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Composite Materials Based on Biocompatible Metal-Organic Framework and Anthocyanins from *Hibiscus sabdariffa* for Active Food Packaging

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Abstract—The biocompatible metal-organic framework $[Zn_4(GA)_4(H_2O)_4]\cdot 4H_2O$ (H_2GA = glutamic acid) was used as a container for anthocyanins from *Hibiscus sabdariffa* in composite films based on kappa-carrageenan and hydroxypropyl methylcellulose. The obtained composite materials showed high antioxidant activity and ability to undergo pH-induced color change upon reactions with gaseous products of pathogen development and, hence, possess the potential for practical application as functional materials for food packaging.

Keywords: biocompatible metal-organic frameworks, anthocyanins, active packaging, hydrocolloids, composite materials

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INTRODUCTION

Active food packaging [1] is one of the most rapidly growing research areas of modern food chemistry. Owing to the presence of biologically active components of different nature, composite materials can increase the shelf life of food products by inhibiting the processes that cause food spoilage [2]. Anthocyanins are often used as active agents in these materials [3]. These water-soluble colored flavonoids abundant in plants, which impart color to the flowers, leaves, and fruits of many plants, are used as natural colorants in foods and beverages [4]. Anthocyanins change their color from red (in highly acidic solutions) to violet (in neutral solutions) and to green-yellow (in alkaline solutions) [5]; therefore, anthocyanin-based materials are suitable [6] for determination of gaseous products produced by pathogenic organisms such as biogenic amines and CO2, accumulated in food packaging. Due to their polyphenolic nature, anthocyanins have a wide range of bioactivity, including antioxidant, antibacterial, and anti-inflammatory activities. For example, anthocyanins present in Sudan rose (*Hibiscus sabdariffa*) calyces exhibit antimicrobial [7] and antioxidant [8] properties, decrease the cholesterol level [9], prevent kidney disease [10], and reduce arterial hypertension in patients with type II diabetes mellitus [11].

Composite materials based on natural hydrocolloids play an important role in modern research in the field of active food packaging [12]. Water-soluble biopolymers of polysaccharide and protein nature have long been used in the food industry as emulsifiers [13], thickening agents [14], stabilizers [15], and gelling agents [16]. The interest of the scientific community in hydrocolloids is due to their ability to form three-dimensional gel networks in aqueous and alcohol solutions, which are converted into strong film coatings after removal of the solvent [17]. The films thus formed (unlike packaging materials made of traditional synthetic polymers) are fully biocompatible and biodegradable [18], which makes the studies of materials based on hydrocolloids especially relevant.

The introduction of anthocyanins into hydrocolloid matrix is complicated by the high sensitivity of their molecules to light, oxygen, heat, and the presence of enzymes [3], which restricts their use in long-term food packaging. One of the ways to address this problem is nanopackaging of anthocyanin molecules into porous materials such as zeolites [19] and natural clays [20]. This approach makes it possible to stabilize anthocyanin molecules, and in the case of substrates that also have active properties, it is possible to manufacture multiple-action composite materials [21].

Metal-organic frameworks (MOFs) are a unique class of porous crystalline materials [22] that possess a large specific surface area and controlled pore structure, which is determined by the structural components chosen for the synthesis [23]. MOFs are actively used in various fields of science, e.g., in catalysis [24], separation of gas mixtures [25] and optically active compounds [26], targeted drug delivery [27], and biomedical imaging [28]. However, they have not yet been considered as substrates for unstable molecules in active food packaging materials. Previously, we described examples of using ZnGlu MOF, $\{[Zn_4(GA)_4(H_2O)_4]\cdot 4H_2O\}_n$ (H_2GA = glutamic acid), as carriers for antimicrobial hydrophobic molecules in composite materials [29] for this purpose.

In this study, we obtained composites based on hydrocolloid matrix consisting of kappa-carrageenan and hydroxypropyl methylcellulose, biocompatible ZnGlu MOF, and anthocyanins from *Hibiscus sabdariffa*. The obtained materials showed good antioxidant activity for the use as active packaging materials for determining gas products of pathogen development.

EXPERIMENTAL

All operations involved in the synthesis of MOFs and preparation of composite films were performed in air using commercial reagents and solvents. Analysis for carbon and hydrogen was carried out on a Carlo-Erba microanalyzer, model 1106.

Extraction of anthocyanins was performed by taking 5 g of powdered *Hibiscus sabdariffa* calyces, which were placed into ethanol acidified with citric acid (30 mL, pH 2) and kept in an ultrasonic bath at 80°C for 30 min. The resulting *Hibiscus sabdariffa* extract was separated by centrifugation and stored in a closed vessel in a cold dry place.

Synthesis of ZnGlu was carried out by an adapted protocol reported previously [30]. A solution of zinc nitrate hexahydrate (50 mmol, 14.86 g) in water (100 mL) was added dropwise with stirring to a solution of L-glutamic acid (50 mmol, 7.36 g) and sodium hydroxide (100 mmol, 4 g) in distilled water (100 mL). The reaction mixture was stirred at room temperature for 30 min. The resulting precipitate was collected on a filter, washed with water, and dried at room temperature. The yield was 13.57 g (97%).

For $C_{24}H_{12}O_{13}Zn_4$

Anal. calcd., %	C, 24.36	H, 4.51	N, 5.68
Found, %	C, 24.43	H, 4.68	N, 5.64

Synthesis of ZnGlu-HE. The insertion of anthocyanin molecules into MOF particles was carried out by stirring the ZnGlu powder in the ethanol extract of *Hibiscus sabdariffa* for 12 hours. The violet powder that formed was collected on a filter, washed with ethanol, and dried at room temperature.

Preparation of composite films. A ZnGlu or ZnGlu-HE powder was added in various amounts (5, 15, 30 wt % of the total mass of hydrocolloids) to a solution of glycerol (0.80 g) and potassium sorbate (0.02 g) in distilled water (100 mL). The mixture was stirred with an ultrasonic bath for 3 min and then heated to 80°C. A mixture of kappa-carrageenan (1.60 g) and hydroxypropyl methylcellulose (0.40 g) was added with stirring, and the resulting homogeneous suspension was cooled down with stirring to 50°C. The solution was poured onto glass preheated to 50°C, flattened using a blade coater with 3 mm blade height, and left on the heated substrate until it was completely dry. The resulting film was separated from the glass and stored in a dry place at room temperature.

Powder X-ray diffraction studies were carried out on a Proto AXRD diffractometer with a copper anode, nickel K_β-filter (K_α = 1.541874 Å), and a Dectris Mythen 1K 1D detector in the Bragg – Brentano geometry in the 5°–50° range of 2θ angles with 0.02° step.

The ferric reducing antioxidant power (FRAP) assay was performed using a Shimadzu UV-2600 spectrophotometer. Samples of composite films (50 mg) were heated to 50°C in an aqueous solution of potassium hexacyanoferrate(III) (1 wt %, 2.5 mL) for 3 h, and then aqueous solutions of acetic acid (10%, 2.5 mL) and iron(III) nitrate (0.1 wt %, 5 mL) were added. After completion of the reaction, the presence of which was indicated by the appearance of blue color, the solution was centrifuged and withdrawn to record the absorption spectrum at a wavelength of 700 nm.

RESULTS AND DISCUSSION

ZnGlu was synthesized by the previously reported, environmentally benign protocol by direct precipitation from an aqueous solution at room temperature [30]. The X-ray diffraction data for ZnGlu (Fig. 1), which coincided with the theoretically calculated data for pure ZnGlu, confirmed the formation of this MOF. The insertion of anthocyanins, obtained by ultrasonic extraction from a powdered *Hibiscus sabdariffa* calyces, into MOF particles was carried out by keeping the ZnGlu powder in the ethanol extract for 12 h. The ZnGlu powder turned from white to violet.

The composite films based on ZnGlu and ZnGlu-HE and hydrocolloid matrix made of kappa-carrageenan and hydroxypropyl methylcellulose in 4 : 1 ratio [29] were prepared by doctor blade casting of the film-forming solution using a blade type membrane filling machine [31]. Glycerol as a plasticizer and potassium sorbate as a preservative and source of potassium ions were also added to the composite mixture to reduce the repulsion between the sulfate groups of kappa-carrageenan and produce elastic gel [32]. The ZnGlu and ZnGlu-HE powders were distributed in a solution of the above additives using ultrasonic stirring for 3 min prior to the addition of the hydrocolloid mixture. A hydrocolloid film (KcHm) that contained no MOF particles served as the control sample.

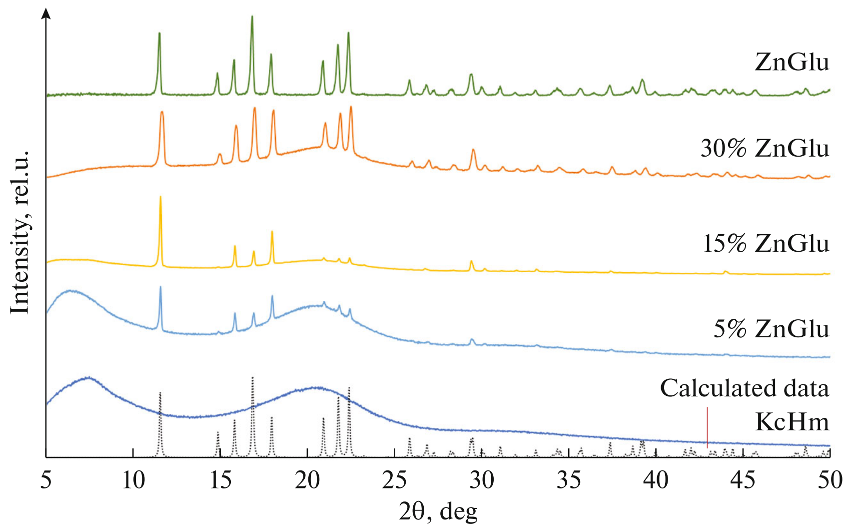

Fig. 1. Powder X-ray diffraction data for ZnGlu samples and composite films containing 5, 15, and 30% ZnGlu relative to the total mass of hydrocolloids in comparison with the theoretically calculated X-ray diffraction pattern of ZnGlu.

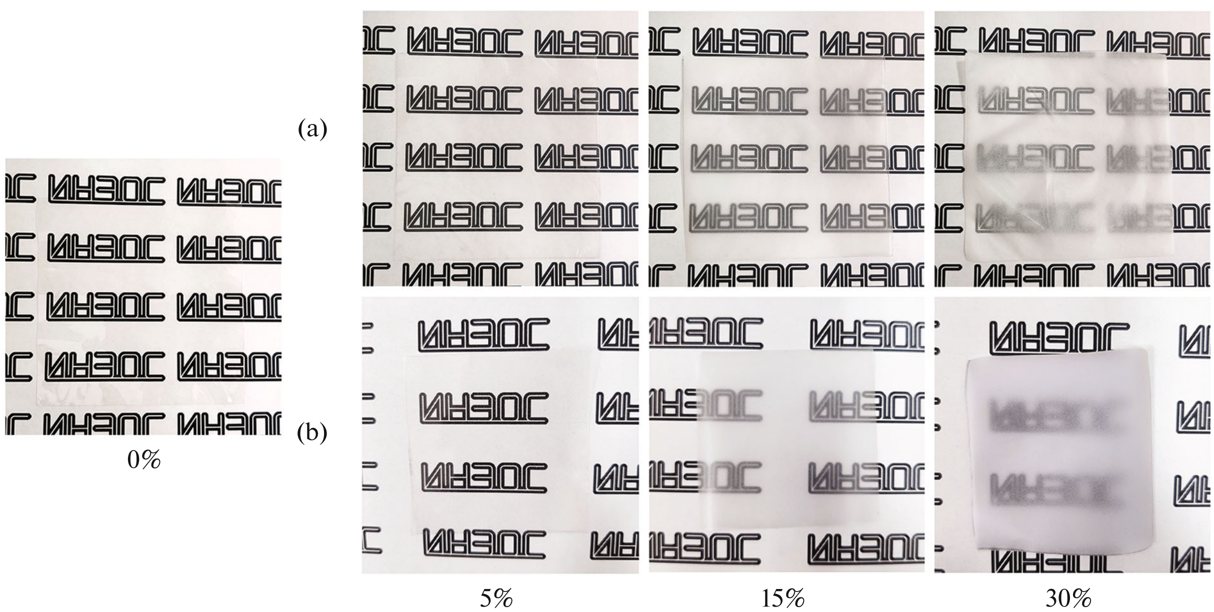

Fig. 2. Photographs of composite films based on ZnGlu and ZnGlu-HE with different compositions.

All the fabricated composite films (Fig. 2) had high elasticity, while their transparency decreased with increasing MOF concentration. Besides, films containing ZnGlu-HE were colored violet, with the color intensity increasing with increasing ZnGlu-HE concentration. Analysis of the X-ray diffraction patterns (Fig. 1) of the composite films confirmed the presence of a crystalline phase corresponding to ZnGlu (except for the control sample).

For determining the pattern of color variation in the solution of *Hibiscus sabdariffa* extract as a function of medium acidity, minor amounts of the extract were placed into solutions with different pH (Fig. 3). As this was done, the pink color (present in acid medium) turned into blue (neutral to slightly alkaline medium) and green (alkaline medium).

The incubation of samples of the obtained composite films containing ZnGlu-HE in closed vessels over acetic acid and ammonia solutions for more than 5 min resulted in a change in the film color corresponding to the expected pH change (Fig. 4). As the MOF content increased, coloring of the composite films became more intense; as a result, a clear-cut

Fig. 3. Color change of the *Hibiscus sabdariffa* calyx extract depending on the medium acidity indicated on the vials.

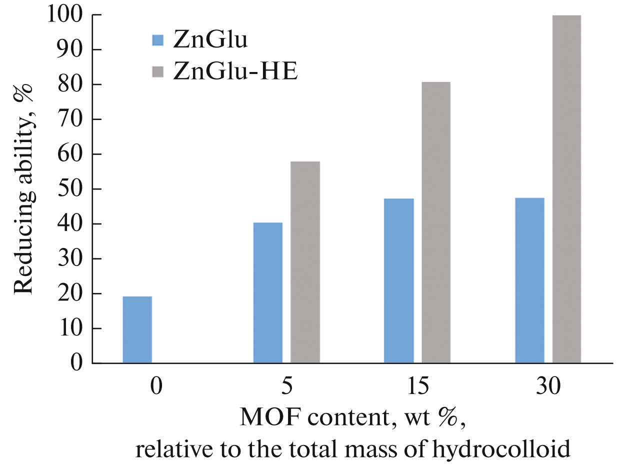

Fig. 5. Reducing power of ZnGlu-HE-based composite films compared to ZnGlu-containing composite films.

transition was observed for samples with MOF contents of 15 and 30%.

The results of FRAP assay of the antioxidant activity of composite films based on the ability of antioxidants to reduce iron(III) ions demonstrated that an increase in ZnGlu-HE content leads to an increase in the reducing power of composite films (Fig. 5). The observed slight increase in the reducing ability of composite films containing initial MOF compared to the control sample may be due to the synergistic effect between kappa-carrageenan and MOF.

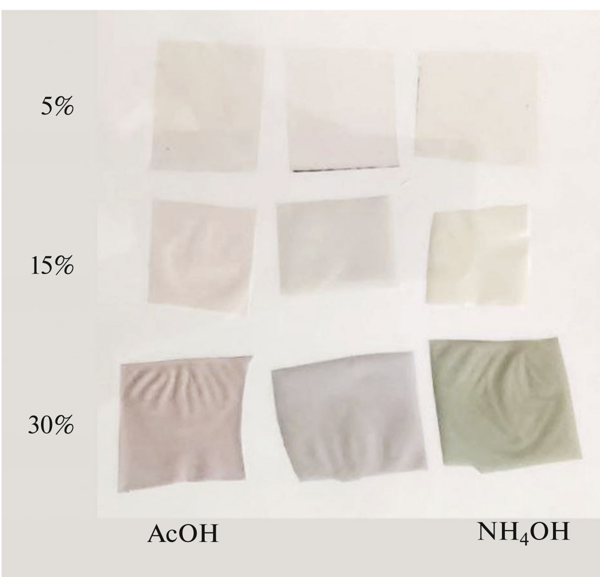

Fig. 4. Change in the color of ZnGlu-HE-based composite films upon exposure to acetic acid and ammonia vapors. The weight percentage of MOF relative to the total weight of the hydrocolloid matrix is indicated to the left of the photo.

Thus, we obtained new composite films based on hydrocolloid matrix consisting of a mixture of kappa-carrageenan and hydroxypropyl methylcellulose and containing ZnGlu MOF particles with anthocyanins obtained by ultrasonic extraction from the *Hibiscus sabdariffa* calyx powder. These materials were characterized by powder X-ray diffraction and spectrophotometry. The presence of antioxidant activity and pH-sensitive color change for these composite materials indicates the possibility of subsequent use of MOF as a substrate for active agents in functional materials for active packaging of food products

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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