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ORIGINAL PAPER

Sunflower Oil Industry By-product as Natural Filler of Biocomposite Foams for Packaging Applications

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Abstract

The use of agroindustry by-products as reinforcements and/or composites filler is an innovative and economically attractive option that is still under study. Hence, the present work aims to study composite foams based on cassava-starch and sunflower oil press cake (SOPC), an oil industry by-product, using urea as an additive to enhance the biocomposites foaming capacity. Filler content (0, 20, and 40 wt%) and urea addition effect on foam morphology, physical properties and mechanical behaviour were analysed and compared to a benchmark polystyrene (PS) foam. In comparison with conventional PS foams, biofoams containing urea presented comparable mechanical properties yet higher hydrophilicity. Besides, formulations containing SOPC resulted in denser and harder materials and higher water uptake capacity than starch-based foams. Results provide further insights into biobased biodegradable foams development using agroindustrial residues as raw material and urea as foaming agent, with promising characteristics for food packaging.

Keywords Starch foams · Renewable materials · Biodegradable · Fibrous fillers · Disposable packaging

Introduction

Global plastic pollution awareness has launched numerous investigations on biodegradable materials in the last decades. Reports show that packaging is one of the main plastics demanding industries as well as one of the major plastic waste sources, especially due to single-use containers production [1]. In this context, starch is considered the natural polymer with the greatest possibilities of being used on an industrial scale, due to its availability, performance, and low cost [2]. Nowadays there are some starch-based commercially available bioplastics, mainly composite blends of starch with other biodegradable polymers such as polylactic acid (PLA), polybutylene adipate terephthalate (PBAT), polycaprolactone (PCL), polybutylene succinate (PBS) and polyhydroxyalkanoates (PHAs) [3]. Moreover, foamed materials are widely used in the packaging industry, thus the use of starch for obtaining biodegradable biobased foams is a promising alternative to petroleum-based polymer expanded materials for single-use packaging. Some results have shown that starch-based foams require lower consumption of non-renewable energy resources (50%) and have lower greenhouse gas emissions (60%) compared to conventional expanded polystyrene (PS) containers [4]. Furthermore, biodegradable polymers also contribute to the reduction of plastic waste generation, especially those derived from food containers and disposable cutlery for which recyclability is water demanding and rather difficult, hence not preferred. Consequently, biodegradable foam-like materials have been developed using a wide range of bioplastics [5–9].

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Several processing methodologies have been reported in the literature to obtain biodegradable foams. As reviewed by Soykeabkaew et al. [2], the most common are extrusion, baking (thermoforming), microwave, freeze-drying/solvent exchange, and supercritical fluid extrusion. Thermoforming process starts with a starch–water based suspension preparation in a mechanical stirrer until a homogeneous batter is obtained. This paste is later added to a preheated mould and subjected to the baking process at standardised moulding time, temperature, and pressure according to the batter formulation [10]. During this process, starch gelatinisation occurs, the surplus water is evaporated, and the vapour generated favours the batter expansion, filling the mould. Some additives have been reported to be typically used in starch-based foam formulation: magnesium stearate is used as release agent, guar gum as solids stabilisers, and glycerol as plasticiser [11].

A key problem of starch-based materials is their inherent hydrophilic and brittle character that restrict their development and applications. One of the alternatives to overcome these limitations is the incorporation of natural fibres as reinforcement agents [2, 12–14]. In this respect, Machado et al. [15] indicated that cassava-starch expanded materials containing 20% or more of sesame cake particles as reinforcing agent, presented similar mechanical properties than those of expanded PS. Other agroindustrial by-products and residues have been studied as fillers of biobased foams, such as peanut skin, coconut fibre, and fish scales [16–18]. In this regard, one of the main by-products from sunflower oil extraction: SOPC, is a fibre and protein rich residue, which has proven to be a promising raw material for biocomposites [19–21].

Urea is a compound with a highly polar structure, which has been reported to have a plasticizing effect [22–27] and crosslinking capacity on starch matrices [28–30]. Over 150 °C urea decomposes in urea-TPS matrices [27, 31],], forming NH_3 and CO_2 as pyrolysis reaction products [32–34], which can contribute to the foaming process [31].

Consequently, the present work intends to study the effect of sunflower oil by-product addition as reinforcing agent (0, 20, and 40 wt%) on morphology and properties of expanded materials based on cassava starch obtained by thermocompression. Urea was also studied as additive, considering both its plasticising and cross-linking properties in starch matrices and its foaming capacity.

Experimental Section

Materials

Cassava (*Manihot esculenta*) starch from Cooperativa Agrícola Mixta de Montecarlo (Misiones, Argentina) and sunflower oil press cake (SOPC) pellet from AGD (Córdoba, Argentina) were used. Dried SOPC was crushed, sieved (through a 500 µm mesh sieve), and its main components were determined using AOAC (1990) standardized methods: lipids (Soxhlet), proteins (Kjeldahl), ash (gravimetric), fibre (Neutral Detergent Fibre), and moisture content [35]. All results were expressed as percentage on a dry basis over a minimum of two replicates.

Particle size distribution (PSD) of SOPC was studied using a Horiba Partica LA-950 Laser Diffraction Particle Size Distribution Analyzer (Kyoto, Japan) analysing approximately 5 g samples. Thermal gravimetric analysis (TGA) of SOPC was carried out in a thermogravimetric balance TA Instrument Discovery Series (New Castle, USA); approximately 10 mg samples were heated from 30 to 700 °C at 10 °C/min under nitrogen flow. For both tests four measurements were performed yielding the same results, thus only one of each them are presented.

Glycerol and urea (CAS# 56-81-5 and CAS# 57-13-6, Biopack, Argentina) were used as plasticizer and foaming agent, respectively. Besides, guar gum (Saporiti SA, Argentina) was employed as suspension stabilizer and magnesium stearate (CAS# 557-04-0 Parafarm, Argentina) as a removal agent.

Foams Preparation

Water-based batters containing 50 wt% of cassava starch with different contents of ground SOPC (R) were prepared: 0, 20, and 40 wt% (with respect to total solids content). In all formulations, glycerol (5 wt%), guar gum (1 wt%), and magnesium stearate (1 wt%) were added. Other batters also contained urea (5 wt%) as foaming agent. Samples were named #R and #RU, being # the amount of SOPC percentual content and U was used as an indicator of urea addition. The final composition of the studied formulations is shown in Table 1. The resulting batters were stirred for 10 min with a mechanical mixer.

Expanded materials were obtained by thermocompression in a steel mould (3 mm × 12.5 mm × 75 mm) with a steam exhaust vent, using a hydraulic press at 100 bars. The mould was preheated to the processing temperature and approximately 3 g of batter were placed in the centre of the mould before closing the lid. The pressing temperature and time were optimized for each formulation, being the assayed conditions: 130, 140, 155, and 170 °C and 3.5, 5, and 7 min, respectively.

Commercially available expanded PS sheet samples (4 mm thick) from Bandex (Argentina) were used as benchmark material.

Table 1 Batter formulations for cassava starch and sunflower oil press cake (SOPC) based biocomposite foams

Sample	Starch	SOPC	Glycerol	Urea	Guar gum/ $Mg(C_{18}H_{35}O_2)$	Water
0R	50	–	2.5	–	0.5/0.5	46.5
20R	40	10	2.5	–	0.5/0.5	46.5
40R	30	20	2.5	–	0.5/0.5	46.5
0RU	50	–	2.5	2.5	0.5/0.5	44
20RU	40	10	2.5	2.5	0.5/0.5	44

All contents are expressed as wt%

Foams Characterization

Samples were cryofracture with liquid nitrogen for foams cross-sections observation by scanning electron microscopy (SEM), using an electron microscope JEOL 35-F (Japan). Cryofractured biofoams were mounted on bronze stubs using a double-sided graphite tape and covered with a thin gold layer (40–50 nm). All samples were analysed using an acceleration voltage of 10 kV under high vacuum mode. Cell diameters were measured using a licence free image editing software (ImageJ).

Samples colour was studied with a Konica colorimeter (CR 400, Japan), according to CIELab scale [36]; eight measures were made along the surface on each side of foam specimens.

Density was determined considering the weight and the volume (determined by means of sample length, width, and thickness measured with a thickness gauge) of at least 10 probes.

Materials moisture content and their water uptake were assessed by drying until constant weight in an oven at 105 °C and by weight gain kinetics study over 4 days in a controlled atmosphere (100% RH and 20 °C), respectively. Swelling and solubility in water were determined gravimetrically after immersion in distilled water at room temperature for 1 h and, in the case of solubility determination, further drying until constant weight in a ventilated oven at 105 °C. Both assays were performed at least in triplicate.

Mechanical properties were studied by three types of assays: compression and puncture tests in a Brookfield CT3 texturometer (USA) and three-point flexure test in a TAxT2i texturometer (UK) according to standardized methods ASTM D1621-10 (2010), ASTM F1306-90 (2001), and ASTM D 790-03 (2003), respectively. For compression tests 12.5 mm × 12.5 mm foam samples were compressed to a 40% of the original thickness using a 12.7 mm diameter disc probe at 0.01 mm/s compression rate. Puncture tests were performed with a 2 mm cylindrical probe at a 1 mm/s rate until complete perforation of the sample on foam square samples (12.5 mm × 12.5 mm). Three-point flexure tests were conducted on 75 mm × 12.5 mm × 3 mm samples until a 40% deformation at 0.4 mm/s. At least 6 to 10 replicates were assayed per sample.

Biodegradation under composting conditions was performed as described in a previous work [37], employing three test samples per extraction time.

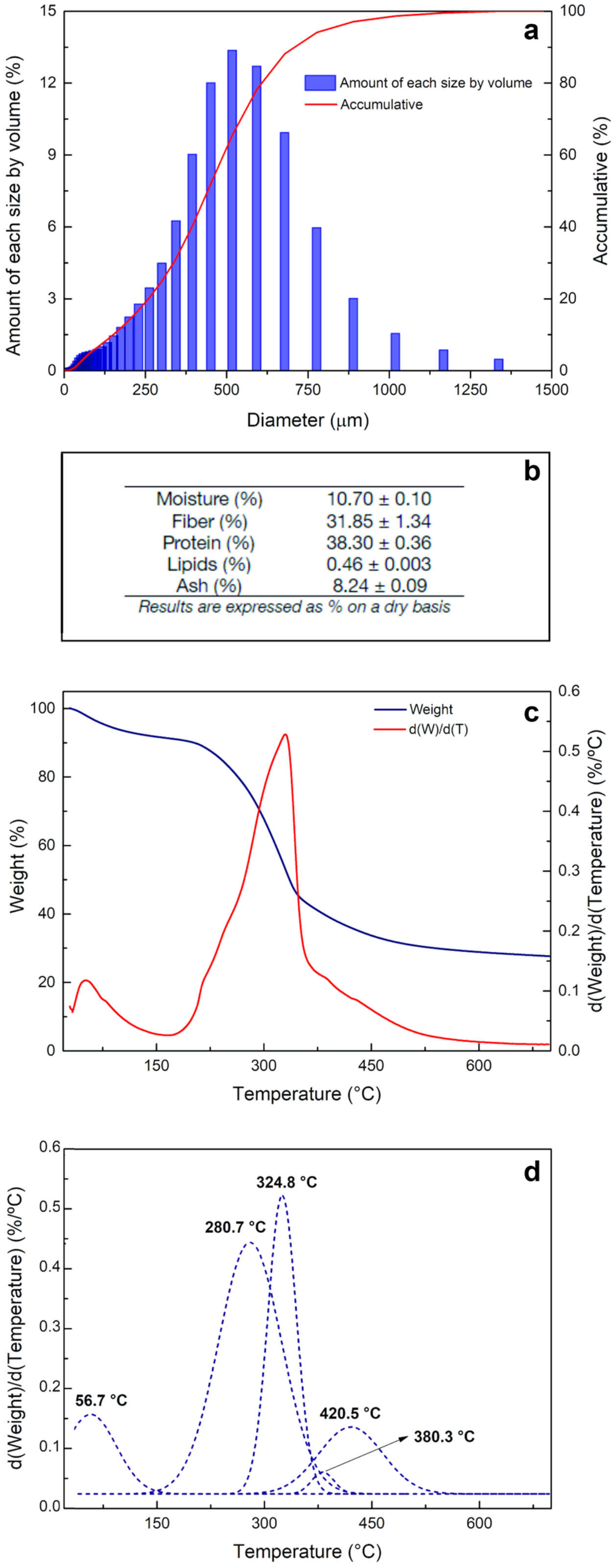
Statistical Analysis

Fisher's minimum square difference (LSD) test was used for means comparison in the data analyses of variance (ANOVA) with a significance level of $\alpha = 0.05$ and the Statistical Software InfoStat [38].

Results and Discussion

SOPC Characterization

Particle size distribution of the ground and sieved SOPC pellet presented a non-symmetrical gaussian distribution with a media of 462.02 µm, a mode of 502.78 µm, and a standard deviation of 261.01 µm (Fig. 1a). Chemical composition of SOPC pellet showed, as expected, a large proportion of fibre and protein, which are the main constituents of the seeds husk, and a low total lipid content since these solid results from sunflower oil extraction process (Fig. 1b). These results, as well as water and ash contents, are in line with previous reported values [19, 20, 39]. Regarding thermal degradation of SOPC, TGA curve evidenced the occurrence of two weight loss steps (Fig. 1c). The first one, which approximately extended to 170 °C, was attributed to water evaporation and the weight loss associated was around 8.3%, slightly lower than the moisture percentage determined gravimetrically. The second thermal event began at 190 °C to 530 °C and was associated with the degradation of organic compounds. From a DTGA peaks deconvolution, five degradation events can be identified (Fig. 1d). The first one, as it was described previously, corresponds to a dehydration process; the following three steps could be associated with the simultaneous breakdown of proteins, hemicellulose and cellulose; meanwhile the last thermal event corresponds to the thermal degradation of lignin. Similar results were



Moisture (%)	10.70 ± 0.10
Fiber (%)	31.85 ± 1.34
Protein (%)	38.30 ± 0.36
Lipids (%)	0.46 ± 0.003
Ash (%)	8.24 ± 0.09

Results are expressed as % on a dry basis

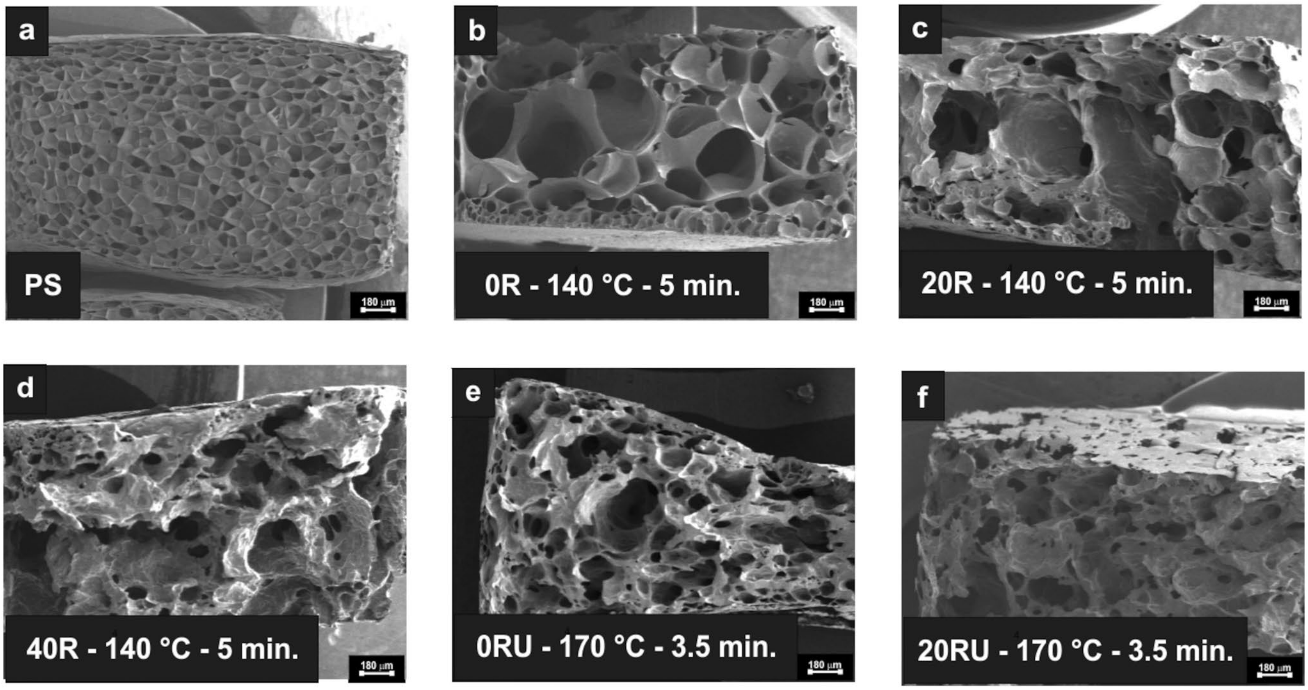
Fig. 1 Sunflower oil press cake (SOPC) particles characterisation: **a** particle size distribution; **b** chemical composition, **c** TGA and DTGA curves, and **d** TGA curve deconvolution

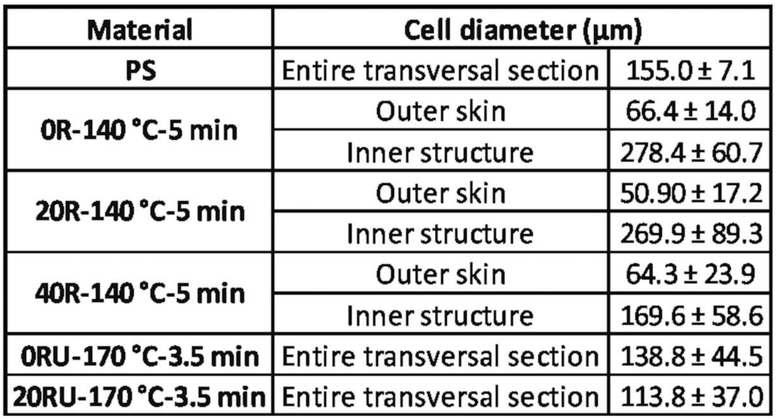
reported by Evon et al. [19]. The weight loss achieved by the degradation of organic compounds was ≈ 63%, close to the fibre and protein content (Fig. 1b). The undegraded material was ≈ 28%, significantly higher ($p < 0.05$) than the ash value determined by calcination. This difference could be attributed to the inert atmosphere (N_2) used in TGA assays that avoid the complete sample degradation; meanwhile calcination was carried out in the presence of oxygen allowing the total combustion of the organic matter.

Foams Morphology

Even though under all tested conditions starch-based foam-like materials could be obtained by thermocompression from every studied formulation, processing parameters were adjusted to achieve a good material expansion and make sure that it filled the mould completely. The morphology of foams cross-sections was analysed by SEM and Fig. 2 shows the corresponding micrographs. Control sample of PS evidences the typical structure of these materials conformed by a polymeric net containing entrapped air bubbles [40]. As it can be observed, PS presents a compact structure with small air cells inside with an average size of 155 ± 7.1 µm and cell density of 1.6×10^5 cells/cm^3. Chen et al. [33] reported smaller size cell (19.2 µm) and consequently higher cell density (1.1×10^8 cells/cm^3) for polystyrene foams. It is important to highlight that the processing method employed to obtain the foams conditions cell size and density.

Regarding the microstructure of starch/SOPC foams developed in this study, they show a sandwich-type structure with denser outer skins that enclose small cells whereas the inner structure is less dense with larger cells. This observation is in accordance with the description given by Machado et al. [15] for baked foams based on cassava starch with sesame cake residue. Processing temperature and time were adjusted considering foam morphology of starch-based foams without SPOC addition (0R and 0RU). Concerning the processing temperature for starch-control foams (0R), samples obtained by thermocompression at 140 ºC presented a more homogeneous inner structure with air cells well-defined. Meanwhile, foams obtained at 130 °C and 155 °C evidenced a more disrupted and heterogeneous structure. The outer skin thickness decreased when the processing temperature increased. These results could be explained considering that the lower temperature tested (130 °C) allowed the starch batter to gelatinize and dry more slowly, developing a thicker outer skin. This thicker skin or crust would hinder the water vapour permeation, which could lead to an increase in internal pressure and, finally, to the collapse or rupture of some cells when the materials are removed from the mould. At 155 °C, due to a higher heat transfer, the outer skin would form faster leading to a thinner layer which would allow the steam to partially exit the mould and





Material	Cell diameter (µm)	
PS	Entire transversal section	155.0 ± 7.1
0R-140 °C-5 min	Outer skin	66.4 ± 14.0
	Inner structure	278.4 ± 60.7
20R-140 °C-5 min	Outer skin	50.90 ± 17.2
	Inner structure	269.9 ± 89.3
40R-140 °C-5 min	Outer skin	64.3 ± 23.9
	Inner structure	169.6 ± 58.6
0RU-170 °C-3.5 min	Entire transversal section	138.8 ± 44.5
20RU-170 °C-3.5 min	Entire transversal section	113.8 ± 37.0

Fig. 2 SEM micrographs of expanded polystyrene—PS (**a**); cassava starch foams obtained at 140 °C and 5 min containing glycerol and 0 wt% SOPC—0R (**b**), 20 wt% SOPC—20R (**c**), and 40 wt% SOPC—40R (**d**); and cassava starch foams obtained at 170 °C and 3.5 min containing glycerol, urea and 0 wt% SOPC—0RU (**e**) and 20 wt% SOPC—20RU (**f**). Average cell-diameter estimated by SEM images processing are presented in the inserted table

the development of smaller inner cells, even though some of them would still suffer a rupture when pressure was released from the mould. Meanwhile, at 140 °C an outer skin with a suitable thickness would be achieved to allow controlled water evaporation and release through the steam exhaust vent during the thermocompression, preventing the cells disruption when the foams were removed from the mould and developing more expanded structures. Analysing the three assayed thermocompression times (3.5, 5, and 7 min), a similar morphology was observed, showing detectable changes in cell size. Samples thermocompressed for 3.5 min presented large inner pores which could weaken the foam structure, compromising their mechanical performance. No significant differences were observed in the foam structure integrity between 5- and 7-min processing times. The corresponding SEM micrographs are shown in Online Figure A1 as supplementary material. From these observations and considering the process energy consumption, chosen conditions were 140 °C and 5 min.

The addition of the residue notably modified the sandwich-type structure of developed foams (Fig. 2 c, d). The outer denser skin was less evident, and the morphology resulted in a more compact and heterogeneous structure with the presence of smaller cells distributed non-uniformly. It was expected that the presence of the SOPC would allow the development of a more expanded structure with denser outer skins, as it was reported by other authors. Polat el al. [41] stressed that the addition of fibre, kaolin or beeswax increased the cell size in the centre of starch foams. Besides, Matsuda et al. [42] found that the addition of the nanoclays improved the foaming ability of starch pastes and Machado et al. [15] showed similar results using sesame cake as reinforcement of cassava starch foams, resulting in cells walls more resistant to collapse during water evaporation. The fact that residue addition did not lead to increased cell size inside the foams structure nor to the development to more dense outer skins could be an indicative that the SOPC did not sufficiently reinforce the starch matrix. Besides, particles dimensions as well as their concentration could be responsible for the presence of stress concentration points which hinder the material expansion during the thermal process. This is an aspect that should be improved to obtain reinforced starch foams with a more open structure and, consequently, with lower density.

When starch batters with urea (0RU) were processed under the same conditions as starch control ones (0R, 140 °C, and 5 min), the typical sandwich-type structure was detected, but the samples were collapsed in the centre (Online Figure A2). Such effect could be ascribed to changes in the batter viscosity due to the higher plasticizers content [27]. Besides, as reported by Wang et al. [34] few decomposition products were detected at 140 °C. Consequently, higher processing temperatures were tested on urea containing batters (155 °C and 170 °C). Over 150 °C, NH_3 and CO_2 decomposition products are produced along with water vapour, therefore higher expansion was detected at 5 min for higher processing temperatures than 140 °C (Online Figure A2). Similar morphology was observed for 155 °C and 170 °C, yet a thinner outer layer was formed at 170 °C. The higher the heating-plates temperature the higher the heat transfer driving force and thus the higher heat transfer rate, which could lead to a faster outer layer formation by batter dehydration in contact with the mould. On the other hand, processing assayed times affected materials morphology when urea was added as foaming agent. As it can be observed in Online Figure A2, the lowest processing time (3.5 min.) led to a more homogenous structure. Higher processing times could favour gases formation and pressure increase, causing larger pores formation. Based on these observations, for formulations with urea, the chosen processing conditions were 170 °C during 3.5 min.

Lastly, the SOPC addition influence on the morphology of starch foams containing urea was also analysed (Fig. 2e, f). As it was aforementioned, the residue presence led to a denser structure.

The table inserted in Fig. 2 shows the cell diameter of PS and starch foams developed in this study. For materials without urea it was possible to calculate cell diameters corresponding to the outer skin and the inner structure. As it can be observed, outer skins presented a more closed morphology conformed by cells with lower size than the inner structure. This observation is in accordance with the sandwich-type structure for these materials. Cell diameters of the inner structure were significantly higher than those of the PS control samples, especially those of starch materials without residue and with the lowest assayed SOPC concentration. In the case of starch foams processed in the presence of urea, it was calculated diameters of the entire transversal section, as in the case of PS, due to the thinness of outer skins. The cell-size of biofoams with urea resulted like those of the PS samples, being this aspect relevant to develop materials potentially substitutes for synthetic foams.

Foams Properties

Properties of the developed foam materials in this study and the PS control are included in Table 2. The obtained results show a higher density of the starch-based materials, that increased with the addition of SOPC and decreased with urea addition. This effect is correlated with the samples pore size and density, as it was observed by SEM (Fig. 2). Even though the density of the starch-based composite foams

Table 2 Properties of foam-like materials based on: polystyrene (PS); cassava starch biocomposites containing glycerol and 0, 20, and 40 wt% SOPC (0R, 20R, and 40R); and cassava starch biocomposite foams with glycerol, urea, and 0 and 20 wt% SOPC (0RU and 20RU)

Material	Density (g/cm^3)	Moisture (%)	Water uptake (g $_{agua}$/g $_{DB}$)	Swelling (%)	Solubility (%)	Compression	
						Hardness (gf)	Energy (mJ)
PS	0.03 ± 0.001^{a}	2.0 ± 0.14^{a}	2.5 ± 0.14^{a}	0.9 ± 0.3^{a}	0.1 ± 0.01^{a}	2562 ± 90^{a}	28.5 ± 1.6^{a}
0R	0.20 ± 0.016^{c}	12.0 ± 0.19^{b}	41.9 ± 1.38^{bc}	1075 ± 45^{e}	5.9 ± 0.19^{bc}	3907 ± 589^{ab}	31.2 ± 1.3^{a}
20R	0.32 ± 0.007^{e}	14.3 ± 0.40^{e}	50.4 ± 1.52^{e}	642 ± 42^{c}	8.8 ± 0.34^{d}	8305 ± 916^{c}	62.3 ± 4.5^{b}
40R	0.40 ± 0.006^{f}	12.9 ± 0.26^{d}	46.4 ± 1.52^{cd}	421 ± 17^{b}	11.8 ± 0.01^{e}	$21{,}692 \pm 4382^{d}$	118.2 ± 21.7^{c}
0RU	0.15 ± 0.001^{b}	12.8 ± 0.06^{c}	40.4 ± 0.83^{b}	902 ± 13^{d}	5.2 ± 0.62^{b}	2391 ± 157^{a}	18.4 ± 2.1^{a}
20RU	0.23 ± 0.017^{d}	12.3 ± 0.11^{b}	46.9 ± 1.08^{d}	378 ± 41^{b}	7.9 ± 1.05^{cd}	6903 ± 589^{c}	50.8 ± 2.7^{b}

Different letters within the same column indicate significant differences among samples ($p < 0.05$)

DB dry basis

herein studied were higher than that of the expanded PS benchmark, our findings are in line with densities reported by other authors working on starch-based foams with different fillers [15, 16, 43–45]. According to Razza et al. [4] for the industrial development of this type of expanded materials, more studies are needed to reduce the density of biodegradable foams.

The visual aspect of foam-like biocomposites was appreciably different from that of the white PS control; presenting lower luminosity (L*), a more brownish tone (hue angle), higher colour saturation (chroma), and grater colour differences from the white standard (ΔE) as shown in Table 3. These effects were accentuated by SOPC filler content regardless of urea addition, which could be ascribed to the residue inherent colour. Besides, the high processing temperature favours Maillard reactions of proteins and sugars from the residue. Samples including urea presented a lesser effect on colour parameters, possibly due to their lower density (Table 2).

Given the hydrophilic character of all components of the developed materials, moisture and water absorption capacity of samples was significantly ($p < 0.05$) higher than that of the synthetic counterpart, increasing with filler content (Table 2). These results correlate with the chemical composition of the filler, (Fig. 1b). Nevertheless, 40R samples presented an atypical behaviour, presenting a significant decrease in swelling capacity, water absorption and moisture content (Table 2), presumably due to a more compact structure as it was observed in Fig. 2d. Accordingly, solubility results presented a similar trend (Table 2), indicating higher chain interactions among starch molecules in foams without filler.

Conversely, swelling by immersion was significantly ($p < 0.05$) higher for biofoams without filler and decreased with filler content, being this effect lower when urea was added in the formulation. These results suggest that urea could be acting as a crosslinking agent for starch reducing the number of free hydroxyl groups available to interact with water, as was also proposed by Chen et al. [31].

On the other hand, mechanical tests indicate a greater mechanical resistance and hardness of the starch-based materials in relation to the expanded PS (Table 2; Figs. 3, 4). However, when observing the mechanical profile of the materials a similar behaviour is identified among the non-reinforced samples (0R and 0RU) and the synthetic control (PS). Biobased foams showed a greater capacity to resist both flexion and puncture than the PS benchmark, though with larger hardness values (Figs. 3, 4). Nonetheless, compression response of the unreinforced starch-based foams and PS samples showed no significant differences ($p > 0.05$) (Table 2).

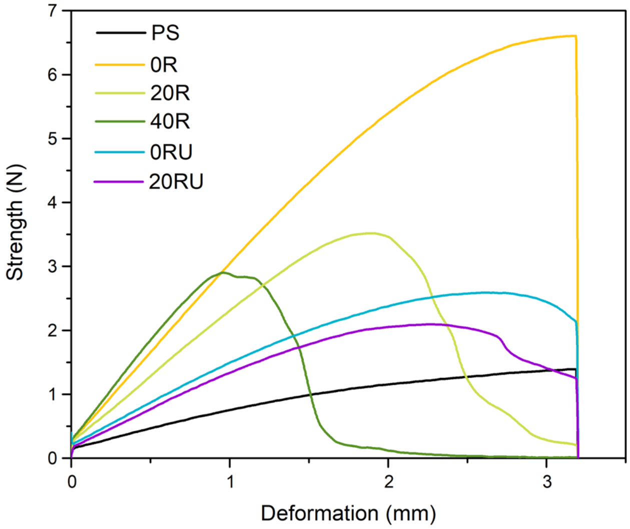


Fig. 3 Mechanical profiles of three point flexural tests of foam-like materials based on polystyrene (PS); cassava starch biocomposites containing glycerol and 0, 20, and 40 wt% SOPC (0R, 20R, and 40R); and cassava starch biocomposites containing glycerol, urea, and 0 and 20 wt% SOPC (0RU and 20RU)

Table 3 Colour parameters according to CieLab scale of foam-like materials based on: polystyrene (PS); cassava starch biocomposites containing glycerol and 0, 20 and 40 wt% SOPC (0R, 20R and 40R); and cassava starch biocomposites containing glycerol, urea, and 0 and 20 wt% SOPC (0RU and 20RU)

Material	Luminosity (L*)	Hue angle (h°)	Chroma (C*)	Colour difference[#] (ΔE)
PS	88.3 ± 0.29^{e}	99.2 ± 1.32^{f}	0.9 ± 0.04^{a}	7.00 ± 0.28^{a}
0R	76.4 ± 1.38^{d}	90.8 ± 0.45^{d}	8.0 ± 0.82^{c}	19.27 ± 1.40^{c}
20R	52.3 ± 1.42^{b}	80.7 ± 0.55^{b}	13.2 ± 0.95^{d}	44.0 ± 1.39^{e}
40R	43.5 ± 1.29^{a}	76.8 ± 0.75^{a}	13.4 ± 0.69^{d}	52.62 ± 1.22^{f}
0RU	79.0 ± 1.26^{d}	92.8 ± 0.81^{e}	6.4 ± 0.54^{b}	16.38 ± 1.18^{b}
20RU	59.2 ± 3.81^{c}	83.7 ± 1.93^{c}	14.3 ± 1.06^{e}	37.75 ± 3.45^{d}

Different letters within the same column indicate significant differences among samples ($p < 0.05$)

[#] Colour difference were measured in comparison to a white control pattern

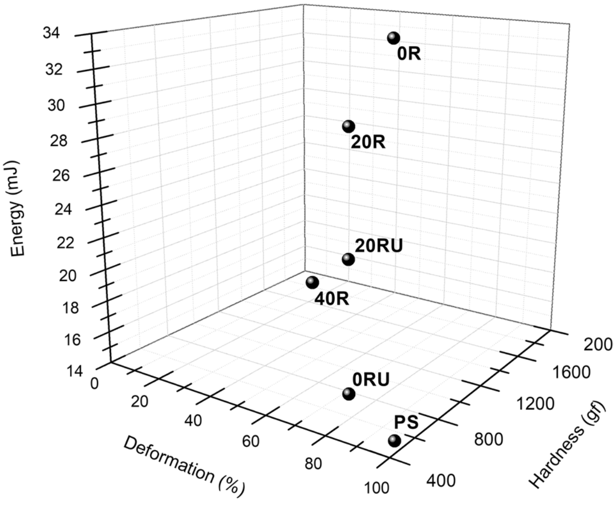


Fig. 4 Mechanical parameters from puncture rupture tests of foam-like materials based on polystyrene (PS); cassava starch biocomposites containing glycerol and 0, 20, and 40 wt% SOPC (0R, 20R and 40R); and cassava starch biocompositescontaining glycerol, urea, and 0 and 20 wt% SOPC(0RU and 20RU)

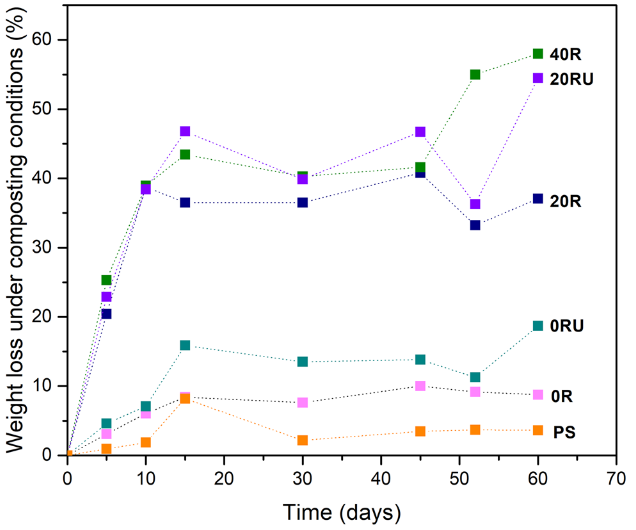


Fig. 5 Biodegradation measured as weight loss percentage under compositing conditions in soil during 60 days of foam-like materials based on polystyrene (PS); cassava starch- biocomposites containing glycerol and 0, 20, and 40 wt% SOPC (0R, 20R, and 40R); and cassava starch biocomposites containing glycerol, urea, and 0 and 20 wt% SOPC (0RU and 20RU)

Likewise, the reinforced materials were significantly ($p < 0.05$) harder than PS and starch foams, which was attributed to their higher densities (Table 2). Yet, these composite materials presented lower resistance to bending reflected in intermediate flexural strength values and the occurrence of small fractures during the test, detected as abrupt decreases in strength values versus deformation during three-point flexion tests.

It should be remarked that composites with urea addition presented better mechanical energy absorption characteristics, being 0RU samples the most like PS control foams. Such results were attributed to the relatively more homogenous pore size of samples containing urea in comparison to those without the foaming agent (Fig. 2) and their lower density (Table 2), which could be responsible for the better mechanical performance.

Considering the obtained results, the materials herein studied without urea (0R, 20R, and 40R) would be more suitable for the manufacture of expanded containers, for instance disposable food trays, than loose-fill materials. Meanwhile, formulations containing urea, especially those not reinforced with SOPC (0RU) would be a promising alternative to replace loose-fill protective packaging materials for dry products, such as electronic products, being necessary the study of lower SOPC contents to obtain more sustainable materials without rendering their mechanical performance. Besides, as reported by Chen et al. [31] ammonia was detected during processing of starch-urea materials at high temperature processing conditions, thus applications where traces of this compound are not acceptable are not recommended. Moreover, starch modifications or multilayering with biodegradable but more water-resistant polymers, such as polylactic acid (PLA) should be considered as alternatives to improve the products hydrophilicity.

Finally, biodegradation results showed as expected a greater biodegradability of biobased foam-like composites though total degradation was not achieved for any of the samples within 60 days after burial (Fig. 5). Samples containing SOPC degraded faster and to a larger extent than samples without filler, showing fungi growth on their surface within the first 5 days under composting conditions (Online Figure A3). Nansu et al. [17] also found that starch-based foams with up to 8 wt% of coconut residue fibre as filler an 0.1 wt% of boric acid as crosslinking agent degraded up to 60% in 30 days while unreinforced samples showed a significantly lower biodegradation ratio (≈ 25%).

Regarding the sustainability of the materials, considering that the biobased materials herein studied present higher densities than the PS counterpart, it would be expected that in a life cycle assessment (LCA) higher greenhouse emissions would result due to transport of the packages produced with these materials and all the products packed with them. Madival et al. [46], carried out a comprehensive study on LCA of different polymer containers in the USA. In this study, the authors concluded that the transportation stage of both the resins and the containers was a determining factor in all impact categories in the package LCA. Therefore, future research will be aimed at reducing the biocomposites density. Nonetheless, as regards expandable PS as packaging material, the major environmental impact is related to the non-renewable energy sources depletion and climate change—associated with greenhouse-effect gases emissions—derived from the resin production itself and electricity required for tray manufacturing [47]. Consequently, the biobased origin of materials herein studied could help reduce the use of non-renewable energy sources as raw material for plastic production.

In a study, which compared PLA to PS boxes, it could be seen that when land-use-change was considered the cradle to consumer gate environmental impact of PLA products was slightly higher than PS one [48]. Yet, in general, PLA boxes impact diminished with starch inclusion in the formulation, indicating a minor impact of this crop on the material life cycle. Besides, the cradle to grave was not considered in Suwanmanee et al. [48] work, though as the authors indicated is a significant issue that needs to be assessed especially regarding biodegradable materials. Composting helps reduce solid waste generation and therefore landfill occupation, as well as greenhouse gas emission in residue transport especially if a house composting system is applied.

In addition, sustainability should be assessed as well from a socio-economic perspective. The use of agroindustry by-products as raw material not only helps reducing cost production and minimising effluents generation, which would imply that the impact of the same production system is cushioned by the full use of the crop, but also leads to new productions systems that can strengthen local economies were the crops are produced favouring both social equity of the region and economic value of the crops production. Besides, a further diminution could be achieved if lower environmental impact crop production systems are employed.

Conclusions

Composite foams based on cassava-starch and sunflower oil press cake (SOPC), an oil industry by-product, were developed by thermocompression. The modification of processing conditions (temperature–time) allowed obtaining materials with different morphological characteristics. Thus, in cassava starch-based materials, processing at 140 °C during 5 min led to the development of foams with a sandwich-type structure and a greater number of uniform and small size cells. The inclusion of SPOC notably modified the sandwich-type structure of developed foams, leading to denser and harder materials with higher water uptake capacity Moreover, filler addition significantly modified colour parameters of starch foams obtaining more opaque and brownish materials. When urea was included in formulations, chosen processing conditions were 170 °C for 3.5 min to ensure the urea decomposition producing gases that act as internal foaming agents. Starch foams containing SOPC and urea were more flexible to flexural deformation than composites without the foaming agent.

Finally, opting for foamed starch materials instead of traditional polystyrene is based mainly on the renewable origin and the biodegradable character of the materials proposed in this work. However, the density of bio-foams is one of the characteristics that should be improved to reduce the transporting cost of these packages and also improve their LCA impact.

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