

Development of a novel regenerated cellulose composite material



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ABSTRACT

We report for the first time on a new natural composite material achieved by blending cotton and duck feather using an ionic liquid. The addition of duck feather was found to improve the elasticity, strain at break, by 50% when compared to regenerated cellulose alone. This is a significant finding since regenerated cotton using ionic liquids often suffers from poor elasticity. The improved elasticity is likely due to the regenerated duck feather maintaining its helical structure. The new regenerated cellulose composites were characterized using a combination of dynamic mechanical analysis, Fourier transform infrared spectroscopy, thermal gravimetric analysis, contact angle measurements and scanning electron microscopy.

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1. Introduction

Cellulose, the structural component of plant walls, is the most abundant raw material on Earth, with millions of pounds of this biopolymer produced every year (Wakelyn et al., 2007; Wang & Zhang, 2009). Given that cellulose is biodegradable, biocompatible, thermally and chemically stable, plentiful and inexpensive, it makes for a versatile and valuable resource (Belgacem & Gandini, 2008; Klemm, Heublein, Fink, & Bohn, 2005; Morton & Hearle, 2008; Netravali, Huang, & Mizuta, 2007; Wakelyn et al., 2007). Due to the recalcitrance of cellulose to both chemical and enzymatic processing, the development of new materials often encounters disadvantages such as long reaction times, harsh conditions or the use of toxic chemicals. Regenerated cellulose fibres can be achieved in a variety of different ways, which ultimately depends on the processing solvent. The most common methods for the preparation of regenerated cellulose are the viscose rayon along with non-viscose rayon methods (Kotek, 2007; Woodings, 2000). In the viscose method, the cellulose is converted into sodium cellulose xanthate, which is soluble in NaOH making it possible to wet-spin the polymer into a fibre or film (Gibril & Yue, 2012; Klemm et al., 2005; Kotek, 2007). The major disadvantage of this process is the use of carbon disulfide (CS₂), a volatile and toxic gas, which is harmful to both the environment and human health (Heinze & Liebert, 2001; SIGMA-ALDRICH, 2013; Zhu et al., 2006). In the non-viscose rayon processes the cellulose is not modified but directly dissolved in a solvent system, such

as *N*-methylmorpholine-*N*-oxide (NMMO)/H₂O system or *N,N*-dimethylacetamide (DMA)/lithium chloride (LiCl) (Fink, Weigel, Purz, & Ganster, 2001; Heinze & Koschella, 2005; Heinze & Liebert, 2001; Kotek, 2007). Again, these processes suffer from long treatment times, high temperatures and have environmental concerns associated with effluent waste entering waterway. In recent times, ionic liquids (ILs) have been used for the dissolution of cellulose (Gibril & Yue, 2012; Heinze & Koschella, 2005; Kosan, Michels, & Meister, 2008; Swatloski, Spear, Holbrey, & Rogers, 2002; Vitz, Erdmenger, & Schubert, 2010) as direct solvents. Ionic liquids are composed entirely of ions with numerous possibilities for cation and anion combinations (Marsh, Boxall, & Lichtenthaler, 2004; Matsumoto et al., 2000; Rogers & Seddon, 2003; Zhu et al., 2006). The dissolution of cellulose, along with other polymers, in ionic liquid is ever expanding, with increasing numbers of ionic liquids capable of dissolving cellulose reported (Kosan et al., 2008; Pinkert, Marsh, Pang, & Staiger, 2009; Xie, Li, & Zhang, 2005; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik, 2010; Zavrel, Bross, Funke, Büchs, & Spiess, 2009; Zhu et al., 2006). The impact of ionic liquids in cellulose dissolution has expanded so greatly that companies such as BASF have even developed a pilot line utilizing 1-ethyl-3-methylimidazolium acetate (EmimOAc) as the solvent to regenerate cellulose (Hermanutz, Meister, & Uerdingen, 2006).

The material properties of regenerated cellulose can depend greatly on the processing methods, however in general, cellulose regenerated using ionic liquids suffers from poor elasticity (Cao, Li, Zhang, Zhang, & He, 2010; De Silva, Wang, & Byrne, 2013; Hameed & Guo, 2010). Therefore, in this study we have sought to improve the properties of regenerated cellulose by blending.

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Polymer blending is a well-known technique used in the polymer industry to develop new materials with improved properties (Wang & Zhang, 2009; Yu, 2009; Yu, Dean, & Li, 2006). The blending of natural polymers using ionic liquids has been previously reported by us and others (De Silva et al., 2013; Hameed & Guo, 2009, 2010), however as is the case with any polymer blending, the selection of the starting materials ultimately impacts the material properties of the final polymer. We found that using wool or silk blended with cellulose did not significantly improve the material properties of the regenerated cellulose. The use of duck feather as a blending material has not been previously reported (Idris et al., 2013; Zhao et al., 2010). Duck feathers are a keratin based protein material consist about 90% keratin which contains about 7% cysteine (Idris et al., 2013; Sun, Liu, & Liu, 2009; Ullah, Vasanathan, Bressler, Elias, & Wu, 2011). It is considered largely to be a waste material (Idris et al., 2013; Zhao et al., 2010). Only a small quantity is utilized in the textile industry for the manufacture of manchester (i.e. beddings and pillows) (Ullah et al., 2011) and duck feathers are also used in the shuttlecock for the sport badminton. (Li, Mao, & Yaniv, 2007). Duck feather is under-utilized as it is a difficult material to solubilize due to the tight arrangement of the α -helix and β -sheet in the polypeptide chain (Idris et al., 2013; Sun et al., 2009; Ullah et al., 2011). Therefore, to utilize these natural polymers by converting them into suitable materials, there is a need for alternative common solvents which are efficient in dissolving both cellulose and duck feather keratin.

It was recently shown that ionic liquids can dissolve duck feather however the material properties were not measured. Here we blend cotton, which was previously separated from polyester–cotton blend wastes (De Silva, Wang, & Byrne, 2014) with duck feather and show a significant improvement in the strain properties of the composite material. In this report the new bio-composites are characterized using a combination of dynamic mechanical analysis (DMA), fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), contact angle measurements, and scanning electron microscopy (SEM).

2. Experimental method

2.1. Dissolution of natural polymers

Single and blended natural polymer solutions of 10wt% of the total polymer content were made using dried 1-allyl-3-methylimidazolium chloride (AmimCl) (purchased from Sigma–Aldrich, NSW, Australia) in 20 mL vials under inert N₂ atmosphere. Other cellulose dissolving ionic liquids such as 1-butyl-3-methylimidazolium acetate (BMIMOA) can be used as a solvent to blend natural polymers. Duck feather obtained from purchases duck feather pillows from spotlight, Australia. The cellulose based materials (yarns) were obtained from Leading Textiles, VIC, Australia. These yarns have not been pre-treated such as scouring or bleaching. The degree of polymerization (DP) of the starting material was measured to be 1260.

Ionic liquids were dried under reduced pressure at 85 °C for 10 h to remove water before dissolution of the polymers was carried out. The water content of the ionic liquid was measured to be less than 0.2% by Karl Fisher titration. The dissolution process was carried out using a pre-heated heating block with a thermocouple at 100 °C. The cotton and duck feathers were oven dried for 24 h at 105 °C. The polymers were added at increments of 1 wt% under magnetic stirring. After total polymer dissolution, a clear and viscous bio-polymer solution was obtained. The complete dissolution was observed and verified using a Nikon 80i eclipse polarizing light microscope (PLM). A dissolved solution was obtained when no crystallinities in the polymer solution were detected.

Table 1
Polymer blends prepared.

Sample name	Polymer blend composition
C100	100% cotton
DF100	100% duck feather
CDF97.5	97.5% cotton; 2.5% duck feather
CDF95	95% cotton; 5% duck feather
CDF90	90% cotton; 10% duck feather
CDF80	80% cotton; 20% duck feather

Measurements of regenerated polymer blends.

2.2. Preparation of regenerated films

The dissolved polymer solution (approximately 1 mL) was spread evenly between two glass slides and immersed in water for 10 min. This was repeated 3 times to ensure removal of the IL from the film. During immersion in the 2nd and 3rd bath, the film was removed from between the glass slides. After which, the film was again immersed in water for 24 h and dried for 48 h at room temperature. The measured film thickness was 65 μ m. After film preparation, the residual solvent was collected separately to recycle the IL. The IL was recycled by water evaporation as described (Cao et al., 2009; Wu, Wang, Wang, Bian, & Li, 2009). No difference in the neat IL and recycled IL was detected in ¹H NMR spectra (¹H NMR spectra are shown in the supplementary graph document). Additionally, the recycled IL was used for further dissolution studies. The regenerated films prepared in this study are shown in Table 1.

2.3. DMA measurements

The stress–strain properties of the regenerated films were measured using dynamic mechanical analysis. Tensile properties of films were measured on a TA Q800 DMA testing machine in tensile mode, with a maximum load capacity of 18 N. Stress–strain curves for the thin rectangular bio-film strips having the dimension of 25 mm $\times$ 5 mm $\times$ 0.065 mm were obtained at room temperature at a controlled force rate of 0.25 N/min. DMA measurement were repeated with 5 specimens of each sample type. Young's modulus was obtained from calculating the gradient of the linear part of the stress–strain curve.

2.4. FTIR spectroscopy

FTIR spectra of the regenerated films were measured on a Bruker LUMOS FTIR microscope. Firstly, samples were scanned in the frequency range of 600–4000 cm^{−1} at the scan resolution of 4 cm^{−1} with a background and sample scan time of 64 scans. Then the samples were again scanned in the regions of interest in the OH stretch region in 2900–3600 cm^{−1} and amide I region in 1590–1710 cm^{−1} for the deconvolution. FTIR measurement was repeated 3 times, taken over 3 places on the same film.

The hydroxyl region (2900–3600 cm^{−1}) was deconvoluted, and the curve was fitted adopting Gaussian model using OPUS 7 software. Deconvolution was carried out adapting a Lorentzian model using a deconvolution factor of 2 and noise reduction factor 0.3. A straight baseline correction of FSD spectrum was performed followed by curve fitting using a Gaussian model. Deconvoluted spectra were automatically adjusted by the autofit programme using a local least square algorithm. Band positions were determined based on fixed number bands determined according to the second derivatives of the original spectra. Three peaks were found in the hydroxyl region which represent inter- and intra-molecular hydrogen bonding of the regenerated films. The intra-molecular hydrogen bonds for O(2)H...O(6), and O(3)H...O(5) (endocyclic oxygen) and the inter-molecular hydrogen bonds for O(6)H...O(3) in the cellulose of the bio-films appeared between

Table 2
Stress–strain values of the regenerated cotton/duck feather blends in AmimCl.

Sample ID	Stress at breakage (MPa)	Strain at breakage (%)	Young's modulus (GPa)
C100	54.89 ± 4.37	4.20 ± 0.26	1.76 ± 0.11
CDF97.5	53.35 ± 3.67	4.48 ± 0.34	1.73 ± 0.15
CDF95	49.82 ± 2.32	6.17 ± 0.23	1.67 ± 0.20
CDF90	47.16 ± 3.02	11.63 ± 0.38	1.66 ± 0.22
CDF80	26.43 ± 2.98	6.30 ± 0.41	1.64 ± 0.19

3455–3410, 3375–3340 and 3310–3230 cm^{-1} respectively (Fan, Dai, & Huang, 2012; Griffiths & De Haseth, 2007; Kondo & Sawatari, 1996; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004). Finally, the spectrum was area normalized to obtain percentage conformations of three bands which represent inter-molecular and intra-molecular hydrogen bonding of the regenerated films.

The amide I region (1595–1705 cm^{-1}) was deconvoluted, and the curve was fitted as described above. Three peaks were found in the amide I region in 1654–1658 cm^{-1} (α -helix), 1621–1630 cm^{-1} (β -sheet) and 1646–1652 cm^{-1} (random coils) (Barth, 2007; Kong & Yu, 2007; Marshall, Orwin, & Gillespie, 1991; Wojciechowska, Włochowicz, & Weselucha-Birczyńska, 1999)

2.5. TGA measurements

Thermal stability of the samples were measured using Thermogravimetric analyses (TGA) on a Netzsch STA 409 Thermogravimetric analyzer. Measurements were performed using 5–8 mg of the samples. The specimens were heated from 30 °C to 500 °C at a heating rate of 10 °C/min under N_2 atmosphere. The thermal degradation temperature at which the weight loss begins (T_d) was calculated as the onset.

2.6. SEM images

The morphologies of bio-films were observed using a Zeiss Supra 55VP scanning electron microscope (SEM) at an accelerating voltage of 5.00 kV. The surface of the bio-film was gold coated before observation.

2.7. Contact angle measurements

The contact angle of the regenerated films was measured using a Malvern contact angle measurement instrument.

3. Results and discussion

The material properties of the regenerated films were measured using DMA. For the films prepared in AmimCl, the Young's modulus, maximum stress and strain at breakage are given in Table 2 (stress–strain curves are shown in the supplementary graph document). C100 shows the highest stress, 54.89 MPa with a strain at break of 4.20 breakage. The addition of duck feather significantly improved the elasticity as measured by improvements in the strain at break. The addition of 10 wt% duck feather gives the greatest strain at break value, 11.63% which is an improvement of greater than 50%, when compared to the 100% regenerated cellulose sample, C100. A small decrease of 13% in the stress at break is measured with the 10 wt% duck feather addition, interestingly with the addition of 20 wt% duck feather, a significant decrease in the stress at break is measured while a decrease in the strain at break (relative to the 10 wt% duck feather sample) is also measured. This suggests that the optimum duck feather concentration is 10 wt%.

The material properties mainly depend on compositions in the film since it is likely that the cellulose component of the blend gives the strength to the material. At low amounts the addition of the

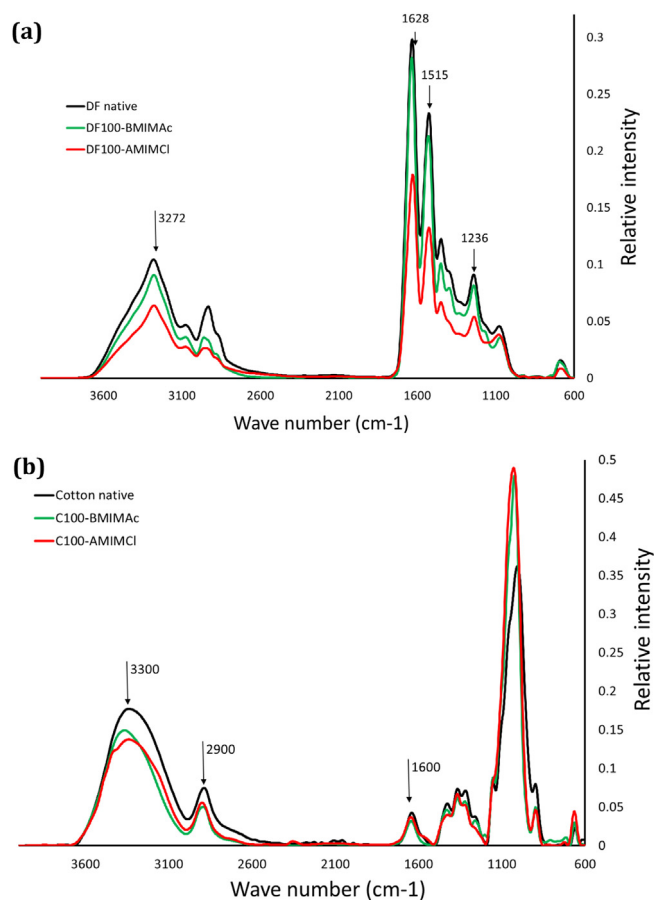


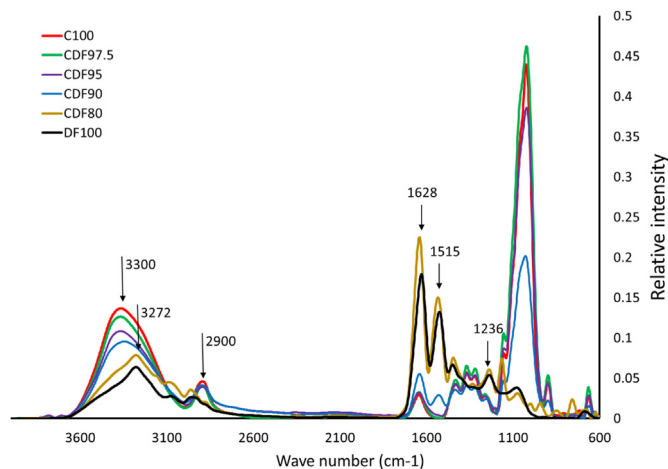
Fig. 1. FTIR spectra of native and regenerated (a) duck feather and (b) cotton. Where native polymers are in black line, regenerated polymers in BmimOAc in green line and regenerated polymers in AmimCl in red line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

duck feather to the cotton improves elasticity due to its α -helix conformation, regenerated duck films do not have good tensile strength (attempts to measure 100% regenerated duck feather films failed). Therefore, it is completely predictable to anticipate that at some duck feather loading the properties of the blended material will decrease, from our measurements at duck feather loadings beyond 10 wt% a significant decrease in material properties is measured.

To determine what interactions are responsible for the improved elasticity with the addition of duck feather to the cellulose, we used FTIR to measure the structural interactions. Fig. 1a shows the FTIR spectra of native duck feather and the regenerated duck feather. The medium absorption band appeared at 3272 cm^{-1} is due to the N–H stretching of the amide A region. A strong band appearing at 1628 cm^{-1} is due to the C=O stretching in the amide I region. The peak found at 1515 cm^{-1} was attributed to C–N stretching and N–H bending of the amide II region. The peak observed at 1236 cm^{-1} relates to C–N and C–O stretching, N–H and O=C–N bending vibrations in amide III region (Barth, 2007; Kong & Yu, 2007; Pribic, Vanstokkum, Chapman, Haris, & Bloemendal, 1993;

Table 3
Secondary structure conformations of native and regenerated duck feathers.

Sample ID	α -helix (1654–1658 cm^{-1})	β -sheet (1621–1630 cm^{-1})	Random coil (1646–1652 cm^{-1})
DF native	54.14%	33.88%	11.98%
DF100-AmimCl	46.78%	46.22%	7.00%
DF100-BmimOAc	44.81%	50.13%	5.06%

**Fig. 2.** FTIR spectra of regenerated films in AmimCl. Where C100 is red, CDF97.5 is green, CDF95 is purple, CDF90 is blue, CDF80 is gold and DF100 is black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Wojciechowska et al., 1999). Here, the spectra of regenerated duck feather in both AmimCl and BmimOAc is very similar to that of the native duck feather. Normally when natural protein fibres such as wool and silk are regenerated, the degree of beta sheet is increased, resulting in a brittle material (De Silva et al., 2013; Du et al., 2009; Kweon, Ha, Um, & Park, 2001). However upon close inspection of the amide I region, shown in the insert, it clearly shows the regenerated duck feather maintains its helical structure. Table 3 shows the deconvolution of the region, where a very slight decrease in helical content is observed. Also the choice of IL as the dissolving solvent seems to have little effect on the structure of the regenerated duck feather with both films regenerated using water. Fig. 1b shows the spectra of native and regenerated cotton. The spectra of regenerated cotton is similar to the native cotton with both showing a broad peak around 3300 cm^{-1} due to the O–H stretch vibration and the peak observed at 2900 cm^{-1} is due to the C–H stretching (Fan et al., 2012; Kondo & Sawatari, 1996; Schwanninger et al., 2004).

Fig. 2 shows the FTIR spectra of the regenerated cotton/duck feather blends using AmimCl as the dissolving solvent. Increasing the duck feather concentration in the composite resulted in a narrowing as well as a shift of the OH peak in the 3000–3500 cm^{-1} region. This peak can be used to understand the hydrogen bond network with a shift to lower wavelengths suggesting an increase in the intermolecular hydrogen bonds with duck feather addition. This suggests that as the duck feather is added, a strong interaction between the cotton and the duck feather exists. This also suggests that a homogenous blend is formed. Table 4 gives the deconvoluted data for this region for the various blends.

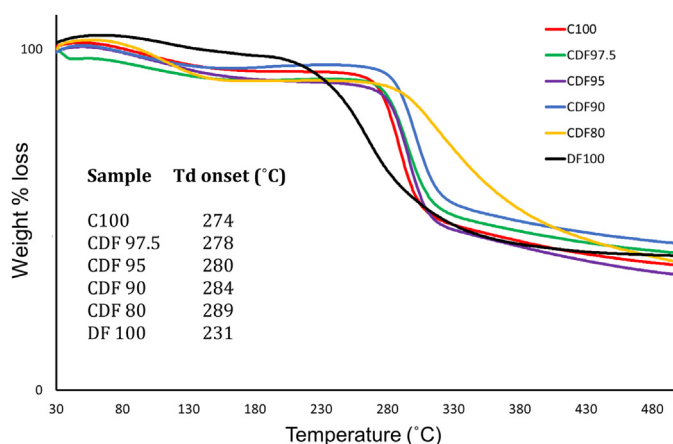
The peak near 1620 cm^{-1} of the regenerated cotton is overlapped with the amide I region. Therefore it was not possible to deconvolute the amide I region for the cotton/duck feather blends.

The thermal degradation curves of the regenerated films in AmimCl are shown in Fig. 3.

It can be seen that the blend composition plays a significant role in the thermal degradation temperature (T_d) of the films. The

Table 4
Hydrogen bond conformations of regenerated cotton/duck feather blends in AmimCl.

Sample ID	Intra-molecular hydrogen bonds		Inter-molecular hydrogen bonds
	O(2)H ... O(6) (3455–3410 cm^{-1})	O(3)H ... O(5) (3375–3340 cm^{-1})	O(6)H ... O(3) (3310–3230 cm^{-1})
C100	4.28%	70.62%	25.10%
CDF97.5	3.88%	69.40%	26.72%
CDF95	3.72%	67.42%	28.86%
CDF90	4.41%	63.18%	32.41%
CDF80	4.18%	59.87%	35.95%

**Fig. 3.** TGA curves of cotton/duck feather blends prepared in AMIMCl.**Table 5**
Contact angles of native and regenerated cotton/duck feather blends in AmimCl.

Sample name	Water contact angle (°)
DF native	152.64
Cotton native	142.45
C100	119.70
DF100	77.97
CDF97.5	117.25
CDF95	101.52
CDF90	95.52
CDF80	82.07

T_d increases as the duck feather content of the blend increases, with CDF80 showing the highest T_d , which is 289 °C.

The increase in the measured thermal stability is likely due the result of the new bonding occurred between – NH groups of duck feathers and – OH groups of cellulose in the blend which increased the intermolecular hydrogen bonds as measured in FTIR deconvolution.

Surface properties of the native and regenerated materials were measured from water contact angle (contact angle images are shown in the supplementary graph document). The contact angle averages provided in Table 5 shows that the native duck feather is a super hydrophobic material with a water contact angle of 152.64°. The super hydrophobic materials have a water contact angle greater than 150° (Liu, Liang, Zhou, & Liu, 2012; Neinhuis & Barthlott, 1997). Therefore duck feather may act as hydrophobic materials such as crude oil. In contrast, the water contact angle of regenerated duck feather was 77.97°, which indicates hydrophilicity (hydrophilic materials have water contact angle less than 90° Sun et al., 2009). It is interesting that the surface of the regenerated duck feather changed from hydrophobic to hydrophilic during the regeneration. This could possibly be due to the changes of the secondary structure of duck feather during the dissolution process. Furthermore,

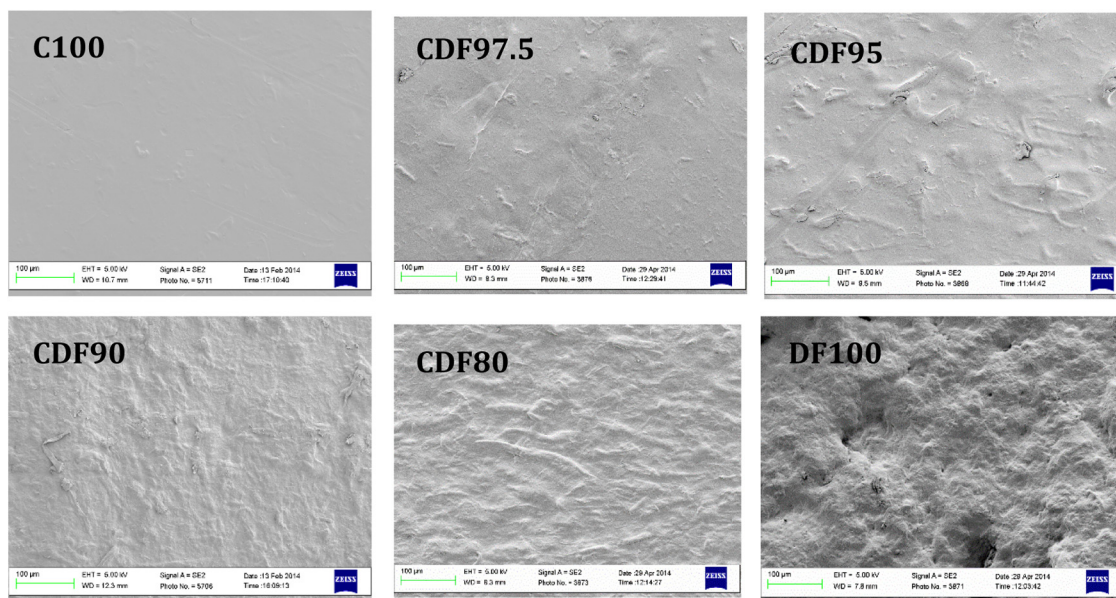


Fig. 4. SEM images of the regenerated cotton/duck feather blends in AmimCl.

when the dissolved duck feather is regenerated using water, the hydrophilic groups such as the amino and carboxyl groups may tend to self-assemble towards the water phase, making the surface of the regenerated duck feather hydrophilic.

The water contact angle of the native cotton fibres was 142.45° . This hydrophobicity is imparted due to the waxes present in the raw cotton fibre. The cotton used for the dissolution was not scoured to remove these waxes. The water contact angle of the regenerated cotton was reduced to 119.70° , which means it retains hydrophobic properties. The removal of waxes during the dissolution process may account for the slight contact angle reduction.

For the regenerated cotton/duck feather blended films, the addition of duck feather resulted in a reduction in the water contact angle. The CDF80 blended film has the most hydrophilic properties, with a contact angle of 82.07° . This phenomenon is due to the hydrophilicity imparted from the presence of the duck feather.

The surface morphologies of the regenerated films in AmimCl are shown in Fig. 4. It reveals the continuous morphology of the blend films, which suggest that there was no phase separation. That means that the cellulose is miscible with duck feather keratin. Also the film surface becomes more irregular with the addition of the duck feather. This may be due to the difference in the way that cellulose and duck feather keratin coagulate in water. The difference in diffusion kinetic behaviour between the two materials may account for the rapid coagulation to form a clotted structure. The SEM observations, suggests that pure duck feather coagulates or refolds much faster than pure cotton giving it an irregular morphology. Interestingly, the surface of the films regenerated in BmimOAc, (SEM images are shown in the supplementary graph document) were different to the films regenerated in AmimCl. This is likely driven by the different diffusion kinetics, which occurred due to the different ionic liquid–water interactions caused by the anions, acetate and chloride in BmimOAc and AmimCl. The acetate anion interaction with water is stronger than that of the chloride anion. Thus BmimOAc removal from the polymer into the water phase was easier than the removal of AmimCl during the coagulation resulting in different diffusion kinetics. Future work will be explored to understand the diffusion kinetics to explain this phenomenon.

4. Conclusion

We successfully regenerated new cotton/duck feather blended materials using two imidazolium based ionic liquids as the blending solvent. The new blended films showed enhanced elastic properties as well as thermal stability in comparison with the single component films regenerated in ionic liquids. The CDF90 film showed the highest elasticity properties whereas CDF80 was shown to have the highest thermal degradation temperature. The amount of α -helix in the blend film accounts to improve the elastic properties and the increase in intermolecular hydrogen bonds for the increase in thermal degradation as measured. The choice of the ionic liquid did not impact the material properties of the films apart from their different surface morphologies observed from SEM. That could possibly be due to the different diffusion kinetics present with the choice of ionic liquid. Current work is in progress to understand this diffusion kinetics in coagulation process and to develop new cotton/duck feather blend fibres using wet spinning technology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2014.12.018>.

References

- Barth, A. (2007). Infrared spectroscopy of proteins. *Biochimica et Biophysica Acta (BBA) – Bioenergetics*, 1767(9), 1073–1101.
- Belgacem, M. N., & Gandini, A. (Eds.). (2008). *Monomers, polymers and composites from renewable resources*. Amsterdam: Elsevier.
- Cao, Y., Li, H., Zhang, Y., Zhang, J., & He, J. (2010). Structure and properties of novel regenerated cellulose films prepared from cornhusk cellulose in room temperature ionic liquids. *Journal of Applied Polymer Science*, 116(1), 547–554.
- Cao, Y., Wu, J., Zhang, J., Li, H., Zhang, Y., & He, J. (2009). Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, 147(1), 13–21.

- De Silva, R., Wang, X., & Byrne, N. (2013). Tri-component bio-composite materials prepared using an eco-friendly processing route. *Cellulose*, 20(5), 2461–2468.
- De Silva, R., Wang, X., & Byrne, N. (2014). Recycling textiles: The use of ionic liquids in the separation of cotton polyester blends. *RSC Advances*, 4(55), 29094–29098.
- Du, C., Jin, J., Li, Y., Kong, X., Wei, K., & Yao, J. (2009). Novel silk fibroin/hydroxyapatite composite films: Structure and properties. *Materials Science and Engineering C*, 29(1), 62–68.
- Fan, M., Dai, D., & Huang, B. (2012). Fourier transform infrared spectroscopy for natural fibres. In *Fourier transform—materials analysis*. ISBN 978-953.
- Fink, H. P., Weigel, P., Purz, H. J., & Ganster, J. (2001). Structure formation of regenerated cellulose materials from NMMO-solutions. *Progress in Polymer Science*, 26(9), 1473–1524.
- Gibril, M. E., & Yue, Z. (2012). Current status of applications of ionic liquids for cellulose dissolution and modifications: Review. *International Journal of Engineering Science and Technology*, 4, 3556–3571.
- Griffiths, P., & De Haseth, J. A. (2007). *Fourier transform infrared spectrometry*. New Jersey: Wiley-Interscience.
- Hameed, N., & Guo, Q. (2009). Natural wool/cellulose acetate blends regenerated from the ionic liquid 1-butyl-3-methylimidazolium chloride. *Carbohydrate Polymers*, 78(4), 999–1004.
- Hameed, N., & Guo, Q. (2010). Blend films of natural wool and cellulose prepared from an ionic liquid. *Cellulose*, 17(4), 803–813.
- Heinze, T., & Koschella, A. (2005). Solvents applied in the field of cellulose chemistry: A mini review. *Polimeros*, 15, 84–90.
- Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, 26(9), 1689–1762.
- Hermanutz, F., Meister, F., & Uerdingen, E. (2006). New developments in the manufacture of cellulose fibers with ionic liquids. *Chemical Fibers International*, 56(6).
- Idris, A., Vijayaraghavan, R., Rana, U. A., Fredericks, D., Patti, A. F., & MacFarlane, D. R. (2013). Dissolution of feather keratin in ionic liquids. *Green Chemistry*, 15(2), 525–534.
- Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, 44(22), 3358–3393.
- Kondo, T., & Sawatari, C. (1996). A Fourier transform infra-red spectroscopic analysis of the character of hydrogen bonds in amorphous cellulose. *Polymer*, 37(3), 393–399.
- Kong, J., & Yu, S. (2007). Fourier transform infrared spectroscopic analysis of protein secondary structures. *Acta Biochimica et Biophysica Sinica*, 39(8), 549–559.
- Kosan, B., Michels, C., & Meister, F. (2008). Dissolution and forming of cellulose with ionic liquids. *Cellulose*, 15(1), 59–66.
- Kotek, R. (2007). Regenerated cellulose fibers. In M. Lewin (Ed.), *Handbook of fiber chemistry* (Vol. 16). Boca Raton: CRC Press.
- Kweon, H., Ha, H. C., Um, I. C., & Park, Y. H. (2001). Physical properties of silk fibroin/chitosan blend films. *Journal of Applied Polymer Science*, 80(7), 928–934.
- Li, X., Mao, D., & Yaniv, Z. (2007). *Nylon 11/filler/modifier composites*. USA: Nano-Proprietary, Inc (5 pp.).
- Liu, X., Liang, Y., Zhou, F., & Liu, W. (2012). Extreme wettability and tunable adhesion: Biomimicking beyond nature? *Soft Matter*, 8(7), 2070–2086.
- Marsh, K. N., Boxall, J. A., & Lichtenthaler, R. (2004). Room temperature ionic liquids and their mixtures – A review. *Fluid Phase Equilibria*, 219(1), 93–98.
- Marshall, R. C., Orwin, D. F. G., & Gillespie, J. M. (1991). Structure and biochemistry of mammalian hard keratin. *Electron Microscopy Reviews*, 4(1), 47–83.
- Matsumoto, H., Yanagida, M., Tanimoto, K., Nomura, M., Kitagawa, Y., & Miyazaki, Y. (2000). Highly conductive room temperature molten salts based on small trimethylalkylammonium cations and bis(trifluoromethylsulfonyl)imide. *Chemistry Letters*, 29(8), 922–923.
- Morton, W. E., & Hearle, J. W. S. (2008). *Physical properties of textile fibres*. Cambridge: Woodhead Publishing Limited.
- Neinhuis, C., & Barthlott, W. (1997). Characterization and distribution of water-repellent, self-cleaning plant surfaces. *Annals of Botany*, 79(6), 667–677.
- Netravali, A. N., Huang, X., & Mizuta, K. (2007). Advanced 'green' composites. *Advanced Composite Materials*, 16(4), 269–282.
- Pinkert, A., Marsh, K. N., Pang, S., & Staiger, M. P. (2009). Ionic liquids and their interaction with cellulose. *Chemical Reviews*, 109(12), 6712.
- Pribic, R., Vanstokkum, I., Chapman, D., Haris, P., & Bloemendal, M. (1993). Protein secondary structure from Fourier transform infrared and/or circular dichroism spectra. *Analytical Biochemistry*, 214(2), 366–378.
- Rogers, R. D., & Seddon, K. R. (2003). Chemistry. Ionic liquids—solvents of the future? *Science*, 302(5646), 792–793.
- Schwanninger, M., Rodrigues, J., Pereira, H., & Hinterstoisser, B. (2004). Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vibrational Spectroscopy*, 36(1), 23–40.
- SIGMA-ALDRICH. (2013). *Material Safety Data Sheet (carbon disulfide)*. SIGMA ALDRICH.
- Sun, P., Liu, Z. T., & Liu, Z. W. (2009). Particles from bird feather: A novel application of an ionic liquid and waste resource. *Journal of Hazardous Materials*, 170(2–3), 786–790.
- Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *Journal of the American Chemical Society*, 124(18), 4974–4975.
- Ullah, A., Vasanathan, T., Bressler, D., Elias, A., & Wu, J. (2011). Bioplastics from feather quill. *Biomacromolecules*, 12(10), 3826–3832.
- Vitz, J., Erdmenger, T., & Schubert, U. S. (2010). Imidazolium based ionic liquids as solvents for cellulose. *Chemistry*, 1033, 299–317.
- Wakelyn, P. J., Bertoniere, N. R., French, A. D., Thibodeaux, D. P., Triplett, B. A., Rouselle, M.-A., et al. (2007). Cotton fibres. In M. Lewin (Ed.), *Handbook of fiber chemistry* (Vol. 16). Boca Raton: CRC Press.
- Wang, Y., & Zhang, L. (2009). Blends and composites based on cellulose and natural polymers. In L. Yu (Ed.), *Biodegradable polymer blends and composites from renewable resources* (pp. 129–161). Hoboken, NJ, USA: John Wiley & Sons Inc.
- Wojciechowska, E., Wlochowicz, A., & Wesolucha-Birczyńska, A. (1999). Application of Fourier-transform infrared and Raman spectroscopy to study degradation of the wool fiber keratin. *Journal of Molecular Structure*, 511–512, 307–318.
- Woodings, C. (2000). Fibers, regenerated cellulose. In *Kirk-Othmer encyclopedia of chemical technology*. John Wiley & Sons Inc.
- Wu, R.-L., Wang, X.-L., Wang, Y.-Z., Bian, X.-C., & Li, F. (2009). Cellulose/soy protein isolate blend films prepared via room-temperature ionic liquid. *Industrial and Engineering Chemistry Research*, 48(15), 7132–7136.
- Xie, H., Li, S., & Zhang, S. (2005). Ionic liquids as novel solvents for the dissolution and blending of wool keratin fibers. *Green Chemistry*, 7(8), 606.
- Yu, L. (Ed.). (2009). *Biodegradable polymer blends and composites from renewable resources*. New Jersey: John Wiley & Sons, Inc.
- Yu, L., Dean, K., & Li, L. (2006). Polymer blends and composites from renewable resources. *Progress in Polymer Science*, 31(6), 576–602.
- Zakrzewska, M. E., Bogel-Lukasik, E., & Bogel-Lukasik, R. (2010). Solubility of carbohydrates in ionic liquids. *Energy and Fuels*, 24(2), 737–745.
- Zavrel, M., Bross, D., Funke, M., Büchs, J., & Spiess, A. C. (2009). High-throughput screening for ionic liquids dissolving (ligno-)cellulose. *Bioresource Technology*, 100(9), 2580–2587.
- Zhao, L., Tang, Y.-x., Zhao, R.-f., Mao, W.-k., Chen, S., & Hua, J. (2010). Dissolution and regeneration of feather keratins in ionic liquids. *Maofang Keji*, 38(8), 1–5.
- Zhu, S., Wu, Y., Chen, Q., Yu, Z., Wang, C., Jin, S., et al. (2006). Dissolution of cellulose with ionic liquids and its application: A mini-review. *Green Chemistry*, 8(4), 325–327.