



Research Article

Application of Waste Bovine Bone-derived Hydroxyapatite to Biodegradable Coatings for Paper-based Food Packaging

Netnapid Ongsuwan and Waefarida Chelee

Department of Food Science and Nutrition, Faculty of Science and Technology, Prince of Songkla University, Pattani, Thailand

Saowapa Chotisuwan*

Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani, Thailand

* Corresponding author. E-mail: saowapa.c@psu.ac.th DOI: 10.14416/j.asep.2024.10.015

Received: 18 August 2024; Revised: 17 September 2024; Accepted: 30 September 2024; Published online: 15 October 2024

© 2024 King Mongkut's University of Technology North Bangkok. All Rights Reserved.

Abstract

Hydroxyapatite (HAp) powder was produced by utilizing food waste bovine bones through alkaline treatment and calcination. The biodegradable coatings on paper-based food packaging that contained synthesized HAp were subsequently prepared and characterized. The slurry of 5 wt% of bovine bones synthesized HAp, 2 wt% of polyvinyl alcohol, and glycerol was coated on a grey back duplex board (GB) by dipping and spraying. The morphology, color, penetration strength, water and oil absorption, and biodegradability of the coated GB were observed. The color of the spray-coated GB was still slightly brighter (L^*) than others due to its good coating ability before and after being heated at 800 W in a microwave oven for 1 minute. The penetration strength of coated GB was higher than that of noncoated GB after containing hot water. The coated GB had 8% water absorption, which was lower than that of the noncoated GB (10%), while oil absorption was nearly the same (3%). Moreover, the biodegradable properties of both coated GBs were not significantly different compared to the non-coated samples.

Keywords: Biodegradable films, Bovine bone, Food packaging, Grey back duplex board, Hydroxyapatite

1 Introduction

Food packaging has a responsibility to maintain food quality. Popular materials include paper and plastic. The most common material is plastic since it can block air and moisture penetration. However, the drawbacks of plastic stem from environmental contamination. Paper is lightweight and inexpensive, but it cannot stop moisture, which some types of food require. Some paper-based food packaging was coated with synthetic polymers; nowadays, much research focuses on bio-based polymers such as polylactic acid (PLA), polybutylene succinate (PBS), polyglycolic acid (PGA), polyhydroxyalkanoates (PHAs), and petrochemical-based synthetic biodegradable polyvinyl alcohol (PVA) [1]–[4]. These biodegradable coating materials have many advantages, such as good

barrier properties for packaging, good optical transparency, and high mechanical strength. However, some drawbacks have been observed, e.g., PBS has a high synthetic cost, PLA has poor barrier properties for oxygen and water vapor permeability, PHAs have physical aging at room temperature, inherent brittleness, a narrow processing window, etc. Among those polymers, PVA offers the most environmentally favorable qualities of any biopolymer, including low cost and wide availability of raw materials, minimal energy use during production, and the capacity to degrade in both water and soil [2], [5]. Furthermore, much research has concentrated on the incorporation of functional inorganic fillers, which are already extensively employed in the paper-based packaging industry as a top varnish to enhance the moisture barrier properties of the coated substrates or to

enhance printability and glossiness [6]. Consequently, additional inorganic materials such as aluminium, alumina, silicate, kaolinite, montmorillonite, bentonite, etc., applied with these bio-based and biodegradable polymers can improve those properties and also the barrier properties, mechanical strength, and oil and grease resistance of the coatings and packaging [7]–[9]. In addition to these inorganic substances, renewable, naturally abundant, nontoxicity, biocompatibility, photocatalyst, low cost, and good organic adsorbent materials such as hydroxyapatite (HAp) have been interested in being used as composite materials along with biodegradable binders, for example, PVA/HAp composites for biomedical applications [10]–[14] and coating materials [15], [16].

A calcium phosphate molecule, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, called hydroxyapatite (HAp), naturally found in animal bones, has good physical, and chemical properties, and organic adsorbent including biocompatibility [17]. It can be made from natural resources, such as fish scales [18] and animal bones such as fish bones [19], [20] and bovine bones [17], or by chemical reactions such as CaO from cuttlebones reacted with ammonium hydrogen phosphate [21]. Animal bones are a popular and long-lasting natural polymer that can be used to create composite films with other components for various applications. Many halal soup beef restaurants in Pattani normally dispose of the waste from boiling and consuming beef soup, which includes large beef bones such as hip and leg bones. In addition, some compounds can be further utilized, including collagen, which is found in about 20% of the common bone composition by weight. Calcium phosphate is about 69% by weight, found in the form of HAp [22]. These waste bones can be used to synthesize HAp and utilized as an inorganic material for composite films and bio-based and biodegradable coating materials for paper-based food packaging. Moreover, HAp can play an important role as an antioxidant material [23] due to its photocatalyst that can produce superoxide radicals and hydroxyl radicals to be effective in reducing the reactive oxygen species (ROS) levels and degradation of other organic pollutants [24], [25]. HAp has been used with quercetin to develop an alginate-based edible coating to extend the shelf life of papaya [26]. Thus, coating HAp on a paper base can be a promising to achieve a biodegradable, low cost, nontoxic, antioxidant paper-based food packaging.

Hooi and co-workers also reported that using the casting method to form a PVA-HAp composite bone scaffold showed higher interaction than the extrusion method [20]. PVA is hydrophilic, so it can interact well with the hydroxyl group on the HAp surface [27]. The composite film composed of HAp, binders as PVA [13], [15], [16], carboxymethyl cellulose (CMC), and plasticizers as glycerol (Gly), polyethylene glycol, and sorbitol was prepared, and it was found that the film formed by 2–10 wt% HAp derived from waste bovine bone, 2 wt% PVA, and 2 wt% Gly showed good physical properties among other films such as brightness and water solubility [28]. While the composite film of HAp-CMC-Gly shows too high viscosity of slurry to cast composite films. The optimum HAp weight of HAp in HAp-PVA-Gly composite film was found to be 5 wt%, whereas 2 and 10 wt% HAp composite films were too brittle due to low HAp dispersion and HAp self-aggregation.

Consequently, in this work, the green HAp composite formula, which consists of 5 wt% HAp derived from waste bovine bone, 2 wt% PVA, and 2 wt% Gly, was employed to coat grey back (GB) duplex board by casting and spraying method for use as paper-based food packaging. The composite was characterized by certain physical and mechanical properties, including biodegradable properties.

2 Experimental

2.1 Materials

Sodium hydroxide (Loba chemie), polyvinyl alcohol (PVA) (Sigma-Aldrich), and glycerol (Gly) (AnaPure) used in this work were analytical grade and used without further purification.

2.2 Preparation of bovine waste derived HAp

The food waste bovine bones were collected at a local beef soup restaurant (namely Soup Jehyoh) in Mueang, Pattani, Thailand. Before drying, they were cleaned with deionized water and then immersed in a 2 wt% sodium hydroxide (NaOH) solution to remove waste meat and hydrolyze fat and lipid. After drying, the size of these cleaned waste bones was reduced into small pieces and then calcined at 900 °C for 2 h [28]. The pale-yellow HAp powders were obtained after grinding the calcined bones, and they were kept in a desiccator before characterization and preparation of

composite films as shown in the research scheme in Figure 1.

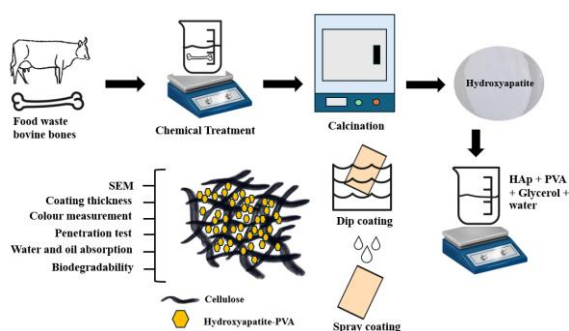


Figure 1: Schematic of laboratory process to prepare bovine waste derived HAp powder, HAp composite films, and grey back duplex board coated with HAp composite film.

2.3 HAp composite film preparation

Composite films namely HAp-PVA-Gly made of HAp (5 wt%), PVA as binding agent (2 wt%), and glycerol (Gly) as plasticizer (2 wt%) were prepared by casting method using distilled water as the solvent. PVA was first dissolved in distilled water at 90 °C while well stirred, and then at room temperature, it was combined with an aqueous glycerol solution. Using a homogenizer and an ultrasonicator, HAp powders were slowly added to the solution and well blended. The films were eventually created by casting them into a round plastic mold and dried at 50 °C in a hot air oven.

2.4 Preparation of grey back duplex board coated with HAp composite film

Coating paper-based or grey back duplex board (GB) with a dipping coating and spraying technique was performed by preparing a viscous liquid containing HAp-PVA-Gly at a ratio of 5-2-2 wt%. The GB was dipped in such a viscous liquid for 20 s under ultrasonic waves three times; letting it drip for around 1 min to remove excess solution before the next dipping. The spraying techniques using a spray gun connected to an air compressor were also repeated three times; it was also let drip to remove excess solution before next dipping. The coated papers were sprayed with 0.02 M potassium oleate and dried at 50 °C for about 24 h. The morphology of the samples was observed by a stereomicroscope (Olympus stemi 2000 °C)

and a scanning electron microscope (SEM) (FEI Quanta 400 England).

2.5 Physical property for packaging usage

2.5.1 Color measurement

A color meter (Hunter Lab ColorQuest XE/CQX 382) was used to measure the Commission Internationale de l'Éclairage (CIE) $L^*a^*b^*$ color and brightness of the films and the GB food packaging coated with HAp composite films while containing water before and after being heated by an 800 W microwave oven for 1–8 min.

2.5.2 Penetration test

The force (g) for penetration testing of the samples coated with HAp composite films containing water was tested by a texture analyzer (Stable Micro systems Ltd., TA.XTplus) after heating GB food packaging coated with HAp composite films in an 800 W microwave oven for 1–8 min.

2.5.3 Water and oil absorption

The percentages of water and oil absorption of the GB food packaging coated with HAp composite films were investigated before and after containing oily and juicy food such as French fries and watermelon, as the Equation (1). The non-coated and coated HAp GB were folded into a small cup with the same volume before being weighed at m_1 and the food samples were added until the cup was filled. Before removing the food samples and obtaining the m_2 , allow the food samples to stand for one hour.

$$\text{Water/Oil absorption (\%)} = \frac{m_1 - m_2}{m_1} \times 100 \quad (1)$$

Where m_1 and m_2 are the weights (g) of the sample before and after containing the food sample, respectively.

2.6 Biodegradable paper-based food packaging coating by HAp composites

The biodegradable property of the GB food packaging coated with HAp composite films was tested for 3 replicates by burying the samples (10×10 cm) in the soil at room temperature. The moisture of the soil and humidity were recorded. The percentage of weight lost

and the morphology of the samples at 7 and 14 days were investigated using Equation (2) [29].

$$\text{Weight lost (\%)} = \frac{W_1 - W_2}{\text{Time (week)}} \times 100 \quad (2)$$

Where w_1 and w_2 are the weights of the dried sample before and after the biodegradability test, respectively.

2.7 Statistical analysis

Experimental data were obtained at least three times and analyzed by one-way analysis of variance (ANOVA) for statistically significant differences among the averages (p -value < 0.05).

3 Results and Discussion

3.1 Morphology of HAp composite films and the GB food packaging coated with HAp composite films

3.1.1 HAp composite films

The HAp powders (5 wt%) derived from waste bovine bones were mixed with PVA as a binding agent (2 wt%) and glycerol (Gly) as plasticizer (2 wt%) to form HAp composite films by casting, as shown in Figure 2. The opaque white films with a thickness 0.28 ± 0.06 mm showed the color parameters 65.00 ± 5.45 (L*), -0.08 ± 0.65 (a*), and -0.91 ± 0.64 (b*). The water solubility of the film was $17.33 \pm 1.23\%$, which was low compared to other films using HAp and PVA (25–52%) [28]. The front, back surface, and cross-section of this film were investigated by stereomicroscope (Figure 3(a)–(c)), indicating a nearly smooth surface with homogeneous blending of HAp, PVA, and Gly. These materials contain hydroxyl groups and have hydrophilic properties; thus, they can form homogeneous films through hydrogen bonding at this ratio (5:2:2), while PVA can form cross-linking between the polymer chains and interact with HAp [27].



Figure 2: Dried HAp composite film consists of HAp-PVA-Gly at 5, 2, and 2 wt%, respectively.

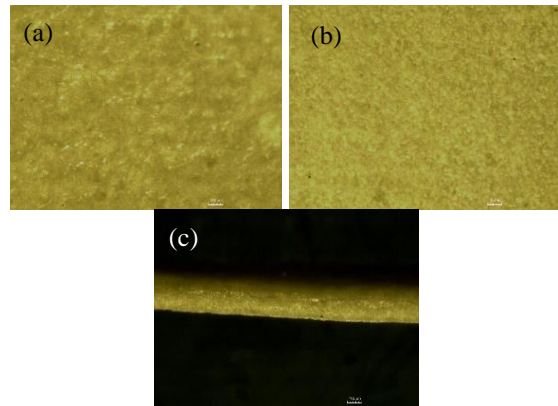


Figure 3: Dispersion characteristics of HAp on hybrid HAp film (a) front surface, (b) back surface, and (c) cross-section, at 100X magnification.

3.1.2 The morphology of the GB and grey back duplex board coated with HAp composite film

Before the coating dried, the GB surface and the HAp slurry interacted through the hydroxyl group (-OH) of cellulose and the water-based solvent, as well as the positively charged HAp and the -OH groups of PVA [27], [30], [31]. After drying, the dried GBs coated with HAp composite film by dipping and spraying techniques were characterized by SEM compared to non-coated GB (Figure 4(a)–(c)). Figure 4(b) demonstrates a minimal deposition of white HAp composite on the GB by the dipping technique. This suggests the presence of small clusters of HAp composite particles, approximately 1 μm in size, adhering to the surface of cellulose fibers and the pores of the cellulose sheet due to adsorption interaction between surface hydroxyl group (-OH) of cellulose and positive charge of HAp surface. Figure 4(c) shows that large amounts of the HAp composite were coated on the GB by the spraying method after drying, demonstrating small particles and aggregated HAp composite dispersed on the surface of the cellulose sheet. This indicates that the spraying technique using a spray gun connected to an air compressor is suitable for coating the GB and will thus affect the barrier properties and other physical properties of the coated GB.

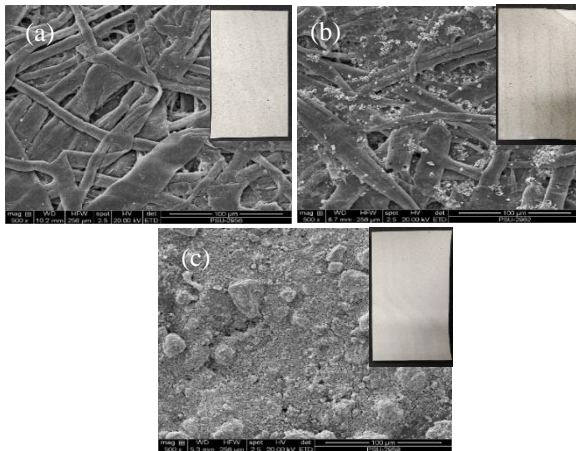


Figure 4: SEM images compared with photos of grey back duplex board (inserted photos) demonstrate the surface of (a) grey back duplex board, (b) grey back duplex board coated with HAp by dipping, and (c) grey back duplex board coated with HAp by the spraying method.

3.2 Physical, mechanical, and biodegradable properties of coated GB

3.2.1 Color

Table 1 displays the measured (CIE) $L^*a^*b^*$ color, thickness, and coating ability of GB coated by dipping and spraying. The L^* values representing lightness and coating ability evidenced by the weight gain for GB coated by spraying (16%) were higher than dip coating, indicating well dispersion of white HAp composite on the surface of GB as shown in SEM

images (Figure 4), even though the thickness measured by vernier caliper of the coated paper board was nearly the same. After coating, the thickness of GB did not significantly change, ranging from 0.40 ± 0.02 to 0.40 ± 0.04 mm for dipping and 0.37 ± 0.01 to 0.37 ± 0.02 mm for spraying.

3.2.2 Physical and mechanical properties after heating the GB packaging coated with HAp composite film with a microwave oven

The coated packaging was put into a microwave oven heated at 800 W for 1 min and repeated heating 1–8 times. The maximum time of non-coated GB, GB coated by dipping, and GB coated by spraying that can be heated in a microwave oven at 800 W is 7, 4, and 8 min, respectively.

The color of the paper packaging on both the front (non-coating) and back sides (coated with HAp composite) after heating was measured, as shown in Table 2.

It was found that for the GB, the bright whiteness or lightness (L^* values) significantly decreased with the duration of heating (1–7 min) from 83 to 47 for the front (non-coated) side and 76 to 51 for the back (coated side), while a^* and b^* increased. The dipped coating GB shows a slight decrease in L^* values from 73 to 67 for the front (non-coated) side and 73 to 63 for the back (coated side) during 1–5 min of heating. The L^* values of spray-coated packaging for the front (non-coated) side were not significantly decreased from 83 to 71, and the L^* values for the back (coated) side were not significantly decreased from 81 to 71 during 1–8 min heated by a microwave.

Table 1: Color values of GB paper packaging before and after coating with HAp composite films.

Coating Methods	Color Values			Thickness of GB Sample after Coating (mm)	Coating Ability (g/m ²)
	Back (HAp Film Coating)				
	L^*	a^*	b^*		
Grey back duplex board	76.86 ± 0.10^b	1.76 ± 0.04^b	5.05 ± 0.07^b	-	-
Dipping	73.61 ± 1.26^c	1.90 ± 0.04^a	5.75 ± 0.14^a	0.40 ± 0.04^a	11.01 ± 0.23^b
Spraying	80.88 ± 0.90^a	1.27 ± 0.09^c	3.10 ± 0.31^c	0.37 ± 0.02^b	16.15 ± 0.18^a

The data is presented as a mean \pm SD. For each variable parameter, the mean values are denoted by various lowercase letters within the same column to signify statistical significance (p -value < 0.05).

Table 2: Color values of non-coated and coated GB paper packaging coated with HAp composite films after being used in an 800 Watt microwave oven for heating food.

Coating Methods	Heating Time (min)	Color Values					
		Front (Non-Coated)			Back (HAp film coating)		
		L^*	a^*	b^*	L^*	a^*	b^*
Grey back duplex board	1	83.85 ± 0.04^a	2.33 ± 0.02^c	-10.77 ± 0.11^d	76.92 ± 0.08^a	1.71 ± 0.02^d	5.17 ± 0.10^d
	2	83.79 ± 0.19^a	2.29 ± 0.04^c	-10.44 ± 0.16^d	76.94 ± 0.15^a	1.69 ± 0.04^d	5.17 ± 0.10^d
	3	82.64 ± 0.90^a	0.71 ± 0.46^d	-2.24 ± 4.03^c	75.24 ± 1.41^a	1.50 ± 0.30^d	10.30 ± 3.03^c
	4	74.52 ± 1.92^b	2.61 ± 0.89^c	16.04 ± 2.07^{ab}	69.17 ± 1.88^b	3.39 ± 0.69^c	17.10 ± 1.00^a

Table 2 (Continued).

Coating Methods	Heating Time (min)	Color Values					
		Front (Non-Coated)			Back (HAp Film Coating)		
		L*	a*	b*	L*	a*	b*
	5	71.09 ± 0.38 ^c	2.90 ± 0.40 ^c	14.31 ± 1.09 ^b	74.37 ± 0.36 ^a	1.60 ± 0.15 ^d	12.90 ± 0.51 ^b
	6	70.83 ± 2.21 ^c	4.15 ± 0.87 ^b	18.71 ± 1.71 ^a	66.53 ± 2.08 ^b	4.29 ± 0.54 ^b	18.50 ± 0.49 ^a
	7	47.05 ± 4.14 ^d	8.32 ± 0.21 ^a	18.97 ± 1.77 ^a	51.28 ± 3.78 ^c	7.04 ± 0.21 ^a	18.73 ± 0.94 ^a
Dipping	1	73.96 ± 1.21 ^a	2.35 ± 1.00 ^b	5.98 ± 2.03 ^a	73.61 ± 1.26 ^a	1.90 ± 0.04 ^b	5.75 ± 0.14 ^c
	2	78.50 ± 2.33 ^a	2.22 ± 0.53 ^b	-3.68 ± 8.15 ^b	72.25 ± 2.55 ^a	1.87 ± 0.32 ^b	7.98 ± 3.64 ^c
	3	71.11 ± 4.04 ^b	3.01 ± 1.31 ^b	17.73 ± 4.34 ^a	69.93 ± 2.58 ^a	2.42 ± 0.51 ^b	14.59 ± 3.05 ^b
	4	67.16 ± 3.11 ^c	4.98 ± 0.97 ^a	21.73 ± 1.28 ^a	63.43 ± 1.33 ^b	4.75 ± 0.47 ^a	19.52 ± 0.44 ^a
Spraying	1	83.63 ± 0.26 ^a	2.37 ± 0.04 ^b	-10.60 ± 0.19 ^d	81.28 ± 0.42 ^a	1.15 ± 0.04 ^{bc}	3.20 ± 0.24 ^c
	2	82.34 ± 1.02 ^a	0.82 ± 0.25 ^c	-2.35 ± 3.18 ^{bc}	81.56 ± 0.65 ^a	0.79 ± 0.03 ^c	5.28 ± 0.45 ^c
	3	81.19 ± 3.39 ^a	1.81 ± 0.46 ^{bc}	-7.87 ± 1.97 ^c	81.83 ± 1.38 ^a	0.72 ± 0.21 ^c	3.57 ± 0.75 ^c
	4	81.91 ± 1.17 ^a	1.03 ± 0.35 ^c	-2.13 ± 3.66 ^{bc}	79.64 ± 0.66 ^a	0.69 ± 0.16 ^c	5.24 ± 1.87 ^c
	5	79.46 ± 3.25 ^a	1.05 ± 0.83 ^c	4.07 ± 6.92 ^b	79.49 ± 1.82 ^a	1.00 ± 0.35 ^c	9.30 ± 1.96 ^b
	6	74.70 ± 3.08 ^b	2.26 ± 1.32 ^{ab}	13.01 ± 4.63 ^a	74.80 ± 2.53 ^b	1.86 ± 0.42 ^b	13.17 ± 0.93 ^a
	7	72.82 ± 4.29 ^b	3.22 ± 1.56 ^a	16.14 ± 3.78 ^a	72.02 ± 4.72 ^b	2.75 ± 0.98 ^a	14.79 ± 153 ^a
	8	71.73 ± 2.34 ^b	3.87 ± 0.94 ^a	17.47 ± 2.05 ^a	71.56 ± 1.27 ^b	2.91 ± 0.29 ^a	13.53 ± 0.30 ^a

The data is presented as a mean ± SD. For each variable parameter, the mean values are denoted by various lowercase letters within the same column to signify statistical significance (p -value < 0.05).

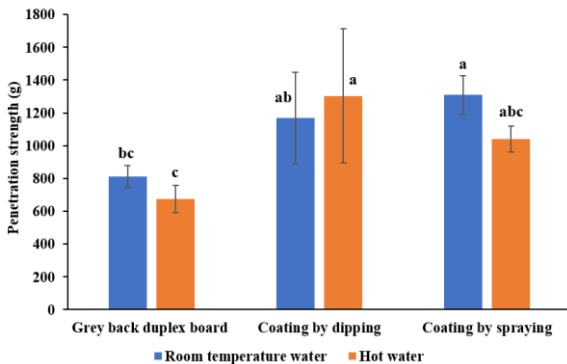


Figure 5: Penetration strength of coated grey back duplex board packaging when filled with room-temperature and hot water.

To form ceramic using casting methods such as dipping and spraying, the particles, or HAp in this work, must be formed in a colloidal system dispersed in solvent, dispersant, binder, and plasticizer [32]. Even though dip-coating is the simplest and most effective method, the HAp mixture used in this work was diluted or had a low HAp amount, which resulted in a low coating of HAp on the surface of GB. Furthermore, spray-coating expedites the process by minimizing contact between the solvent and the GB, while also applying pressure through an air compressor via a spray gun, resulting in increased coating ability. Thus, the spray-coated packaging has longer heat resistance than non-coating and dip-coated packaging due to the high coating ability and heat resistance of the HAp composite.

The HAp particles are inorganic materials with a high melting point and heat resistance; thus, heating in the microwave for a short time cannot decompose the structure and whiteness of HAp. However, PVA can degrade or decompose during the thermal process [33] and microwave irradiation [34], resulting in decreasing the brightness and increasing a^* and b^* .

Practical use of all 3 types of GB paper packaging by containing hot water at 80 °C and room temperature water was set up and the penetration strength was measured of the paper packaging after practical usage as shown in Figure 5.

The penetration strength values of dipping and spray-coated packaging when filling room-temperature water and hot water were not significantly different (p -value < 0.05). However, both coating papers show significantly (p -value > 0.05) higher penetration strength testing values (1,000–1,250 g) than non-coated GB (700–800 g) when filled with room temperature and hot water due to the HAp coating and lower wettability of the coated surface. The increase in penetration strength is mainly due to the HAp coating. The Vickers (HV) hardness of HAp particles is approximately 600 kg.mm⁻¹, higher than that of metals [35]. It depends on HAp grain size, which can increase if grain size decreases from submicron to nanometer.

3.2.3 Water and oil absorption

Cellulose, a hydrophilic material in nature, has good water absorption due to the hydroxyl groups (-OH) found in homopolysaccharide polymers; however,

some natural cellulose fibers, such as kapok [36] and *Metaplexis japonica* seed hair fibers [37], show a high value of oil absorption. In this work, watermelon and French fries were used as samples to represent food containing water or soup and oily food, respectively, to determine the ability of water and oil absorption by coated GB food packaging, as shown in Figure 6.

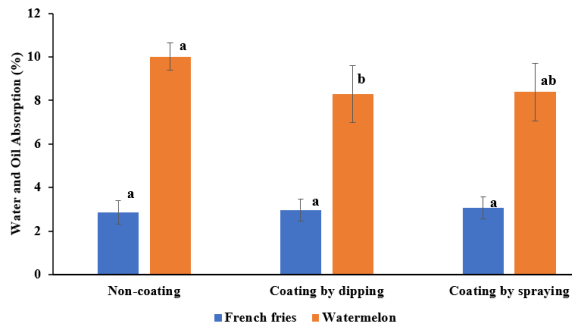


Figure 6: Water and oil absorption (%) of non-coated and coated packaging containing French fries and watermelon.

The oil absorption percentages for French fries in coated GB food packaging (2.97% for dipping and 3.06 for spraying) are slightly higher than those in non-coated packaging (2.86%) but not significantly different (p -value < 0.05). The water absorption of dipping-coated GB (8.28%) is significantly (p -value > 0.05) lower than that of non-coated GB (10.01%), but not different from spray-coated GB (8.38%) (p -value < 0.05). The decreased water absorption of coated GB is due to the decreasing hydrophilicity of the coated surface by modification with potassium oleate.

This data indicates that the non-coated and coated GB food packaging is suitable for both greasy and short-term containers for juicy food.

3.3 Biodegradability of coated GB

The main composition of GB is cellulose, a linear homopolysaccharide polymer containing many glucosyl units linked by β -1,4 glycosidic linkage [38]. This natural polymer can undergo biological degradation slowly; the time it takes to degrade depends on various factors such as moisture content,

soil pH, soil texture, temperature, oxygen availability, light exposure, and microbial abundance such as bacteria and fungi [38]–[40]. The cellulose biodegradation will be 80% in around 180 days [41]. In this work, the weight losses of the samples at 7 and 14 days in soil burial were studied. The morphology of the surface and percentage weight lost after burying the coated GB in soil for 7 and 14 days compared with GB are shown in Figures 7 and 8, respectively. The surface morphology of these samples before buried and obtained by stereomicroscope is different; dip-coated GB shows a lower amount of HAp on the GB surface than that of spray-coated Gb surface, the same results have been observed by SEM as in Figure 4 indicating these coated GB can slowly degrade in soil.

The morphology of both coating samples remains nearly the same after soil burial at 7 and 14 days, with the white HAp coating still dispersed on the coated sample's surface. The weight lost after 7 and 14 days is 6–8%, not significantly different (p -value < 0.05),

In this work, factors that affect biodegradability, such as moisture content and temperature, were controlled during the experiment. The HAp particle size and physical properties of coated GB may have an impact on biodegradability. Higher HAp coating ability or coating thickness, as well as lower hydrophilicity or wettability, may decrease moisture and oxygen permeation to cellulose, resulting in slow biodegradation of cellulose. Additionally, some inorganic materials, such as metal and metal oxide coatings, can slow down the biodegradation of cellulose buried in soil by suppressing microbial growth on cellulose [42]. However, nanosizes such as nanowire HAp (HNWs) can degrade rapidly in slightly acidic burial soil (pH 6.4) due to solubility in acidic condition, and TEMPO oxidized cellulose nanofiber (TOCNF)/nanowire HAp (HNWs) composite films (20% HNWs) can also degrade rapidly in burial soil (pH 6.4) [43]. Therefore, the application of nano HAp as a coating on paper-based food packaging may facilitate the rapid degradation of cellulose in acidic environments. It is necessary to investigate the possible mechanism and model of biodegradation of HAp/PVA-coated cellulose that is buried in soils in order to obtain additional information.

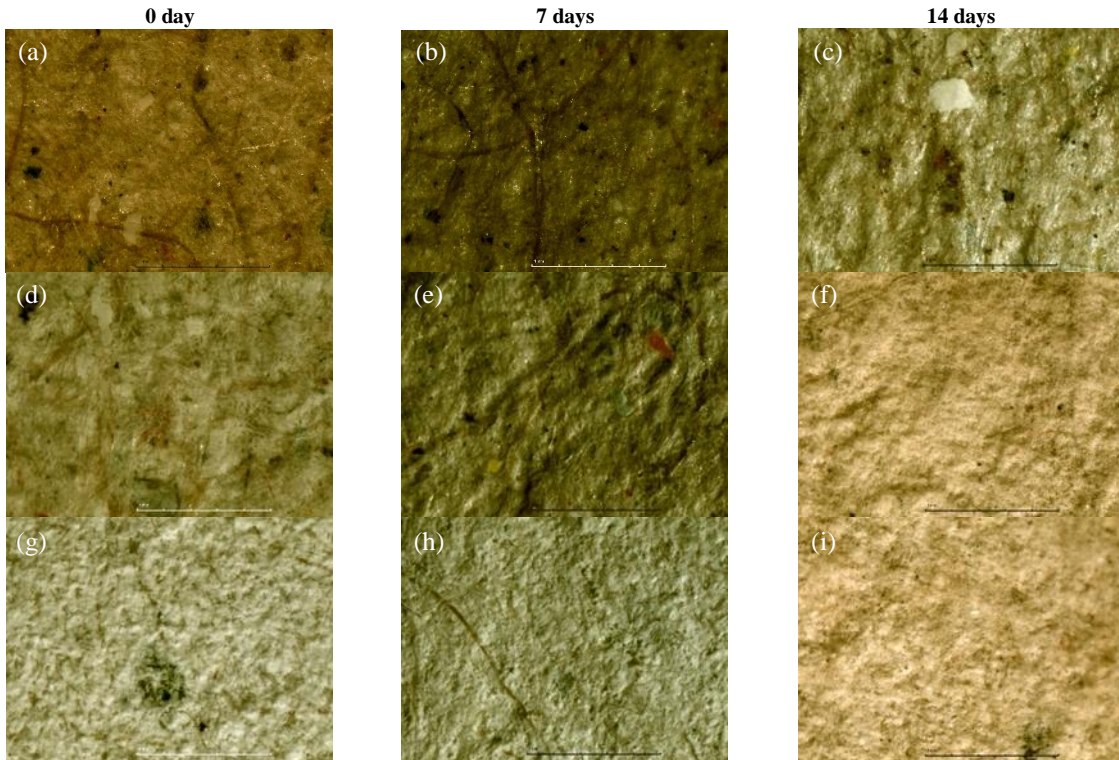


Figure 7: Surface images from the stereomicroscope of grey back duplex board at (a) 0, (b) 7, (c) 14 days; coating by dipping at (d) 0, (e) 7, (f) 14 days; coating by spraying at (g) 0, (h) 7, (i) 14 days for the biodegradability test (20x magnificent).

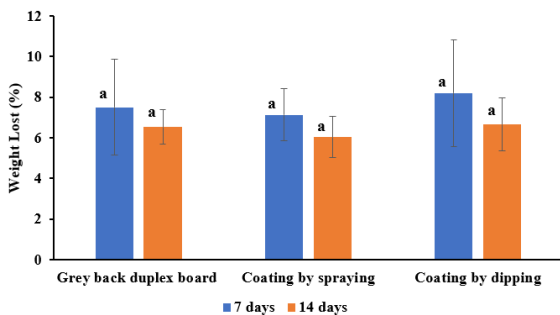


Figure 8: Biodegradability of grey back duplex board paper packaging coated with HAp composite film at room temperature (23–33 °C), 10–11% soil moisture, and 80–85% relative humidity.

4 Conclusions

The composite films, consisting of 5 wt% bovine bone waste-derived hydroxyapatite (HAp), 2 wt%

polyvinyl alcohol (PVA), and 2 wt% glycerol, were successfully prepared and effectively applied on the grey back duplex board (GB) food packaging using the dipping and spraying methods. The spray coated GB food packaging had $16.15 \pm 0.18\%$ coating ability and showed increased brightness (L^*) compared to dip coated and noncoated GB. The brightness of the spray coated GB packaging only had small changes. Additionally, after heating the spray coated GB packaging four times at 800 W in a microwave oven, the brightness of the other packaging rapidly reduced. The coated GB had a higher penetration strength than the noncoated GB after absorbing water. The biodegradable properties at 7 and 14 days (6–8%) were not significantly different for the coated GB before and after coating. Consequently, a simple HAp, derived from waste bovine bone, and coating HAp-PVA-Gly coated on GB by spraying technique promises a potential to be commercially applied as biodegradable paper-based food packaging.

Acknowledgments

This work was funded by the Establishment Project of Halal Food Science Center, Department of Food Science and Nutrition, Faculty of Science and Technology, Prince of Songkla University, Pattani (SAT6104073S).

Author Contributions

N.O.: Conceptualization, statistical analysis, funding acquisition, project administration, writing-review and editing; W.J.: Methodology and experiments; S.C.: Data curation, writing-original draft, review, and editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

- [1] K. K. Dash, P. Deka, S. P. Bangar, V. Chaudhary, M. Trif, and A. Rusu, "Applications of inorganic nanoparticles in food packaging: A comprehensive review," *Polymers*, vol. 14, no. 3, pp. 1–17, 2022, doi: 10.3390/polym14030521.
- [2] P. K. Kunam, D. Ramakanth, K. Akhila, and K. K. Gaikwad, "Bio-based materials for barrier coatings on paper packaging," *Biomass Conversion and Biorefinery*, vol. 14, no. 12, pp. 12637–12652, 2024, doi: 10.1007/s13399-022-03241-2.
- [3] S. Imam, G. Glenn, B.-S. Chiou, J. Shey, R. Narayan, and W. Orts, "Types, production and assessment of biobased food packaging materials," in *Environmentally Compatible Food Packaging*, E. Chiellini, Ed. Florida: CRC, pp. 29–30, 2008, doi: 10.1533/9781845694784.
- [4] S. M. Rangappa, S. Siengchin, H. N. Dhakal, "Green-composites: Ecofriendly and sustainability," *Applied Science and Engineering Progress*, vol. 13, no. 3, pp. 183–184, 2020, doi: 10.14416/j.asep.2020.06.001.
- [5] F. Fitriani, M. R. Bilad, S. Aprilia, and N. Arahman, "Biodegradable hybrid polymer film for packaging: A review," *Journal of Natural Fibers*, vol. 20, no. 1, 2023, doi: 10.1080/15440478.2022.2159606.
- [6] A. Marinelli, M.V. Diamanti, M. Pedferri, and B. D. Curto, "Kaolin-filled styrene-butadiene-based dispersion coatings for paper-based packaging: Effect on water, moisture, and grease barrier properties," *Coatings*, vol. 13, no. 1, pp. 195, 2023, doi: 10.3390/coatings13010195.
- [7] T. Hirvikorpi, M. Vähä-Nissi, T. Mustonen, A. Harlin, E. Iiskola, and M. Karppinen, "Thin inorganic barrier coatings for packaging materials," in *TAPPI PLACE Conference*, 2010, pp. 2444–2484.
- [8] R. Coles and M. Kirwan, *Food and Beverage Packaging Technology*, 2nd ed. New Jersey: Blackwell Publishing Ltd., 2011, p. 219.
- [9] G. L. Robertson, *Food Packaging Principles and Practice*, 3rd ed. Boca Raton, Florida: CRC, 2013, p. 33.
- [10] S. M. Stella and U. Vijayalakshmi, "Development of nano-hydroxyapatite polymer composite and its in vitro activity for biomedical applications," *Asian Journal of Chemistry*, vol. 35, no. 6, pp. 1361–1368, 2023, doi: 10.14233/ajchem.2023.27741.
- [11] P. Turon, L. J. del Valle, C. Alemán, and J. Puiggali, "Biodegradable and biocompatible systems based on hydroxyapatite nanoparticles," *Applied Sciences*, vol. 7, no. 1, 2017, doi: 10.3390/app7010060.
- [12] T. Başargan, N. Erdöl-Aydin, and G. Nasün-Saygili, "In situ biomimetic synthesis to produce hydroxyapatite-polyvinyl alcohol biocomposites: Precipitation and spray drying methods," *Polymer - Plastics Technology and Engineering*, vol. 55, no. 5, pp. 447–452, 2016, doi: 10.1080/03602559.2015.1098674.
- [13] O. N. Musskaya, A. I. Kulak, V. K. Krut'ko, S. A. Ulasevich, L. A. Lesnikovich, and L. F. Suchodub, "Composite films based on hydroxyapatite and polyvinyl alcohol," *Journal of Nano- and Electronic Physics*, vol. 7, no 1, pp. 1022–1025, 2015.
- [14] A. N. Itua, O. I. Oluwole, D. O. Ojo, and A. M. Hope, "Abrasion resistance and water absorption characteristics of Ti-HAp hybrid reinforced polyetheretherketone biocomposites," *Applied Science and Engineering Progress*, vol. 16, no. 3, 2023, Art. no. 6728, doi: 10.14416/j.asep.2023.02.005.
- [15] Aminatun, F. F. S. B. Tenong, D. Hikmawati, and E. M. Setiawati, "Characterization of vickers hardness and corrosion rate of stainless steel-316L coated with hydroxyapatite-polyvinyl alcohol," *Journal of Physics: Conference Series*,

- vol. 1816, no. 1, 2021, Art. no. 012012, doi: 10.1088/1742-6596/1816/1/012012.
- [16] D. Moreau, A. Villain, D. N. Ku, and L. Corté, "Surface exposure of hydroxyapatite Poly (vinyl alcohol) hydrogel coatings with tunable surface exposure of hydroxyapatite," *Biomatter*, vol. 4, no. 1, 2014, Art. no. e28764, doi: 10.4161/biom.28764.
- [17] M. Akram, R. Ahmed, I. Shakir, W. A. W. Ibrahim, and R. Hussain, "Extracting hydroxyapatite and its precursors from natural resources," *Journal of Materials Science*, vol. 49, no. 4, pp. 1461–1475, 2014, doi: 10.1007/s10853-013-7864-x.
- [18] Y. Liu, J. Li, D. Wang, F. Yang, L. Zhang, S. Ji, and S. Wang, "Enhanced extraction of hydroxyapatite from bighead carp (*Aristichthys nobilis*) scales using deep eutectic solvent," *Journal of Food Science*, vol. 85, no. 1, pp. 150–156, 2020, doi: 10.1111/1750-3841.14971.
- [19] B. L. Do, T. G. T. Ho, H. P. Phan, and T. Nguyen, "Green fabrication of effective silver loading on fishbone-derived hydroxyapatite: A robust catalyst for 4-nitrophenol reduction," *Arabian Journal for Science and Engineering*, 2024, doi: 10.1007/s13369-024-09167-3.
- [20] M. T. Hooi, S. W. Phang, H. Y. Yow, E. David, N. X. Kim, and H. L. Choo, "FTIR spectroscopy characterization and critical comparison of poly(vinyl)alcohol and natural hydroxyapatite derived from fish bone composite for bone-scaffold," *Journal of Physics: Conference Series*, vol. 2120, no. 1, 2021, doi: 10.1088/1742-6596/2120/1/012004.
- [21] N. Jamarun, A. Prasejati, Z. Zulhadjri, and S. Caniago, "Effect of chitosan concentration on hydroxyapatite/chitosan composite synthesis using the in-situ method as a dye adsorbent," *Kuwait Journal of Science*, vol. 51, no. 4, 2024, Art. no. 100252, doi: 10.1016/j.kjs.2024.100252.
- [22] R. Kumar and S. Mohanty, "Hydroxyapatite: A versatile bioceramic for tissue engineering application," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 32, no. 12, pp. 4461–4477, 2022, doi: 10.1007/s10904-022-02454-2.
- [23] V. Murugesan, G. Easwaradas, and K. Manju, "Evaluation of the antioxidant, antimicrobial, haemolytic and cytotoxic effect of eggshell based hydroxyapatite," *Journal of Cluster Science*, vol. 33, no. 2, pp. 825–834, 2022, doi: 10.1007/s10876-021-02153-x.
- [24] R. L. P. Rocha, L. M. C. Honorio, R. D. d. S. Bezerra, P. Trigueiro, T. M. Duarte, M. G. Fonseca, E. C. Silva-Filho, and J. A. Osajima, "Light-activated hydroxyapatite photocatalysts: New environmentally-friendly materials to mitigate pollutants," *Minerals*, vol. 12, no. 5, pp. 1–27, 2022, doi: 10.3390/min12050525.
- [25] M. T. D. C. Español, ER J. G. Garcia, L. A. V. Maligaya, C. M. S. Santos, J. A. H. Santos, N. G. Suarnaba, R. V. C. Rubi, and R. Raguindin, "Ultrasound-assisted biomimetic synthesis of MOF-Hap nanocomposite via 10xSBF-like for the photocatalytic degradation of metformin," *Applied Science and Engineering Progress*, vol. 17, no. 2, 2024, Art. no. 7251, doi: 10.14416/j.asep.2023.11.002.
- [26] A. M. I. Montone, F. Malvano, P. L. Pham, L. Cinquanta, R. Capparelli, F. Capuano, and D. Albanese, "Alginate-based coatings charged with hydroxyapatite and quercetin for fresh-cut papaya shelf life," *International Journal of Food Science and Technology*, vol. 57, no. 8, pp. 5307–5318, 2022, doi: 10.1111/ijfs.15860.
- [27] Hartatiek, Yudyanto, M. I. Wuriatika, J. Utomo, M. Nurhuda, Masrurroh, and D. J. D. H. Santjojo, "Nanostructure, porosity and tensile strength of PVA/Hydroxyapatite composite nanofiber for bone tissue engineering," *Materials Today: Proceedings*, vol. 44, pp. 3203–3206, 2020, doi: 10.1016/j.matpr.2020.11.438.
- [28] N. Ongsuwan, W. Jehlee, and S. Chotisuwat, "Preparation of hydroxyapatite composite films derived from waste bovine bones," in *the Pure and Applied Chemistry International Conference*, 2022, pp. 497–501.
- [29] M. M. Afiq and A. R. Azura, "Effect of sago starch loadings on soil decomposition of Natural Rubber Latex (NRL) composite films mechanical properties," *International Biodeterioration and Biodegradation*, vol. 85, pp. 139–149, 2013, doi: 10.1016/j.ibiod.2013.06.016.
- [30] G. Wang, T. Lu, X. Zhang, M. Feng, C. Wang, W. Yao, S. Zhou, X. Zhu, W. Ding, and M. He, "Structure and properties of cellulose/HAP nanocomposite hydrogels," *International Journal of Biological Macromolecules*, vol. 186, pp. 377–384, Sep. 2021, doi: 10.1016/j.ijbiomac.2021.07.060.

- [31] W. Wei, W. Song, and S. Zhang, "Preparation and characterization of hydroxyapatite-poly(vinyl alcohol) composites reinforced with cellulose nanocrystals," *BioResources*, vol. 9, no. 4, pp. 6087–6099, 2014, doi: 10.15376/biores.9.4.6087-6099.
- [32] M. N. Rahaman, *Ceramic Processing and Sintering*, 2nd ed. Florida: CRC Press, 2003, pp. 316–317, 364–374.
- [33] R. Wulandari, Y. A. Swasono, M. Z. N. Ichsan, and A. Rifathin, "Thermal behavior and kinetic of degradation of PVA and PVA/CS/AL blend," *Saintekno : Jurnal Sains dan Teknologi*, vol. 21, no. 1, pp. 1–10, 2023, doi: 10.15294/saintekno.v21i1.42675.
- [34] D. T. Nguyen, K. L. Ly, N. M.-P. Tran, M. H. Ho, T. T.-P. Tran, T.-H. Nguyen, D. N. T. Nhi, and V. T. Vo, "Effect of microwave irradiation on polyvinyl alcohol as a carrier of silver nanoparticles in short exposure time," *International Journal of Polymer Science*, vol. 2019, no. 1, 2019, doi: 10.1155/2019/3623907.
- [35] O. A. Osuchukwu, A. Salihi, I. Abdullahi, B. Abdulkareem, and C. S. Nwannenna, "Synthesis techniques, characterization and mechanical properties of natural derived hydroxyapatite scaffolds for bone implants: A review," *SN Applied Sciences*, vol. 3, no. 10, 2021, doi: 10.1007/s42452-021-04795-y.
- [36] K. Hori, M. E. Flavier, S. Kuga, T. B. T. Lam, and K. Iiyama, "Excellent oil absorbent kapok [*Ceiba pentandra* (L.) Gaertn.] fiber: Fiber structure, chemical characteristics, and application," *Journal of Wood Science*, vol. 46, no. 5, pp. 401–404, 2000, doi: 10.1007/BF00776404.
- [37] Z. Wang, D. Wang, Z. Li, and Y. Wang, "Metaplexis japonica seed hair fiber: A hydrophobic natural fiber with robust oil–water separation properties," *Cellulose*, vol. 27, no. 5, pp. 2427–2435, 2020, doi: 10.1007/s10570-020-02976-3.
- [38] R. Datta, "Enzymatic degradation of cellulose in soil: A review," *Heliyon*, vol. 10, no. 1, 2024, Art. no. e24022, doi: 10.1016/j.heliyon.2024.e24022.
- [39] F. Bueno, L. Fultz, C. Husseneder, M. Keenan, and S. Sathivel, "Biodegradability of bacterial cellulose polymer below the soil and its effects on soil bacteria diversity," *Polymer Degradation and Stability*, vol. 217, 2023, Art. no. 110535, doi: 10.1016/j.polymdegradstab.2023.110535.
- [40] E. Hoque, A. M. Rayhan, and S. I. Shaily, "Natural fiber-based green composites: Processing, properties and biomedical applications," *Applied Science and Engineering Progress*, vol. 14, no. 4, pp. 689–718, 2021, doi: 10.14416/j.asep.2021.09.005.
- [41] V. Caligiuri, G. Tedeschi, M. Palei, M. Miscuglio, B. Martin-Garcia, S. Guzman-Puyol, M. K. Hedayati, A. Kristensen, A. Athanassiou, R. Cingolani, V. J. Sorger, M. Salerno, F. Bonaccorso, R. Krahne, and J. A. Heredia-Guerrero, "Biodegradable and insoluble cellulose photonic crystals and metasurfaces," *ACS Nano*, vol. 14, no. 8, pp. 9502–9511, 2020, doi: 10.1021/acsnano.0c03224.
- [42] B. Tomšič, D. Marković, V. Janković, B. Simončič, J. Nikodinovic-Runic, T. Ilic-Tomic, and M. Radetić, "Biodegradation of cellulose fibers functionalized with CuO/Cu₂O nanoparticles in combination with polycarboxylic acids," *Cellulose*, vol. 29, no. 1, pp. 287–302, 2022, doi: 10.1007/s10570-021-04296-6.
- [43] L. Xia, C. Tan, W. Ren, X. Liu, X. Zhang, J. Wu, X. Zhang, F. Guo, Y. Yu, and R. Yang, "Robust, biodegradable and flame-retardant nanocomposite films based on TEMPO-oxidized cellulose nanofibers and hydroxyapatite nanowires," *Carbohydrate Polymers*, vol. 324, 2024, Art. no. 121495, doi: 10.1016/j.carbpol.2023.121495.