A New Green Thermoplastic Polymer with Improved Hydrophobic Character

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Summary: A green thermoplastic polymer based on wheat flour was modified by the addition of a natural crosslinker genipin. Films of the polymer modified with different composition of genipin were prepared by extrusion. Free surface energy using contact angle method, moisture absorption test and hardness test were used to characterize the products. From moisture absorption and contact angle measurements, it was seen that for genipin amounts higher than 0.2% w/w, a hydrophobic character is achieved. Results obtained indicate enhancement in hydrophobic properties of the films.

Keywords: contact angle; crosslinking; genipin; green polymers; hardness; wheat flour

Introduction

In recent years, great progress has been achieved in the development of biodegradable products based on agricultural materials. Several natural polymers have been examined for the use in biodegradable plastic composites where starch has been considered as one of the most promising materials for this purpose because of its universality, renewability and low cost. It usually has two major components and appears as a mixture of two glucosidic macromolecules: amylose consisting of α – (1-4)-linked D-glucose and amylopectin having the same backbone as amylose but with myriad α-(1-6)-linked branch points. The uses of agricultural biopolymers which are easily biodegradable provide a potential new use for surplus farm production.[1]

The use of a by-product of wheat flour milling has been recently proposed with thermo physical properties very close to what it is expected by using starch alone.[2] In absence of additives, films made from starch or amyloses are brittle and sensitive to water (hygroscopic). These drawbacks can be overcome by the chemical modification of starch,[3] by crosslinking of starch,[4] and by blending starch with synthetic polymers,[5]

Genipin ($C_{11}H_{14}O_5$), with a dihydropyran ring (Figure 1) is found in the fruit of *Gardenia jasminoides Ellis*. Because it is a naturally occurring, biodegradable molecule with low cytotoxicity (About 5000–10,000 times less cytotoxic than glutaraldehyde), genipin has recently been investigated as a crosslinking agent in many biological applications.[6–9] This work report on the results concerning the modified wheat flour polymer by the help of a natural crosslinking agent namely genipin.

Experimental Part

Materials

The wheat flour was provided by Grands Moulins (Paris, France). After a dry division

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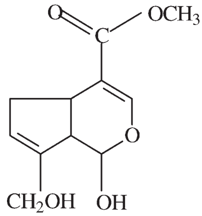

Figure 1.
Chemical structure of genipin.

of the cereal, the flour (which is a by-product of the food production) containing 7% w/w protein and 90% w/w of starch (amylose 20–30% and amylopectin 70–30%) were used for this work. Additives used for the fabrication of the films are glycerol, sorbitol, silicon dioxide and magnesium stearate of weight fractions 12.8%, 7.2%, 1%, 1.8% respectively having the laboratory quality. Genipin was provided by Wako pure chemical industries Ltd, Japan.

Preparation of the Blends

The wheat flour with different additives (sorbitol as plasticizers, magnesium stearate and silicon dioxide as the lubricants for extrusion) and genipin (0%, 0.02%, 0.1%, 0.2%, 0.3% and 0.4% w/w) were mixed well in a thermo regulated turbo mixer at a rotating speed of 750 rpm for three minutes. Then the plasticizers (glycerol mixed with water) were introduced slowly through a valve fixed on the lid. The mixture was extruded using a single screw extruder at 120 °C with a screw rotating speed of 60 rpm. Stress relaxation and stabilisation were performed on the pellets obtained by the above method by keeping the pellets at room temperature for one hour. A second extrusion using the same temperature and screw speed was performed to get the final films of thickness ≈2 mm, and kept under a constant temperature of 22 °C.

Sample Characterization

Moisture absorption measurements were done on samples ≈ 10 g (7 cm × 5 cm × 2 mm). Samples were dried in desiccators with P_2O_5 for 10 days. Then the samples were placed over saturated salt solutions of relative humidity equal to 75% in desiccators at room temperature (≈ 23 °C). The exposed samples were drawn out periodically to measure the moisture absorbed by the samples. The moisture absorption content (weight gain, W %) is calculated using the weight difference ratio

$$W(\%) = \left(\frac{W_1 - W_0}{W_0}\right) \qquad (1)$$

where W_1 is the weight after moisture absorption (saturation weight) and W_0 is the dry mass of the blends. The measurements were carried out on three specimens and the average value is calculated.

Surface tension measurements of films were calculated using contact angle measurements method. The contact angle of a drop of liquid on the surface of the material is an accurate way to determine the wettability and free surface energy. Three reference liquids, ultra pure water (milli-Q Water system resistivity 18 Ω/cm), glycerol and diiodomethane were used. All measurements were carried out at room temperature (23 °C). For each liquid, we made an average of five measurements. A drop of 3 μL deposited with a micro syringe was photographed with a black and white CCD camera (500 × 500). Contact angle (θ) was determined from a computerized contact angle meter (NFT communications company, Tours, France).

Hardness tests were carried out using Shore A durometer (Zwick 3100 Sodexim S.A, France) with ISO 868 providing a weight of 1 kN during 15 ± 1 seconds.

Results and Discussion

The composition of the material (wheat flour, plasticizers and lubricants) and role of each component were discussed in the previous works.[2,10] The results of moisture absorption for the matrix and blends are displayed in Figure 2(a). The expected sigmoid curves are obtained for all the samples but the steady state seems not

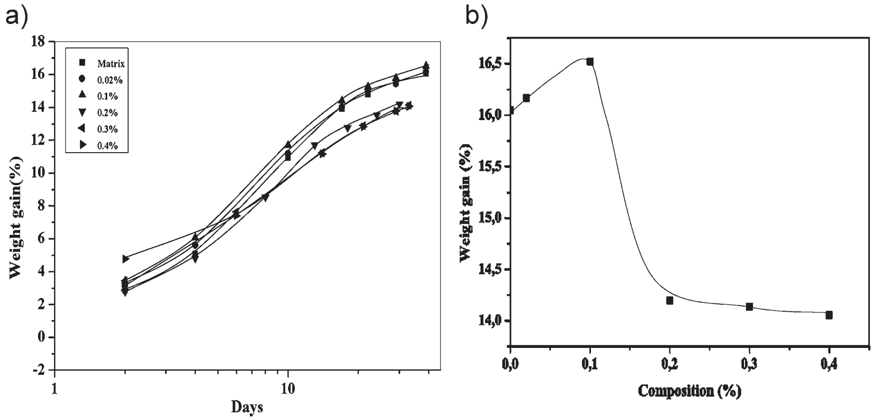

Figure 2.
Moisture absorption properties (a) Percentage weight gain of films with different composition of genipin (b) Total percentage weight gain (after one month) for films with different composition of genipin.

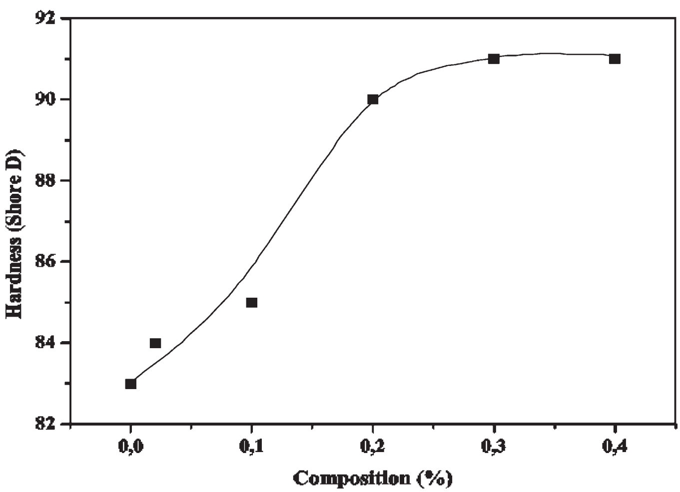

Figure 3.
Hardness of films with varying concentration of genipin.

reached for any composition. The value of the moisture absorption after one month as a function of the composition is given on Figure 2(b). A threshold is observed for a composition of 0.2% of genipin. Up to this composition, no effect of genipin against moisture absorption is observed, while for compositions greater than 0.2% a large decrease of the ability to water absorption is obtained. After this period, we observed the degradation of the samples by micro-organisms.

Keeping in mind that the nature of the sample surface can play a great role on the moisture absorption, we have tested the surface properties by means of mechanical and free surface measurements. Figure 3 displays the values of surface hardness for different composition of genipin. For composition greater than 0.2 w/w % the hardness of the surface has increased. This must be due to the crosslinking effect of genipin in the films resulting in harder and denser products.[11] At least 0.2% of

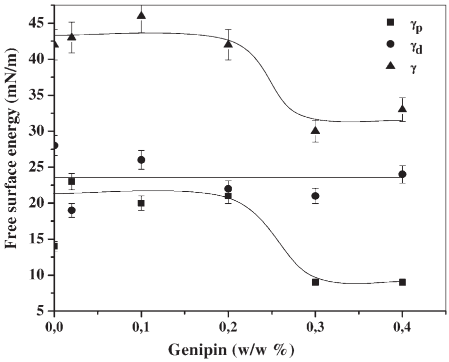

Figure 4.
Surface energy γ, polar factor γ_p and dispersive factor γ_d values for the different percentage of genipin (0, 0.02, 0.1, 0.2, 0.3, and 0.4w/w).

genipin was needed to modify the surface property of the blends.

The free surface energy of the blends has been obtained according to the Young-Dupré formula [12] and using the Owens Wendt calculation method for the contact angle.[13] With this method, the free surface energy (γ) is decomposed in two contributions γ_P for the polar part and γ_d for the dispersive part, i.e. $\gamma = \gamma_p + \gamma_d$. The measurement of free surface energies reveals the same tendencies. As Figure 4 shows, the free surface is modified if the amount of genipin is greater than 0.2 w/w %, and with a decrease of the polar component. The dispersive character of the free surface energy remains quasi constant. The change in polar component as shown by the reduction in the γ_p values explains the modification from hydrophilic to hydrophobic character [14].

From this last result and in agreement with previous observation concerning surface properties and moisture absorption measurement, it appears that the genipin incorporated in the matrix. The genipin crosslinks with the amino groups present in the proteins in the flour (proteins like Gliadin, Glutenin) through the reaction mechanisms shown in Figure 5. This explains for the increase of hydrophobic character by the reduction of primary amino groups, which is more hydrophilic than the tertiary amines.

Conclusion

The films of wheat flour polymer modified with a natural crosslinker, genipin, were successfully obtained by extrusion. The moisture absorption and surface properties of the blends were studied. The surface tension and absorption studies display a decreasing character in water absorption behaviour of the blends. It explains how

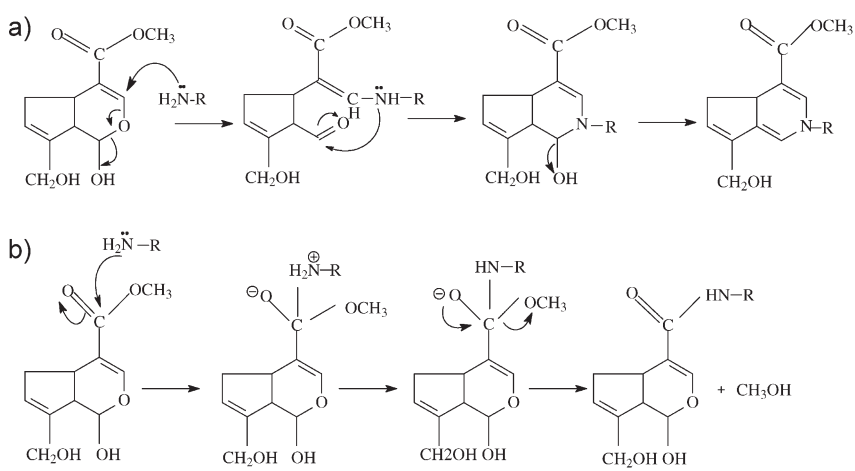

Figure 5.
The possible reaction mechanisms of genipin with amino group.

some of the hydrophilic amino groups are finally modified by crosslinking with genipin.

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