European Polymer Journal 82 (2016) 324–333

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

A novel approach to manufacture porous biocomposites using extrusion and injection moulding

Alaitz Etxabide, Koro de la Caba, Pedro Guerrero *

BIOMAT Research Group, University of the Basque Country (UPV/EHU), Engineering College of Gipuzkoa, Plaza Europa 1, 20018 Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form 31 March 2016
Accepted 1 April 2016
Available online 1 April 2016

Keywords:
Biocomposite
Microstructure
Porosity
Processing
Extrusion
Injection moulding

ABSTRACT

Gelatin biocomposites were successfully manufactured by extrusion followed by injection. The employment of these industrial techniques, which have not been widely used in the case of biopolymers such as gelatins, represents an important advance for the development of gelatin-based biocomposites. Furthermore, the use of a non-enzymatic reaction to cross-link proteins provides a new approach to improve and control some functional properties, such as solubility and swelling. The addition of lactose in the formulations, as well as the heating of injected biocomposites, caused gelatin cross-linking, changing the protein structure towards the formation of pores and thus, solubility, density, and swelling decreased. Additionally, the cross-linked biocomposites showed good mechanical properties.

1. Introduction

Gelatin is the hydrolyzed product of the native collagen, an abundant structural protein found in animal tissues, including tendons, ligaments and skin [1]. Approximately 50,000 tons of gelatin are produced annually for medical purposes due to features such as biodegradability, hydrogel or film forming ability, biocompatibility, and commercial availability at a relatively low cost [2]. These characteristics allow gelatin to be an attractive candidate for the production of biocomposites [3–5]. However, the main limitation of gelatin for its use arises from its rapid solubility in aqueous media. With this regard, chemical cross-linking has been used to decrease solubility and natural compounds such as sugars have been added into the formulations to promote cross-linking [6,7].

Considering that the world production of freshwater fish in 2010 consisted of 33.7 million tonnes, of which up to 75% represents residues from filleting, and that approximately 30% of such residues consists of skin and bones with high collagen contents [8,9], fish gelatin seems to be an available biopolymer for industrial applications. Furthermore, due to its relative low melting point, gelatin can be processed by extrusion, which could increase its commercial feasibility. Thermoplastic extrusion is a versatile, highly efficient and continuous manufacturing technology, in which a wide range of thermo-mechanical and thermo-chemical processes are involved, resulting in physical and chemical modifications of the extruded materials [10,11]. Although extrusion is a well-established industrial technique, it has not been widely used for proteins. However, some recent works focused on the extrusion of soy protein [6], whey protein [12] and pea protein [13] suggest the possibility of extrusion as a suitable processing method for proteins.

* Corresponding author.
E-mail address: pedromanuel.guerrero@ehu.eus (P. Guerrero).

http://dx.doi.org/10.1016/j.eurpolymj.2016.04.001

The novelty of this work lies in the use of extrusion and injection as processing methods to manufacture fish gelatin biocomposites. Furthermore, different contents of lactose were incorporated into the formulations to give rise to chemical cross-linking by a non-enzymatic reaction, promoted by heating the biocomposites. Functional properties, such as solubility, swelling and mechanical properties, were analyzed and related to the changes observed in gelatin structure by differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Materials

A commercial cod fish gelatin type A was employed in this study. It has bloom 200, 11.06% moisture and 0.15% ash. Fish gelatin was kindly supplied by Weishardt International (Liptovsky Mikulas, Slovakia). Glycerol and lactose, supplied by Panreac Química S.A. (Barcelona, Spain), were used as plasticizer and cross-linking agent, respectively.

2.2. Biocomposite preparation

A co-rotating conical twin screw extruder, micro compounder Thermo Haake MiniLab II model (Thermo Fisher Scientific, Karlsruhe, Germany), was used to produce gelatin sheets. Extruder feed was prepared by mixing 40 g gelatin, 10 wt% glycerol (on gelatin dry basis) and different lactose contents (10, 20 and 30 wt% on gelatin dry basis) in distilled water (50 wt% on gelatin dry basis). The mixture was manually mixed until getting a homogeneous mixture. Afterwards, the extruder was fed at 1.6 g/min, barrel temperature was fixed at 90 °C, screw speed was set at 70 rpm, and the torque values ranged from 25 to 30 N cm. The thickness and width of the sheets obtained were 1.06 ± 0.19 mm and 3.79 ± 0.33 mm, respectively (Fig. 1a).

After cooling sheets, gelatin samples were cut into small squares and pellets were subsequently injected. An injector, Thermo Haake MiniJet II model (Thermo Fisher Scientific, Karlsruhe, Germany), was used to obtain fish gelatin biocomposites. Different injection moulds were used, depending on the properties analyzed, spherical moulds or bone-shaped moulds. Injected biocomposites were heated at 105 °C for 270 min (Fig. 1b). Heating time was selected according to a previous work [14], which showed that 270 min were required to promote changes in the secondary structure of fish gelatin by the addition of lactose, regardless of lactose content.

All samples were conditioned in an ACS Sunrise 700 V bio-chamber (Alava Ingenieros, Madrid, Spain) at 25 °C and 50% relative humidity for 48 h before testing.

2.3. Biocomposite characterization

2.3.1. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric measurements were performed in a Mettler Toledo TGA SDTA 851 (Mettler Toledo S.A.E., Barcelona, Spain). Tests were running from 25 °C up to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere (10 mL/min) to avoid thermo-oxidative reactions.

2.3.2. Differential scanning calorimetry (DSC)

DSC measurements were performed using a Mettler Toledo DSC822, provided with a robotic-arm and with an electric intercooler as a refrigeration unit (Mettler Toledo S.A.E., Barcelona, Spain). Samples (4.0 ± 0.1 mg) were hermetically

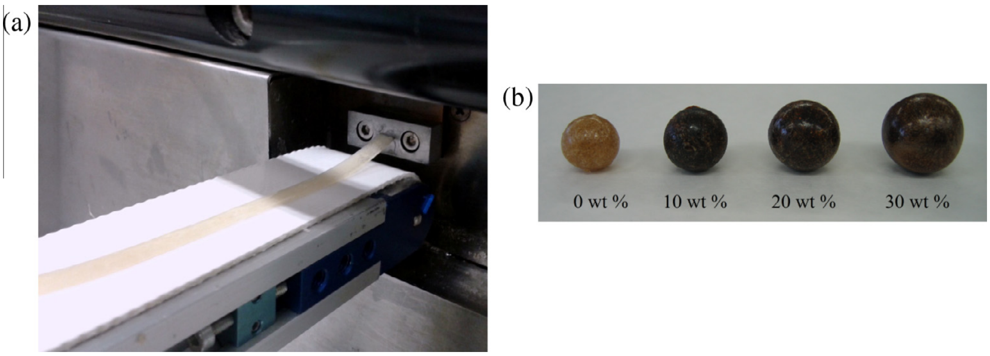

Fig. 1. (a) Continuous production of gelatin sheets by extrusion and (b) gelatin biocomposites obtained by injection after being heated at 105 °C for 270 min.