Industrial Crops & Products 108 (2017) 756–766

Contents lists available at ScienceDirect

Industrial Crops & Products

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

Effect of concentrated natural rubber latex on the properties and degradation behavior of cotton-fiber-reinforced cassava starch biofoam

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ARTICLE INFO

Keywords:
Cassava starch biofoam
Concentrated natural rubber latex
Cotton fiber
Degradation

ABSTRACT

Eco-friendly starch biofoams derived from natural rubber were fabricated in this study. To overcome their two main shortcomings, i.e., lack of flexibility and susceptibility to moisture, cotton fiber and concentrated natural rubber latex (CNRL) were incorporated into the biofoam products. Cotton-fiber-reinforced cassava starch biofoams were successfully prepared by compression molding using water as the solvent, a processing aid, and a blowing agent. The morphology and the physical, flexural, and thermal properties of the starch biofoams as a function of the CNRL content were investigated. The moisture adsorption capacity of the foam decreased with increasing CNRL content up to 5 phr (−73.4% and −41.78% at 0 and 100% RH, respectively). With increasing CNRL content, the hydrophobicity of the biofoam increased, as evidenced by contact angle measurements; this result suggested better moisture resistance and dimensional stability. The flexural properties of the biofoams were tuned by adjusting the CNRL content. With the addition of the CNRL content of 2.5 phr, the elongation of the biofoam clearly improved by 24%, with an acceptable decrease (−2.2%) in the bending modulus. Biodegradation by the soil burial test revealed that the degradation of the biofoam mainly proceeds by hydrolysis, and the addition of CNRL retards the degradation of the biofoam.

1. Introduction

Synthetic-polymer-derived plastic packaging adversely affects the environment. Recently, several efforts have been focused on the replacement of petroleum-based packaging products with biodegradable polymers. Starch biofoams have been widely recognized as one of the best choices for single-use packaging applications. Starch biofoams can be easily processed by extrusion, baking or compression, injection molding, and microwave heating using water as the blowing agent (Soykeabkaew et al., 2015). However, starch foams exhibit several disadvantages, e.g., poor flexural properties and high water absorption, that need to be resolved. The rigidity and water adsorption ability of the starch foams, as well as their flexibility, can be tremendously improved by the incorporation of hydrophilic reinforcing fillers, e.g., soft wood (Glenn et al., 2001), jute and flax (Soykeabkaew et al., 2004), sugarcane fiber and chitosan (Debiagi et al., 2011), wheat bran (Robin et al., 2011), natural fiber and chitosan (Kaisangsri et al., 2012), sugarcane bagasse fibers and montmorillonite (Vercelheze et al., 2012), nanoclays (Matsuda et al., 2013), lignin (Bhat et al., 2013), kraft fiber (Kaisangsri et al., 2014), malt bagasse (Mello et al., 2014), barley straw fiber, cardoon waste, and grape waste (Lopez-Gil et al., 2015), and cellulose (Rodríguez-Castellanos et al., 2015). Moreover, the blending of starch with other flexible, biodegradable polymers leads to the enhanced ductility of starch foam products with an acceptable level of reduction in other mechanical properties and provides environmentally compatible solutions for waste disposal.

Natural rubber (NR) is a biodegradable polymer that exhibits high elongation, high tensile strength, and good impact properties. Hence, the ductility of thermoplastics can be improved by blending with NR without the deterioration of its biodegradable property. For easy, efficient blending, concentrated NR latex (CNRL), which can flow at room temperature, was used rather than high-molecular-weight solid NR (Panrat et al., 2012). To formulate thermoplastic blends, easy processing via the mixing of CNRL with other ingredients can be carried out without energy consumption; therefore, the cost of manufacturing products decreases. Undoubtedly, the mechanical properties, e.g., strain at break, tensile strength, tear strength, impact resistance, and heat shrinkability, of most of the common packaging thermoplastics (polyethylene (PE) and polypropylene (PP)), have been improved by the addition of CNRL (Mahapram and Poompradub, 2011; Senna et al., 2008; Hassan et al., 2003; Ismail and Suryandiansyah, 2002; Oh et al., 2003; Shamsuri et al., 2009). Therefore, CNRL is a suitable plasticizer

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http://dx.doi.org/10.1016/j.indcrop.2017.07.046
Received 2 December 2016; Received in revised form 14 June 2017; Accepted 30 July 2017

for thermoplastics.

As mentioned earlier, starch biofoam is one of the most favorable renewable materials for replacing petroleum-based synthetic plastics. However, starch biofoams exhibit disadvantages of the lack of flexibility and adsorption of high moisture. To surmount these drawbacks, the use of cotton fiber and CNRL for the preparation of cassava-starch biofoams is examined. To the best of our knowledge, a limited number of studies have reported the use of CNRL as a hydrophobic filler for improving not only the flexural properties and water resistance but also the biodegradation behavior of starch biofoams. In this study, cotton-reinforced cassava starch biofoam filled with different content of CNRL was prepared by conventional compression molding. The morphology and the thermal, physical, and flexural properties of the starch biofoam were investigated as a function of CNRL. Finally, the biodegradation behavior of the two selected starch biofoams (e.g., with and without CNRL, respectively) was examined by the soil burial test. The blending of starch with cotton fiber and flexible NR in appropriate amounts leads to the increased flexural strength and hydrophobicity of starch foam products with an acceptable level of reduction in other properties and provides environmentally compatible solutions for waste disposal.

2. Materials and methods

2.1. Materials

Cassava starch was purchased from Bangkok Interfood Co., Ltd. Guar gum, bee wax, kaolin, and magnesium stearate (food-grade materials) were purchased from Chemipan Co., Ltd. Low-ammonia grade CNRL with a dry rubber content of 60% was obtained from Thai Rubber Latex, Suratthani, Thailand. Aqueous solutions of vulcanization ingredients included 10% KOH (0.3 phr), 50% zinc oxide (0.25 phr), 50% sulfur (0.5 phr), and 50% zinc diethyldithiocarbamate (0.5 phr). Glycerol (analytical grade) was purchased from Orec. Cotton fiber (Chopped into a length of 1 mm) was purchased from Bangplee Cotton Industry Co., Ltd. Calcium chloride and sodium chloride (analytical grade) were obtained from Merck. All chemicals were used as received without any further purification.

2.2. Preparation of starch biofoam

Various formulations of cassava starch biofoam (Table 1) were prepared using a conventional compression molding machine. Starch, cotton fiber, CNRL (pre-mixed with an appropriate amount of vulcanization ingredients), distilled water, and all additives were mixed using a kitchen Aid mixer at room temperature for 5 min or until a homogenous batter was obtained. Next, the homogenous batter was poured into a 300 × 300 × 3 mm^3 mold, which was placed in the compression molding machine. The mold temperature was set at 220 °C. The process was carried out at a pressure of 1000 atm for 4 min.

Table 1
Compositions of the starting materials per 100 g of dry cassava starch[a] and the areal porosity of the biofoams.

Sample name	CNRL (mL)	Cotton fiber (g)	Areal porosity (%)
CS	0	0	52.60
CS-C6	0	6	43.37
CS-C6-2.5NR	2.5	6	37.76
CS-C6-5.0NR	5.0	6	34.96
CS-C6-7.5NR	7.5	6	28.58
CS-C6-10NR	10.0	6	29.00

[a] Other additives, e.g. Guar gum (1 g), magnesium stearate (2 g), kaolin (15 g), beewax (20 g), glycerol (4 mL), and distilled water (115 mL) were added at fixed quantities for all foam formula.

2.3. Measurements

Foam density was calculated from the weight and volume (calculated from the apparent dimension) of a specimen. The specimens were conditioned at an RH of 50% at room temperature for 14 days prior to testing. The averaged values of density of at least five specimens were reported for each sample.

The dimensional stability test of a specimen was carried out by soaking a specimen with dimensions of 30 × 30 × 3 mm^2 in distilled water for 24 h. The dimensional change was observed by visualization.

The moisture adsorption of a specimen at an RH of 0 and 100% was examined by a gravimetric method. Prior to the test, five specimens of each sample were dried in an oven at 105 °C for 24 h and conditioned at an RH of 50% for 14 days. The specimen was weighed (W_o) before placing it into a desiccator in which the RH was controlled at 0% (silica gel) and 100% (distilled water). Then, the weight of the specimen (W_t) was recorded every hour for 12 h. The moisture content was calculated by the following equation:

$$\textit{Moisture content}\ (\%) = \frac{(W_t - W_o)}{W_o} \times 100 \quad (1)$$

The moisture adsorption rate was calculated from the slope of moisture content (y-axis) versus the time (x-axis) plot.

The water contact angle (WCA) on the foam surface was measured after a drop of DI water with an average sessile volume of 7 μL was set on the foam surface, and the side-view pictures of the droplet were recorded. Similarly, the oil contact angle (OCA) on the foam surface was measured after a drop of vegetable oil was set on the foam surface, and side-view pictures of the oil droplet were recorded. The averaged WCA and OCA values were obtained by the measurement of five randomly selected droplets.

The cross-sectional morphologies of the starch biofoams were investigated by scanning electron microscopy (SEM). The dried foam was mounted on a metal stub using a double-sided adhesive carbon tape and coated with gold. SEM micrographs of the composite films were recorded on a LEO-1450VP SEM instrument at an accelerating voltage of 15 kV.

To analyze the area porosity of the starch biofoam, the SEM micrographs were processed using the MATLAB program. First, image noise was eliminated using a median filter. Then, binarization was carried out, which separates the pore from the starch matrix via the selection of a suitable threshold. The values above the threshold were expressed by one value, and the zero value was used to replace the values below the threshold. Third, every region of the object in the image was labeled, and its pixel number was calculated. The area porosity of the biofoam was then calculated from the ratio of the pixel number of the pore to the pixel number of the total area.

Flexural tests were carried out in the three-point bending mode using a Testometric Micro 350 universal tensile testing machine, with a 50 N load cell equipped with tensile grips. Foam samples were cut into 25-mm-wide and 125-mm-long strips, and their thickness was measured using a digital micrometer. The support span and cross-head speed were set at 60 mm and 1 mm/min, respectively. The tests were carried out at 23 °C and at an RH of 55%. At least 10 specimens were measured, and the averaged values of the bending modulus, flexural strength, and elongation at break were estimated.

The thermal stability of a composite film was measured on a Pyris I Perkin Elmer thermogravimetric analyzer (TGA). A weighed sample (4–6 mg) was placed in a stainless pan and heated from 35 to 650 °C at a heating rate of 10 °C min^{-1} under nitrogen.

2.4. Biodegradation by the soil burial test

To study the biodegradation behavior of the starch biofoams, the soil burial test was carried out on a laboratory scale. Square specimens (25 × 25 mm^2) were buried in plastic cups containing gardening soil,