MECHANICAL PROPERTIES OF CHEMICALLY AND PHYSICALLY CROSSLINKED POLY(VINYL ALCOHOL) CRYOGELS

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Introduction

Poly(vinyl alcohol) (PVA) is one of the most popular macromolecule capable of hydrogel structure formation [1]. PVA hydrogels are weak materials therefore their structure is stabilized by chemical crosslinking with glutaraldehyde, acetaldehyde, formaldehyde and other monoaldehydes [2] in the presence of sulfuric acid, acetic acid or methanol. This method of crosslinking is not suitable, however, for biomedical or pharmaceutical applications because of residual amount of toxic crosslinking agents or catalyst which can be leached out. Therefore, to eliminate toxic and elutable agents from hydrogels, another chemical methods of crosslinking can be used, including electron beam or g - irradiation [3,4].

An alternative method of hydrogel's preparation without using toxic additives, is the freezing-thawing process in cycles repeated up to several times [5]. In this process aqueous solutions of PVA are frozen at -20°C±2 and then thawed at room temperature, with formation of crystallites [6]. Such variables as number of freezing- thawing cycles, time of each operation and also molecular weight and concentration of PVA determine final properties of produced cryogels [7,8].

In order to improve mechanical strength of hydrogels, we used low molecular weight, biocompatible molecules of di- and multifunctional metabolites such as succinic acid and gluconic acid as crosslinking agents, thus eliminating problem of toxicity associated with conventional chemical crosslinkers such as aldehydes. These low molecular weight functional metabolites can form additionally hydrogen bonds in the PVA network. The systems were subjected to the freezing/thawing process, which can finally lead to cryogels of mechanical properties useful for articular cartilage repair.

Experimental

Preparation of hydrogels by combined chemical and physical process

PVA with M_n=48 400- 52 800 Da and M_w=89 500- 97 700 Da (Elvanol, du Pont with degree of hydrolysis 99-99,8%) was used to prepare an aqueous solutions of 25 wt% PVA with 3 wt% gluconic acid (Aldrich, aqueous solution 45-50%) and 25 wt% PVA with 3 wt% succinic acid (Aldrich, powder 99%). Samples were heated in an oven at 90°C for 12-16 hours. Hydrogel solutions were placed in teflon moulds in order to prepare samples for mechanical testing. Samples were subjected to freezing at -18°C for 12 h and thawing at 18°C for 12 h for 4,7, and 9 cycles.

Mechanical testing

Compression tests of prepared hydrogels were performed on MTS QTest\10 apparatus at crosshead speed of 5 mm/min according to EN ISO 604:2002 standard. Compressive stress was determined at 60% strain. Additionally, relation between compression strength of the hydrogel and number of freezing-thawing cycles applied during material production was investigated. Results were averaged from 4-6 samples.

Results and discussion

PVA hydrogels blends containing succinic and gluconic acids, respectively, subjected to freezing-thawing process were relatively strong, white materials. It is already know from the literature, that cryogel's properties, especially the degree of crystallinity is highly dependent on the number of freezing-thawing cycles [5,9]. Therefore novel blends were subjected to variable number of cycles in order to find the correlation between the overall mechanical properties and number of freezing-thawing cycles .

It has been found that mechanical properties of produced blends were strongly dependent on the crosslinking density. FIGURE 1 shows that blend containing gluconic acid has the highest values of compressive strength, which increases with increasing number of freezing-thawing cycles. It is worth noting that these values are higher as compared to the PVA/PVP system, already described in the literature (the highest crosslinking density has been found for this system among all prepared blends).

It has been also found that blends containing metabolite's molecules were characterized by elastic modulus of E_c=7.23-14.09 MPa at 60% strain (FIG.2), what compares very well

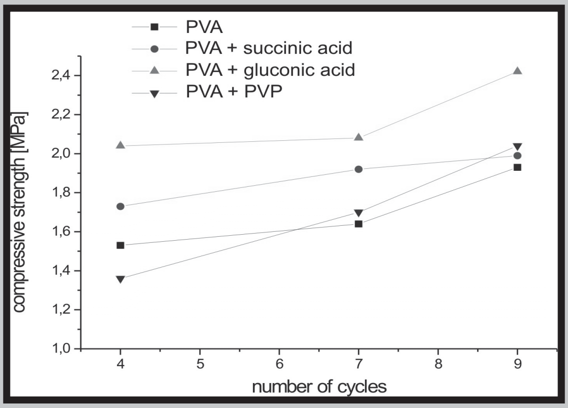

FIG. 1. Compressive strength as a function of freezing-thawing cycles.

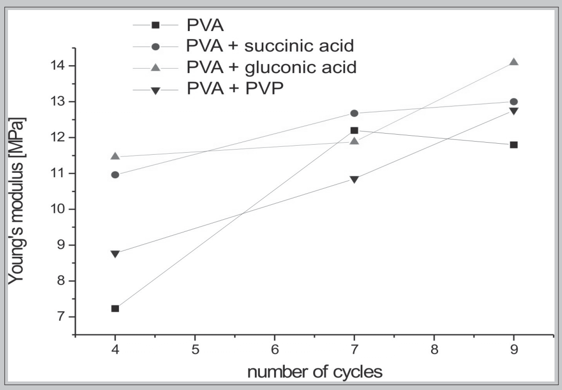

FIG. 2. Young's modulus at 60% strain as function of freezing-thawing cycles.

to properties of natural articular cartilage (E_c=1.9-14.4 by 30% of strain [12]).

Conclusions

PVA hydrogels were prepared by combined chemical and physical process including chemical reaction between PVA and low molecular weight metabolite molecules, such as succinic and gluconic acid, respectively, followed by repeated freezing-thawing cycles. The highest compressive stress has been found for a blend containing 25% PVA and 3% gluconic acid after four cycles. After nine cycles, this blend showed still higher values as compared to the neat 25% PVA cryogel and PVA/PVP system (the last one was characterized by the highest crosslinking density). We demonstrated that usage of di- and monofunctional metabolites as crosslinking agents for PVA hydrogel in combination with repeated freezing-thawing process is an effective method for preparation of strong cryogels. Their mechanical properties compare very well with these of natural cartilage and can be considered for articular cartilage reconstruction.

Acknowledgements

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REPEATABILITY OF SOL-GEL BIOCOATINGS ON OPTICAL FIBERS EXAMINED BY STATISTICAL PATTERN RECOGNITION METHODOLOGY

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Introduction

The sol-gel production technology enables to obtain variously shaped materials from liquid precursors. The sol-gel coatings are the subject of many examinations, since they can find plethora of applications [1,2,3,4]. Coated subjects may gain new characteristics [5,6,7,8], like corrosion resistance [9], improved biocombatibility [10] or better electrical insulating properties [11]. Silica based sol-gel coatings may be used for production of fiberoptic applicators for laser therapies [12]. Interstitial laser thermotherapy is a quite new treatment of pathologic tissues in difficult to access environments (e.g. brain, liver), whereas the applicator is inserted into the pathologic lesion and curing laser light is guided through the fiber [13]. The other area of applications are bio- and chemosensors. This work presents the results of examination of sol-gel biocoatings surfaces.

Experimental

Materials

Sol-gel coatings were produced from solvents and reagents obtained from commercial sources and used without further purification: 96% ethyl alcohol (Merck), 98% tetraethylorthosilane (TEOS) (Fluka) and 37 % hydrochloride acid (Merck). The various coatings were prepared with R ratios equal 20, 32, and 40, where R denotes the number solvent moles to number of precursor moles. The HCl was added as the catalyst in proportion to ensure the acid hydrolysis (pH=2). The mixture was stirred for 4 hours by means of magnetic stirrer with the speed 400 rot/min at the room temperature. Optical fibers from Thorlabs (Hard Clad Silica, low OH) were used (core diameter ϕ_1=400 μm, HCS cladding ϕ_2=430 mm with external coating ϕ_3=730μm). First, the external jacket was mechanically removed on the distance of 2 cm. Next, the cladding was removed chemically by acetone and washed with ethyl alcohol. The sol-gel coatings were produced from freshly prepared hydrolyzates by dip-coating method, whereas the bar fiber tip was placed in liquid hydrolizate, which flow out form the container in the controlled manner (the outflow speed was calculated).

Procedures and methodology

All prepared fibers (20 for each ratio R) were dried for 24 hours in room temperature. After that, the microscopic pictures were taken by means of microscope (Nikkon optical microscope with PC interfaced digital camera) and stored in PC for further processing. The preprocessing was applied in order to obtain images compressed to 80x80 pixels bitmaps. The Linear Discriminant Analysis (LDA) for the feature selection and dimensionality reduction of data was exploited [14]. Then the classification based on Single Linkage method was performed. The picture in statistical pattern recognition methods is treated as a two-dimensional array of intensity values I(x,y). The recognition process was perform in order to find out the similarity between images. We divided the data base into 3 groups (corresponding to the types of applicators; one group for one R).

Results and discussion

The recognition procedure was applied to find out in which group the similarity score was the highest one. The higher the number of similar images, the higher is the repeatability of production process, thus the better quality of coatings. FIGURE 1 shows light distribution around the sol-gel coated applicator. The exemplary microscopic image of the coating surface is depicted by FIG.2.