

Composite Films Based on Hydroxyapatite and Polyvinyl Alcohol

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Composite films based on hydroxyapatite (HA) gel and polyvinyl alcohol (PVA) were obtained. Light scattering of composite films in the PVA film is increased with growth of HA content from 0.5 to 33.0 %. The introduction of HA into PVA film leads to the inhibition of thermal degradation of the polymer without changing the position of the main spectral bands in UV-Vis absorption spectra. The introduction of HA into the PVA film promotes their hydrophobicity, while UV light leads to the significant increase in the hydrophilicity, especially after its heating at 180 °C.

Keywords: Polyvinyl alcohol, Hydroxyapatite, Thermal decomposition, UV treatment, UV-Vis absorption spectra.

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1. INTRODUCTION

Due to biocompatibility, elasticity and chemical stability polyvinyl alcohol (PVA) is widely used in medical practice as a component of artificial articular cartilage [1], matrix for immobilization of proteins, ferments, DNA [2, 3], in prolonged action preparations [4]. Hydrogel composites based on PVA, collagen and hydroxyapatite (HA) which stimulate adhesion, proliferation and differentiation of osteoblast cells are also known [5].

As it was noted in [6-9], thermal and UV action are suitable methods to influence the physical and chemical properties of PVA and PVA-based materials. A partial dehydration of PVA with the formation of a system of polyene bonds [7] can occur in this case. Introduction of acid catalysts (aluminum, iron, bismuth, cuprous chlorides or hydrochloric acid) allows to substantially decrease the initiation temperature of the PVA dehydration processes [10, 11].

Taking into consideration the fact that biocompatible calcium phosphates, mainly HA [12-14], often enter into the composition of biomaterials, study of the influence of these phosphates on the PVA properties are of an interest. Much of the research in this field was devoted to the study of the mechanical and biological properties of the composites based on calcium phosphates and PVA [15-18]. However, the action of UV radiation and temperature factor – important components of the sterilization process of ready biomaterials of the given type – remain poorly studied until now.

The aim of the work was to obtain the film composite materials containing HA in a PVA matrix as well as the investigation of the influence of the temperature and UV radiation on their physical and chemical properties.

2. DESCRIPTION OF THE OBJECTS AND METHODS OF RESEARCH

Aqueous solution of 10 % PVA was prepared by dissolution of PVA (11/2 top grade with content of acetate groups of 5-6 %) in distilled water when heated in a water bath. HA gel was synthesized by the interaction of

diammonium phosphate with calcium chloride (Sigma-Aldrich) at pH of 10-11 according to the previously developed technique [19, 20].

Film composite HA/PVA materials were manufactured by irrigation of the mixture of 5 % HA gel and 10 % PVA solution in volumetric ratios of 1 : 1; 1 : 5; 1 : 10; 1 : 20; 1 : 50; 1 : 100 (Table 1) on the glass substrate of the size of 2 × 7 cm followed by drying in air at room temperature. The obtained HA/PVA films of thickness of about 0.2 mm were separated from the substrate and heated at 85, 135, 150 and 180 °C during 1 hour.

Table 1 – Composition of the initial HA gel/PVA solution mixture, content of HA (C_{HA}), optical density (D_T) and reflection coefficient (R) except the background for film composite HA/PVA materials

Initial mixture HA gel /PVA solution		C_{HA} , wt. %	D_T , rel. un.	R , %
HA gel /PVA solution ratio, vol. un.	Content of HA gel, wt. %			
1 : 100	1	0.5	0.21	1
1 : 50	2	1.0	0.41	7
1 : 20	5	2.4	0.47	11
1 : 10	9	4.8	0.54	24
1 : 5	17	9.1	1.24	49
1 : 1	50	33.0	1.51	68

X-ray phase analysis of PVA and HA/PVA films was performed on the diffractometer DRON-3 with radiation $CuK_{\alpha} = 1.5405 \text{ \AA}$. Optical transmission spectra of the film samples were recorded on the spectrophotometer Agilent 8453 (USA); measurement of the optical reflection coefficient of the samples was carried out using spectrodensitometer SpectroDens (TECHKON GmbH, Germany) against the black paper with the reflection coefficient of 6 %. Hydrophilic and hydrophobic properties of the samples were determined by the contact wetting angle method on the device Contact angle Measuring system G10.

Irradiation of PVA and HA/PVA films was performed by the entire spectrum of a medium pressure mercury quartz lamp DRSh-250; distance between the lamp and the sample was 10 cm; exposure time – 10 min.

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3. DESCRIPTION AND ANALYSIS OF THE RESULTS

Diffraction patterns of the investigated samples are illustrated in Fig. 1. Presence of the main crystalline peak near 2θ 20° with the orthorhombic unit cell [21] and insignificant amorphous halo near 2θ 40° is typical for pure PVA film (Fig. 1, curve 1). We should also note the presence of the peak near 2θ 29°, which, taking into account its crystallinity different from the basic PVA reflexes, is probably conditioned by some impurity.

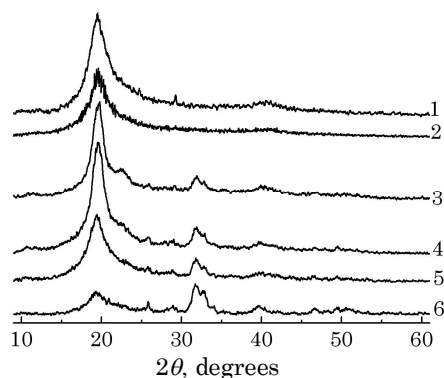


Fig. 1 – X-ray patterns of PVA and HA/PVA films containing different amount of HA: 1 – PVA; 2 – 0.5 % HA; 3 – 4.8 % HA (150 °C); 4 – 4.8 % HA (135 °C); 5 – 4.8 % HA; 6 – 33.0 % HA

Addition of even insignificant (0.5 %) amount of HA leads to the fact that PVA phase becomes more amorphous (Fig. 1, curve 2). Starting from a certain concentration (4.8 %), HA begins to be identified on the diffraction patterns (Fig. 1, curves 3-6). However, in all these samples main peaks of apatite are poorly distinguished because of its low crystallinity. The basic reflexes of HA are located near 2θ 26° (plane (002)) and 2θ 30-35° (superposition of four peaks (211), (112), (300) and (202)). We should note that with increasing HA content in the composite, crystallinity of PVA becomes worse (Fig. 1, curves 5, 6) as a result of weakening of intermolecular interactions. Increase in the crystallinity of PVA phase is observed under thermal treatment of the films containing PVA and HA as evidenced by the increase in the reflexes intensities (Fig. 1, curves 3, 4).

Electronic transmission spectrum of the initial (cold) PVA film is characterized by insignificant absorption by acetate groups in the range of 200-400 nm (Fig. 2a, curve 1) [22]. With increasing baking temperature of PVA films from 135 to 150 °C, band intensity in the range of 260-300 nm appreciably increases; warm-up at 180 °C leads to a subsequent (12-20-fold) increase in the optical density in the absorption maxima, and appearance of a number of new absorption bands, according to [10, 11], can be associated with the overlap of intense bands from polyene fragments with three conjugated bonds on the absorption bands of un-saturated carbonyl fragments of the types $R-(CH=CH)_2-CO-OH$, $R-(CH=CH)_2-CO-H$, $R-(CH=CH)_2-CO-R$, where R is the fragment of the chain $PVA-(CH_2-CHOH)_m-$ with m links.

Introduction of HA into PVA film promotes the increase in the total absorption, mainly, due to the strengthening of light scattering effects (Fig. 2b, c). The value of the optical density determined from the transmission spectra in the range of 600-800 nm significantly increases

es with increasing HA content – from 0.21 to 1.51 rel. un. with the increase in the HA content from 0.5 to 33 % (Table 1). When determining the reflection coefficient R conditioned by the optical reflection from HA particles, the similar dependence takes place, namely, the growth from 1 to 68 % with increasing HA content in the film from 0.5 to 33 % (Table 1).

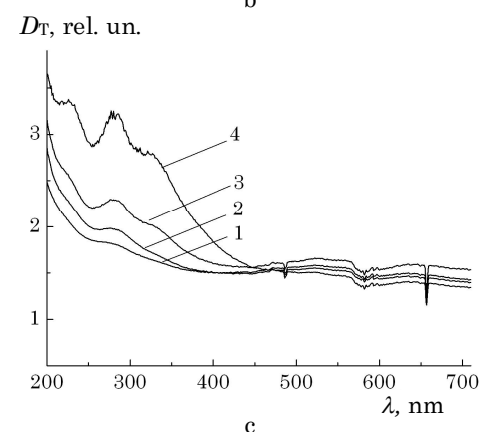
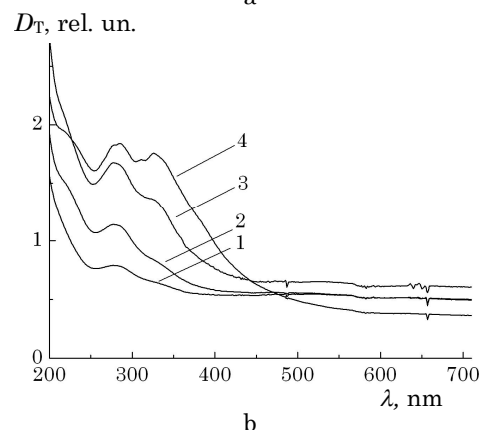
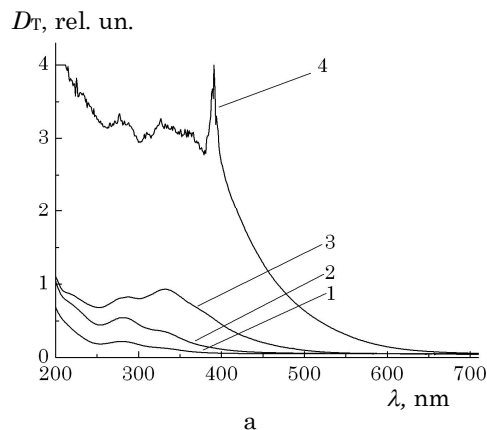


Fig. 2 – Absorption spectra of PVA (a) and HA/PVA films containing 4.8 % (b) and 33.0 % (c) of HA: 1 – 20; 2 – 135; 3 – 150; 4 – 180 °C

Warm-up of HA/PVA film in the range of 135-180 °C, as well as in the case of PVA films, leads to the increase in the band intensity in the range of 260-300 nm especially significantly with increasing HA concentration (see Fig. 2b, c, curves 2-4).

Thus, increase in the baking temperature of HA/PVA films leads to both the growth of absorption in the region of spectral maxima and the increase in the level of total

absorption (background) in the visible and UV regions. To compare the values of the optical density of the samples with the varied HA content the given background conditioned by the scattering effects was deducted. It is established that the value of the first maximum of the optical density determined except the scattering background ($D'_{Tmax(280\text{ nm})}$) in the temperature range of 20-135 °C increases insignificantly with rise of HA content from 0 to 30 %, and then it is constant (see Fig. 3a, curves 1-3). When warming up the films at 150-180 °C the change of the optical density occurs in a different way: introduction of 0.5-5 % of HA leads to the 1.5-fold decrease in the optical density and further increase in the HA content to 10-33 % leads to the increase in the optical density. Based on this data, one can conclude that inhibition of the PVA destruction process is mostly expressed at 180 °C that is clearly confirmed by the change in the optical density obtained in the reflection D_R for the samples with different HA content (Fig. 3b).

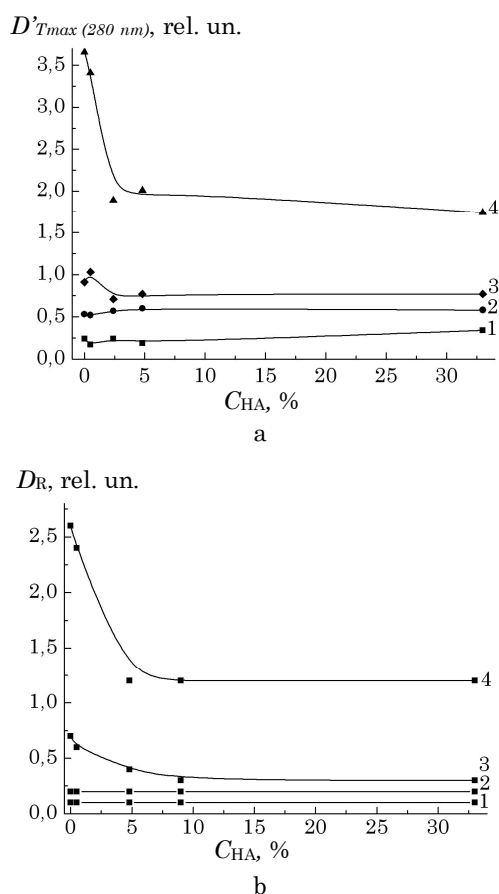


Fig. 3 – Dependence of $D'_{Tmax(280\text{ nm})}$ (a) and D_R (b) on the HA content in a film composite HA/PVA material: 1 – 20; 2 – 135; 3 – 150; 4 – 180 °C

Thus, the data of the X-ray phase analysis and optical spectrophotometry implies that the warm-up of PVA films as well as the HA introduction into their content influences the polymer structure and the processes of its thermal destruction. Taking into account the fact that dehydration occurs during the polymer warm-up, the study of the hydrophilic and hydrophobic properties of

the surface of PVA films both initial and with introduced HA is also of interest.

The value of the contact angle of the film of studied PVA is equal to 48°, and when warming up from 20 to 180 °C it slightly increases because of the hardening of the polymer (Table 2). Treatment by UV during 10 min of the PVA film both cold and warmed up at 135-180 °C promotes an additional increase in the value of the contact angle by 8-17°.

Introduction of HA into the PVA film content leads to the insignificant increase in its hydrophobicity; the contact angle increases by 3-5° (Table 2). In contrast to the PVA films, hydrophilicity of the HA/PVA composites after UV treatment somewhat increases. In particular, contact angle of the samples preheated at 180 °C after UV treatment decreases by $23 \pm 10^\circ$.

Table 2 – The values of the contact angle of the PVA film and composite HA/PVA material

Sample	Baking temperature, °C	Contact angle, degrees	
		UV free	After UV (10 min)
PVA	20	48 ± 1	59 ± 8
	135	58 ± 2	65 ± 10
	150	62 ± 1	62 ± 1
	180	66 ± 2	56 ± 10
HA/PVA (HA content of 4.8 %)	20	53 ± 2	51 ± 2
	135	59 ± 3	57 ± 3
	150	66 ± 5	60 ± 3
	180	69 ± 10	46 ± 10

We should note that changes in the absolute value of the contact angle of PVA films and HA/PVA under the action of UV irradiation are relatively small and characterized by a significant spread conditioned by the amphiphilicity of the polymer and considerable oscillations of the initial values of the contact angle – 44-72° [23-26].

4. CONCLUSIONS

Film composite materials with the content of HA of 0.5-33 % have been obtained based on the HA gel and PVA solution. Analysis of the optical spectra of these films implies the presence of the pronounced light scattering effects increasing with the rise of the HA content. Introduction of HA into the content of PVA films leads to the inhibition of thermal destruction of the polymer without changing the position of the main spectral bands of the optical absorption. Hydrophobicity of PVA films increases with introduction of HA, and action of the UV treatment of HA/PVA films, otherwise, leads to the strengthening of the hydrophilic properties especially after warm up of the films at 180 °C.

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