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Biomaterials based on polyvinylalcohol / hydrolysed collagen blends

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This paper deals with obtaining and characterization of some bioartificial materials based on polyvinyl alcohol(PVA)/hydrolysed collagen (HC) blends. The film samples have been obtained by mixing of the solutions of polyvinyl alcohol and hydrolyzed collagen of 10 wt% concentration in different proportions. By a complex of physico-chemical and structural methods such as DSC, thermogravimetry, IR-spectroscopy etc., the compatibility and interactions between components has been established. On the basis of the obtained data can be concluded that optima compatibility ratios are 95-70 PVA wt %/5 – 30 wt% HC**.**

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1. Introduction

Blends of polymeric materials for different applications should possess physico-chemical and mechanical properties adequate to their final use and also the components should be compatible. Synthetic polymers have many of physico-chemical and mechanical properties requiered for biological polymers they have to replace, but they do not provide satisfactory biocompatibility, and after their use they lead to a large amount of waste. Natural polymers such as fibrin, collagen, elastin, etc., possess high biocompatibility, but their mechanical properties are often inadequate and, furthermore, their processing is difficult.

Blending techniques were used to combine synthetic and natural polymers to realize processable biomaterials combining physico-chemical properties of the synthetic component with the biocompatibility of the biological one.

Polyvinyl alcohol (PVA) a water-soluble synthetic polymer has been produced for many industrial applications. It is used as emulsifier, colloid stabiliser, sizing agent, coating in the textile industry, adhesives, and house building industry, as suture fibers, protection colloid, replacing material for leather, soil conditioner etc [1]. All these end-uses of PVA are based on its exceptional properties such as: water solubility, good thermal stability, good film forming, high tensile strength, no static charge, resistance to organic solvents and oils, non toxicity and non carcinogenity and good biodegradability [2].

In the future, water-soluble polymers, hydrogels and water-soluble packing will be designed to completely biodegrade in composting plants or waste treatment facilities [3]. This goal is receiving in our days a great attention.

PVA has been blended with natural polymers such as starch, chitin, gelatin, silk fibroin, cyclodextrin and other lignocellulosic fillers [3], because of its hydrophilic characteristics that allows for good compatibility Also, blending with natural polymers get low cost of final materials, they show good properties, they are easy to process and recyclable [3 - 9].

Natural polymers allow for cost reduction of the final items and are supposed to speed up the degradation process [4].

Collagen is the most abundant protein in the animal kingdom, including man. It is a major component of extra-cellular matrix in many tissues, and its metabolism is directly associated with many physiological processes of biological adaptations and tissue regeneration. Many vital processes of tissue repair and growth following injury of any kind depend largely on the rate of self-assembly of collagen molecules [10]. The collagen addition in blends in different proportions increase the biodegradation rate, enhance adhesion of epidermal cells to the polymer surface and prevent failure in case of implants [11]. Understanding the factors that influence collagen interactions with solid surfaces is of great importance in medicine and pharmacology.

Manufacture of blends containing collagen hydrolysate (HC) [12-16], a proteinaceous material produced by enzymatic hydrolysis of solid waste generated down stream to chrome tanning (leather shavings) in the presence of organic amines, thus contributes also to solving a worldwide recognized disposal problem of the tannery industry [17, 18]. The use of HC is also supposed to be valuable as a natural fertilizer in agriculture applications due to the relatively high nitrogen content (~13%) and, moreover, it may act as a promoter for degradation of the blends based on water-soluble continuous matrices. HC is readily degradable both in an aqueous environment and with standard activated sludge at a rate higher than in soil.

Studying the PVA/HC blends, Alexy *et al.* [10, 19] showed the positive effect of the HC on biodegradation in anaerobic conditions. The HC addition in the blend significantly increases biodegradation rate at 5 °C.

Blends of PVA with natural polymers increase the number of new materials with applications in medicine, agriculture, pharmacy, etc.

PVA/HC blends properties are of practical relevance for applications as hospital laundry bags and containers of water-soluble substances, such as chemical agents for treatment of waste and potable water, fertilizers, washing agents, sanitary products, entraping materials for immobilisation of enzymes in biosensors, packing materials, drug release systems and so on.

The aim of our study was to increase the compatibility and biocompatibility of a synthetic polymer - PVA, by incorporation a natural one, HC. By a complex of physico-chemical and structural methods such as DSC, thermogravimetry, IR-spectroscopy, etc., the compatibility and interactions between components will been studied.

2. Experimental

2.1. Materials

PVA with a number-average molecular weight of 71 000 Dalton, a polymeric degree of 1600 and a degree of saponification of 95.8 mg KOH/g was obtained from SA Romacril Râşnov- România.

The hydrolyzed collagen was supplied by the National Institute of Research and Development for Biological Science – Bucharest, Romania. It has been obtained by acid hydrolysis of bovine derma. The powdered sample was obtained by a spray-drying process with a BÜCHI 190 MINI SPRAY DRYER. It is a type I and III collagen and it consists of a mass of peptides with the following elemental composition: 42.7 wt%C, 10.8 wt% H, 12.2 wt% N and 34.3 wt% O and has a number average molecular weight determined by GPC on solution in dimethyl formamide of 99 000 Daltons and a polydispersity of 1.66. It is thermally resistant up to 180 ºC. HC is a highly hydrophilic polymer.

2.2. Blends preparation

There have been obtained 2 solutions of polyvinyl alcohol and hydrolyzed collagen, respectively of a 10 wt% concentration.

For the solution of polyvinyl alcohol there were weighed 20 g PVA and sprinkled in 200 ml of twice distilled water under continuous stirring. After it has completely dissolved, it was heated in thermostated bath at 60-70 ºC for 5 hours, under continuous stirring. By cooling, a white viscous solution was obtained. This was centrifuged and the resulted solution was completed to 200 ml with twice distilled water. The concentration was re-evaluated by evaporation of a known quantity of solution and resulted solid was repeated weighing to constant mass.

20 g HC were sprinkled in 200 ml of twice distilled water under continuous stirring. The resulted solution is brown-yellowish and weakly viscous.

There have been prepared blends by mixing of the resulted solutions in various proportions which are presented, in the first column of the Table 1.

The blends were stirred for 15 minutes and left to room temperature for 48 hours. After this period of time, the blends were homogeneous, they present neither separation nor colour changes. The blends that have been left to room temperature for a seven-day period of time are strongly microbially contaminated. Therefore, should be necessary to add stabilizers and antimicrobial preservatives.

After 24 h mixing, the blends were again stirred and films with a thickness of approximately 0.02 mm have been made from these solutions by solvent casting method. 2 ml of each solution has been laid on polymethyl methacrylate (PMMA) plates of dimensions of 10×15 cm, and then were dried at 60-70 ºC in for one hour.

2.3. Investigation methods

Optical microscopy

The obtained films were examined by means of an optical Axiolab.re Carl Zeiss microscope, J/902553, with a magnification of 400 X. No structures can be evidenced because the samples are homogeneous and transparent, and there have not been used any techniques of colouring the components.

DSC analysis

The DSC analyses were achieved by means of a Mettler DSC 12E instrument. Before starting measuring, the calorimeter was calibrated with indium standard, which has T_m =156.6 ºC and heat of fusion of 28.43 J/g.

The samples were thermically scanned in two cycles of heating under temperature range between 25-216 ºC with a heating rate of 10ºC/min, followed by a cycle of cooling at a cooling rate of 10 ºC/min. The samples having masses comprised between 6 and 8.2 mg were put into aluminium crucibles. A nitrogen flow of 30 ml/min was passed through the calorimeter. The DSC curves for these blends were drawn for the two heating cycles and for one cooling cycle

IR analysis

FT-IR spectra of the films of PVA/HC were recorded at 4 cm^{-1} resolution by means of a DIGILAB Scimitar Series FT-IR spectrometer (USA). Processing of the spectra was done by means of Grams/32 program (Galactic Industry Corp.).

The thickness of the films was measured and a correction of the recorded spectra was made due to the fact that the thickness of the films was slightly different. For the hydrolysed collagen, the spectra were recorded in KBr pellets because this sample does not form film.

Table 1. Macroscopic aspect of the obtained solutions and films.

Blend	Notation	Solution aspect	Films aspect
1HC/9PVA	1	Opalescent white-yellowish viscous	Semitransparent, continuous
2HC/8PVA	2	Opalescent white-yellowish viscous	Semitransparent, continuous
3HC/7PVA	3	Opalescent white-yellowish viscous	Semitransparent, continuous
4HC/6PVA	4	Opalescent yellowish weakly viscous	Semitransparent, continuous
5HC/5PVA	5	Opalescent yellowish weakly viscous	The film is brittle and transparent
PVA	PVA	Opalescent white viscous	Semitransparent, continuous

3. Results and discussion

The DSC curves of PVA, HC and their blends are given in Fig. 1-3 where endothermal water desorption peak, glass transition temperatures and endothermal melting peak of PVA are recorded; and also crystallisation of PVA after first heating run.

The physically adsorbed water is released in very different temperature range depending on the chemical nature of the components. The peak temperature of this process is 90 ºC for HC and 130 ºC for PVA – Fig. 1.

The peak temperatures for the blends, lie between those of the components, but the shape of the peak is characteristic for each blend. All peaks of water desorption corresponding to the blends are wider than those of components and peak temperatures of the blends 1-4 with composition 95-40 wt% PVA/5-60 wt% HC are shifted to lower temperatures (95-100 ºC).

This change could be due to the different interaction with adsorbed water because the compatibility between components creates other arrangement of functional interacting groups. The melting temperature of PVA in the first run is almost unchanged of 185 ºC.

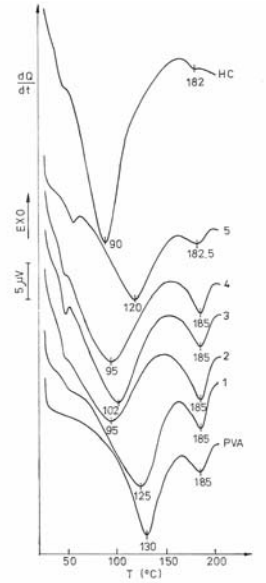

Fig. 1. DSC curves of PVA, HC and their blends in the first heating run.

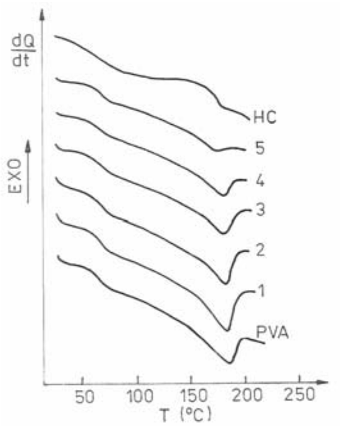

Fig. 2. DSC curves of PVA, HC and their blends in the second run.

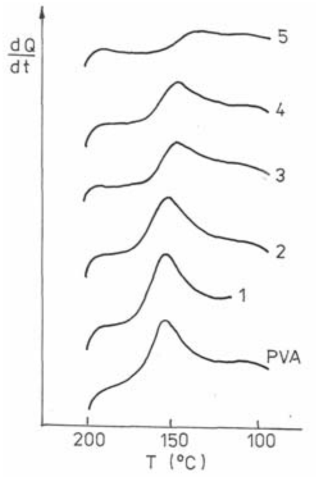

Fig. 3. DSC curves for crystallization.

In the second run – Fig. 2 – the water desorption peak does not appear more, that means that water was totally removed and the sigmoid corresponding to a second order transition is present in 50 - 80 ºC range. Also endotherm corresponding to melting is recorded, its area decreasing with HC content. The HC starts to decompose at temperature higher than 180 ºC.

PVA crystallizes at about 150 ºC Fig. 3, the peak is shifted to high temperature and area decreases with increasing HC content.

The DSC results for the process of water desorption, melting and crystallization corresponding to the cycles of heating and cooling are also plotted in Table 2 and also in Fig. 4-9.

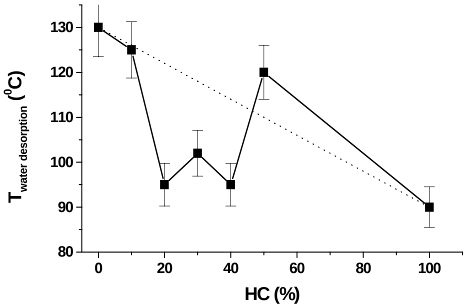

Fig. 4. Temperature corresponding to water desorption variation versus HC content (Dotted line calculated by additivity rule).

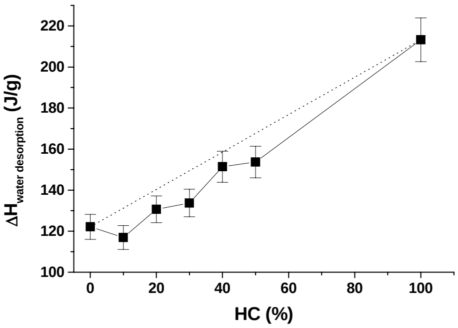

Fig. 5. Variation of the enthalpy corresponding to water desorption versus HC content (Dotted line calculated by additivity rule).

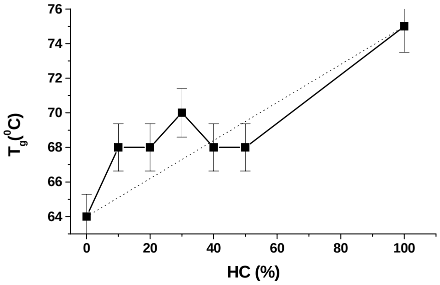

Fig. 6. Glass transition temperature variation versus HC content. (Dotted line calculated by additivity rule).

Comparison with values evaluated additively shows that experimental values of temperatures are inferior to those calculated – Fig. 4 - while heat of desorption are smaller. The enthalpy corresponding to the desorption of water from the samples rises as the content of the hydrolysed collagen in blends increases as it is shown in Fig. 5. That should means, as it was already mentioned, that interaction of the components with physically absorbed water is changed in the blends because their reciprocal influence.

In the case of PVA, the glass transition temperatures at 64ºC and a process of melting around the temperature of 180ºC (Table 2) were found. There can be noticed for the values of glass transition temperature their slight increase with HC content, the most considerable increase being observed for the 3HC/7PVA blend. The glass transition temperatures have higher values than additives ones for blends with prevalent content of PVA.

The modification of the transition temperature can be explained by the interactions between the components of the blend. (Fig. 6).

Generally, the melting endotherm of the polyvinyl alcohol decreases in intensity as the content of hydrolysed collagen in blends increases mainly in the second run as it is shown in Fig. 7.

Table 2. DSC results for the PVA, HC and their blends.

Sample	T_D (ºC)	ΔH_D (J/g)	T_g (ºC)	Tm (ºC)	ΔHm (J/g)	T_{cr} (ºC)	ΔH_{cr} (J/g)
PVA	130	122.13	64	Run I 185 Run II 185 Run III 185	12.35 34.16 38.3	155	27.82
1HC/9 PVA	125	116.9	68	Run I 185 Run II 185	18.6 44.1	155	22.43
2HC/8 PVA	95	170.64	68	Run I 185 Run II 185	17.03 51.08	155	17.92
3HC/7 PVA	102	133.71	70	Run I 185 Run II 185	14.47 34.77	150	9.7
4HC/6 PVA	95	151.4	68	Run I 185 Run II 185	9.81 28.54	150	13.92
5HC/5 PVA	120	153.68	68	Run I 182.5	16.92	140	11.26
HC	90	213.25	75	182			

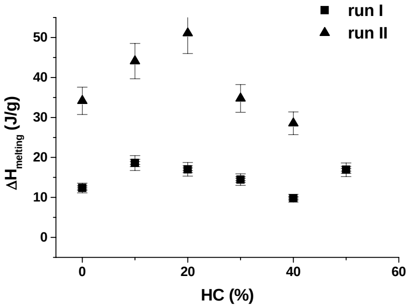

Fig. 7. Variation of the melting enthalpy versus HC content during the two cycles of heating.

The enthalpy variations corresponding to the melting process offers lower values than in the first cycle of heating, the curves described by these values having a similar aspect. The melting heats are higher than that of PVA especially for blends containing prevalent content of PVA indicating increased order in these blends because of higher compatibility degree (Fig. 7).

In the process of crystallization, the temperature and enthalpy variation shows a minimum value for the 3HC/7PVA sample (Fig. 8, 9); therefore HC hinders the PVA crystallization. It can conclude that this blend exhibits a higher compatibility degree.

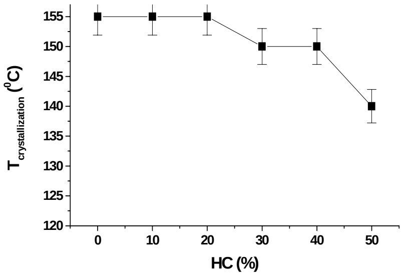

Fig. 8. Crystallization temperature of the PVA/HC blends vs HC content.

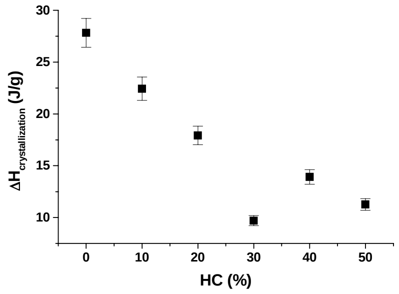

Fig. 9. Crystallization enthalpy of the PVA/HC blends vs HC content.

The FT-IR spectra are given in Fig. 10.

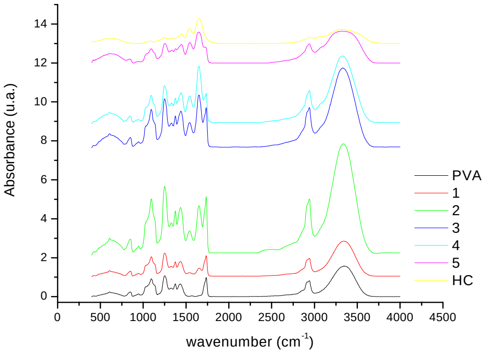

Fig. 10. FT-IR spectra of the blends based on PVA.

The band from 3350 cm^{-1} region, typical for polyvinyl alcohol, presents a maximum intensity for the 2HC/8PVA blend and its intensity considerably decreases as the HC content rises.

The band from 2939 cm^{-1} region, typical for C-H bond, presents a shoulder for the blends with a high content of PVA, this shoulder disappears in the case of 5HC/5PVA blend. The intensity of this band decreases as the HC content rises.

The band from 1651 cm^{-1} region (typical for terminal groups interactions) appears in the spectra of all blends and it is more obvious at high collagen content.

The band from 1541 cm^{-1} is typical for HC and rises in intensity as the collagen content increases.

The changes in the normalized bands' intensities for the same film thickness indicate the presence of the interactions between components.

4. Conclusions

Both DSC and IR-spectroscopy evidenced the physical and chemical interactions between the functional groups. It has been established the compatibility "window" and specific interactions between components. The values of the glass transition temperature increase with increasing HC content; the most significant increase being observed for the 3HC/7PVA blend. The IR spectra have maxim intensity values for this blend which are typical for the interactions between functional groups.

On the basis of the obtained data can be concluded that optima compatibility ratios are 95-70 PVA wt%/5 – 30 wt% HC**.** These blends may find application in agriculture and medicine. as ecologically expedient seeds polymeric covers, as matrix for controlled drug release of bioactive substances and chemical means of plant protection.

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