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Short communication

Natural wool/cellulose acetate blends regenerated from the ionic liquid 1-butyl-3-methylimidazolium chloride

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ABSTRACT

Dissolution and blending one of the most commonly used natural polymers, i.e., wool using a green solvent ionic liquid is described. The cleaned natural wool from merino sheep was directly dissolved and regenerated from 1-butyl-3-methylimidazolium chloride (BMIMCl) without any modifications. BMIMCl was subsequently used to develop wool/cellulose acetate (CA) blends. Blending modification of wool in this IL green solvent led to significant increase in glass transition temperature (T_g) and thermal stability compared to the pure components. It was found that there exist strong intermolecular hydrogen bonding interactions between regenerated wool and CA. Moreover homogeneous surface morphology was observed in the blends with higher CA concentrations. At the final stage of the blending process, the IL solvent was recycled completely. This work presents a green processing route for development of novel natural wool blended materials.

1. Introduction

Natural wool is one of the most abundant natural polymers, which has evolved over thousands of years to insulate and protect sheep. It has been estimated that wool contains about 20 amino acids linked together in ladder-like polypeptide chains (Block, Bolling, Brand, & Schein, 1939). This heterogeneous composition is responsible for the highly complex and versatile physical and chemical structure of wool, unlike cotton and majority of other natural fibers. The insulating and moisture absorbing properties of wool make it into extremely comfortable textiles. It is noted that everyday large amount of wool is wasted during wool weaving and disposal of used cloths. Wool is renewable, biodegradable, and biocompatible, but difficult to process by directly dissolving into common solvents. This is due to the molecular close chain packing and various inter- and intra-molecular hydrogen bonding (Hames & Hooper, 2003). For functional applications and chemical modifications, it is essential to form a stable homogeneous wool solution in order to improve the efficiency of the application. Multiple methods have been utilized to prepare wool solutions. Solvent systems like carbamide/H_2O_2/H_2O and carbamide/2-mercaptoethanol were used for the processing (Garrett & Grisham, 2002). However, the limitations of these solvents such as volatility, toxicity, cost, difficulty for solvent recovery, and moreover, strong environmental impact of the waste solution prompted researchers to develop new dissolving techniques.

A new class of solvent, ionic liquids (ILs) have recently received much attention as green solvents and as very promising replacements for the traditional volatile organic solvents due to their characteristics such as non-volatility, non-flammability, thermal stability and ease of recycling (Earle & Seddon, 2000; Novoselov, Sashina, Kuzmina, & Troshenkova, 2007; Ueki & Watanabe, 2008; Zhang et al., 2006). In fact, the properties of ILs can be manipulated according to the requirements since they offer great flexibility in designing cationic and anionic structures and their combinations; therefore they have been termed the "designers solvent" (Earle & Seddon, 2000; Novoselov et al., 2007; Ueki & Watanabe, 2008; Zhang et al., 2006). Ionic liquids possess exceptional solubility characteristics due to their special structures compared to the traditional molecular solvents. Recently, Swatloski, Spear, Holbrey, & Rogers (2002) showed that cellulose can be easily dissolved in ionic liquids without the formation of any derivatives. They prepared concentrated solutions of cellulose in an imidazole-based ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl), and cellulose can be regenerated by coagulation in water or ethanol. Another highly efficient direct cellulose solvent 1-allyl-3-methylimidazolium chloride (AMIMCl) was used by Zhang and coworkers (Wu et al., 2004; Zhang, Wu, Zhang, & He, 2005; Zhang et al., 2007) and they found that regenerated cellulose exhibited good mechanical properties. This new technology therefore opens up great potential for cellulose processing. Xie, Zhang, and Lib (2006) found that chitin and chitosan can be dissolved in BMIMCl. Moreover, a novel application of chitin and chitosan as substitutes for amino-functionalized synthetic polymers for capturing and releasing CO_2 has also been exploited based on this processing strategy. Ionic

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liquids can also be used for dissolving other carbohydrates (Murugesan & Linhard, 2005) and silk fibroin (Phillips et al., 2004, 2005).

Xie, Li, and Zhang (2005) reported the dissolution and solubility of wool keratin fibers in various ILs at different temperatures. Even though they indicated the efficacy of ILs as a natural polymer blend medium, to date research with natural polymers and ILs has largely focussed on single component natural polymer systems. It is well known that blending is an expedient technique for the development of new polymeric materials with improved properties (Guo & Zheng, 1999; Guo et al., 1990; Guo, 1999, chap. 6; Zheng, Hu, Guo, & Wei, 1996). The phase behavior and properties of polymer blends are highly dependent on the extent of intermolecular association. The existence of a favorable intermolecular interaction between two polymers can promote their miscibility and also has a significant effect on the properties of the blends. In this paper, we investigate the dissolution of natural wool and development of regenerated wool/cellulose acetate (CA) blends using IL green solvent. CA is a commercial renewable polymer possessing good toughness and high transparency. CA has huge applications in the manufacture of textiles, tools, frames, photographic films, etc. The effect of phase behavior and specific interactions in regenerated wool/CA blends were investigated using differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy, respectively. The surface morphology of the blends was examined using scanning electron microscopy (SEM). The regenerated wool/cellulose acetate (CA) blends show strongly synergistic behavior, providing an example of wool blended biodegradable and renewable materials with improved properties using an ionic liquid green solvent.

2. Experimental

2.1. Materials and preparation of samples

Natural raw wool, shorn from an Australian merino sheep, was cleaned using acetone/ethanol solvent mixture in a Soxhlet extractor for 48 h. Then it was washed several times with deionized water and finally dried in vacuum oven at 100 °C for 15 h. Cellulose acetate (CA) was purchased from Aldrich with an average $M_n = 50000$ and with 39.7 wt% acetyl content. 1-Buthyl-3-methylimidazolium chloride (BMIMCl) (assay >95%, water content <0.5%) was obtained from Fluka. The chemicals were used as received. Wool fibers were cleaned as described before. A known amount of wool was dispersed into 20 mL molten BMIMCl in a 100 mL flask, and the mixture was heated at 100 °C and stirred until wool samples were completely dissolved to give a clear and viscous wool solution. The concentration of wool was calculated about 5 wt% in BMIMCl. The regenerated wool was obtained by coagulating the wool solution in water as BMIMCl was completely miscible with water in any ratios. The regenerated wool membrane could be obtained by casting the BMIMCL/wool solution onto a glass slide and then soaked in the water bath to allow the ionic liquid to diffuse from the membrane. After the washing with deionized water several times for the complete removal of the ionic liquid, the regenerated wool was then filtered and dried in a vacuum oven. The BMIMCl was recovered completely by evaporating water from the precipitate. The BMIMCL was recovered by the distillation of the water/BMIMCL mixture under reduced pressure both in rotary evaporator and distilling apparatus as described by other authors (Zhang et al., 2005).

The wool/CA blends were prepared by the mutual mixing of wool/BMIMCl and CA/BMIMCl solutions together to get a 5 wt% solution. The mixture solution was stirred at 100 °C again for 12 h in order to ensure the complete intermixing. Regenerated wool/CA blends were obtained in the same way as that of regenerated wool.

2.2. Methods

DSC experiments were carried out using a TA-DSC model Q200 instrument. The measurement was performed using 5–10 mg of the sample under an atmosphere of nitrogen gas. The samples were first heated to 100 °C and held at that temperature for 5 min to remove the thermal history. Then the samples were cooled to 0 °C at a rate of 20 °C/min, held for 5 min, and subsequently heated from 0 to 200 °C at 20 °C/min (second scan). Glass transition temperature (T_g) values were taken as the midpoint of transition in the second scan of DSC thermograms. Thermogravimetry analysis (TGA) measurements were performed on Netzsch STA 409 thermogravimetric analyzer over a temperature range of 25–500 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The decomposition temperature (T_d) was obtained from the onset value of the weight loss curve. The FTIR spectra of all the samples were measured on a Bruker Vetex-70 FTIR spectrometer. The KBr disk method was adopted to conduct the FTIR experiments. The blend sample was mixed with KBr powder, ground well and prepared to KBr disks. The disks were dried under vacuum in an oven at 100 °C before the measurements. The spectra were recorded at the average of 32 scans in the standard wavenumber range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. The morphology of free surfaces of regenerated wool/CA blends was examined with a Leica S440 scanning electron microscope (SEM) at an activation voltage of 5 kV. The free surfaces were coated with thin layers of gold before the observation.

3. Results and discussion

3.1. Surface morphology and phase behavior

The surface morphology of the regenerated wool and wool/CA blends was investigated using SEM. Fig. 1a and b show SEM images of pure wool fibers and regenerated wool, respectively. As can be seen, the surface morphology of the regenerated wool fiber is significantly changed. The fibers of the regenerated wool seem to be diffused into a relatively homogeneous dispersed structure (Fig. 1b). SEM image of regenerated wool/CA blends containing 20 and 40 wt% CA are given in Fig. 1c and d, respectively. It can be observed that these blends are not homogeneous. However, the wool-rich phase and the CA-rich phase cannot be easily distinguished in these images. It can also be seen that the regenerated wool interact with CA in the blends and there is excellent adhesion between the interfaces of two phases. The SEM micrographs of blends containing 60 and 80 wt% CA are given in Fig. 1e and f, respectively. However, no obvious evidence of phase-separated structure or inhomogeneity can be observed; these blends appear homogeneous. The morphology can be correlated with the DSC results (Fig. 2). Regenerated wool/CA blends containing 20 and 40 wt% CA showed two T_g's as observed by DSC, which is due to the existence of two phases as revealed by SEM. On the other hand, the single T_g observed in 60 and 80 wt% CA blends by DSC can be due to the intermixing between the components to form a single phase at these compositions. Morphological observations support the results obtained by DSC that the blends with 60 wt% and higher CA content exhibit a single phase.

Thermal behavior of wool/CA blends was investigated using DSC. The DSC curves of the second scan of wool/CA blends with various compositions are shown in Fig. 2a. Regenerated wool and CA show a T_g of 156 and 163 °C, respectively. As can be seen, the blends with 20 and 40 wt% CA show two distinct T_g's corresponding to the wool-rich phase and the CA-rich phase. It is noted that

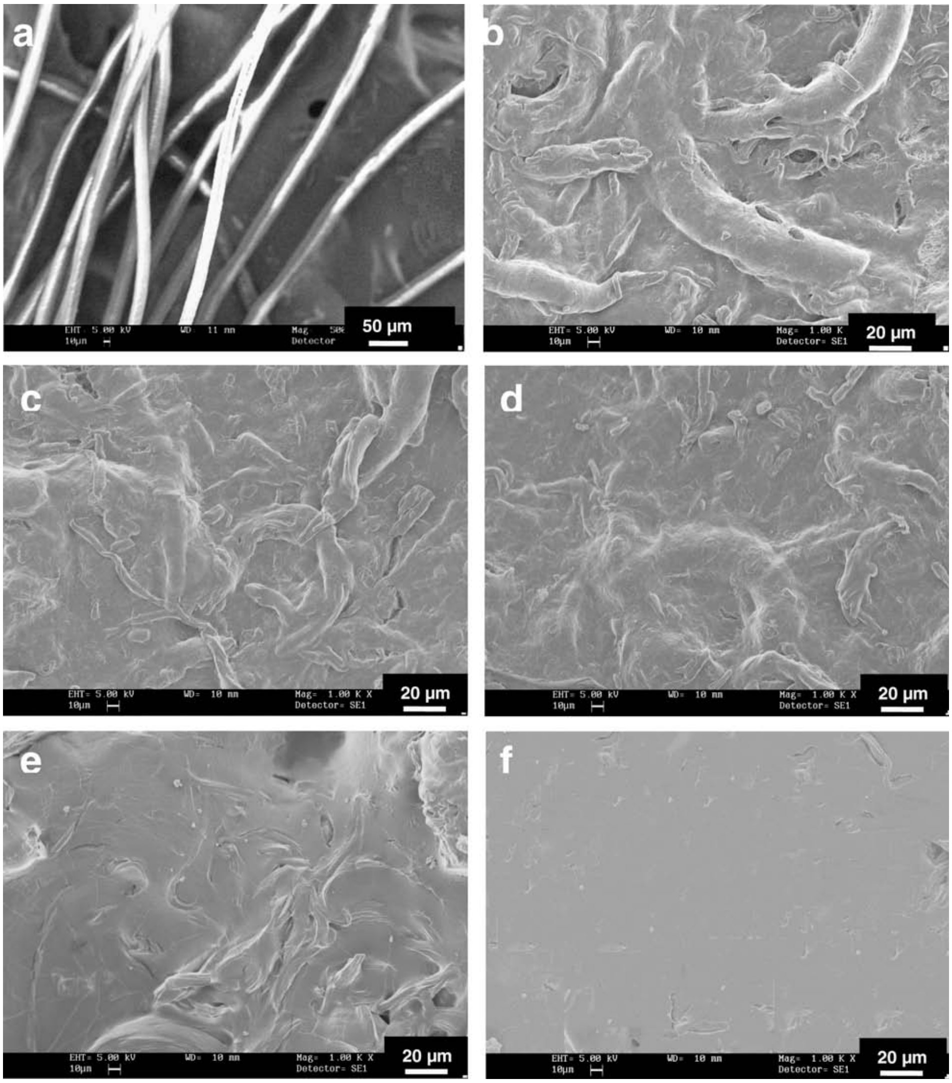

Fig. 1. Scanning electron micrographs of (a) natural wool, (b) wool regenerated from BMIMCl, (c) 80/20, (d) 60/40, (e) 40/60, and (f) 20/80 regenerated wool/CA blends.

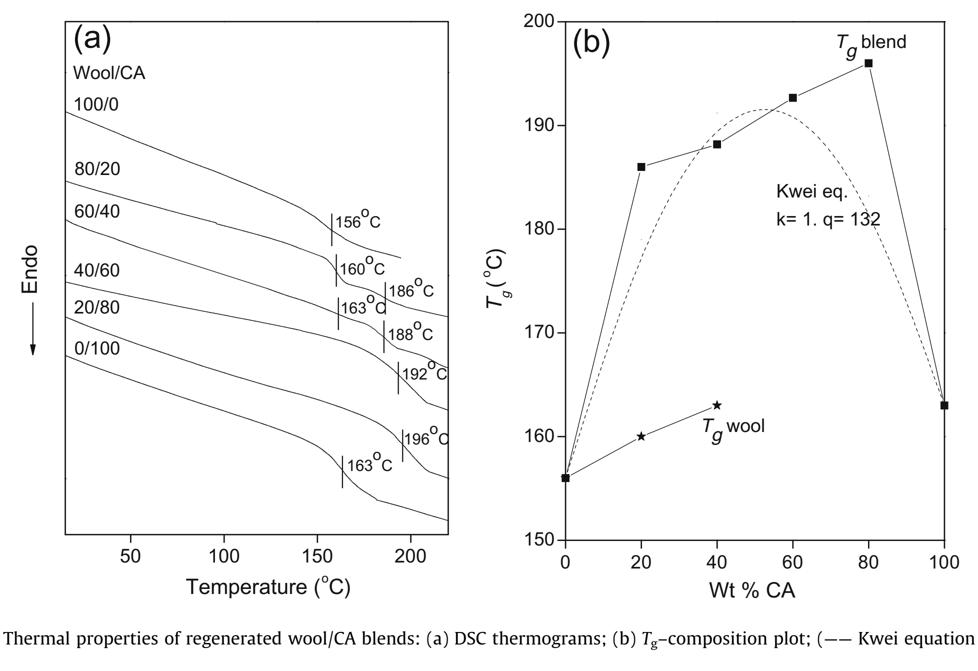

Fig. 2. Thermal properties of regenerated wool/CA blends: (a) DSC thermograms; (b) T_g–composition plot; (—— Kwei equation fitting).

the T_g values of the CA-rich phase are 20–30 °C higher than those of individual components. Furthermore, the blends with 60 and 80 wt% CA show a broad single T_g which is, to our surprise, higher than the those of individual components by 20–30 °C. The dependence of T_g on the composition of the wool/CA blends is illustrated in the T_g–composition plots shown in Fig. 2b. It can be seen that the T_g shows a positive deviation from the linearity. Usually, miscible polymer pairs show a single T_g intermediate between those of the pure polymers. However, if the interactions are fairly strong, the T_g value shows a positive deviation from the linearity rule, i.e., the T_g of the blend is higher than that from simple additivity of the individual T_g's of the components (Hameed & Guo, 2008; Hameed, Liu, & Guo, 2008). Usually, this type of positive deviation occurs in polymer complexes where intermolecular interactions exist between the individual components. Here the unusual large increase in T_g values may be due to the existence of strong intermolecular mixing between CA and wool components, which is facilitated by the IL media. Therefore, the positive deviations in T_g and thus increased thermal properties can be attributed to the intermolecular interactions in the blends.

The existence of a single T_g is usually indicative of miscibility in polymer blends (Guo, 1990a; Guo, 1990b; Zheng, Zheng, & Guo, 2003). The T_g–composition curve of the blends can be correlated by the Kwei equation (Kwei, 1984):

$$T_g = \frac{W_1 T_{g1} + qW_2 T_{g2}}{W_1 + kW_2} + qW_1W_2 \tag{1}$$

where W_1 and W_2 are the weight fractions of the components in the blend, T_{g1} and T_{g2} represent the corresponding glass transition temperatures, and k and q are the fitting parameters which can be obtained from the least squares best fit values. Here, q is the parameter corresponding to the strength of hydrogen bonding in the blend and is considered as the balance between the breaking of the intra-association hydrogen bonding and the forming of inter-association. Kwei equation fitting has been carried out for all compositions for the best fit values and is also given in Fig. 2b. The fitting was based on Eq. (1) and was calculated manually. Here the fitting leads to a result of $k = 1$ and $q = 132$ for wool/CA blends. In this study, a large positive q value is obtained, indicating the interaction between the wool and CA (Zheng, Guo, & Mi, 1998). It is noticed that the experimental results are not well-fit with Kwei equation which is due to the remarkably strong interactions between the components in the blends.

3.2. Thermal stability

The thermal decomposition of the blends and the pure components were performed. It has been reported that the thermal stability of the regenerated wool is higher than the raw wool fibers (Xie et al., 2005). The TGA curves of regenerated wool/CA blends are given in Fig. 3. It can be observed that the blends at any composition show higher decomposition temperature (T_d) than the plain regenerated wool and CA. In fact, the T_d of regenerated wool/CA blends increases with increase in CA content. However, the maximum thermal stability was exhibited by blend containing 40 wt% regenerated wool and the T_d value is 35 °C higher than the plain regenerated wool. The significant improvement on thermal stability of wool can be achieved through the dissolution and regeneration of wool in IL. Xie et al. (2005) observed that the thermal stability of regenerated wool keratin is slightly superior to that of natural wool keratin fibers. It is also reported that crystalline phase of wools was destroyed during the dissolution process in IL and could not be regenerated. The enhanced thermal stability of the blends can be attributed to the strong interaction between wool and CA as revealed by FTIR and facilitated by the IL media.

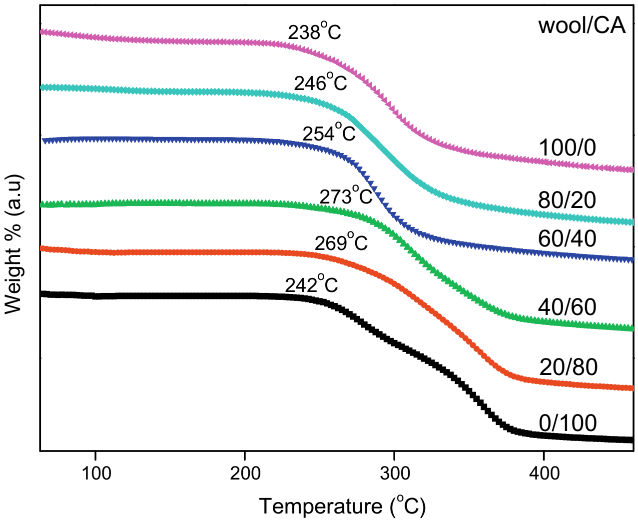

Fig. 3. TGA curves of regenerated wool/CA blends.

3.3. Hydrogen bonding interactions in the blends

Hydrogen bonding interactions in polymer blends can be revealed using FTIR spectroscopy (Zheng, Zheng, & Guo, 1997; Zhong & Guo, 1998). The chemical structures of the components support the possibility of hydrogen bonding between hydroxyl groups of wool and carbonyl groups of CA. The hydroxyl region in the FTIR spectra of regenerated wool/CA blends regenerated from BMIMCl is given in Fig. 4a. For the plain regenerated wool, the broad peak at 3400 cm^{-1} is due to the intra-molecular hydrogen bonding of hydroxyl groups collectively from the amino acids and the comparatively sharp peak at 3280 cm^{-1} can be attributed to the stretching vibrations of N–H groups (Church & Millington, 1996; Slark & Hadgett, 1999). In the general secondary structure of a protein, the α-helix is a right- or left-handed coiled conformation, in which every backbone N–H group is hydrogen bonded with the backbone C═O group of the amino acid. The peak at 3280 cm^{-1} can be attributed to this hydrogen bonding. In the blends, the relative intensity of the peak corresponding to N–H groups in wool (3280 cm^{-1}) decreases without any shift as the concentration of wool deceases. However, the hydroxyl band at 3400 cm^{-1} changes its position upon blending. CA can act as a proton accepting and donating polymer due to the presence of carbonyl group and unsubstituted hydroxyl groups. The CA regenerated from BMIMCl shows a distinct band centered at 3515 cm^{-1} which can be attributed to the stretching vibrations of the hydroxyl groups in regenerated CA.

It is known that the inter-associated hydroxyl band shifts towards the lower wavenumber if the intermolecular hydrogen bonding is stronger than the intra-molecular hydrogen bonding and vice versa (Coleman, Graf, & Painter, 1991; He, Zhu, & Inoue, 2004). However, here the blends show a hydrogen bonded hydroxyl band in between the pure components. In other words, upon blending the 3400 cm^{-1} band (intra-molecular hydrogen bonded hydroxyl groups) of the wool reduces in intensity and moves towards higher wavenumber region. This indicates that the intermolecular hydrogen bonding between hydroxyl groups of wool and CA is weaker compared to the intra-molecular hydrogen bonded hydroxyl groups in regenerated wool.

The hydrogen bonding between hydroxyl groups of wool and carbonyl groups of CA can be investigated by analyzing the carbonyl region. The carbonyl region ranging from 1820 to 1700 cm^{-1} in the IR spectra of regenerated wool/CA blends at room temperature is presented in Fig. 4b. The spectrum of pure CA shows a sharp peak at 1760 cm^{-1} corresponding to the acetate

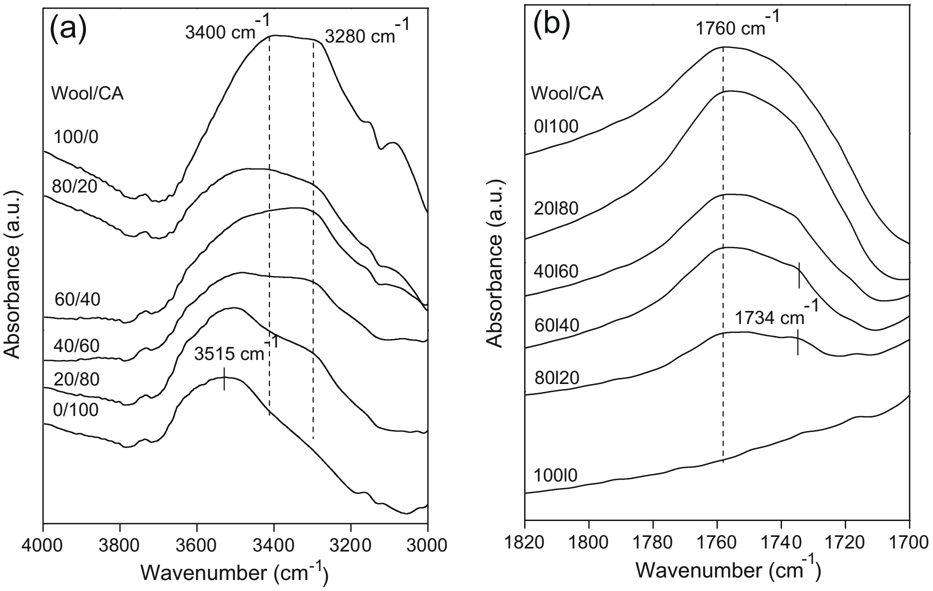

Fig. 4. Infrared spectra of regenerated wool/CA blends in (a) hydroxyl stretching region and (b) carbonyl region.

groups in CA. In regenerated wool/CA blends, as the concentration of wool increases, this peak decreases in intensity and a new peak appears at 1734 cm^{-1}. This peak can be attributed to the hydrogen bonding interaction between CA carbonyl groups and wool hydroxyl groups. There is also chance for the hydrogen bonding interaction between amide–carbonyl groups in the amino acid and hydroxyl groups in CA. However, this interaction cannot be detected as this region of the spectra is more complicated.

From the FTIR results it is confirmed that there are intermolecular interactions in wool/CA blends. The inter-associations between wool hydroxyl groups and CA carbonyl groups as well as between CA hydroxyl groups and wool amide groups can be formed.

Wool is a natural fiber composed of keratin-type protein that grows from the follicles of the sheep's skin (Block et al., 1939). Chemically these proteins contain five elements: carbon, hydrogen, oxygen, nitrogen and sulphur which are combined into amino acids. It is known that wool contains more than 20 amino acids linked together. The structure and chemical nature of wool have been studied extensively. The three dimensional structure of wool is formed by various kinds of secondary interactions including hydrogen bonding and ionic interactions. Therefore, in order to dissolve wool, these inter- and intra-molecular interactions have to be disrupted. It is reported that high chloride concentration in BMIMCl is highly efficient in breaking down the highly networked hydrogen bonding and thereby dissolving wool (Swatloski et al., 2002). Wool comprises of many functional groups where proton accepting and donating groups present, so as in CA. A possible dissolution mechanism of cellulose in AMIMCL was given by Zhang et al. (2005). Similarly, BMIMCl exists as dissociated $BMIM^+$ and Cl^- ions. The free Cl^- anions possibly associated with hydroxyl protons of wool and CA and the free $BMIM^+$ cations associated with hydroxyl and carbonyl oxygen (Zhang et al., 2005). Such an association would disrupt the hydrogen bonding and lead to the dissolution of both wool and CA in BMIMCl solution. A homogeneous solution is formed upon the mutual mixing of wool/BMIMCl and CA/BMIMCl. Intermolecular hydrogen bonding would be developed between proton accepting and donating groups in wool and CA, resulting in a miscible blend. However, further investigation is required to understand the basic mechanism of interaction between the two components in such systems.

4. Conclusions

The dissolution, regeneration and blending of natural wool have been performed in an ionic liquid. Natural wool/CA blends were prepared in BMIMCl ionic liquid and the blends are partially miscible. FTIR investigations suggested the intermolecular interactions between regenerated wool and CA. DSC experiments revealed the partial miscibility between regenerated wool and CA. The blends showed two T_g's corresponding to wool-rich and CA-rich phase, respectively at lower CA concentrations. However, a single T_g remarkably higher than those of either blend components was observed at higher CA contents. DSC results along with SEM observations suggested that regenerated wool/CA blends are partially miscible. That is, blends containing low CA contents showed a phase-separated structure, whereas at higher CA concentrations the blend was homogeneous and no evidence of phase separation was observed. The unusual increase in thermal stability was also observed for the blends, which can also be due to the strong intermolecular interactions between the components. The regenerated wool/CA blends showed increased T_g and thermal stability which can be applied for the development of renewable materials.

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