Industrial Crops and Products 66 (2015) 194–205

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Cellular structure and mechanical properties of starch-based foamed blocks reinforced with natural fibers and produced by microwave heating

A. Lopez-Gil[a,*], F. Silva-Bellucci[b], D. Velasco[a], M. Ardanuy[c], M.A. Rodriguez-Perez[a]

[a] *Cellular Materials Laboratory, (CellMat), Condensed Matter Physics Department, University of Valladolid, Paseo de Belén 7, 47011, Valladolid, Spain*
[b] *Ministério da Ciência, Tecnologia e Inovação–MCTI, Rua: Esplanada dos Ministérios, Bloco E, 01, CEP 70067-900 Brasília, DF, Brazil*
[c] *Departament d'EnginyeriaTèxtil i Paperera.UniversitatPolitècnica de Catalunya–Barcelona TECH, C/Colom, 11, E-08222 Terrassa, Spain*

ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form
17 November 2014
Accepted 13 December 2014
Available online 8 January 2015

Keywords:
Starch
Foam
Bicomposites
Biodegradable
Microwave heating
Natural fibers

ABSTRACT

The cellular structure and mechanical properties in compression of starch-based foams filled with natural reinforcements, such as grape wastes, cardoon wastes and barley straw fibers, have been studied in this work. The foams were produced by a microwave foaming process in which water is the plasticizer and at the same time the blowing agent. The use of thermoformed sheets as solid precursors for foaming allowed the production of foamed blocks with cells elongated in the expansion direction and with better properties in terms of rigidity and strength than foams produced in previous works by microwave heating of pellets. Moreover, the natural reinforcements increased not only the rigidity and strength, but also the toughness of these foams. Finally, the modeling of the compressive modulus using scaling laws shows how the stabilization of the cellular structure by the drying of the polymer matrix increases the rigidity of the solid cell walls. The flexible solid thermoplastic starch based precursor turns while foaming into a rigid starch-based foam, which could be suitable either for structural applications, due to its high stiffness and strength, or for packaging due to its complete biodegradability under controlled conditions.

1. Introduction

The plastic industry have made great efforts during the last decades to replace common petroleum-based polymers by biobased and biodegradable polymers as an alternative approach to recycling, incineration and energy recovery of plastic waste (Davis and Song, 2006; Taurino et al., 2010; Zare, 2013). Biodegradable polymers (Chandra and Rustgi, 1998; Yu et al., 2006; Gisha et al., 2011) are completely degraded by microorganisms in a few weeks under controlled conditions and the resulting compost is generally employed in agriculture fields (Lörcks, 1998; Kale et al., 2007). Among them starch is one of the most promising because of its low price and abundant world production. It is extracted from cereals and tubers in the form of semicrystalline granules composed of amylose and amylopectin (James and Roy, 2009; Andréa and Bertolini, 2010). Starch was originally used as filler in blends with synthetic polymers with the aim of increasing the biodegradability and at the same time the stiffness of the blend (Thakore et al., 2001; Park et al., 2002; Pedroso and Rosa, 2005). Later, the production of thermoplastic starch (TPS) extended the range of applications of this polymer. TPS is a mostly amorphous polymer that possesses properties similar to those of conventional thermoplastics. However, it is highly hydrophilic and therefore, its use in applications such as food packaging is not possible without being chemically modified or blended with other polymers. Currently, TPS can be found in packaging applications such as plastic bags (DaRóz et al., 2006; Leon and Leszek, 2009; Prachayawarakorn et al., 2010; Canché-Escamilla et al., 2011; Da Róz et al., 2011; Olivato et al., 2013; Lopez-Gil et al., 2014).

Starch based foams have been produced by several techniques but one of the most employed has been extrusion foaming to produce snacks in the food industry (Moraru and Kokini, 2003; Chanvrier et al., 2007; Elisa et al., 2012a; Elisa et al., 2012b) and loose fill chips for protective packaging (Lee et al., 2007; Pushpadass et al., 2008; Pushpadass et al., 2010). Baking is another technology that has been studied in detail (Shogren et al., 1998a; Shogren et al., 1998b; Shogren et al., 2002). It is a very simple process, which takes place in only one step. Nevertheless, cycle times are high and the cellular structures obtained are in general non-homogeneous. Microwave foaming is one of the most

* Corresponding author. Tel.: +34 983184035; fax: +34 983423192.
E-mail address: alopgi@fmc.uva.es (A. Lopez-Gil).

http://dx.doi.org/10.1016/j.indcrop.2014.12.025
0926-6690/

promising technologies for the production of foamed starch products. The origin of this technology dates back to the microwave expansion of popcorn (Hoseney et al., 1983) and to the production of a third-generation of snacks expanded by microwave radiation (Boischot et al., 2002). The main advantage of this method is that the increase in temperature comes from the interaction of water with the microwave radiation. The volumetric heating of the polymer and subsequent generation of steam is more homogeneous than in conventional techniques such as baking because water is homogeneously distributed throughout the polymer matrix after plasticization. Moreover, cycle times and energy consumption can be reduced with respect to conventional heating methods. There are a few previous works in literature in which thermoplastic starch pellets produced by extrusion are foamed inside microwave ovens either by free expansion (Boischot et al., 2002; Zhou et al., 2006) or by using molds to obtain specific shapes (Zhou et al., 2007). Boischot et al. (2002) reported the basics of starch foams nucleation and expansion under microwave radiation and the stabilization of the cellular structure by drying of the polymer matrix. This paper used starch based pellets as raw materials for the microwave foaming process. In the work of Zhou et al. (2007) a method to produce starch-based foamed blocks is described in which plasticized starch pellets are placed inside the cavity of a PTFE mold and later foamed by microwave radiation. However, the adhesion between the foamed pellets was poor resulting in foamed blocks with low mechanical properties in terms of stiffness and strength. In the work of Peng et al. (2013)a a microwave heated thermo-mechanical analyses was carried out to study the influence of additives such as glycerol and PVOH in the foamability of starch-based materials under microwave radiation. Moreover, the effect of microwave expansion in the dielectric properties of thermoplastic starch was studied by using a microwave calorimeter (Peng et al., 2013a; Peng et al., 2013b). Finally, the work of Sjöqvist and Gatenholm (2005) focused on foaming batters of starch containing water by microwave radiation instead of thermoplastic starch pellets produced by extrusion. In this way a production step is taken off from the production process because extrusion is not needed (Sjöqvist and Gatenholm, 2005).

Natural fillers based on cellulose have been widely used in blends with biopolymers to enhance their mechanical properties. In the particular case of starch-based foams several works were found in literature. In the works of Shogren et al. (2002) and Lawton et al. (2004) baked starch foamed trays for food packaging reinforced with aspen fibers were produced and characterized (Shogren et al., 2002; Lawton et al., 2004). Aspen fiber addition up to 15% resulted not only in increasing the strength of the foamed trays but also their flexibility. Jute and flax fibers with different aspect ratios were mixed with starch and later foamed by baking in the work of Soykeabkaew et al. (2004). When the amount of both jute and flax fibers increased up to 10%, the flexural modulus and the flexural strength of these foams also increased (Soykeabkaew et al., 2004). Kaisangsri et al. (2012) developed by using the baking process cassava starch-based trays in which kraft fibers were added in several concentrations resulting in an increase of both tensile strength and elongation at break (Kaisangsri et al., 2012). Glenn et al. (2001) produced several foams of starch with softwood fiber by baking resulting in an improvement of their flexibility (Glenn et al., 2001). Moreover, these properties were compared with those of commercial extruded polystyrene and paper board trays. Bénézet et al. (2012) also reported an increment of the mechanical properties when using different kinds of natural fibers such as wheat straw, hemp, cotton linter and cellulose in the production of starch-based foams by extrusion foaming (Bénézet et al., 2012). Nevertheless, as far as we know there are not papers dealing with the foaming by microwave radiation of starch-based composites reinforced with natural fillers.

In this work, starch based foamed blocks were obtained by a production method which consists of three steps: plasticization of starch with water by extrusion, thermoforming of cylindrical solid precursors and foaming by means of microwave radiation. The main difference with respect to previous works is that foams were obtained from thermoformed sheets instead from individual pellets with the aim of obtaining continuous foamed blocks with higher mechanical properties. Moreover, natural reinforcements such as barley straw fibers, grape waste and cardoon waste were blended with thermoplastic starch in order to improve the mechanical properties of the starch-based foamed blocks produced. These foams were characterized in detail by image analysis of the cellular structure and by mechanical tests in compression from where mechanical parameters such as the compressive modulus, the compressive strength and the energy absorbed were analyzed and discussed in terms of the materials structure.

2. Materials and production process

2.1. Raw materials

Native wheat starch (Meritena 200) provided by Tereos Syral was selected as the polymer matrix. Water was employed not only as the plasticizer of the polymer matrix but also as the blowing agent. Three natural reinforcements were selected with the aim of improving the mechanical properties of the polymer matrix: barley straw fibers, cardoon waste and grape waste. Barley straw fibers, which were kindly provided by the Department of Textile Engineering of the Unversitat Politècnica de Catalunya, were previously treated with hot water and with an alkaline solution with the aim of isolating the cellulosic fibers (Ardanuy-Raso et al., 2011). Matarromera Group (Spain) and Riberebro Group (Spain) provided grape and cardoon wastes, respectively, in the form of particles. These two last wastes were not chemically treated and they were used as received. These reinforcements from different natural origins were selected on the one hand, because of their chemical affinity with starch. They are mainly composed of cellulose which is a polysaccharide as well as starch. On the other hand, they were selected because each one have a different morphology in terms of shape, size and aspect ratio as will be described in the following sections. The inherent humidity of starch powders is 13 wt% (weight percentage) while that of barley straw, grape and cardoon fillers are 4.2, 3.5 and 5.1 wt% as specified by the suppliers. Finally, conventional salt was also employed because increases the absorption of microwave radiation and as a consequence allows reducing foaming times (Zhou et al., 2006).

2.2. Production of the solid precursors

Four formulations based on thermoplastic starch were produced: one of them without reinforcement and the other three with the addition of the natural reinforcements. These four formulations and their compositions expressed in weight percentage (wt%) are shown in Table 1.

First of all, a 3 mol/l solution of salt in water was prepared which in turn was employed to obtain a starch-based batter (70% in weight

Table 1
Starch based formulations.

Formulation	Thermoplastic starch[a]	Barley	Grape	Cardoon
WS	100	–	–	–
WSB	95	5	–	–
WSG	95	–	5	–
WSC	95	–	–	5

[a] 70% Starch/30% water solution of salt.