Comparison of chickpea and soy protein isolate and whole flour as biodegradable plastics

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Abstract

The objective of the present work is to compare some different crop products such as protein isolates and defatted whole flours from legumes, as chickpea and soy bean, involved in the molded compression processing to obtain plastics. The present work analysed the possibility of forming new plastic materials with products of chickpea, and soy bean seeds typically from the North West of Argentina, conditioned as chickpea isolate (CI), chickpea whole flour (CWF) in relation with soy protein isolate (SI) and soy whole flour (SWF). The blends containing isolates or defatted whole flour of chickpea, with the addition of glucopolysaccharide, glycerol and water as plasticizers were compression molded at 120°C, at 20 MPa, for 7 min. The glucopolysaccharide employed from this vegetals presented a ratio of amylose to amylopectin structure 95:5. The molded specimens were calculated for their tensile strength, percent elongation at break and water absorption. The chickpea isolate would be important in the production of plastic materials because of the best mechanical properties and the smallest water absorption. The chickpea whole flour product gave better material than soy whole flour product, even if the mechanical properties of both are lower than chickpea and soy isolates, respectively. Addition of boric acid in the blend induced a fall in water absorption in the case of soy plastics, but was not important in chickpea plastics. The effect of irradiation was to decrease water absorption in soy plastics and chickpea whole flour, while the effect on mechanical properties was not important.

Keywords: Biodegradable plastics; Chickpea proteins; Soy proteins; Agricultural plastics

1. Introduction

There is a continuous interest in the development of plastic materials that are biodegradable and that come from renewable resources. At the same time, there is interest in agricultural regions, to diversify the utilisation of their production to non-food products, in order to increase the value of their crops.

The truly biodegradable plastics are those that can be consumed by micro-organisms and reduced to simple compounds. One way to produce
biodegradable plastics is by using natural polymers based on starch, proteins and cellulose.

It has been shown that commercially available soy protein products such as soy isolates, soy concentrates and soy flour are useful for plastic production. One of the commercial soy products is the soy isolate. It consists of dehydrated storage proteins, and is prepared by precipitation at pH 4.5; its protein content is about 90%. The soy flour is characterised by protein content of about 56% and about 34% carbohydrates (Wolf, 1970; Kinsella, 1979; Salt et al., 1982). The North West of Argentina is a region where legume production is traditional. Chickpea and several kinds of beans, including soybean are among the main crops. Chickpea has been historically grown in that region and accounts for about 75% of the Argentine production of that legume. The production is either used as food or exported without any industrial processing. To obtain industrial uses of traditional crops is one of the goals for the technological development of the region (SECYT, 1997).

Our objective was to compare some different crop products of such legumes like soy and chickpea through processing them by compression molding to obtain plastics.

We avoided as far as possible to introduce modifications on the biopolymers in order to maintain the biodegradability, for this reason we choose plasticizers that would not alter this condition and are non toxic.

Boric acid is reported to be able to react in mixtures of glycerol and starch forming a network among starch chains and glycerol molecules (Yu et al., 1998).

We have also studied the effect of $\gamma$ radiation on protein isolates and defatted whole chickpea and whole soy flour on the properties of molded compounds.

Gamma radiation has been reported to affect starch by degradation (Pruzinek and Hola, 1987) and to promote protein crosslinking (Ressouany et al., 1998).

In an industrial process, irradiation is being used to improve reactivity of cellulose chains in the production of viscose (Stepanik et al., 1998).

2. Materials and methods

2.1. Materials

2.1.1. Cultivation

Chickpea (Chañarito) and soybean (6445) were obtained from the experimental stations belonging to the National Institute for Agricultural Technology (INTA) from Salta and Tucuman respectively, Argentina.

2.1.2. Protein isolates and flours

(1) Soy isolate (SI) was prepared in the laboratory by defatting the grounded seeds. Then, after an aqueous process the alkaline suspension was acidified to the isotonic point (pH 4.5), when the proteins precipitated. After neutralisation, the protein fraction was centrifuged and lyophilised. The material was kept at 4°C. (2) The chickpea isolate (CI) was prepared in a similar way; the isotonic point of predominant proteins was at pH 6 (patent pending). (3) Soy whole flour (SWF) and chickpea whole flour (CWF): were prepared at the laboratory by defatting the grounded seeds by Soxhlet extraction, milling and sieving the resulting material through a 230 ASTM mesh.

2.1.3. Glucopolysaccharides isolation

The powdered seeds were soaked in NaHSO$_3$, homogenised in a blender with water and the resultant slurry was squeezed in cheesecloth. The supernatant was decanted. The precipitated was submitted to several washes with: NaCl aqueous solution, NaCl/toluene (140:1), and ethanol/water in the ratios (1:3); (2:3) and (3:1) successively. The starch obtained was finally washed, dried and defatted by the Soxhlet method.

2.1.4. Purification

The $\alpha$-$\beta$, $\alpha$-$\beta,\alpha,\beta$ glucopolysaccharides were purified in Biogel P6 (100–200 mesh) before analysing its structural characteristics (the wavelength of maximum absorption and the polysaccharide spectra were analysed in a UV-VIS Beckman spectrophotometer).

The structural analysis of the $\alpha$-$\beta$, $\alpha,\beta$ linked glucopolysaccharides, was described in a previous paper (Salmoral et al., 1993).
2.1.5. Proteins:
Were quantified in the washing solutions by the Lowry method (Lowry et al., 1951).

2.2. Composition of blends

2.2.1. Isolate fractions
(SI) was prepared by mixing in a blender the isolate with glycerol (21.7%); starch (11.7%) and water (28%) (w/w in total batch basis). Chickpea blend (CI) was prepared in a similar way (patent pending).

The starch employed was obtained from legume species under study. It was purified and its structure was characterised; the ratio of amylose to amylopectin structure was found to be 95/5.

2.2.2. Whole flour fractions
To prepare the blends from CWF and SWF the same additives, proportions and conditions used for the isolates were followed.

2.2.3. Addition of boric acid
By adding 3% of boric acid the specimens were prepared as described before (w/w in total batch basis).

All the blends were kept at 4°C, 24 h for stabilisation in closed containers. Water content was chosen at 28% because we had previously found that mechanical properties of molded products gradually impoverished when the water content of the blend increased. We had also found that the addition of a plasticizer like glycerol was necessary to avoid excessive brittleness of the product (Salmoral et al., 1998).

2.3. Specimen preparation

Specimens were prepared from chickpea products (isolate and whole flour) with the same composition and following the same technique employed for soybean products that was reported elsewhere in detail (Salmoral et al., 1998). For comparison soybean specimens were simultaneously prepared, processed and tested.

The carefully homogenised mixture was left to stand to reach room temperature (23°C) in the same container and then submitted to compression-molded under the following conditions: compression load, 20 MPa; molding temperature, 120–130°C and molding time 7 min. In this way, plates of 0.7-mm thickness were obtained. Specimens for microtensile tests according to ASTM D-1708 (ASTM, 1984) were cut out of the plates and conditioned at 23°C and 70% of relative humidity for 48 h. The borders and edges were sanded as well as the surfaces with abrasive sandpaper. This kind of specimens was chosen in order to be able to prepare large numbers of specimens with relatively small amounts of material, for each kind of composition tested. The mechanical properties in this work are for comparative purposes among the different materials employed, not intending to define basic properties of the materials.

2.4. Irradiation

Part of the samples previously mixed and homogenised were irradiated with γ beams from a Co-60 source to a total dose of 50 kGy, at a dose rate of 9.5 kGy/h. The samples were packed in polyethylene flasks and no attempt was done to eliminate air. The temperature in the irradiation chamber never surpassed 30°C. The dosimetric measurements were performed by means of dichromate dosimeters for high doses. The homogeneity of dose within the samples was of 30%. The time elapsed from sample preparation to irradiation was kept constant at 24 h. From irradiation to compression molding it was also kept to about 24 h. In all cases irradiated and non irradiated samples were processed and tested in the same batch.

2.5. Mechanical testing

Tensile tests were performed by means of an Instron Model 1122 testing system. Crosshead speed was 1 mm/min. Tensile strength at breakage and percent elongation at breakage were measured using at least five specimens for each composition or treatment tested. The reported results are averages of the experimental values. We did not intend to measure the modulus due to the limitations pointed by ASTM D-1708. Tensile tests were performed after 48 h of conditioning specimens at 23°C and 70% relative humidity.
We considered it necessary to measure the moisture content of samples before mechanical testing (it was founded always lower than 1%) because the relative humidity conditioned was different from the standard condition of 50%.

2.6. Water absorption

The test applied was according to ASTM D 570 95 (ASTM, 1995). Three specimens having the same surface volume, ratio and area were conditioned for each treatment.

The specimens were stabilised for 24 h at 50 ± 3°C, then cooled in desiccator and weighed to a nearest 0.001 g. Then, the samples were immersed in distilled water for 2 h at 23 ± 1°C and immediately weighed to determine the absorbed water. The process was repeated.

2.7. Statistic of results

The results were analysed by means of the Student test.

3. Results

The mechanical properties, tensile strength (MPa) and % elongation of chickpea and soy bean shown in Fig. 1A, B.

We can see that the isolate product are superior to whole flour. The chickpea isolate product gives a plastic not significantly weaker, less strong but much isolates (CI), (SI) are comparing with chickpea and soy whole flour (CWF) (SWF) as it is more elongable than chickpea whole flour product (0.001 < P < 0.005).

In the case of soy plastics, the isolate compound has higher tensile strength and no significant difference in elongation than their whole flour plastic (0.05 < P < 0.1).

On the other hand, when both whole flours are compared the chickpea whole flour (CWF) has higher tensile strength (P < 0.001), than soy bean whole flour (SWF) but no significant difference in % elongation.

This behaviour of chickpea isolate shows a remarkable improvement in relation with brittleness with respect to the soy isolate plastic (P < 0.005).

Water absorption properties of the obtained plastics are shown in Table 1. Water absorption of the whole flours plastics is higher than that of the isolate products.

The soy bean whole flour (SWF) reaches almost 100% while the value for soy isolate (SI) is 39% (σ = 2). Water absorption for chickpea products resulted remarkably lower than the corresponding soy products 26% (σ = 0.7) in the chickpea whole flour (CWF) and 15% (σ = 0.43) in chickpea isolate (CI). The water absorption of chickpea whole flour is a quarter of that of soy bean whole flour.

3.1. The effect of boric acid in the blend

The effect on mechanical properties of the obtained plastics due to the addition of boric acid to the blends for molding can be seen in Fig. 2. The mechanical property of elongation was in general, slightly improved in (SWF) (P < 0.05), not important in the others materials, but decreased for (CI).

The tensile skength, neither presented significant changes with the exception of the soy bean whole flour product which was improved by about 75% (P << 0.001) with respect to the plastic without boric acid.

Regarding water absorption, the effect of boric acid addition does not benefit chickpea whole flour and chickpea isolate because such addition increases the water absorption slightly in both cases. On the other hand, soy products showed significantly less water absorption after the boric acid treatment; the ability to absorb water falls by about 20% in the case of soy bean whole flour.

3.2. The effect of γ radiation

The effect of γ radiation on mechanical properties of chickpea plastics can be seen in Fig. 3. In the conditions of irradiation employed there are no important effects except for the reduction in elongation of chickpea isolate plastic by about 50% (P < 0.001).

Tensile strength shows a slight improvement for chickpea whole flour plastic (0.01 < P < 0.02).
Irradiation treatment of both mixtures, chickpea isolate and chickpea whole flour reduced the water absorption, significantly in particular in the case of chickpea whole flour. In the case of soy products the effect of irradiation was slightly significant only for soy bean whole flour water absorption (74%, $\sigma = 1.9$) (Table 1).

4. Discussion

To interpret these results we should take into account the remarkable difference in chemical composition between the protein soluble isolates and the defatted whole flours. These flours have a heavy load of cellulose material that amounts to

Fig. 1. Mechanical properties of soy protein isolate (SI); chickpea isolate (CI); in comparing with soy whole flour (SWF); and chickpea whole flour (CWF). (A) Tensile strength expressed in MPa. (B) Elongation %. Blend, 66.4% of isolated or defatted flour; 11.7% starch; 21.7% glycerol.
17% in the case of chickpea and 21.9% in the case of soybean whole flour. This non protein material is absent in the case of isolates. The presence of other strong hydrophilic carbohydrate chains should also be considered like galactomannans in the ease of soy.

The protein quality is also important in the gelification process. The much higher elongation of chickpea isolate with respect to chickpea whole flour (Fig. 1B) can be understood in terms of improved protein–protein interactions but there may also be a better possibility of plasticization in the absence of cellulose material, because tensile strength did not result proportionally improved. The presence of cellulosics produces the same tendency in soy plastics, but in this case the mechanical properties of soy bean whole flour plastic proved to be poor in comparison with chickpea.

In this research we are using a glucopolysaccharide with a high content of amylose with respect to amylopectin and with a relatively low degree of branching points.

This composition proved advantageous with respect to the use of starch from different vegetal species that have high branching degree (Salmoral et al., 1998).

Polysaccharides possess complex structures because there are many types of inter-sugar linkages involving different monosaccharide residues. They can form secondary structures which depend on the conformation of component sugars, their weight, and the inter and intra chain hydrogen bonding (Srivastava and Kulshreshtha, 1989).

It would be easier to understand the proteic functionality if the model system submitted to test had only one type of protein. However, most of the protein ingredients available for industrial processing consist of protein mixtures and contain also appreciable amounts of carbohydrates, mineral salts, phenolics and other compounds. This is also the ease of the whole flours tested in this work.

Even if the protein isolates are purified, the structure as well as the functionality of their proteins could have been affected by the purification process.

There is remarkably different behaviour of chickpea isolate with respect to soybean isolate. Chickpea isolate produced a plastic about four times more elongable than soybean isolate with a tensile strength about 30% lower and a value of water absorption 2.5 times lower than soybean isolate.

It is known that total water absorption can increase with protein concentration and with pH changes through its influence on ionization; the amount of net change of protein molecules can alter the interactive forces of the proteins modifying their ability to associate with water.

In our case the chickpea isolate has a content of 70% protein and soybean isolate has 90%.

The water absorption is also influenced by pH. Isoelectric point of chickpea isolate is at pH 6 while for soybean isolate it is at pH 4.5.

In consequence, the plastic with highest water absorption is the one from soy whole flour (Table 1). In general the ability to absorb water was
about three times lower for plastics from chickpea than for soybean plastics.

Ionizing radiation affects organic compounds in general by breaking covalent bonds. This initial event is followed by reactions of the reactive species produced in the system. The reactions involved can produce, in the case of macro-molecules, new covalent bonds between chains (crosslinking) or rupture of chains with the consequent lowering of molecular weight.

There may be also oxidation products and insaturations. The magnitude of the effects depend on several factors: the chemical composition and structure of the irradiated material; the environ-

![Graph showing tensile strength and elongation of soy protein isolate (SI), chickpea isolate (CI), soy whole flour (SWF), and chickpea whole flour (CWF).](image)

Fig. 2. Effect of boric acid and mechanical properties of soy protein isolate (SI); chickpea isolate (CI); in comparing with soy whole flour (SWF); and chickpea whole flour (CWF). (A) Tensile strength expressed in MPa. (B) Elongation %. Blend, isolate or defatted whole flour + 11.7% starch + 21.70% glycerol + 3% boric acid.
Fig. 3. Effect of γ radiation and mechanical properties of chickpea isolate (CI) and chickpea whole flour (CWF). (A) tensile strength expressed in MPa. (B) Elongation %. Blend, isolated or defatted whole flour + 11.7% starch + 21.70% glycerol + boric acid 3%; irradiation 50 kGy.

...ment (presence of oxygen or water, temperature) and the intensity of the treatment (absorbed dose).

In our case, the irradiated material is a complex mixture that can experience molecular degradation in the special case of the starch; then, the crosslinking of protein chains and finally structure alteration of cellulose chains, with possible reduction in molecular weight and increased reactivity (report in preparation). The presence of water in the mixture would enhance the effect of radiation because of reactions of radiolysis products of water. On the other hand, glycerol could have an effect of radiation protection.

The expected effect of blend irradiation before molding was to improve the mechanical proper-
ties of molding compounds by the introduction of crosslinks. However, a positive effect could also be obtained in the case of whole flours water absorption by the rupture of bonds in the hydrocarbonated material, which that would eventually become more reactive.

Moreover, degradation of starch could result in the smaller molecules acting as plasticizers.

The obtained results in mechanical properties suggest that chickpea isolate blend could have some degree of crosslinking that would be responsible for the strong fall in elongation but the improvement in tensile strength is too small to be caused by an extended crosslinked structure. The small reduction of water absorption, suggests a minor structural change upon irradiation. On the other hand, there are evidences that no improvement in plasticization was produced, by the non appreciable effects on elongation and tensile strength. However, the fall in water absorption (from 26%, \(\sigma = 0.70\) to 18%, \(\sigma = 0.15\)) suggests that a structural change was induced by radiation.

The similar effects of radiation on soy plastics, regarding water absorption, suggests similar mechanisms but should be confirmed by results of mechanical testing which will be reported in the future.

Radiation effects on these mixtures should be further studied, possibly by investigating the behaviour of individual components in the conditions employed.

The boric acid effect observed (Fig. 3A, B) in the mixtures under study was a non important increase in elongation. However the chickpea isolate, became more rigid.

The effect on tensile strength was only important in soy whole flour and crosslinkings were induced by boric acid. This behaviour can be attributed to the carbohydrate content of SWF material.

However, in the case of soy plastics, a structural change is suggested also by water absorption which falls by about 20% both for soy isolate and soy whole flour.

5. Conclusion

A legume as chickpea would be important in the production of plastic materials.

Compression molding of blends containing either protein isolates or defatted whole flour of chickpea, with the addition of glucopolysaccharides characterised as predominantly amylosic with respect to amylpectin (95/5), water and glycerol as plasticizers produced plastic materials of acceptable properties.

The best mechanical properties and the smallest water absorption corresponded to chickpea isolate plastic (CI).

Chickpea whole flour product gave a better material than soy whole flour product, even if the mechanical properties of both are lower than chickpea and soy isolates.

The effect of boric acid in the blend was to induce a fall in water absorption at about 20% in the case of soy plastics, but was not important in chickpea plastics.

The effect of blend irradiation was to decrease water absorption in soy plastics and chickpea whole flour, while the effect on mechanical properties was not important.

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