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# Blends of Cellulose and Silk Fibroin in 1-butyl-3-methylimidazolium chloride-Based Solutions

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## Abstract

*Cellulose/fibroin blends in 1-butyl-3-methylimidazolium chloride-based solutions (BMIMCl) were studied using TGA, IR-spectroscopy, X-Ray and viscometry methods. The strongest intermolecular interaction occurred with 20% fibroin in the blend. As a result an amorphous and homogeneous film structure was formed. The solution of this blend has the highest viscosity than those obtained from not mixed solutions.*

**Key words:** cellulose, fibroin, blends, rheological properties, thermal destruction.

meric materials. For example, hydrate-cellulose fibres have a high degree of fibrillation and low strength in wet conditions in comparison with natural cotton fibres. Obtaining cellulose-based blends has a huge practical interest in terms of achieving different structures and properties of films and textile materials.

The most homogenous blend can be obtained from solutions in common solvent. There is information in the literature about a blend of cellulose with synthetic materials obtained by coagulation from tri-fluoroacetic acid solutions [1]: LiCl/dimethylacetamide (DMAA) [4 - 8], binary system dimethyl sulfoxide (DMSO)-paraformaldehyd and DMAA-paraformaldehyd [9, 10]. Polyvinyl alcohol (PVA) and polyethylene oxide (PEO) have the best compatibility with cellulose [2, 6]. The compatibility of cellulose with PVA in films was studied using the DSC (differential scanning calorimetry) – method [2]. The interaction energy of cellulose with PVA in films depends on the temperature, varying from  $-42$  to  $-75$  J/cm<sup>3</sup>; these values are higher than those for other polymer pairs known from literature data. The value of interaction parameter  $\chi_{12}$  for this polymer pair is about  $-0.9$ . The density of the interaction energy and interaction parameter  $\chi_{12}$  of cellulose with polyethylene oxide also has negative values [3]. In solutions of cellulose with polyamide-6, -66 phase separation is observed in any mixing ratio [6, 7]. In a cellulose blend with poly- $\epsilon$ -caprolactam, phase separation is also observed in some mixing ratios [7]. The molecular compatibility of cellulose with synthetic polymers decreases in the following order: polyacrylonitrile > polyvinyl alcohol > poly( $\epsilon$ -caprolactam) > polyamide-6, which was found by using nuclear magnetic resonance (NMR) <sup>13</sup>C analysis [6].

The homogeneity of blend films characterised by medium sized domains decreases in the same order. Cellulose and polyacrylonitrile regenerated as blends from LiCl-DMAA and DMFA-CO<sub>2</sub> solutions could interact in an amorphous way only when the cellulose content is more than 50 wt.% [11]. Cellulose/polyethylene terephthalate blends are incompatible and represent the dispersion of one polymer in the matrix of another, depending on the ratio of components. Primary hydroxyl groups of cellulose are mainly involved in the formation of intermolecular hydrogen bond interactions between the protons of OH- groups of cellulose and nitrogen from poly(4-vinylpyridine) [12]. This was confirmed by NMR, IR (infrared)-spectroscopy, DSC methods for cellulose blends with polyvinyl pyrrolidone [13], PVA and PEO [14]. Analysing cellulose behavior during heating is a method of assessing the compatibility of components: whether the compatibility of cellulose with synthetic polymers correlates with the measure of thermal stability of cellulose in blends [9].

Cellulose blends with other polymers could be obtained by coagulation from NMMO (N-methylmorpholine-N-oxide) solutions [15 - 20]; however, almost no research has been devoted to physical and chemical aspects of the interaction of components in these mixtures. A homogeneous solution and fibres from cellulose blends with aromatic polyamide poly-2,6-dichloro-1,4-phenyleneterephthalamide was obtained [17]; however, the solubility of this polyamide in NMMO is limited to 1.5 - 2 wt.%. Fibres of cellulose blends with polyethylene oxide and polyethylene from solutions in NMMO were obtained [18 - 20]. In these works the physical and mechanical characteristics of the fibres are presented, but no data are

## Introduction

Such processes as the dissolution and regeneration of natural polymers are basic technologies for producing fibres and films for different purposes obtained from wood cellulose, chitosane, non-spinable natural silk waste and wool. Good biocompatibility and biodegradation are undoubted advantages of products regenerated from fibre-forming polymers. However, the properties of regenerated polymers are quite different from those developed during the biosynthesis of pol-

given on the interaction of components or phase separation in cellulose blends with these polymers in NMMO.

Cellulose was mixed with fibroin in aqueous solutions of  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$  [21, 22] and NaOH [23]. An IR-spectral study of films from cellulose/natural fibroin silk blends from copper ammonium complex  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$  showed [21, 22] that there is an intermolecular interaction between polymers in the solution and in the amorphous regions of the films. By reducing the additive density of films from blends and increasing the humidity, it was concluded that the number of amorphous regions increases during the crystallisation of cellulose/fibroin blends. With an increase in cellulose content, the fibroin in cellulose/fibroin blends becomes more regular; the degree of cellulose crystallinity also changes when mixed with fibroin. These data indicate that the prerequisites for the interaction of active groups of components are in aqueous solutions.

The compatibility of cellulose with fibroins of silk in blends, obtained from the common solvent N-methylmorpholine-N-oxide has been already studied [24]. It is shown that in films from these blends there is a strong interaction of components; the material also has good physical-mechanical properties and thermal stability. However, in recent years the possibility of developing technologies for processing cellulose from a new class of solvents – ionic liquids – has been widely investigated [25]. In ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl), fibroin and some other polymers are also soluble [26, 27]. Therefore the aim of this work was to obtain and study cellulose/fibroin blends in imidazolium-based ionic liquids.

## Materials and methods

Ionic solvent – 1-butyl-3-methylimidazolium chloride (BMIMCl) from Merck – Schuchardt; bleached wood sulfated cellulose with a polymerisation degree (DP) of 495, containing  $\alpha$ -cellulose 95.8%; silk fibres from *Bombyx mori* of 346  $\mu\text{m}$  diameter, washed from fatty and waxy substances. Fibroin polymerisation degree was 250 kDa.

Polymers were dissolved in BMIMCl at 90 °C with constant stirring. The concentration of solution was 5 wt% mass. The

completeness of dissolution was determined using a microscope (magnification of 160 $\times$ ) with Baiotise table.

The viscosity was measured by a Reologica Rheometer using the cone-plate system with a sample volume of 25 ml. The measurement was carried out within a shear rate range of 5 – 120  $\text{s}^{-1}$  and temperature 90 °C.

Films from solutions of cellulose and its blends with fibroin were cast on a Teflon plate in isopropyl alcohol bath followed by repeated washing with distilled water till the solvent was completely removed (BMIMCl and water are completely miscible). The films were then dried in air. The most of films obtained were optical transparent. Films of blend with 40 - 60 wt% of cellulose have a low degree of turbidity. Thermogravimetric analysis (TGA) was carried out on a Setaram instrument in the temperature range of 20 - 800 °C at a heating rate of 10 °/min in air. The weight of samples was about 5 g. The measurement error was  $\pm 0.1\%$ .

X-ray (roentgen diffraction) patterns of the films were taken using Advantage diffractometer with  $\text{Cu}\alpha$  radiation. The volume of the samples was 3 g.

Physic-mechanical properties of the films were analysed using Instron in accordance with tensile tester DIN EN ISO 527.

## Results and discussions

On the basis of the polymer blends analysed, the ultimate aim was the formation of a thermodynamically stable polymer - polymer system due to the presence of a strong interaction between the macromolecules of both components. On the basis of results of isometric studies, it is possible to evaluate the interaction of polymers in a solution. The dependence of viscosity on the composition of the mixture could reveal different types of interaction between macromolecular components of blends. Methods of thermal analysis: differential thermal analysis, thermogravimetric and thermo-mechanical analysis, differential scanning calorimetry, Kalve-type differential calorimetry are widely used to assess the interaction of polymers in a solid state. Using these analyses in combination with spectroscopic, X-ray diffraction, and mechanical relaxation methods allow to describe the features of interaction between the components of blends sufficiently.

Figure 1 shows the viscosity of solutions of cellulose and fibroin blends with different ratios of components within a shear rate range of 5 - 120  $\text{s}^{-1}$  at 90 °C.

Figure 1 shows a significant change in the viscosity of solutions with an alteration in the ratio of components.

The nonlinear behavior of the curves indicates a large influence of the spe-

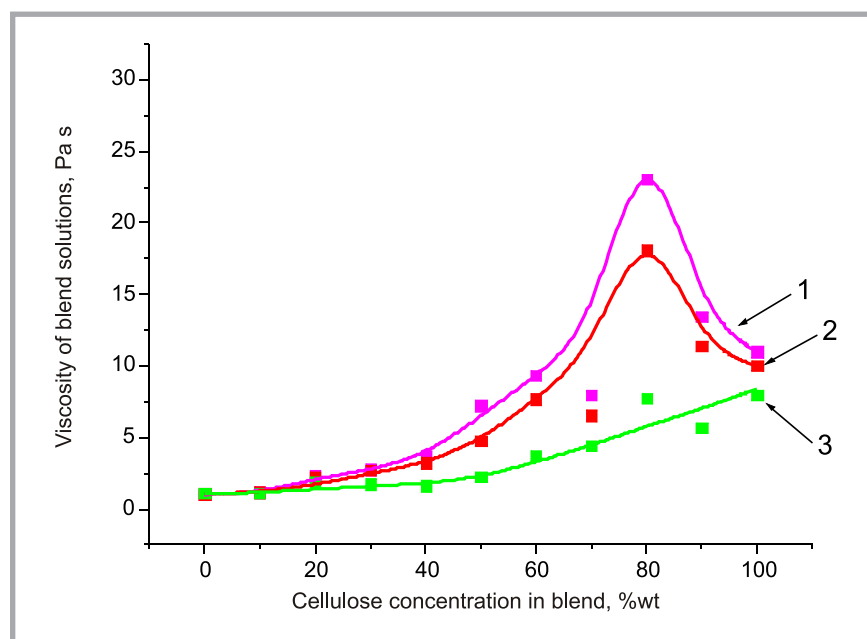
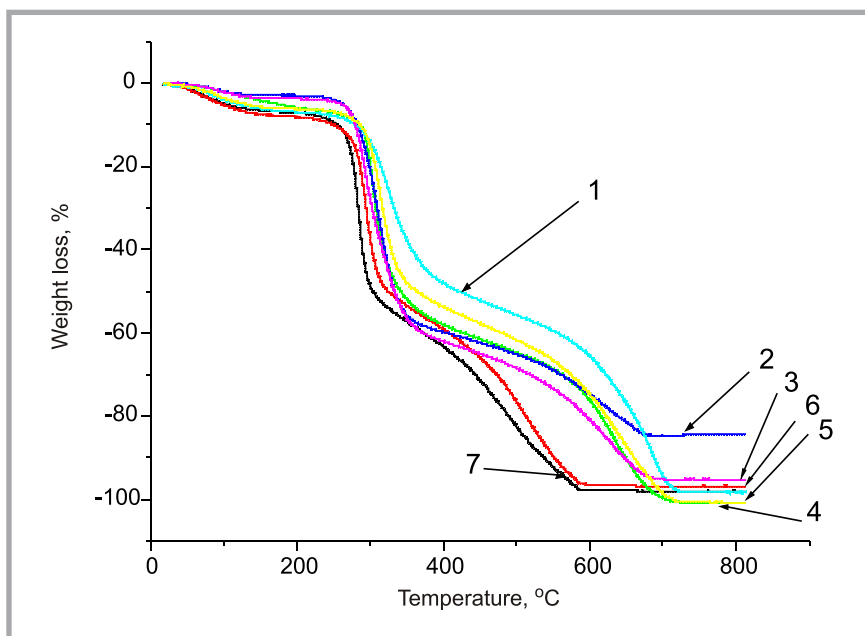
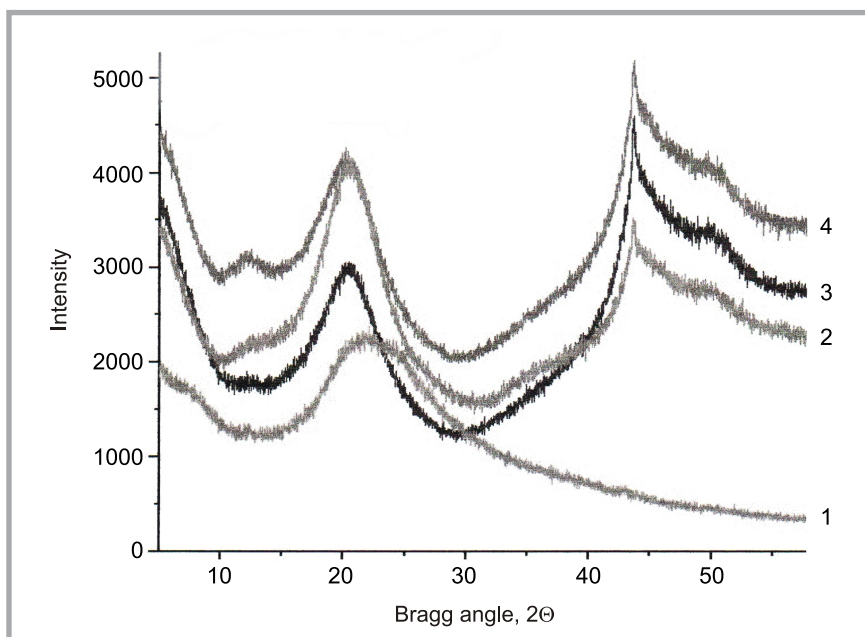


Figure 1. Dependence of the viscosity of solutions of cellulose/fibroin blends on their ratio in the composition at a temperature of 90 °C with the following shear rates: 1 - 5  $\text{s}^{-1}$ , 2 - 10  $\text{s}^{-1}$ , 3 - 60  $\text{s}^{-1}$



**Figure 2.** TGA data for films of cellulose / fibroin blends with the following ratio of components: 1 - 100% cellulose; 2 - 20:80; 3 - 40:60; 4 - 50:50; 5 - 60:40; 6 - 80:20; 7 - 100% fibroin



**Figure 3.** X-Ray data for films of cellulose / fibroin blends with the following ratio of components: 1 - 20:80; 2 - 50:50; 3 - 70:30; 4 - 90:10.

cific intermolecular interactions between components on the viscosity. As can be supposed, the most powerful interaction between the functional groups of macromolecules of cellulose and silk fibroin in the solution occurs at the following ratio of components: 80% wt cellulose and 20% wt fibroin. This conclusion can be made on the basis of the increase in viscosity values of the compositions with concentrations at low shear rates ( $5 - 10 \text{ s}^{-1}$ ). By increasing the shear rate to  $60 \text{ s}^{-1}$ , the flow mechanism changes:

fluid layers start to move simultaneously, hence the intrapolymer interaction stops affecting the viscosity. The samples shows non-newtonian behaviour, and interaction between macromolecules becoming weaker. This is typical for shear thinning fluids.

The films obtained from solutions of blends were transparent, hard but fragile. They were studied by TGA, IR and X-ray analysis. **Figure 2** shows the curves of weight loss of films from cellulose/

broin blends with different proportions of components during heating in the range  $20 - 800 \text{ }^\circ\text{C}$ .

From the curves presented we can see, that thermostability of the films is depends on concentration of the components. The thermostability of films from cellulose/fibroin blends is higher than thermostability of the pure fibroin film (curve 7), but lower than thermostability of the pure cellulose film (curve 1). Hence, the destruction behavior of the samples is different. On the first stage of destruction (below  $100 \text{ }^\circ\text{C}$ ) weight loss of samples is due to the evaporation of sorbed water. With further heating the destruction is slowed down. At this temperature a rupture of the amorphous sections of the samples occur. With continued heating above  $250 - 280 \text{ }^\circ\text{C}$  the weight of ordered sections of polymeric films is reduced. At this temperature, the break of hydrogen bonds in ordered region take place, followed by a thermal destruction of the main polymer chains.

At the temperature of  $250 - 280 \text{ }^\circ\text{C}$  the film with cellulose:fibroin ratio 80:20 shows the slowest destruction of the amorphous section (**Figure 2**, curve 2). It means that the strongest components interaction takes place in the cellulose/fibroin film with a ratio of 80:20. Such strong components interaction could prevent an ordered structure formation in certain segments (crystallisation processes in the different phases). Perhaps, this is why, after solvent removal the most amorphous structure was formed in this film. Actually, with continuing heating this film is destroyed faster than others because of a higher amorphous degree. It should be stated that this film is also the most homogeneous. In the temperature range of  $700 - 800 \text{ }^\circ\text{C}$  this film has the lowest weight loss in comparison with other samples. At this finely stage the cellulose/fibroin film with a ratio of 50:50 has the maximum weight loss (curve 4). Thus can be assumed the weakest intermolecular interaction take place in the blend with equal mass ratio of components.

**Figure 3** shows X-Ray diffraction patterns data for films of cellulose/ fibroin blends casted from 5% solutions in BMIMCl.

From the data represented, it follows that with an increase in fibroin content in the sample, the ordering of cellulose in the film decreases. The X-ray curve of a



**Table 1.** Physic-mechanical properties of films from fibroin/cellulose blends.

Fibroin concentration in blend, %	0,8-hydrate N-methylmorpholine-N-oxide [1]		1-butyl-3-methylimidazolium chloride	
	Breaking strength, MPa	Elongation at break, %	Breaking strength, MPa	Elongation at break, %
100	31.1	2.9	34.3	2.5
90	31.2	3.1	36.0	3.0
50	35.0	9.5	37.6	8.0
30	47.5	10.4	48.2	8.5
10	45.3	10.3	49.7	8.5
-	50.1	10.4	54.2	8.7

film from cellulose with a fibroin ratio of 20:80 almost resembles the curve of an amorphous polymer, what confirms the TGA-analysis conclusion.

The physical and mechanical properties of films from cellulose/ fibroin blends obtained from the common solvent 0.8-hydrate N-methylmorpholine-N-oxide and 1-butyl-3-methylimidazolium chloride are represented in the table below.

From the data in the table, it follows that the strength characteristics of films of fibroin/cellulose blends obtained from solution in ionic liquid are slightly higher than for similar films from the 0.8-hydrate N-methylmorpholine-N-oxide. The data presented confirm the efficiency of ionic liquids as solvents in the technology of natural polymer processing.

## Conclusion

According to research solutions and films of cellulose/fibroin blends obtained from the 1-butyl-3-methylimidazolium chloride, it can be concluded that the strongest intermolecular interaction of components of the blend occurs at a fibroin content of 20%; an amorphous and the most homogeneous film structure forms as a result. The solution of this blend (cellulose: fibroin 80:20) has the highest viscosity in comparison with other samples.

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