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Bicompatible Metal-Organic Framework for Functional Packing of Food Products

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Abstract—Biocompatible metal-organic framework $[Zn_4(GA)_4(H_2O)_4]\cdot 4H_2O$ (H_2GA is glutamic acid) is tested as a "container" with bioactive hydrophobic components of jasmine essential oil for the preparation of functional composite materials based on a hydrocolloid matrix containing kappa-carrageenan and hydroxypropyl methylcellulose. The prepared composite film coatings exhibit high antimicrobial and antioxidant activities in the model experiment with a long-term storage of fruits, which indicates broad prospects for the practical use of these materials as an active packing of food products.

Keywords: biocompatible metal-organic framework, functional packing, hydrocolloids, composite materials, X-ray diffraction

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INTRODUCTION

The preparation of an active packing for food products [1] is an innovative approach to the prolongation of the expiration date of food products based on the inhibition of processes associated with food product damage via direct or indirect contact with the product of active agents in the composite packing composition [2]. Intense studies on preparing these composite materials based on natural hydrocolloids [3] have been conducted in the last three decades. Hydrocolloids are water-soluble biopolymers widely used in the food industry as emulsifiers [4], thickening agents [5], stabilizers [6], and gelling agents [7]. The ability of a number of hydrocolloids to form a three-dimensional gel framework in aqueous or alcohol solutions makes it possible to prepare strong film coatings that can be an environmentally friendly alternative to packing materials made from traditional synthetic polymers [8].

Plant essential oils and extracts are widely used as components of nontoxic functional composite materials for packing food products [9–12]. Essential oils are mixtures of various organic compounds with a broad range of active properties, including antimicrobial [13], antioxidant [14], and anticancer [15] activities. However, the direct functionalization of a hydrocolloid matrix with essential oils is conjugated with a number of difficulties [16, 17], the most important of which is their high hydrophobicity leading to the phase separation of the components during drying composite materials [18].

To solve this problem, it was proposed to encapsulate hydrophobic active agents into pores of metal-organic frameworks (MOFs) [19], which are representatives of a unique class of crystalline materials with a periodical three-dimensional structure [20]. The MOFs consisting of metal-containing nodes and organic linkers have recently been used actively in various fields of science and technology owing to their huge specific surface area and controlled pore structure predetermined by the nature of the structural components [21]. For instance, the biocompatible MOFs are used in catalysis [22] and for the separation of gas mixtures [23] and optically active compounds [24], address drug delivery [25], and biomedical visualization [26]. Both MOFs themselves and their decomposition products are not toxic [27] and, in addition, their hydrolytic stability under aqueous conditions [28] close to biological conditions is an important characteristic of MOFs used as "containers" for active components in biological systems. The most promising MOFs in biomedicine or food industry are the materials based on biomolecules present in the human organism, such as amino acids, nucleic bases, and polybasic carboxylic acids [29].

Zinc glutamate $[Zn_4(GA)_4(H_2O)_4]\cdot 4H_2O$ (H_2GA is glutamic acid, ZnGlu) refers to the class of MOFs containing conformationally mobile linkers capable of changing sizes of the formed pores and channels depending on the contents in the pores and channels [30]. The three-dimensional structure of ZnGlu is formed by zinc ions connected by glutamate linkers (1 : 1) that form channels ~5 × 10 Å^2 in size filled with water molecules [31]. An approach of MOF "assembling" around a guest molecule in the reaction mixture facilitating the encapsulation of guest molecules in MOF channels was successfully used in the previous studies on the encapsulation of the bioactive molecules in channels of ZnGlu [31, 32].

In this work, we prepared materials for the functional packing of food products. The materials are based on the biocompatible MOF ZnGlu containing the hydrophobic active components of jasmine essential oil distributed over the hydrocolloid matrix of kappa-carrageenan and hydroxypropyl methylcellulose. The prepared materials demonstrated a good protection from the growth of pathogenic microorganisms and enzymatic oxidation of polyphenols in the model experiment with freshly cut apples.

EXPERIMENTAL

All procedures associated with the synthesis of the MOF and preparation of composite films were carried out in air using commercially available reagents and solvents. Analyses to carbon and hydrogen were conducted on a CarloErba (model 1106) microanalyzer.

Synthesis of ZnGlu was carried out according to the earlier published adapted protocol [33]. 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 formed precipitate was filtered off, washed with water, and dried at room temperature. The yield was 13.568 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-JEO. The active components of jasmine essential oil (JEO) were encapsulated at the stage of MOF assembling according to the synthesis of ZnGlu with the dropwise addition of an alcohol solution of JEO (1 mL per 10 mL of EtOH). The formed precipitate was additionally washed with alcohol.

Preparation of composite films. Powders of ZnGlu or JEO-ZnGlu were added in different amounts (5, 15, 30, and 50 wt % of the total weight of hydrocolloids) to a solution of glycerol (0.8 g) and KOH (0.02 g) in distilled water (100 mL). The mixture was stirred for 3 min in an ultrasonic bath and heated to 80°C. After this, kappa-carrageenan (1.6 g) and hydroxypropyl methylcellulose (0.4 g) were supported on the mixture with stirring. The resulting homogeneous suspension was cooled with stirring to 50°C. The solution was poured onto a glass heated to 50°C, leveled using a blade device with a knife height of 3 mm, and left on the heated support to complete drying. The prepared film was separated from the glass and stored at room temperature in a dry place.

Images of scanning electron microscopy (SEM) for the films placed on a 25-mm aluminum stage and fixed by a conducting carbon ribbon were obtained in the secondary electron mode at an accelerating voltage of 5 kV and in the medium vacuum mode on a Hitachi TM4000Plus desktop electron microscope. The film thickness was measured with a micrometer at 10 random sites.

The water vapor permeability (WVP) was measured by the gravimetric method according to the ASTM E96-80 standard [34]. A film sample was tightly fixed on a glass vial filled with dry silica gel to maintain 0% relative humidity, and the cell was placed in a desiccator with a saturated solution of NaCl to maintain 75% relative humidity and was left at room temperature (25°C) for 2 h. The weight of water vapors passed through the film was determined from a change in the weight of the vial with silica gel. Weighing was carried out at an interval of 2 h for 10 h. The WVP was measured using the equation

$$\mathrm{WVP} = \frac{A\Delta x}{(p_1 - p_2)S},$$

where A (g/h) is the slope of the linear regression of the weight on time, Δx (mm) is the film thickness, $(p_1 - p_2)$ (kPa) is the difference in partial pressures inside and outside the cell, and S (m^2) is the surface area of the film.

Studies by X-ray diffraction (XRD) were carried out on a Proto AXRD θ–2θ diffractometer equipped with a copper anode, a nickel K_β filter ($\lambda(\mathrm{Cu}K_\alpha)$ = 1.541874 Å), and a Dectris Mythen 1 K 1D detector in the Bragg–Brentano geometry in the angular range 5°–60° with an increment of 0.02° over the 2θ range.

To determine the incorporation of the JEO components into ZnGlu-JEO, a ZnGlu-JEO powder (100 mg) was placed in a solution of 1 M HCl (2 mL) and diluted with distilled water (8 mL). After the complete dissolution of the precipitate, the aqueous phase was extracted with dichloromethane (10 mL), and the organic fraction was separated and studied on a GCMS-QP2020 gas chromatograph/mass spectrometer (Shimadzu, Japan) equipped with a quadrupole detector. Analysis conditions were the following: the sample volume was 1 μL, the injector temperature was 250°C, and the SH-RTx-5MS column (30 m × 0.25 mm × 0.25 μm) was used. The temperature regime of a thermostat was as follows: 40°C, 1 min: heating to 290°C with a rate of 30°C/min, 2 min: 290°C; helium served as the carrier gas, the flow rate through the column was 1 mL/min, the temperature of the ion source was 200°C, and the interface temperature was 250°C. Detection was carried out in the regime of monitoring the chosen ion current (*m*/*z* 108, molecular ion of benzyl alcohol).

For testing the composite films, the moisture on samples of freshly cut ripe Golden Delicious apples 5 × 5 × 5 mm in size was thoroughly sopped up, and the apple pieces were put on a needle and immersed into a film forming solution. An excess solution was let to flow down, and the solution on the needle was dried by permanent turning over. After the gel congealed, the apples were transferred to Petri dishes and left in air to the complete drying of the film. Then all samples were stored at room temperature for 7 days in an increased (50%) humidity medium.

RESULTS AND DISCUSSION

The previously published environmentally friendly approach of the direct precipitation from an aqueous solution of the zinc salt and sodium glutamate in a ratio of 1 : 1, which requires no organic solvents, was used for the synthesis of ZnGlu. The synthesis was carried out at room temperature for 3 h. The formed crystalline product was washed with distilled water, filtered off, and dried at room temperature. The incorporation of the JEO components into pores of this MOF was carried out similarly with the simultaneous dropwise addition of an alcohol solution of the essential oil. The MOF retained its structure, which was confirmed by the XRD data for the ZnGlu and ZnGlu-JEO powders (Fig. 1) that coincided with the theoretically calculated values for pure ZnGlu. Although the encapsulation of the guest molecules did not result in a change in the positions of the diffraction peaks of ZnGlu-JEO, the change in their relative intensity indirectly indicated a conformational change in the channel structure with a change in the content in the channels.

To confirm the encapsulation of the active components, the prepared ZnGlu-JEO powder was soaked in dichloromethane with vigorous stirring for 24 h, after which the solution was centrifuged and analyzed by mass spectrometry. Unfortunately, a low concentration of the active components did not allow us to estimate their content in the solution. Therefore, the ZnGlu-JEO powder was placed in a solution of HCl until the complete decomposition of the MOF, after which the aqueous phase was extracted with dichloromethane. The organic fraction was analyzed by mass spectrometry. In this case, the determination was carried out by monitoring the current of the molecular ion corresponding to benzyl alcohol, because the main active components of JEO (benzyl acetate and benzyl benzoate) also undergo acidic hydrolysis to benzyl alcohol under the conditions of acidic decomposition of the MOFs. The signal of the molecular ion of benzyl alcohol was experimentally found in the mass spectrum, but its low concentration impedes the quantitative estimation of its content in the sample.

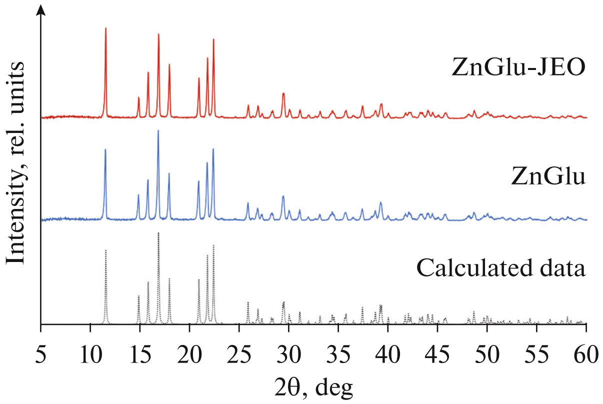

Fig. 1. XRD data for the ZnGlu and ZnGlu-JEO samples compared with the theoretically calculated diffraction pattern for pure ZnGlu.

A mixture of kappa-carrageenan and hydroxypropyl methylcellulose in a ratio of 4 : 1 was chosen as a hydrocolloid matrix for the preparation of composite films based on ZnGlu and ZnGlu-JEO [35]. The mixture was molded by the "doctor blade" method using a membrane-coating machine of the blade type [36]. Glycerol (40 wt % of the total weight of hydrocolloids) as a plasticizer and KOH (1 wt % of the total weight of hydrocolloids) as a source of potassium ions, which decrease the repulsion between the sulfate groups of kappa-carrageenan to form an elastic gel [37], were added to the film forming solution to improve the mechanical properties of the films. The uniform distribution of the MOF particles was provided by ultrasonic stirring of a suspension of ZnGlu or ZnGlu-JEO in an aqueous solution for 3 min before the addition of the indicated mixture of hydrocolloids. A hydrocolloid film (KcHm) containing no MOF particles served as a control sample.

The prepared composite films (Figs. 2a, 2d) were highly transparent and elastic. The addition of the MOF to the composition resulted in a decrease in these parameters and the appearance of texture changes on the upper side of the films related to the aggregation of the MOF particles violating the monolithic character of the hydrocolloid matrix, which followed from the SEM data (Figs. 2b, 2c, 2e, 2f). The observed aggregates consisting of 200–500-nm particles are 5–40 μm in size even at a minimum studied concentration of the MOF (5%). An analysis of the XRD patterns (Fig. 3) of the composite film samples confirmed that they contained the crystalline phase corresponding to ZnGlu (except for the control sample). A noticeable shift of the signal positions and signal broadening for the samples with the high content of ZnGlu (30 and 50%) are due to the rough film surface related to the aggregation of the MOF particles leading to the nonuniform compression of the composition during drying.

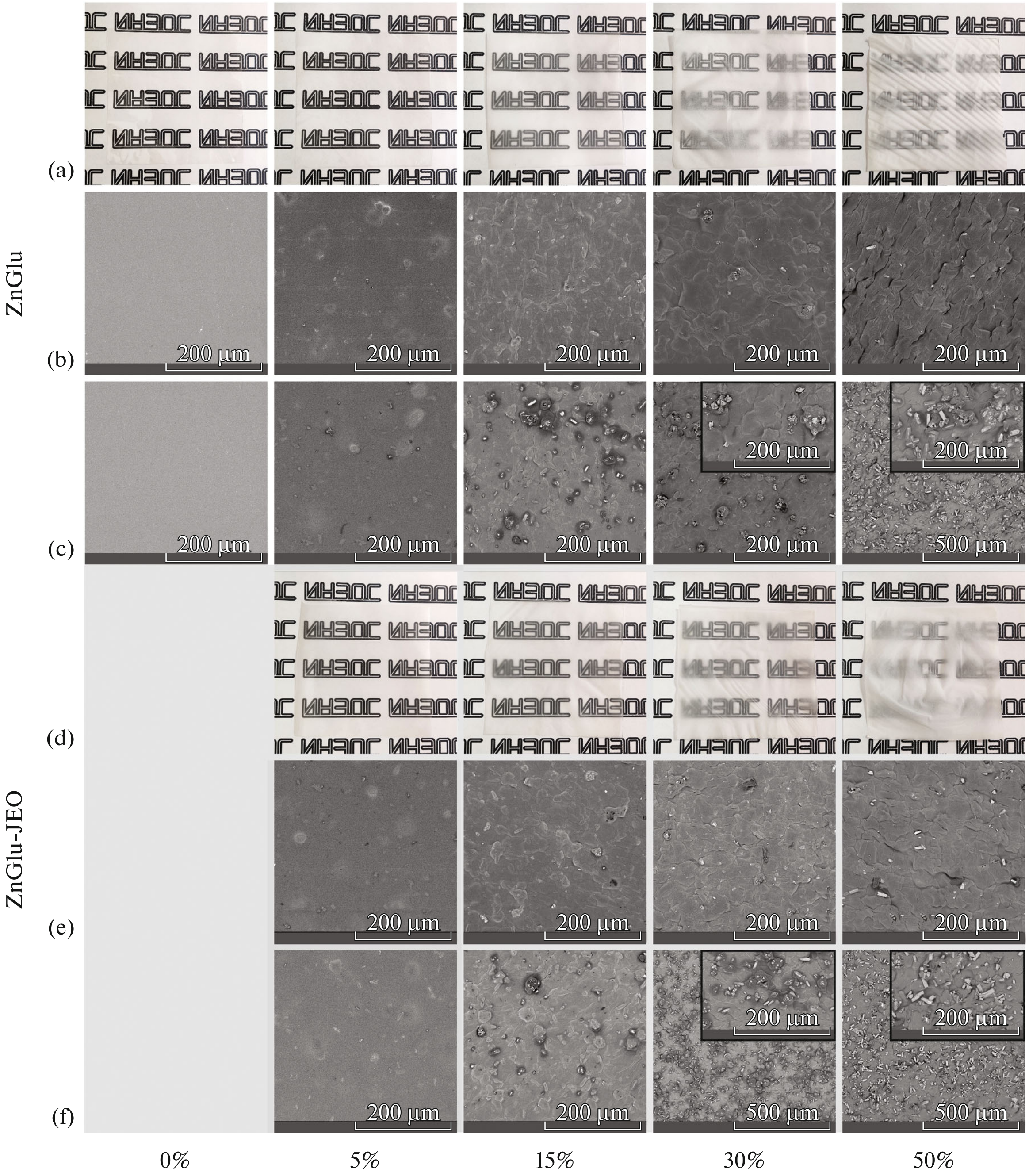

Fig. 2. Photographs of the (a) ZnGlu- and (d) ZnGlu-JEO-based composite films. (b, c, e, f) SEM images of the surface fragments from two sides of the composite films with different compositions obtained immediately after film preparation.

The easiness of moisture penetration through the formed composite films was evaluated by measuring WVP. In addition to an increase in the film thickness with an increase in the concentration of the MOF particles, an increase in the WVP was observed (Table 1) related to the violation of the monolithic character of the composite film upon the aggregation of the MOF particles. In addition, water molecules can move along the MOF channels thus increasing the efficiency of the water vapor transfer through the composite films. For the same MOF concentrations, the film samples containing ZnGlu-JEO have a lower vapor permeability than the ZnGlu-containing samples, which is due to the hydrophobic contents of the channels in ZnGlu-JEO.

In the model experiment (Fig. 4), to evaluate the practical potential of the prepared composite films as a material for the active packing of food products, we coated samples of freshly cut apples with these films.

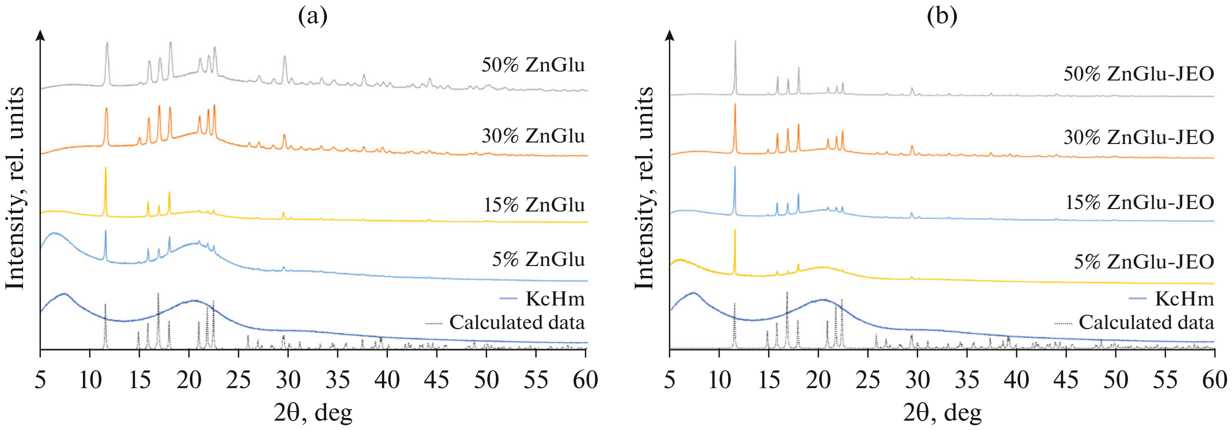

Fig. 3. XRD data for the (a) ZnGlu- and (b) ZnGlu-JEO-based composite films compared with the theoretically calculated diffraction pattern of ZnGlu.

Then the coated samples were stored at room temperature in a chamber with an increased humidity (RH = 50%) for 7 days. The hydrocolloid coatings in the pure form are excellent nutrient media for the development of potentially pathogenic microorganisms. The apple samples coated with the hydrocolloid composition without MOFs manifested the first properties of contamination with microorganisms on the second day, and the introduction of ZnGlu increased the storage period to 4 (for 5 and 15%) and 5 days (for 30%). No properties of pathogen growth were revealed on the apple samples with 50% ZnGlu for all concentrations of ZnGlu-JEO within the whole time of experiment. In this case, darkening of the sample surface because of the inhibition of enzymatic oxidation processes was less pronounced. The antimicrobial activity of the composite coatings with ZnGlu containing no active agents of jasmine oils is due to two factors. First, the MOF particles can act as a physical barrier for the penetration of pathogens onto the food product surface. Second, zinc ions that are slowly washed from the MOF particle surface can be responsible for the antimicrobial activity [38].

Thus, we studied the composite films based on the hydrocolloid matrix of a mixture of kappa-carrageenan and hydroxypropyl methylcellulose containing the ZnGlu MOF particles with the active components of jasmine essential oil incorporated into the MOF channels. The prepared materials were characterized by powder XRD and scanning electron microscopy. The antimicrobial and antioxidant activities of these composite materials found by the model experiment with apples are observed even at the minimum studied concentration of ZnGlu-JEO (5%) and indicate that the MOFs are promising for the use as “containers” or other type carriers of active agents in functional materials for the active packing of food products.

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Table 1. Barrier properties of the composite films

Parameters of film	KcHm	ZnGlu				ZnGlu-JEO			
		%							
		5	15	30	50	5	15	30	50
Film thickness, μm	51	59	69	82	107	55	63	81	93
WVP, g mm kPa^{-1} h^{-1} m^{-2}	0.723	0.832	0.967	1.229	1.524	0.816	0.931	1.122	1.302

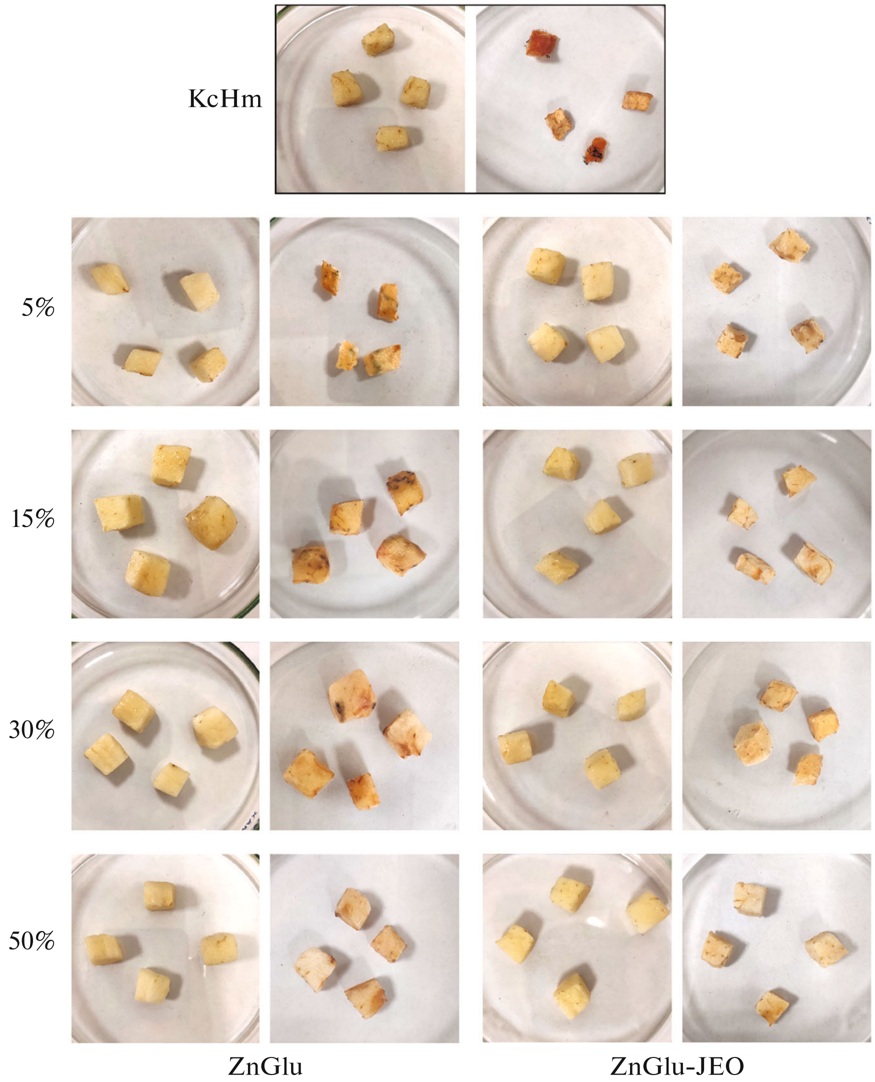

Fig. 4. Photographs of the freshly cut apple samples covered with the composite film materials before and after 7 days of storage in the wet medium.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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