

Research article

Eco-friendly biocomposite foam from natural rubber latex and rice starch for sustainable packaging applications

Wannarat Chueangchayaphan¹, Phatchariya Nooun¹, Nittaya Ummarat²,
Narong Chueangchayaphan^{1*} 

¹Faculty of Science and Industrial Technology, Prince of Songkla University, Surat Thani Campus, 84000 Surat Thani, Thailand

²Faculty of Innovative Agriculture and Fishery Establishment Project, Surat Thani Campus, Prince of Songkla University, 84000 Surat Thani, Thailand

Received 2 August 2023; accepted in revised form 27 September 2023

Abstract. An environmental pollution problem is caused in part by packaging materials made from non-biodegradable synthetic polymers derived from petroleum. In this study, eco-friendly biofoams derived from natural rubber (NR) latex and rice starch (RS) were manufactured on a laboratory scale using the Dunlop process. Rice starch content was varied from 0 to 50 phr. The morphological, thermal, physical, mechanical, and biodegradability properties of the NR/RS biocomposite foams were characterized. Scanning electron microscopy (SEM) was used to assess the morphology of the foam cells. Dynamic mechanical thermal analysis (DMTA) and Thermogravimetric analysis (TGA) were used to investigate the thermal characteristics. When RS was present, it was discovered that the biocomposite foams had decreased thermal stability and enhanced biodegradability. Introducing RS into the NR/RS biocomposite foams also decreased tensile strength, elongation at break, and rebound resilience but increased the 100% modulus, hardness, compression force deflection (CFD), and compression set. The NR/RS biocomposite foams better preserved the banana fruit than the absence of foam, with lower ethylene accumulation, lower total soluble solids (TSS), higher pulp firmness, and good color preservation. This demonstrated that these NR/RS biocomposite foams helped to preserve banana fruit quality during storage and could be used in sustainable packaging applications.

Keywords: biocomposite foam, natural rubber, rice starch, mechanical properties, banana packaging

1. Introduction

Everyday waste from consumed goods, such as bottles, food scraps, plastic bags, food wrappers, and other packaging, is discarded as municipal solid waste. Unfortunately, many waste products, particularly those made from synthetic petroleum polymers with non-renewable components, are not biodegradable [1]. Several factors, including the depletion of oil and gas reserves, rising prices, concerns about the effects of degradation or incineration on the environment and particularly on global warming, contamination-prone recycling processes, and the

potential toxicity of the finished product, have led to increased interest in using biopolymers as alternatives to petroleum-based polymers [2]. Biopolymers are made from natural materials and have recently attracted scientific attention because of their reusability, eco-friendliness, accessibility, sustainability, and level of usefulness [3].

Natural rubber (NR), a biopolymer and environmentally benign elastomer is extracted from the *Hevea Brasiliensis* tree as latex, a milky-appearing liquid. Because it is renewable, non-toxic, has excellent physical properties, and is inexpensive, NR is the

*Corresponding author, e-mail: narong.c@psu.ac.th
© BME-PT

most often used elastomer globally in industry and in many applications where the finished goods come into contact with food or drinkable water [4]. Although NR is categorized as a natural polymer, its biodegradability is still poor due to the high molecular weight of NR macromolecules and the additional chemical crosslinking created during vulcanization [5].

Starch is a biopolymer composed of two distinct components, amylose and amylopectin, with the proportions depending on the botanical source, such as corn, cassava, potatoes, sago, rice, *etc.* [6]. Rice is the most widely grown cereal grain and is considered the primary source of nutrition for approximately half of the world's population [7]. Among all the starches, rice starch (RS) is a popular raw material for many food and non-food applications due to its non-allergenicity, easy digestion, white color, tiny grains (3–10 mm), and wide range of amylose/amylopectin ratios [8]. Because it is abundant, inexpensive, biodegradable, and has good film-forming properties, several studies have been published on the use of starch as a biodegradable packaging material or as a bio-coating to increase the shelf life of fresh fruit, either alone or in combination with other biopolymers [9].

For NR composites, biodegradability has been pursued by incorporating various kinds of starches, such as corn starch [10–12], waxy corn starch [13, 14], cassava starch [15–20], potato starch [4, 21, 22], sago starch [23], rice starch [24, 25], and unspecified starch [26, 27]. Such prior studies, however, have often constructed rubber films or adhesives. In addition to tires, gloves, condoms, and so on, the utilization of NR foam products has also increased recently. NR foam is commonly used in the production of a variety of products, including mattresses, pillows, dolls, cushions, and flooring, because it provides both good mechanical and distinct morphological features, in addition to providing a good balance between strength and weight [28]. This type of foam is among the many products that can be manufactured from both NR latex and dry NR.

Protective and cushioning materials are crucial in packing, preserving, and enhancing the quality of food products throughout the distribution, storage, and consumption processes [29, 30]. These cushioning materials must have a low density to save transport costs, barrier properties against moisture, and good processing abilities. Petroleum-based plastic

foams dominate the current market of protective and cushioning packing products, including expanded polystyrene foams, expanded polyethylene foams, expanded polypropylene foams, and polyurethane foams [31–33]. Consequently, finding alternative biobased and sustainable packaging to replace petroleum-based packaging materials and meet cushion packing standards has been actively pursued in research. The developments of foams prepared from natural rubber and starch as agricultural resources have been reported [1, 34–36]. However, these studies have one thing in common: either starch was used as the primary matrix, or the foams were prepared using dry NR under compression moulding. The only study that reported on the production of NR foam as the primary polymer matrix in biocomposites using NR latex as a starting material for foam preparation was by Prasopdee *et al.* [37], in which the cassava starch served as a light filler to improve the recovery properties of natural rubber foam (NRF) prepared through the Dunlop process. Cassava content was varied from 0 to 16 phr. NRF possessed better compression strength and shape recoverability with increasing cassava content and showed the optimum properties at 8 phr. This NRF was intended for high resilience or high shape recoverability applications [37]. After an extensive review, no previous report on NR/rice starch foam used in food packaging applications was found by the authors of this current study.

The objective of this work was to prepare cushion biocomposite foam sheets. Following the concept of green and sustainable materials, the biocomposite foams were produced via the Dunlop method in this study, using a straightforward strategy that combines natural rubber (NR) latex and rice starch (RS) as renewable and biodegradable filler in the absence of any organic solvent. The effects of RS content on morphological, physical, mechanical, and thermal properties and biodegradability of the NR/RS biocomposite foam are reported. Additionally, in an application case study, the NR/RS biocomposite was utilized as a cushion foam sheet to extend the shelf life of bananas.

2. Experimental

2.1. Materials

High-ammonia-grade concentrated natural rubber latex with a dry rubber content of 60% and the suspension vulcanizing additives listed in Table 1 were

Table 1. Composition of the NR/RS biocomposite foams.

Ingredients	Starch content [phr]					
	0	10	20	30	40	50
60% NR latex	100.0	100.0	100.0	100.0	100.0	100.0
20% Potassium oleate	1.0	1.0	1.0	1.0	1.0	1.0
50% Sulfur	2.0	2.0	2.0	2.0	2.0	2.0
50% ZDEC	1.5	1.5	1.5	1.5	1.5	1.5
50% ZMBT	1.5	1.5	1.5	1.5	1.5	1.5
50% CPL	2.0	2.0	2.0	2.0	2.0	2.0
50% ZnO	5.0	5.0	5.0	5.0	5.0	5.0
30% DPG	0.85	0.85	0.85	0.85	0.85	0.85
1% Sodium metabisulfite	0.025	0.025	0.025	0.025	0.025	0.025
20% SSF	0.60	0.65	0.70	0.75	0.8	0.85
50% Rice starch	0.0	10.0	20.0	30.0	40.0	50.0

obtained from Boss Optical Limited Partnership, Songkla, Thailand. Sodium metabisulfite was obtained from Merck, Darmstadt, Germany. Rice starch was produced by Cho Heng Rice Vermicelli Factory Co., LTD., Nakhon Pathom, Thailand. All the chemicals were used as received.

2.2. NR/RS biocomposite foam preparation

NR/RS biocomposite foam samples were prepared using the Dunlop method, which entails foaming compounded latex, adding chemical agents, and then adding a gelling agent to solidify the foam. Table 1 provides a complete list of the components with their respective pph amounts in proportion to the NR component (the dry rubber content). Using a multipurpose kitchen blender, we mixed the concentrated NR latex to reduce ammonia for 2 min at a low speed. To make the foam, K-oleate was added, and the mixture was whisked for 2 min at high speed until it had expanded to around three times its original volume. The mixing speed was slowed to medium before applying

sulfur (S), zinc diethyl dithiocarbamate (ZDEC), zinc-2-mercaptobenzothiazole (ZMBT), and antioxidant (Lowinox CPL). After that, the RS was added to the mixture, and the blend was stirred for two minutes. We slowed down the blender and added more diphenylguanidine (DPG) and zinc oxide (ZnO), then pounded it for a full minute. Finally, 35 s were allotted to incorporate the major gelling ingredient, sodiumsilicofluoride (SSF). The SSF content is based on the rice starch content to keep the gelling time constant. The mold was filled with a non-gelled foam left to gel at room temperature. In a hot air oven set to 100 °C, the gelled foam was allowed to cure for an hour. After the foam had been set, it was taken out of the mold and given a thorough rinsing with water to remove any remaining soap residue or unreacted components. Once again, the resulting foam spent 24 h drying at 60 °C. Figure 1 provides a high-level view of the research and development of biocomposite packing foam sheets and their effects on the absorption of ethylene in postharvest bananas.

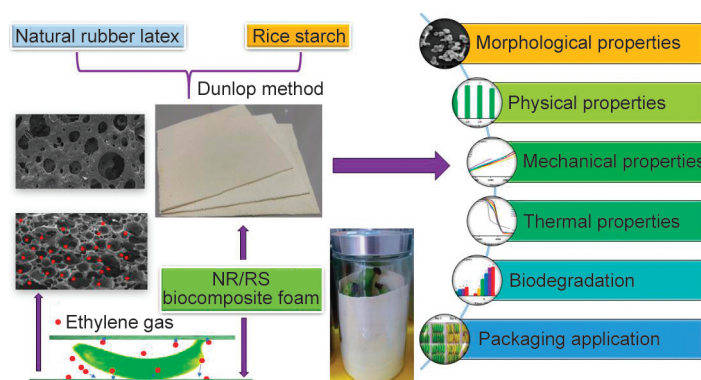


Figure 1. A high-level view of the research and development of biocomposite packing foam sheets and their effects on the absorption of ethylene in postharvest bananas.

2.3. Characterization and mechanical property testing of NR/RS biocomposite foam

Scanning electron microscopy (Quanta 250, FEI Company, Eindhoven, Netherlands) revealed the foam had fractured surfaces. Cell size and number were observed from SEM images using a cooling tech microscope program. A laser particle sizer (ANALYSETTE 22 NeXT Nano, FRITSCH GmbH, Germany) was used to test and analyse the particle size of rice starch powder as a wet dispersion. The density of a specimen was calculated using the mass and volume of the foam in grams and cubic centimeters, respectively (estimated based on the apparent dimensions). The average density of at least five specimens was recorded for each sample type. According to ASTM D2240, a Shore AO hardness test was conducted on a specimen with a 10 mm thickness. Based on ASTM D2632, the rebound resilience was measured by dropping a 16.3 g metal ball from a height of 500 mm onto a 50 mm-thick test piece. The distance the ball traveled after striking the specimen was measured. The compression set was evaluated based on ASTM D395. The test specimens measured 50×50×25 mm. Each sample was examined three times. The samples were placed between the plates of the compression device and compressed to 50% of their initial thickness. The apparatus and compressed specimens were placed within 15 min in a 70 °C air oven for 22 h. After 22 h, the samples were removed from the apparatus and given 30 min to recover. After recovery, the specimen thickness was determined. The compression force deflection (CFD) was measured using an ASTM D 3574-95 universal testing machine. The test specimens measured 100×100×100 mm. The samples were compressed to half their original size. Test specimens for ASTM D412 (tensile testing) and ASTM D624 (tear testing) were evaluated using a universal testing machine with a crosshead speed of 500 mm/min at 25±2 °C. The average results of five samples were exhibited. The dynamic mechanical thermal analysis (DMA 1, Mettler Toledo, Switzerland) was used to perform the dynamic mechanical thermal testing with a specimen dimension of 10×30×2.5 mm over the temperature range from –100 to 100 °C at a heating rate of 5 °C/min, a frequency of 10 Hz, and a strain magnitude of 1%, under nitrogen gas. Thermal degradation of native rice starch powder and NR/RS biocomposite foam samples was assessed using a Thermogravimetric

analysis (TGA8000, Perkin Elmer, United States of America) with a heating rate of 10 °C/min from 25 to 800 °C under N₂ gas atmosphere.

2.4. Soil burial test

The foams were cut into 2.0×2.0 cm pieces and buried in the soil at a depth of 7 cm in an ambient environment. Every two weeks, the weights of the samples were measured. The degradation rate was calculated as Equation (1):

$$\text{Weight loss [\%]} = \frac{W_b - W_a}{W_b} \cdot 100 \quad (1)$$

where W_a and W_b are the corresponding weights of the foam materials after and before the test. The presented data are averaged from three independent samples of each type.

2.5. Application of NR/RS biocomposite foam to the preservation of bananas

A local banana plantation in Surat Thani, Thailand, provided us with freshly picked bananas (*Musa acuminata* (AAA Group)) at commercial maturity (70–80% maturity). The bananas were harvested and then delivered to the lab the same day. This particular fruit was selected because it consistently met our criteria for size and weight, and the samples were free of physical defects. The fruit was then rinsed in running water and allowed to dry naturally before use in the planned experiments.

2.6. Ethylene measurement

A multi-gas analyzer was utilized to ascertain the NR/RS biocomposite foam's level of ethylene absorption (F-950 model, Felix Instruments Inc., United States). Randomly choosing three bananas, measuring their weight, and packing them with two biocomposite foams was done. After that, they were placed in a 1.7 l airtight glass jar with a lid that held a rubber septum for sampling headspace gas, and they were kept at a temperature of 25±2 °C for twenty-four hours. Throughout the storage period, ethylene gas was measured on the hour, and the results are expressed in µl/(kg·h) C₂H₄.

2.7. Quality evaluation of banana preservation

Bananas from the same batch were randomly separated into two lots for the control (no foam) and for NR/RS biocomposite foam treatments, with five

replicates in each treatment. The bananas had uniform size, weight, and maturity levels. After placing each set of three bananas between two foam sheets, the sets were placed in corrugated boxes and kept at a temperature of $25 \pm 2^\circ\text{C}$ for twelve days. Every three days, fruit samples were taken and analyzed for weight loss, pulp hardness, peel color, and total soluble solids (TSS). A penetrometer was utilized to evaluate the cohesiveness of the pulp of banana fruits (FHR-1, Nippon Optical Works Co. Ltd., Tokyo, Japan). The brightness (L^*) and hue angle (h^*) were both determined for the color of the peel by measurement using a colorimeter (NH310 model, Shenzhen Three NH Technology Co. Ltd., China). The total soluble solids (TSS) in fruit juice were analyzed with a refractometer (Master-M, Atago Co. Ltd., Japan), and the results are presented in degrees Brix.

2.8. Statistical analysis

The statistical homogeneity of variance was determined using data from repeated experiments. To compare significant effects at the $p \leq 0.05$ level, a one-way analysis of variance (ANOVA) was used, followed by the calculation of Tukey's Honestly Significant Difference (HSD).

3. Results and discussion

3.1. Morphological studies

The particle size distribution of RS is displayed in Figure 2a. RS had a trimodal size distribution with small, middle, and prominent peaks over the ranges 0.3–1.7, 1.7–21.3, and 21.3–116.3 μm , respectively. The large-sized particles were caused by granule aggregation, as indicated by SEM images. The particles were also characterized by equivalent diameters at 10% cumulative volume (D10) and 90% cumulative volume (D90). The values of D10 and D90 were 2.4 and 47.5 μm , respectively. Such supplementary information describes the particle size distribution

more precisely. In addition, the D50 particle size was 9.4 μm . The granular structure (shape and size) of RS was also observed by scanning electron microscopy (SEM), as shown in Figure 2b. These RS granules exhibited a particle size of around 3–5 μm , predominantly polyhedral and irregular shape, and smooth surfaces, in agreement with prior literature [7, 8]. SEM images of surfaces and cross-section views of NR/RS biocomposite foams are presented in Figures 2 and 3, respectively. An open cell structure was mostly present. An open cell structure typically results from the high-speed mixing of latex used in the Dunlop method, which creates gas bubbles of various sizes [28]. The biocomposite foam without RS has a small, uniform foam cell structure (Figure 4a). Moreover, the NR/RS biocomposite foams did not present starch granular morphology. This demonstrated that the starch had undergone gelatinization. The use of RS granules as a filler in NR foam prepared with the Dunlop method caused swelling and disintegration of the RS granules. This was validated by both surface and cross-sectional views without distinction between RS and NR particles. As the RS content was increased, the biocomposite foam had a large, irregular foam cell character, and the cell wall became thicker (Figures 4b–4f). The Dunlop method is a mechanical foaming procedure that poorly regulates pore production, resulting in an inhomogeneous foam dispersion [38]. The number of cell foams also decreased with increasing RS content (Figure 5a). On the surface of an NR/RS biocomposite foam containing RS, open macropores were discovered. The pores were considerably larger in size compared to the biocomposite foam without RS. This might be because after being baked at 100°C , the RS particles that had been incorporated in the NR latex phase during mixing had been gelatinized. This could make the foam structure more unstable and induce more connected cells from the loss of walls. This

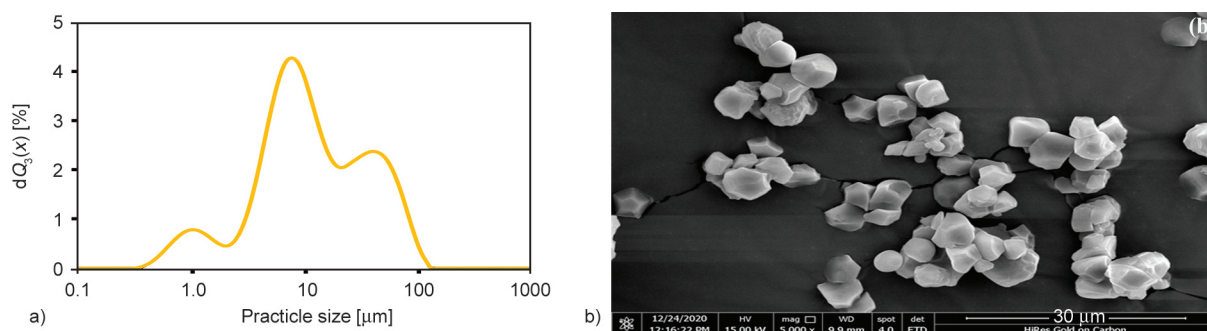


Figure 2. Granule size distribution and morphology of RS a) granule size distribution of RS as measured by a laser particle size analyzer, b) morphology of RS as imaged by scanning electron microscopy.

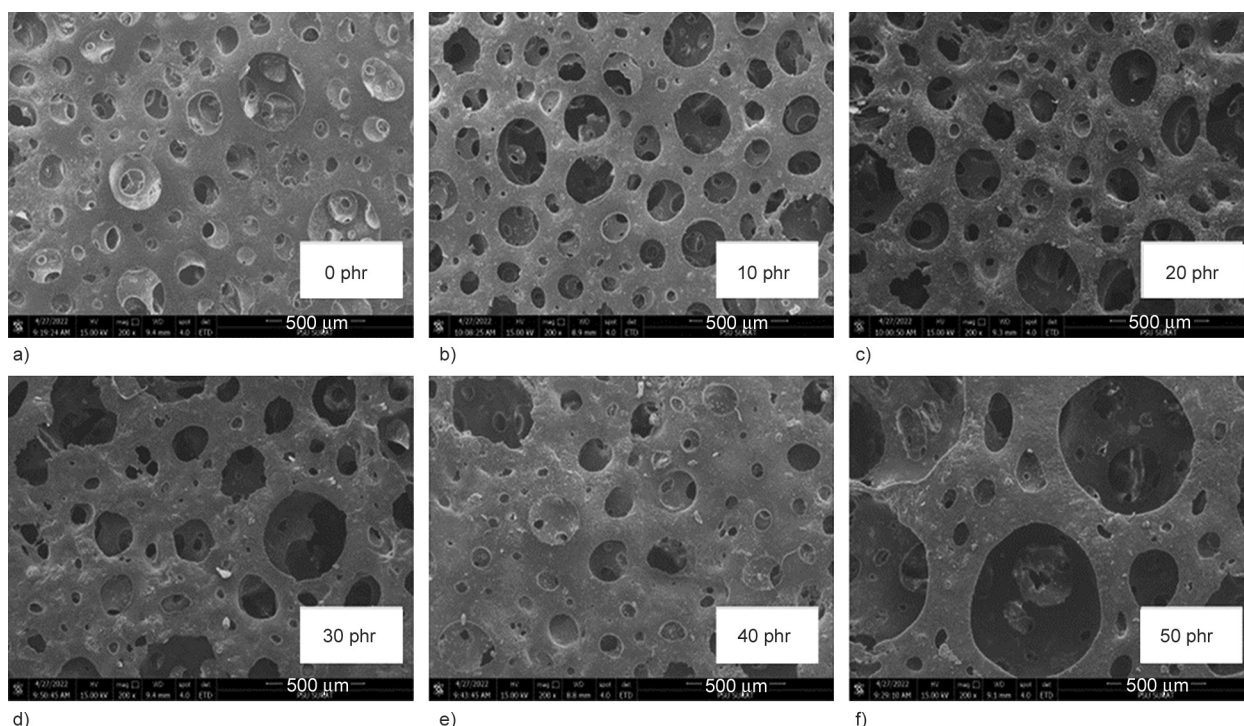


Figure 3. SEM images of surfaces of NR/RS biocomposite foams with RS a) 0 phr, b) 10 phr, c) 20 phr, d) 30 phr, e) 40 phr, and f) 50 phr.

was clearly seen in the NR/RS biocomposite foam with RS content of 50 phr (Figures 3f and 4f).

The density increased with RS content, as seen in Figure 5b. This might be because there were fewer cells and the creation of large-sized cells occurred throughout the matrix. The density and porosity

exhibit opposite trends to each other, as could be expected. Furthermore, it is common knowledge that increasing the filler content tends to increase the density due to the higher density of the filler [39]. In this instance, the density of NR is 0.92 g/cm³, while the density of RS is 1.530 g/cm³ [40].

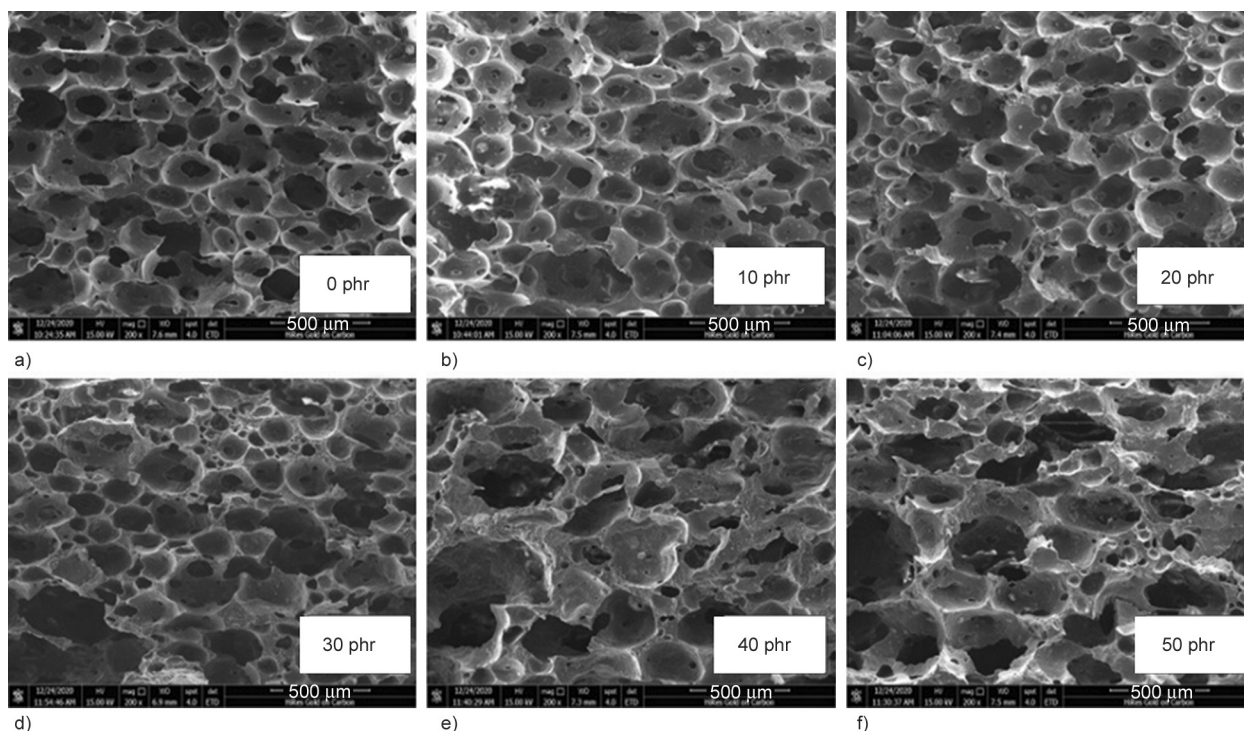


Figure 4. SEM images of cross sections of NR/RS biocomposite foams with RS a) 0 phr, b) 10 phr, c) 20 phr, d) 30 phr, e) 40 phr, and f) 50 phr.

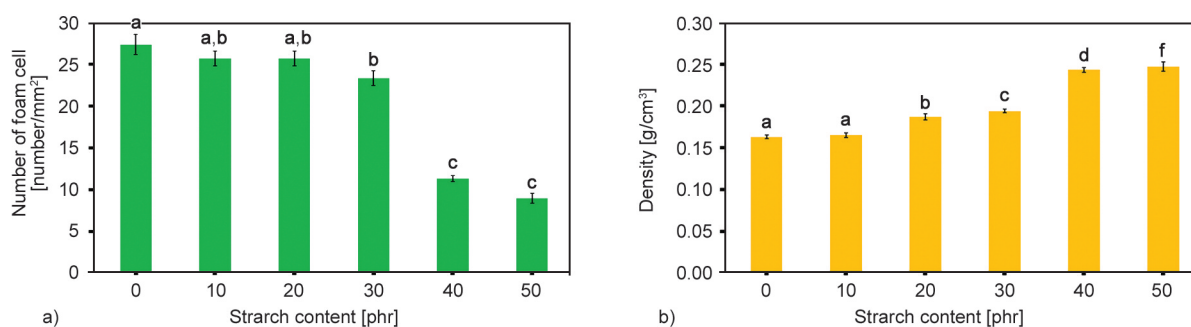


Figure 5. Physical properties of NR/RS biocomposite foams: a) number of foam cells, and b) bulk density of foam. **a, b, c, d, e, f:** different letters denote a significant difference between the two values according to ANOVA analysis (Section 2.8.)

3.2. Thermal properties

Thermogravimetric analysis (TGA) was used to determine the thermal stability of samples. Thermal stability was evaluated in terms of weight loss as a function of temperature in a nitrogen atmosphere. TGA and Derivative Thermogravimetry (DTG) profiles of native RS powder and NR/RS biocomposite foams are exhibited in Figure 6. All samples tested demonstrated a weight loss zone in the 30–100 °C temperature range, indicating moisture evaporation. The significant degradation of native RS powder and the NR biocomposite foam was observed at approximately 300 and 380 °C, respectively. During thermal decomposition, the NR/RS biocomposite foams

exhibited two main degradation stages, one before 330 °C and the other around 350–450 °C, corresponding to RS and NR degradation, respectively. The NR/RS biocomposite foams are thermally degraded at a lower temperature than the unfilled RS foam. Evidently, composites with a high RS content had reduced thermal stability. The characteristic temperatures of thermal degradation are summarized in Table 2. The deterioration of NR/RS biocomposite foam's thermal stability with increasing RS loading was attributed to the lesser thermal stability of RS compared to NR.

Figure 6c presents the storage modulus vs. temperature for the NR/RS biocomposite foams with different

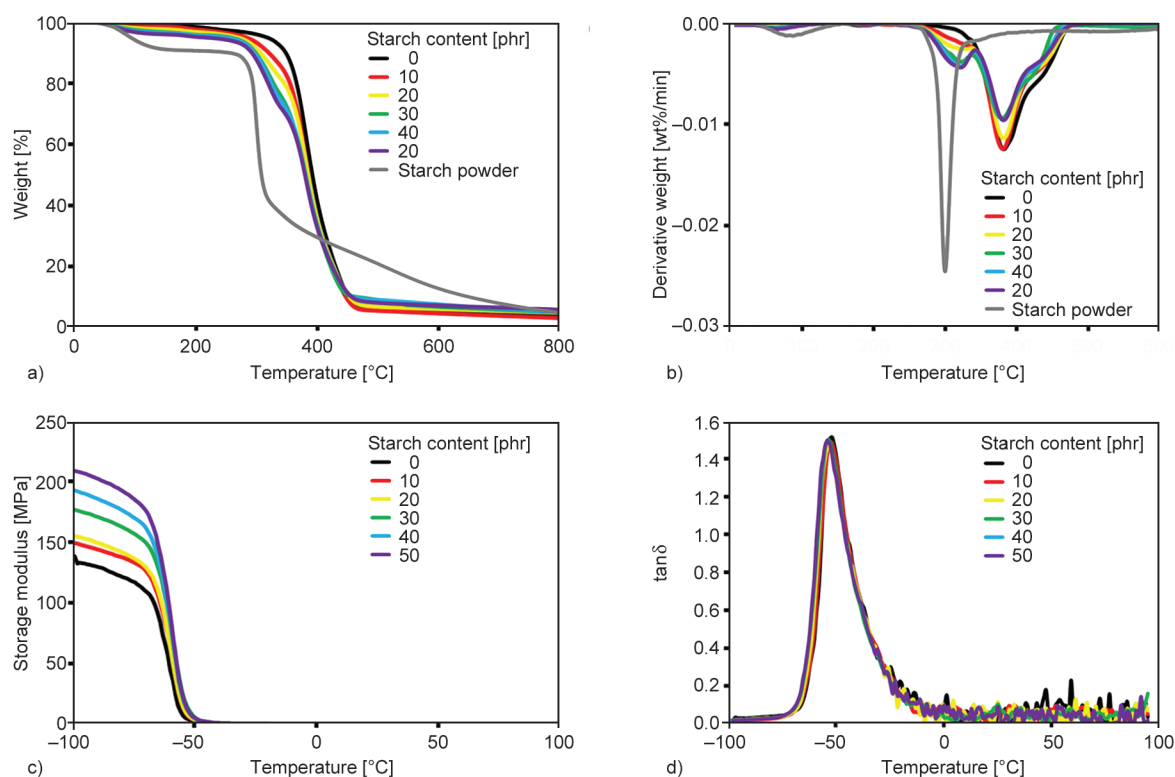


Figure 6. Thermal responses of the NR/RS biocomposite foams, a) TGA thermogram, b) DTG thermogram, c) storage modulus, d) $\tan \delta$.

Table 2. Thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA) data for starch powder and NR/RS biocomposite foams.

Starch content [phr]	TGA					DMTA	
	T_{10} [°C]	T_{50} [°C]	T_{70} [°C]	T_{90} [°C]	Residue [%]	T_g [°C]	$\tan \delta$ max
0	348	392	414	451	4.15	−51.7	1.51
10	320	385	407	447	3.18	−52.7	1.49
20	306	384	407	453	4.81	−53.2	1.47
30	298	380	405	467	4.98	−53.8	1.50
40	297	380	405	460	5.14	−53.8	1.45
50	292	379	404	457	5.99	−53.9	1.49
Starch powder	254	308	395	653	4.75		–

RS contents. It was found that the storage modulus tended to increase with RS content. This was due to the stiffness imposed by the RS. Figure 6d displays $\tan \delta$ vs. temperature. On adding more RS, the glass transition temperature T_g slightly shifted to a lower value. This indicates only weak interactions between RS and NR due to their different polarities. However, compared to the pure NR biocomposite foam,

there was no significant change in $\tan \delta$ when the starch content was increased.

3.3. Mechanical properties

Figure 7a shows the stress–strain curves of the NR/RS biocomposite foams. It can be seen that an increase in RS content generally decreased tensile strength and elongation at break. In contrast, the

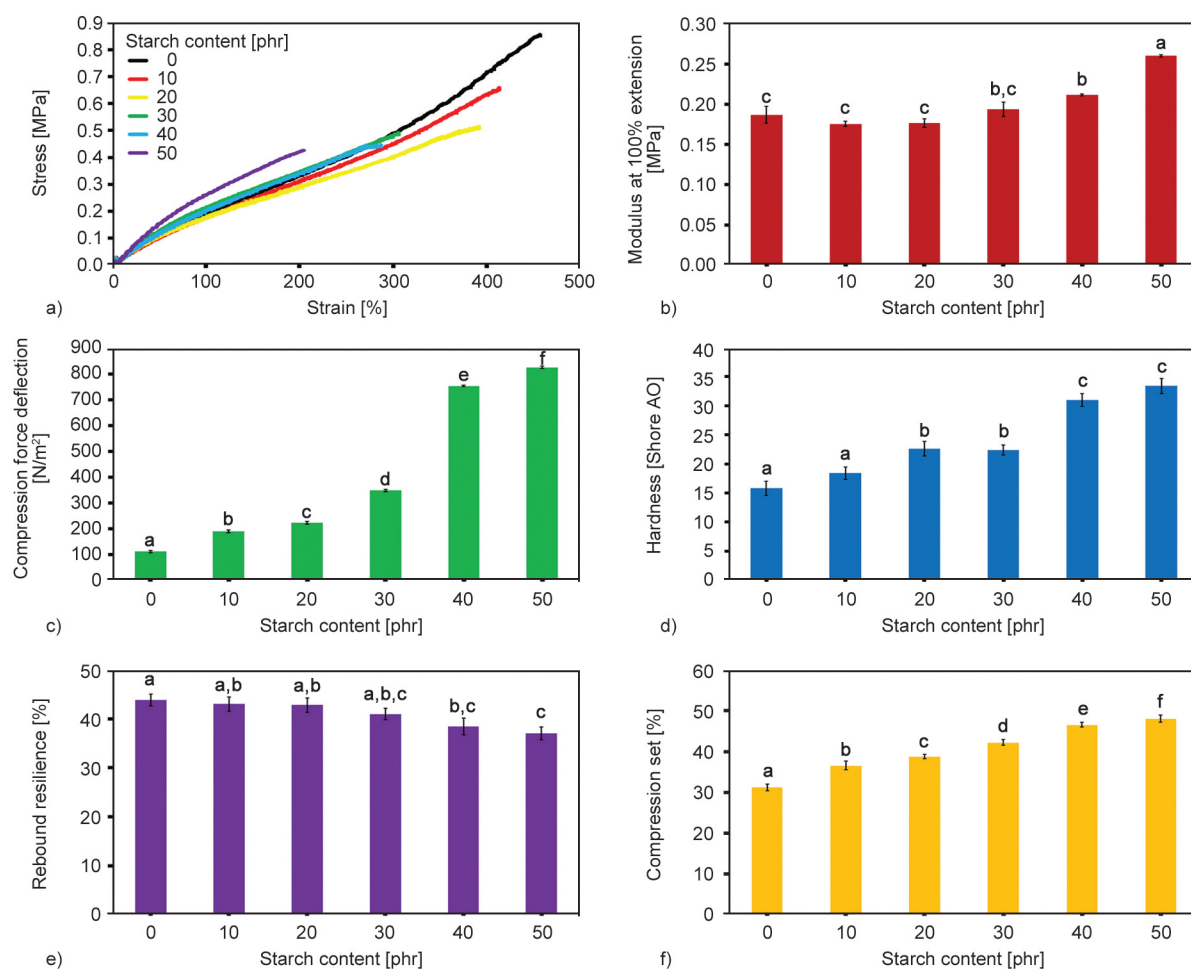


Figure 7. Mechanical properties of the NR/RS biocomposite foams, a) stress vs. strain, b) modulus at 100% extension, c) compression force deflection, d) hardness, e) rebound resilience, and f) compression set. **a, b, c, d, e, f:** different letters denote a significant difference between the two values according to ANOVA analysis (Section 2.8.)

100% modulus and compression force deflection (CFD) presented in Figures 7b and 7c, respectively, increased remarkably with the proportion of RS in the NR/RS biocomposite foams. They had trends similar to the hardness presented in Figure 7d. The biocomposite foam without RS had the least hardness of 15.8 Shore AO while adding 50 phr RS increased the hardness of the NR/RS biocomposite foam to 32.2 Shore AO. This was because RS is hard and brittle. Thus, adding a harder filler to a soft and flexible rubber matrix led to increases in hardness, modulus, and CFD but decreased tensile strength and elongation at break. The rebound resilience of the NR/RS biocomposite foams is shown in Figure 7e. It was found that the addition of RS caused a decrease in rebound resilience. This was due to stiff and rigid starch that diminished the flexibility of the NR composites. In addition, a substantial reduction in resilience was induced by larger cell sizes with decreased NR chain flexibility. The biocomposite foams had an inverse relationship between hardness and resilience, consistent with Vahidifar *et al.* [41]. This observation agreed with the compression set displayed in Figure 7f. The compression set measures the capacity of a foam material to keep its elastic properties at a specific temperature when compressed for an extended period. The lower the compression set, the more flexible the material is, and the less it changes permanently [42]. So, the material has better elastomeric properties when the compression set is low. Figure 7f displays the compression set for the NR/RS biocomposite foams. The compression set was greater than 0% in all cases, showing that the NR/RS biocomposite foams did not return to their original shape after being deformed. The NR biocomposite foam without RS exhibited the least compression set, and on increasing RS content, the compression set increased. Apparently, the NR/RS biocomposite foams lost elastomeric properties due to a dilution effect.

3.4. Biodegradability

The NR/RS biocomposite foams were buried in soil for 12 weeks under ambient conditions to observe biodegradation. The biodegradation was measured by calculating the weight loss as a percentage of initial weight, as shown in Figure 8. As the RS contents increased, the biodegradation of NR/RS biocomposite foams linearly increased. At the end of the 12th week, the NR/RS biocomposite foam with 50 phr

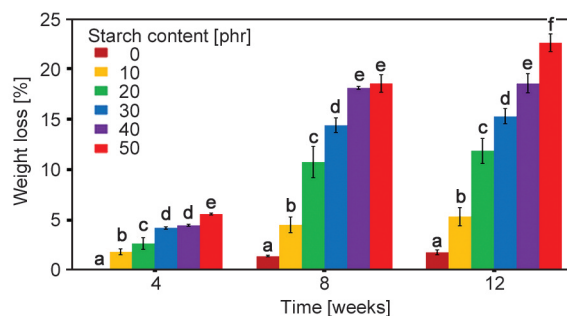


Figure 8. Average weight loss [%] by degradation time for the NR/RS biocomposite foams during burial in soil for up to 12 weeks. **a, b, c, d, e, f:** different letters denote a significant difference between the two values according to ANOVA analysis (Section 2.8.)

RS reached its maximum biodegradation value of roughly 20%. In contrast, the pure NR biocomposite foam showed only a <5% weight loss over the same time period. Because the RS is quickly destroyed by bacteria and fungi in the soil [16], the NR/RS biocomposite foams with high RS contents biodegrade at a faster rate. In a study by Watcharakul *et al.* [43], the presence of starch enabled the degradation of NR. Because the starch was digested first and served as a growth substrate for the bacteria, the bacterium population grew rapidly, and the rate of NR breakdown increased [43]. This agreed with Bhatt *et al.* [44], who reported that NR was slowly destroyed in nature by particular microbes [44]. In addition, Tanrattanakul and Chumeka [35] mention that a longer time was required for deterioration with increased NR content. The addition of NR lowered foam water absorption. Because water is required for fungal development and the physical parameters impact enzyme activity, a decrease in water absorption and a high average molecular weight resulted in a lower rate of biodegradation [35]. Therefore, it was confirmed that RS as filler can increase the degradation rate of the NR/RS biocomposite foams.

3.5. Quality of banana

Biocomposite foam was developed as a new alternative cushioning foam sheet for mechanical damage protection during transport and storage. The NR/RS biocomposite foam exhibited higher tensile strength, elongation at break and tear strength compared to a commercial cushion foam sheet, as shown in Table 3. Furthermore, it showed high rebound resilience and low compression set, as seen in Figures 7e and 7f, indicating that the biocomposite foams had better flexibility properties. If the biocomposite foam can

Table 3. Mechanical properties of the commercial foam and NR/RS biocomposite foams.

Properties		Tensile strength [MPa]	Elongation at break [%]	Tear strength [N/mm]
Commercial foam		0.35±0.13	90.3±3.7	2.41±0.56
Starch content [phr]	0	0.85±0.02	455.1±3.5	4.48±0.12
	10	0.65±0.04	417.0±9.8	4.02±0.19
	20	0.51±0.01	392.9±3.6	5.49±0.06
	30	0.49±0.01	304.7±3.7	3.72±0.26
	40	0.44±0.01	283.7±6.8	3.51±0.16
	50	0.42±0.01	204.8±5.4	3.95±0.25

also absorb ethylene emitted from the fruit, it will have further useful functionality. Accordingly, the NR/RS biocomposite foam with RS 30 phr was chosen for further study as a cushioning foam sheet to extend the life of bananas because it contained the greatest amount of RS in the foam rubber composite without a reduced number of cells foam, as seen in Figure 5a. Fleishy fruit ripening represents the unique coordination of developmental and biochemical pathways that change peel color, texture, aroma, and nutritional quality. Ethylene (C_2H_4), a gaseous plant hormone, influences the ripening of numerous fruits. It has been demonstrated that packaging with ethylene removal systems significantly delays the effects of ethylene on storage-related deterioration. As a result, numerous initiatives have been made to reduce the rate at which ethylene-induced deterioration of fresh produce occurs [45].

Figure 9a presents the ethylene release rate of bananas in sealed glass jars. Over the storage duration, the C_2H_4 concentration rose in each case. Bananas without the NR/RS biocomposite foam (the control) reached their ethylene level peak on the 9th day, after which there was a declining trend. However, the bananas packed with NR/RS biocomposite foam had their climacteric peak delayed to the 12th day. In addition, the bananas packed with NR/RS biocomposite foam had less ethylene accumulated in the headspace of the glass jar throughout the storage period monitored. The NR/RS biocomposite foam was successful in absorbing ethylene and preventing ethylene accumulation in the glass jar because of its porosity with open cell structure. Sittinun *et al.* [46] mention that the interconnecting pores made this composite an efficient sorbent by facilitating the adsorption of additional chemical species. The average weight loss per treatment, with weight loss tending to rise from the start to the end, is shown in Figure 9b. The weight

loss was greater the longer the fruit was stored. However, bananas in the control treatment and those packed with NR/RS biocomposite foam had no difference in weight loss. This indicates that the biocomposite foam could not act as a water vapor barrier for the banana fruit. In addition, the notably thick peels of bananas, which protect them from excessive transpiration, were responsible for their weight maintenance. Fruit firmness is an important characteristic that represents quality and determines consumer acceptability. As presented in Figure 9c, banana pulp firmness reduced dramatically on the sixth day of storage and gradually declined thereafter. The softness was generated by the depolymerization and de-esterification of protopectin in the middle lamella of the cell wall [47]. This occurrence resulted in a weak texture. The impact of storage time on banana TSS is depicted in Figure 9d. All the banana samples showed stable TSS levels within the first three days. Then the TSS dramatically increased in all samples. The hydrolysis of starch and other carbohydrates produced total soluble sugars like sucrose, glucose, and fructose [48], which increased the TSS. Control bananas exhibited a sharp increase in TSS and peaked on day 6 of storage, subsequently becoming steady. In contrast, the NR/RS biocomposite foam treatment presented a delay of the TSS peak to day 12 of storage. On the sixth day, bananas packed with NR/RS biocomposite foam showed lower TSS than the control bananas and a higher pulp firmness. This suggests that using NR/RS biocomposite foam delayed the transformation of starch to sugars and suppressed the activity of cell wall hydrolase enzymes in the banana fruit during storage. Fruit color is the most essential and the most often used quality indicator. As a banana ripens, its green surface turns yellow, which affects its quality and marketability. The transformation of chloroplasts into chromoplasts causes the color change in fruit, corresponding to a decrease in chlorophyll and an increase in carotenoids [49]. Figures 9e, 9f displays the time profiles of the peel color of bananas in terms of lightness (L^*) and hue angle, respectively. The hue angle is representative of the color changes, whereas lightness is correlated with the pigmentation level [50]. Bananas in the control group and those with NR/RS biocomposite foam had increasing L^* throughout the storage. The control bananas changed from green to yellow on day 6 of storage, which correlated with the decrease in hue. Bananas packed with NR/RS biocomposite

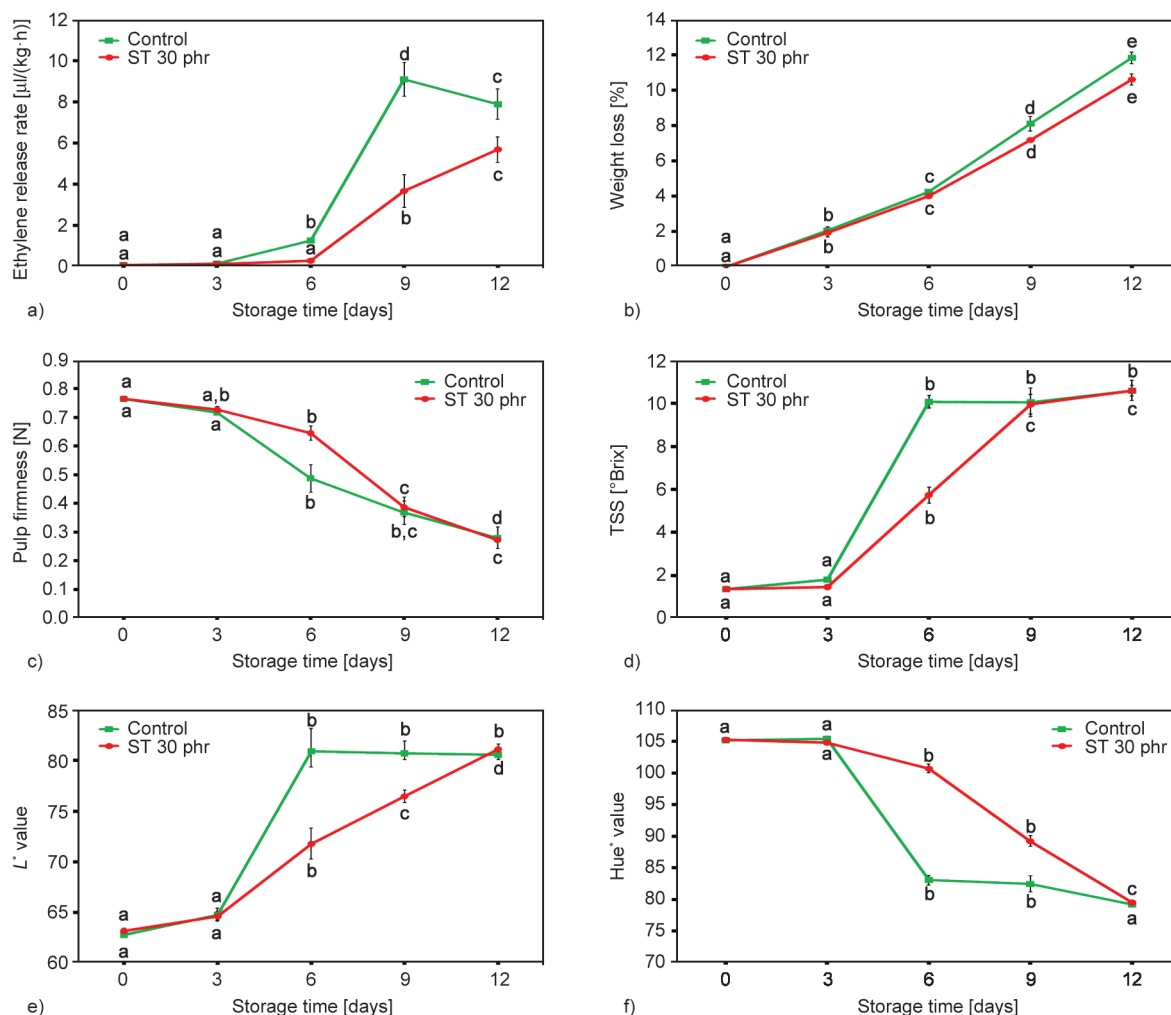


Figure 9. a) Ethylene release rate, b) weight loss, c) pulp firmness, d) TSS, e) lightness (L^*), and f) hue angle of bananas fruit during storage at $25\pm 2\text{ }^{\circ}\text{C}$ for up to 12 days. **a, b, c, d, e, f:** different letters denote a significant difference between the two values according to ANOVA analysis (Section 2.8.)

foam had a reduced L^* over the first 9 days of storage, but it peaked on day 12, correlating with the greater hue. This demonstrates that the NR/RS biocomposite foam could absorb ethylene, resulting in less chlorophyll breakdown and a delayed banana peel color change. This was supported by the quality changes in the bananas after storage for 12 days, illustrated in

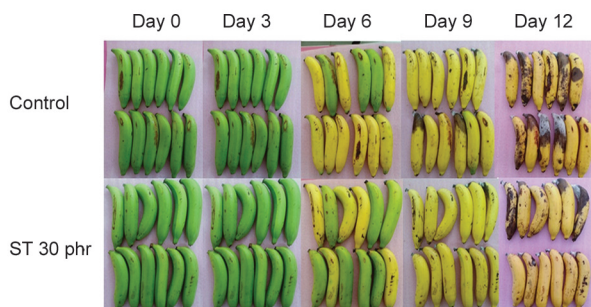


Figure 10. Peel colors of bananas in the control group and those packed with NR/RS biocomposite foam during storage at $25\pm 2\text{ }^{\circ}\text{C}$ for up to 12 days.

Figure 10. The bananas in the experiment had green peel for the first three days. On day 6, the peel color had changed. The yellowness intensified until brown patches appeared on day 9. In the control group, they abruptly changed and became rotten in 9 days, which could be attributed to the quick activity of the enzymes that cause bananas to change color as well as the influence of infections. On the other hand, the NR/RS biocomposite foam packing gave steady color changes. The impact of packing might be attributed to the reduction of ethylene accumulation, resulting in a delay in the ripening of bananas.

4. Conclusions

This study demonstrated straightforward and environmentally friendly strategies to prepare natural rubber latex (NR) foams with open pore structure by introducing rice starch (RS) as a biofiller and applying the Dunlop method. The RS content had an effect

on foam cell size, cell wall thickness and reduced the number density of cells while increasing foam density. The incorporation of RS into the NR biocomposite foams relatively improved 100% modulus, hardness, and compression force deflection (CFD). At the same time, it diminished tensile strength, elongation at break, and rebound resilience, suggesting that the RS reduced the flexibility of the NR/RS biocomposite foam. However, the biodegradability was also improved by adding RS, as the starch provided nutrition to bacteria and fungi in the soil. Finally, the NR/RS biocomposite foam could be used as green packaging that extends the shelf life of climacteric fresh fruits because it reduces ethylene accumulation and improves the shelf life of bananas.

References

- [1] Shey J., Imam S. H., Glenn G. M., Orts W. J.: Properties of baked starch foam with natural rubber latex. *Industrial Crops and Products*, **24**, 34–40 (2006).
<https://doi.org/10.1016/j.indcrop.2005.12.001>
- [2] Nagalakshmaiah M., Afrin S., Malladi R. P., Elkoun S., Robert M., Ansari M. A., Svedberg A., Karim Z.: Biocomposites: Present trends and challenges for the future. in ‘Composites science and engineering, green composites for automotive applications’ (eds.: Koronis G., Silva A.) Woodhead, Cambridge, 197–215 (2019).
<https://doi.org/10.1016/B978-0-08-102177-4.00009-4>
- [3] Mohiuddin M., Kumer B., Haque S.: Biopolymer composites in photovoltaics and photodetectors. in ‘Biopolymer composites in electronics’ (eds.: Sadasivuni K. K., Ponnammma D., Kim J., Cabibihan J.-J., AlMaadeed M. A.) Elsevier, Amsterdam, 459–486 (2017).
<https://doi.org/10.1016/B978-0-12-809261-3.00017-6>
- [4] Manaila E., Stelescu M. D., Craciun G.: Degradation studies realized on natural rubber and plasticized potato starch based eco-composites obtained by peroxide cross-linking. *International Journal of Molecular Sciences*, **19**, 2862 (2018).
<https://doi.org/10.3390/ijms19102862>
- [5] Syuhada D. N., Azura A. R.: Waste natural polymers as potential fillers for biodegradable latex-based composites: A review. *Polymers*, **13**, 3600 (2021).
<https://doi.org/10.3390/polym13203600>
- [6] Thomas S. K., Parameswaranpillai J., Krishnasamy S., Begum P. M. S., Nandi D., Siengchin S., George J. J., Hameed N., Salim N. V., Sienkiewicz N.: A comprehensive review on cellulose, chitin, and starch as fillers in natural rubber biocomposites. *Carbohydrate Polymer Technologies and Applications*, **2**, 100095 (2021).
<https://doi.org/10.1016/j.carpta.2021.100095>
- [7] Wani A. A., Singh P., Shah M. A., Schweiggert-Weisz U., Gul K., Wani I. A.: Rice starch diversity: Effects on structural, morphological, thermal, and physicochemical properties – A review. *Comprehensive Reviews in Food Science and Food Safety*, **11**, 417–436 (2012).
<https://doi.org/10.1111/j.1541-4337.2012.00193.x>
- [8] Thakur R., Pristijono P., Golding J. B., Stathopoulos C. E., Scarlett C., Bowyer M., Singh S. P., Vuong Q. V.: Effect of starch physiology, gelatinization, and retrogradation on the attributes of rice starch- κ -carrageenan film. *Starch*, **70**, 1700099 (2018).
<https://doi.org/10.1002/star.201700099>
- [9] Thakur R., Pristijono P., Scarlett C. J., Bowyer M., Singh S. P., Vuong Q. V.: Starch-based films: Major factors affecting their properties. *International Journal of Biological Macromolecules*, **132**, 1079–1089 (2019).
<https://doi.org/10.1016/j.ijbiomac.2019.03.190>
- [10] Wu Y.-P., Ji M.-Q., Qi Q., Wang Y.-Q., Zhang L.-Q.: Preparation, structure, and properties of starch/rubber composites prepared by *co*-coagulating rubber latex and starch paste. *Macromolecular Rapid Communications*, **25**, 565–570 (2004).
<https://doi.org/10.1002/marc.200300125>
- [11] Leksawasdi N., Chaiyaso T., Rachtanapun P., Thanakkasaranee S., Jantrawut P., Ruksiriwanich W., Seesuriyachan P., Phimolsiripol Y., Techapun C., Sommano S. R., Ougizawa T., Jantanasakulwong K.: Corn starch reactive blending with latex from natural rubber using Na^+ ions augmented carboxymethyl cellulose as a crosslinking agent. *Scientific Reports*, **11**, 19250 (2021).
<https://doi.org/10.1038/s41598-021-98807-x>
- [12] Senna M. M., Mohamed R. M., Shehab-Eldin A. N., El-Hamouly S.: Characterization of electron beam irradiated natural rubber/modified starch composites. *Journal of Industrial and Engineering Chemistry*, **18**, 1654–1661 (2012).
<https://doi.org/10.1016/j.jiec.2012.03.004>
- [13] Valodkar M., Thakore S.: Thermal and mechanical properties of natural rubber and starch nanobiocomposites. *International Journal of Polymer Analysis and Characterization*, **15**, 387–395 (2010).
<https://doi.org/10.1080/1023666X.2010.500543>
- [14] Angellier H., Molina-Boisseau S., Lebrun L., Dufresne A.: Processing and structural properties of waxy maize starch nanocrystals reinforced natural rubber. *Macromolecules*, **38**, 3783–3792 (2005).
<https://doi.org/10.1021/ma050054z>
- [15] Wang Z.-F., Peng Z., Li S.-D., Lin H., Zhang K.-X., She X.-D., Fu X.: The impact of esterification on the properties of starch/natural rubber composite. *Composites Science and Technology*, **69**, 1797–1803 (2009).
<https://doi.org/10.1016/j.compscitech.2009.04.018>
- [16] Riyajan S.-A., Sasithornsonti Y., Phinyocheep P.: Green natural rubber-g-modified starch for controlling urea release. *Carbohydrate Polymers*, **89**, 251–258 (2012).
<https://doi.org/10.1016/j.carbpol.2012.03.004>

- [17] Vudjung C., Chaisuwan U., Pangan U., Chaipugdee N., Boonyod S., Santawitee O., Saengsuwan S.: Effect of natural rubber contents on biodegradation and water absorption of interpenetrating polymer network (IPN) hydrogel from natural rubber and cassava starch. *Energy Procedia*, **56**, 255–263 (2014).
<https://doi.org/10.1016/j.egypro.2014.07.156>
- [18] Riyajan S-A.: Robust and biodegradable polymer of cassava starch and modified natural rubber. *Carbohydrate Polymers*, **134**, 267–277 (2015).
<https://doi.org/10.1016/j.carbpol.2015.07.038>
- [19] Riyajan S-A., Patisat S.: A novel packaging film from cassava starch and natural rubber. *Journal of Polymers and the Environment*, **26**, 2845–2854 (2018).
<https://doi.org/10.1007/s10924-017-1172-5>
- [20] Li K., You J., Liu Y., Zhu K., Xue C., Guo X., Wang Z., Zhang Y.: Functionalized starch as a novel eco-friendly vulcanization accelerator enhancing mechanical properties of natural rubber. *Carbohydrate Polymers*, **231**, 115705 (2020).
<https://doi.org/10.1016/j.carbpol.2019.115705>
- [21] Bouthegourd E., Rajisha K. R., Kalarical N., Saiter J. M., Thomas S.: Natural rubber latex/potato starch nanocrystal nanocomposites: Correlation morphology/electrical properties. *Materials Letters*, **65**, 3615–3617 (2011).
<https://doi.org/10.1016/j.matlet.2011.07.069>
- [22] Rajisha K. R., Maria H. J., Pothan L. A., Ahmad Z., Thomas S.: Preparation and characterization of potato starch nanocrystal reinforced natural rubber nanocomposites. *International Journal of Biological Macromolecules*, **67**, 147–153 (2014).
<https://doi.org/10.1016/j.ijbiomac.2014.03.013>
- [23] Ab Rahman M. F., Norfaizal N. S., Azura A. R.: The influence of sago starch dispersion on mechanical properties of biodegradable natural rubber latex films. *Materials Today: Proceedings*, **17**, 1040–1046 (2019).
<https://doi.org/10.1016/j.matpr.2019.06.507>
- [24] Akbari S., Gupta A., Khan T. A., Jamari S. S., Ani N. B. C., Poddar P.: Synthesis and characterization of medium density fibreboard by using a mixture of natural rubber latex and starch as an adhesive. *Journal of the Indian Academy of Wood Science*, **11**, 109–115 (2014).
<https://doi.org/10.1007/s13196-014-0124-0>
- [25] Soubam T., Gupta A.: Eco-friendly natural rubber latex and modified starch-based adhesive for wood-based panels application – A review. *Maejo International Journal of Energy and Environmental Communication*, **3**, 49–53 (2021).
<https://doi.org/10.54279/mijeec.v3i1.245163>
- [26] Liu C., Shao Y., Jia D.: Chemically modified starch reinforced natural rubber composites. *Polymer*, **49**, 2176–2181 (2008).
<https://doi.org/10.1016/j.polymer.2008.03.005>
- [27] Wu J., Li K., Pan X., Liao S., You J., Zhu K., Wang Z.: Preparation and physical properties of porous starch/natural rubber composites. *Starch*, **70**, 1700296 (2018).
<https://doi.org/10.1002/star.201700296>
- [28] Suethao S., Phongphanphane S., Wong-ekkabut J., Smitthipong W.: The relationship between the morphology and elasticity of natural rubber foam based on the concentration of the chemical blowing agent. *Polymers*, **13**, 1091 (2021).
<https://doi.org/10.3390/polym13071091>
- [29] Sid S., Mor R. S., Kishore A., Sharanagat V. S.: Bio-sourced polymers as alternatives to conventional food packaging materials: A review. *Trends in Food Science and Technology*, **115**, 87–104 (2021).
<https://doi.org/10.1016/j.tifs.2021.06.026>
- [30] Nabels-Sneiders M., Platnieks O., Grase L., Gaidukovs S.: Lamination of cast hemp paper with bio-based plastics for sustainable packaging: Structure-thermomechanical properties relationship and biodegradation studies. *Journal of Composites Science*, **6**, 246 (2022).
<https://doi.org/10.3390/jcs6090246>
- [31] Georges A., Lacoste C., Damien E.: Effect of formulation and process on the extrudability of starch-based foam cushions. *Industrial Crops and Products*, **115**, 306–314 (2018).
<https://doi.org/10.1016/j.indcrop.2018.02.001>
- [32] Japra-Parra M., Chen L.: Applications of plant polymer-based solid foams: Current trends in the food industry. *Applied Sciences*, **11**, 9605 (2021).
<https://doi.org/10.3390/app11209605>
- [33] Nechita P., Năstac S. M.: Overview on foam forming cellulose materials for cushioning packaging applications. *Polymers*, **14**, 1963 (2022).
<https://doi.org/10.3390/polym14101963>
- [34] Kiatkamjornwong S., Suruchanajirasakul P., Tasakorn P.: Natural rubber–cassava starch foam by compression moulding. *Plastics, Rubber and Composites*, **30**, 318–327 (2001).
<https://doi.org/10.1179/146580101322913419>
- [35] Tanrattanakul V., Chumeka W.: Effect of potassium persulfate on graft copolymerization and mechanical properties of cassava starch/natural rubber foams. *Journal of Applied Polymer Science*, **116**, 93–105 (2010).
<https://doi.org/10.1002/app.31514>
- [36] Riyajan S-A., Keawittarit P.: A novel natural rubber-graft-cassava starch foam for oil/gasohol absorption. *Polymer International*, **65**, 491–502 (2016).
<https://doi.org/10.1002/pi.5062>
- [37] Prasopdee T., Shah D. U., Smitthipong W.: Approaches toward high resilience rubber foams: Morphology–mechanics–thermodynamics relationships. *Macromolecular Materials and Engineering*, **306**, 2100337 (2021).
<https://doi.org/10.1002/mame.202100337>
- [38] Phomrak S., Nimpaiaboon A., Newby B. Z., Phisalaphon M.: Natural rubber latex foam reinforced with micro- and nanofibrillated cellulose *via* Dunlop method. *Polymers*, **12**, 1959 (2020).
<https://doi.org/10.3390/polym12091959>

- [39] Basuli U., Lee G. B., Jang S. Y., Oh J., Lee J. H., Kim S. C., Jeon N. D., Huh Y. I., Nah C.: Foaming behavior, structure, and properties of rubber nanocomposites foams reinforced with zinc methacrylate. *Elastomers and Composites*, **47**, 297–309 (2012).
<https://doi.org/10.7473/EC.2012.47.4.297>
- [40] Mark J. E.: *Polymer data handbook*. Oxford University Press, New York (1999).
- [41] Vahidifar A., Esmizadeh E., Rostami E., Khorasani S. N., Rodrigue D.: Morphological, rheological, and mechanical properties of hybrid elastomeric foams based on natural rubber, nanoclay, and nanocarbon black. *Polymer Composites*, **40**, 4289–4299 (2019).
<https://doi.org/10.1002/pc.25290>
- [42] Amaraweera S. M., Gunathilake C., Gunawardene O. H. P., Dassanayake R. S., Fernando N. M. L., Wanninayaka D. B., Rajapaksha S. M., Manamperi A., Gangoda M., Manchanda A., Fernando C. A. N., Kulatunga A. K., Manipura A.: Preparation and characterization of dual-modified cassava starch-based biodegradable foams for sustainable packaging applications. *ACS Omega*, **7**, 19579–19590 (2022).
<https://doi.org/10.1021/acsomega.2c01292>
- [43] Watcharakul S., Umsakul K., Hodgson B., Chumeka W., Tanrattanakul V.: Biodegradation of a blended starch/natural rubber foam biopolymer and rubber gloves by *Streptomyces coelicolor* CH13. *Electronic Journal of Biotechnology*, **15**, 1–14 (2012).
<https://doi.org/10.2225/vol15-issue1-fulltext-10>
- [44] Bhatt R., Shah D., Patel K. C., Trivedi U.: PHA-rubber blends: Synthesis, characterization and biodegradation. *Bioresource Technology*, **99**, 4615–4620 (2008).
<https://doi.org/10.1016/j.biortech.2007.06.054>
- [45] Mariah M. A. A., Vonnie J. M., Erna K. H., Nur'Aqilah N. M., Huda N., Abdul W. R., Rovina K.: The emergence and impact of ethylene scavengers techniques in delaying the ripening of fruits and vegetables. *Membranes*, **12**, 117 (2022).
<https://doi.org/10.3390/membranes12020117>
- [46] Sittinun A., Pisitsak P., Manuspiya H., Thiangtham S., Chang Y-H., Ummartyotin S.: Utilization of palm olein-based polyol for polyurethane foam sponge synthesis: Potential as a sorbent material. *Journal of Polymers and the Environment*, **28**, 3181–3191 (2020).
<https://doi.org/10.1007/s10924-020-01834-4>
- [47] Jirukkakul N., Chanshotikul N.: The effects of wrapping paper coated with banana flour on physical properties of banana fruit. *International Journal of Food Engineering*, **5**, 200–204 (2019).
<https://doi.org/10.18178/ijfe.5.3.200-204>
- [48] Soradech S., Nunthanid J., Limmatvapirat S., Luangtananan M.: Utilization of shellac and gelatin composite film for coating to extend the shelf life of banana. *Food Control*, **B**, 1310–1317 (2017).
<https://doi.org/10.1016/j.foodcont.2016.10.059>
- [49] Das D. K., Dutta H., Mahanta C. L.: Development of a rice starch-based coating with antioxidant and microbe-barrier properties and study of its effect on tomatoes stored at room temperature. *LWT – Food Science and Technology*, **50**, 272–278 (2013).
<https://doi.org/10.1016/j.lwt.2012.05.018>
- [50] Wantat A., Rojsitthisak R., Seraypheap K.: Inhibitory effects of high molecular weight chitosan coating on ‘Hom Thong’ banana fruit softening. *Food Packaging and Shelf Life*, **29**, 100731 (2021).
<https://doi.org/10.1016/j.fpsl.2021.100731>