

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Recycling textiles: the use of ionic liquids in the separation of cotton polyester blends.

Rasike De Silva<sup>1</sup>, Xungai Wang<sup>1</sup> and Nolene Byrne<sup>1\*</sup>

<sup>1</sup>Institute for Frontier Materials, Deakin University, Pigdons Road, Waurn Ponds, Victoria, Australia, 3217. Fax: +61 3 5227 1103

**Textiles are commonly made from intimate blends of polyester and cotton, which makes recycling very difficult. We report for the first time the use of ionic liquid in the separation of polyester cotton blends. By selective dissolution of the cotton component, the polyester component can be separated and recovered in high yield. This finding presents as an environmentally benign approach to recycling textile waste.**

## Introduction

One of the challenges facing society today is the recycling of textiles. It has been reported that the United States generates 25 billion pounds of textiles per year and only 15% of this is recycled with 85 % being sent to landfills<sup>1-3</sup>. The U.S EPA estimates that textile wastes occupies 5% of land fill mass<sup>1, 2</sup>. As such, many campaigns exist to improve the consumers' awareness towards recycling textiles. While donating or selling clothing has resulted in a decrease in the disposal of textiles this is not a complete recycling solution. Currently, only 15% of all textiles material is recycled back into the original fibre form<sup>2-4</sup>. A significant limitation associated with the recycling of clothing back into the original fibres is that the majority of clothing is comprised of blended fibres<sup>3</sup>. The most common blend used in clothing is a polyester/cotton blend<sup>5, 6</sup>. While the individual components, cotton and polyester, can be easily recycled, mechanical separation techniques cannot be used for intimately mixed polyester/cotton blends<sup>5-14</sup>. Limited attempts have been made to separate these blends chemically, however polyester is only soluble in very harsh solvents such as hexafluoroisopropanol<sup>15</sup> and phenol/tetrachloroethane<sup>16</sup>. High concentration acid solutions have also been investigated, such as 70-75 % aqueous sulphuric acid<sup>17</sup> and 85 % aqueous phosphoric acid<sup>18</sup>. However these are not environmentally sustainable solutions

and the acid solutions promotes hydrolysis of the glycosidic linkage of the cellulose chain resulting in the degradation of the cotton fibre <sup>19</sup>.

Here we use ionic liquids, ILs, as environmentally friendly processing solvents for the chemical separation of polyester/cotton blends. The IL selected for this study is the cellulose dissolving 1-allyl-3-methylimidazolium chloride (AMIMCl) <sup>20</sup>. The benefit of using ILs in this process is the ease with which the polyester and cotton can be separated. The AMIMCl selectively dissolves the cotton component, with the added advantage that the IL can be recycled and reused. We show that the polyester is recovered in high yield and that the cotton can be regenerated into various forms, such as wet spun into fibres or cast as films. In 2012, 88.5 million tonnes of fibres were produced <sup>21</sup>, and this amount is expected to continue to increase with demand from developing countries. This technology reported here shows a facile route to the recycling of clothing in the form of polyester/cotton blends. We measure the material properties of the recovered polyester and cotton and show that no significant differences can be seen between the recovered polymers and the as received 100% polymers.

## Materials and Methods

### Dissolution studies

1-allyl-3-methylimidazolium chloride AMIMCl and 1-butyl-3-methylimidazolium acetate BMIMAc were purchased from Sigma Aldrich and vacuum dried for 6 hours at 80°C prior to each dissolution experiments. The water content of the ionic liquid (IL) was measured to be less than 0.2% by Karl Fisher titration. To determine if this IL would dissolve polyester, 100% polyester as received was submerged in the AMIMCl at 80°C and monitored using polarising optical microscopy. Over a 48 hour period, no dissolution was observed.

### Separation of cotton and polyester

All the yarn specimens were oven dried at 105°C for 24 hours prior to dissolution to remove the moisture in yarns. All the yarn samples were obtained from Leading Textiles, Australia. The yarn was added to AMIMCl at 80°C at 2wt% increments up to 10wt%. After 6 hours, the undissolved component was removed, rinsed with water and weighed. Table 1 shows the

weight of the blend before cotton dissolution and the recovered amount. The IL was able to be recovered and recycled as previously reported as water is the coagulating solution<sup>22, 23</sup>.

**Table 1:** Dissolved cotton % and undissolved polyester of the blend samples in AMIMCL

Sample ID	Initial blend weight (mg)	Residue (mg)	Undissolved polyester from the blend %	Dissolved cotton from the blend %
A	1602.25	803.60	50.15	49.85
B	<u>1598.23</u>	<u>798.85</u>	<u>49.98</u>	<u>50.02</u>
C	1600.40	801.72	50.09	49.91

### Characterization of recovered polyester and regenerated cellulose

#### FTIR

FTIR spectra of the samples were measured on Bruker Alpha FT-IR spectrometer. Samples were scanned in the frequency range of 600  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  at the scan resolution of 4  $\text{cm}^{-1}$  and background and sample scan time of 64 scans. FTIR measurement was repeated 3 times, taking over 3 places on the test specimen.

For the cotton films regenerated, the hydroxyl region 2990  $\text{cm}^{-1}$  – 3900  $\text{cm}^{-1}$  was deconvoluted, and curve was fitted adopting Gaussian model using OPUS 5.5 software. Finally, auto fitted spectrum was area normalized to obtain percentage conformations of three bands which represent inter molecular and intra molecular hydrogen bonding of the cotton films regenerated.

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 were appeared in 3455-3410, 3375-3340 and 3310-3230  $\text{cm}^{-1}$  respectively<sup>24, 25</sup>.

### **$^{13}\text{C}$ -CP-NMR**

The solid state of  $^{13}\text{C}$  NMR spectra of the samples were recorded on Bruker AVANCE III 300 MHz Wide Bore using 4.00 mm MAS HX probe. The experiments were carried out at the spinning rate of 12.5 kHz at 25°C for 5677 scans.

### **SEM**

The morphology of samples was observed using Zeiss Supra 55VP scanning electron microscope (SEM) at an accelerating voltage of 5.00 kV. The sample surface was gold coated before observation.

### **DSC**

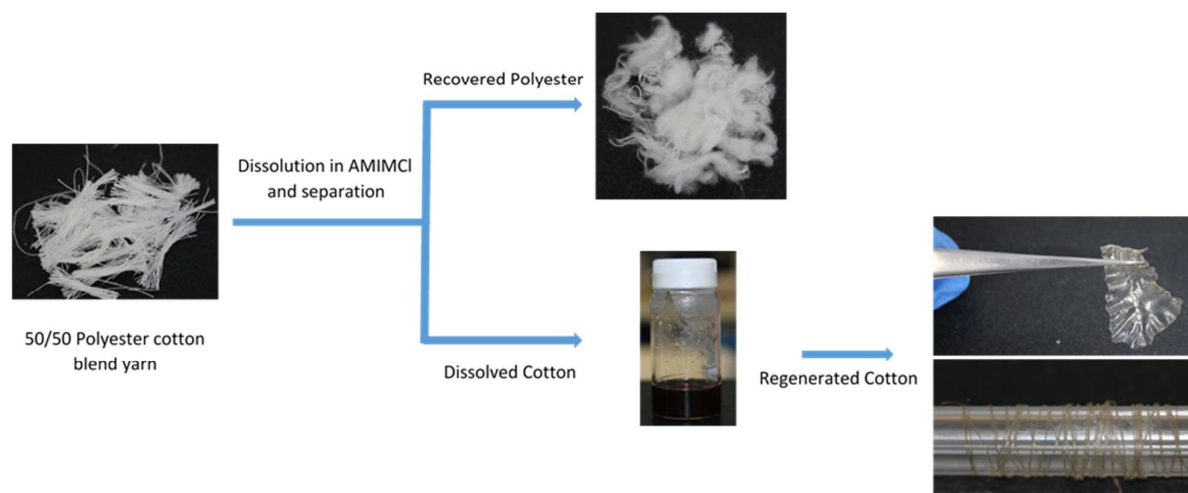
The DSC experiments were performed on TA DSC Q 200 differential scanning calorimetry using 4-6 mg of the sample. Firstly the samples were heated to 100°C at a heating rate of 10°C/min under  $\text{N}_2$  atmosphere. Then the samples were held at 100°C for 5 minutes to delete the thermal history. The samples were cooled down 0°C at a cooling rate of 10°C/min and held for 5 minutes. Subsequently, the samples were heated from 0°C to 300°C at a heating rate of 10°C/min (second scan). The second scans of the samples are shown.

### **TGA**

The samples were subjected to Thermogravimetric analyses (TGA) on Netzsch STA 409 Thermogravimetric analyser. Test was performed using 5-8 mg of the samples. The specimens were heated from 25°C to 600°C at a heating rate of 10°C/min under  $\text{N}_2$  atmosphere. The decomposition temperature at which the weight loss begins ( $T_d$ ) calculated as the onset.

### **Results and discussion**

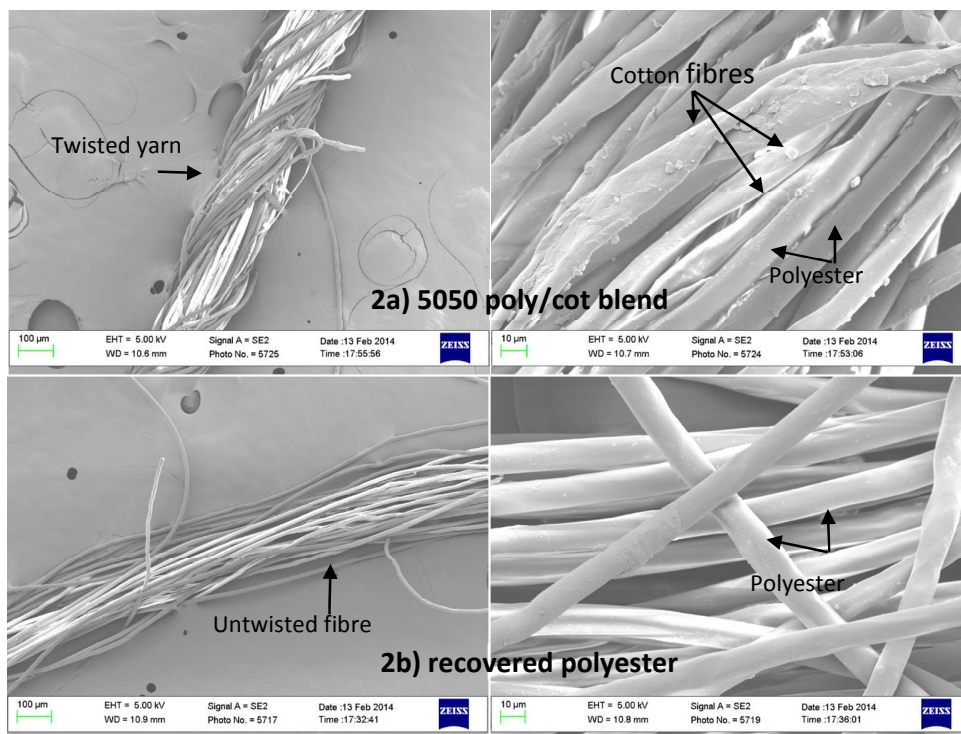
Figure 1 shows the general scheme for the separation of the cotton/polyester blend using AMIMCl. The IL was able to be recovered and recycled as previously reported as water is the coagulating solution<sup>22, 23</sup>



**Figure 1:** Separation and utilisation of polyester/cotton blends using AMIMCl

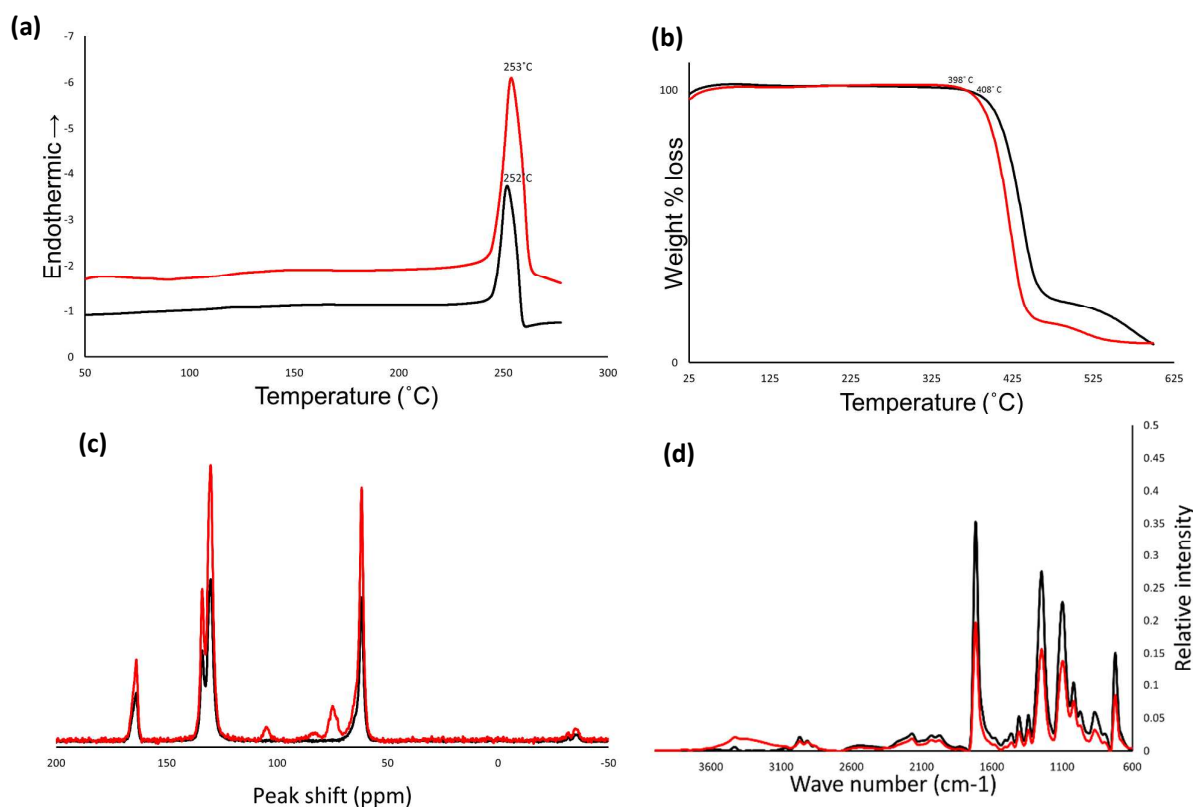
For this process we have studied both AMIMCl and BMIMAc, these ILs have been selected on the basis of their cellulose dissolving capabilities, both ILs show some of the highest cellulose dissolving capabilities<sup>26</sup>. Little difference in the separation capabilities was noted under the conditions investigated here. We also studied the impact of temperature on the separation process and found little difference in the time it took to dissolve the cotton component in either BMIMAc or AMIMCl at 80°C, 100°C and 120°C. The dissolution of the cotton was considerably faster at 120°C for both ILs as expected (see Table 1, supporting information).

Figure 2a shows scanning electron image of the polyester cotton blend; prior to separation both cotton and polyester fibres can be observed. Figure 2 b shows the recovered polyester, only polyester fibres are observed.



**Figure 2:** (2a)-SEM of polyester/cotton blend; (2b)-SEM of recovered polyester

We also characterized the structure of the recovered polyester, using a combination of DSC, TGA, NMR and FTIR shown in Figure 3a-d. For comparison we include the as received 100% polyester. It can be seen that no change in the melt temperature of the recovered polyester is measured, which is important since polyester can be recycled by melting the polyester and reshaping the polyester into the desired form (fibres, bottles, etc.). The  $^{13}\text{C}$  NMR spectrum and FTIR do indicate that some small amount (less than 2%) of cotton may remain with the recovered polyester as evidenced by the additional peaks observed at 60 and 110 ppm<sup>27, 28</sup>, and the presence of the hydroxyl peak at  $3300\text{ cm}^{-1}$ <sup>25, 29</sup> in the FTIR spectrum.

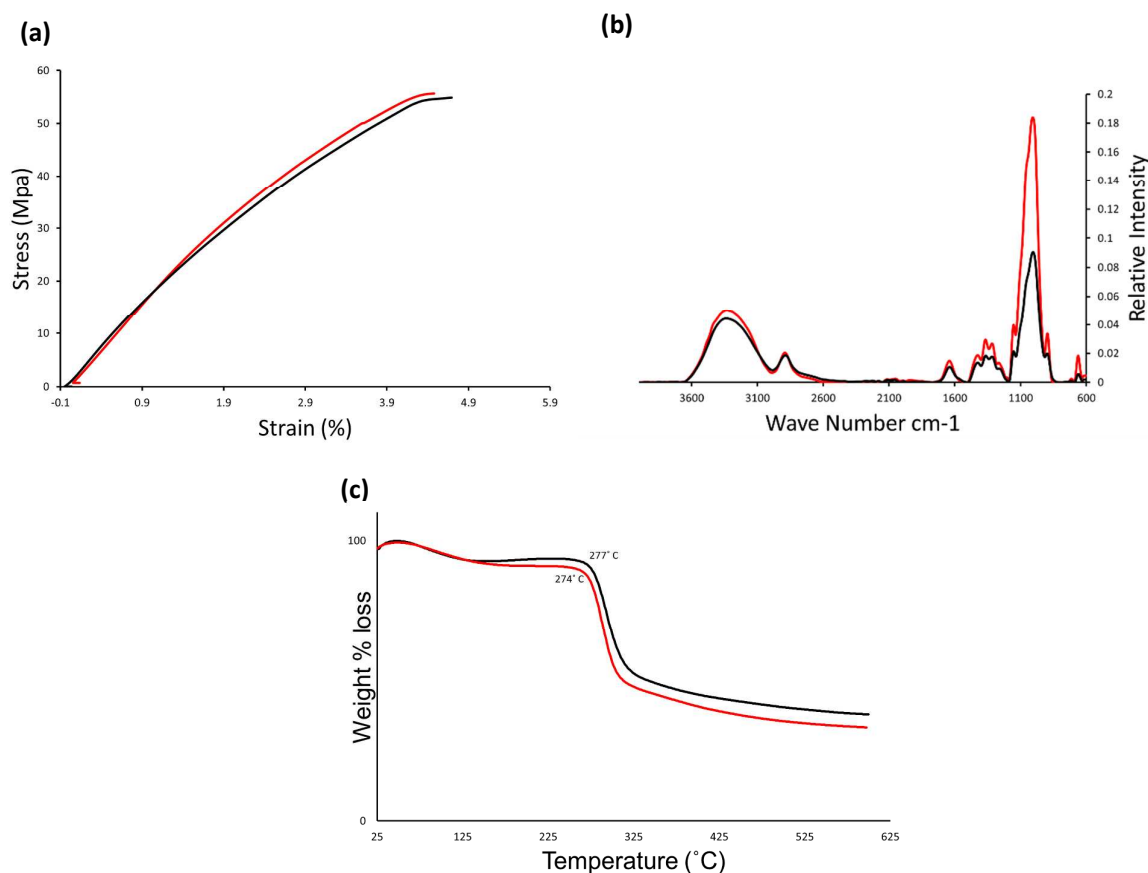


**Figure 3a-d:** Characterization of the recovered polyester (red curve) compared with the as received polyester (black curve) a) DSC curves b) TGA curves, c) <sup>13</sup>C- CP-NMR and d) FTIR , all show little to no difference between the two polyester samples.

We now turn our attention to the regenerated cotton. We show that fibres and/or films can easily be prepared from the cotton/AMIMCl solution. Regenerated cellulose fibres have a considerable market share and are growing in popularity, common regenerated cellulosic fibres are viscose, rayon and lyocel<sup>30, 31</sup>. Figure 4a-c shows a series of material characterization experiments performed on the recovered cotton from the blend compared with as received cotton dissolved and regenerated from the same IL, AMIMCl. As can be seen no difference in the tensile properties are observed between the two cotton samples (Fig 4a, stress and stain at breakage and Young's modules provided in Table 2 ESI). Similarly



the thermal degradation temperature and FTIR show no appreciable differences (deconvolution of the OH region provided in Table 3 ESI).



**Figure 4a-c:** Characterization of the recovered cotton (red curve) compared with as received cotton (black curve) a) DMA curves b) TGA curves, c) FTIR, all show little to no difference between the two cotton samples. Both samples are regenerated cotton.

Here we described the facile and efficient separation of polyester/cotton blends into their individual components. This was achieved by selective dissolution of the cotton component using the ionic liquid AMIMCl. We showed that the cotton could be regenerated using water as the coagulated solvent. Regenerated cotton is a material finding increased use in the textiles industry<sup>30-32</sup>, in the carbon fibre industry as low cost precursor materials<sup>33, 34</sup> and as the starting material for bioethanol production<sup>20, 35, 36</sup>.

## References

1. Council for Textile Recycling, <http://www.weardonaterecycle.org/index.html>, Accessed 1st March 2014.
2. Wastes - Resource Conservation - Common Wastes & Materials, <http://www.epa.gov/wastes/conserves/materials/textiles.htm>, Accessed 03rd March 2014, 2014.
3. Y. Wang, ed., *Recycling in textiles*, Woodhead Publishing Limited, Cambridge England, 2006.
4. Business Recycling, <http://businessrecycling.com.au/recycle/clothes>, Accessed 03rd March 2014.
5. Y. Zou, N. Reddy and Y. Yang, *Composites Part B: Engineering*, 2011, **42**, 763-770.
6. E. M. Kalliala and P. Nousiainen, *AUTEX Research Journal*, 1999, **1**, 8-20.
7. G. Güçlü, T. Yalçinyuva, S. Özgümüş and M. Orbay, *Polymer*, 2003, **44**, 7609-7616.
8. F. Liu, X. Cui, S. Yu, Z. Li and X. Ge, *Journal of Applied Polymer Science*, 2009, **114**, 3561-3565.
9. G. P. Karayannidis and D. S. Achilias, *Macromolecular Materials and Engineering*, 2007, **292**, 128-146.
10. D. E. Nikles and M. S. Farahat, *Macromolecular Materials and Engineering*, 2005, **290**, 13-30.
11. D. Carta, G. Cao and C. D'Angeli, *Environmental Science and Pollution Research*, 2003, **10**, 390-394.
12. S. R. Shukla, A. M. Harad and L. S. Jawale, *Waste Management*, 2008, **28**, 51-56.
13. S. R. Shukla and A. M. Harad, *Polymer Degradation and Stability*, 2006, **91**, 1850-1854.
14. M. E. Tawfik and S. B. Eskander, *Polymer Degradation and Stability*, 2010, **95**, 187-194.
15. A. Moroni and T. Havard, in *Chromatography of Polymers*, American Chemical Society, 1999, vol. 731, pp. 249-262.
16. F. Galil, *Textile Research Journal*, 1973, **43**, 615-623.
17. I. Negulescu, H. Kwon, B. J. Collier, J. R. Collier and A. Pendse, *Text Chemistry Color*, 1998, **30**, 31-35.
18. F. Shen, W. Xiao, L. Lin, G. Yang, Y. Zhang and S. Deng, *Bioresour Technol*, 2013, **130**, 248-255.
19. P. J. Wakelyn, N. R. Bertoniere, A. D. French, D. P. Thibodeaux, B. A. Triplett, M.-A. Roussele, W. R. Goynes, Jr., J. Vincent Edwards, L. Hunter, D. D. McAlister and G. R. Gamble, in *Handbook of fiber chemistry*, ed. M. Lewin, CRC Press, Boca Raton, 2007, vol. 16.
20. S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding and G. Wu, *Green Chemistry*, 2006, **8**, 325-327.
21. The Fibre Year - 2013, [http://www.thefiberyear.com/media/pdf/Tfy\\_Toc\\_2013\\_05.pdf](http://www.thefiberyear.com/media/pdf/Tfy_Toc_2013_05.pdf), Accessed 26th February 2014.
22. Y. Cao, J. Wu, J. Zhang, H. Li, Y. Zhang and J. He, *Chemical Engineering Journal*, 2009, **147**, 13-21.
23. B. Li, J. Asikkala, I. Filpponen and D. S. Argyropoulos, *Industrial and Engineering Chemistry Research*, 2010, **49**, 2477-2484.
24. T. Kondo and C. Sawatari, *Polymer*, 1996, **37**, 393-399.
25. M. Schwanninger, J. Rodrigues, H. Pereira and B. Hinterstoisser, *Vibrational Spectroscopy*, 2004, **36**, 23-40.
26. M. E. Zakrzewska, E. Bogel-Łukasik and R. Bogel-Łukasik, *Energy & Fuels*, 2010, **24**, 737-745.
27. S. Köhler, T. Liebert and T. Heinze, *Journal of Polymer Science Part A: Polymer Chemistry*, 2008, **46**, 4070-4080.
28. H. Zhang, J. Wu, J. Zhang and J. He, *Macromolecules*, 2005, **38**, 8272-8277.
29. M. Fan, D. Dai and B. Huang, *Fourier Transform—Materials Analysis*, ISBN, 2012, 978-953.
30. R. Kotek, in *Handbook of fiber chemistry*, ed. M. Lewin, CRC Press, Boca Raton, 3rd edn., 2007, vol. 16.

31. C. Woodings, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.
32. Y. Wang and L. Zhang, in *Biodegradable polymer blends and composites from renewable resources*, ed. L. Yu, John Wiley & Sons Inc, Hoboken, NJ, USA, 2009, pp. 129-161.
33. P. Morgan, in *Carbon Fibers and Their Composites*, CRC Press, Boca Raton USA, 1 edn., 2005, pp. 269-294.
34. A. G. Dumanli and A. H. Windle, *Journal of Materials Science*, 2012, **47**, 4236-4250.
35. M. Balat and H. Balat, *Applied Energy*, 2009, **86**, 2273-2282.
36. B. Hahn-Hägerdal, M. Galbe, M. F. Gorwa-Grauslund, G. Lidén and G. Zacchi, *Trends in Biotechnology*, 2006, **24**, 549-556.