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Strong Cellulosic Film Cast from Ionic Liquid Solutions

Abstract
The article presents a method to prepare films by casting solutions of cellulose in ionic liquid 1-ethyl-3-methylimidazolium acetate [emim][OAc]. Cotton linters and a hydrothermally treated (HT) wood cellulose pulp were used in the investigation. The film was cast from solutions with cellulose concentrations of 2.0, 5.0, 6.0, 10.0 and 14.0 wt% in [emim][OAc] at temperatures in the range of 20 - 80 °C. The influence of the cellulose concentration, composition of the coagulation bath and temperature of the solution and coagulation bath upon the mechanical properties and morphology of the cellulose films were examined. Samples of transparent cellulose film were prepared with a low polydispersity index (PDI) of 2.2, and satisfactory mechanical properties: strength up to 103 MPa and elongation of 30%.

Key words: *cellulosic film, cotton linters, hydrothermal treatment, ionic liquid, mechanical properties, morphology.*

Introduction

Transparent cellulose film has been present on the market for one hundred years under the trade name cellophane. Cellophane is produced via the viscose process from renewable resources, mainly wood dissolving pulp. It shows a broad spectrum of applications such as packaging and decorative material mainly for alimentary products, adhesive bands, labels, etiquettes, or sausage casings. The climax of cellophane's role on the market is long over, though it is still seen as a valuable packaging material for its beneficial properties like transparency, biodegradability and impermeability to certain gases and water vapour. The British company Innovia Films is one of the leading manufacturers of cellulose film under the trade names of Cellophane® and NatureFlex® [1].

The viscose method by which cellophane is made requires toxic and harmful chemicals, thus posing a real thread to the environment and humans. This is the reason why alternative technologies are sought worldwide. The new potential methods are based on the use of solvents that are capable of dissolving cellulose directly: *N*-methylmorpholine *N*-oxide (NMMO) [2], aqueous NaOH combined with ZnO, urea [3 - 7] or thiourea [8]. Few of the new methods bear real commercial potential and a chance to replace the burdensome viscose route.

In recent years, research attempts have been made to harness ionic liquids (ILs) as cellulose solvents and to elaborate optimum conditions to cast films from IL-cellulose solutions. It is anticipated that ILs as cellulose solvents would offer the chance for an environment-friendly, safe-for-humans, low energy-consuming process. Good transparency and high tensile strength is expected from cellulose film cast from IL solutions.

ILs with an imidazole cation in their structure are excellent solvents of biopolymers like cellulose, starch and proteins, forming solutions suitable for spin fibres or cast films [9, 10]. One major advantage of ILs is their ability to dissolve polymers in high concentrations. In addition, the dissolution process proceeds fast due to the low viscosity of some ILs. Within 10 minutes cellulose was dissolved at 90 °C in 1-ethyl-3-methylimidazolium diethylphosphate [emim][DEP]. A 4 wt% solution of cellulose was the effect [11]. Rheological properties of the resulting cellulose solutions are influenced by the type of polymer and solvent, but also by the time and temperature of the dissolving procedure [12]. The resulting visco-elastic characteristics of the IL-polymer solution define the processability and, consequently, the film quality. Furthermore the properties of the final film depend on the coagulation medium [13].

The versatile dissolution properties of ILs offer the possibility to blend different polymers and substrates.

Hameed et al. demonstrated that ILs offer the chance to prepare a wool/cellulose composite film from a solution of 1-butyl-3-methylimidazolium chloride [bmim]Cl coagulated in demineralised water. The films prepared revealed a moderate tensile strength of 54 MPa [14].

Takegawa et al. used a mixture of [amim]Br and [bmim]Cl to prepare a chitin-cellulose composite film. Microcrystalline cellulose (Avicell) represented the cellulosic matrix which was coagulated together with chitin with water as the antisolvent medium. The films showed rather poor mechanical properties: tensile strength 10 MPa and an elongation of 10% [15]. Another composite chitosan-cellulose film was formed from the [bmim][OAc], showing a tensile strength of 10 MPa at an elongation of 10% [16].

An increase in the tensile strength of the resulting cellulose films was observed upon the addition of poly(vinyl alcohol) (PVA) to a solution of cotton linters in 1-allyl-3-methylimidazolium chloride [amim]Cl [17]. From the solution coagulated in water, a transparent film was prepared with a tensile strength of 100 MPa and elongation of 25%.

ILs with an adequate structure [18] may also serve as modifiers of cellulose properties themselves: they may change the affinity to water, increase tensile strength and confer antibacterial properties upon the polymer.

Unlike in the dissolution of MCC, high polymerisation degree (DP) cellulose such as pulp is typically more challenging to dissolve due to a steep increase in the viscosity of the resulting solution.

Hydrothermal treatment enables a controlled reduction of the polymerisation degree and improves cellulose properties: increased solubility in alkali, de-

creased polydispersity, and removal of traces of lignin [3 - 7]. Therefore hydrothermal treatment was proposed as pretreatment for the cellulose pulp before its dissolution in IL. A higher solubility and shorter dissolution time is anticipated for HT cellulose.

The mechanical properties of cellulose film prepared from IL solutions, as in articles hitherto presented [14 - 16], do not satisfy quality demands; the tensile strength, for example, barely reaches 60 MPa. Since high tenacity cellulose fibres could be formed by the dry-wet spinning method from ILs solutions, a film with high tensile strength may be expected too.

The purpose of this work was to elaborate conditions to form cellulose film with a tenacity as high as 100 MPa from IL solutions. Cotton linters and HT wood cellulose pulp dissolved in [emim][OAc] were used in the experiments. The impact of the cellulose concentration in IL solution on the film casting process was investigated. Subsequently the influence of the coagulation bath composition (demineralised water-ethanol mixtures) and temperature on the final film properties was investigated.

Materials and methods

Materials

The following materials were used:

- [emim][OAc], 95%, purchased from BASF, Germany.
- Ethyl alcohol and butanol, made by POCh S.A., Gliwice, Poland.

The cellulosic raw materials were cotton linters (520 ml/g, R10 = 97.5%, R18 = 98.3%), provided by Milouban, Israel, and softwood prehydrolysis kraft (PHK) dissolving pulp (408 ml/g, R10 = 92.5%, R18 = 97.1%), from Buckeye Technologies, USA.

Methods

Pretreatment of the cellulose pulp for dissolving

PHK dissolving pulp was subjected to hydrothermal treatment as described in the European patent [5]. The pulp was processed at 160 °C for 30 minutes, washed afterwards with demineralised water and dried to a humidity content of 7%. The HT cellulose obtained, characterised by a degree of polymerisation (DP) of 255 and polydispersity index (PDI) of 2.2, was used as a cellulose substrate for IL solutions.

Preparation of cellulose/IL solutions

Cotton linters were dissolved in [emim][OAc] within 2 hours at 90 °C using the vertical kneader system. A concentration series of 2.0, 5.0, 6.0, 10.0 and 14.0 wt% was prepared for film casting.

Solutions with a 6.0 and 10.0 wt% concentration of the *HT cellulose* were prepared by wetting the pulp with IL at 20 °C and subsequent heating for 15 minutes at 90 °C. To ensure complete dissolution, heating was continued for another 60 minutes, followed by vacuum de-aeration at 80 °C. The respective solutions were used to cast cellulosic films.

Casting of the cellulose film

The [emim][OAc]-cellulose solution was heated to a temperature in the range of 20 - 80 °C, poured onto a heated glass or metal surface and distributed by means of a simple device equipped with a knife to remove surplus of the solutions with a 0.6 mm slot and then put into a regeneration bath. Various coagulation media were applied: demineralised water, 96% ethanol, aqueous ethanol (20/80 and 80/20 ethanol/water), or butanol at a temperature of 15 - 40 °C. The immersion time was typically 3 - 12 minutes. The film was then placed into a washing bath with 96% ethanol or demineralised water at a temperature of 20 - 90 °C for 1 hour and then treated in another demineralised water bath at 90 °C for 3 hours. The film samples were finally kept for 24 hours in demineralised water at ambient temperature before being dried at 50 °C.

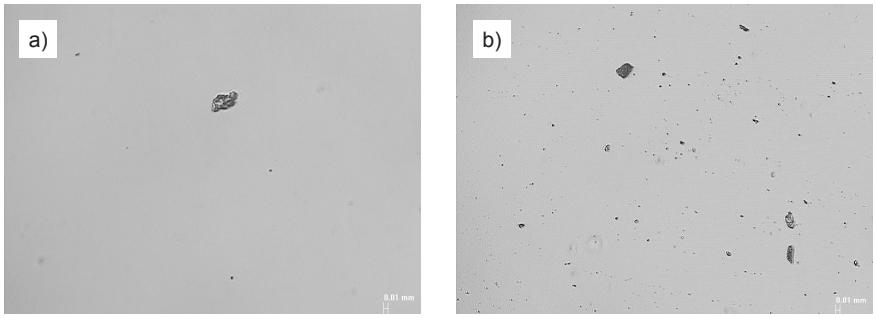


Figure 1. *Microscopic images of solutions of cotton linters with a concentration of 5.0 wt% (a) and 10.0 wt% (b) in [emim][OAc].*

Analytical methods

Assessment of solutions by means of a microscope

A Biolar ZPO optical microscope equipped with an advanced image analysis system (MultiScan V. 14.02) was used to take images of the cellulose-IL solutions and films.

Images of the cross-section and surface of the cellulose films were obtained using a scanning electron microscope, SEM/ESEM, Quanta 200 (W), FEI Co., USA.

Mechanical properties of the cellulose film

Mechanical properties of the cellulose film were examined in accordance with Standards PN-ISO 4593:1999 and 93:1999 PN-EN ISO 527-3:1998 at a relative humidity of 64 ± 4% and temperature of 20 ± 2 °C.

The molecular mass distribution of cellulose was determined by gel chromatography (GPC/SEC). The function of the mass distribution (*MMD*), average molecular mass (M_n, M_w) and polydispersity (M_w/M_n) were determined as described elsewhere [19]. Samples for GPC analysis were prepared according to the Ekmanis [19] procedure: swelling of the cellulose with water for 24 h, exchange of the water with dimethylactoamide (DMAc) employing microwave treatment, and dissolving of the cellulose in DMAc/8% LiCl. GPC/SEC analysis was performed in a solution of 0.5 mg/ml cellulose in DMAc/0.5% LiCl at a flow rate of 1.0 ml/min. The results were calculated by the universal calibration method, with parameters a and k in the Mark-Houwinek equation amounting to a = 0.65, $k = 17.3\times10^{-3}$ ml/g for the PEO/PEG standards, and a = 1.0, $k = 12.78\times10^{-3}$ ml/g for cellulose [20, 21].

Results and discussion

Impact of the cotton linters' concentration in the solution on the film's mechanical properties

Solutions of 2.0, 5.0, 10.0 & 14.0 wt% cotton linters in [emim][OAc] were used in this study. The quality of the solutions

Figure 2. *Images of cellulose film made from 5.0 wt% cotton linters in IL, where a - RCF 2A (coagulation bath - demineralised water); b - RCF 2B (coagulation bath - EtOH); c - RCF 3A (coagulation bath - EtOH, second bath - EtOH).*

was assessed by optical microscopy. ***Figure 1*** presents microscopic images of the solutions.

The cotton linters were completely dissolved in the IL, which is confirmed by the images in ***Figure 1***, where no undissolved fibres can be seen. Tiny particles of below 0.01 mm in size appeared in the solution, probably impurities contained in the linters. The solutions prepared for film casting were not filtered.

Several coagulation media (ethanol, butanol and boiled demineralised water) were tried to form a film from the 2.0 wt% cotton linter solution. Regardless of the coagulant used (20 °C), no film could be prepared suitable for analysing. The samples were weak, brittle and opaque. Supposedly the low cotton linter concentration was the reason for the low tensile strength. The film obtained in the trial with ethanol as the coagulant presented some chance of attaining better results. Further attempts were therefore made employing ethanol as the coagulant, as well as a second bath with ethanol, then demineralised water, and eventually drying at 50 °C. The procedure yielded a transparent film, which is marked as RCF 1.

Further trials were made with a **5.0 wt% solution of cotton linters** in IL. The film was cast as a thin layer on a glass plate (20 °C) and put for 6 minutes into a coagulation bath at 40 °C which was either demineralised water (sample marked RCF 2A) or ethanol (sample marked RCF 2B). Demineralised water was used as a second bath in both trials. Depending on the coagulation bath used, two distinctly different films were obtained: one transparent and the other opalescent. Solidifying proceeds in demineralised water much faster than in ethanol, and the film can be removed from the glass much more easily. The use of ethanol as the second bath and demineralised water as the third remarkably improved both transparency and strength. Upon optimisation of the after-treatment conditions, such as rinsing and drying, a film with even better transparency could be prepared (RCF 3A).

Small changes were observed when the solution was cast at lower temperature (17 °C), followed by the same coagulation and after-treatment protocol as before (RCF 3B). Samples were analysed in terms of mechanical properties.

The most uniform film, marked RCF 3A, was selected for testing. The mechanical properties of selected films are summarised in ***Table 1*** (see page 38).

Properties like adequate thickness with an acceptable variation coefficient, poor tensile strength with very low elongation and a high variation coefficient indicate low uniformity of the film. A uniform fragment of film was obtained and tested (see ***Table 1***).

The thickness is comparable, the tensile strength dropped, and the elongation is low. The storing of the solution caused a decline in tensile strength. The casting temperature of the solution (RCF 4) was changed to 50 °C. Other casting conditions remained the same for the film sample marked RCF 1.

The higher viscosity of the **10.0 wt% cotton linter solution** in IL makes it difficult to evenly spread the solution on the glass plate. The temperature was therefore increased up to 80 °C and large fragments of film were prepared. Depending on the kind of coagulation bath, two quite different film samples were obtained: one transparent and the other opalescent. ***Figure 3*** depicts images of the films (RCF 5A, RCF 5B, RCF 6 & RCF 7). By slightly changing the washing conditions, a film with a yellowish

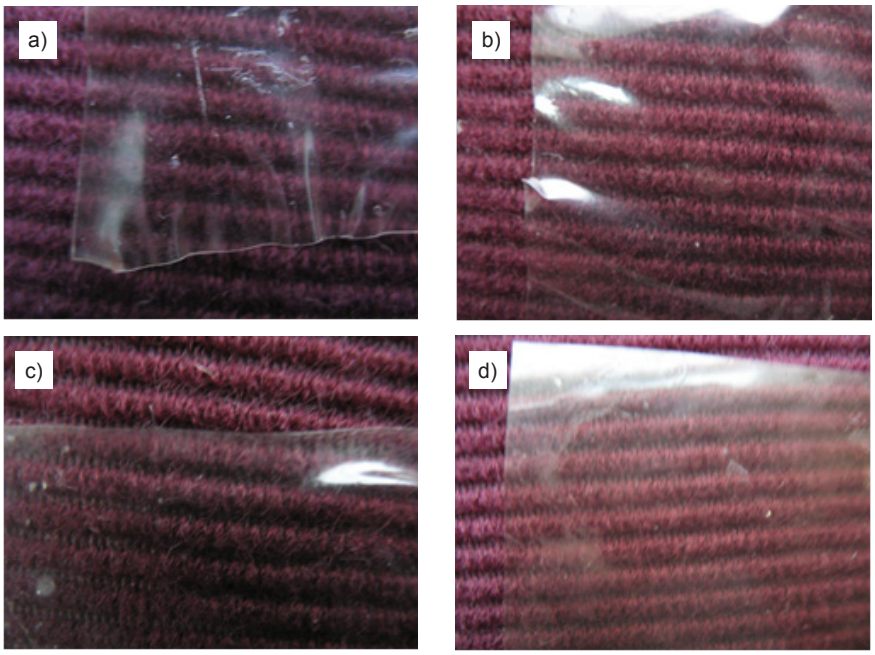


Figure 3. *Images of cellulose film made from 10.0 wt% cotton linters in IL, where a - RCF 5B, b - RCF 5A, c - RCF 6, d - RCF 7.*

Table 1. *Mechanical properties of cellulose films made from cotton linter solution; (*coagulation bath - 96% EtOH, 6 min, 30 °C; second bath - 96% EtOH, 3 min, 30 °C).*

Type of film	Cotton linter content in solutions, wt%	Thickness, mm	Thickness variation index, %	Maximum breaking force, N	Breaking force variation index, %	Tensile strength, MPa	Elongation at maximum stress, %	Elongation variation index, %
RCF 1	2	0.014	10.4	14.80	12.0	70.4	18.3	40.6
RCF 3A	5	0.022	9.78	13.00	35.0	38.5	3.19	58.9
RCF 3B		0.023	7.85	8.22	42.7	23.6	4.10	24.0
RCF 4		0.025	2.16	38.30	3.03	100.5	44.20	14.1
RCF 6	10	0.048	8.47	27.6	23.9	37.9	3.40	18.9
RCF 7		0.129	7.01	14.2	9.71	7.35	103.0	35.5
RCF 8A*	14	0.077	31.6	72.7	27.2	63.2	26.9	2.71
RCF 8B*		0.125	32.7	110	22.2	60.4	27.2	6.89
RCF 8C*		0.441	26.6	246	16.2	39.4	28.8	3.70

hue and better elasticity was obtained (RCF 7), which is probably caused by residual solvent in the film. This calls for examination and clarification in further works. The cellulose film marked RCF 5B was immersed for 3 minutes in ethanol prior to drying. The sample marked RCF 7 was neither rinsed nor kept for 24 hours in demineralised water after coagulation, which resulted in a considerable content of the solvent in the film. The differences in transparency and hue can be seen from ***Figure 3***.

Cellulose films marked RCF 5A and RCF 6 were prepared from the same solution and under the same conditions. Photographic images confirm the uniformity and similarity of the two films.

The mechanical properties of films RCF 6 and RCF 7 are shown in ***Table 2***. The two films only differ in the rinsing procedures.

Both samples are characterised by high thickness, a low allowable variation coefficient, low tensile strength, very low elongation and a very high variation coefficient, which indicate the high heterogeneity of the films. No influence of the increased cotton linter concentration upon the tensile strength was observed. The only changes in properties resulted from different washing conditions - RCF 7 showed an enormous increase in elongation and decrease in tensile strength, probably caused by residual solvent, which acts as a plasticiser. Generally the solution is more difficult in processing, but more interesting, also from an economic point of view.

Due to its very high viscosity (above 500 Pas at 60 °C), the **14.0 wt% solution of cotton linters** in IL (RCF 2B) was the most difficult to process. The preparation of a film was only possible upon further increase of the solution temperature. Prior to casting on the glass surface, the solution was kept at 95 °C for 2 hours. However, the formation of an even solution layer was not possible. Stationary film casting is not a suitable method for film forming from solutions with high cotton linter content. Continuous extrusion would offer a better approach. In this set, the influence of the rinsing time on film properties was investigated, the results of which are presented in ***Table 3***. The film coagulated in ethanol was rinsed with hot demineralised water for 3 (RCF 8A), 4 (RCF 8B) and 5 (RCF 8C) minutes, while the remaining conditions were the same as in previous trials. The film samples obtained were rigid, thick and opalescent.

The high cotton linter concentration in the solution (14 wt%) impeded the formation of thin films via the casting method applied. The film formed required more extensive washing and underwent deformation during drying. The rather high variation coefficients of thickness and force are in line with the macroscopic observation.

The tensile strength was down while the elongation remained practically unchanged with prolonged hot demineralised water washing time after coagulation in ethanol. These are confusing results since a reverse dependence could have been anticipated, that is a higher strength and lower elongation. The unexpected outcome may only be explained by the much increased thickness resulting from the shrinkage of the film, which probably prevented effective leaching of the solvent.

The mechanical strength of the film depends on the concentration of the cotton linters in the IL solution. The film cast from a 5.0 wt% cotton linter solution revealed the highest tensile strength. Processing conditions like the type of coagulation medium and retention time therein, as well as the way of washing and drying also exert an influence upon the mechanical parameters, as demonstrated in the film series prepared from 2.0 wt% cotton linter solution in [emim][OAc]. The use of 96% ethanol as a coagulation bath produced a transparent film with a tensile strength of 70 MPa. Adding a second bath of 96% ethanol caused an increase in transparency.

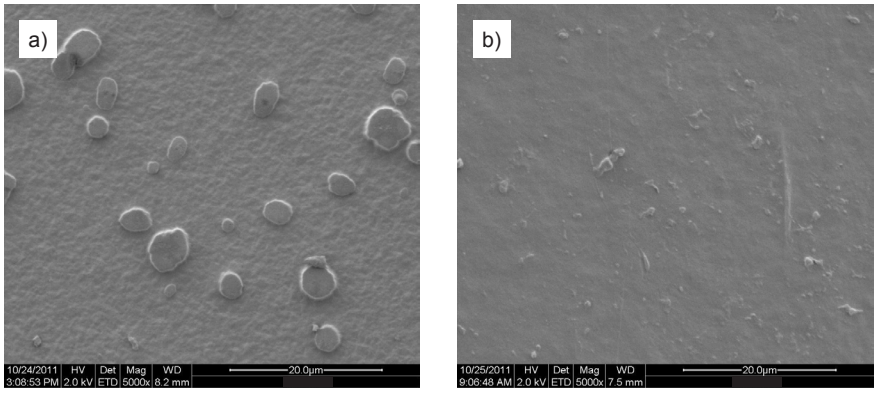


Figure 4. *SEM surface of cellulose film made from 6 wt%/filtered cotton linter/IL solution, where a - RCF 9 and from 6 wt%/not filtered cotton linter/IL solution b - RCF 10.*

Table 2. Mechanical properties of cellulose film made from 6 wt% cotton linter/IL filtered and not filtered solution.

Type of film	Cotton linter content in solutions, wt%	Thickness, mm	Thickness variation index, %	Maximum breaking force, N	Breaking force variation index, %	Tensile strength, MPa	Elongation at maximum stress, %	Elongation variation index, %
RCF 9	6 wt%/filtered	0.023	4.80	35.1	4.39	103.0	20.3	26.9
RCF 10	6 wt%/not filtered	0.022	7.43	31.5	4.89	96.0	20.4	27.7

Based on the results attained, it was concluded that a concentration slightly above 5.0 wt% of the cotton linters in IL would be optimal for the casting of cellulose films. Solutions with a 6.0 wt% cotton linter concentration were therefore prepared for further trials.

Investigation concerning the impact of solidifying conditions of 6.0 wt% cotton linter/IL solutions upon the mechanical properties of the film

The solidifying process of the cotton linter/IL solution was optimised in order to prepare uniform film samples to analyse their mechanical and morphological properties. Care was taken to provide samples uniform in thickness. Two bigger lots of the 6.0 wt% cotton linter solutions in [emim][OAc] were prepared, denoted as 6 wt%/filtered and 6 wt%/not filtered.

The coagulation sequence, based on earlier results, was as follows: coagulation bath - 96% ethanol at 30 °C, coagulation time - 6 minutes, second bath - 96% ethanol for 3 minutes at 30 °C - and third bath - demineralised water at 60 °C for 3 minutes and 24 hours in demineralised water at 20 °C.

Film samples prepared from the two different solutions show no difference in terms of thickness, tensile strength and elongation. Tensile strengths of up to 103 MPa were attained (***Table 2***). SEM microscopic observation at 5000× magnification revealed a large number of nodules on the film surface, in particular in sample RCF 9. These are probably low molecular substances deposited on the film surface after the evaporation of water. Film sample RCF 10 shows a specific surface pattern and some fibre fragments.

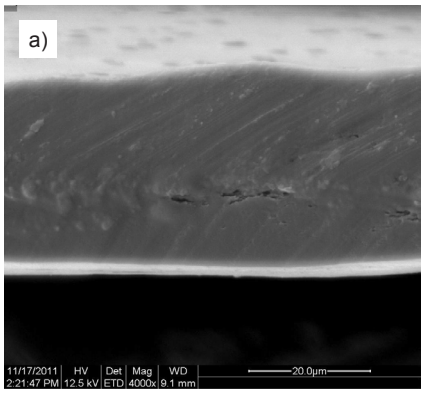
The cross-section of the film shows a uniform thickness and considerable inhomogeneity of the morphology, probably caused by the film casting conditions. Micro-cracks are visible and the singular film layers are displaced against each other.

Adapting the conditions applied for film RCF 9, a film was cast from 6 wt%/filtered cotton linter/IL solution (RCF 11). Merely the coagulation time was prolonged to 10 minutes in a 96% ethanol bath, the other parameters being the same as in earlier trials. It seems that the prolonged coagulation time results in a more homogeneous morphology. Despite numerous micro-pores, the structure is more compact and fewer spots and bubbles appear on the surface. The film cross-sections are presented in ***Figure 6***.

Impact of casting conditions on the films' mechanical properties

The same solutions of 6 wt%/filtered and 6 wt%/not filtered cotton linters in IL, as described in the previous section, were investigated herein. The solution was heated up to 70 °C and a thin film layer was cast and kept at 70 °C for 10 minutes. The films were coagulated in a bath consisting of 80 parts ethanol and 20 parts demineralised water at 15 °C with a retention time of 8 minutes. In contrast to the previous experiments, the coagulation medium contained different shares of 6 wt%/filtered solution. Symbols G 1, G 2 & G 3 in the sample code refer to the differences in coagulation medium composition. IL concentration in the coagulation bath was 0% for G1, 2% for G2 and 4% for G3. The coagulated film was rinsed with warm demineralised water, left in water overnight and then dried at 50 °C. ***Figure 7*** (see page 40) presents SEM pictures and ***Table 3*** an overview of the mechanical properties of the films, respectively.

The films obtained may be considered even and regular for their comparable thickness and low coefficient of thickness variation. The highest variation is observed in elongation: from 14 to 30%. Tensile strength values fall into the range of 75 - 102 MPa regardless of the 6 wt%/filtered of cotton linters/IL solution used. The IL concentration in the coagulation bath had only a minor influence on the tensile strength (***Table 3***, RCF 12/G). SEM images of the films are shown in ***Figure 7***. The film samples are characterised by an uneven cross section, which might result from the high viscosity of the cellulose solution and inadequate speed of the knife device. On the surface, many dots are visible for all the samples. It was observed that a reduction in the coagulation time and, in par-



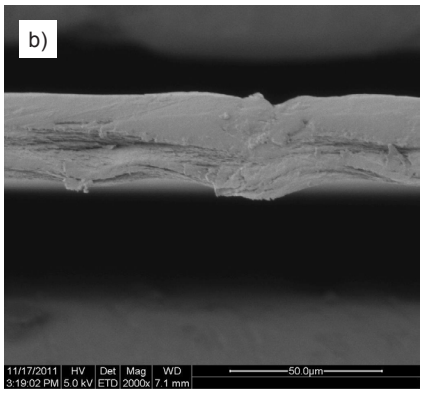


Figure 5. *SEM cross section of cellulose film made from 6 wt%/filtered cotton linter/IL solution, where a - RCF 9 and from 6 wt%/not filtered cotton linter/IL solution b - RCF 10.*

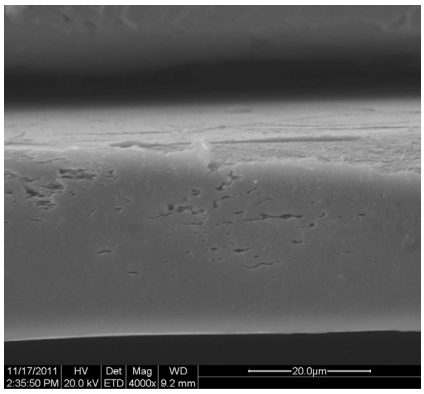


Figure 6. *SEM of cellulose film made from 6 wt%/filtered cotton linters/IL solution RCF 11.*

Table 3. *Mechanical properties of cellulose films made from the 6 wt% of cotton linter /IL solution; (RCF 12 - not filtered, RCF 13, RCF 14 - filtered) The IL concentration in the coagulation bath was: 0% for G1, 2% for G2 and 4% for G3.*

Type of film	Thickness, mm	Thickness variation index, %	Maximum breaking force, N	Breaking force variation index, %	Tensile strength, MPa	Elongation at maximum stress, %	Elongation variation index, %	Modulus of elasticity, MPa
RCF 12/G1	0.031	4.56	39.8	11.2	85.6	36.1	30.4	29.2
RCF 12/G2	0.029	3.94	41.8	13.4	95.4	24.6	40.1	66.5
RCF 12/G3	0.034	2.66	43.7	11.4	86.6	30.1	21.3	51.7
RCF 13/G1	0.030	2.94	40.6	5.55	89.0	20.9	27.4	31.2
RCF 13/G2	0.034	2.66	43.8	3.55	86.9	22.8	13.2	17.9
RCF 13/G3	0.030	4.71	34.0	10.3	75.7	13.9	21.3	11.2
RCF 14/G1	0.029	3.52	44.2	5.44	100.5	32.2	25.7	28.0
RCF 14/G2	0.030	2.69	46.4	4.11	102.0	30.2	12.3	26.4
RCF 14/G3	0.030	2.69	43.9	5.83	96.6	26.4	26.8	10.5

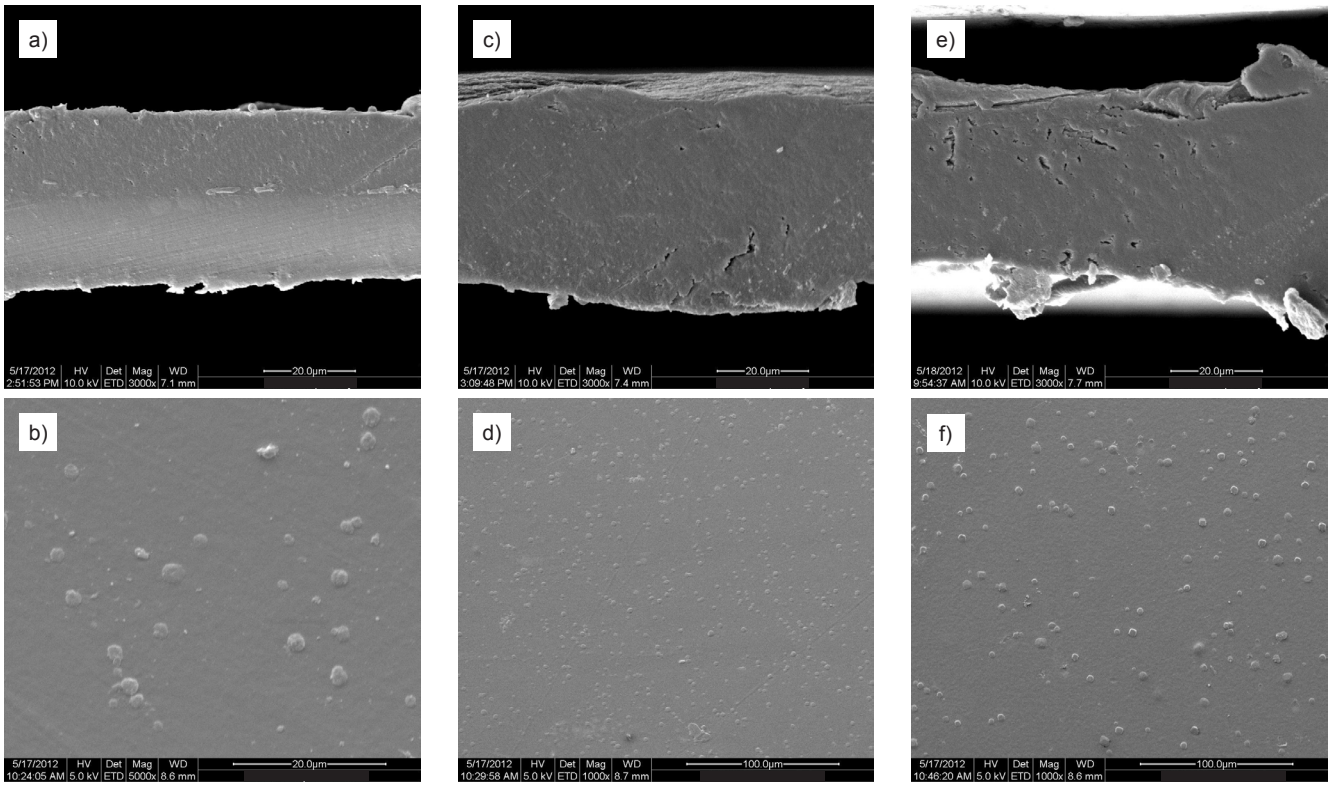


Figure 7. *SEM images of surface and cross section of cellulose film made from 6 wt%/filtered cotton linter/IL solution, where a), b) - RCF 12 G2: c), d) - RCF 12 G3 and from 6 wt%/not filtered cotton linter/IL solution e), f) - RCF 14 G3.*

ticular, the extent of demineralised water rinsing affect the amount of nodules.

From the mechanical properties of the films summarised in ***Table 3***, one can perceive an essential influence of the coagulation bath composition. The use of demineralised water as a coagulant results in opalescent, brittle and weak films, while ethanol regenerates films with much better quality in terms of both transparency and strength. Ethanol, however, bears one disadvantage: the film prepared show a porous bulk structure. Porosity is observed after a certain coagulation time and increases with the prolonged residence time of the film in the bath. Most of the pores are inside the film, with only few visible on the surface. The pores have a negative effect on the strength of the films and limit the range of its application. The generation of pores can be curbed by changing the coagulation bath composition to ethanol/water in the proportion of 80/20. Films with a tenacity of around 100 MPa were prepared with 80 - 96% ethanol as a coagulation medium, which was applied in most of the following trials, since it allowed the preparation of films with satisfactory tensile strength and good transparency.

Use of hydrothermally treated (HT) wood pulp in the preparation of cellulose films

It was assumed that the PHK dissolving pulp after hydrothermal treatment could be suitable for the preparation of cellulose film with properties comparable to those of the linter-originated film. HT cellulose pulp with DP = 255, low polydispersity PDI = 2.2 and a water content of 7% was used in the experiments. The pulp could be completely solubilised in [emim][OAc] within 15 minutes. Solutions with 6.0 and 10.0 wt% content of cellulose were prepared for subsequent film casting. In microscopic images taken both in polarised and regular light, the presence of swollen fibres can be seen at the beginning of the dissolution; these disappeared after 15 minutes, yielding clear solutions. The film was cast after one day of de-aeration of the solution at 70 °C. Two coagulation media with varied ethanol concentration were used, fol-

Table 4. Mechanical properties of cellulose films made from 6.0 and 10.0 wt% cellulose HT/IL Solution; RCF – 15, RCF – 16A - 80/20 (EtOH/water) as coagulation medium, RCF – 16B - 20/80 (EtOH/water) as coagulation medium.

Type of film	DP of cellulose HT	Cellulose HT content in solutions, wt%	Thickness, mm	Thickness variation index, %	Maximum breaking force, N	Breaking force variation index, %	Tensile strength, MPa	Elongation at maximum stress, %
RCF-15	255	10	0.044	5.87	63.5	5.00	91.2	21.6
RCF-16A		6	0.026	0.00	31.8	7.27	81.6	17.1
RCF-16B				3.39	28.9	10.30	73.1	12.4

lowed by a demineralised water bath at 50 °C. The film formed was then left in demineralised water for 24 hours and afterwards dried at 50 °C. ***Table 4*** presents the mechanical properties and ***Figure 8*** shows SEM images of the respective cellulose films.

The cellulose films cast from 10.0 wt% solution were slightly stronger (tensile strength of 91 MPa) than those from 6.0 wt% solutions (tensile strength of 81 MPa) prepared under the same conditions, confirming the impact of cellulose concentration on the films' mechanical properties. Changing the solidifying medium composition by lowering the ethanol content from 80 to 20 caused a drop in the tensile strength of about 10 MPa.

All films showed tensile strength values in the vicinity of 100 MPa, which is close to commercial cellophane. The use of HT treated wood cellulose with a DP of 255 did not cause a considerable drop in the tensile strength in comparison to the films made of linters.

GPC analysis of cellulose film

The molecular mass distribution of the cellulosic substrate and respective films was determined. ***Figure 9*** shows that the films prepared from cotton linters do not differ in terms of MMD. Minor polymer degradation happens during the dissolution procedure. However, in the course of film preparation the cellulose is perfectly preserved, which is also reflected by the curves of HT cellulose and film prepared thereof. Due to the very fast dissolution of the cellulose, the shape of the molecular mass distribution is almost preserved, resulting in only a slight drop in DP and decrease in PDI to 2.1.

Table 5 presents the number and weight average molar mass, PDI and DP of the original cellulose substrates and films prepared thereof (see page 42).

Herein it was demonstrated that films with a tensile strength of around 100 MPa and elongation of about 30% can be prepared from solutions of linters or hydrothermally treated dissolving pulp in IL by coagulation in a bath containing ethanol, demineralised water, IL or a mixture thereof. Films formed from the solution of HT cellulose with a much lower DP than cotton linters are characterised by a tensile strength of about 91 MPa.

HT cellulose dissolves within 15 minutes with moderate heating. Solutions of cellulose with a concentration above 10 wt% require a prolonged de-aeration time. A higher cellulose concentration had a positive effect on the mechanical properties of the films prepared.

Conclusions

1. Conditions were elaborated to form transparent film from solutions of cotton linters in [emim][OAc] with tensile strengths up to 103 MPa and elongation of 30%.
2. It was demonstrated that thermally treated dissolving pulp is suitable for the purpose of preparing cellulose films. HT wood cellulose with a polydispersity index of DPI = 2.2 and degree of polymerisation DP = 255 is a suitable substrate for the forming of cellulose film.
3. Adequate processing of HT cellulose shortens the dissolution time to only

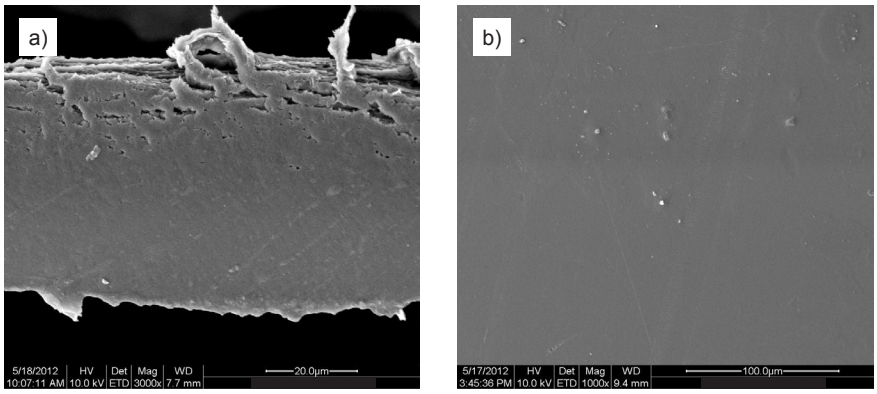


Figure 8. *SEM images of cross section (a) and surface (b) of cellulose film made from 10.0 wt% cellulose HT/IL solution RCF – 15.*

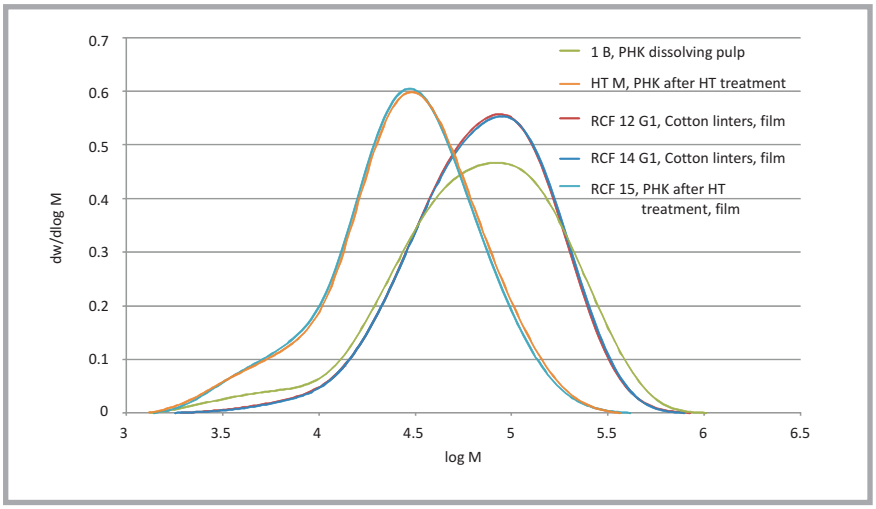


Figure 9. *Molecular mass distribution of cellulose and respective cellulose films.*

Table 5. *Key parameter calculated from the MMD analyses of the cellulose substrates and respective films.*

Parameter	Symbol of samples						
	1 B	RCF 18 film	HT M	RCF 15 film	RCF 16A film	RCF 12 G1 film	RCF 14 G1 film
	PHK dissolving pulp		PHK after HT treatment			Cotton linters	
Mn, kDa	35.5	33.5	18.6	18.1	18.5	43.8	45.0
Mw, kDa	102.5	86.6	41.3	39.4	38.8	94.3	97.0
Polydispersity PDI (Mw/Mn)	2.9	2.6	2.2	2.2	2.1	2.2	2.2
DP	633	534	255	243	242	582	599

15 minutes, which prevents cellulose degradation during the IL-treatment sequence.

4. A concentration of 10 wt% of HT cellulose in the IL solution results in high tensile strength of the film prepared.

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