ENVIRONMENTALLY PROTECTION BY PREPARING OF BIOMATERIALS BASED ON SYNTHETIC AND BIOPOLYMERS

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ABSTRACT. In the last decades, the synthetic polymers are used in large scale in many areas. These macromolecular substances are usually of petroleum origin and are not biodegradable. The oil resources are limited and the use of non-biodegradable polymers causing serious environmental problems. In addition, non-biodegradable polymers are not suitable for temporary use. The advantages of synthetic polymers are obvious, including adequate physical and mechanical properties and low cost price. Natural polymers are abundant, renewable and biodegradable. Disadvantages of natural polymers refer to the decreasing of physical and mechanical properties. Mixtures of synthetic polymers with natural polymers that contain hydrolytic or enzymatic labile links show the advantage of improving the physical and mechanical properties and are biodegradable. The aim of this paper is to prepare biocomposites by melt blending of the polyvinyl alcohol (PVA) with natural polymers, such that these mixtures will provide suitable properties required for use in the medical field, respecting the environment.

Key words: *synthetic polymer, biopolymer, mechanical properties, thermal properties*

INTRODUCTION

In the last decades, the synthetic polymers are used in large scale in many areas. These macromolecular substances are usually of petroleum origin and are not biodegradable. The oil resources are limited and the use of non-biodegradable polymers causing serious environmental problems. In addition, non-biodegradable polymers are not suitable for temporary use. The advantages of synthetic polymers are obvious, including adequate physical and mechanical properties and low cost price.

Natural polymers are abundant, renewable and biodegradable. Polymers from natural sources are particularly useful as biomaterials in medicine, given their similarity to the polymers in the human body (extracellular matrix EMC) as well to the chemical versatility and biological performance. Disadvantages of natural polymers refer to the decreasing of physical and mechanical properties.

Mixtures of synthetic polymers with natural polymers that contain hydrolytic or enzymatic labile links show the advantage of improving the physical and mechanical properties and are biodegradable (Sionkowska, 2011). The main biopolymers used for biomedical applications are collagen, hyaluronic acid, chitosan, etc.

Collagen is the primary protein component of animal connective tissues. The major structural protein of the extracellular matrix (ECM) is collagen (Lullo et al., 2002; Karsenty and Park, 1995) and represents 90% of the bone protein content (Kern et al., 2001). There are 22 types of collagen, characterized by the formation of a triple helix, the three polypeptide chains are tightly twisted around each other in a circular structure.

Collagen is composed of different polypeptides, which contain mostly glycine, proline, hydroxyproline and lysine. The flexibility of the collagen chain depends on the glycine content. More flexibility is obtained with an increase content of glycine. Collagen is enzymatically degradable and has unique biological properties. It has been extensively investigated for biomedical applications (Vroman and Tighzert, 2009).

Discovered first time in the vitreous humour of bovine eyes in 1934 and subsequently synthesized *in vitro* in 1964, hyaluronic acid (HA) is made up of glucuronic acid and N-acetyl-glucosamine macromolecules which polymerized in units of more than 30,000. It is the longest component of EMC (Price et al., 2007). In the vitreous humour of the human eye it represents 0.1–0.4 mg/g wet weight, in synovial joint fluid, between 3–4 mg/ml, and in the matrix produced by the cumulus cells around the oocyte prior to ovulation, about 0.5 mg/ml). Rooster comb has high amounts of hyaluronan, up to 7.5 mg/ml (Collins and Birkinshaw, 2013). Also, its presence has been reported in the skin, aorta, brain, and cartilage. More recently HA has been extracted from bacteria-streptococci through fermentation, thereby eliminating the possibility of inter-species disease transfer.

Hyaluronic acid (HA) is widely used for numerous medical applications, such as eye surgery and drug delivery, scaffolding for tissue engineering, dermatological fillers, viscosupplementation for osteoarthritis treatment and as a potential modulator of growth and differentiation of stem cells (Palumbo et al., 2013; Davidenko et al., 2010; Collins and Birkinshaw, 2013; Yoo et al., 2005; Schanté et al., 2011; Fakhari and Berkland, 2013).

Chitosan is an abundant and renewable natural polymer that has excellent properties of biodegradability, biocompatibility, non-toxicity, antitumor, antimicrobial and adsorption activity (Maazouz et al., 2003; Dash et al., 2011; Mourya et al., 2010; Sashiwa and Aiba, 2004). The literature of the period 1994 to 2010 reported properties, processing and applications of chitosan in various industrial and medical fields: water engineering, paper, textiles, food processing, agriculture, photography, chromatographic separations, LED, tissue engineering, artificial skin, treatment of burns, drug delivery systems (Sashiwa and Aiba, 2004; Liu et al., 2011; Bonvin and Bertorello, 1994), artificial kidney membrane (Sashiwa and Aiba, 2004), cosmetics (Mourya et al., 2010).

It is known the use of polyvinyl alcohol (PVA) - based hydrogels in the presence of polysaccharides, such as sodium hyaluronate, or sodium chondroitin sulfate (Dutta et al., 2004). Films based on mixed chitosan / PVA were obtained by solvent casting (Agostino et al., 2012; Liang et al., 2009). Blends of PVA with collagen and gelatin, prepared from aqueous solution by solvent casting, were investigated by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) (Sarti and Scandola, 1995).

Little research has been conducted in the melt blending of synthetic polymer with natural polymers. Hybrid blends based on PVA and hydrolysed collagen (CH), an abundant, added value waste product of the leather industry, have been processed by melt blow extrusion to environmentally degradable films (Alexy et al., 2003). Chitosan between 25 % up to 70 % wt. was melt blended with poly ε-caprolactone (PCL), poly(butylene succinate) (PBS), poly(lactic acid) (PLA), poly(butylene terephthalate adipate) (PBTA), and poly(butylene succinate adipate) (PBSA) (Zhuang et al., 2012). Hyaluronic acid has been used to make biodegradable melt blends based of PLA (Zhang and Cui, 2012).

The aim of this paper is to prepare biocomposites by melt blending of the polyvinyl alcohol with natural polymers, such that these mixtures will provide suitable properties required for use in the medical field, respecting the environment.

MATERIALS AND METHOD

Materials

Polyvinyl alcohol from DuPont ELVANOL 71-30 was used as powder shape. It shows full degree of hydrolysis, viscosity of 27.0-33.0 cps, pH 5.0-7.0, volatile max. 5.0 % and ash max. 0.70 %. This grade is soluble in boiling water, but insoluble in cold water or common organic solvents. Glycerol having density 1.26 g/cm^3 was used as a plasticizer and supplied by REDOX.

As natural polymers were used: hydrolysed collagen (HC) with pH 5.5, supplied by THE LEATHER AND FOOTWEAR INSTITUTE, Bucharest, hyaluronic acid, sodium salt from bovine vitreous umor (HA), chondroitin sulphate A 70 sodium salt (CS) from bovine trachea and chitosan, all provided by SIGMA-ALDRICH.

It was performed 4 recipes based on PVA, collagen (up to 12.5 % wt.), chondroitin sulphate (0.2 % wt.), acid hyaluronic (2 % wt.) and chitosan (3.6 % wt.) by melt technique, as it is shown in table 1.

Table 1. *Recipes based on ELVANOL 71-30 and biopolymers*

Code	PVA, wt. %	Glycerol, wt. %	HC, wt. %	HA, wt. %	CS, wt. %	Chitosan, wt. %
Biomed_1.1	72	28	-	-	-	-
Biomed_1.2	65	25	10	-	-	-
Biomed_1.3	65	25	8.9	1	0.1	-
Biomed_1.4	59	22.7	12.5	2	0.2	3.6

The mixing of components was made with BRABENDER Plastograph with twin screws. After blending, PVA and was kept in oven at 105 ^{0}C for 4 h, for maturation. Homogenization of mixtures was achieved at following conditions: mixing chamber capacity: 300 cm^3, temperature: 175 ^{0}C ± 5 ^{0}C, mixing time: 10 minute, rotation speed of screws: 80 rpm.

After blending, the melted samples were processed by twin rolls and sheets with dimensions (150x150x1) mm and respectively, (150x150x4) mm were obtained by press. Table 2 shows the technological conditions for achieving the sheets.

Table 2. *Technological conditions for sheets*

Property	U.M.	Value
Rolling temperature	^{0}C	140-157
Rolling time	minutes	10
Pressing temperature	^{0}C	170
Preheating time	minutes	8
Preheating pressure	kN	150
Pressing time	^{0}C	10
Pressure	kN	600
Cooling time	minutes	11

The specimens were from these sheets in order to be characterized by DSC, tensile properties, density, hardness Shore and VICAT softening point. The purpose of tests is to estimate the behavior of polymeric materials to mechanical and thermal conditions to determine their compliance with product standards.

DSC

The DSC tests were performed using a METTLER-TOLEDO apparatus DSC-823^e model, using STAR^e software, version 9.10, and previously calibrating with indium standard. The weighted samples were sealed in 40 µl aluminum crucibles with a small hole in the lids, and the first heating curves were measured from room temperature to 250°C at a heating rate of 10°C/min. The melting of the samples were determined and defined as peak maximum (T_m) temperatures. For control, was used PVA 71-30.

Tensile properties

Tensile strength and elongation at break were performed on INSTROM 3345 (USA) mechanical tester. It was used test specimens of 1 mm thickness and a crosshead speed of 10 mm min^{-1}. At least five samples were tested for each composition, and the average value was reported.

124

Density

Density was performed with analytical balance RADWAG AS 220/X with kit density on sheets with 1 mm thickness.

Hardness Shore D

Hardness Shore was tested using a Durometer with Shore D scale, according to ISO 868. Test specimens of 4 mm thickness and a loading force of 4536 g were used. At least five points were tested for each composition, and the average value was reported.

VICAT softening point (VST)

VICAT softening point (VST) was performed with HDT/VICAT Aparatus (CEAST Italy). It was used A50 Method (load 10 N and heating rate 50 ^{0}C/h). It was used three specimens for each sample from sheets having the dimensions 25x10x4 mm.

RESULTS AND DISCUTION

DSC

Figure 1 shows the values obtained for melting temperature of biocomposites against the PVA sample (control) as peak maximum.
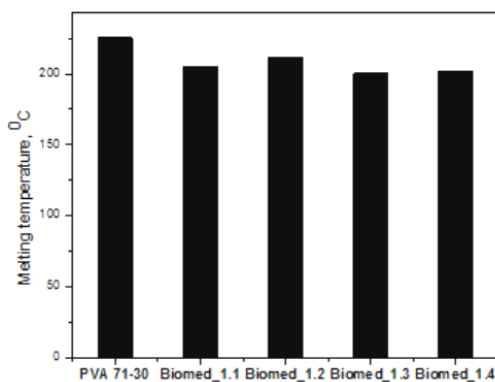

Fig. 1. T_m for samples based on PVA 71-30 and biopolymers

It can be seen from Figures 1 that the melting temperature decreases for all composites compared with the PVA control that shows T_m of 204.72 ^{0}C. This is due to glycerol that has the effect to decrease the melting temperature. From the point of view of extrusion workability at industrial level, it is desirable to reduce the energy consumption by the use of suitable polymers and additives. For this reason, the recipe Biomed_1.3 having lower value of temperature melting (T_m = 200.13 ^{0}C) is preferred.

Tensile properties

Tensile strength and elongation at break are illustrated in figure 2 and figure 3. From figure 2 and figure 3 is noticed that the mechanical properties for sample containing HC 10% (Biomed_1.2) were worse than the composition without HC (Biomed_1.1). Much better compatibility between PVA and biopolymers could be obtained by using of hyaluronic acid and condroitine sulphate (Biomed_1.3), when the tensile strength reaches 6.96 MPa and elongation at break is 26.58 %.
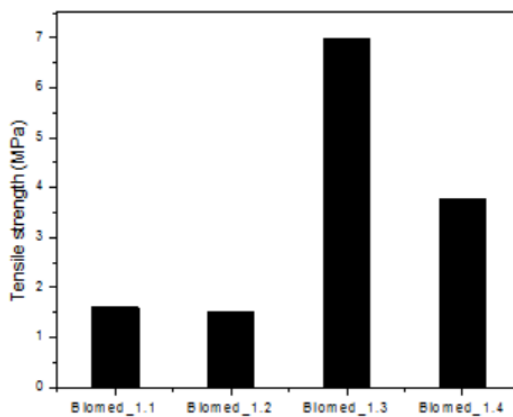

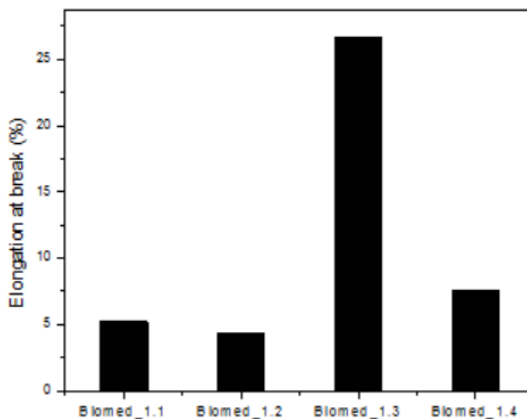**Fig. 2.** *Tensile strength for samples based on PVA 71-30 and biopolymers*

Fig. 3. *Elongation at break for samples based on PVA 71-30 and biopolymers*

By adding of chitosan (Biomed_1.4) the tensile properties suddenly decrease up to 3.77 MPa for tensile strength and 7.56 % for elongation at break.
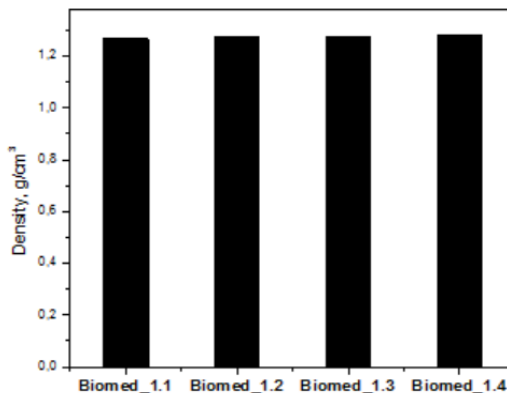
Density

Density of samples is shown in Figure 4.

Fig. 4. *Density of samples based on PVA 71-30 and biopolymers*

All composites show the same density.

Hardness Shore

Figure 5 shows the hardness Shore for the formulations made by melting.
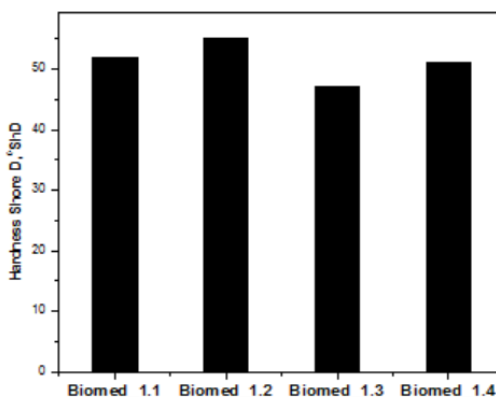

Fig. 5. *Hardness Shore D for samples based on PVA 71-30 and biopolymers*

The introduction of collagen at mixtures based on PVA (Biomed_1.2) has the effect of increasing the hardness up to 55 ^{0}Shore D comparative with samples without collagen that has 51 ^{0}Shore D (Biomed_1.1). Together with introduction of HA and CS (Biomed_1.3), the hardness Shore decreases up to 47 ^{0}Shore D. By introduction of chitosan (Biomed_1.4), the hardness Shore increases up to 51 ^{0}Shore D.

VST

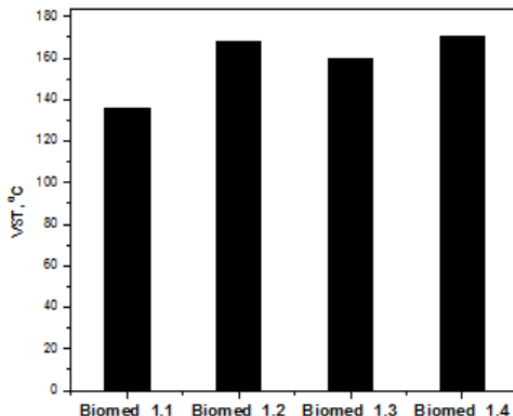The representation of VICAT softening point is shown in Figure 6.

Fig. 6. *VST for samples based on PVA 71-30 and biopolymers*

Adding of natural polymers to blends of PVA leads to increase of VICAT softening point, with about 23 %.The highest VST is registered by Biomed_1.4 (170 ^{0}C). VST is important to apreciate the behaviour of materials at thermal stresses.

CONCLUSIONS

Composites based on polyvinyl alcohol and natural polymers are prepared by melt processing.

Blend based of PVA and 10 % collagen shows the worse mechanical and thermal properties than those of control sample.

Mixture based of PVA, hydrollysed collagen, hyaluronic acid and condroitin sulphate reveals o good compatibility.

Chitosan leads to decrease of mechanical properties (tensile properties, hardness Shore) but to increase of thermal properties (melting temperature and VICAT softening point) compared with control sample.

The obtained biocomposites are very attracted for making suitable items by tailoring the compositions depending of desired properties.

Acknowledgements

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