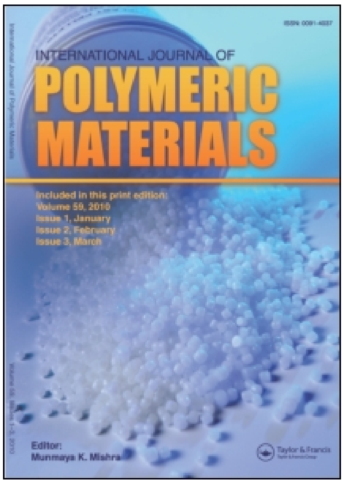

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effects of gamma radiation on a plastic material based on bean protein

M. E. Gonzalez[a]; E. M. Salmoral[b]; K. Traverso[b]; M. E. Floccari[c]
[a] Comision Nacional de Energia Atomica, Buenos Aires, Argentina [b] Faculty de Ingenieria, University Buenos Aires, Buenos Aires, Argentina [c] Faculty de Cs. Exactas y Naturales, University Buenos Aires,

To cite this Article Gonzalez, M. E. , Salmoral, E. M. , Traverso, K. and Floccari, M. E.(2002) 'Effects of gamma radiation on a plastic material based on bean protein', International Journal of Polymeric Materials, 51: 8, 721 — 731
To link to this Article: DOI: 10.1080/714975831
URL: http://dx.doi.org/10.1080/714975831

International Journal of Polymeric Materials, 51:721–731, 2002

0091-4037/02 $12.00 + .00
DOI: 10.1080/00914030290046273

EFFECTS OF GAMMA RADIATION ON A PLASTIC MATERIAL BASED ON BEAN PROTEIN

M. E. Gonzalez
Comision Nacional de Energia Atomica,
Buenos Aires, Argentina

E. M. Salmoral and K. Traverso
Faculty de Ingenieria, University Buenos Aires,
Buenos Aires, Argentina

M. E. Floccari
Faculty de Cs. Exactas y Naturales,
University Buenos Aires

The effect of gamma radiation applied to a system used for the preparation of biodegradable plastics was studied. The system was composed of the proteins and glucopolysaccharides previously isolated from Phaseolus vulgaris beans, mixed with glycerol and water as plasticizers.

The irradiation of mixtures with doses of 25, 50 and 100 kGy was carried out in two conditions: (a) before the compression molding process and (b) after mixtures were molded.

When the maximum applied dose (100 kGy) was applied to mixtures before the molding process, the plastic product obtained presented a deformation reduction of 62%, while the water absorption capacity increased by 20%.

When the previously molded products were submitted to gamma radiation, their tensile strength decreased by 20%.

The observed effects were attributed to different water content in each mixture and the eventual possibility of rearrangements giving rise to different structural interactions among starch and protein chains.

Received 27 December 2000; in final form 31 December 2000.

The authors wish to thank the Research and Doctorate Department, Engineering Faculty of Buenos Aires University, for financial support; Eng. L.F. Medina and the Experimental stations of National Institute for Agricultural Technology (INTA) for provision of seeds; the Semi-industrial Co-60 Irradiation Facility of Ezeiza Atomic Center for irradiation of samples; and the Dosimetry Laboratory of Ezeiza Atomic Center for dosimetric controls.

Address correspondence to M. E. Gonzalez, Comision Nacional de Energia Atomica, Av. del Libertador 8250 (C.P. 1429) Buenos Aires, Argentina. E-mail: maegonz@cae.cnea.gov.ar

A comparative analysis of biodegradability between irradiated and non-irradiated products is being carried on, with no differences observed up to the present state of the experiments.

Keywords: gamma radiation, biodegradable plastics, bean protein plastics

INTRODUCTION

The interest in using natural polymers to obtain materials for industrial use is due to, among other reasons, the problem of the final disposition of wastes and the convenience of employing renewable resources.

Proteins of vegetal and animal origin have been employed in films and thermoformed plastics [1, 2]. There are precedents about the preparation of biodegradable plastics from soy isolate and concentrate by means of compression molding [3].

The use of starch in plastic materials has been proposed as well as its incorporation as granule or gelatinized, in synthetic polymer matrixes to make them biodegradable or to obtain plastic materials exclusively from starch [4, 5].

In relation to ionizing radiation, gamma radiation or electron beams have been studied for decades regarding their interaction with polymers. Main effects observed in polymer irradiation are chain scission, with eventual reduction in molecular weight, and crosslinking, leading to the formation of 3-dimensional networks resulting in important changes in physicochemical and mechanical properties [6].

Based on those effects, the treatment of synthetic polymers with ionizing radiation originated well-established processes in the industry of pneumatics, cables, thermo-shrinkable materials, and radiation sterilization.

The effect of radiation on natural polymers such as proteins and polysaccharides has been studied mainly for food preservation and decontamination [7, 8]. However, since a few years ago, cellulose irradiation is being employed for viscose industrial production [9].

In contrast with certain chemical treatments of natural products, radiation processing does not interfere with the attack on natural products by biological agents. This aspect was utilized by several authors that have proposed radiation treatment of agricultural wastes for enhancement of different forms of bioconversion of lignocellulosic materials into chemicals, fuel or food [10 – 12]. In addition, natural rubber latex is claimed to be more readily biodegradable if it is radiation vulcanized than the conventionally sulfur vulcanized latex [13].

Ionizing radiation has also been proposed for the modification of starch destined to industrial use with different objectives: facilitate starch dissolution, important in paper industry and facilitate the incorporation of starch in mixtures of polyolefines to induce biodegradability [14, 15].

Irradiation of proteins to improve the mechanical properties of films and plastics has been reported [16–18].

In our laboratory we are engaged in the evaluation of the potential of diverse bean cultivations from the Argentine Northwest for the preparation of plastics based on polymers of protein and glucoside matrix obtained from by-products of beans [19, 20].

The object of the present work is to study the effect gamma radiation induces on a system constituted by a protein matrix with starch, glycerol and water. The system is destined to the production of biodegradable plastics.

We adhere to the concept that defines biodegradability as the intrinsic capacity of the material to be degraded by microbial attack to progressively simplify its structure and to be finally converted into CO_2, H_2O and/or CH_4 and a new biomass [21]. We are interested in evaluating the biodegradability of the materials that undergo an irradiation process.

EXPERIMENTAL

Cultivation

Phaseolus vulgaris bean was provided by Agr. Eng. Federico Medina, from Obispo Colombres Experimental Station and National Institute of Agricultural Technology (INTA) from Tucumán, Argentina.

Protein Soluble Fraction

It is a soluble protein fraction isolated from peeled and pulverized seeds, ground in a mill and defatted by the Soxhlet method. After homogenization at pH not higher than 7 the material was squeezed in cheesecloth to separate the cellulose material. It was decanted and the remaining suspension was concentrated by evaporation and finally lyophilized. It was kept at 4°C. The protein content was 50%.

Glucopolysaccharides

Process of isolation: the pulverized seeds were soaked, homogenized and squeezed in cheesecloth thus obtaining a supernatant that was decanted. The precipitate was submitted to several washes with NaCl in aqueous solution, NaCl in aqueous solution/toluene (140 : 1), ethanol/water (1 : 3), (2 : 3) and (3 : 1) successively. The starch obtained was finally washed, dried and defatted by the Soxhlet method.

The purification process: the α1,4–α1,6 glucopolysaccharides were purified in Biogel P6(100–200 mesh) before analyzing its structural characteristics (the wavelength of maximum absorption and the polysaccharide spectra were analyzed in a UV-VIS Beckman spectrophotometer).

The structural analysis of the $\alpha 1{,}4-\alpha 1{,}6$ linked glucopolysaccharides, was described in a previous paper [22].

Mixtures for Molding

The blends consisted in a matrix of protein and starch with glycerol and water as plasticizers. To obtain the blend, the starch was gelatinized with water. Glycerol was incorporated in the protein soluble fraction. The composition tested consisted of 51% protein, 30% of glycerol, 10% water and 9% starch. Proportions are given w/w with respect to total mixture weight.

Glycerol was of analytical quality and was employed without further purification.

Molding Conditions and Preparation of Specimens for Tensile Tests

Compression molding was carried out following the same technique described elsewhere [19].

The carefully homogenized blends were left to stand overnight. Then they were placed in a stainless steel mold to obtain type V specimens (ASTM D638-97), of 1.5-mm thickness. The molding was performed by means of a press with heating in both platens at 120 – 130°C, with a pressure of 20 MPa for 7 minutes. After having been taken out of the mold, the specimens were sanded with abrasive sandpaper to eliminate imperfections.

Irradiation

Radiation treatment was performed at the Co-60 facility of Ezeiza Atomic Center. Dose rate was 0.37 kGy/min., total applied doses were 25, 50 and 100 kGy. Applied doses were verified by means of high dose dichromate dosimeters. When the samples were irradiated as blends before molding they were packed in closed containers without elimination of residual air. When they were irradiated as tensile specimens, after molding, they were placed in sealed polyethylene bags.

Tensile Properties

Tensile strength (T, MPa) and percent elongation at break (e%) were measured. The specimens had been previously conditioned at constant temperature of 25°C and relative humidity 60% rh, during 48 h. Measurements were done by means of an Instron dynamometer model 1122. Tensile properties were measured using five probes for each composition. The measurement was done for comparative purposes, not intending to define basic properties of the materials.

Water Absorption Capability

The ability of the molded products to absorb water was measured according to ASTM D-570 1995. Samples of 8.0 mm × 15 mm and 1,5 mm thick were conditioned for 24 hrs at 50°C ± 3°C and weighed. The samples were immersed in distilled water for 2 hrs at 23°C and immediately weighed to determine the absorbed water.

Biodegradability

Biodegradability studies were carried out on the specimens utilized for tensile tests.

The degradation analysis of irradiated and non irradiated samples is carried out on 1500 ml Biometer flasks following ASTM 5988-96. The test fragments are buried in a laboratory mixture of 70% freshly collected top soil and 30% mature compost, and incubated at a constant temperature (23°C + − 2), constant water content (28%) and initial pH = 6.0. The rate of degradation is determined by CO_2 production trapped by KOH. The experiment is performed by triplicate using pure starch as a positive control.

Statistical Analysis of Results

The Student test was applied to analyze the results ($p < 0.05$).

RESULTS AND DISCUSSION

Our objective was focused on the evaluation of the radiation treatment for the improvement of some properties of molded compounds, without reducing the product biodegradability.

We intended to establish the influence that the conditions of the system at the time of irradiation have on the properties of the resultant products. For this purpose the system was irradiated in two different conditions: (1) before the preparation of the molded compound and (2) after the compression molding of the mixture.

Irradiation before the Molding Process

The proteins and the starch used to prepare the blends for molding were extracted from Phaseolus vulgaris seeds. All components included in the blends were non-toxic.

The blends prepared in quadruplicate were irradiated to total doses of 0, 25, 50 y 100 kGy and afterwards subjected to compression molding.

The specimens prepared as indicated in the experimental section were employed to carry out the tests for tensile properties, water absorption, and biodegradability. Specimens prepared from non irradiated blend were used as control.

We observed that when increasing radiation doses were applied to mixtures prepared in the same conditions, the % elongation at break gradually decreased from 134% (corresponding to the non-irradiated control.) to 50% (corresponding to 100-kGy radiation dose), what implies a reduction of 62% in elongation as can be seen in Figure 1.

This means that the material reduces its deformation capacity with growing dose, increasing its rigidity and becoming less flexible.

However, the tensile strength remains unchanged in the same conditions. In the same figure it is shown that no significant changes were detected on increasing radiation dose. This suggests that no outstanding changes in the material structure were produced.

We can assume that mainly the protein matrix component provides the cohesion that gives rise to tensile strength in this material, while the starch reinforces the structure. This assumption is based in the relation of proteins to starch in the mixture (about 5.7 : 1.0). In another work, dealing with soy plastics, we proved that the incorporation of a small amount of starch to the protein matrix rendered a product showing an increase of about 50% in

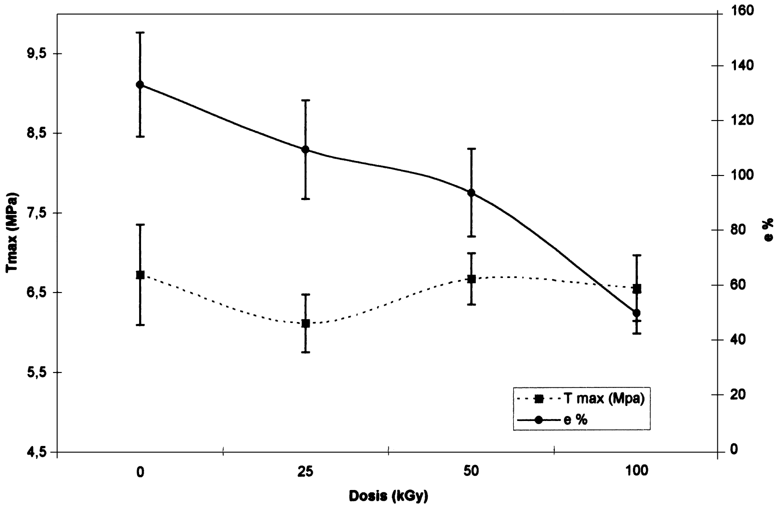

FIGURE 1 Tensile strength and % elongation at break of plastics molded after irradiation of the blend.

tensile strength while strongly reducing the % elongation [23]. The reinforcing effect of starch may be attributed to its ability to form intermolecular connections through hydrogen bonds and Van der Waals forces between glycoside chains and peptides.

Radiation effects on mechanical properties are usually most strongly reflected in % elongation, which is a property very sensitive to small structural changes [24].

When in our product the % elongation diminishes because of irradiation without noticeable improvement of tensile strength, it seems that the cohesion remains unchanged, that is, the structure formed by protein chains and additives present in the blend does not change significantly. Nevertheless, the lowered extensibility suggests that some kind of reinforcement effect has occurred.

It is well known that ionizing radiation affects the rheological behavior of starch, even with very low doses [25, 26]. This effect of radiation is attributed to covalent bond ruptures that modify the network interactions of polysaccharide molecules and to chain scissions that lower the average molecular weight.

The starch employed in this case possesses a high ratio of amylose with respect to amylopectin (95 : 5). It has been shown that amylose starch is more prone to degradation upon irradiation than amylopectin starch [14]. It might be assumed that chain scission of starch molecules occurs, lowering the molecular weight, particularly with the highest applied dose. Smaller chains formed in this way would have increased mobility allowing for more dispersed interactions with peptide chains. Moreover, it has been proved that a lowering of molecular dimensions in amylose-amylopectin systems would reduce the elongation because of the reduction in the range of the interactions domain, that is, a diminution results in the long-range coherence [27].

The water absorption ability increased by about 20% with applied dose of 100 kGy, while the effect of lower radiation doses was not remarkable (Tab. 1).

Although we could attribute the small initial reduction to crosslinking in the protein phase, the important increase observed after irradiation to a

TABLE 1 % Water absorption capacity of compression molded plastics. Measurements according to ASTM D-570 1995

Dose (kGy)	*Irradiation of blend before molding*	*Irradiation of molded plastic*
0	47.30	47.30
25	44.03	44.29
50	47.54	46.60
100	56.47	47.20

dose of 100 kGy could be better explained by the molecular modifications experienced by the starch. It would eventually have a structure with a much lower degree of intermolecular interaction allowing the incorporation of water to a greater extent.

On the other hand, we can not ignore the role played by glycerol in the mixtures studied. It has been demonstrated that the strong interaction between glycerol and starch in the presence of water influences the gelatinization and melting of granular potato starch when the ratio starch:water is 1 : 1, provoking disruption of the macroscopic, spherical ordering of amylopectin and amylose [27].

Glycerol interacts also with the protein matrix; the enhancing effect of glycerol on protein crosslinking by gamma radiation in the presence and water has been reported [28].

The high interaction forces between glycerol and starch and glycerol and polypeptide chains in the presence of water would thus influence the macromolecular structure and the reactions upon irradiation.

We can not neglect the possibility of crosslinking occurring to some extent in the protein phase, although we expected this effect would improve the tensile strength. This possibility must be studied in another experiment.

Irradiation of Moulded Specimens

The blend was prepared in the usual way and the compression molded specimens, after conditioning at constant temperature and humidity, were irradiated in separate bags to total doses of 25, 50 y 100 kGy. A set of specimens prepared at the same time was kept as non-irradiated control.

The specimens, irradiated and control, were used for the measurement of tensile properties, water absorption capacity and biodegradability analysis.

The results of tensile testing showed that Irradiation of molded specimens had scarce influence on % elongation. In contrast, tensile strength fell about 18% on application of the lowest dose, but no significant differences were noticed on increasing the dose (Fig. 2).

The product became less strong without losing its ability to elongate.

It has to be taken into account that when the mixtures were irradiated before the molding process, they contained about 10% water. On the one hand, in the case of molded product, irradiation was carried out after conditioning at 60% R.H. Water content of the product in this condition was found to be less than 1%. The difference in water content affects the effect of radiation due to reactions induced by ions and radicals formed as a consequence of the radiolysis of water. As a consequence, stronger effects would be expected when irradiation is carried out in the presence of water.

On the other hand, irradiation of molded product may affect the structures formed during the molding process but the heat and pressure

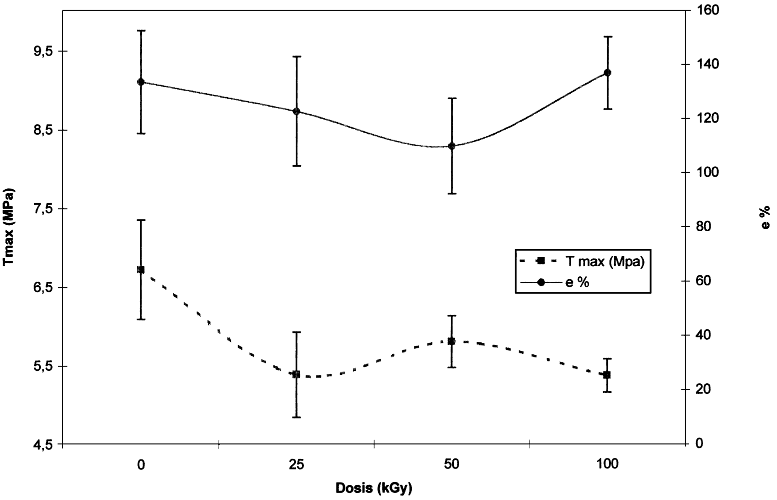

FIGURE 2 Tensile strength and % elongation at break of irradiated compression molded plastics.

process has already fixed the morphology. During the blending and molding process, the gelatinized starch disperses in the protein matrix achieving a certain order. The resultant morphology will not be able to change upon irradiation as long as no further heat processing is applied. Starch chains may suffer chain scission and become shorter but they will be kept fixed; the expected effects would be a lowering in the tensile strength because of lowering of high intermolecular interactions and increase in % elongation. In our case, we observed a moderate fall in tensile strength without alteration of % elongation. This effect could be attributed to a loss of the reinforcing ability of starch chains.

When we observe the results of water absorption capacity (Tab. 1), we can see a reduction of about 6% for the specimens irradiated with the 25-kGy dose but no changes for the applied doses of 50 and 100 kGy.

This results confirm that no remarkable changes in structure have been produced by irradiation in the dry state after the molding process.

Biodegradability

Although irradiation of natural products is not likely to make difficult the later attack by microorganisms, we considered important to compare the biodegradability of our irradiated products to those of non-irradiated controls. In this aspect, we applied the definition given in the Introduction.

The study on biodegradability was initiated utilizing the specimens for tensile testing corresponding to materials irradiated under both conditions: before and after the compression molding process, and to non irradiated controls.

After 10 days from the beginning of the experiment for biodegradability, a gradual degradation of plastics is observed.

During the indicated elapsed time, no significant difference was observed in the behavior towards degradation between control and irradiated materials.

The studies will continue with periodical controls. The results will be reported separately.

CONCLUSIONS

Irradiation of the blends containing protein, glycerol, starch and water, before the molding process occurs in the presence of enough water to render significant the effect of radiolysis of water. Besides, the mobility acquired by the lower molecular weight polysaccharide chains allows for the relocation of these fragments increasing the reinforcing effect in the protein matrix. We found a remarkable influence on product deformability that diminished by 62% and water absorption capability that increased by 20% when it is irradiated to 100 kGy.

The irradiation of previously molded products occurred under conditions of very low moisture and on a structure and morphology fixed by the molding process, The effects of low radiation dose (25 kGy) on plastic compound produced a reduction of 18% in tensile strength but it was not sufficient to affect % elongation or water absorption. Extensibility of the molded compound was not affected by irradiation.

Irradiated materials are biodegrade gradually up to 10 days of the beginning of the experience, without showing any evidence of differences between control and irradiated materials.

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