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The Influence of Ultrasound and Ultraviolet Irradiation on the Nanocomposite Calcium Phosphate-Polymeric Gel

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An influence of high-intensive ultrasound and ultraviolet (UV) irradiation on the nanocomposite calcium phosphate-polymeric gels has been investigated. The action of UV light leads to a significant increase in shear stress and viscosity of hydroxyapatite (HA) / polyvinyl alcohol (PVA) gel while HA / sodium carboxymethyl cellulose (Na-CMC) gel is insensitive to the UV action. Ultrasonic treatment of HA / PVA gel plays an important role only at small shear rates. UV treatment of HA / Na-CMC gel has no effect on its structure and can be used for low temperature UV sterilization.

Keywords: Hydroxyapatite, Biomaterials, Nanocomposites, Ultrasound activation, Ultraviolet treatment, Calcium phosphate-polymeric composite.

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1. INTRODUCTION

Calcium phosphates, mainly hydroxyapatite $Ca_{10}(PO_4)_3(OH)_2$ (HA), in combination with biocompatible polymers are well known as biomaterials for tissue engineering [1]. Polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and its sodium salt (Na-CMC) are biodegradable and nontoxic water-soluble polymers [2]. These polymers were widely used for the preparation of biomaterials [3].

It is known that the influence of ultraviolet (UV) light on PVA leads to the crosslinking of polymer chains [4] while the ultrasound action can destruct the polymer structure [5]. In this research, we have studied the influence of calcium phosphate hydrogel additive on ultrasonic and ultraviolet induced process in PVA or Na-CMC binder of phosphate-polymer composite. The structural-rheological properties of the composite under action of powerful low-frequency ultrasound and high-intensive UV light have been investigated.

2. MATERIALS AND METHODS

2.1 Materials

Aqueous solutions of 12 – 14 wt % PVA (M_w ~ 72000) and Na-CMC were prepared by dissolving preweighted amount of PVA and Na-CMC in distilled water and heating for 1 h at 90°C. The HA gel was synthesized by interaction of calcium chloride and ammonium hydrophosphate at pH 11 [6]. Composite gel was prepared by the mixture of 12 – 14 wt % HA gel and 12 – 14 wt % aqueous polymer solution (PVA, Na-CMC) in 1 : 1 ratio.

2.2 Methods

Composite gels were treated by ultrasound using USD3-20 generator, 120 W, 44 KHz, for 5 min. For the UV treatment the medium-pressure mercury lamp DRT 250, 240 W was used on 5 cm distance between lamp and sample surface during 10 min. An RHEOLAB MC1 rheometer (Physica Medtechnik, Stuttgart, Germany) with a standard steel-parallel-plate geometry of 13.56 mm diameter was used for the rheological characterization of HA / PVA or HA / Na-CMC composites. Test methods of oscillatory stress sweep and frequency sweep were used. The stress sweep was performed at a constant temperature (20°C) and with shear stress factor 1.1418 Pa. The viscosity range was performed at 0.118-100 Pas, and shear rate factor was 1.291.

The structure of synthesized samples was examined using an X-ray diffractometer ADVANCED D8 (Brucker, Germany); Ni-filtered Cu*K*α radiation (wavelength 0,154 nm) was used.

3. RESULTS AND DISCUSSION

According XRD data HA/PVA composite consists of nanocrystalline HA and amorphous PVA binder. The mean crystalline size of HA particles is 10 – 30 nm.

Shear viscosity of a colloidal HA / PVA gel at the initial shear rates of $1 - 5\ s^{-1}$ is 0.6 Pa·s. Sharp decrease of shear viscosity up to 0.01 Pa·s connected with destruction-reduction of colloidal structure takes place in the range from 5 to 50 s^{-1}. The transfer to the flowable state at the shear rates higher 50 s^{-1} is occurred (Fig. 1).

Ultrasonic treatment of a colloidal HA / PVA gel leads to the twofold increasing the viscosity at the initial shear rates range ($1 - 5\ s^{-1}$). In the range of 5 – 50 s^{-1} the viscosity decreases in 14 times from 1.4 to 0.1 Pa·s. The transfer to the flowable state takes place at the shear rates higher 250 s^{-1}.

Ultraviolet treatment of a colloidal HA / PVA gel does not lead to the changes in the viscosity at the initial shear rates range ($1 - 5\ s^{-1}$). In the range of 5 – 50 s^{-1} the viscosity decreases in 3 times. The transfer

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to the flowable state takes place at the shear rates higher 250 s^{-1} but the viscosity is 12-fold higher than that for non-treated and ultrasonically treated samples.

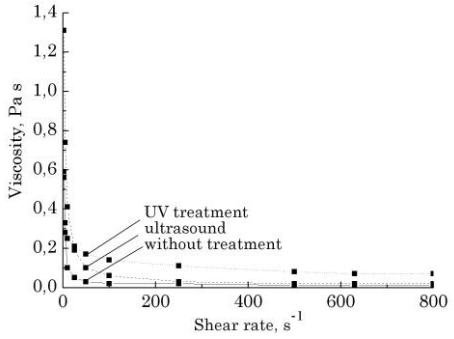

Fig. 1 – Share rate dependences of HA / PVA gel shear viscosity after UV and ultrasound treatment

The shape of the flow curves (Fig. 2) for the initial HA / PVA gel as well as for UV and ultrasonic activated gels corresponds to the pseudoplastic behavior. As is seen in Fig. 2 shear stress values for UV treated gel is significantly higher than that for initial gel in the wide range of share rates. This increase of shear stress values is probably connected with the formation of polyene links under UV irradiation. One of the evidence of the double-bound formation is yellow coloring of UV irradiated HA / PVA gel after its drying.

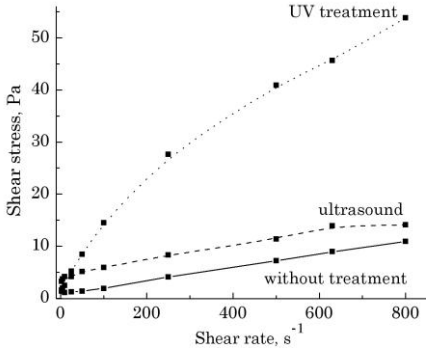

Fig. 2 – Share rate dependences of HA / PVA gel shear stress after UV and ultrasound treatment

In contrast to HA / PVA gel the structural-rheological properties of HA / Na-CMC gel is insensitive to the UV and ultrasound treatment. This allows using UV irradiation for low-temperature sterilization of HA / Na-CMC gel in medicinal practice.

4. CONCLUSIONS

An influence of ultrasonic and UV action on the structural-rheological properties of HA / PVA and HA / Na-CMC gel has been investigated. The action of UV light leads to an essential increase in shear stress and viscosity of HA / PVA gel while HA/Na-CMC gel is insensitive to the UV action. Ultrasonic treatment of HA / PVA gel plays an important role only at the initial range of shear rates.

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