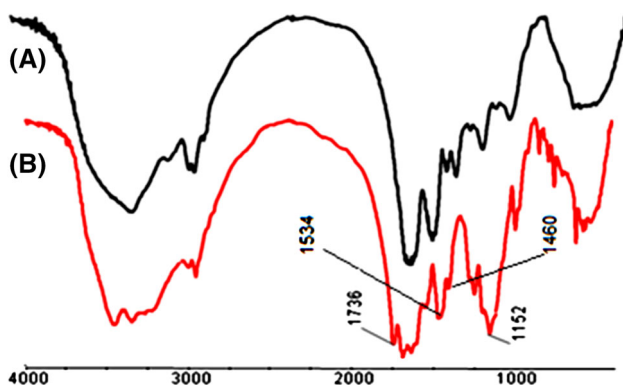


Fig. 1 FTIR spectra of SPI (a) and SPI-g-PMMA copolymer (b)

After the grafting reaction, the determination of the achieved grafting degree (%G) and the grafting efficiency (%E) was performed. %G denotes the amount of polymer grafted onto the backbone (SPI) and %E indicates the efficiency of conversion of the initial vinyl monomer on the grafted polymer. These values were calculated on the basis of the increase in matrix weight after reaction. From the respective determinations, it was found that %G was 27.04 % and %E was 15.34 %. By analyzing these results, the percentage of graft achieved was not high; yet, the modification yielded a product with good properties.

After obtaining this material, films were prepared following the compression methodology with temperature. SPI and SPI-g-PMMA films were obtained showing a homogeneous and yellowish aspect for SPI films. On the other hand, SPI grafted films showed a similar aspect in relation to control films. However, we observed the presence of areas where the intensity of the yellow coloration varied. In some areas, color was less intense, while in others, points of higher color intensity were observed. This effect was also reported by Shi et al. [36] who attributed this lack of homogeneity to points of unmelted material. Thickness values of control and grafted films were similar since equal amounts of soy protein and grafted-soy protein powders were used in the hydraulic press under equal compression conditions for the preparation. Table 1 displays thickness values and Fig. 3 shows the macroscopic appearance of the films.

Physical Characterization

The determination of the angle that forms the surface of the film with a water drop measured by the tangent at the three-phase interface (solid–liquid–vapor) serves to analyze the

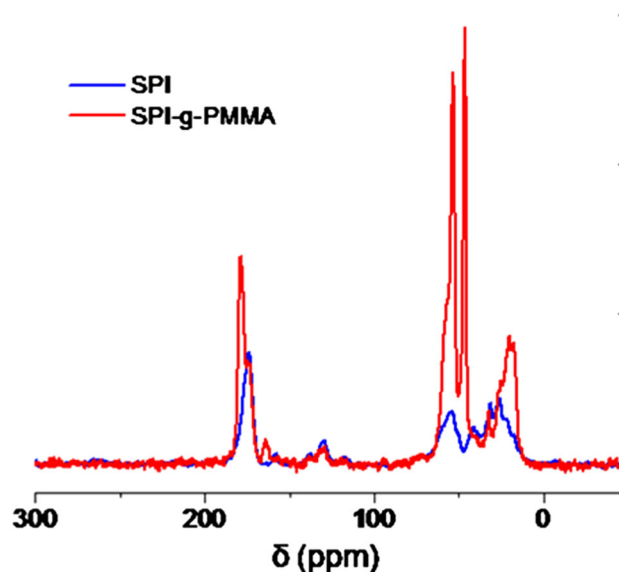


Fig. 2 SPI and SPI-g-PMMA RMN- ^{13}C spectra

structure of film surface, giving an idea of its hydrophilic/hydrophobic character. Due to the incorporation of a hydrophobic component such as PMMA, the value of the contact angle is expected to increase in the grafted film as compared to that in the SPI film. Table 1 shows the values of the contact angle (θ) determinations. A significant increase in contact angle was observed in the modified film, which becomes more hydrophobic in relation to the control film. As stated above, the greater hydrophobic character is directly attributed to the presence of PMMA that forms part of the film.

The increase in the hydrophobicity of the film causes changes in properties such as MC and TSM, where water plays an important role. From the results shown in Table 1, it can be observed that both MC and TSM decreased in PMMA grafted film. Undoubtedly, this behavior is attributed to an increase in the matrix hydrophobicity caused by the presence of PMMA, whose interaction with water is low.

Kaith et al. reported that MC of PMMA grafted SPI fibers decreased after grafting reactions. This decrease depended on the variation of the grafting yield. Similarly, these authors evaluated TSM in 1 M HCl and 1 M NaHO solutions, revealing that this value decreased with the increase in grafting yield. As we have previously stated, these authors affirmed that soy protein fiber became hydrophobic on graft copolymerization due to incorporation of PMMA chains, resulting in blockage of sites vulnerable to moisture absorbance [37].

Figure 4 shows the swelling in water determined for the films, as a function of time. The percentage of maximum swelling was reached at the same time for both films (6 min); yet, the maximum value in each sample was clearly different since the value reached in the modified film was markedly lower (60 %) than that observed in SPI film.

These effects can be ascribed to the increase in film hydrophobicity, where water has less affinity by the sample, showing less tendency to be incorporated within the matrix. In addition, the diffusion of water vapor is also diminished by this effect. This can be seen in the WVP values shown in Table 2.

Furthermore, mechanical properties were assayed in order to evaluate changes in the tensile behavior of the films according to the methodology described by ASTM [30]. A universal testing instrument was used to record the stress–strain curves for each specimen. From these, tensile

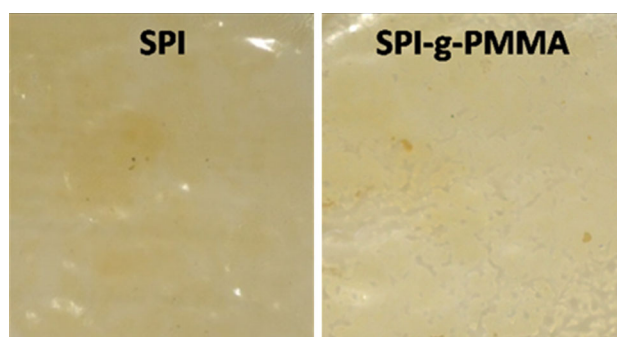


Fig. 3 Macroscopic aspect of SPI and SPI-g-PMMA films obtained by heat compression

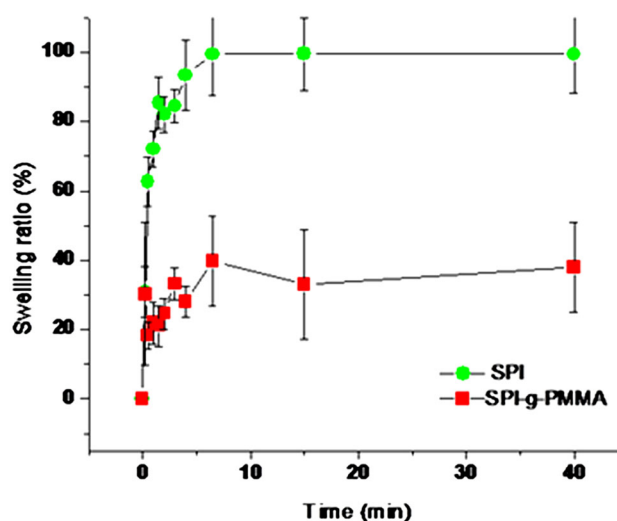


Fig. 4 Swelling in water as a function of time for control and grafted films

strength (TS), elongation at break (EB) and Young's modulus (E) were determined (Table 2).

PMMA is a highly rigid material, thus it is expected that the grafted material exhibits greater rigidity with respect to the unmodified material. The results evidenced this effect since grafted PMMA was more rigid with greater TS and E. The interactions between grafted PMMA chains are mainly responsible for the rigidity of the final material. Likewise, reduction in EB values was achieved yielding a less extendible material. An increase in TS was also reported by Shi et al. [36] for SPI-g-PMMA in relation to that for SPI film. However, an increase in breaking elongation values was reported by these authors ascribed to the presence of

Table 1 Determination of thickness, contact angle (θ), moisture content (MC) and total soluble matter (TSM) in control and grafted films

Film	Thickness (μm)	θ ($^\circ$)	MC (%)	TSM (%)
SPI	171 \pm 23 ^A	37.29 \pm 1.38 ^A	25.93 \pm 2.37 ^A	29.24 \pm 2.43 ^A
SPI-g-PMMA	168 \pm 16 ^A	43.13 \pm 1.08 ^B	19.09 \pm 1.15 ^B	20.58 \pm 2.76 ^B

Any two means in the same column followed by the same letter are not significantly ($P \geq 0.05$) different according to Turkey test

Table 2 Tensile strength (TS), elongation at break (EB), Young's modulus and water vapor permeability (WVP) of control and grafted films

Film	TS (MPa)	EB (%)	E (Mpa)	WVP (10^{-11} kg m Pa ⁻¹ s ⁻¹ m ⁻²)
SPI	8.7 ± 2.7 ^A	44.1 ± 5.5 ^A	1676 ± 325 ^A	19.9 ± 0.7 ^A
SPI-g-PMMA	19 ± 3.3 ^B	25.8 ± 3.1 ^B	3826 ± 379 ^B	9.4 ± 1.3 ^B

Any two means in the same column followed by the same letter are not significantly ($P \geq 0.05$) different according to Turkey test

PMMA homopolymer. It is important to note that this effect is produced by the addition of PMMA homopolymer to SPI matrix. In our study, the grafting of PMMA onto SPI produced a decrease in EB since a more rigid material was obtained with respect to SPI film. The grafting of PMMA onto SPI made films more resistant and durable.

Conclusions

In this research, a graft modification of SPI with PMMA and subsequent preparation of films are described. The use of this synthetic methodology for proteins was not widely reported in the literature. However, the methodology presented in this work was shown to be valid to improve the poor properties of natural materials with low grafting percentage. Films prepared from SPI-g-PMMA showed a greater hydrophobicity behavior than SPI films, resulting in a variation of important properties where water plays a fundamental role. In these determinations, improved water resistance was observed since the modified films were less swell able and less soluble than the control film. In addition, grafted films also showed a marked decrease in WVP in relation to the control film. Mechanical properties were enhanced yielding more rigid materials with higher TS and E.

This research represents an interesting advance in the preparation of hybrid biocomposites since physicochemical properties not properly reported in the literature were evaluated. The determinations reported here reveal that the grafted films are more resistant to the action of water. This modification increases the potential application of this material as food packaging where this property is needed.

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