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Gluten-Based Bioplastics for a Controlled-Release of Active Agents

Diana Gómez-Martínez[1], Pedro Partal[1], Inmaculada Martínez[1]*, Antonio Guerrero[2], Críspulo Gallegos[1]

[1] Dpto. Ingeniería Química, Q. Física y Q. Orgánica, Universidad de Huelva. imgarcia@uhu.es
[2] Dpto. Ingeniería Química, Universidad de Sevilla.

In recent years there has been a great interest to utilize renewable biomass in the manufacture of high-quality, cost-competitive and biodegradable consumer goods as a means of reducing the dependence and consumption of petrochemical feedstock and of diminishing environmental pollution. This work focuses on the development of new bioplastic materials based on wheat gluten proteins containing an antimicrobial agent (i.e. lisozyme, formic acid, sorbic acid and/or essential oil compounds) by means of direct mixing of the proteins with a plasticizer, glycerol and active agent, and, eventually, a thermal and moulding process which shapes the materials and gives them suitable mechanical properties to be used as substitutive materials of synthetic polymers in certain applications. These mechanical properties have been evaluated by Dynamic Mechanical Thermal Analysis (DMTA) on both intermediate process material and on the final bioplastics. Diffusion and water absorption tests were carried out in order to study the influence of the above-mentioned treatments on the physico-chemical characteristics, controlled-release properties and rheological behaviour of these bioplastic samples. Protein-based bioplastics containing biocide have demonstrated antimicrobial activity and a suitable biocide release, which depend on the formulation and thermo-mechanical processing.

1. Introduction

Biopolymers from agricultural sources are becoming an interesting alternative not only as biodegradable films, suitable for food packaging, but also as plastic stuffs which require improved mechanical and controlled-release properties. These novel biopolymer applications include matrices for enzyme immobilization, matrices for controlled-release devices, active packaging, high water absorption and reswelling, etc. (Chen and Tan, 2006; Gómez-Martínez, et al., 2009).

In this sense, many different thermoplastic biopolymers have been developed and commercially produced using current levels of technology (Lörck et al., 2000). The main renewable sources of biopolymers are proteins, polysaccharides and lipids. Proteins are thermoplastic heteropolymers of both polar and nonpolar amino acids that are able to form numerous intermolecular linkages, and undergo different interactions, yielding a wide range of potential functional properties. Moreover, plant proteins are inexpensive, renewable and abundant raw materials (Song and Zheng, 2008).

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A way of processing protein-based biomaterials is the mechanical method, or thermoplastic processing, which consists of mixing proteins and plasticizer to obtain a dough-like material (Attenburrow et al., 1999; Jerez et al., 2007). The use of plasticizers reduces the intermolecular forces and increases the mobility of polymeric chains, thereby improving the flexibility and the extensibility of the film (Gao et al., 2006). Therefore, bioplastics can be processed using existing plastics processing machinery, including thermoforming, various types of injection moulding, compression-moulding, extrusion (films and fibers), and extrusion coating and lamination (Kim, 2008).

One advantage of these materials is that they can serve as vehicles of several types of additives, including antioxidants and antimicrobial agents, vitamins, flavors and colorants. Thus, there are several reports on the inclusion of such additives in biopolymer-based formulations in order to prolong the life span of foods (Han and Krochta, 2007; Gómez et al., 2009).

The aim of this work was to incorporate antimicrobial agents into gluten based bioplastics, manufactured by thermo-plastic or thermo-mechanical methods, and to determine their inhibitory effects against selected food pathogens for several aplications. In addition, it should be possible to use the advantage of the low solubility of proteins in water, as well as their water up-taking (swelling) properties, in order to develop controlled-realease matrices.

2. Materials and Methods

Wheat gluten was provided by RIBA S.A. Protein content was 83 wt.%, lipids 1.5–2 wt.%, and ashes 0.7–0.8 wt.%. Its moisture content was 8 wt.% on dry basis. Glycerol, from Panreac Química, S.A. (Spain), was used as protein plasticizer. The antimicrobials used in this study were formic acid, by Panreac Química, oregano essential oil from Destilerías Muñoz Gálvez, S.A. (Murcia, Spain) and clove essential oil supplied by Sigma-Aldrich (Spain). Plasticizer and antimicrobial agent/protein ratio was 0.5.

The thermo-mechanical processing was carried out in the kneading tool (Rheomix 600p) of a torque-rheometer (Polylab, Thermo Haake GmbH, Germany), equipped with two counter-rotating rollers turning at 50 rpm (Jerez et al., 2005). Both torque and temperature were recorded during the mixing process. The mixing chamber can be considered adiabatic. Compression-moulded biomaterials were prepared by compressing the dough-like materials obtained after the mixing process at 100 bar of pressure, in a 50x10x3 mm mould (Jerez et al., 2005). The compression-moulding process was carried out at 90ºC.

DMTA experiments were developed with a Seiko DMS 6100 (Seiko Instruments, Japan), using 50x10x3 mm samples in double cantilever bending mode. All the experiments were carried out at constant frequency (1 Hz) and strain (within the linear viscoelastic region), selecting a 2ºC/min temperature ramp with a temperature range from 20 to 170ºC.

Tests of the antimicrobial activity of the active packaging materials and the bioactive agents were performed in Petri dishes, where the appropriate solidified agar culture medium was inoculated with a solution of one of the microorganisms studied: *Aspergillus niger, Candida kefir, Bacillus cereus and Escherichia coli*. The inhibition of each tested microorganism by each of the tested materials was calculated by measuring the inhibition zone.

3. Result and Discussion

3.1 Processing of protein-based bioplastics

Bioplastic manufacture needs a complete mixing of all the components during the so-called thermoplastic processing. Figure 1 shows the evolution of both torque and temperature during the mixing process, at 50 rpm, for the different blends studied. Thus, the gluten/glycerol (G/WG) blend, without an active agent in its formulation, and the blends which contain in their formulation essentials oils (oregano and clove oil), present three different regions in their torque profiles. In the first region, also known as induction region, which corresponds to low mixing times, there is not a significant increase in torque. In the second region, torque undergoes an exponential increase with mixing time up to a maximum value. Finally, in the last region, an apparent torque decay is observed (Jerez et al., 2005). In the same way, three different temperature zones have been also found along the mixing process which are related to the above described torque regions.

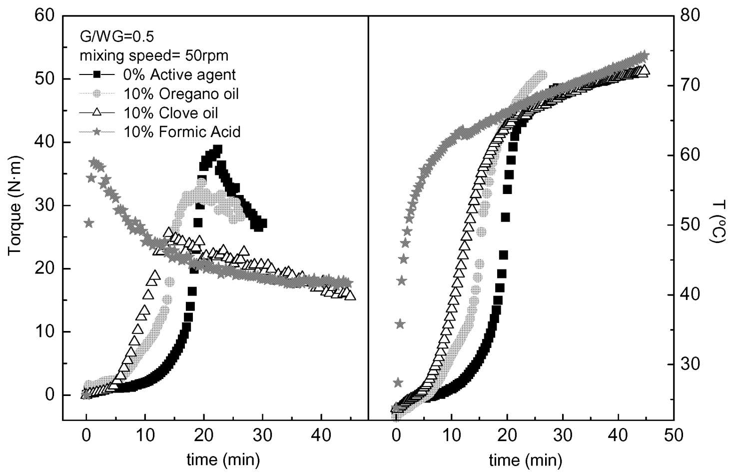

Figure 1: Mixing torque curves and temperature profiles during the bioplastic manufacture.

On the contrary, the sample containing formic acid in its formulation only presents two regions, characterized by an instantaneous increase in torque, up to a maximum value, and then a continuous decay down to steady state values.

Regarding mixing time, the occurrence of a torque overshoot suggests a dramatic evolution of gluten structure upon mixing. The final torque decay is associated with a change in consistency from powder/plasticizer dispersion to a cohesive and elastic material (Redl et al., 1999). When an active agent is added, the maximum value of torque (torque overshoot) is reached much faster than that obtained for the G/WG blend. The final temperature of the mixing process is close to 75ºC in all cases.

3.2 Thermo-mechanical behaviour

Protein-based bioplastics with very broad rheological characteristics can be obtained by combining different formulations and processing conditions. Figure 2 shows DMTA temperature sweep curves for different bioplastics manufactured by compression moulding and thermosetting of the dough-like materials obtained after mixing.

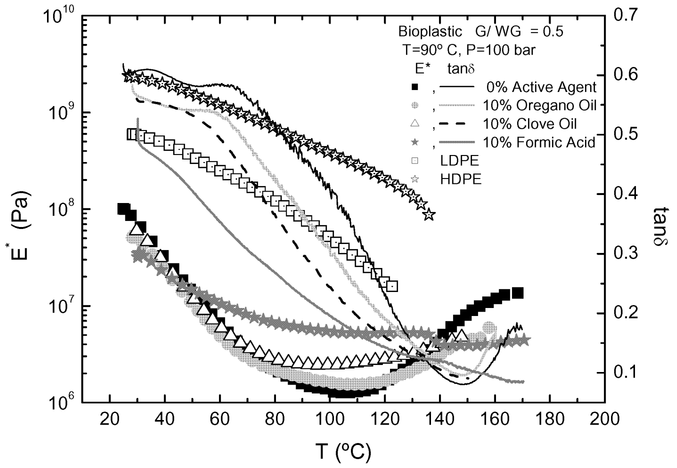

Figure 2: DMTA tests performed on bioplastics containing active agents.

Figure 2 shows the values of the complex modulus (E*), for gluten-based bioplastics, obtained by moulding at 100 bar and thermosetting temperatures of 90ºC. Initially, the complex modulus decreases down to lower values, showing a rubbery-like plateau region at ca. 100º C. However, a further increase is observed above this temperature of which extent depends on sample formulation. Thus, it is more evident for materials containing oregano essential oil and vanishes when clove essential oil or formic acid is present in the formulation (Figure 2). This last region would suggest that an apparent thermosetting potential remains in the sample without an active agent or with oregano essential oil. In order to compare the mechanical properties of these bioplastics with those corresponding to widely used synthetic polymers, complex modulus values, from DMTA temperature sweep tests, for commercial LDPE and HDPE are also shown in Figure 2. Gluten-based bioplastics with a plasticizer/protein ratio of 0.5 shows lower values of the complex modulus in the whole temperature range studied.

3.3 Antimocrobial activity

The antimicrobial effectiveness of bioplastics containing the bioactive agent on a selected microorganism was measured by the inhibition zone assay (Table 1). The inhibitory activity showed clear inhibition zones for all the microorganisms studied. The clove essential oil was more effective on *Aspergillus niger*. Bioplastic containing the tested bioactive agents have demonstrated a suitable antimicrobial activity (Table 1).

Table 1: Antimicrobial activity of bioplastics containing different bioactive agents Inhibition diameter (cm).

	Oregan oil	Clove oil	Formic Acid
Aspergillus niger	++	+++	++
Candida kefir	++	++	++
Bacillus cereus	++	++	++
E.coli	++	++	++

Inhibition diameter:
+++ (d >70 mm)
++ (20 mm< d <70 mm)
+ (d < 20 mm)

3.4 Controlled-release matrices

The release of an active agent from biopolymer systems has received considerable attention in the last years, because of their important applications in the fields of food packaging, biomedical, pharmaceutical, environmental and agricultural engineering. Previous results have pointed out that both processing conditions and bioplastic formulation may lead to materials with a wide range of mechanical responses and, therefore, microstructures. As a result, different swollen and release abilities should be expected. Figure 3 shows the kinetics of biocide release for bioplastics containing different antimicrobial agent. As may be observed, gluten based matrices are able to control the diffusion of the oregano essential oil for, at least, one week.

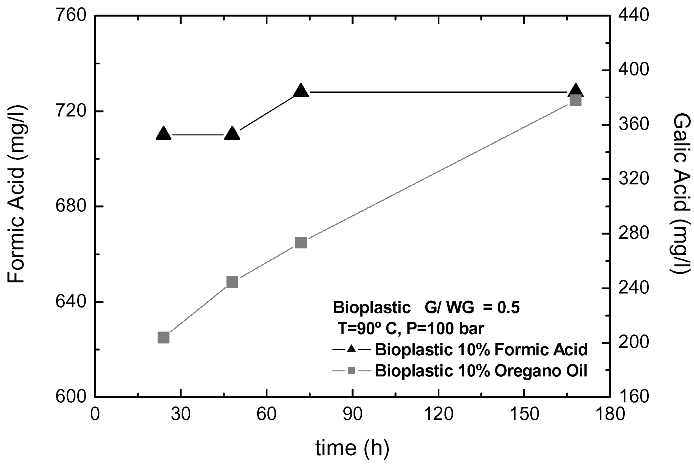

Figure 3: Controlled-release behaviour of bioplastics containing different biocide.

4. Conclusions

Gluten-based bioplastics with very broad rheological characteristics can be obtained by combining different formulations and processing conditions. Bioplastics containing the tested bioactive agents have demonstrated a suitable antimicrobial activity. In addition, gluten based matrices are able to control the diffusion of the active agent for, at least, one week.

Acknowledgements

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