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# Physical property and water absorption capacity of paper coated with hydroxyapatite composite film

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**Abstract**

Paper packaging for food products is lightweight and low price but not moisture-proof. This makes it unusable for certain foods. Therefore, this research created the concept of synthesis of hydroxyapatite (HAp) from bovine bone, studying the optimum of HAp for composite material consisting of sodium alginate (SA) and cassava starch (CA) for physical and water absorption capacity properties. The HAp was synthesized from waste bovine bones by calcination at 900 °C. The synthesized HAp powders were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The results showed HAp with the surface functional group of hydroxyl and phosphate groups. The molar ratio of calcium to phosphorus was 1.53. After that, it was prepared as a composite film coating on brown paper with SA and CA at the concentration of 2 % wt using HAp at 0, 1, 3, and 5 % wt. The result found that coated paper with the HAp 1 % wt composite with CA showed water absorption capacity ($p<0.05$), 15.17 ± 0.30 %, the paper had a thickness of 0.21 ± 0.01 mm, moisture content 17.51 ± 1.30 %, tensile strength 31.50 ± 2.30 MPa, and elongation of paper 9.23 ± 1.63 %.

**Keywords:** bovine bone; hydroxyapatite; paper; coating; composites

## 1. Introduction


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Packaging for food products has to prevent food quality changes. The popular materials used are plastic, paper, etc. Plastic is the most popular because it can prevent moisture and air permeability. But its disadvantage is caused by the pollution of the environment. Paper is lightweight and cheap, but it cannot contain water. Papar food packaging can be coated with a biodegradable polymer, such as polylactic acid (PLA), polybutylene succinate (PBS), polyhydroxyalkanoates (PHAs), and polyglycolic acid (PGA), to improve barrier and mechanical properties. Inorganic compounds like montmorillonite were mixed with the polymer coating [1-3]. Hydroxyapatite (HAp) is an inorganic compound in the form of calcium phosphate with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$. It can be prepared by chemical reactions or natural materials, such as animal bones [4-5]. A natural and edible polymer is durable and popular, e.g., sodium alginate (SA) and starch, which can form a composite film with other substances for application but still has poor properties for water absorption [6]. Therefore, this research aimed to synthesize HAp from bone waste from beef soup restaurants, study the amount of HAp, and composite it with sodium alginate (SA) and cassava starch (CA). Then, study the physical properties and water absorption capacity of coated paper.

## 2. Materials and Methods

### 2.1 Preparation of hydroxyapatite

The waste bovine bones collected from beef soup restaurants were used as a HAp source. They were washed, reduced in size, and burned at 900 ° C for 2 hours [7]. After cooling, the calcined bones were crushed into fine powder and characterized the surface functional groups by Fourier transform infrared spectroscopy (FT-IR) (Bruker, Spectrometer, Tensor27). The crystal structure was analyzed by X-ray powder diffraction (XRD) (X'Pert MPD Philips Netherlands), and morphology was examined by the scanning electron microscope (SEM) (FEI Quanta 400 England).

### 2.2 Preparation of hydroxyapatite composite coating solution

#### *2.2.1 SA/HAp solution*

Bionanocomposite was synthesized via the modified procedure of Xu and co-workers [8]. Sodium alginate (SA) homogeneous mixture was added gradually for 4 h into nanostructured hydroxyapatite solution at 0%, 1%, 3%, and 5% wt to promote flexibility, plasticity, and to decrease brittleness of nanocomposite samples film. A Glycerol plasticizer was added dropwise to the SA/HAp nanocomposite solution, homogenized at 9200 rpm for 7 min at ambient temperature, followed by sonication for 5 min.

#### *2.2.2 CA/HAp solution*

Cassava starch (CA) and polyvinyl alcohol (PVA) were mixed at 80 °C stirred for 48 hours at 60 °C. Then, HAp powders were added into this polymer solution at 0, 1, 3, and 5 % wt concentrations and sonicated for 15 min.

### 2.3 Characterization method

#### *2.3.1 Paper coating thickness (mm)*

The sample thickness was measured by Digimatic Indicator ID-SX (Mitutoyo).


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### *2.3.2 Moisture content (MC) of coated paper*

The size of the sample specimens was (3 x 3 cm), and the MC (%) of the sample was analyzed overnight and dehydrated in a hot air oven at 103 °C, as shown in equation (1).

$$MC\% = \frac{H_2O \text{ weight}}{\text{Wer sample weight}} \text{ x } 100 \quad (1)$$

### *2.3.3 Mechanical properties of coated paper*

Elongation at break (E%) and tensile strength (TS) of the samples were determined based on the ASTM D882-02 standard method using an Instron Universal Testing Machine (Model 200, Hiwa Engineering Co., Iran). The specimens were cut into pieces (1.5 x 10 cm). Primary grip separation was fixed at 50 mm, and then all samples were tested employing a cross-head speed of 50 mm/min. The E% and TS experiments were iterated three times.

### *2.3.4 Cobb test*

Cobb test was used to analyze the water absorption capacity of coated paper, performed as described in T-441 om-90 (TAPPI,1994a) [9]. Three samples of dimensions 10×10 cm were preconditioned in a desiccator for 72 h at room temperature (25 ± 2°C). Samples were individually weighed on a semi-analytical scale with a precision of 0.01g and attached to the Cobb test equipment (Regmed, Brazil). Moreover, 100 mL of water was added to contact with the surface delimited by the apparatus ring. After removing the specimen, it was placed between two sheets of absorbent paper and pressed by a conditioning roller (Regmed, Brazil) to remove excess water. Lastly, the samples were weighed. Water absorption capacity (Abs, g/m²) was determined using equation (2), where $M_f$ and $M_i$(g) were final and initial sample weight, respectively, while A was the surface of the sample (m²).

$$Abs\ (\%) = \frac{M_f - M_i}{A} \text{ x } 100 \quad (2)$$

### *2.3.4 Statistic method*

The data such as thickness, moisture content, elongation at break, tensile strength, and water absorption capacity were analyzed for scientific data using the ANOVA method.

## 3. Results and Discussion

### 3.1. Characterization of HAp

Surface functional groups of HAp obtained from FT-IR are shown in Figure 1. The HAp showed the unit peak of pure HAp at wavenumber 630.69 and 3572.97 $cm^{-1}$, presenting O-H bending and O-H stretching, respectively. These peaks represented the hydroxyl function group (-OH) of HAp. The peak at the wavenumber at 1030-1071, 1090, 961, and 570.90 $cm^{-1}$ represent phosphate stretching of the phosphate functional group [10]. The synthesized substances' functional groups correspond to pure HAp's functional groups.


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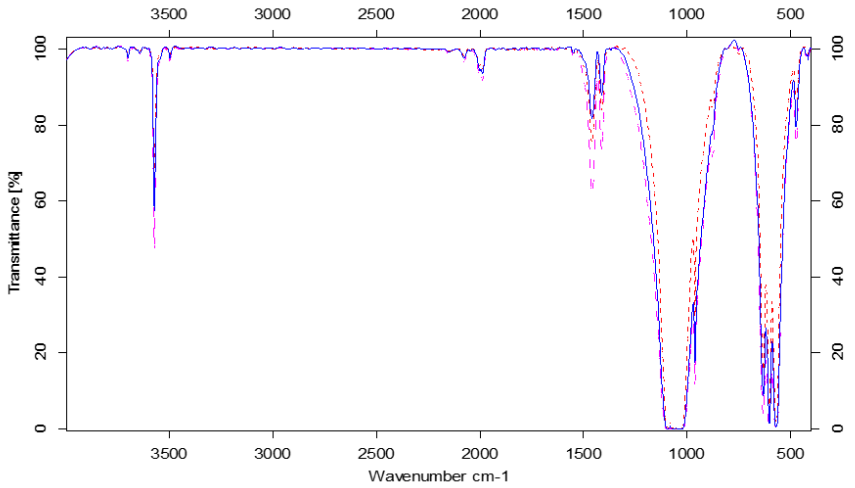


**Figure 1**. FT-IR spectrum of bovine-derived HAp after calcined at 900°C.

The XRD pattern of synthesized HAp is shown in Figure 2. It showed the XRD peak at 2θ, equal to 31.83º, 32.23º, and 32.93º, and other peaks at 25.88, 34.13, 39.83, 46.73, and 49.48, showed the unique characteristics of pure HAp [11].

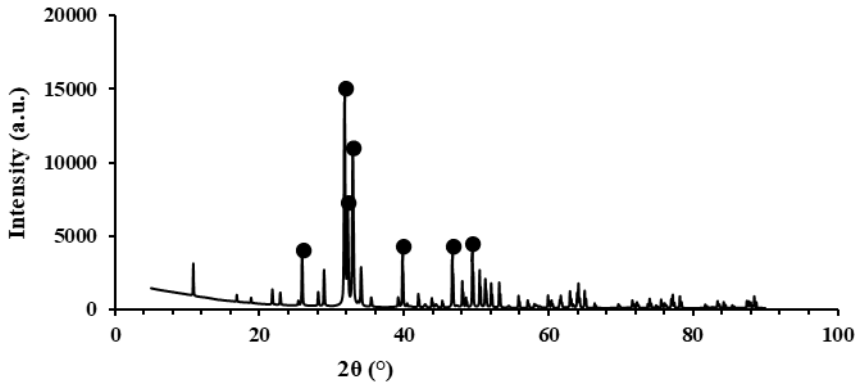


**Figure 2**. XRD pattern of bovine derived HAp after calcined at 900°C.

SEM studied the morphology of HAp powder, shown in Figure 3. SEM image showed dispersion of HAp crystals with a hexagon shape. The hydroxyl function groups of HAp particles can form hydrogen bonds with nearby HAp particles, forming aggregate HAp particles. The HAp particles are porous and have a rough surface due to the decomposition of organic substances, such as proteins (collagen) and carbohydrates. These impurities decompose to carbon dioxide and water


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during calcination of the bones and remain inorganic substances, mostly HAp, which decomposes at temperatures above 1000°C [10].

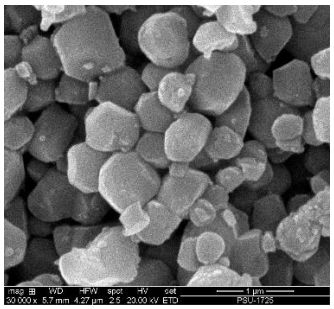

**Figure 3**. SEM image of bovine derived HAp after calcined at 900°C.

### 3.2 Physical properties test of coated paper

#### *3.2.1 Thickness*

The thickness of paper coated by SA/HAp and CA/Hap concentrations 0, 1, 3, and 5% wt were significantly different ($p \leq 0.05$), as shown in Table 1. The paper thickness was increased with the percentage of HAp composite. The increasing amount of HAp in composite coatings affected the integration of HAp particles. The hydrophilic functional group in HAp is the hydroxyl group, which can form interaction through hydrogen bonds, making the paper thicker [12-13]. The thickness of SA/HAp and CA/HAp differed ($P \leq 0.05$). CA/HAp composite paper can absorb water and form film and gelatinization.

**Table 1.** Thickness, moisture content (MC), tensile strength (TS), elongation, and water absorption capacity (Abs) of coated paper with 4 different levels of HAp (0, 1, 3, 5 % wt) composite with SA and CA

| Type of coating | Thickness (mm) | MC (%) | TS (MPa) | E (%) | Abs ($g/m^2$) |
|---|---|---|---|---|---|
| SA/HAp 0% | $0.19 \pm 0.00^{d}$ | $19.21 \pm 2.74^{a}$ | $36.95 \pm 1.17^{d}$ | $8.73 \pm 0.60^{ab}$ | $24.15 \pm 2.46^{bc}$ |
| SA/HAp 1% | $0.21 \pm 0.00^{cd}$ | $18.64 \pm 1.29^{a}$ | $77.44 \pm 2.62^{a}$ | $4.38 \pm 1.14^{c}$ | $24.56 \pm 0.55^{bc}$ |
| SA/HAp 3% | $0.21 \pm 0.01^{cd}$ | $17.93 \pm 0.04^{ab}$ | $35.18 \pm 0.92^{d}$ | $7.15 \pm 1.14^{bc}$ | $38.40 \pm 1.98^{a}$ |
| SA/HAp 5% | $0.22 \pm 0.00^{c}$ | $18.70 \pm 0.27^{a}$ | $42.90 \pm 2.10^{c}$ | $5.28 \pm 2.67^{bc}$ | $32.48 \pm 3.93^{ab}$ |
| CA/HAp 0% | $0.21 \pm 0.01^{cd}$ | $19.81 \pm 2.33^{a}$ | $35.27 \pm 3.82^{d}$ | $7.64 \pm 2.95^{bc}$ | $28.88 \pm 6.15^{b}$ |
| CA/HAp 1% | $0.21 \pm 0.01^{cd}$ | $17.51 \pm 1.30^{ab}$ | $31.50 \pm 2.30^{e}$ | $9.23 \pm 1.63^{ab}$ | $15.17 \pm 0.30^{c}$ |
| CA/HAp 3% | $0.24 \pm 0.00^{b}$ | $15.83 \pm 0.21^{b}$ | $49.05 \pm 0.65^{b}$ | $11.74 \pm 2.63^{a}$ | $33.20 \pm 6.05^{ab}$ |
| CA/HAp 5% | $0.28 \pm 0.02^{a}$ | $15.61 \pm 0.40^{b}$ | $43.28 \pm 0.83^{c}$ | $6.95 \pm 2.07^{bc}$ | $34.00 \pm 1.68^{ab}$ |

#### *3.2.2 Moisture content*

The moisture content (MC) of paper coated by SA/HAp and CA/HAp 0, 1, 3, and 5 % wt was shown in Table 1. They were not significantly different ($p>0.05$) when increasing the amount of HAp in composite SA and CA, resulting in a decrease in MC content. The CA/HAp coated paper had less moisture due to the gelatinization of starch molecules with


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more hydroxyl groups that could interact via hydrogen bonds when heated. The CA/HAp absorbed more water than the SA/HAp sample, which made it dense due to the remaining free water molecules around the starch.

#### *3.2.3 Tensile strength and elongation at break*

Tensile strength (TS) and elongation at break (E)) of paper coated by SA/HAp and CA/HAp 0, 1, 3, and 5 % wt were significantly different ($p \leq 0.05$, as shown in Table 1. The increasing HAp content decreases TS and E values because high HAp particles have been interfered with by hydrogen bonding between the plasticizer molecules and surface hydroxyl groups of HAp.

#### *3.2.4 Water absorption capacity*

Table 1 showed water absorption capacity (Abs) properties of paper coated by SA/HAp and CA/HAp 0, 1, 3, 5 % wt, and they were not significantly different ($p > 0.05$). The paper coated with CA/HAp 1%wt was the best prevention of water absorption due to the consistent distribution of HAp particles in the coating solution. Moreover, the occurrence of retrogradation from starch molecules that can be combined, resulting in a strong interaction of starch, can prevent water absorbability.

## 4. Conclusions

The HAp synthesized from waste bovine bones was successfully prepared and mixed with CA, SA, and glycerol to form the coating solution. These coating formulas with 0, 1, 3, and 5 % wt HAp were coated on brown paper and characterized the physical, mechanical, and water absorption capacity properties. When increasing the amount of HAp content, the paper thickness was significantly increased ($p \leq 0.05$, while the moisture content decreased significantly. ($p \leq 0.05$), and the use of CA/HAp composites results in less paper moisture than SA/HAp. The amount of HAp increased from 0, 1, 3, and 5 % wt also decreased TS and E values. The type of polymers, SA and CA, did not significantly affect the water absorption of coated paper ($p \geq 0.05$). The coated paper with the composite CA/HAp at 1% wt prevented water absorption more than other formulas.

## 5. Acknowledgements

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