Research of Dissolution Ability of Ionic Liquids for Polysaccharides such as Cellulose

Dissertation

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Gutachter:

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Abbreviations

BDMIMCl 1–butyl–2,3–dimethylimidazolium chloride
BMIMAc 1–butyl–3-methylimidazolium acetate,
BMIM BF_4 1–butyl–3-methylimidazolium tetrafluoroborate
BMIMCl 1–butyl–3–methylimidazolium chloride
BMIM PF_6 1-butyl-3-methylimidazolium hexafluorophosphate
CED cupri-ethylene-diamine
Cuam cupri-ammonium hydroxide
Cuen cupri-ethylene-diamine hydroxide
DA degree of acetilation
DEE diethyl ether
DLS dynamic light scattering
DMAC dimethylacetamide
DMF dimethylformamide
DMSO dimethyl sulfoxide
DMSO-d_6 dimethyl-d_6 sulfoxide
DNS 3,5-dinytrosalicilic acid
DP degree of polymerisation
EAc ethyl acetate
E_{act} activation energy
EMIMAc 1–ethyl–3–methylimidazolium acetate
Eq. equation
EWNN iron (III) sodium tartrate complex solution
FA formamide
Fig. figure
FTIR fourier-transform infrared spectroscopy
GPC gel permeation chromatography
ITCF Institut für Textilchemie und Chemiefasern
IL ionic liquid
LC_{50} lethal concentration at which 50 per cent mortality occurs
NMMO N-methylmorpholine-N-oxide
NMR nuclear magnetic resonance
POE polyoxyethylene
R_g radius of gyration

R_h hydrodynamical radius

SEM scanning electron microscopy

SLS static light scattering

SRV solution retention value

TBAF tetrabutylammonium fluoride trihydrate

TGA thermogravimetric analysis

TG-IR thermogravimetry with infrared-coupling

TITK Thüringisches Institut für Textil- und Kunststoff-Forschung

WRV water retention values,

v wave length measured in cm^{-1}

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1. Introduction

1.1 General aspects of using of ionic liquids in polysaccharides dissolution.

Ionic liquids (ILs) are an exciting re-found class of substances. Some representatives of this class were described as early as 1914 (Keskin et al., 2007), yet the earliest ILs in the literature were mentioned in 1934 by Graenacher, who patented to use molten *N*-ethylpyridinium chloride, in the presence of nitrogen-containing bases for cellulose dissolution. During the long time after Graenacher patent, ILs were forgotten as a cellulose solvents. In the late 1990s, ILs became known as some of the most promising solvents. Researchers discovered that ILs are more than simply “green” solvents, and they have found application in the replacement of volatile organic solvents, making new materials, conducting heat effectively, hosting a variety of catalysts, purification of gases, homogenous and heterogeneous catalysis, biological reactions media and removal of metal ions (Baker et. al. 2009). In 2002 Swatloski et al. open this class of organic solvents as a cellulose solvent second time.

Cellulose is the most widespread renewable resource on the planet, its derivatives were used both in primitive and hi-tech societies. However, its applications in industrial technologies are almost unchanged from the beginning of the chemical industry. The most popular chemical transformation of cellulose is esterification; esters of cellulose have great value in the paper industry, for the manufacture of fibres and textiles, polymers and films (Swatloski et al. 2002). Mixtures of esters of cellulose, for example, acetate/propionate or acetate/butyrate are used for manufacture of plastics. However the full potential of cellulose and its derivatives has not been appreciated due to the limited number of solvents for cellulose. Traditional dissolution processes of cellulose, including copper-ammonium and viscose processes, are often cumbersome (viscose process utilizing carbon disulfide as both reagent and solvent, emits zinc and hydrogen sulfide) and the solvents typically have a high ionic strength and involve relatively harsh conditions (at first, few steps of dissolution) (Kirk-Othmer, 1993). With increasing industrial pollution and consequent governmental regulations, the need to provide “green” processes to prevent pollution, to reduce waste production and to utilize renewable resources has become increasingly important.

In 2002 Swatloski et al. have suggested the dissolution of cellulose in ionic liquids. Ionic liquids have a number of advantages in comparison with other used solvents (Keskin et al., 2007). It is known that cellulose can be dissolved in ionic liquids without derivatization (Heinze et al. 2005b; Massone et al., 2009; Pagoria et al., 2009; Maase et al. 2008; Myllamaki et al. 2008). In systems based on ionic liquids it is possible to obtain cellulose fibres and films for various purposes (Wu et al. 2007; Kadokawa et al. 2008; Sumnicht et al. 2008; Kokko et al., 2008; Kadokawa et al. 2009). Moreover, it is possible to make chemical modification of cellulose in mild conditions using ionic liquids as the reactive medium (Buchanan et al. 2008; Ebner et al. 2008; Cao et al., 2009; Heinze et al. 2001). Cellulose could be blended with other polymers in ILs to produce, for example, “green” composite films from cellulose, starch and lignin (Wu et al., 2009), cellulose/fibroin (Kuzmina et al. 2009), cellulose/chitin (Takegawa et al. 2010) and cellulose/chitosan composites (Dai et al., 2010; Li et al., 2010; Pang et al., 2009). Many solvents for cellulose are already known, some of them are used nowadays to produce cellulose-based materials (viscose fibres, Lintex, copper-ammonium fibres, lyocell and etc.). The most commonly used direct solvent is N-methylmorpholine-N-oxide (NMMO), which has certain advantages (Rosenau et al., 2001) and disadvantages (Rosenau et al., 2001; Yang et al., 2005) when compared to other solvents which can be avoided through the use of ILs. The dissolution of cellulose in "direct" solvents depends not only on its molecular weight (Schulz et al., 2000; Roder et al., 1999), but also on preliminary activation (Roder et al., 1999), and on presence of low molecular weight liquids (Cao et al., 2009; Bochek et al., 2002).

The water is one of the low molecular weight liquids accompanying cellulose-containing plants during growth and at all stages of processing. Water can influence the dissolution ability of ILs toward cellulose (Mazza et al., 2009; Kuzmina et al., 2010).

In order to reduce the viscosity of solutions, the cost of solvent, and make dissolution more efficient, the addition of thinners to IL solutions can be expedient. Protic and aprotic organic solvents and their mixtures have been studied as thinners for cellulose/ionic liquid solutions by Menghuj Luo et al. (2009), and described according to their solvatochromic parameters (Gericke et al., 2011).

There is still lacks plentiful information on cellulose film production in the literature (Liua et al., 2011). To improve the final mechanical properties of the cellulose films plasticizers such as glycerin, polyoxyethylene (POE-400) and mixtures thereof was added to the spinning solution and washing bath. There is not current industrially viable methodology for cellulose manufacture using ILs. There are only reports of lab-scale apparatus’ for fibres manufacturing from cellulose/IL solutions, for example, the “Institut für Textilchemie und Chemiefasern” (ITCF) in Denkendorf and BASF, which investigate the properties of fibers spun from solutions of cellulose dissolved in IL in a pilot plant (Hermanutz et al., 2006). Nowadays the researches on dependence of the dissolution process from water content (Mazza et al., 2009; Kuzmina et al., 2010), influence of co-solvents (Gericke et al., 2011), purity (Stark et al., 2008) and toxicity (Studzinska et al., 2009) of ILs and etc. are carried out. There are still studies on recovering of

ILs after cellulose dissolution and coagulation (Wu et al., 2009). The recyclability of ILs is one of challenges on which scientists and technologists of cellulose manufacturing pay attention.

The relevance of this work on study of ILs as a polysaccharide's solvents defined by the need of the industry in more economically effective and environment safe manufacturing of polysaccharides, especially cellulose.

1.2. Aims and objectives

The aim of this work was to study dissolution process of polysaccharides cellulose and chitosan in ILs. The first objective was to prepare cellulose solutions in ILs, and to find its maximum concentration therein. To study the dissolution process of polysaccharides in ILs, determine the influence of water on dissolution process of cellulose in ILs.

My second objective was to blend cellulose with chitosan. Consequently the solubility of the 2 polysaccharides in ILs was studied. Solutions were obtained either via simultaneously blending of polysaccharides in a common IL, or via preparation of separate solutions of each polysaccharide and subsequent blending of these solutions.

The third objective was the production of films composed of cellulose and mixtures of cellulose and chitosan. To study the homogeneity of these films, polymer content by means of FTIR, degradation of the polysaccharides by GPC and their mechanical properties. The use of plasticizers to improve the mechanical properties of films and modify the degradation profile of the films was studies by means of thermogravimetric (TG) analysis.

My final objective was to study IL recovery by distillation and determine the potential for using ILs for polysaccharide dissolution.

1.3. Literature review

1.3.1. Ionic liquids. History, structure, properties and applications.

Ionic liquids (ILs) are now perceived as revolutionary "green" solvents by the chemical industry, owing to their unique properties and a wide variety of structural variations. To describe this class of substances, the following terms - «ionic liquids of a room temperature (RTILs)», «waterless ionic liquids», «molten salts» or «liquid organic salts» (Welton, 1999) are used.

1.3.1.1. The join history of ILs and cellulose industry.

As noted above, ionic liquids are not new substances. At the Fig. 1.1 the history of cellulose dissolution development and IL discovery is shown.

There are different literature data on cellulose discovery date. Cellulose was discover in 1838 by Anselme Payen (Young, 1986), and in 1839 by Anselme Payen[1]. First, Graenacher suggested to use quaternary ammonium salts (a kind of ILs) for cellulose dissolution. His idea was too novel, and only after discovery of copper-ammoniun and viscose processes, after development of Lyocell process in 2002 ILs were re-found as a cellulose solvents. Since 2002 numerous numbers of patents for dissolution of different polysaccharides and their mixtures, which are discussed in chapter 1.3.3 were published worldwide.

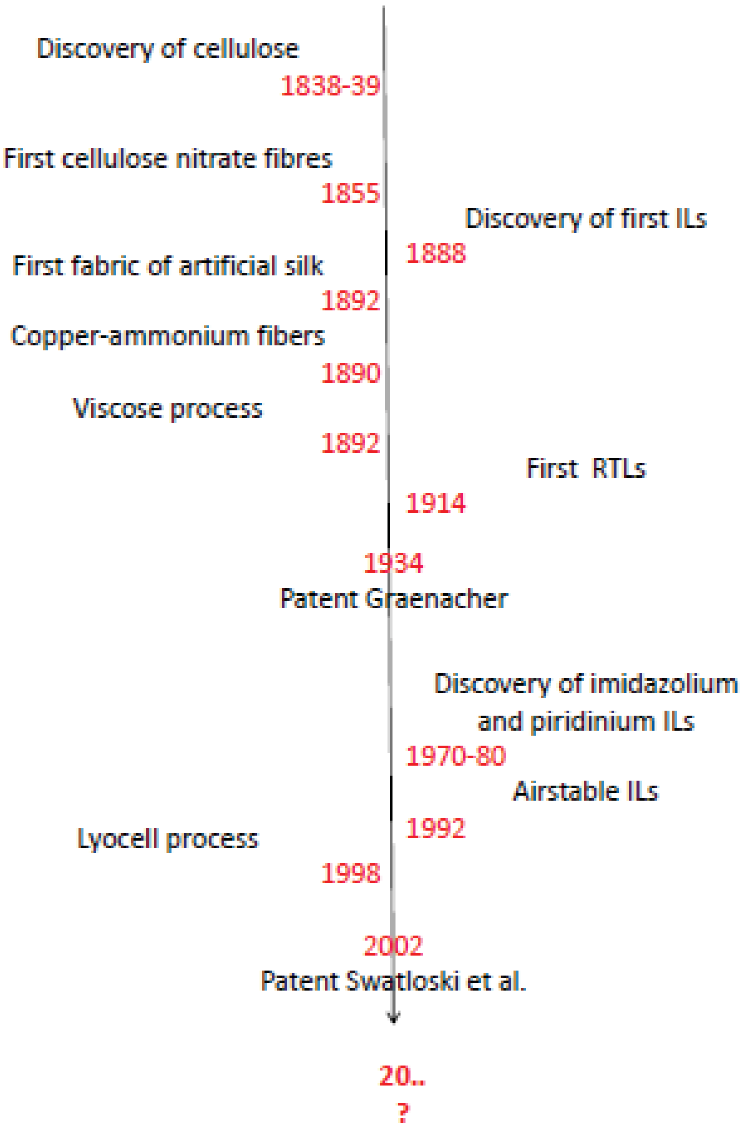

Fig. 1.1. The brief history of cellulose dissolution development and ILs discovery.

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[1] http://www.nonwoven.co.uk/reports/History%20of%20Cellulosics.html

1.3.1.2. The structure and synthesis of ILs

Ionic liquids consist of positive and negatively charged ions. The structure of ILs is similar to other salts, such as sodium chloride, however, the key difference is that ILs remain liquid at temperatures below 100 °C, whereas the melting point of sodium chloride is 801 °C. The most widely used ILs are based on imidazolium, pyridinium, phosphonium and ammonium cations, and Fig. 1.2 presents the most common cations of ILs.

Two important groups of ILs are those based on imidazolium and pyridinium cations with PF_6^- and BF_4^- anions (Fig. 1.3, 1.4).

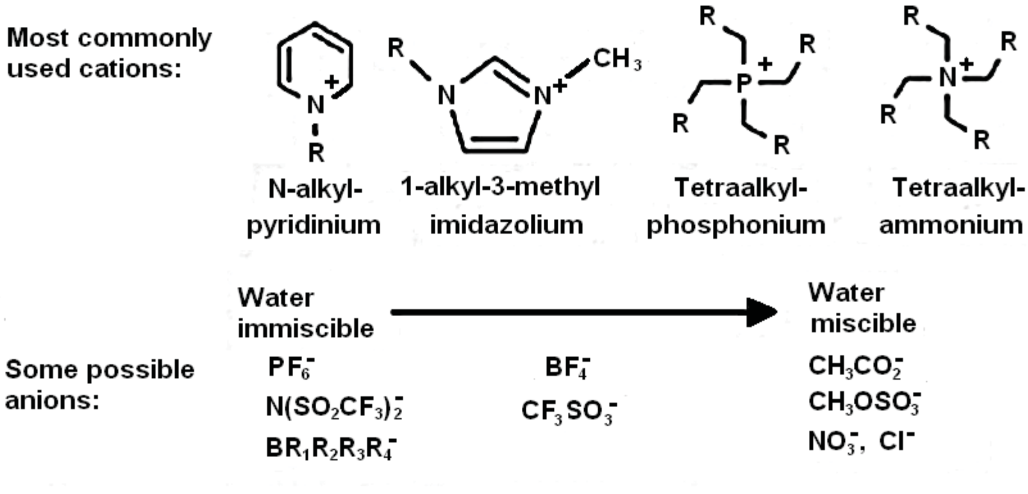

Fig. 1.2. Most commonly used cation structures and possible anion types (Keskin et al., 2007)

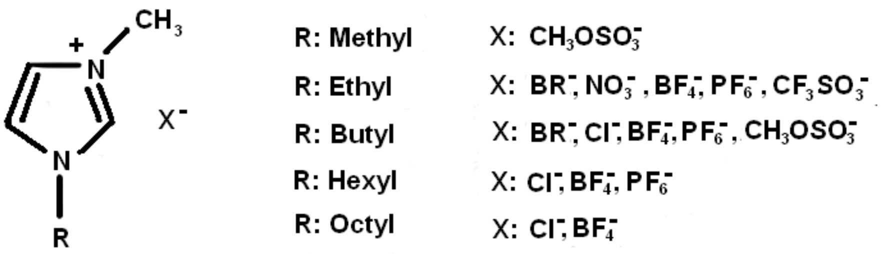

Fig. 1.3. Imidazolium derivatives of ILs[2].

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[2] www.sigmaaldrich.com

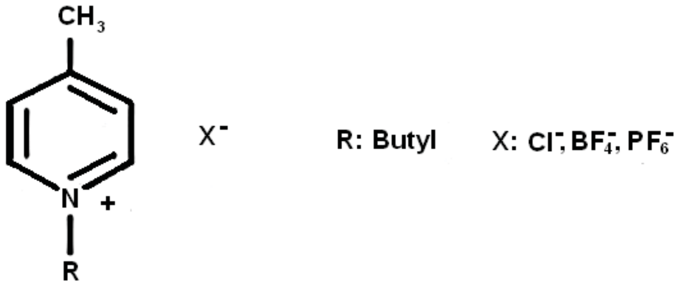

Fig. 1.4. Pyridinium derivatives of ILs[3].

Both the ionic species influent the final properties of ILs. Usually, the anion controls the water miscibility, but the cation also has an influence on the hydrophobicity or hydrogen bonding ability. If the size and asymmetry of the cation increases, the melting point decreases (Keskin et al., 2007). There are three basic methods to synthesize ILs: metathesis reactions, for example, of a halide salt with an ammonium salt of the desired anion, acid–base neutralization and direct combination (Welton, 1999; Keskin et al., 2007; Novoselov et al., 2008). For example, to produce imidazolium ILs 1-methylimidazole could be alkylated or imidazol can be first alkylated to 1-alkylimidazol and then methylated (Adelwohrer et al., 2008). After synthesis, ILs are processed under vacuum to remove any excess water.

1.3.1.3 Basic properties of ILs

Properties of ILs can be defined mainly by a combination of organic cation and inorganic anion. As solvents, ILs possess several advantages over conventional organic solvents, which make them environmentally compatible (Keskin et al., 2007):

- ILs have the ability to dissolve many different organic, inorganic and organometallic materials.
- ILs are highly polar.
- ILs consist of loosely coordinating bulky ions.
- ILs do not evaporate since they have very low vapor pressures.
- ILs are thermally stable, most of ILs are liquids from 25 °C up to 200 °C.
- ILs have high thermal conductivity
- ILs are immiscible with many organic solvents and miscible with inorganic (water, alcohols, acetone, etc.).

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[3] www.sigmaaldrich.com

- ILs are non-aqueous polar alternatives for phase transfer processes.
- The solvent properties of ILs can be tuned for a specific application by varying the anion/cation combinations.

1.3.1.3.1 ILs as solvents

Ionic liquids are capable of the dissolution of substances such as salts, fats, fibers, amino acids, sugars and polysaccharides. ILs show strong dissolving abilities in relation to many organic molecules, including oil, ink, plastic and even DNA (Dai et al., 2008). ILs are called "green" solvents because their vapor pressures are extremely low (and are effectively negligible). ILs are considered "green" solvents because unlike the volatile organic compounds (VOCs) that they could replace, many of these compounds have negligible vapor pressure, they are not explosive and it may be feasible to recycle and repeatedly reuse them. ILs are also known as "designer solvents" since they offer the opportunity to tune their specific solvation properties for a particular application. Researchers can design task-specific ILs by choosing negatively charged small anions and positively charged large cations, and these specific ILs may be utilized to dissolve a certain chemicals or to extract a certain materials from a solution. By combining various kinds of cation and anion structures, it is estimated that 10^{18} ILs can be designed (Hecht et al., 2006). The ability of ILs to dissolve solutes is defined by their ability to undergo donor-acceptor interactions.

1.3.1.3.2 Toxicology of ILs

The "green" character of ILs has been usually correlated with their negligible vapor pressure (the order 10^{-11} (Keskin et al., 2007)), however data about their toxicological characteristics are sparse. Research shows that the toxicity of ILs is directly connected to their lipophilicity and length of alkyl chains (Renner, 2001; Dai et al., 2008). Ecotoxicologists use the concept of the lethal concentration at which 50 per cent mortality occurs (LC_{50}). Concentration is measured in mg/l. If the value of LC_{50} is less or equal to 10 the substance possesses extreme toxicity; if $10 < LC_{50} < 100$ chemical is very poisonous; if $100 < LC_{50} < 1000$, chemical possesses low toxicity; and lastly, if $1000 < LC_{50} < 10000$ the given substance is practically nontoxic.

In Table 1.1, LC_{50} data for two ILs are presented in comparison with other common solvents. Apparently from Table 1.1, ILs appear to have rather low toxicity in comparison with others industrially used solvents.

Table 1.1. Values LC_{50} for some solvents (Keskin et al., 2007; Eichinger et al., 1995)

Compound	LC_{50}, mg/l
BMIM PF6	250-300
BMIM BF4	225-275
Acetone	30
Dichloromethane	310
Phenol	5
Ammonia	0.53-4.94
Chlorine	0.028
NMMO	31

1.3.1.3.3 Air and moisture stability of ILs

Many ILs are both air and moisture stable, some are even hydrophobic. The hydrophobicity of an IL increases with increasing length of the alkyl chain attached to one of the ionic species (typically the anion) (Keskin et al., 2007). However it has been shown that the presence of minor quantities of water in ILs essentially reduces ability to dissolve various species (Chiappe et al., 2005; Arning et al., 2008). ILs tend to be hygroscopic and the greatest absorption of water is observed in ILs containing the BF_4^- anion, and the lowest with PF_6[4].

1.3.1.4 Major applications for ILs

The unique chemical and physical properties of ILs bring about several application areas including: solvents for organic/organometallic synthesis and catalysis; electrolytes in electrochemistry, in fuel and solar cells; lubricants; matrices for mass spectrometry; supports for the immobilization of enzymes; in separation technologies; as liquid crystals; templates for synthesis nano-materials and materials for tissue preservation; in preparation of polymer–gel catalytic membranes; in generation of high conductivity materials (Keskin et al., 2007). At Figure 1.5 main application areas of ILs are presented.

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[4] http://www.rsc.org/chemistryworld/Issues/2005/March/Promising.asp

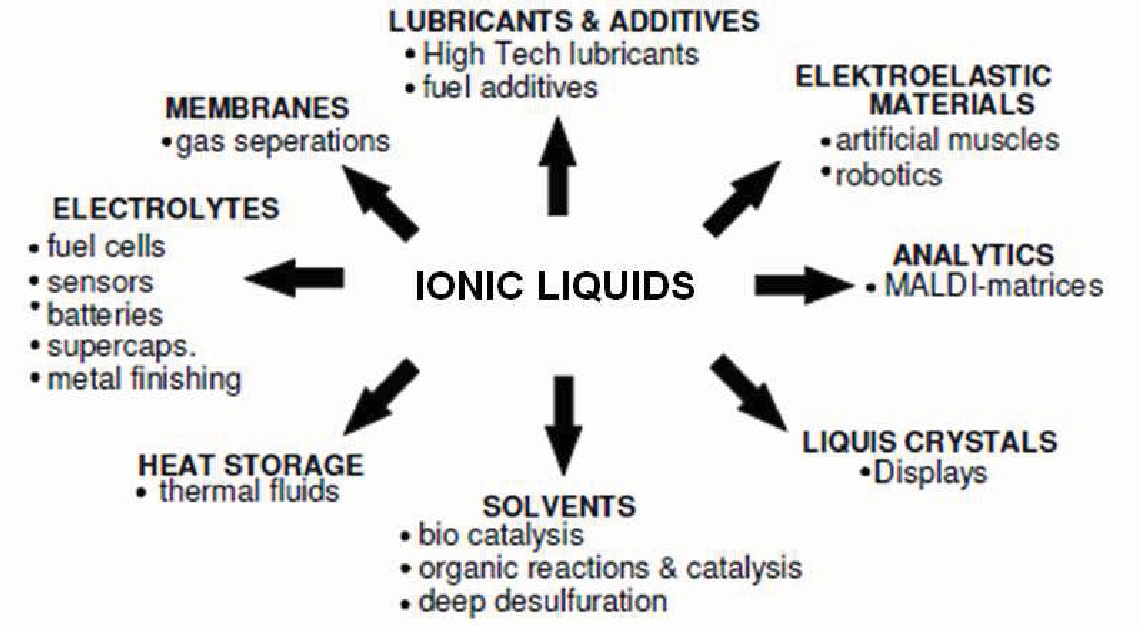

Fig. 1.5. The main application areas of ILs (Schubert, 2005).

1.3.2 Dissolution of cellulose with ionic liquids

1.3.2.1 Cellulose. The basic characteristics.

In recent years, interest in using cellulose materials increases in a wide range of technological processes, including biosorbents, chromatography, etc. This interest is caused by following factors[5]:

1. A wide variety of geometrical and morphological forms of cellulose.
2. Similarity of technological processes for all cellulose derivatives that facilitates their processing.
3. Cellulose is inexpensive and a renewable raw material.

Cellulose is the main building material of flora, forming cellular walls of trees and other plants, and the purest natural form of cellulose are the fibres of cotton seeds.

1.3.2.1.1 Chemical structure

Despite the many industrial applications of cellulose and its derivatives, until the 1920s, many scientists believed that cellulose consisted of a few small molecules of glucose or cellobiose. Its empirical formula $C_6H_{10}O_5$ according to the quantitative analysis of washed out and dried samples was known from 1913: 44,4 % C, 6,2 % H and 49,4 %, but very few scientists permitted

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[5] www.pereplet.ru/obrazovanie/stsoros/201.html

that it is a polymer (Hon, 2004). According to Staudinger and Fritschi (Hon, 2004), cellulose is a linear macromolecule consisting of a large number of hexose units connected by main-valence glucosidic links. Each unit has three OH groups - one primary (RCH_2OH) and two secondary (R_2CHOH) (Fig. 1.6.).

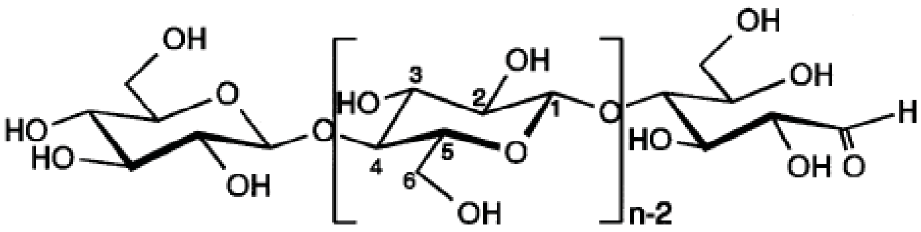


Fig. 1.6. Molecular structure of an elementary unit of cellulose, where n = a degree polymerizations (DP), with numbering atoms of carbon of an elementary part (Heinze et al., 2001).

1.3.2.1.2 Chemical properties of cellulose

As shown at Figure 1.6, cellulose represents the high polymeric carbohydrate, consisting of glucosic rests $C_6H_{10}O_5$, which are linked via ethers bridges in position 1,4. Three OH groups in each glucopyranosic part can be etherified by organic reagents, such as mixtures of acids and anhydrides of acids with the corresponding catalyst (e.g. sulfuric acid). Replacement of free OH groups also impacts upon the degradation profile of the polymer backbone, for example: cellulose nitrate degrades more quickly than either cellulose acetate or propionate.

1.3.2.1.3 Physical properties

In the solid state cellulose chains are packed into long bunches or fibres, in which there are ordered crystalline domains, and less ordered amorphous regions (Fig. 1.7). The degree of crystallinity depends on the type of cellulose, and the technique used to determine it: X-Ray diffraction data indicates a degree of crystallinity of 70 % for cotton and ca. 38-40 % for viscose fibres (Schulz et al., 2000).

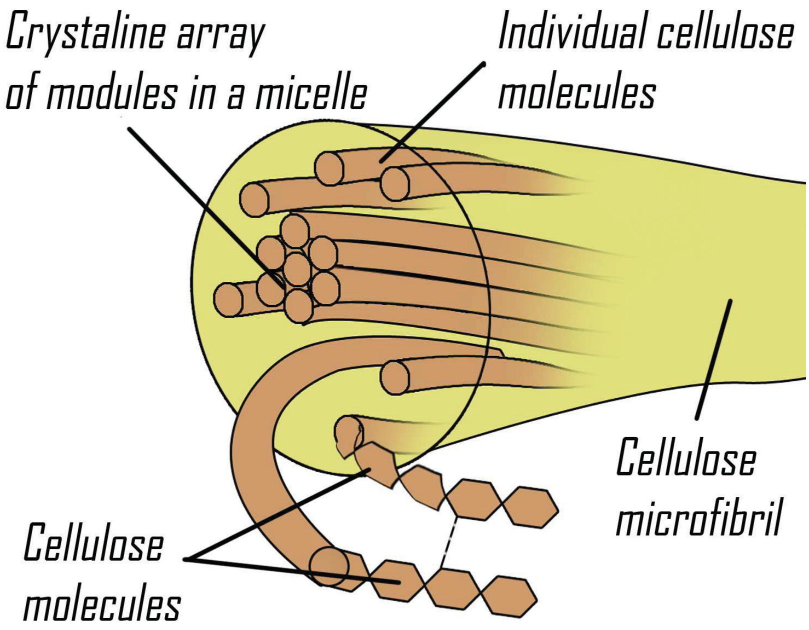


Fig. 1.7. Schematic structure of cellulose

1.3.2.2 Dissolution of cellulose. Specification of cellulose solvents.

Find an effective solvent for cellulose is a topic of intense current research interest in the field of polysaccharides. From the commercial point of view, the viscose process, that is the production of cellulose xanthate using NaOH and CS_2, is certainly an important method of dissolving cellulose. The viscose process discovered in 1892 is currently used all over the world, with an output of about 3 million tons annually (Heinze et al., 2005a). Formation of aqueous solutions of metal complexes of cellulose, for example, copri-ammonium hydroxide (Cuam) is another potential solvent system. In the copper-ammonium process, cellulose is dissolved in copper hydroxide or in a mix of the basic copper salt and concentrated ammonia. Passage through a syringe into a coagulation bath of either water or an aqueous solution of acid yields strings, fibres and membranes and is also used on an industrial scale.

Solvents for cellulose are classified according to the two categories of: non-derivatizing and derivatizing solvents (Fig. 1.8), "non-derivatizing" systems dissolve the polymer by intermolecular interactions only (aqueous transition metal complex solvents are conventionally included in this category despite a very strong interaction, as no covalent interactions occur); whereas the group of "derivatizing" solvents comprises all the systems where dissolution occurs in combination with formation of ether, ester, or acetate derivatives. Both categories of solvents include aqueous and non-aqueous media.

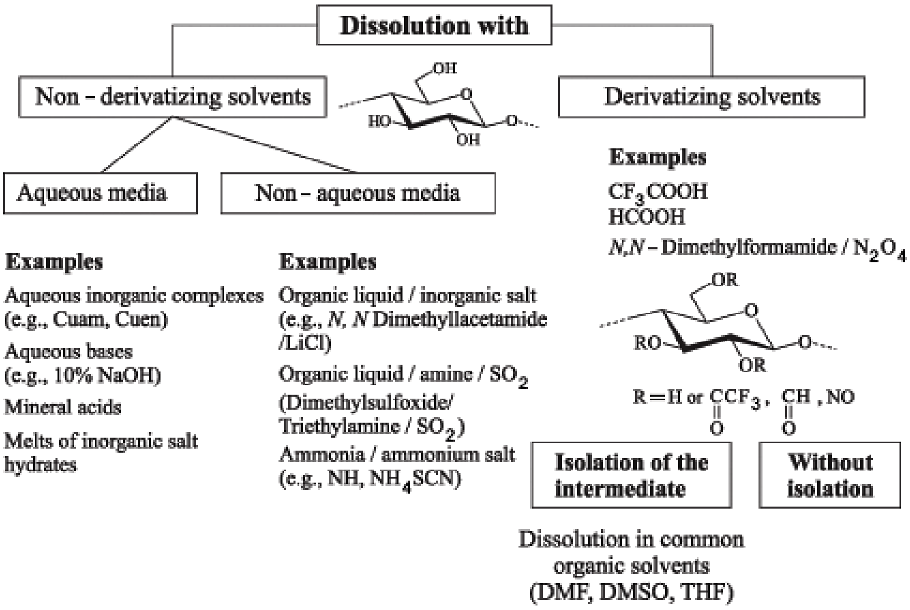


Fig. 1.8. Classification of solvents of cellulose (not including ionic liquids) (Heinze et al., 2005a).

The best known solvents of aqueous solvents are cuprammonium hydroxide (Cuam) and cupri-ethylene-diamine hydroxide (Cuen) (Heinze et al., 2005a). It is possible to dissolve the polymer in about 10 % aqueous NaOH solution, however, the solubility is limited to cellulose of comparably low degree of polymerization (DP) up to 200. The typical aqueous-based solvents of cellulose are solutions of: transition metal complexes with NH_3, transition metal complexes with tartaric acid, ammonium hydroxides, alkali hydroxides (dissolve cellulose with limited polimerization degree only) (Heinze et al., 2005a). Typical direct non-aqueous solvents for cellulose are: N-alkylpyridinium halogenides, oxides of tertiary amines (for example, NMMO), dimethyl sulfoxide (DMSO) containing solvents, liquid ammonia/sodium or ammonium salts, dipolar aprotic solvents/LiCl, NH_3 or amine/salt/polar solvent, NH_3 or amine/SO_2 or $SOCl_2$/polar solvent (Heinze et al., 2005). In most cases of using non-aqueous cellulose solvents preliminary processing of cellulose is necessary. The system N,N-dimethylacetamide (DMAC)/LiCl shows an enormous potential for the analysis of cellulose and for the preparation of a variety of derivatives. From the mentioned mixtures dimethyl sulfoxide (DMSO)/SO_2/diethylamine is most versatile for cellulose dissolution and simple preparation of tri-*o*-substituted cellulose ethers (Kondo et al., 1987). In case of single component solvent the most powerful is *N*-methylmorpholine-*N*-oxide (NMMO), in which high concentrated cellulose solution could be produced (Eichinger et al., 1995).

A powerful new solvent for cellulose consists of the mixture DMSO/tetrabutylammonium fluoride trihydrate (TBAF) (Heinze et al., 2000). The advantage of DMSO/TBAF is that cellulose with a degree of polymerization as high as 650 dissolves without any pretreatment within 15 min.

With the rediscovery of NMMO and with the development of technical processes for the manufacture of textile cellulose fibres and filaments, an environmentally friendly alternative of the viscose process was established (Johnson, 1996a; Johnson 1996b). As a result of industrial achievement, the fibres received from solutions NMMO, of Lyocell type, have begun to compete with viscose fibres. Structural distinctions between Lyocell and fibres of viscose follow from distinctions in supramolecular structure - including a degree of crystallinity, orientation of the non-crystalline chain segments - and in the cross morphology (Fink et al., 2001). Lyocell process has some advantages in comparison with other common processes of cellulose manufacturing (viscose, copper-ammonium processes) such as low number of technological steps, no derivatization, NMMO could be recovered in amount greater than 99%, Lyocell process pertains a significantly low specific environmental challenge, a flexibility of process in terms of the cellulosic raw material, etc. (Rosenau et al., 2001). Usually 10-15 % cellulose solution in NMMO is used for final product manufacturing. There are also some negative points as a results of side reactions and byproduct formation, presented at the Fig. 1.9. As it is shown at the Fig. 1.9, one negative affect lead to another and all together renders processing of cellulose with NMMO is not so attractive.

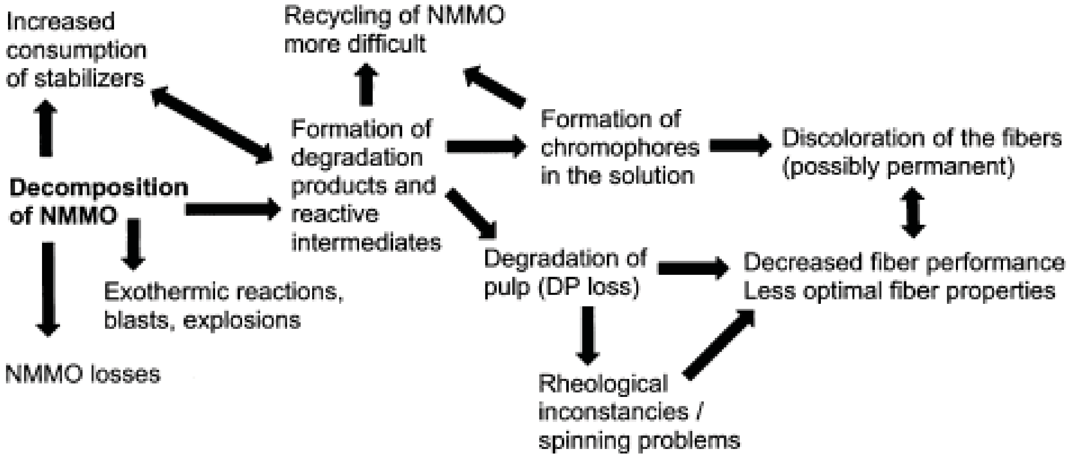


Fig. 1.9. Potentially detrimental negative results of Lyocell process (Rosenau et al., 2001).

Rather recently it was revealed, that ionic liquids (IL), especially those based on imidazolium cations, are capable of dissolving cellulose in a wide range of values of the polymerization degree (even bacterial cellulose) without covalent interactions (Wu et al., 2009). Scientists are currently investigating the application of ILs as the solvent for the chemical modification of cellulose (Wu et al., 2009; Egorov et al., 2007; Scheibel et al., 2007; Zhao et al., 2009; Rogers et al., 2007).

1.3.2.3 Mechanism of cellulose dissolution in ILs

The dissolution mechanism of cellulose in ionic liquids involves the oxygen and hydrogen atoms of cellulose-OH groups in the formation of electron donor – electron acceptor (EDA) complexes which interact with the ionic liquid. For their interaction, the cellulose molecules serve as electron pair donor and hydrogen atoms act as an electron acceptor. In a corresponding fashion, the cations in ionic liquid solvents act as electron acceptor centers, and anions as electron-donor centers. The two centers must be located close enough in space to permit the interactions and to permit the EDA complexes to form. Upon interaction of the cellulose-OH groups and the ionic liquid, the oxygen and hydrogen atoms from hydroxyl groups are distant, resulting in opening of the hydrogen bonds between molecular chains of the cellulose and, finally, the cellulose dissolves. The mechanism of interaction of cellulose and IL is presented at Fig. 1.10. In research (Sashina et al., 2009) on the basis of the analysis of experimental and theoretical data it was concluded, that hydrogen-bond interactions are created between H-atom of OH-groups in cellulose and electron-donor center of the anion of the IL. The cation of the IL doesn’t interact with cellulose directly. The cations role is consists is as a steric obstacle for the prevention of interactions between polymeric chains, shielding them from each other after dissolution.

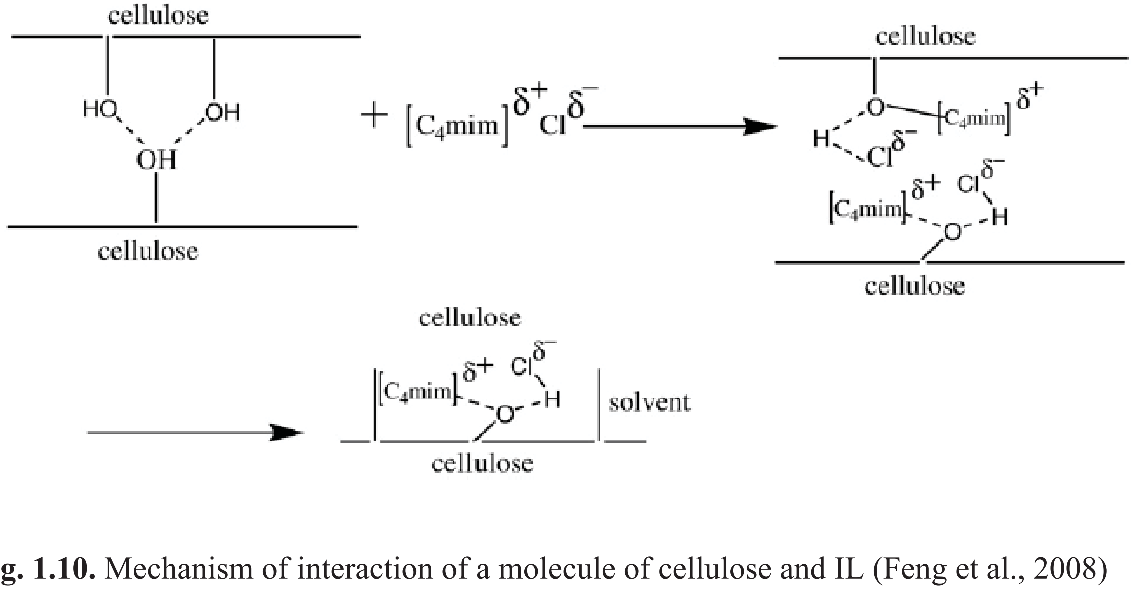


Fig. 1.10. Mechanism of interaction of a molecule of cellulose and IL (Feng et al., 2008)

At Fig. 1.11 the structure of a complex 1-butyl-3-methylimidazolium chloride - cellobiose, obtained by means of computer modeling is presented.

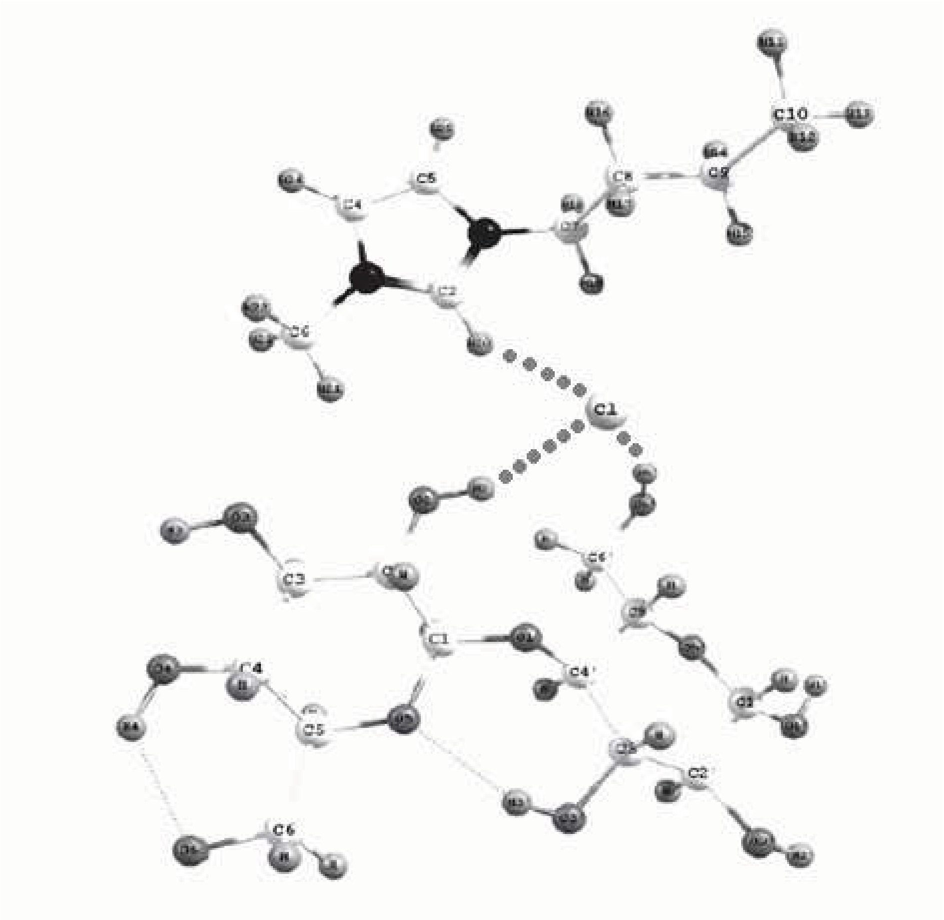


Fig. 1.11. 1-butyl-3-methylimidazolium chloride - cellobiose complex (Novoselov et al., 2007).

Dissolution of cellulose in ILs is usual heated in an oil bath preventing the moisture absorption of a solution, and under an atmosphere of nitrogen (Dai et al., 2008) or air, at mixing and heating, sometimes with microwave heating (Massone et al., 2009; Buchanan et al., 2008; Stegman et al., 2008; Dai et al., 2008, Xu et al., 2008). Turbidity is usually used to assess the degree of dissolution. Turbidity can be observed by microscope or with nephelometer (Mazza et al., 2009). Regeneration of cellulose from solutions made in water (Wu et al., 2009; Zhao et al., 2009; Kosan et al., 2008), or in spirit (Xu et al., 2008). At the same time, ionic liquids transfer to aqueous phase, water molecules form a hydrodynamic shell around the ionic liquid molecules, that inhibits interactions between ILs and cellulose (Zarvel et al., 2009). The ionic liquid can be recycled from a solution by distillation (Sun et al., 2009a). The purity of recycled ILs is about 98-99 % (Maki-Avrela et al., 2010). Schematically simplified manufacturing of cellulose with ILs is presented at Fig. 1.12.

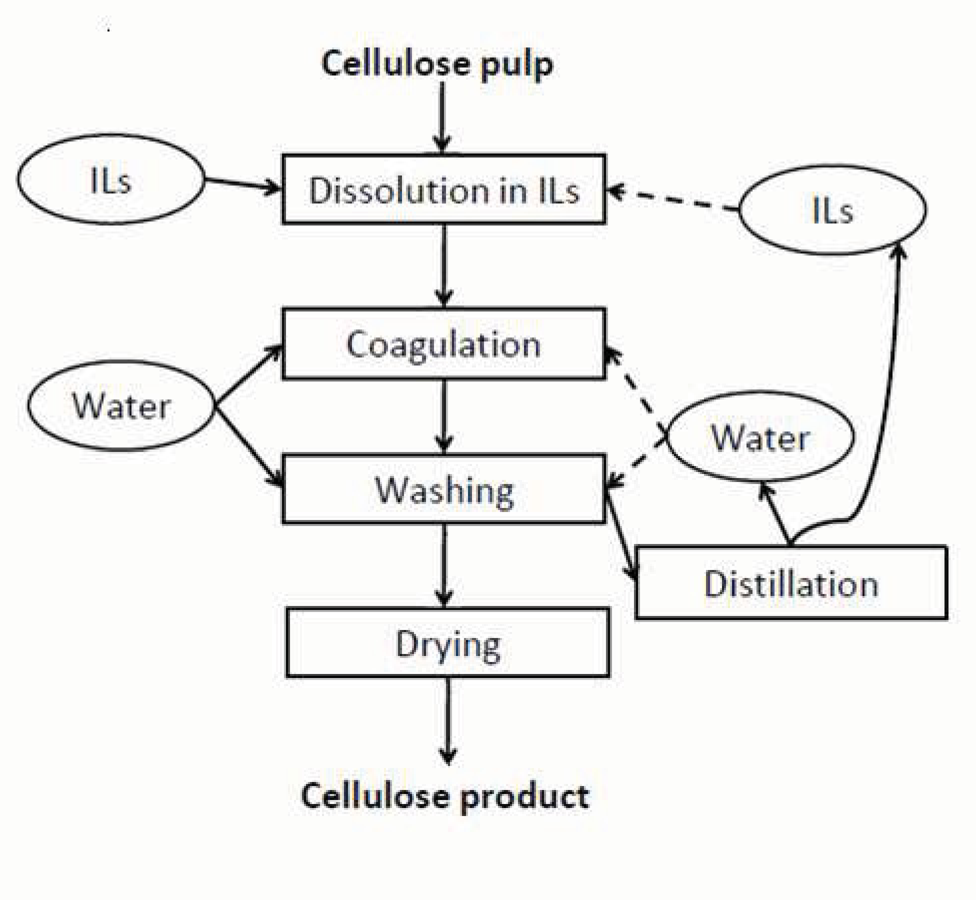


Fig. 1.12. Scheme of cellulose manufacturing using ILs.

It is possible to dissolve a lignocelluloses which contains 35-50 % of cellulose, 20-35 % of hemicellulose and 5-30 % of lignin (Zavrel et al., 2009). It is possibly to dissolve wood in ILs (Maki-Avrela et al., 2010). There are data about solubility of bacterial cellulose in ILs (Keshk, 2008).

1.3.2.4 Factors influencing on dissolution process in ILs

1.3.2.4.1 Influence of presence of water on dissolution process

As is has already been noted, the presence of water reduces the ability of ILs to dissolve solutes such as cellulose due to the solvation of the ionic species and solute by the water. There are a variety of sources of potential contamination: water content in cellulose (ca. 7 % (Mazza et al., 2009)); water content in the ionic liquid or water from the environment (air/glassware etc.).

1.3.2.4.2 Influence of thinners on dissolving ability of IL

In order to reduce the viscosity of IL solutions, and also the cost of the IL, it is common to add thinners to the IL solutions. Thinners, which do not necessarily dissolve the solute independently are commonly studied. Water and organic protic solvents compete for hydrogen bonding interactions with the solute, whereas aprotic thinners such as DMSO and DMF have less effect on a given ILs ability to dissolve the solute (Novoselov et al., 2008). Then less the thinner competes with the IL for formation of H-bonds with cellulose, the lower its negative impact upon the ability of the binary system to dissolve cellulose. Such a statement can be made, comparing donor numbers of investigated thinners, enthalpy value ΔH, and also by results of theoretical calculations of ΔE hydrogen-bond interactions of OH groups cellobiose with thinners (Novoselov et al., 2008). One of the main characteristics of a solvent are Guinman's donor and acceptor numbers. In the Table 1.2. presented the DN and AN of common organic solvents.

Table 1.2. The donor and acceptor number of common organic solvents (Lowry et al., 1987; Moskva, 1999). Solvents used in this work are indicated with color- aprotic blue and protic pink ones.

Solvent	Donor number (DN)	Acceptor number (AN)
Acetone	17.0	12.5
Acetonitrile	14.1	18.9
Benzene	3.5	8.2
Water	18.0	54.8
Hexane	0.0	0.0
Dimethylsulfoxide	28.9	19.3
Dimethylformamide	26.6	16.0
Dioxane	14.8	10.8
1,2 – Dichloroethane	0.0	16.7
Diethyl ether	19.2	3.9
Methanol	19.0	41.5
Pyridine	33.1	14.2
Acetic acid	15.0	52.9
Formamide	24.0	39.8
Dichloromethane	1.0	20.4
Ethanol	19.6	37.9
Ethyl Acetate	17.1	9.3

Dissolution of cellulose in mix DMSO-BMIMCl occurs by swelling of cellulose (Cuissinat et al., 2008). However, use of a thinner is not the optimum solution, owing to a decrease in the kinetics of the dissolution of cellulose. Mixtures of DMSO: BMIMCl with a parity 25:75 accordingly, does not dissolve cellulose at all (Cuissinat et al., 2008).

1.3.3. Other polysaccharides and proteins in ILs.

It was already found, that ILs could dissolve not only cellulose, but other carbohydrates (El Seoud et al., 2007), and proteins such as *Bombyx mori* silk fibroin (Phillips et al., 2005; Kuzmina et al., 2009) and wool keratin (Hameed et al., 2010). It is possible to obtain unique mixtures of polymers in ILs, for example, mixtures of cellulose, starch and lignin (Wu et al., 2009). There are studies on chitin, chitosan (Sun et al., 2009b, Xiao et al. 2011) and starch (Wilpiszewska et al., 2011) dissolution in ILs. Also blending polysaccharide in ILs is actively studied. Binary blends of natural polymers such as cellulose and chitosan are promising systems for creating new polymer materials such as blended films, fibers and sponges. Attention should be paid to the compatibility of the polymers, the type of inter- and intra-molecular interaction between the macromolecules. The reactivity of chitosan is more versatile than cellulose due to the NH_2 groups presented in the chitosan structure (Dutta et al, 2004). As the mechanical properties of most of products obtained from chitin and chitosan are very weak, and producing of amino-cellulose is a technologically complicated process, the blending of these two polymers could be a perspective way to their modification and improving the properties of the final product which can be obtained from the blended solutions.

The similarity in chemical structure of chitosan and cellulose predict their compatibility and the possibility for the preparation of homogeneous blends. Cellulose as most of the naturally occurring polysaccharides is acidic, whereas chitosan is a highly basic polysaccharide (Holmbeg et al., 1997). The research in cellulose-chitosan blending shows the great potential for the materials that can be obtained. The intramolecular interactions between molecules of both polymers were confirmed (Holmbeg et al., 1997), and blended films with high contain (up to 20 wt%) of chitosan in real conditions are stronger than calculated by the additively rule from the component's ratios (Hasegava et al., 1994).

Despite the recent report that 1-ethyl-3-methylimidazolium acetate (EMIMAc) cannot dissolve chitosan (Wendler et al., 2010), Haibo at al. reported in 2006, that the ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl) could dissolve chitosan to 10 wt% after 5 hours heating at 110^{o}C under an inert atmosphere of N_2 with mechanical stirring. There are also a few recent patents describing methods of producing chitosan fibers (Xiong et al., 2009) and films (Yu et al., 2009) from chitosan/IL solutions using carboxyl alkyl imidazolium ionic liquids. The blending of cellulose with chitosan as a perspective idea to modify cellulose materials has also found interest. Some patents (Pang et al., 2009; Li et al., 2010) describe the ways to produce cellulose/chitosan composite films, fibers and foams using ILs. There is also literature on composite biologically active fibers based on chitosan-coated lyocell fibers (Janjic et al., 2009). However, some of these reports suggest the use of aqueous solutions of NaOH as a pretreatment for the chitosan (Yu et al., 2009; Janjic et al., 2009).

2. Results and Discussion

2.1. Characterization of cellulose pulp

The cellulose pulp that was used throughout this thesis (Alicell - Super, supplied by Western Pulp Inc.) was characterized with a variety of techniques and the basic properties are presented in Table 2.1.

Table 2.1. Results of data analysis for Alicell-Super Cellulose.

Analysis	Parameter	Data
Water retention value (WRV)	WRV, %	64.5
Water content	W, %	7.97
Alpha-cellulose content	α, %	93
	Methods for DP analyzes:	
Cupri-ethylene-diamine method (CED)	[η], cm^3/g	540.5
	DP	763
Iron (III) sodium tartrate complex method (EWNN)	[η], cm^3/g	608.5
	DP	748
Gel permeation chromatography (GPC) with LiCl/DMAC as a eluent	Mn, g/mol	34 743
	Mw, g/mol	97 029
	DP	599

It was found that the characteristics of the cellulose samples correspond to the data provided by the supplier. The differences in DP-data between EWNN and CED – methods and GPC – method could be explained by man-factor in EWNN and CED analysis. It was assumed, that GPC results to be more precise and consequently used further in this work.

The FTIR absorbance spectrum of cellulose (Fig. 2.1) was recorded in order to determine if there were any changes of cellulose structure during the dissolution and coagulation processes.

All of the characteristic bands as OH-stretching (3650-3200 cm^{-1}, 1200-1000 cm^{-1}), C-H stretching (2950-2800 cm^{-1}, 1500-1300 cm^{-1}) and C-O stretching (1400-1300 cm^{-1}) are clearly visible in the spectrum of original cellulose.

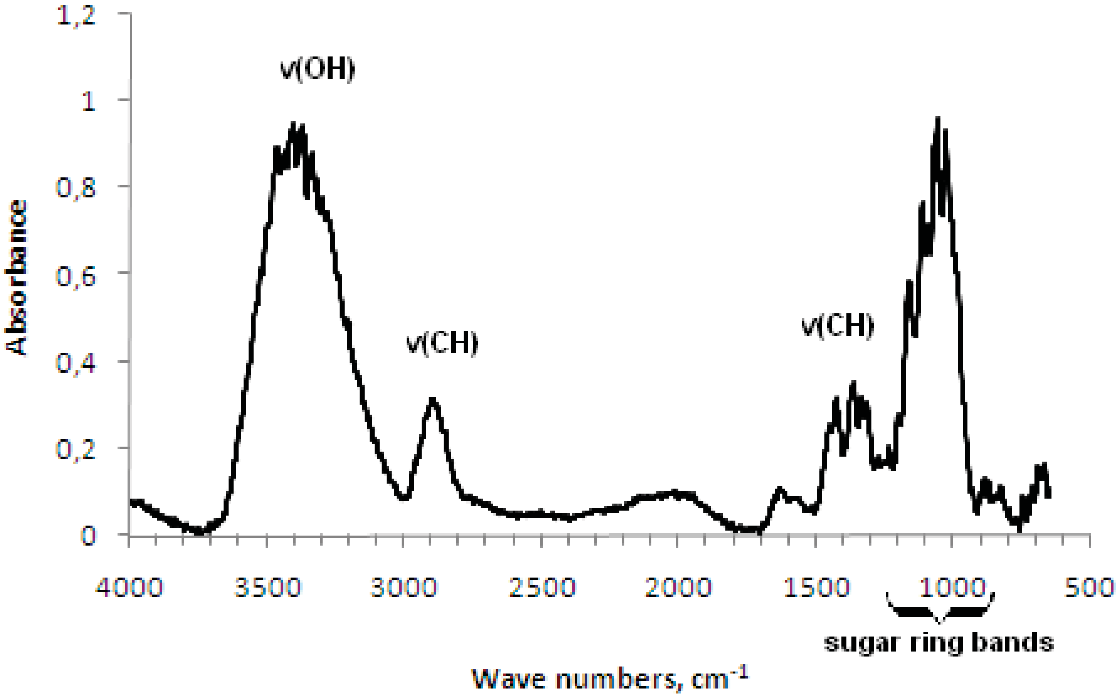


Fig. 2.1. FTIR absorbance spectrum of the cellulose pulp studied.

The molecular weight distribution was determined by GPC analysis. The differences between samples obtained did not exceed acceptable levels of experimental error ± 5 % . As it is shown in Fig. 2.2, the cellulose pulp had a relatively narrow molecular weight distribution with PDI 1.6.

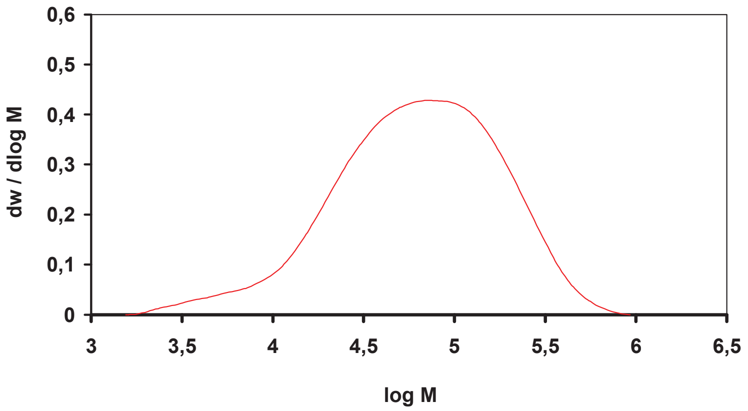


Fig. 2.2. Molecular weight distribution of Alicell- Super cellulose pulp.

2.2. Dissolution of cellulose in IL

The maximum concentration of cellulose soluble in various ILs was determined. In the case of BDMIMCl, EMIMAc and BMIMAc solutions, the dissolution of cellulose was limited by the viscosity of the solutions. Above the maximum concentration of cellulose in BMIMCl, the fibrils of cellulose was observed by microscope (Fig. 2.3).

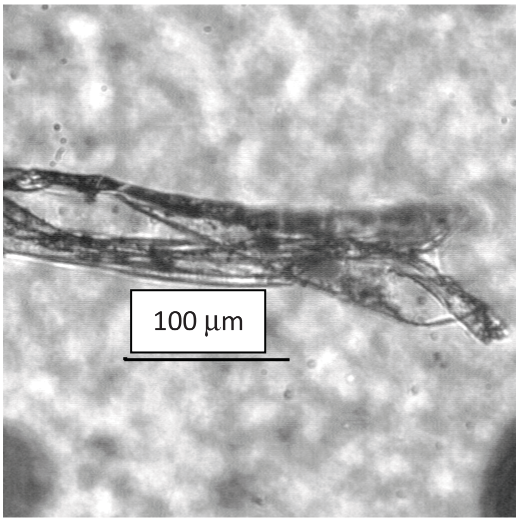


Fig. 2.3. Microscopic photo of cellulose solution (15 wt%) in BMIMCl

At a cellulose concentration of 5 wt% in BDMIMCl, 18 wt% in EMIMAc and 20 wt% in BMIMAc solutions were absolutely transparent, with no signs of cellulose coagulation, although air-bubbles were clearly visible due to their viscosities of solutions (Fig. 2.4).

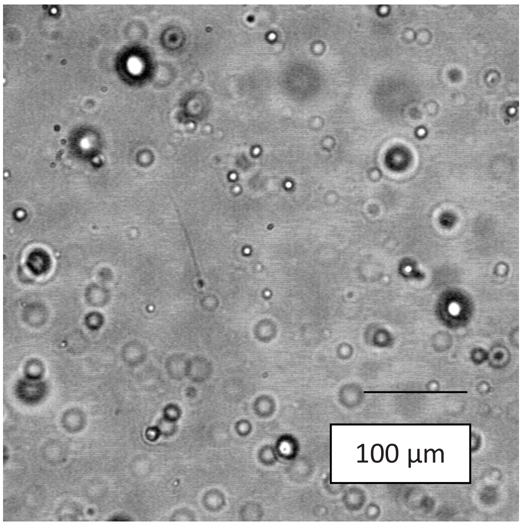


Fig. 2.4. Microscopic photos of 5 wt% cellulose solution in BDMIMCl

The maximum concentration of cellulose obtained by dissolution in various ILs is presented in Table 2.2. Heinze, et. al. in 2005b reported the similar results for cellulose with equal DP with one used in this work.

Table 2.2. The maximum concentration of cellulose in various ILs.

Ionic Liquid	Maximum cellulose concentration, wt%
BMIMCl	14
BDMIMCl	5
EMIMAc	18
BMIMAc	20

The best dissolution ability is shown by ILs with acetate anions. It is possible to dissolve 18 wt% of cellulose at 110 ^{o}C in EMIMAc and up to 20 wt% in BMIMAc. The worst dissolution ability among the studied solvents has shown BDMIMCl, in which it was only possible to dissolve 5 wt% of cellulose under the same conditions. In the case of BMIMCl dissolution stops at concentrations of cellulose exceeding 14 wt%.

By the method used in TITK (Rudolstadt, Germany), swelling of cellulose pulp with water and its subsequent evaporation under vacuum during the dissolution procedure facilitates the preparation of cellulose solutions with up to 20 wt% of cellulose in EMIMAc. It was concluded therefore that swollen cellulose is easy to dissolve in ILs.

2.3. Influence of water on the ability of selected ionic liquids to dissolve cellulose.

The cellulose was dried under vacuum or mixed with a certain quantity of water in order to obtain a pulp with a specific water content. The concentration of cellulose in solution was varied from 0.5 up to 2 wt%.

As it was found early (Kuzmina et al., 2010) cellulose in ILs solutions appears in the form of soft spherical particles. The particle size measured is the diameter of the sphere that diffuses at the same speed as the particle being measured. The size were determined by first measuring the Brownian motion of the particles in a sample using Dynamic Light Scattering (DLS) and then interpreting a size from this using established theories. The particles in a liquid move about randomly and their speed of movement is used to determine the size of the particle. It is known that small particles move quickly in a liquid and large particles move slowly (Fig. 2.5). This movement is carrying on all the time, so if we take two ‘pictures’ of the sample separated by a short interval of time, say 100μS, we can see how much the particle has moved and therefore work out how big it is.

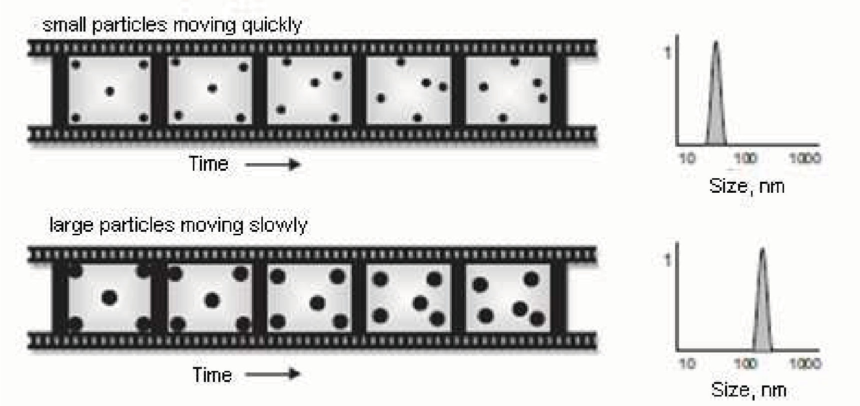
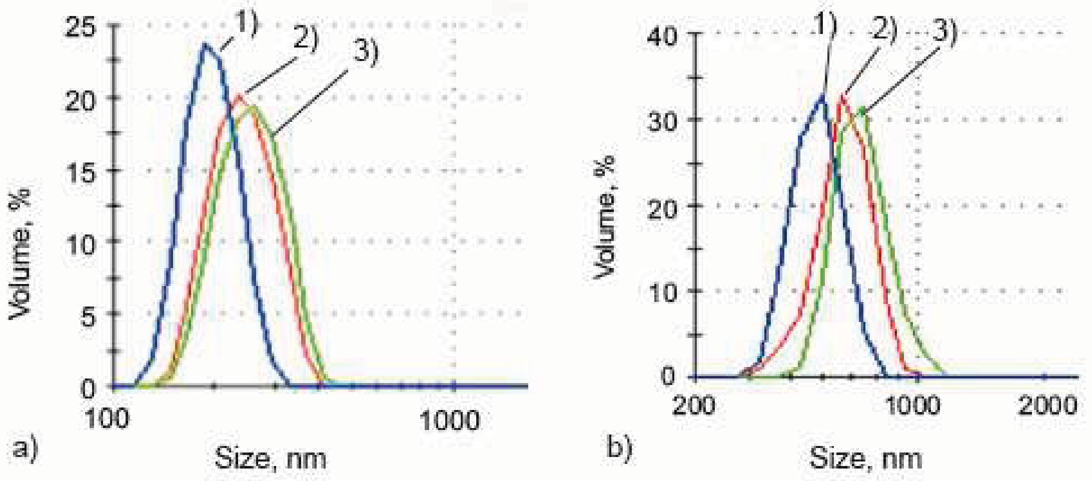


Fig. 2.5. A principle of particle size determination (Malvern Instruments, 2003)

In Fig. 2.5 size distribution by R_h (hydrodynamical radius) of cellulose aggregates in ILs solutions are presented. R_h of cellulose aggregates were determined using dynamic light scattering (DLS) analysis. Apart from static light scattering (SLS), determined Rg (radius of gyration), DLS allows more precisely determine the real size of aggregates. The specific example depicted is for BMIMCl solutions with 0.5; 1 and 2 wt% cellulose concentration and 0.1% and 8% of cellulose water content. The size distributions of cellulose aggregates in the solutions in EMIMAc and BMIMAc look identical. As we can see from the Fig. 2.5, the size of cellulose aggregates increases with an increase in the concentration of cellulose in solution. This is happens due to the agglomeration of cellulose macromolecules.

At infinite dilution, the size of polymer particles are minimal and depend on the polymer-solvent interaction only, and with increasing polymer concentration the macromolecules have a greater likelihood of interacting with each other, therefore the size of the particles increases. Water content also has an influence on the size of cellulose aggregates. The deterioration of solvent quality due to competition for macromolecule solvation is the reason for the progressive changes in aggregation. The dependence of the hydrodynamic radius of cellulose aggregates in BMIMCl, BMIMAc and EMIMAc solutions (calculated at infinite dilution) on the relative content of water in cellulose is presented in Fig. 2.6. The size of cellulose particles is observed to increase with increasing water content, and the cellulose particles in solution in EMIMAc are bigger than in BMIMAc or BMIMCl under equivalent conditions.

In Fig. 2.6. can be seen that the size of cellulose aggregates in IL solutions also increase with an increase of the water content in cellulose. This phenomenon can be explained by the competition between water and IL molecules for solvation of the polymer. Water interacts more strongly with cellulose than ILs, so once the cellulose is fully solvated by water, the "effect of competition" on particle size becomes less noticeable, and the increase in aggregate size is much slower than at low water contents. With water contents greater than 8% water in cellulose, the size of aggregates in solution reached several hundred nm, and they were visible to the eye.



Cellulose concentration in the solution	Average aggregates size [nm] at different cellulose water content	
	a) a water content of 0.1%.	b) a water content of 0.8%.
1) 0.5%	183.4	663
2) 1%	238.2	789
3) 2%	260.9	863

Fig. 2.5. Size distribution by volume for cellulose dissolved in BMIMCl

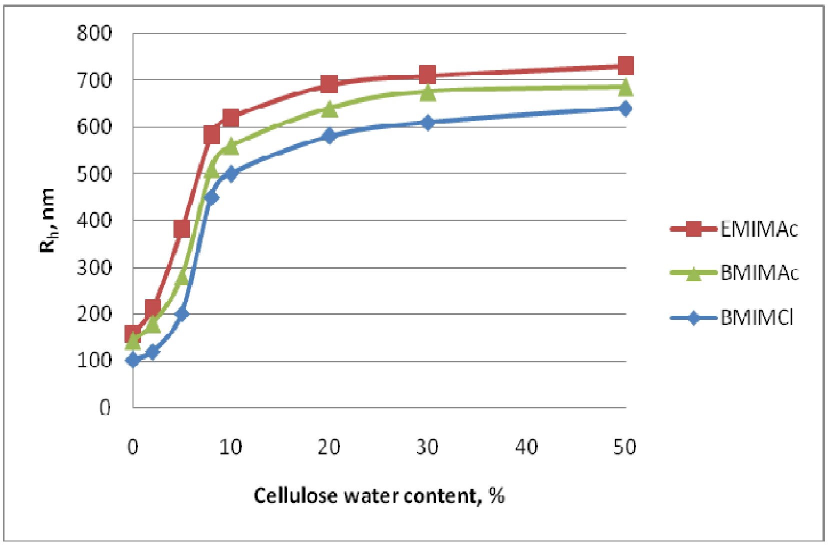


Fig. 2.6. Relationship between the hydrodynamic radius of cellulose aggregates in dilute solutions of EMIMAc, BMIMAc and BMIMCl and the water content of cellulose in solution at 85 °C (calculated at infinite dilution).

For identical samples, the value of the hydrodynamical radius R_h is bigger than the radius of gyration R_g. For dissolved, practically dry cellulose, the values are R_g = 101 nm and R_h = 160 nm, indicative of a certain degree of aggregation potentially including solvent molecules (Kuzmina et al., 2010). For a better understanding of the influence of water on the dissolution of cellulose in ILs, the plot of aggregate size from the mass ratio of components in solution is presented in Fig. 2.7.

In the diagram depicted above at a temperature of 85 °C and atmospheric pressure, three areas of state are found: I – a colloidal solution with aggregates of less than 10^{-7} m, II – suspensions with aggregates of more than 10^{-7} m and less than 10^{-5} m, III –bi-phasic system, characterized by polymer particles above 10^{-5} m.

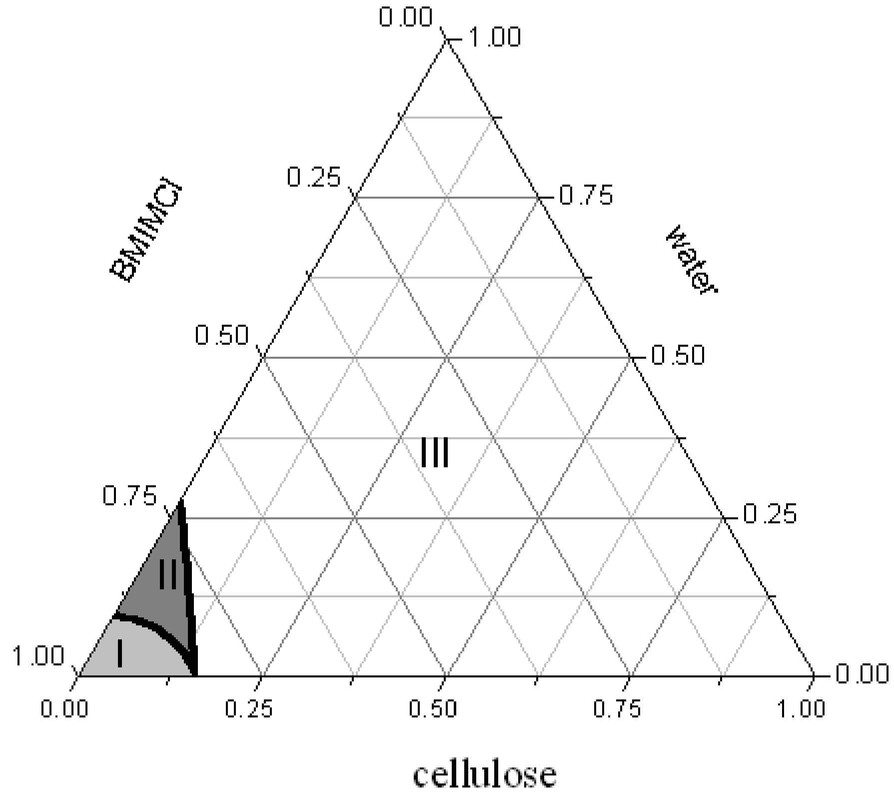


Fig. 2.7. Solubility diagram of cellulose-water-BMIMCl mixtures at 85 °C. I – area of colloid solution; II – area of suspension; III – area of bi-phasic system (large-size dispersion).

A solution with small particle sizes is a prerequisite to obtain a good quality product (fibres or films). Solutions in area I in Fig. 2.7 are in line with this requirement. From area II, the maximum component ratio can be found to obtain a solution suitable for technological processing into fibres or films. If the component ratio in the mix corresponds to area III, the cellulose aggregates in this area are large enough to be observed by the naked eye and it is not possible to produce a homogeneous and good-quality product from this system.

Thus, it was found that solutions of cellulose in ionic liquids represent the steady disperse systems containing the remains of the undissolved structure of the polymer, with a radius of gyration of up to 5 times higher than that of a single macromolecule of cellulose of the same molecular weight. The hydrodynamic radius of particles of cellulose in EMIMAc slightly exceeds those in BMIMAc and BMIMCl, with other conditions being equal (moisture content of cellulose, concentration of the solution, and the temperature). The size of the cellulose aggregates in IL solutions grows with an increase in the water content of cellulose and its concentration in the solutions, which may be interpreted in terms of both the deterioration of the solvent and the swelling of particles in the presence of water. A colloid solution useful for technical purposes could be obtained at water content in the BMIMCl solution below 8%. The excess of water should be removed under vacuum during the dissolution process.

2.4. The influence of thinners on cellulose dissolution in ILs.

For decrease in viscosity of solutions, and efficient dissolution process the addition of thinners to IL solutions was expedient. In my work two ways of the triple systems obtaining is described: standard - with simultaneously mixing of components and second way – swelling of cellulose pulp with thinner and consequence dissolution in ILs. In this work aprotic dimethyl sulfoxide (DMSO), dimethylformamide (DMF), diethyl ether (DEE), ethyl acetate (EAc) and protic formamide (FA) were chosen as thinners for cellulose solutions in ILs. Was assumed, that all this thinners enchased cellulose swelling and make it dissolution in ILs easier. It was interesting to compare thinners with different boiling points and solvatochromic parameters.

To understand the interaction in system cellulose/IL/thinner, two-component systems: cellulose/thinner and ILs/thinner were analyzed. First, interaction between cellulose and thinners were study to find cellulose swelling degree in selected thinners and tsolution retention values (SRVs) for thinners. As is shown in Fig. 2.8, the degree of cellulose swelling is the lowest in DEE and very high in FA. The SRVs are reflected in Fig. 2.9. Intensive cellulose swelling was observed during the first hour of treatment. During that time, the inter- and intramolecular structure of cellulose changed and physical swelling occurred.

The greater the SRV, the greater the chemical affinity of the thinner and cellulose, and the more easily the thinner accepts cellulose active centers (OH-groups) and increases the cellulose pulp surface area. According to data presented in Figure 2.9, the protic solvent FA could swell cellulose more efficiently than aprotic ones, as was proposed previously (Fidale et al. 2008).

After the first hour of swelling, the degree of cellulose swelling increases insignificantly. Thus, in our study cellulose was swollen for one hour only before further treatment to produce systems type II.

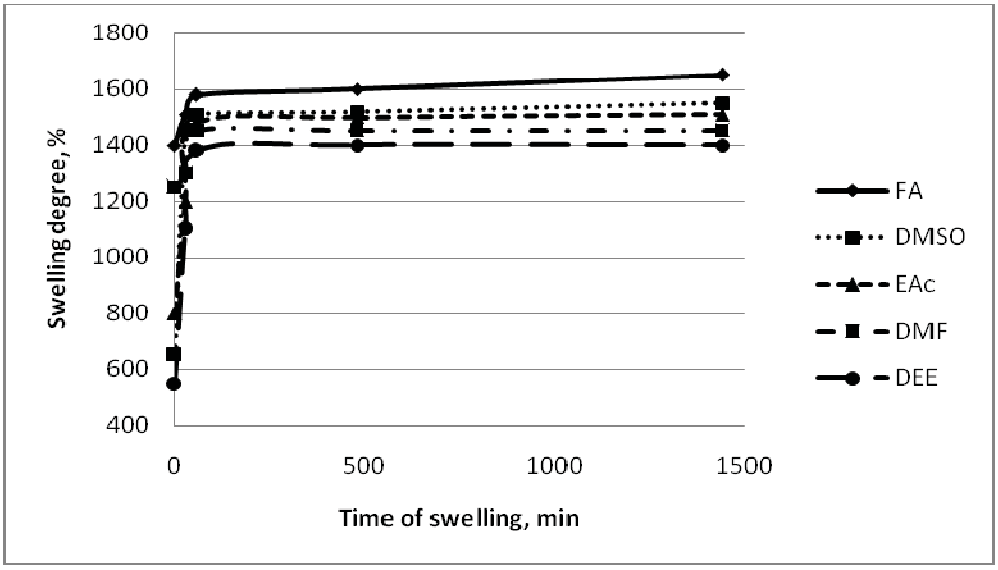


Fig. 2.8. Degree of cellulose swelling in different thinners over 24 hours

As the influence of the thinners on cellulose pulp was studied, the viscosity of ILs/thinner solutions was analyzed at 85°C. Because DEE and EAc were not miscible with ILs, only DMSO, DMF and FA were examined. Data for EMIMAc mixtures are illustrated in Fig 2.10. The results for all ILs were similar. It should be noticed, that despite DEE and EAc thinners are not miscible with ILs, there no formation of bi-phase two-solvents system occur. At the solution preparation by type I all the components (cellulose, IL, thinner) were added to the flask simultaneously, the concentration of thinner is small and surface of cellulose pulp is large, thinner is instantly absorbed by cellulose pulp. Actually we obtained cellulose swelled by thinner and IL in IL media. As it will be discussed later, at heating at dissolution process these thinners evaporate almost completely, only its traces were found and the obtained solutions were homogeneous. Similar effect is occur at preparation of solution type II: DEE and EAc first are absorbed completely by cellulose and then evaporated freeing up space in cellulose swelled structure for ILs. Consequently, due to DEE and EAc are evaporate from the solutions, the term “thinners” is accepted to them conditionally.

The possibility of interactions between solvents was examined by viscosity measurements of their mixtures in different proportions. The concave shape of a curve show that interactions between molecules of IL are stronger than interactions between molecules of IL with molecules of other solvent (Tager, 2007).

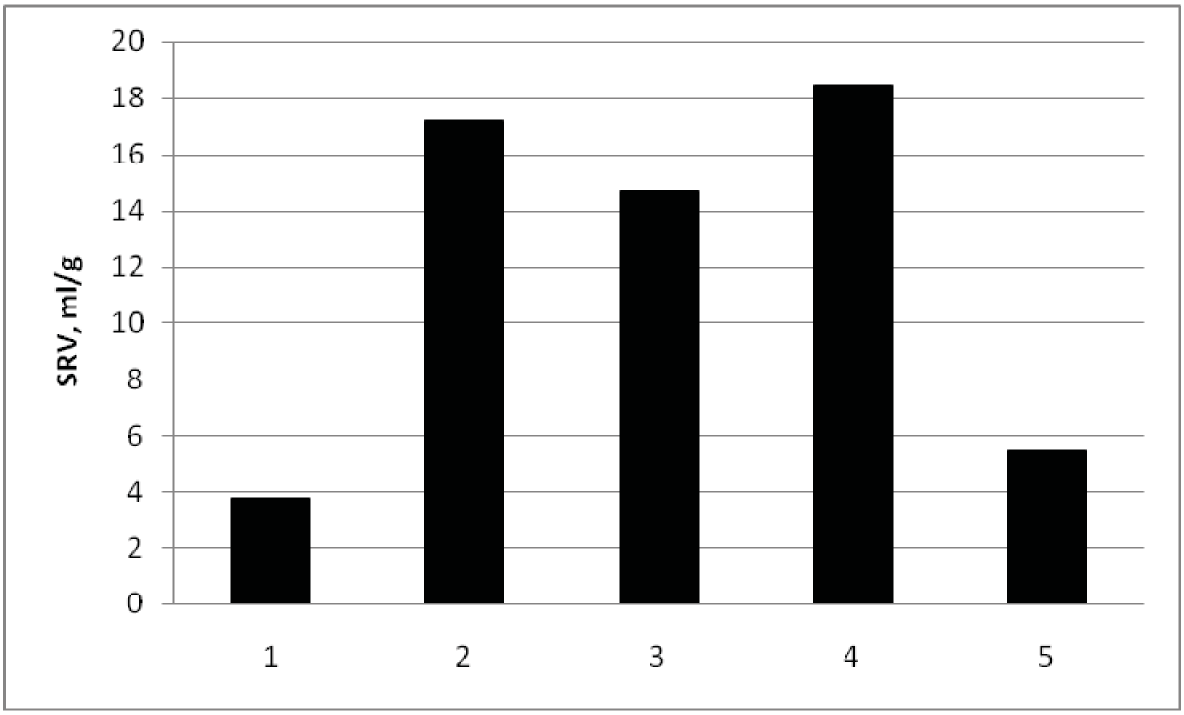


Fig. 2.9. SRVs of the studied thinners toward cellulose: 1) DEE, 2) EAc, 3) DMSO, 4) FA, 5) DMF

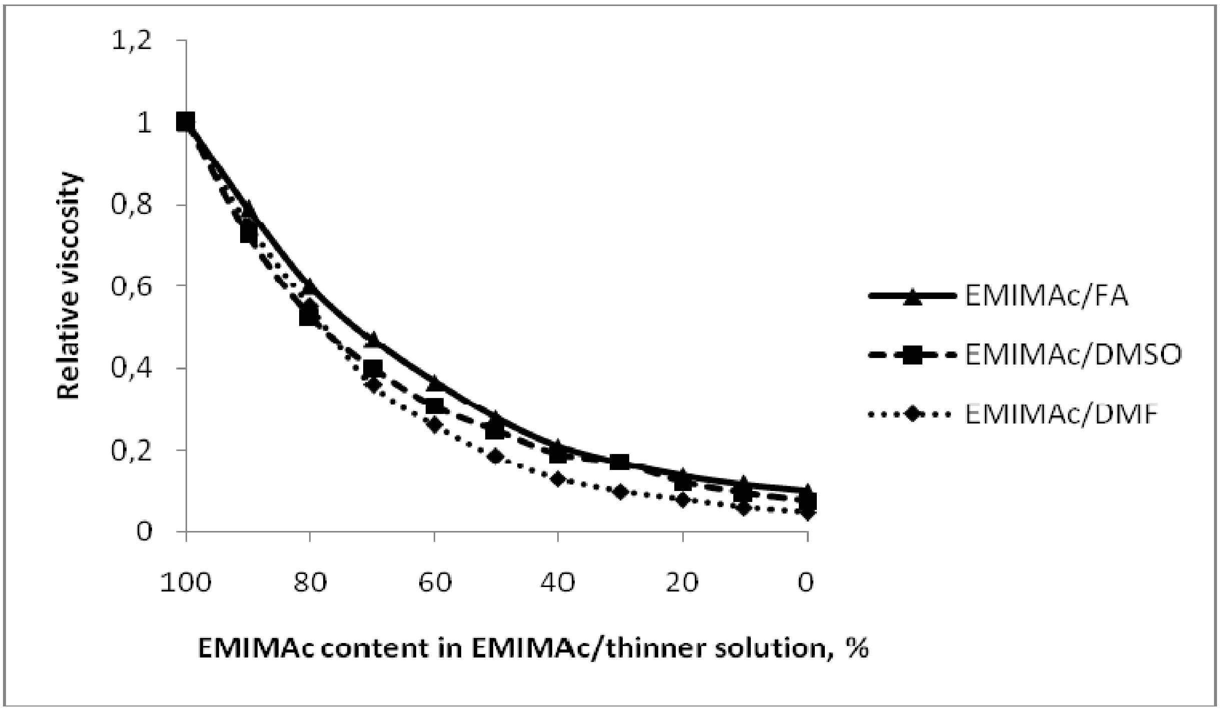


Fig. 2.10. The relative viscosity of EMIMAc/thinner solutions with different component ratios

^{1}H NMR spectroscopy was used to analyze the influence of thinners on the chemical shifts of the ILs and cellulose. Solutions with a component ratio cellulose:IL:thinner of 5:80:15 were analyzed.

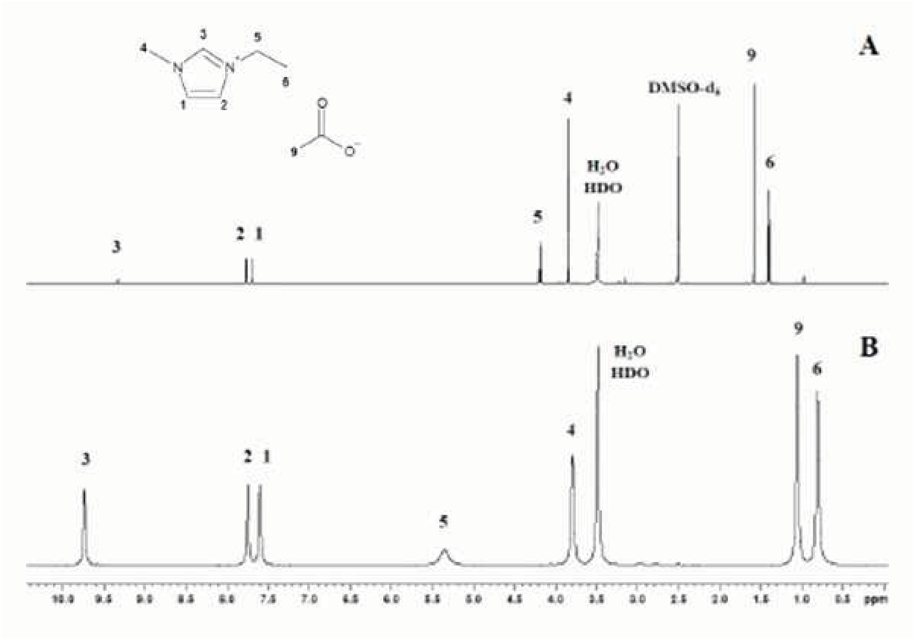


Fig. 2.11. ^{1}H NMR spectra of 5 wt% cellulose/EMIMAc in A) DMSO-d_6 as solvent, B) DMSO-d_6 as an external standard (700 MHz, 100°C). Hydrogen atoms of IL are numbered according to Table 3.4.

The dilution of a sample with a large amount of DMSO-d_6 can obscure the influence of the thinners on chemical shifts in ILs, a method with an external standard was carried out first. The cellulose/IL/thinner mixtures were placed in a NMR tube at 110°C, and then a sealed capillary with DMSO-d_6 (1 mm in outer diameter) was inserted coaxially. The cellulose/IL/thinner systems were too viscous for ^{1}H NMR measurements at room temperature, consequently temperatures of 70°C and 100°C were selected. Even at higher temperatures, only very wide signals of the IL were observed (Fig. 2.11). Thus, we decided to use samples diluted with DMSO-d_6.

In Table 2.3. the influence of thinners on the chemical shifts of hydrogen atoms in ILs (numbered according to Table 3.4) in cellulose solutions is presented. The chemical shifts of imidazolium ring protons H1–H3 depends to a greater degree on the presence of thinners than the shifts of protons in other positions, which is in correspondence with literature data (Hesse-Ertelt et al., 2010). The chemical shifts of the alkyl chain protons, especially H7 and H8 atoms of the butyl-chain, were independent of the presence of thinners. Proton resonances are most shifted in the solution prepared using EAc.

Table 2.3. ^{1}H NMR chemical shifts of ILs in the presence of thinners in DMSO-d_6 (700 MHz, 27°C).

ILs	IL NMR shifts of IL hydrogen atoms*								
BMIMAc	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
DMSO	7.69	7.76	9.32	3.85	4.16	1.76	1.25	0.89	1.58
DMF	7.69	7.76	9.34	3.85	4.16	1.76	1.25	0.89	1.58
FA	7.68	7.75	9.31	3.84	4.16	1.75	1.25	0.89	1.59
EAc	7.73	7.79	9.66	3.86	4.17	1.76	1.25	0.89	1.56
DEE	7.69	7.76	9.36	3.85	4.16	1.75	1.25	0.89	1.58
without thinners	7.69	7.76	9.34	3.85	4.16	1.76	1.25	0.89	1.58
EMIMAc	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
DMSO	7.68	7.77	9.27	3.84	4.19	1.40	-	-	1.58
DMF	7.68	7.77	9.30	3.84	4.19	1.40	-	-	1.58
FA	7.68	7.77	9.28	3.84	4.19	1.40	-	-	1.58
EAc	7.68	7.76	9.30	3.84	4.19	1.40	-	-	1.58
DEE	7.68	7.76	9.32	3.84	4.19	1.40	-	-	1.58
without thinner	7.68	7.77	9.37	3.84	4.19	1.40	-	-	1.58
BMIMCl	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
DMSO	7.70	7.77	9.19	3.85	4.16	1.76	1.25	0.89	-
DMF	7.70	7.77	9.20	3.85	4.16	1.76	1.25	0.89	-
FA	7.70	7.77	9.19	3.85	4.16	1.76	1.25	0.89	-
EAc	7.70	7.76	9.18	3.85	4.16	1.76	1.25	0.89	-
DEE	7.70	7.77	9.18	3.85	4.16	1.76	1.25	0.89	-
without thinner	7.71	7.78	9.23	3.85	4.16	1.76	1.25	0.89	-

* Hydrogen atoms of ILs are numbered according to Table 3.4.

Cellulose shifts are observed in ^{1}H NMR (700 MHz, DMSO-d_6) spectrum (Fig. 2.12.) at δ_H: 3.00 (br s, H-2), 3.24 (1H, br s, H-5), 3.30 (1H, br s, H-4), 3.37 (1H, br s, H-3), 3.61 (1H, br s, H-6’), 3.70 (1H, br s, H-6’’), 4.38 (1H, br s, H-1). The observed chemical shifts are consistent with the values reported in the literature (Hesse-Ertelt et. al, 2010), recorded for the liquid and solid state NMR spectroscopy. It can be concluded that cellulose dissolution occurred without chemical modifications.

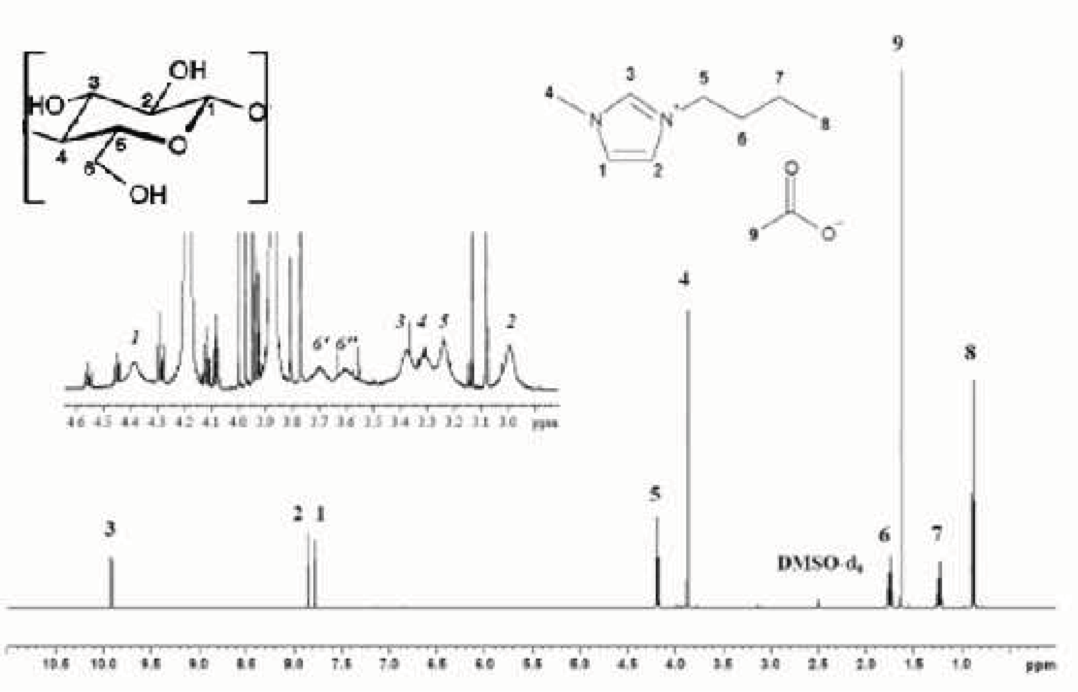


Fig. 2.12. ^{1}H NMR spectrum of 5 wt% cellulose in BMIMAc solution, recorded in DMSO-d$_6$.

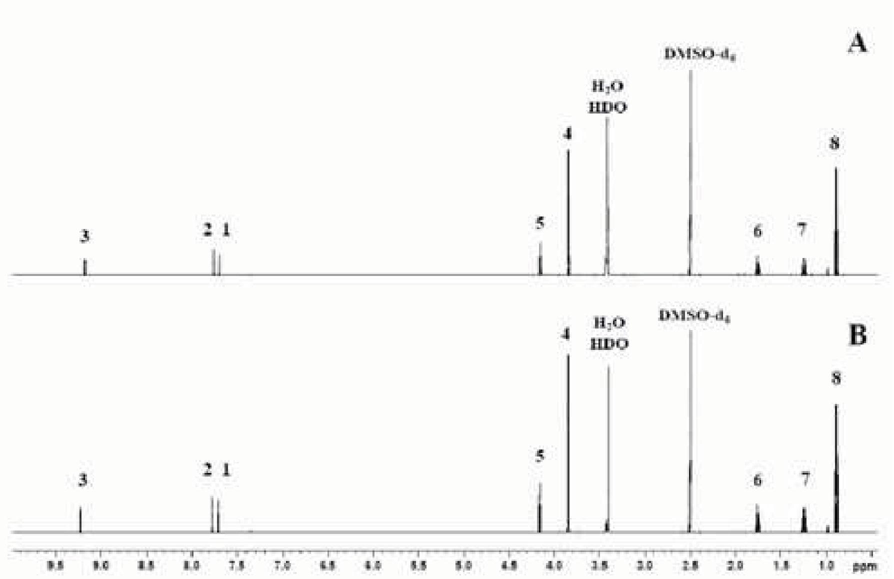


Fig. 2.13. ^{1}H NMR spectra of 5 wt% cellulose/EAc/BMIMCl solutions, recorded in DMSO-d$_6$: A) right after preparation, B) after 4 months. Hydrogen atoms of IL are numbered according to Table 3.4.

The stability of the cellulose/IL/thinner systems was confirmed by identical ^{1}H NMR spectra recorded directly after preparation and after four months at room temperature (Fig. 2.13). The spectra obtained for solutions type I and II are slightly different from each other. The two NMR spectra of cellulose/EMIMAc/EAc solutions are given in Fig. 2.14 as an example.

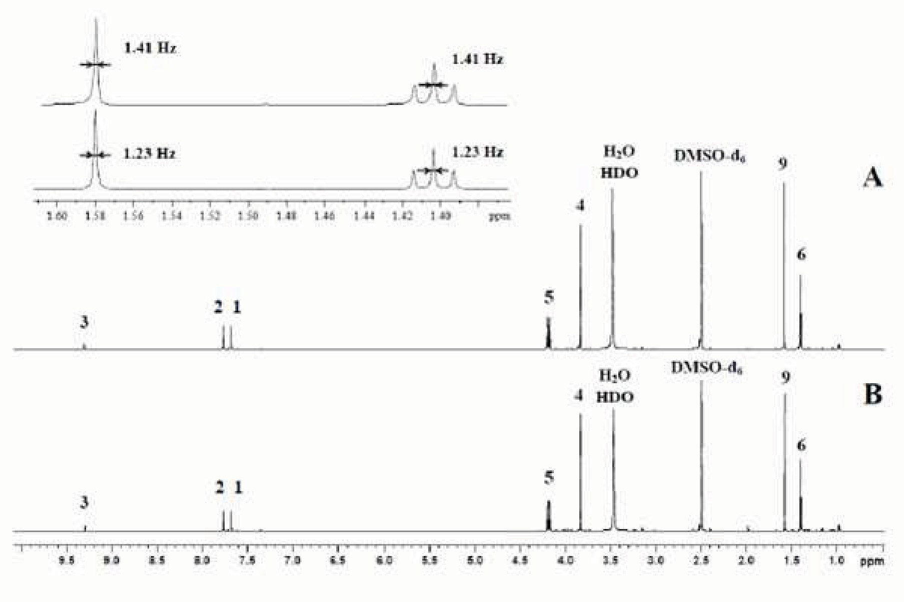


Fig. 2.14. ^{1}H NMR spectra of cellulose/EMIMAc/EAc solutions prepared with a different order of adding components: A) cellulose was added to the EAc/EMIMAc mixture (type I), B) cellulose preliminarily swollen in EAc was added to EMIMAc (type II). Hydrogen atoms of IL are numbered according to Table 3.4.

The order of mixing components had no effect on the shifting of peaks. However, the solutions are not identical, as the IL signals recorded for solution type II are slightly sharper than for type I, and similar to those recorded for the IL alone. This means that the addition of pre-swollen cellulose had a lesser impact on the IL hydrogen bonding system. The peaks corresponding to systems prepared with the addition of EAc and DEE have the same chemical shifts as for the solution without thinner (Fig. 2.15). The signals of EAc or DEE thinners are of very low intensity, which means that these thinners have almost completely evaporated upon heating during the dissolution procedure. The evaporation of EAc and DEE led to a decrease in the time of cellulose dissolution (Table 2.4).

Aprotic thinners facilitated the cellulose dissolution process more efficiently than the protic FA. Based on Table 2.4, it can be concluded that EAc and DEE are more efficient in facilitating the dissolution process. DMSO was also observed to increase the speed of cellulose dissolution in ILs and remained in the solution, decreasing its viscosity (Table 2.4). The air bubbles may have appeared in the cellulose solution due to increased viscosity, as presented in the pictures in Table 2.4.

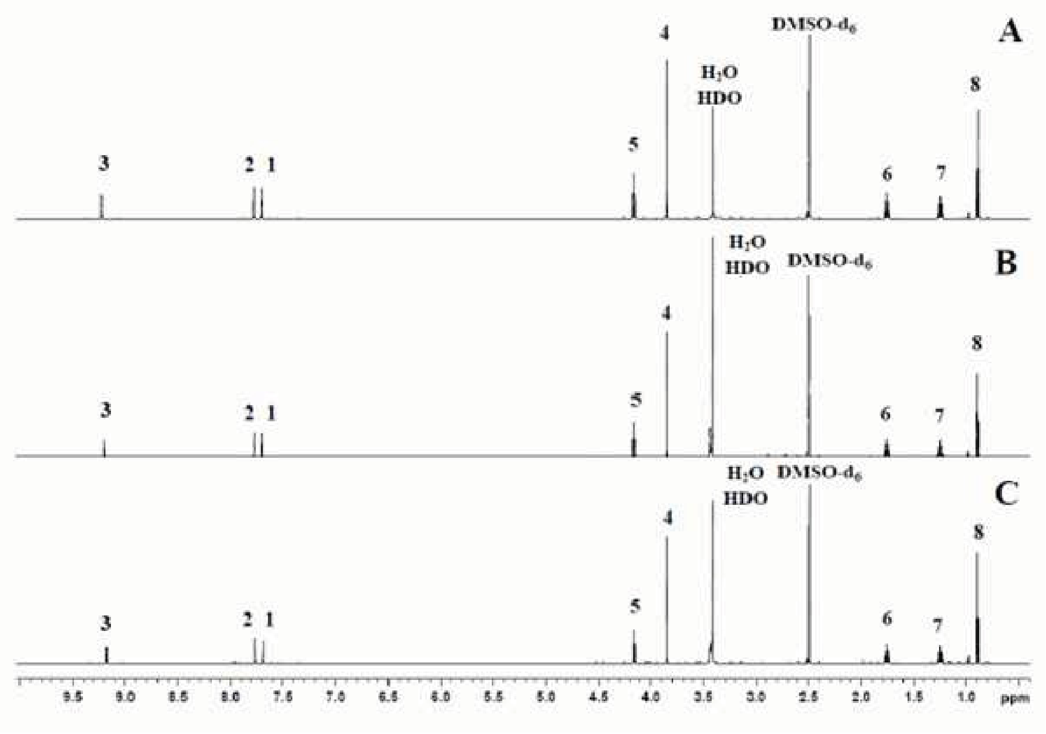


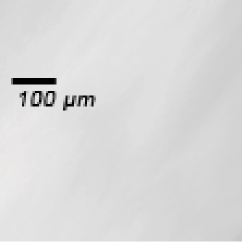
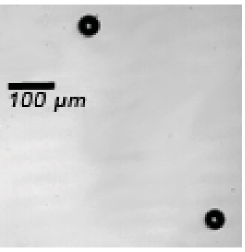
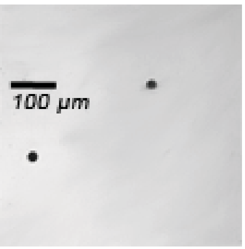
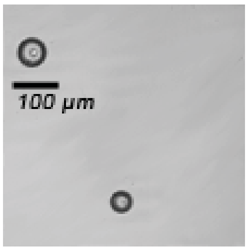
Fig. 2.15. ^{1}H NMR spectra of cellulose solutions in BMIMCl: A) without thinners, B) with DEE, and C) with EAc. Hydrogen atoms of IL are numbered according to Table 3.4.

In most cases, the viscosity of cellulose/IL solutions decreased with the addition of thinners. The thinners added to solutions type II caused an increase in the speed of cellulose dissolution in the order:

$$\text{FA} \rightarrow \text{DMF} \rightarrow \text{DEE} \rightarrow \text{DMSO} \rightarrow \text{EAc}$$

When cellulose pulp was added to the solvent mixture (type I), the dissolution speed was 60 min for all samples. The influence of thinners on the viscosity of 2 wt% cellulose solution in EMIMAc is presented in Fig. 2.16 and 2.17. The results obtained for other ILs were similar. DMF solutions showed the lowest viscosity irrespective of the type of the system. Solutions without thinners exhibited the highest viscosity in all cases. A comparison of Figures 2.16 and 2.17 shows that solutions which were obtained with preliminary swelling of cellulose in DMSO and DMF (type II) have a slightly lower viscosity than solutions in which cellulose was added to the solvent mixture (type I). Only the solution with the cellulose swollen in FA showed a higher viscosity than the solution in which cellulose was added to the FA/ILs mixture.

Table 2.4. The time of dissolution of 2 wt% pre-swollen cellulose with 5 wt% thinners in BMIMCl at 110°C

Cellulose/ IL/thinner system	Dissolution time, min	Microscopic image of solution
Cellulose/ BMIMCl/DMSO	45	
Cellulose/ BMIMCl/DMF	75	
Cellulose/ BMIMCl /FA	100	
Cellulose/ BMIMCl /EAc	40	
Cellulose/ BMIMCl /DEE	50	

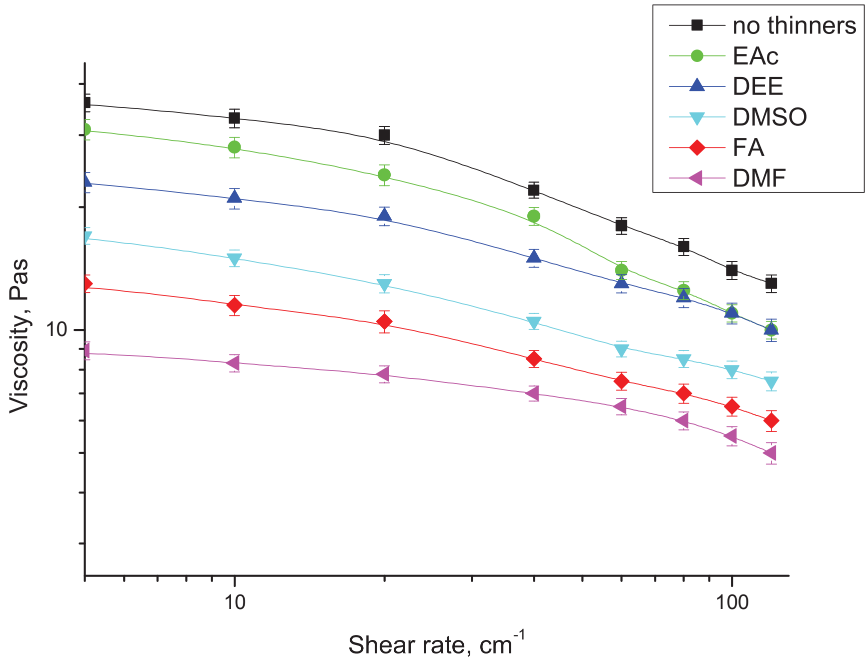


Fig. 2.16. Relationship between the viscosity of 2 wt% cellulose solution in EMIMAc and the shear rate at 110°C; cellulose was added to the thinner/IL mixture (type I).

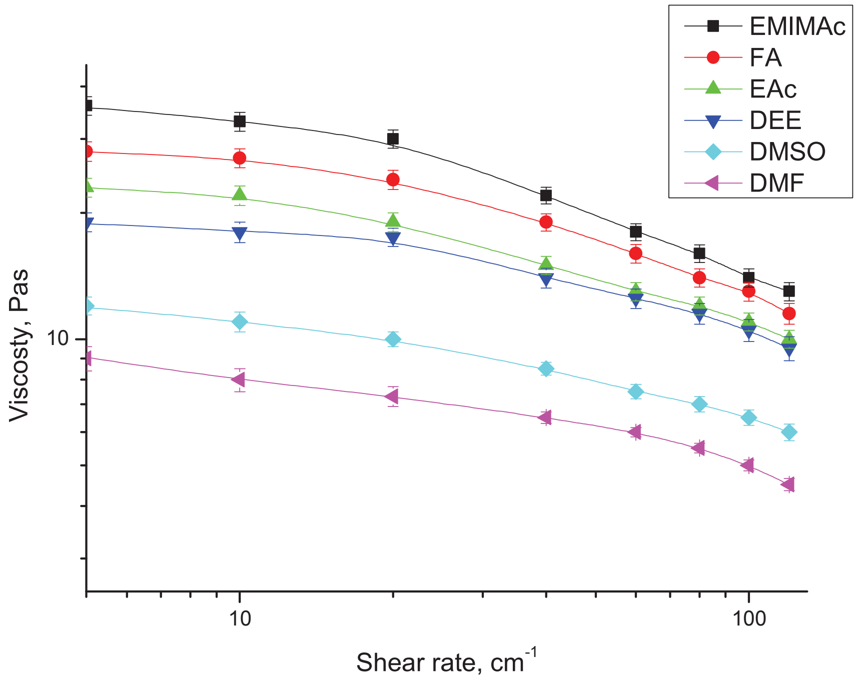


Fig. 2.17. Correlation between the viscosity of 2 wt% cellulose solution in EMIMAc and the shear rate at 110°C; cellulose was swollen for 1 h in different thinners before dissolution in ILs (type II).

Generally, the thinners studied decreased the viscosity of the solutions and this effect is independent on the nature of the thinner or type of solution. The type of the system (the order of component mixing) did not affect the qualitative or quantitative composition of cellulose/IL/thinner systems. The composition of cellulose/IL/thinners systems remained stable even after 4 months.

Ethyl acetate and diethyl ether almost completely evaporated from the solution upon heating and facilitated cellulose dissolution in ILs. DMSO also increased the speed of cellulose dissolution in ILs, but it remained in the solution and lowered its viscosity. All of the thinners used successfully decreased the viscosity of cellulose solutions in ILs.

2.5. Cellulose/Chitosan blends in ILs.

Few types of chitosan, including microcrystalline chitosan were used in this work. First, chitosan was dissolved in ILs in temperature range 25-110 ^{o}C. 1 wt% of chitosan solution was impossible to reach in BDMIMCl and BMIMCl, chitosan started to dissolve at 75 ^{o}C in BMIMAc and at 110 ^{o}C in EMIMAc. Clear solutions were obtained in BMIMAc at 110 ^{o}C (Fig. 2.18).

Optical microscopy confirmed that BMIMAc was able to dissolve 1 wt% of chitosan at 110 ^{o}C. The results for all of the chitosan studied were the same. BMIMAc shown the best dissolving ability toward chitosan, but it was also possible to produce a 1 wt% chitosan solution in EMIMAc. BMIMCl and BDMIMCl weren't able to dissolve even 1 wt% of chitosan under the conditions studied.

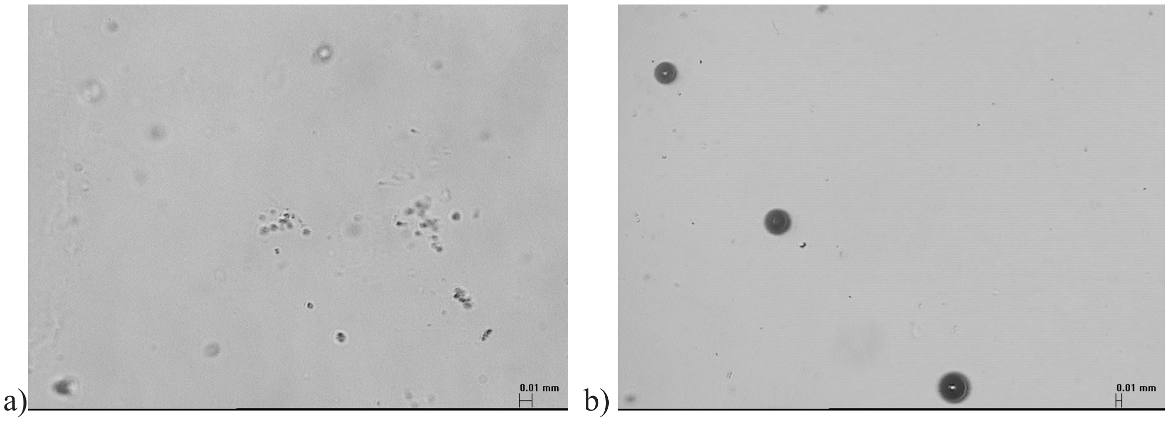


Fig. 2.18. Microscopic pictures of chitosan powder Polymar in BMIMAc after 4 hours of dissolution at a) 75 ^{o}C and b) 110 ^{o}C.

The time of temperature treatment was not more than 4 hours due to the fast degradation of chitosan at high temperatures. To minimize the degradation of chitosan during dissolution in ILs, microwave treatment was tried. The power was 90 Watts, but even at this power degradation was too fast and the appearance of smoke was observed after few seconds of treatment indicating degradation of the chitosan. After only 12 seconds of microwave treatment chitosan powder degraded and was observed to form of black particles that were clearly visible in solution (Fig. 2.19). Thus, because of negative influence of microwaves on chitosan degradation, we did not use this treatment in our further experiments.

Acidic media were also studied to see if they were successful at dissolving chitosan under relatively mild conditions (without heating). Water/IL solutions have different pH values dependent on the water content of the mixture. Thus after the pH measurement of the IL/water solutions the most acid solution was chosen for chitosan dissolution. In Table 2.5 we present the pH-values of the solutions studied (the water used had a pH 6.69).

Chitosan could be more effectively dissolved in 10 wt% BMIMAc/water solution, because of its higher acidity in comparison with the other solutions studied. Chitosan Primex and Polymar (1 wt%) were easy dissolved in BMIMAc/water solution, containing 10 wt% of IL, during 1.5h with magnetic stirring. Due the fact that MCCh has a bigger M_w than the others types of studied chitosan its dissolution times were longer. The concentration of 1 wt% of chitosan could be reached in 10 wt% BMIMAc/water solution during 2.5 h.

The water content of the obtained chitosan/IL/water solution was too high for mixing it with cellulose/IL solution, and an excess of water could precipitate cellulose from its solution. Thus water should be removed from the chitosan/IL/water system. Chitosan degraded fast at high temperatures, thus water should be removed at low temperatures under vacuum.

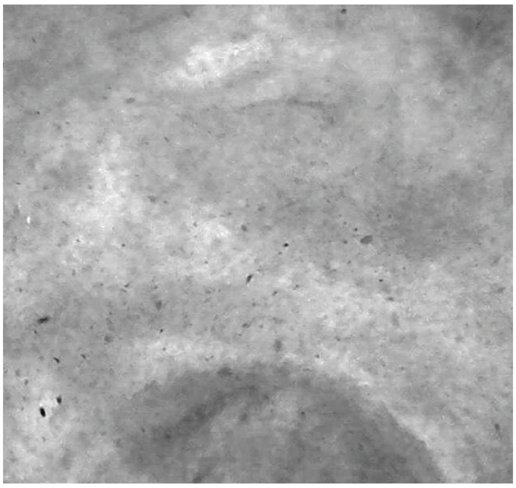


Fig. 2.19. Chitosan powder Primex degraded under microwave treatment in IL.

Table 2.5. The pH-values of the IL/water solutions studied.

IL	pH-values of IL/water solutions at ILs content, wt%		
	10	20	50
BMIMCl	6.85	6.75	6.27
BMIMAc	5.30	5.48	6.54
EMIMAc	6.17	6.36	7.73

Fig. 2.20 presented photos of chitosan/BMIMAc/water solutions and the chitosan/IL system obtained after water removing. An equal amount of cellulose/IL solution was added to chitosan/IL system after calculation the components ratio in obtained chitosan/IL solution. The sample was heated up to 50 °C to blend the polymer solutions without the degradation of chitosan. But even after heating during 24 hours at 50 °C, and even at 110 °C the blending of components was ineffective. The system was a heterophase gel material.

It was found that chitosan/ILs solutions could be obtained after heating at 110 °C for at least 4 hours. Blended solutions could be obtained upon mixing chitosan and cellulose solutions in a common solvent. Cellulose solutions were obtained as described previously (Kuzmina et. al, 2010) after heating at 110 °C for 2 hours.

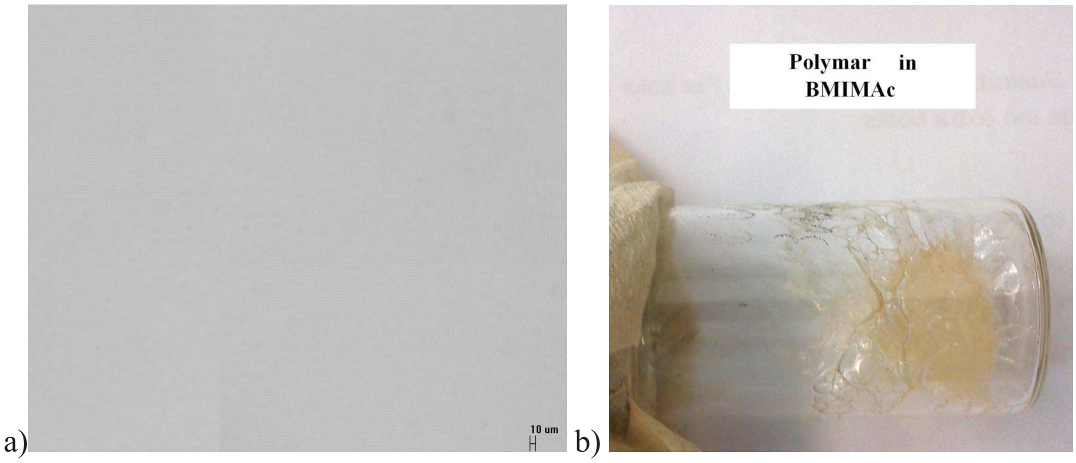


Fig. 2.20. Dissolution of chitosan in IL/water solutions: a)chitosan/BMIMAc/water solutions (example is given for Primex/BMIMAc/water system), b) chitosan/IL system after water removal.

Simultaneously mixing of components of a cellulose/chitosan/IL system by second method using solutions with 5 wt% of polymers content could be easily obtained after heating at 110 °C for 4 h. Few cellulose/chitosan blends were prepared in ILs EMIMAc and BMIMAc at the temperature of 110 °C. The solutions were heated for 4 hours, after that dissolution was confirmed by optical microscopy. Only in the solution with small chitosan content (Fig. 2.21) the dissolution progress could be noticed. The maximum ratio of components cellulose/chitosan/IL systems that were achieved was 4.5/0.5/95 independent on chitosan type, the ratio of polysaccharides was 90 wt% of cellulose to 10 wt% of chitosan.

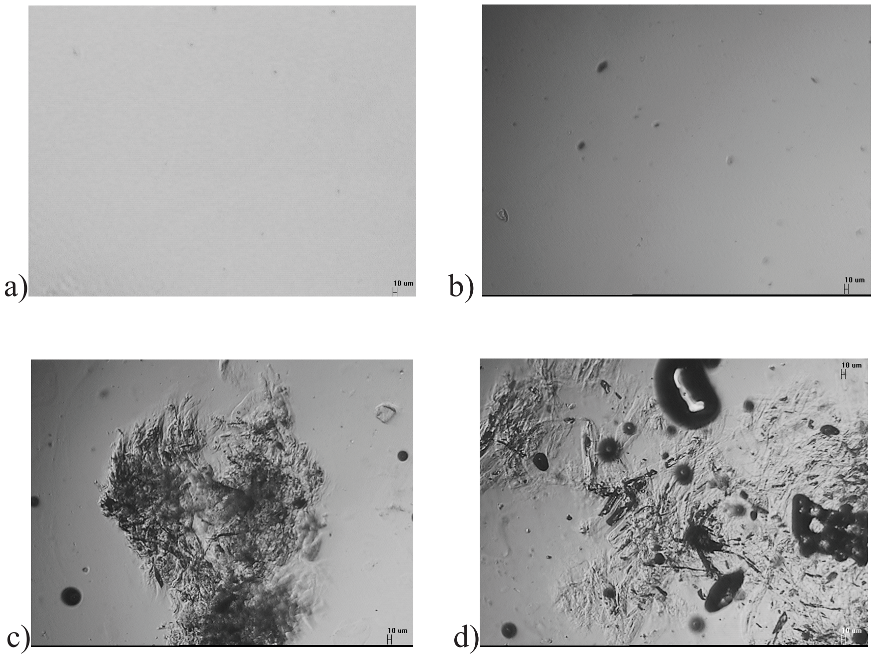


Fig. 2.21. The microphotos of cellulose/chitosan (Primex) blends in EMIMAc with different polymers ratio (cellulose:chitosan = a) 99:1; b)90:10; c)80:20; d)50:50) obtained by heating at 110 °C for 4 hours.

As described above (Kuzmina et al. 2011) it was found that the aprotic solvents DMSO, DEE and EAc were efficient thinners for cellulose dissolution in ILs. These three thinners were chosen to study for cellulose/chitosan solutions in order to facilitate the dissolution process and improve rheological properties of the studied solutions. In Fig. 2.22 the dependence of shear rate on viscosity of cellulose/chitosan solution in BMIMAc with thinners is shown. The example is given for cellulose/MCCh blend, other chitosan powders show the same behavior. It was found for cellulose/chitosan blend solutions that the addition of thinners decrease the viscosity of the blended solutions in ILs. The same dependence was found for cellulose solution in ILs (Kuzmina et al. 2011). Blended solutions both in EMIMAc and BMIMAc have very similar viscosity values.

The temperature dependence of viscosity was studied for cellulose/IL and cellulose/chitosan/IL solutions over the temperature range 273-373 K. In Fig. 2.23 is shown an example of the influence of temperature on viscosity for cellulose/EMIMAc and cellulose/chitosan (Polymar)/EMIMAc solutions with and without thinners addition. The addition of thinners decreases the viscosities of both solutions.

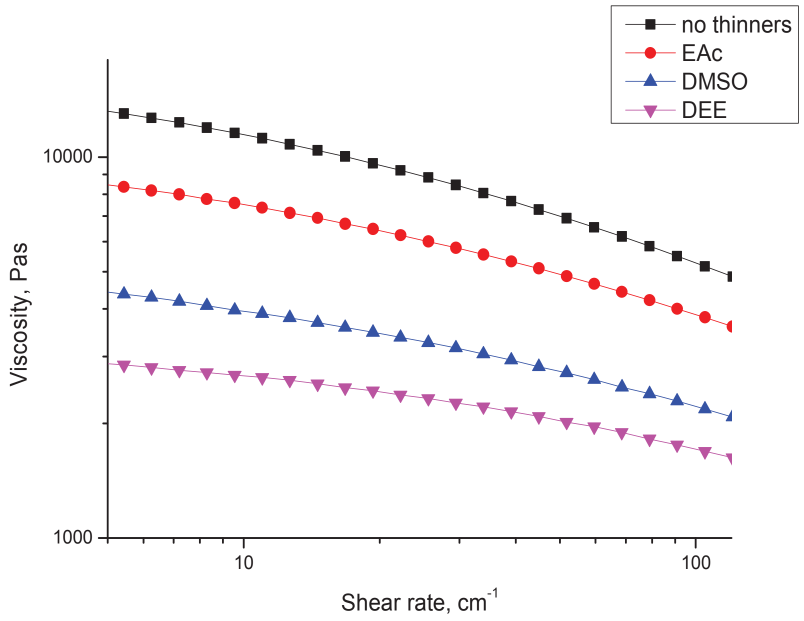


Fig. 2.22. The influence of shear rate on viscosity of cellulose/chitosan (MCCh) solution in BMIMAc with and without thinners at 110 °C. Ratio of components of cellulose:chitosan:BMIMAc:thinner systems is 4.5:0.5:90:5.

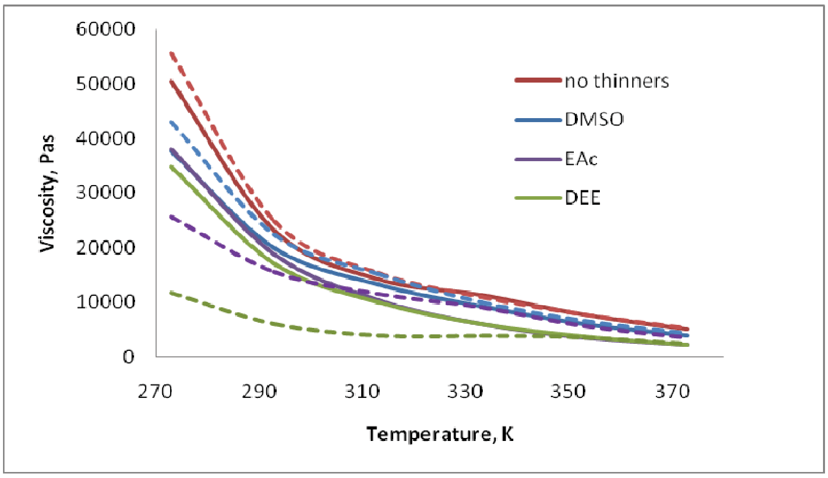


Fig. 2.23. The dependence of viscosity of 5 wt% cellulose solutions in EMIMAc with and without thinners (solid lines) and 4.5 wt% cellulose/ 0.5 wt% chitosan solutions in EMIMAc with and without thinners (dashed lines) on temperature. The concentration of thinners was 5 wt%.

Generally, cellulose/chitosan solution is more viscose that pure 5 wt% cellulose solution, but upon EAc addition the viscosity of the blended solution decreases dramatically and became lower than for pure cellulose solutions. Then the Arrhenius plot for calculating the activation energy (E_{act}) from the temperature dependence of viscosity of cellulose/chitosan solution with and without thinners was plotted (Fig. 2.24).

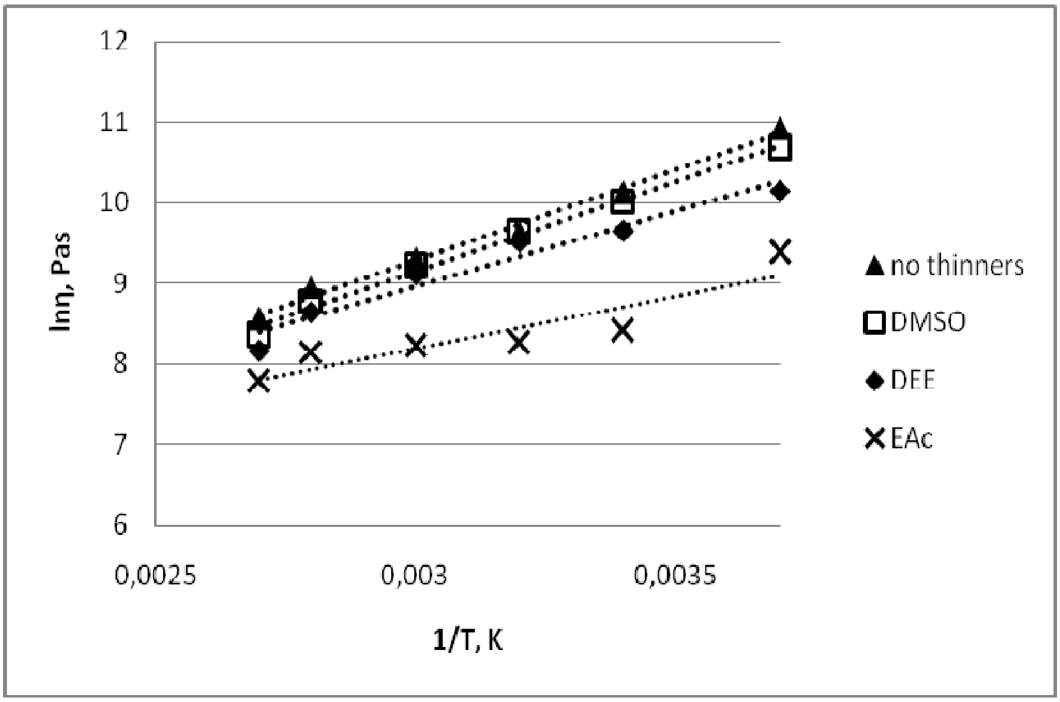


Fig. 2.24. Arrhenius plot for cellulose/chitosan blend solution in EMIMAc with thinners. Trend lines correspond to first Arrhenius approximation. Example is given for solution contained chitosan Primex.

Despite the fact that the plotted dependences weren't exactly linear, according to the literature (Gericke et al. 2011, Sescousse et al. 2010), the activation energies were calculated as a first approximation. The calculated E_{act} for cellulose/IL solution are presented in the Table 2.6. The calculated E_{act} for the cellulose/chitosan/IL solutions are presented in the Table 2.7. All cellulose/chitosan solutions in ILs had concentration as presented for the Fig. 4: 4.5:0.5:90:5 for cellulose:chitosan:IL:thinner solutions and 4.5:0.5:95 for cellulose:chitosan:IL respectively.

The larger is the value of E_{act}, the harder it is for the reaction, in this case- dissolution of polymers in ILs, to occur. E_{act} increases with polymer concentration (Gericke et al. 2011). Thinners added to cellulose/chitosan solutions at 5 wt% concentration decrease its E_{act} (Table 2.6, 2.7). As greater amounts of thinner were added to the solution, the lower the was E_{act} of this system (Table 2.6).

Table 2.6. The E_{act} of cellulose/EMIMAc solutions with and without thinners

Thinners	Thinner concentration, %	E_{act}, kJ/mol
DMSO	5	19
	15	18
DEE	5	19
	15	17
EAc	5	18
	15	16
No thinners	-	23

Table 2.7. The E_{act} of cellulose/chitosan (Primex)/IL solutions with thinners.

IL	Thinner	E_{act}, kJ/mol
EMIMAc	No thinners	24
	DMSO	21
	DEE	21
	EAc	19
BMIMAc	No thinners	27
	DMSO	25
	DEE	21
	EAc	20

The sizes of polymer aggregates were analyzed. In Table 2.8 is shown that the polymer aggregates sizes are bigger in EMIMAc solution than in BMIMAc solutions. The polymer aggregates size in cellulose solutions are smaller than in cellulose/chitosan solutions. The addition of thinners decreases the size of polymer aggregations in both IL solutions, which means the cellulose and chitosan molecules are better dissolved and the solutions with these thinners are more homogeneous.

Thus, ionic liquids EMIMAc and BMIMAc are suitable solvents to produce cellulose/chitosan blends by heating. Microwave treatment wasn't efficient for polymer dissolution. Simultaneous blending of components in solution (the second way), is more efficient than mixing of separately prepared chitosan and cellulose solutions in a common solvent (first way of preparation of blended solution) The addition of thinners decreased the size of polymer aggregates in ILs solution, the viscosity of cellulose and cellulose/chitosan solutions in ILs and the E_{act} of solutions.

Table 2.8. The sizes of polymer aggregates in the cellulose/chitosan (Primex) solutions with thinners in comparison to cellulose solutions in ILs.

IL	Thinner	Concentrations of components in the solutions, wt%				Aggregates sizes, nm
		cellulose	Chitosan	IL	thinner	
EMIMAc	-	5	0	95	0	419
	-	4.5	0.5	95	0	600
	DMSO	4.5	0.5	90	5	552
	DEE	4.5	0.5	90	5	203
	EAc	4.5	0.5	90	5	368
BMIMAc	-	5	0	95	0	197
	-	4.5	0.5	95	0	208
	DMSO	4.5	0.5	90	5	199
	DEE	4.5	0.5	90	5	196
	EAc	4.5	0.5	90	5	175

2.6. Producing of films from ILs solutions

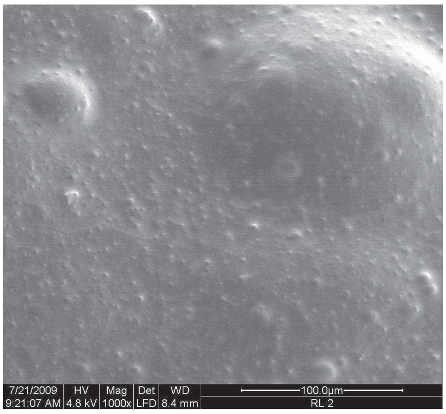


Fig. 2.25. Surface of cellulose film. 1000X.

Films were obtained from the studied solution of cellulose and cellulose/chitosan blends. In Fig. 2.25 a microscopic photo of the surface of a cellulose film obtained from 5wt% cellulose solution in EMIMAc is presented. The roughness on the surface of films shows that there are air pockets, as a result of incomplete air-removal from the solutions, because of its high viscosity.

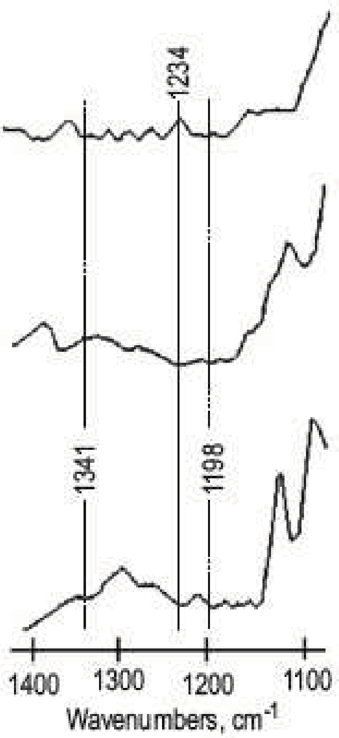


Fig. 2.26. FTIR spectrum of native cellulose (2) and film obtained from the solution in BMIMCl (1) and EMIMAc (3).

The film samples obtained from ILs solutions of cellulose with equilibrium water moisture were also examined by the FTIR method (Fig 2.26.). The absorbance spectra of the film are compared with the spectrum of the cellulose pulp. Very interesting peaks appear in the IR-spectra of cellulose film obtained from the BMIMCl solution at wave numbers of ~ 1198 - 1334 cm^{-1} and in the IR spectrum of cellulose film obtained from the solution in EMIMAc at wave numbers of ~ 1201 - 1341 cm^{-1}, characteristic of the symmetric stretching of the C-N group. The peak of the acetyl group stretching (1234 cm^{-1}) is also present in the spectrum of the film obtained from the EMIMAc solution. The appearance of these groups is evidence of the presence of solvent in the film. Macromolecules of cellulose strongly absorb the molecules of the ionic liquid, traces of which remain in the pulp, even after careful washing.

Different thinners, added to cellulose simultaneously with ILs at the solution preparation, influence on M_w and DP_w of films obtained in different ways (Table 2.9).

Table 2.9. The influence of the thinner on M_w and DP_w of 2 wt% cellulose films obtained from the cellulose/EMIMAc/thinner systems type I (with 10 wt% of thinner content) in comparison with cellulose/ILs solution.

System used for film preparation	M_w, g/mol	DP_w
Cellulose/EMIMAc/DMSO	98130	600
Cellulose/EMIMAc/DMF	93188	575
Cellulose/EMIMAc/FA	94149	581
Cellulose/EMIMAc/DEE	101682	606
Cellulose/EMIMAc/EAc	98533	608
Cellulose/EMIMAc/-	84913	524
Original cellulose	97027	599

Cellulose degrades somewhat during dissolution in ILs from DP = 599 to DP = 524. DMSO, DEE and EAc addition could help keep the same DP as for the initial sample. Generally the addition of thinners inhibits the degradation of cellulose during dissolution and coagulation processes in ILs. The thinner added change not only the properties of solutions, but the properties of the final product, too. The residue of these thinners could be kept in the cellulose films obtained from the spinning solutions.

Table 2.10. The shifts observed in the FTIR of cellulose films obtained from the solution type I and type II, belonged to the thinners used.

Thinner	Characteristic stretched groups	Characteristic bands (Kinugasa S, 2005; Silverstein et al. 2005) in		Bands observed in the films obtained, cm^{-1}
		Film	Solution	
DMSO	S=O-	1050	1050	1050
DMF	Valence vibrations N-H	-	2940-2852	2919-3013
EAc	Asymmetrical stretching C=O*	-	1743	1744
FA	Deformation stretching N-H	-	1686-1608	1429
DEE	Asymmetrical stretching C=O*	-	1126	1109

* These bands could also belong to acetate anion of EMIMAc.

- No information found

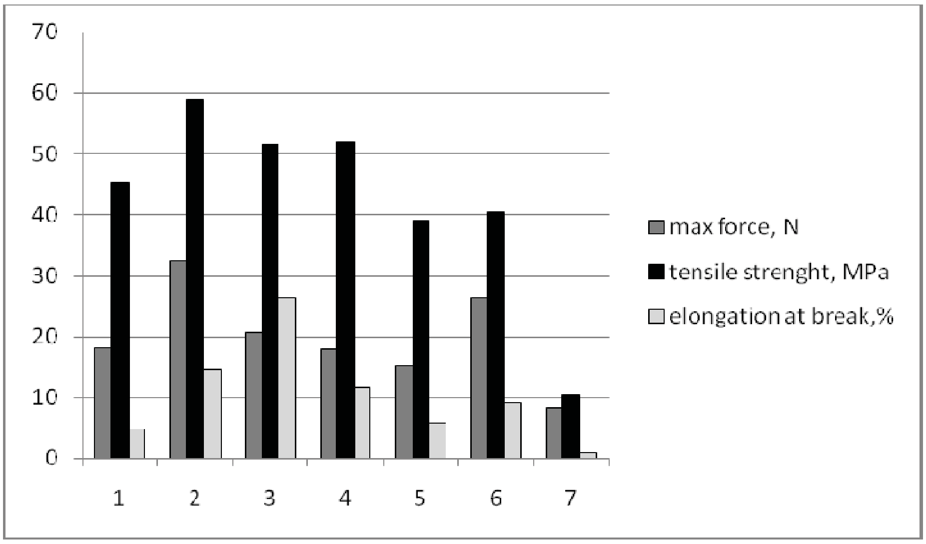


Fig. 2.27. Mechanical properties of cellulose films obtained from 5 wt% cellulose solutions in BMIMAc with 5 wt% of thinners content in comparison with 5wt% cellulose film from cellulose/BMIMAc solution. Films were obtained from the solutions in which thinners were added to cellulose simultaneously with IL (type I): 1) DMSO, 2) DEE, 3) FA; cellulose was pre-swelled with thinners (type II): 4) DMSO, 5) DEE, 6) FA; 7) no thinners.

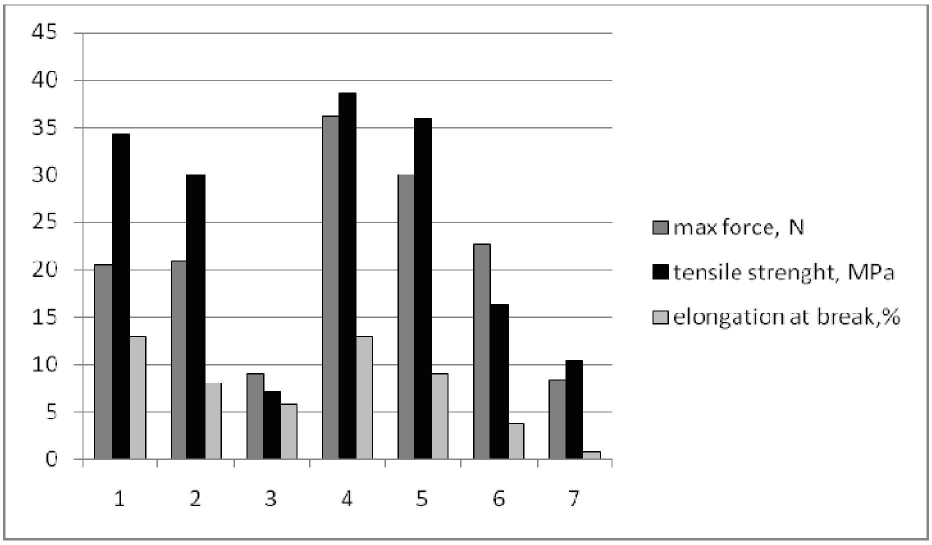


Fig. 2.28. Mechanical properties of cellulose films obtained from 5 wt% cellulose solutions in BMIMAc with 15 wt% of thinners content in comparison with 5 wt% cellulose film from cellulose/BMIMAc solution. Films were obtained from the solutions in which thinners were added to cellulose simultaneously with IL (type I): 1) DMSO, 2) DEE, 3) FA; cellulose was pre-swelled with thinners (type II): 4) DMSO, 5) DEE, 6) FA; 7) no thinners.

The films were obtained from the solution type I and type II (from solutions with composition corresponded to ones from Table 2.9). In both of cases, independent of the system types, the bands belonging to the thinners are noticeable at FTIR-spectrum of the films obtained. In the Table 2.10 the shift belonging to thinners are presented. Only in case of DEE and EAc thinners, which are evaporate from the solutions, the bands found may belong to acetate anion of ILs. These bands weren't found in films produced from BMIMCl solutions. It could be concluded that washing with water alone is not enough good remove ILs (Kuzmina et al. 2010) or the thinners.

The type of solvent and its quantity also affects the mechanical properties of the final product. Some mechanical properties of films obtained from these systems on example of 5 wt% cellulose solutions in BMIMAc with 5 wt% and 15 wt% of thinners content are presented at the Figures 2.27, 2.28.

The strongest films could be obtained with aprotic DMSO at low concentrations (5 wt%) added to cellulose simultaneously with IL or at high concentration (15 wt%) using DMSO as pre-swelling solvent. Generally the mechanical properties of the films obtained deteriorate with increasing thinner content. The mechanical properties of the films obtained from the high concentrated solution show the same behavior as already described for films obtained from diluted solutions.

Thus, both protic and aprotic thinners inhibit the cellulose degradation which is occur at it dissolution in ILs. DMSO, DEE and EAc adding could help keep the same DP as for the initial sample. The films with the highest mechanical properties could be obtained with using aprotic solvents. The mechanical properties of the films obtained became weaker with increasing thinner content. Aprotic solvents are more useful for cellulose films obtaining and facilitating the cellulose dissolution in ILs.

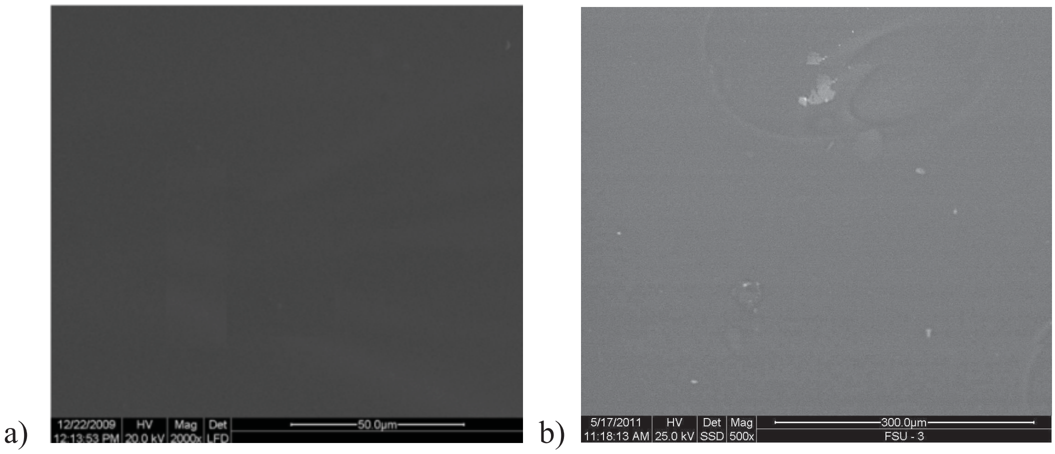


Fig. 2.29. SEM-photos of cellulose (a) and cellulose/chitosan (Polymar) (b) films obtained from 5 wt% cellulose solution and 4.5 wt% of cellulose and 0.5 wt% of chitosan blended solution in EMIMAc.

Cellulose/chitosan blended films were produced as final products from the studied solutions. Comparison of SEM photos of cellulose and cellulose/chitosan films shows worse quality and heterogeneity of blended film (Fig. 2.29).

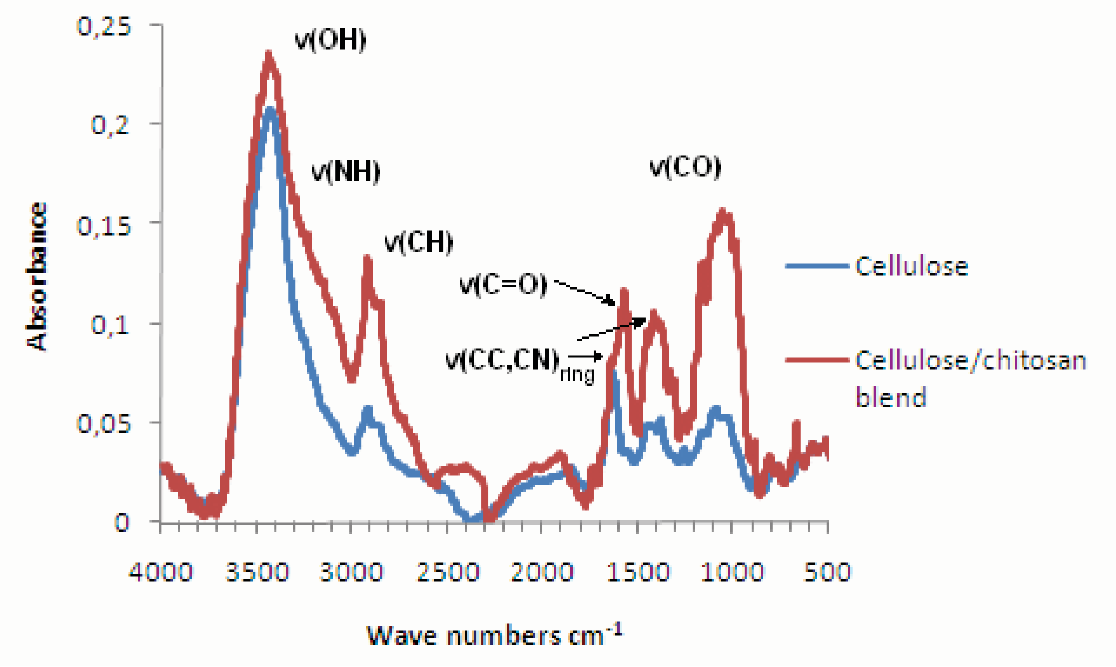


Fig. 2.30. Comparison of FTIR spectra of films produced from EMIMAc solutions: 1) cellulose film produced from 5 wt% cellulose/EMIMAc solution; and 2) blended cellulose/chitosan film produced from 4.5 wt% of cellulose/ 0.5 wt% of chitosan/EMIMAc solution.

Obtained blended films produced from the solutions with cellulose/chitosan solutions with concentrations 4.5 wt%/0.5 wt% consist theoretically of 90 wt% of cellulose and 10 wt% of chitosan. Not only the cellulose bands corresponded to the OH-stretching (3650-3200 cm^{-1}, 1200-1000 cm^{-1}) and C-H stretching (2900-2850 cm^{-1}, 1500-1300 cm^{-1}) were found in FTIR spectra (Fig 2.30) of blended films, but also the peaks corresponded to NH-bounding (3500-3250 cm^{-1}) of chitosan and C-C and C-N bonding of an imidazolium ring (1500-1700 cm^{-1}) were observed. All peaks corresponded to OH, CH and CO- stretching were much more intense for blended film than for pure cellulose. The presence of C-C and C-N stretching at 1500-1700 cm^{-1} at the spectrum of both films confirms the presence of ILs residues in the films after washing. The calculated from absorbance of FTIR peaks amount of ILs observed in cellulose film is 0,7%.

From DTG analysis we found that at cellulose/chitosan blended film degradation the 2 peaks are observed (Fig. 2.31). The first peak corresponds to chitosan degradation and the second to cellulose degradation (Fig. 2.32). The OH-degradation occurs in larger amounts, for example for cellulose film prepared from EMIMAc, water-products, which evaporate first, presented 8.00 % of mass, and for blended films 9.32 % (Fig 2.31).

The influence of polymers blending on cellulose degradation at producing of blended films was studied by means of GPC. The amount of extracted chitosan is about 3 wt%.

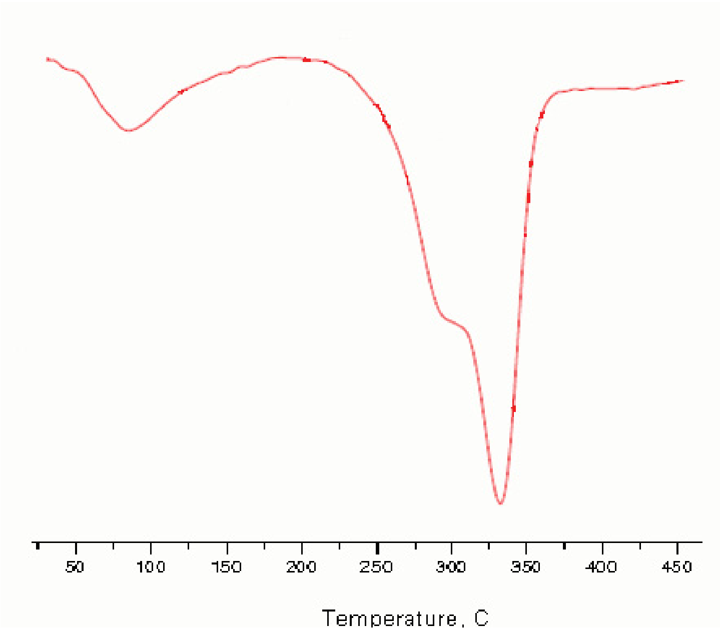


Fig. 2.31. DTG of cellulose/chitosan (Polymar) blended film, obtained from BMIMAc solution.

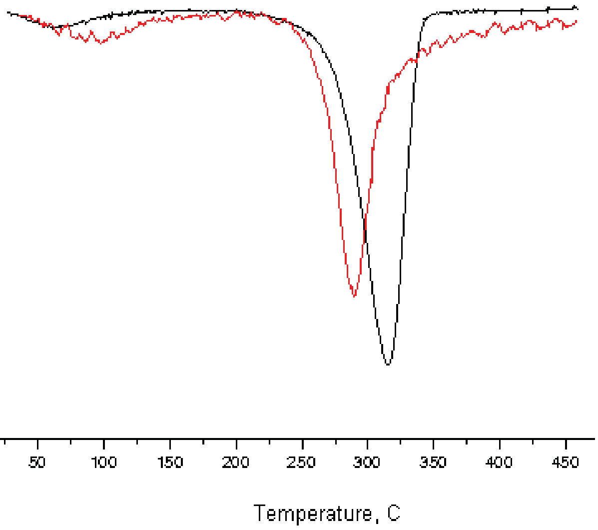


Fig. 2.32. DTG of cellulose (black curve) and chitosan Polymar (red curve).

After the analysis of the extracted cellulose part was found that the increase of chitosan content toward cellulose leads to a decrease of the cellulose DP in the produced blended films

(Table 2.11), that could lead to decreases in their mechanical properties. DMSO and DEE used as a thinners could improve the mechanical properties of blended films (Fig. 2.33).

Table 2.11. Influence of amount of chitosan (Polymar) in blended film on M_w and DP of its cellulose part degradation.

Components ratio in solutions for films producing			Analysis of cellulose part extracted from blended films.	
Cellulose	IL	Chitosan	M_w	DP
4.5	85	0.5	64681	399
4.9	85	0.1	69995	432

The molecular weight of chitosan decreases dramatically in solution in ILs. Upon its blending with cellulose in IL, chitosan degrades even more and thinners do not inhibit chitosan degradation, as they do for cellulose (Table 2.12).

Table 2.12. M_w of chitosan Polymar contained if blended films obtained from cellulose/chitosan/IL and cellulose/chitosan/IL/thinner systems.

Chitosan Polymer	M_w, kDa
Original chitosan powder	54.4
Chitosan obtained from films prepared from:	
chitosan/EMIMAc (0.5 wt% of chitosan) solution	12.4
4.5 wt% cellulose/0.5 wt% chitosan/EMIMAc solution	7.6
4.5 wt% cellulose/0.5 wt% chitosan/EMIMAc/ 5 wt% DMSO solution	7.4
4.5 wt% cellulose/0.5 wt% chitosan/EMIMAc/ 5 wt% DEE solution	6.9

It was found recently (Kuzmina et al. 2011) that DMSO improves the mechanical properties of cellulose films obtained from ILs solutions. DMSO addition has the same effect on the mechanical properties of the blended films (Fig. 2.33).

The blended film has an equal maximum force and elongation at break in comparison with cellulose film, but better tensile strength. Addition of DMSO and DEE improves the mechanical characteristics of the blended films, but addition of EAc decreases slightly its values. It was assumed that the dissolution of the polymer blends is very intensive in the presence of EAc and the molecular structure of polysaccharides is destroyed, which leads to decreases in the mechanical properties of the blended films.

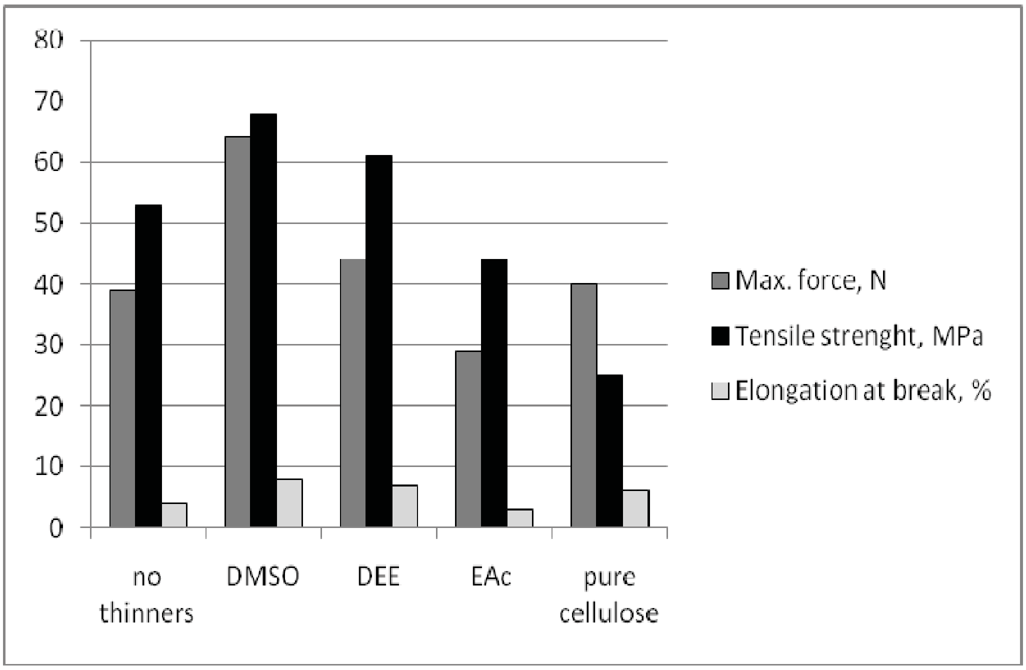


Fig. 2.33. Influence of thinners on mechanical properties of cellulose/chitosan (Primex) films, obtained from 4.5 wt% cellulose/0.5 wt% chitosan/90 wt% EMIMAc/5 wt% thinner solutions.

Thus, the blended films were prepared from the studied solutions. The increase of chitosan concentration in blends increased the degradation of the cellulose part. DMSO and DEE improve the mechanical properties of the blended films. Chitosan is a promising polysaccharide for cellulose modification, but the process of blend production in ILs still needs to be studied in more detail.

To improve the mechanical properties and facilitate the process of films obtained it is necessary to add the plasticizers to the wash-bath or to the spinning solutions. Glycerine, polyethylene oxide (POE-400) and their mixture were used as plasticizers, which could be added to the solution or to wash-bath.

The plasticizing agents were added to cellulose solution in concentration of 10%, in case of glycerine-POE mixture in concentration of 5% each. The mechanical properties of the film obtained using plasticizers for producing cellulose films from it 2 wt% solution in BMIMAc are presented in Fig. 2.34. Films obtained with adding of the mixture of plasticizing agents shows the optimal mechanical properties in comparison with others films studied, it shows the maximum tensile strength ~ 15 MPa, relatively good elongation at break ~ 12 % and relatively high maximal force ~ 12 N.

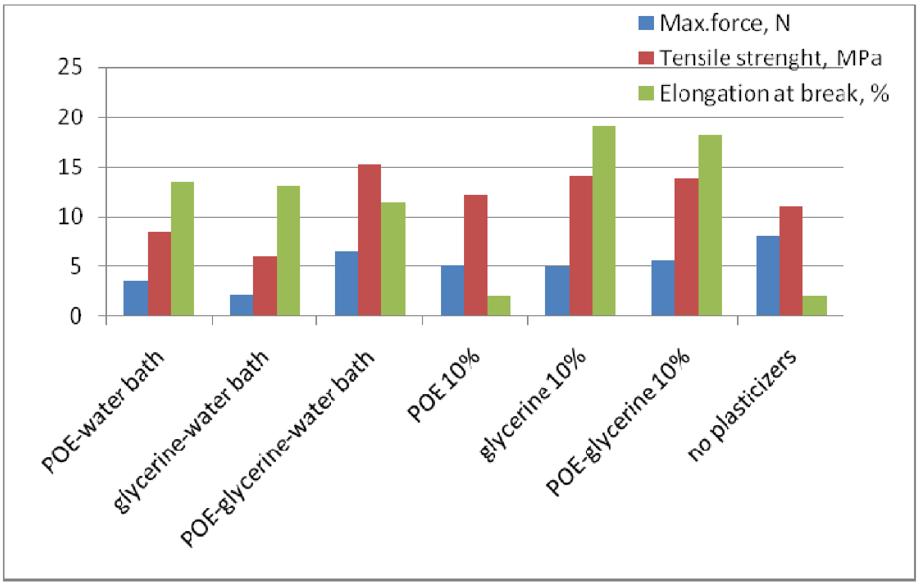


Fig. 2.34. Mechanical properties of cellulose films obtained from 2 wt% cellulose/EMIMAc solution.

Table 2.13. The data from TGA for cellulose films obtained from 2 wt% cellulose solution in EMIMAc with adding 10 wt% of glycerine/POE-400 mix to the spinning solution or to the wash-bath.

glycerine/POE-400 added to	T of the thermal decomposition, °C	T of the thermal destruction, °C
Solution	100,91	223,63
Wash-bath	54,97	334,24

By mean of TGA-IR analysis was found, that films obtained from the cellulose/IL solutions with 10 wt% of glycerin/POE-400 mix decompose when heated to isocyanates, carbon dioxide, formic acid and etc., films obtained with addition of plasticizers to the wash-bath are less thermostable than the films obtained from the spinning solution containing plasticizers (Fig. 2.35, Table 2.13).

Solutions of glycerin/POE-400 undergo thermal decomposition in three stages, first- loss of water, second-loss of isocyanates and finally, full destruction (Fig. 2.35, a). If glycerine/POE-400 mix was added to the wash-bath the second stage is absent at thermal decomposition (Fig. 2.35, b). This minimizes emissions, thus the adding of plasticizers to wash-bath is more preferable.

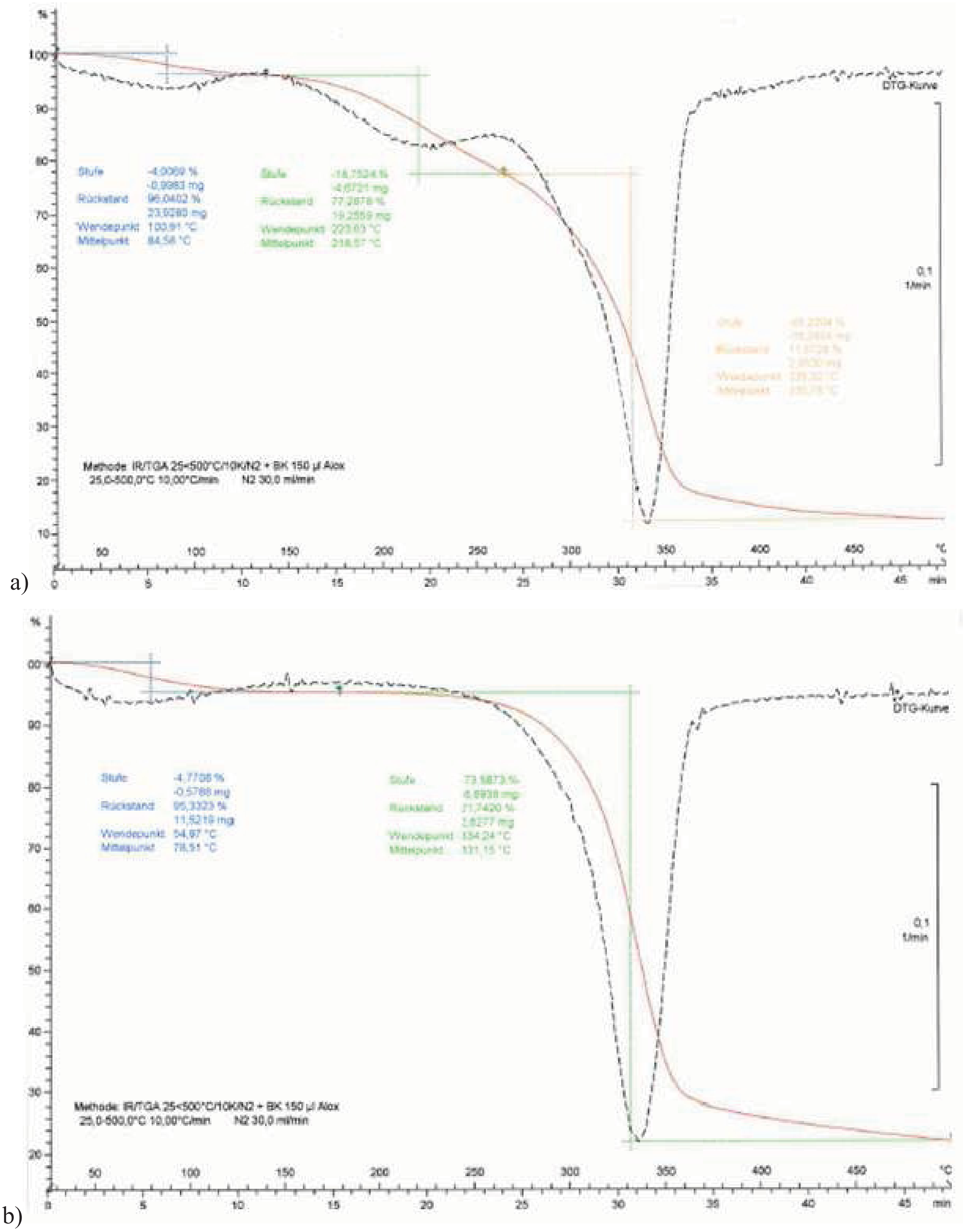


Fig. 2.35. The TGA curves of the films obtained from the 2 wt% cellulose solution in EMIMAc with plasticizing agents added to: a) spinning solution, b) wash-bath.

2.7. Recovery and reuse of ILs.

5 wt% cellulose pulp can be dissolved in BMIMCl during 6 hours at 100 ˚C (Fig. 2.36) or in 2 hours at 120 ˚C. But at 100 ˚C the same concentration could be achieved in EMIMAc in 4 hours. EMIMAc faster dissolve cellulose and less decrease its DP at dissolution and coagulation (Table 2.14).

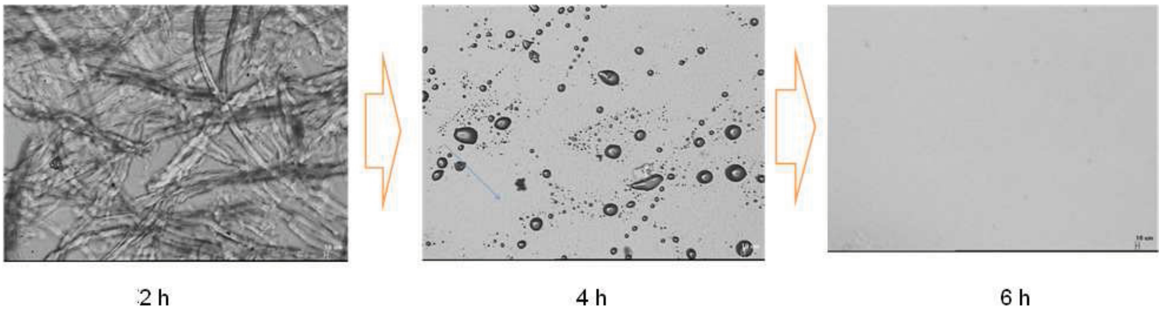


Fig. 2.36. Dissolution of cellulose pulp in BMIMCl at 100 °C during 6 hours.

The DP of origin cellulose was 599, and after dissolution in ILs its DP decreases, more in BMIMCl than in EMIMAc. The DP of dry cellulose after dissolution in BMIMCl decreases dramatically from 599 to 25. At the same conditionals, described in Table 2.13, DP of cellulose dissolved in EMIMAc decreases only to 280. It is important to keep the high level of DP of coagulated cellulose, because it can influent the properties of final product. Thus, was concluded that EMIMAc is a more efficient and preferable solvent for cellulose dissolution and reformation.

Table 2.14. Decreasing of cellulose DP at 24 hour heating in ILs. DP of original cellulose is 599.

IL	Cellulose moisture, %	DP of cellulose, dissolved at		
		100 ˚C	110 ˚C	120 ˚C
BMIMCl	0	173	90	25
	8	213	205	189
EMIMAc	0	353	314	280
	8	428	417	387

After cellulose coagulation the water wash-bath was analyzed. The presence of sugars in wash-bath indicates the degradation of cellulose. As it might be predicted, the sugar content increased with increasing of time and temperature of dissolution process. The dependence of sugar content in the wash-bath from cellulose dissolution time is almost linear. Much more sugar was found in the wash-bath of the preliminary dried cellulose after its dissolution during long times (Fig. 2.37).

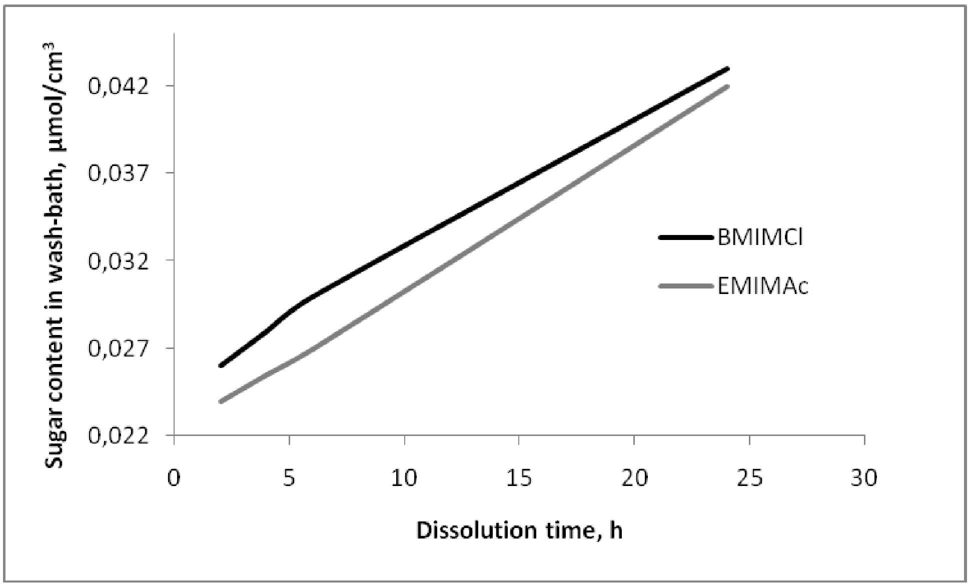


Fig. 2.37. Sugar content in wash-bath after cellulose coagulation. Cellulose with 0 % of moisture was dissolved at 120 ˚C.

The FTIR analysis of coagulated cellulose shows slightly differences between samples of cellulose dissolved at different temperatures. Cellulose coagulated after dissolution in higher temperatures has more intensive absorbance peaks of free and bounded OH-groups stretching at 3400-3600 cm^{-1}, stretching of aromatic compound at 2900 and 1600 cm^{-1}, stretching of others group corresponding to IL-ring (C-C and C-N stretching at 1700-1500 cm^{-1}) (Fig. 2.38). In a spectrum of pure cellulose, there should not be much absorption in the region 1700-1500 cm^{-1}. Cellulose on its own has only a small band at ~ 1630 cm^{-1} due to the dOH deformation. The increasing of intensivity of absobtion in this area confirm the presents of chitosan in blended film. The FTIR spectrum of the wash-bath is very similar to that of water (Silverstein, 2005) (Fig. 2.39) with symmetrical stretching of OH-groups at 3652 cm^{-1}, asymmetrical stretching at 3756 cm^{-1} and scissoring at 1596 cm^{-1}. The 3 small bands at 1800, 1440 and 1200 cm^{-1} may stem from dissolved BMIM cation.

The presence of ILs in cellulose after coagulation could be undesirable for future applications of the cellulose product. Quantitative FTIR analysis showed that there could remain up to 3 % of IL and up to 0.05 % of thinners in the cellulose films. It is therefore necessary to improve the wash-bath for more efficient removal of solvents. ILs could be recovered from the wash-bath by distillation. A simple distillation process for the water bath allows the recovery of ILs with water concentrations as low as 7 - 11 wt%. Recovered ILs have the same dissolution ability as fresh ones with the same water content (Table 2.15).

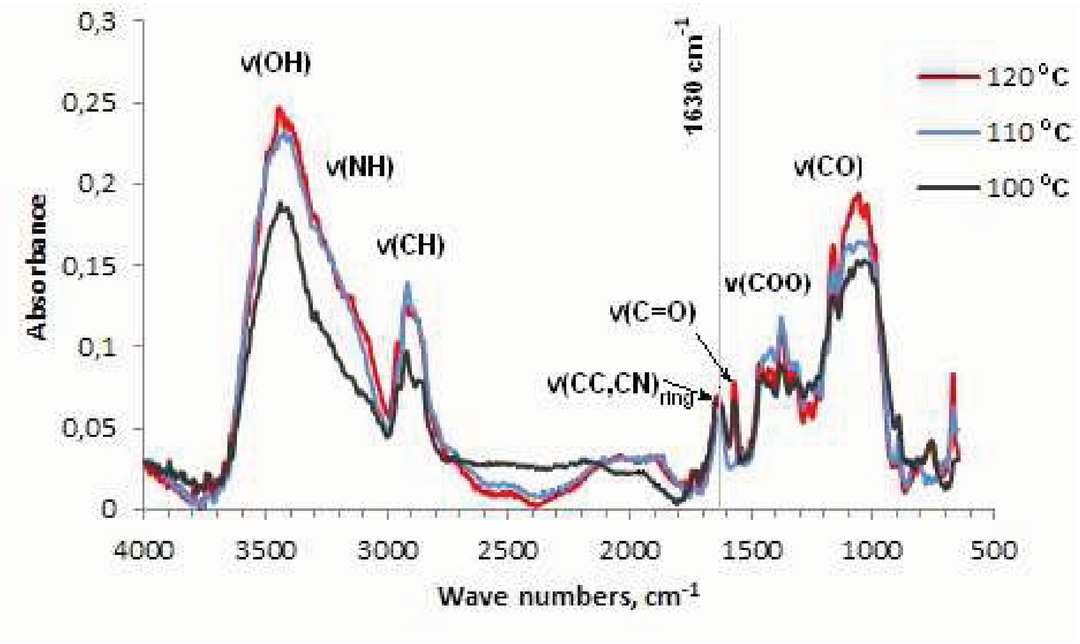


Fig. 2.38. FTIR spectra of cellulose dissolved in BMIMCl in different temperatures.

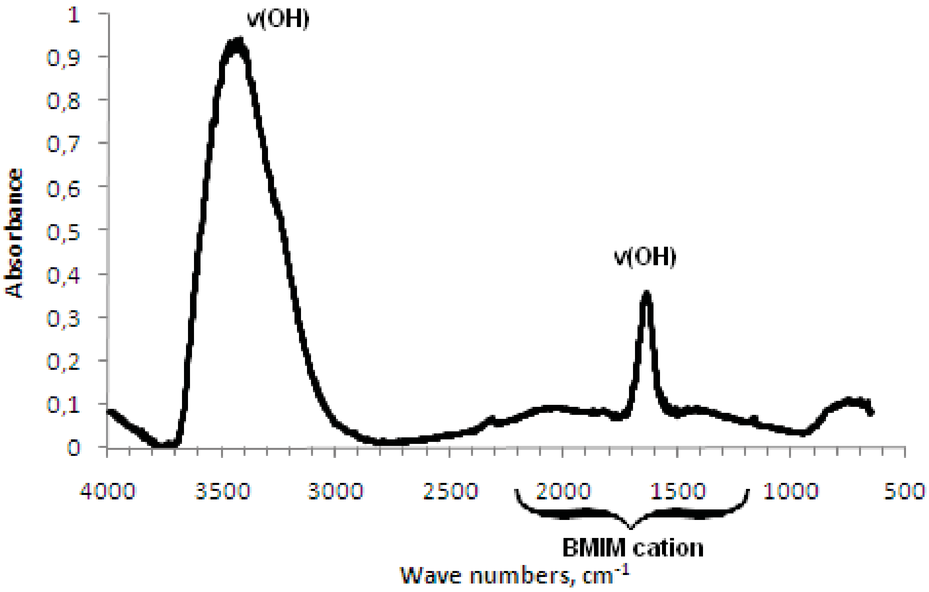


Fig. 2.39. FTIR spectra of wash-bath after cellulose coagulation. (Cellulose was dissolved in BMIMCl solution at 110 ^{o}C).

Table 2.15. The maximum concentration of cellulose which could be dissolved in recovered and fresh EMIMAc.

IL	Max. cellulose concentration (wt%) at ILs water content	
	7 %	10 %
Fresh	11	5
Recovered	11	5

During the distillation process, the water is removed but sugars and impurities remain in the IL. That could influence the final properties of the cellulose product. In Fig. 2.40 the comparison of mechanical properties of films produced from 5 wt% cellulose solutions in fresh and recovered EMIMAc are presented. The mechanical properties of the film produced from recovered IL are weaker, especially in terms of their tensile strength. This confirms the negative influence of impurities, kept in ILs and the necessity to further study the recovery process.

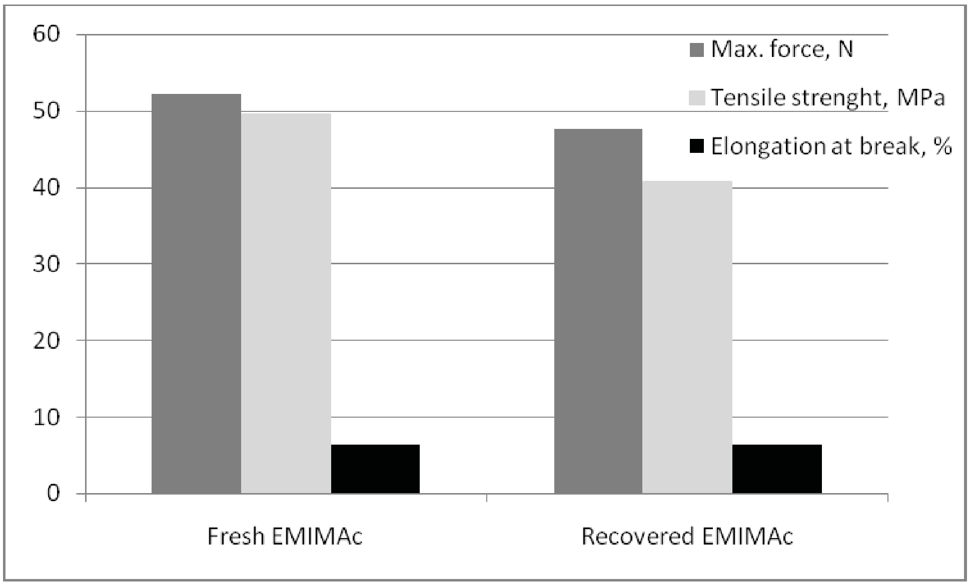


Fig. 2.40. Mechanical properties of films produced from 5 wt% cellulose solutions in fresh and recovered EMIMAc.

Thus, very little sugar residues were found in the wash-bash, its amount increases slightly at longer dissolution times. The traces of ILs were observed in FTIR spectra of cellulose films, thus water alone is not efficient at removal ILs during cellulose coagulation. It is possible to recover ILs from the water-bath by distillation. Recovered ILs have a moisture content of about 7-11 %, and despite the same dissolving ability, the mechanical properties of the films obtained from recovered ILs are worse than those obtained from fresh ILs.

3. Experimental part

3.1. Materials

Alicell-Super cellulose produced by Port Alice B.P., is a high purity, wood derived chemical cellulose. Western hemlock, the predominant species of the region, permits easy pulping by the acid sulphite system. A blenching process gives a pulp of high brightness, uniform viscosity and controlled alpha level. Typical analytical properties of Alicell-Super are represented in table 3.1. Cellulose was mechanically dispersed during the pulping process to make the dissolution process easier and faster.

Table 3.1. Typical properties of Alicell-Super

Property	Value
Calculated alpha content, %	93.5
ISO brightness, %	91.0
Density, g/sm^3	0.77
Oven dry, %	93.0

Chitosan Polymar (Brazil), chitosan Primex Chito-Clear FG 90 after NaOH-washing and Microcristaline chitosan (MCCh). Typical analytical properties of Alicell-Super are represented in table 3.2.

Table 3.2. Typical properties of used chitosan.

Chitosan	M_w, g/mol	moisture content, %	deacetylation degree (DA), %	ash content, %	nitrogen content, %
Polymar	54400	9.70	76.90	3.10	6.90
Primex	121500	10.75	83.20	0.40	6.84
MCCh	341800	10	83	0.40	6.84

1–butyl–2,3–dimethylimidazolium chloride (BDMIMCl), 1–butyl–3–methylimidazolium chloride (BMIMCl), 1–ethyl–3–methylimidazolium acetate (EMIMAc) and 1–butyl–3-methylimidazolium acetate (BMIMAc) were obtain from Merk KGaA, Germany, and were used without any pretreatment.

Methanol, purity 100%; ethanol (antibacterial line) 96% from Linegal Chemicals Co. Ltd.; dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), formamide (FA), diethyl ether (DEE) and ethyl acetate (EAc) from POCH, Poland. Glycerine from POCH, Poland; polyoxyethylene (POE) – 400, from "Rokita", Poland; Solvent for NMR: Dimethyl-d_6 sulfoxide (DMSO-d_6) from Sigma-Aldrich, Germany. The characteristics of used thinners are presented in the table 3.3.

Table 3.3. The characteristics of thinners had chosen (Lowry et al., 1987; Markus, 1993; Moskva, 1999; Gericke et al. 2011).

Characteristic	Dimethyl sulfoxide	Dimethyl-formamide	Formamide	Ethyl acetate	Diethyl ether
Molecular formula	C_2H_6OS	C_3H_7NO	CH_3NO	$C_4H_8O_2$	$(C_2H_5)_2O$
Molar mass, g/mol	78.13	73.09	45.04	88.11	74.12
Density, g/cm^3	1.1004	0.944	1.133	0.9	0.7134
Melting point	18.5 °C	-61 °C	2-3 °C	-83 °C	-116.3 °C
Boiling point	189 °C	153 °C	210 °C	77 °C	34.6 °C
Solubility in water	Unlimited	Unlimited	Unlimited	75g/l	69 g/l
Viscosity at 20 °C, cP	1.996	0.92	3,75	0.426	0.224
Donor number	28.0	26.6	24.0	17.1	19.2
Acceptor number	19.3	16.0	39.8	9.3	3.9

3.2. Methods

3.2.1. Method for cellulose pulp drying

The pulp was dried in an oven at 105 ^oC for 4 hours to get a water content of about 4%.

To obtain less moisture of cellulose it was dried with using of alcohols (such as methanol and ethanol). Cellulose pulp was put in a glass vial and filled with alcohol. After that, cellulose with alcohol were stirred for 10 min. The pulp was then filtered via vacuum filtration and dried in an oven with infrared lamps at 115 ^oC. The duration of drying was from 4 to 6 hours depended on the required water content value of the cellulose from 0,2 – 3 %.

3.2.2. The water retention values (WRV) analysis

WRV was determined by international standard ISO/FDIS 23714:2006 (E). A test pad consisting of pulp fibres is formed by drying a pulp suspension on a glass- fibre filter. The test pad is centrifuged under a specified centrifugal force (4000 g) for a specified time (10 min), weighed, dried and weighed again. The water retention is calculated from the wet mass of the centrifuged test pad and dry mass of the test pad, Equation 1.

$$WRV = (\frac{m_1}{m_2} - 1)\,, (\%) \qquad \text{Eq. 1}$$

m_1 - wet mass of the centrifuged test pad,
m2 - dry mass of the test pad

3.2.3. Assessment of cellulose and chitosan water content

Data on the water content of polymers was obtained by the weight-drier - apparatus WPE 30S. Apparatus WPE 30S was used for polymers, in which the content was more than 1% of water. Karl Fisher's method was used for more precise data if expected cellulose moisture was less than 1%. Karl Fisher (KF) titrater has drying oven with temperature range 50- 300 ^{o}C (temperature used for drying cellulose is 100 ^{o}C), and titration cell. The mixing time was 30 min.

3.2.4. Assessment of α-cellulose content

Cellulose samples of about 3 g were swollen in 17.5% NaOH-solution during 15 min at 20 ^{o}C. After that 15 ml of distilled water was added. The solution was mixed and the mass washed with 750 ml of cold water subsequently was washed twice with 30 ml of 10%-solution of CH_3COOH. Finally the mass was washed with 750 ml of hot water. The obtained cellulose mass was dried at 103±2 ^{o}C till constant weight. Content of α-cellulose was calculated with Equation 2 according to the literature (Modrzejewski et al., 1977).

$$\alpha = \frac{m_1 - m_2}{m_2 * s} * 100 * 100\,,\ (\%) \ \text{Eq. 2}$$

m_1 = mass of the dry pad, g
m_2 = mass of the start pad, g
s – dryness, %

3.2.5. Preparation of cellulose solution in ILs

Cellulose was dissolved in ILs at up to 110°C for 1-5 h. Cellulose solutions with thinners were produced in 2 ways: thinners were added to ionic liquids simultaneously with cellulose and heated at 110°C with periodical mechanical stirring (system type I) or cellulose was pre-swollen with thinners at room temperature and then dissolved in ILs at 110°C with periodical mechanical stirring (system type II). The time of cellulose swelling in thinners was varied from 10 min to 24 hours. Temperature treatment was held till cellulose completely dissolved, dependent on the thinner – from 45 to 100 min. To equate the conditions for all of the studied systems, the total time of temperature treatment was prolonged for all of the solutions till 2 h. Triple systems with cellulose concentration 2-5 wt% were produced. Thinner content in the systems was from 0 to 15 wt%. Turbidity, being an indicator of complete dissolution, was confirmed with an optical microscope.

3.2.6. Preparation of blended solutions in IL

The blends of cellulose and chitosan were obtained by 2 methods: simultaneously mixing of cellulose, chitosan and ILs or separately preparation of polymers solutions in IL with its subsequent mixing. First chitosan powder was dissolved in selected ILs at room temperature, 50, 75 and 110 ^{o}C using an oil-bath (to evacuate the ambient moisture) over a period of 4 h with periodical mechanical stirring. Chitosan in IL/thinner systems was dissolved at the same temperatures. Microwave treatment was also tried to improve the dissolution of polysaccharides in ILs. Blended polysaccharides were tried to dissolve in ILs using oil-bath at different temperatures during 4 hours with periodical mechanical stirring.

3.2.7. Preparation of high concentrated cellulose solutions (TITK method)

A pre-weighed mass of cellulose pulp was mixed with EMIMAc:H_2O = (3:1) or EMIMAc:thinner = (3:1) mixture, stirred and left swelling for 12 hours. Afterwards, the suspension was poured into a horizontal kneader, vacuum closed and heated by means of a thermostat with mineral oil running through its coating jacket. The water was removed by gradually raising the temperature from 20 ^{o}C up to 110^{o}C at a vacuum of 30 mbar and constant stirring rate of 40 rpm.

3.2.8. Viscosity measurements

Viscosity measurements were carried out with a Rheometer (Rheologica Instruments Inc.) in the plate-plate system. The volume of the sample was 2 ml. Viscosity measurements carried out with a shear rate in the range of gradient 5 - 120 s^{-1} (at 110 ^{o}C) and temperature heating from 0 to 110 ^{o}C at constant shear rate.

3.2.9. Dynamic Light Scattering (DLS)

Zetasizer Nano (Malvern Instruments Ltd., UK) was used for determination polymer aggregates size at 85 °C. The size range measured by this apparatus is 10^{-9} – 10^{-5} m. Quartz square glass cuvettes were used instead of polystyrenes ones, because of the high temperature of our experiment.

3.2.10. Method for cellulose and blended films obtaining

Cellulose and cellulose/chitosan films were obtained from solutions with or without deaeration at 105 ^{o}C in vacuum. Solutions were cast onto a warm glass plate, were smoothed with a glass stick to obtain a thickness in 0.5, 1.0 or 2.0 mm, and put into a water bath to remove solvent. All solvents utilized are miscible with water. Solvent removal was carried out in water in a tub, with a at least 30 minutes between each of 3 washes.

3.2.11. Determination of average polymerization degree (DP)

The DP of cellulose was measured with cupri-ethylene-diamine (CED) methods according to ISO 5351/1:1981, with iron (III) sodium tartrate complex solution (EWNN $_{\text{mod NaCl}}$ method) and with GPC (Gel Permeation Chromatography).

1) Method in cupri-ethylene-diamine (CED) solution

25 ml of the cupri-ethylene-diamine solution were mixed with 25 ml of distilled water. After thermal stabilization at 25 ^{o}C, the viscosity of a solvent was measured. The expected viscosity was about 550 ml/g. Chosen concentration of cellulose solution is 0.0025 g/ml. 25ml of distilled water was added to a sample, together with 2 g of copper. It was shaken until the samples has been completely disintegrated. Then 25 ml of CED solution was added, and this was shaken for 2 h, and put in the constant-temperature bath until the temperature of 25±0.1 ^{o}C has been

reached. The efflux time was determined both for the solvent and for cellulose solution. DP and limiting viscosity number were calculated according to Equations 3 and 4.

$$DP^n = K \cdot [\eta] \quad \text{Eq. 3}$$

n = 0.905

K = 0.75

[η] = limiting viscosity number

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{\eta_0 \cdot c} \right) \quad \text{Eq. 4}$$

2) Method in EWNN- solution

EWNN was prepared first with using of ferric chloride hexahydrate ($FeCl_3*6H_2O$), sodium tartrate dehydrate [$Na_2(C_4H_4O_6)2H_2O$], sodium hydroxide solution, containing 96.0 g of sodium hydroxide (NaOH) per 180 ml of water.

217.09 g of the sodium tartrate and 550 ml of distilled water were put into the stainless steel container (fig. 3.2). Sodium tartrate was dissolved with vigorous stirring. Then 81.09 g of iron (III) chloride was added. The solution was mixed until completely dissolving of reagents. Ice-bath was made to maintain the temperature of solution less that 20 ^{o}C during the addition of the sodium hydroxide solution. The EWNN solution is light green and fully transparent.

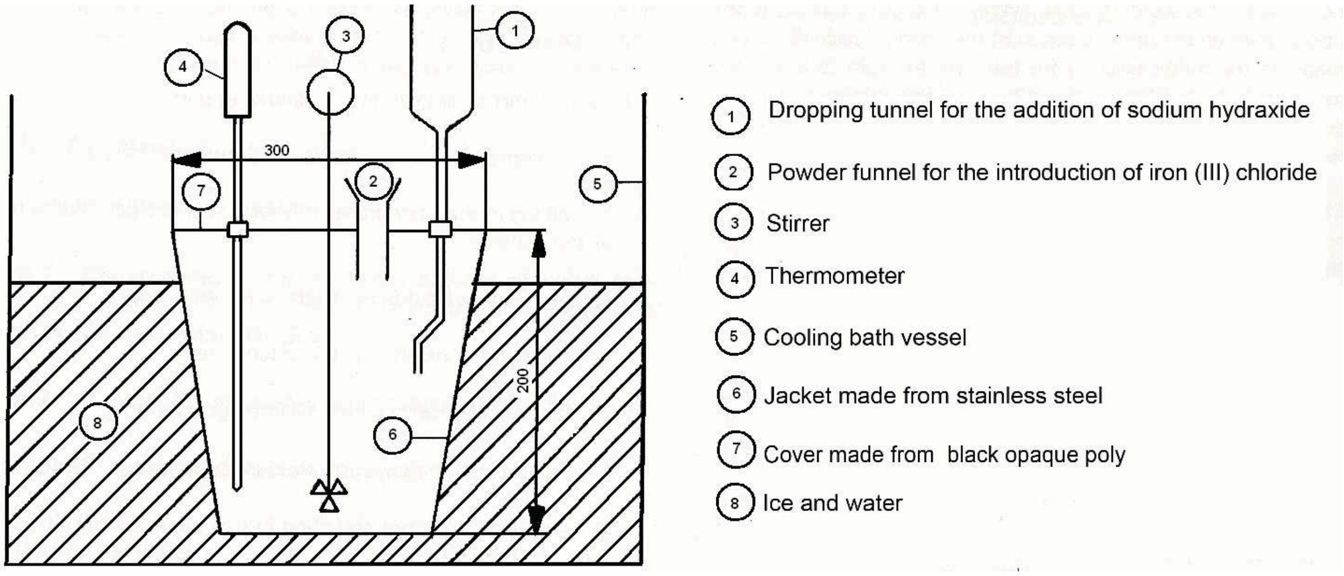


Fig. 3.1. Apparatus for preparation of iron (III) sodium tartrate complex solution

50 ml of EWNN solution was added to the sample (weight about 0.1g), it was shaken for about 16 h by a shaking machine. The efflux time was determined both for the EWNN solution and for the cellulose solution in EWNN.

3.2.12. Gel Permeation Chromatography (GPC)

Number and weight molecular weights (M_n and M_w), polydispersity (Pd), polymerization degree (DP) of the pulp and films were determined by this method.

The weight of the samples was about 0.02g. Distilled water was added to samples and then samples with water were put into cold storage (to avoid a degradation processes) for 20 h. After excess water was removed push-ups with textiles. 20 ml of DMAC solution was added and solution was twice heated in a microwave oven. 8.3%LiCl/DMAC solution was added to the pulled samples. Than samples were left for 24 hours, after which, DMAC was added to the obtained cellulose solution to obtain a total volume of 10 ml. Obtained solution was diluted with DMAC to the ratio 1:2, and heated in a hot water bath (T= 60-70 ^{o}C) for 15 min. For future research it is necessary to select a sample of 2 ml, which will be injected into GPC-apparatus.

The data were obtained from four solutions with one GPC run per one solution. The parameter values of the Mark-Houwink equation were used for calculation: for polystyrene standards a = 0.65 and K = 17.3×10^{-5} ml/g, and for cellulose a = 1.0 and K = 12.78×10^{-5} ml/g.

The GPC system consists of a DG-700 degasser (Viscotek, Houston Texas USA), HP 1050 pump (Hewlett-Packard, Waldrom, Germany), a sample injector (Rheodyne Inc. Model 7125 Cofati Taxas USA), on-line filter (2 µm), a set of 3 columns PLgel Mixed A (300*7.5mm) with a guard column (Polymer Laboratories Ltd. Shropshire, UK), differential viscometric detector H502B Viscotek, Texas USA) and refractive index detector HP 1047 (Hewlett-Packard).

Chromatographic parameters: eluent - DMAC/0.5 % LiCl; temperature of columns set 80^{o}C; flow rate of the eluent 1.0 ml/min; volume of the injection 100 µl; concentration of cellulose solution ~0.7 mg/ml

3.2.13. Scanning electron microscope analysis (SEM)

The SEM observations of films were carried out with a Quanta 200 SEM from FEI at a magnification of 2000x. Structural investigations were performed under a high vacuum, in a natural state, without sputter coating.

3.2.14. Fourier transform infrared spectrometry (FTIR)

Fourier transform infrared spectroscopy (FTIR) was made with apparatus Genesis Series FTIR^{TM} (Unicam ltd.). The measurements were provided in the mid-infrared region, approximately 4000–500 cm^{-1}, used to study the fundamental vibrations and associated rotational-vibration structure.

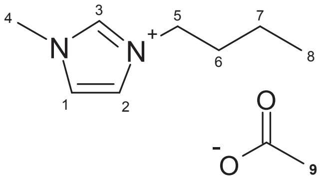
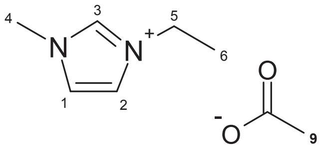
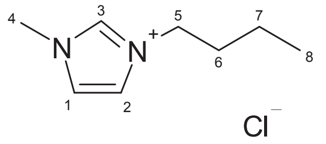
The method of samples preparation is to grind a quantity of the sample with a specially purified salt (potassium bromide). This powder mixture is then pressed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass. Calculations of ILs remained in cellulose films were provided according to quantitative method described in literature (Smith, 1981).

3.2.15. Solution Retention Value (SRV)

The volumes of liquor retained in fibers (SRV) were determined from fiber weights after centrifugation and their initial dry weighs derived from their conditioned weights and moisture content, as described in literature (Quan et al., 2010) at 20 °C.

3.2.16. Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

Table 3.4. Structures of the selected ILs, with hydrogen atoms marked as observed in ^{1}H NMR

IL		Chemical structure
BMIMAc	1-n-butyl-3-methylimidazolium acetate	
EMIMAc	1-ethyl-3-methylimidazolium acetate	
BMIMCl	1-n-butyl-3-methylimidazolium chloride	

Proton nuclear magnetic resonance spectroscopy (^1H NMR) measurements were determined with Spectrometer NMR Avance II plus 700MHz, Bruker, Germany. The temperature in the probe, where the sample sits, is controlled by a variable temperature controller and is typically set to 25-27°C. Samples require deuterium solvent for a lock signal. Deuterated DMSO (DMSO-d_6) was used as the deuterium containing solvent. As the NMR chemical shifts depend on the concentration of the IL, samples were at a concentration of 15 mg/ml. The protons in ^1H NMR spectra were indicated according to Table. 3.4.

3.2.17. Mechanical measurements

The thickness of the films obtained was measured with micrometric screw. Max force, tensile strength and elongation at break of the films obtained were measured with "Instron-5544" apparatus. With speed 10mm/min, and samples 10x15mm according to ISO 527-3:1998.

3.2.18. Thermogravimetric analysis (TGA)

TG-analysis was performed using a heating rate of 25 °C/min in a temperature range between 20 to 500 °C.

3.2.19. Thermogravimetry with Infrared-Coupling (TG-IR)

TG-IR analysis does not require any kind of sample preparation; the amount of sample has to be weighed before analysis. TG-IR analysis was performed using a PYRYS TGA thermo-balance infrared via a data transmission link to a FTIR Spectrum 2000 infrared spectrophotometer. Samples were heating with heating ramp of 25 °C/min in a temperature range between 25 and 500 °C.

3.2.20. pH-measurements of IL/water solutions

pH-measurements of IL/water solution with IL content 10, 20, 50 wt% were provided with pH-meter Metler Toledo, Germany.

3.2.21. IL/water bath separation

IL was recovered from its water solution with evaporator IKA RV 10 connected with pump KNFLAB and heating bath IKA HB 10 digital at 80 °C. All recovered ILs were analyzed to determine their water content by Karl Fisher titration.

3.2.22. Determination of reducing sugars by colorimetric method with 3.5- dinitrosalicylic acid (DNS).

This procedure is based on literature (Wood, 1988). 1 cm^3 of sample solution is diluted by 1 cm^3 of 0.05 mol/l acetate buffer (pH 4.8). 3 cm^3 of 3,5-dinitrosalicilic acid (DNS) is added and heated in boiling water bath during 5 min. Then sample was cooled and analyzed comparing with zero-standard at wave length 540nm with spectrometer HELIOS γ. Content of reduced sugars is calculated by Equation 5.

$$X = d * R \text{, µmol/cm}^3 \quad \text{Eq. 5}$$

d- multiplicity of sample dilution

R-concentration of D-glucose, found from calibration curve

4. Summary

Imidazolium-based ionic liquids were studied as solvents for cellulose and chitosan. Cellulose solutions and cellulose/chitosan blends were produced in ILs. The best dissolution ability among the studied ILs show acetate containing ILs. It is possible to dissolve up to 18 wt% of cellulose at 110 °C in EMIMAc and up to 20 wt% in BMIMAc. The worst dissolution ability among the studied solvents was shown by BDMIMCl. It was possible to dissolve only 5 wt% of cellulose under the same conditions. In case of BMIMCl, dissolution stops when the concentration of cellulose is more than 14 wt%. The dissolution in EMIMAc, BMIMAc and BDMIMCl was limited by the viscosity of the solutions. By DLS was found that solutions of cellulose in ionic liquids BMIMAc, BMIMCl and EMIMAc represent the steady disperse systems containing polymer aggregates, with sizes of up to 5 times higher than that of a single macromolecule of cellulose of the same molecular weight. The hydrodynamical radius of particles of cellulose in EMIMAc slightly exceeds those in BMIMAc and BMIMCl, with other conditions being equal (humidity of cellulose, concentration of the solution, and the temperature). The influence of water on dissolution ability of ILs was determined. Generally, water has negative influence on cellulose dissolution in ILs, and excess of water should be removed from solution. The size of cellulose aggregates in ILs solutions grows with an increase in the water content of solutions, which may be interpreted in terms of both the deterioration of the solvent and the swelling of particles in the presence of water. The phase diagram of cellulose/BMIMCl/ water system was plotted. A colloid solution useful for technical purposes could be obtained at water content in the BMIMCl solution below 8%. Selected thinners were studies in order to find the appropriate one to facilitate cellulose dissolution in ILs. Cellulose/IL/thinner systems were prepared with different orders of component mixing. The type of the system (the order of component mixing) did not affect the composition of cellulose/IL/thinner systems. The composition of cellulose/IL/thinners systems remained stable even for 4 months. Ethyl acetate and diethyl ether almost completely evaporated from the solution upon heating and facilitated cellulose dissolution in ILs, which was confirmed by mean of ^{1}H NMR spectroscopy. DMSO as DEE and EAc increased the speed of cellulose dissolution in ILs, but it remained in the solution and lowered its viscosity. Both protic and aprotic thinners inhibit the cellulose degradation in obtained films which occurred at its dissolution in ILs. DMSO, DEE and EAc adding could help keep the same DP as for initial sample. The films with highest mechanical properties could be obtained with using aprotic solvents. Produced films obtained became weaker and more fragile with increasing of the thinners content. Aprotic solvent are more efficient for cellulose films production and facilitating the dissolution of cellulose in ILs. Among the studied ILs, EMIMAc and BMIMAc are suitable to produce cellulose/chitosan blends by heating. Microwave treatment wasn't efficient for chitosan dissolution. Simultaneously blending of components is more efficient than mixing of separately prepared chitosan and cellulose solutions in common solvent. The addition of thinners decreased the viscosity of cellulose solutions and cellulose/chitosan solutions in ILs. The thinners addition decreased slightly the E_{act} of blended solutions and its values were almost equal to the E_{act} of solutions without thinners. The sizes of polymer aggregates in blended solutions were bigger in EMIMAc solution than in BMIMAc solution. Addition of thinners decreased the size of polymer aggregations in both IL solutions. Blended films with 3 -10 wt% of chitosan were prepared from the studied solutions. The increasing of chitosan concentration in blends increased the degradation of the cellulose part. DMSO and DEE improve the mechanical properties of blended films. We have not found any pertaining to better dissolution of MCCh in ILs and its blending with cellulose. Chitosan is a promising polysaccharide for cellulose modification, but the process of blend production in ILs still needs to be studied. Glycerine/POE-400 mixture was chosen as plasticizer. By means of TG-IR was found that the adding of plasticizers to wash-bath is more preferable. Much less sugar residues were found in wash-bash, and its amount increased slightly at longer dissolution, which indicates that cellulose degrades slowly at the temperatures studied. The traces of ILs were observed in the FTIR spectra of cellulose films and wash-baths. A residual content of 0,7- 3 % ILs, was typically found, therefore water alone is not efficient at the complete removal of ILs during cellulose coagulation. It is possible to recover ILs from the water-bath by distillation. Recovered ILs have a moisture about 7-11 %, and despite the same dissolving ability the mechanical properties of the films obtained from recovered ILs are worse than those obtained from fresh ILs.

The ability of ILs to dissolve polysaccharides was studied in this work. The influence of water, thinners, and other polysaccharides was analyzed and was concluded that ILs are effective reusable solvents for processing polysaccharides into a films, which may also be viable on a technical scale.

5. Zusammenfassung

Ionische Flüssigkeiten bzw. Ionic Liquids (ILs) sind eine äußerst interessante Klasse von Substanzen. Im Jahre 1934 berichtete Graenacher als erster der über ILs. Jedoch gerieten diese Lösemittel für Cellulose lange Zeit in Vergessenheit. Erst in den späteren 90er Jahren des 20. Jahrhunderts wurden sie als sehr versprechende Lösungsmittel wieder entdeckt. Im Jahre 2002 erkannte Swatloski, dass Ils Zellstoff lösen können.

Die herkömmlichen Löseprozesse für Cellulose inklusive des Kupfer-Ammonium- und Viskoseprozesses bergen Nachteile, wie der Verbrauch des Schwefekohlenstoffes als Lösungsmittel und Reagenz sowie Emissionen von Zink im Abwasser und Schwefelwasserstoff. Die angewendeten Lösungsmittel weisen einen hohen ionischen Charakter auf und der Löseprozess benötigt zu Beginn verhältnismäßig drastische Prozessparameter (Kirk-Othmer, 1993). Mit der ansteigenden Umweltbelastung und damit verbundenen Regelungen werden „grüne" Prozesse zunehmend wichtig, damit die Verschmutzung der Umwelt durch Reduzierung der Abfallmenge verringert wird und erneuerbare Rohstoffe genutzt werden können.

Es ist bekannt, dass man Cellulose ohne Derivatisierung in ILs auflösen kann (Heinze et al. 2005b; Massone et al. 2009; Pagoria et al. 2009; Maase et al. 2008; Myllamaki et al. 2008).

Cellulose kann man mit anderen Polymeren in den ILs mischen, um z.B. grüne Kompositfolien herzustellen, die Cellulose, Stärke und Lignin (Wu et al., 2009), Cellulose und Fibroin (Kuzmina et al. 2009), Cellulose und Chitin (Takegawa et al. 2010) bzw. Cellulose und Chitosan enthalten können (Dai et al., 2010; Li et al., 2010; Pang et al., 2009). Gegenwärtig werden die Abhängigkeit des Auflösungsprozesses vom Wassergehalt (Mazza et al., 2009; Kuzmina et al., 2010), der Einfluss anderer Lösungsmittel (Gericke et al., 2011) und der Reinheit der ILs (Stark et al., 2008) sowie deren Toxizität (Studzinska et al., 2009) erforscht. Darüber hinaus wird intensiv an der Rückgewinnung der ILs nach der Auflösung und Regenerierung der Cellulose gearbeitet (Wu et al., 2009). Insbesondere für Papierwissenschaftler und –technologen sowie Celluloseverarbeitern ist die Recyclisierbarkeit der ILs von großer Bedeutung.

Der Inhalt der Dissertation über die Anwendung von ILs als Lösungsmittel für Polysacharide ist eng verbunden mit den Erwartungen der Industrie an effizientere und umweltfreundlichere Prozesse bei der Verarbeitung von Polysachariden, insbesondere der Cellulose.

Ziel dieser Arbeit war es daher, den Auflösungsprozess von Polysachariden in ILs unter Berücksichtigung des Wassergehaltes zu untersuchen, sowie Filme aus Cellulose und Komposite mit Chitosan herzustellen und zu charakterisieren. Darüber hinaus wurde an der Rückgewinnung der ILs und deren Lösepotenzial für Polysaccharide gearbeitet.

Ergebnisse

Imidazolium-basierte ionische Flüssigkeiten wurden als Lösungsmittel für Polysacharide untersucht und Mischungen von Cellulose mit Chitosan hergestellt. Unter den untersuchten ILs wiesen die Imidazoliumacetate das beste Auflösungsvermögen auf. Bei einer Temperatur von 110 °C konnten bis zu 18% Cellulose in EMIMAc und bis zu 20 % in BMIMAc gelöst werden. BDMIMCl zeigte das geringste Lösevermögen; unter denselben Bedingungen konnten nur 5 % Cellulose aufgelöst werden. Die Maximalkonzentration der Cellulose in BMIMCl liegt bei 14%. Das Lösen des Polymers in EMIMAc, BMIMAc und BDMIMC ist durch die Viskosität der Lösungen begrenzt. Mittels DLS wurde gefunden, dass die Celluloselösungen in BMIMAc, BMIMCl und EMIMAc ein kontinuierliches Dispersionssystem darstellen, das Aggregate von ungefähr 5-facher Größe bezogen auf die Cellulosekette enthält. Der hydrodynamische Radius der Cellulosemoleküle in EMIMAc ist im Vergleich zu BMIMAc und BMIMCl unter identischen Bedingungen (Feuchtigkeit des Zellstoffs, Konzentration der Lösung, Temperatur) nur unwesentlich größer

Der Einfluss des Wassers auf das Lösevermögen der ILs für Cellulose wurde untersucht. Es zeigt sich, dass Wasser im Allgemeinen einen negativen Einfluss auf das Auflösen der Cellulose in ILs hat, weswegen das überschüssige Wasser aus der Lösung entfernt werden muss. Die Aggregate in den Celluloselösungen wachsen mit steigendem Wassergehalt. Dieser Vorgang lässt sich mit der abnehmenden Qualität des Lösungsmittels und dem Quellen der Partikel in Anwesenheit von Wasser erklären. Ein Phasendiagramm für das System Cellulose/BMIMCl/Wasser ist in Bild 1 dargestellt.

Eine für technische Zwecke nutzbare kolloidale Lösung kann bei einem Wassergehalt unterhalb 8% erhalten werden. Ausgewählte Verdünnungsmittel sind hinsichtlich der Beschleunigung des Löseprozesses untersucht worden. Hierbei wurde auch die Reihenfolge bei der Lösungsherstellung erforscht. Dabei konnte gezeigt werden, dass die Zusammensetzung der Cellulose/IL/Verdünnungsmittel-Systeme durch die Reihenfolge des Mischens nicht beeinflusst wurde.

Die Zusammensetzung der Cellulose/IL/Verdünnungsmittel-Mischungen blieb über mehr als 4 Monate unverändert. Mittels ^{1}H-NMR-Spektroskopie wurde bestätigt, dass Ethylacetat und Diethylether beim Erwärmen fast völlig aus der Lösung verdampft wurden, was das Auflösen der Cellulose erleichert. DMSO, DEE und EAc beschleunigten das Auflösen der Cellulose in ILs, verblieben aber in der Lösung und erniedrigten deren Viskosität. Alle angewendeten Verdünnungsmittel setzten die Viskosität der Lösungen von Cellulose und Cellulose/Chitosan in ILs herab (Bild 2) .

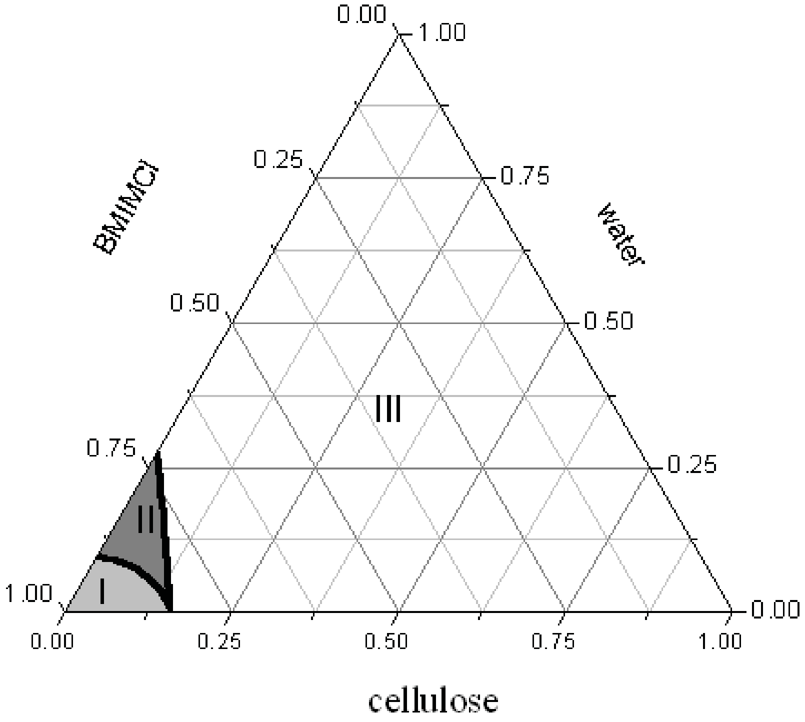


Bild 1. Phasendiagram für Cellulose-Wasser-BMIMCl-Mischungen. I – Kolloidale Lösung; II – Suspension; III – Zweiphasen-System (grobdisperses System).

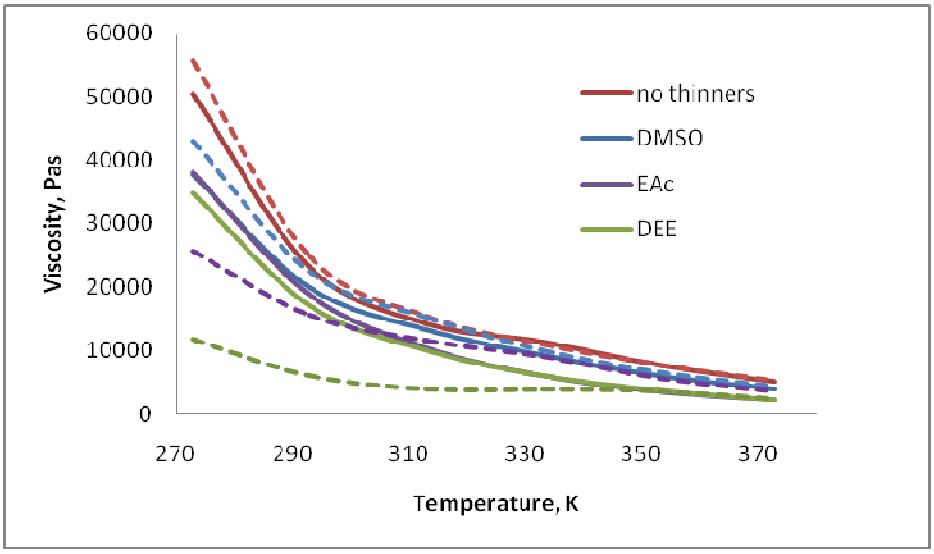


Bild 2. Temperaturabhängigkeit der Viskosität einer 5%-igen Celluloselösung in EMIMAc mit und ohne Verdünnungsmittel (durchgehende Linie) und 4.5 %ige Cellulose-/ 0.5 %ige Chitosanlösung in EMIMAc mit und ohne Verdünnungsmittel (unterbrochene Linie) bei einer Verdünner-Konzentration von 5 %.

Sowohl protische als auch aprotische Verdünnungsmittel verzögern den Abbau der Cellulose während der Auflösung in ILs bei der Folienherstellung. Die Zugabe von DMSO, DEE und EAc konnte zum Beibehalten des DP beitragen. Aprotische Lösungsmitteln ergeben Folien mit den besten mechanischen Eigenschaften. Mit steigendem Gehalt an Verdünnungsmitteln nehmen die mechanische Eigenschaften der Folien jedoch ab. Aprotische Lösungsmittel sind der bei der Herstellung von Cellulosefolien besser geeignet, da sie auch das Auflösen der Cellulose in den ILs erleichtern.

Tabelle 1. Die Größe der Polymeraggregate und Aktivierungsenergie (E_{act}) der Cellulose/Chitosan (Primex)-Lösungen mit Verdünnungsmitteln im Vergleich mit Celluloselösungen in ILs

IL	Verdünner	Konzentration der Komponente in der Lösung, wt%				Größe der Aggregate, nm	E_{act}, kJ/mol
		Cellulose	Chitosan	IL	Verdünner		
EMIMAc	-	5	0	95	0	419	23
	-	4.5	0.5	95	0	600	24
	DMSO	4.5	0.5	90	5	552	21
	DEE	4.5	0.5	90	5	203	21
	EAc	4.5	0.5	90	5	368	19
BMIMAc	-	5	0	95	0	197	24
	-	4.5	0.5	95	0	208	27
	DMSO	4.5	0.5	90	5	199	25
	DEE	4.5	0.5	90	5	196	21
	EAc	4.5	0.5	90	5	175	20

EMIMAc und BMIMAc sind für die Herstellung von Cellulose/Chitosan Mischungen mit konventioneller Erhitzung am besten geeignet. Das Auflösen des Polymers unter dem Einfluss von Mikrowellen hat sich als ungünstig erwiesen. Das gleichzeitige Mischen der Komponenten ist effizienter als das Mischen von separat hergestellten Lösungen von Cellulose und Chitosan in herkömmlichen Lösungsmitteln. Die Zugabe von Verdünnungsmitteln erniedrigte die Viskosität der Cellulose/Chitosan-Lösungen in ILs. EAc erniedrigte die Aktivierungsenergie der Mischungen im Vergleich mit anderen Verdünnungsmitteln nur wenig, und die Werte waren fast gleich mit den Aktivierungsenergien der unverdünnten Lösungen (Tabelle 1). Die

Polymeraggregate in der EMIMAc-Lösung waren größer als in BMIMAc-Lösungen (Tabelle 1). Das Zugeben von Verdünnungsmitteln verringerte die Größe der Aggregate in beiden ILs.

Mischfolien mit einem Chitosananteil von 3-10 % wurden hergestellt. Mit steigender Chitosan-Konzentration erhöhte sich der Celluloseabbau.

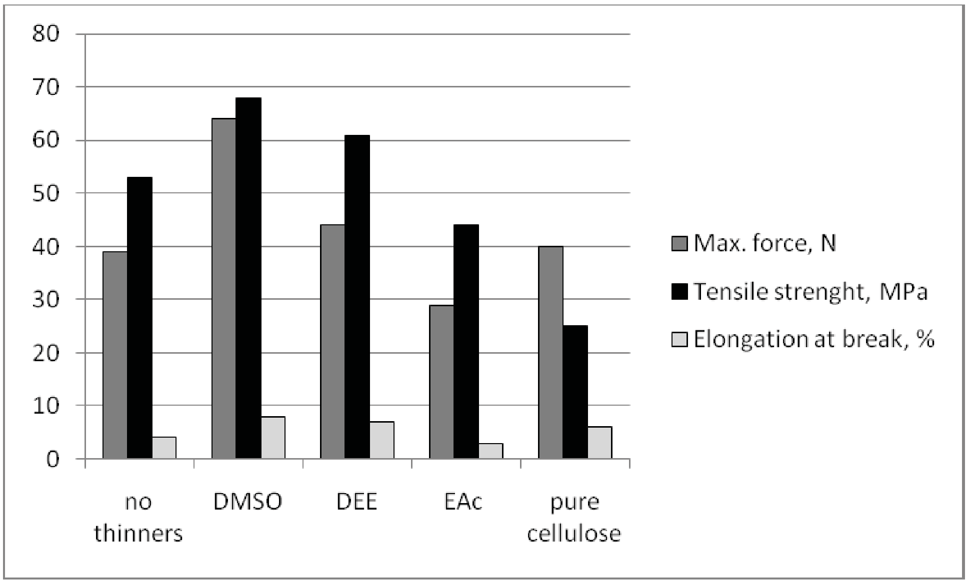


Bild. 3. Einfluss der Verdünnungsmittel auf die mechanischen Eigenschaften der aus EMIMAc–Lösungen hergestellten Cellulose/Chitosan (Primex)-Folien

DMSO mit DEE tragen zur Verbesserung der mechanischen Eigenschaften der Mischfolien bei (Bild 3). Chitosan löst sich in den ILs besser als mikrokristallines Chitosan. Chitosan ist ein für die Modifizierung der Cellulose gut geeignetes Polysaccharid. Jedoch erfordert die Vorbereitung der Mischungen weitere Untersuchungen. Eine Glyzerin/POE-400-Mischung wurde als Weichmacher gewählt. TG-IR-Messungen haben gezeigt, dass die Zugabe von Weichmachern zum Wasch-Bad vorteilhaft ist.

Nach dem Koagulieren konnten in den Waschwässern nur sehr kleine Mengen von Zuckern gefunden werden. Diese Mengen wiesen eine leicht steigende Tendenz mit verlängerter Auflösungszeit auf, was ein Beweis für den geringen Celluloseabbau bei der gewählten Lösetemperatur ist. FTIR-spektroskopisch lassen sich Spuren der ILs in den Folien und Waschwässern nachweisen (Bild. 4).

Die Folien enthalten 0,7-1 % ILs. Demnach ist Wasser ist für das Entfernen der ILs im Koagulationsprozess nicht geeignet. Es besteht die Möglichkeit, die ILs mittels Destillation aus dem Waschwasser zurückzugewinnen.

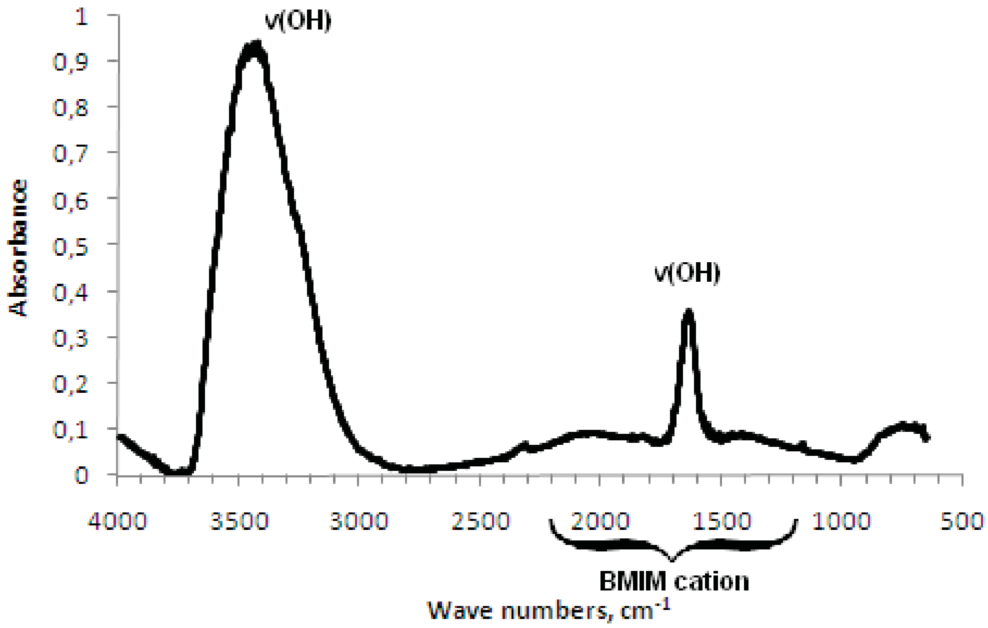


Bild. 4. FTIR-Spektren des Waschwassers nach der Koagulation der Cellulose aus BMIMCl-Lösung).

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Selbständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

Jena, den --

Unterschrift