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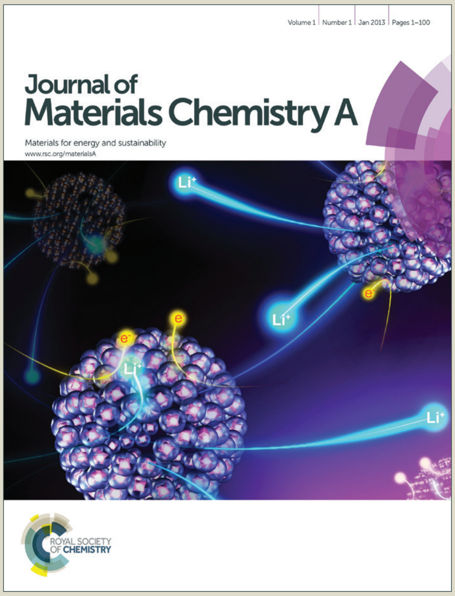

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ARTICLE TYPE

Preparation of polyacrylonitrile-natural polymer composite precursors for carbon fiber using ionic liquid co solvent solutions

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We report on the use of ionic liquid co-solvents in the preparation of polyacrylonitrile – natural polymer carbon fibers as low cost environmentally friendly alternatives to conventional carbon fibers precursors and processing solvents. We have characterized the structure properties of the new composites as a function of dissolving solvent using solid state NMR, DSC , FTIR and TGA. We show that the dissolving solvent plays a significant role in the properties of the new composites, we also find that the incorporation of the natural polymer additive impacts the thermal transition temperatures for the PAN.

Carbon fiber reinforced composites are rapidly becoming one of the leading materials for applications that demand lightweight materials with high strength and high stiffness[1,2]. The benefits of using carbon fiber are well documented[3] however, the cost of the precursor and the environmental footprint of the carbon fiber processing method remains a limiting factor to widespread use[4]. The most commonly used precursors for carbon fiber are pitch, rayon and polyacrylonitrile (PAN), recently graphene nanoribbons and graphene oxide have been used[5]. PAN the most commonly used precursor for structural applications[6,7]. The use of low cost co-monomer additives to PAN based carbon fibers is a research direction gaining momentum[8]. Indeed, lignin[9-11] has been explored as both a precursor material and as an additive to PAN based carbon fibers for the production of general grade carbon fiber[12,13]. In this context, we have explored the use of unprocessed cotton and cellulose acetate as low weight percentage, cheap, additives to blend with PAN. Cellulose is the most abundant renewable material available. We included cellulose acetate in the study due to its higher solubility when compared to unprocessed cotton, as the solution processing of PAN is the other major limitation associated with carbon fiber production.

The manufacture of carbon fiber requires the PAN to be dissolved in a solvent prior to spinning. Currently, harsh volatile and toxic solvents such as Dimethylformamide DMF, Dimethylacetamide DMA and mixtures thereof are used to dissolve PAN[14]. The cost and environmental impact of solvent recovery is detrimental to the carbon fiber industry. As such, the urgent need to replace these environmentally harmful solvents acts as a driving force to explore alternative processing conditions. In the past decade, ionic liquids, ILs have received considerable attention as alternatives to traditional volatile solvents[15]. Ionic liquids are considered to be environmentally friendly alternatives to volatile solvents due largely to the negligible vapor pressure and the recyclability[16]. Ionic liquids pose many advantages, in particular ILs have been shown to be excellent solvents for biopolymer dissolution[17] – a process that normally requires very harsh solvent processing conditions.

In this communication, we explore the use of the IL, 1-butyl-3-methylimidazolium chloride, [BMIM]CI for the dissolution of PAN/cellulose acetate (CA) and PAN/raw cotton (RC) composite fibers. This ionic liquid was used in the first report of natural polymer dissolution[17], and is commercially available. Others have studied PAN dissolution in ILs, the majority of the work so far has explored the rheological properties of the spinning dope important for fiber production[18-21]. Here, we characterize the thermal and structural properties of the new composite fibers using a combination of, solid state NMR, differential scanning calorimetry, DSC, thermogravimetric analysis, TGA and Fourier transform infrared spectroscopy, FTIR. Additionally, while it was possible to dissolve the PAN/CA and PAN/RC composites, at an amount of 8wt% total polymer, in the 100% [BMIM]CI dissolution time at 70° C exceeded 24hours and the solution at room temperature was highly viscous making electrospinning (and any future spinning processes) difficult or requiring elevated temperatures[22]. Therefore, we employed a co-solvent approach to solve this problem. We selected DMSO, as the co-solvent, as this solvent is routinely used to dissolve PAN and is often used to replace the more toxic DMF in industrially processes. We explored two co-solvent ratios, 70: 30 v/v DMSO: [BMIM]CI and 30: 70v/v DMSO:[BMIM]CI. Interestingly, we found that the raw cotton composite fibers were only soluble in the higher IL co-solvent solution, 30: 70 DMSO: [BMIM]CI. Table 1 outlines the various samples prepared in this study. All samples were coagulated using water. The IL was easily recycled by removing the water under vacuum.

Table 1: Samples prepared in this study

	Solvent		Composite at 8 weight % total		
Sample ID	DMSO	[BMIM]CI	PAN	Cellulose acetate	Raw cotton
001	70%	30%	100%	0%	0%
002	70%	30%	90%	10%	0%
003	70%	30%	80%	20%	0%
004	70%	30%	70%	30%	0%
008	30%	70%	100%	0%	0%
009	30%	70%	90%	10%	0%
010	30%	70%	80%	20%	0%
011	30%	70%	70%	30%	0%
012	30%	70%	90%	0%	10%
013	30%	70%	80%	0%	20%
014	30%	70%	70%	0%	30%

It was possible to electrospin all samples, Figure 1 shows the typical morphology of the electrospun fibers investigated in this study (experimental method and additional SEM images of other compositions shown in supplementary information). Non uniformity of the fibers was observed for all samples and most likely due to the lack of control in the feed rate.

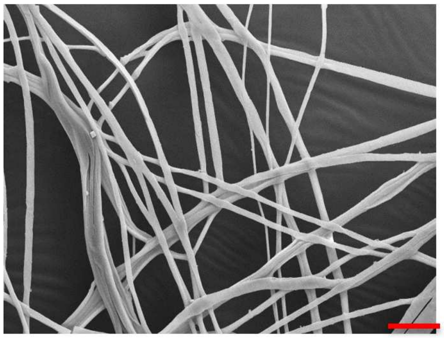

Figure 1: Electrospun PAN from 30: 70 v/v DMSO: [BMIM]CI into a water bath. Scale 10µm. (additional images shown in supplementary information)

We explored the thermal properties of the new composite fibers. Figure 2a shows a comparison of 100% PAN dissolved in 70: 30 v/v DMSO: [BMIM]CI and 30: 70v/v DMSO:[BMIM]CI respectively. Figure 2b and c shows the DSC trace for the PAN: CA composites dissolved using 70: 30 v/v DMSO: [BMIM]CI and 30: 70v/v DMSO:[BMIM]CI respectively. Figure 2d shows the PAN:RC composites dissolved in 30: 70 v/v DMSO: [BMIM]CI. The 100% PAN dissolved in the 70: 30 v/v DMSO: [BMIM]CI shows a broad exothermic event, onset 250° C, with multiple maxima (black curve, Fig2a). In contrast, the PAN dissolved in the 30: 70 v/v DMSO: [BMIM]CI (red curve, Fig2a) shows a single sharp exothermic event, it is likely the PAN exhibiting the broad exothermic reaction is in a more disordered state, which could be attributed to different orientations or short chains due to polymer-solvent complexes. It has been shown that the solvent can play a significant role in the structure of PAN[15,23,24], with DMSO dissolved PAN known to co crystallize resulting in a hexagonal to orthorhombic polymorphic transition[25]. The PAN:CA composites dissolved in the 70: 30 v/v DMSO: [BMIM]CI (Fig2b) show a similar trend to the 100% PAN sample dissolved in the same solvent, a broad exothermic peak with multiple maxima, onset 250° C. In contrast, the PAN:CA dissolved in the high IL co solvent solution, 30: 70 v/v DMSO: [BMIM]CI (Fig2c) shows a single exothermic event again with an onset temperature of 250° C, it is clear that the solvent is playing an important role in the thermal properties of the PAN and the PAN composites, the composite containing 30wt% CA did show two maxima suggesting a change in the polymer structure as a result of the additive. The composites containing the raw cotton (Fig 2d), due to solubility limitations with the high DMSO solvent, where only explored in the high IL co solvent solution, again a similar trend to the CA composites in the same solvent was seen, a single exothermic peak no change in onset, the width of the peak does get broader suggesting some degree of disorder in the polymer structure as a function of additive.

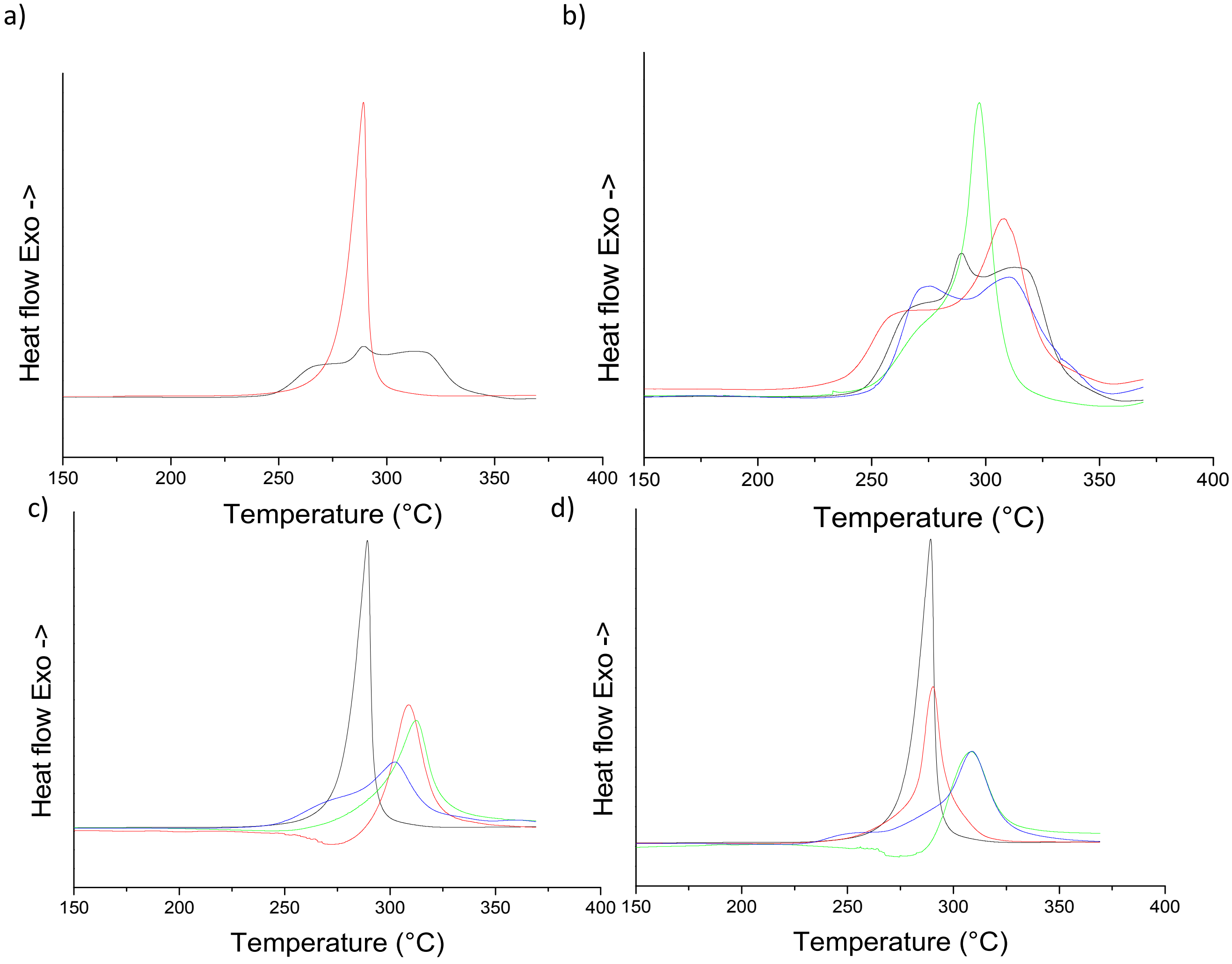

Figure 2: DSC scans of the various PAN composites where a) 100%PAN dissolved in black 70: 30 v/v DMSO: [BMIM]CI, red, 30: 70 v/v DMSO: [BMIM]CI b) PAN:CA composites dissolved in 70: 30 v/v DMSO: [BMIM]CI c) PAN:CA composites dissolved in 30: 70 v/v DMSO: [BMIM]CI and d) PAN:RC composites dissolved in 30: 70 v/v DMSO: [BMIM]CI where black is 100% PAN, red is 90% PAN: 10% additive, green, is 80% PAN: 20% additive blue is 70% PAN: 30% additive.

Thermal degradation of the various composite fibers is shown in Figure 3a-d as measured using TGA in a nitrogen atmosphere. PAN is known to show a degradation transition at 300° C this decomposition step relates to the breakdown of C-N bonds, a 2nd degradation step for PAN occurs at 460° C due to C-C bond breakage[26,27]. Figure 3a shows the thermal degradation for the 100% PAN dissolved in 70: 30 v/v DMSO: [BMIM]CI (black curve) and 30: 70 v/v DMSO: [BMIM]CI (red curve). PAN dissolved in 70: 30 v/v DMSO: [BMIM]CI shows the 1st degradation step at 300° C however the 2nd degradation step appears at a significantly lower temperature 360 °C. The PAN dissolved in the 30: 70 v/v DMSO: BMIMCI has a subtly different profile, the first degradation step occurs at 300° C, similar to previous reports for PAN however this is only associated with a 10% weight loss and a second step occurs at 340 ° C followed by a larger step at 460° C which likely represents the C-C bond breakdown. The addition of either cellulose acetate or raw cotton results in a lowering of the 1st degradation step, by as much as 40 °C at 30wt% cellulose acetate or raw cotton, however the 2nd degradation step is not changed, Figure 3b-d. Previous studies using lignin as an additive to PAN has also shown a decrease in the thermal degradation temperature. The carbon yields of the various blends at 700º C was shown to decrease with the addition of either cellulose acetate of raw cotton with a greater decrease observed for the raw cotton blends. A slightly higher carbon yield is observed for blends and pure PAN dissolved in the higher IL solutions; 30: 70 v/v DMSO: [BMIM]CI, this is an important finding and may be explained by the absence of (or different) solvent – polymer complexes. We have also used 1-butyl-3-methylimidazolium acetate to dissolve the PAN and we find that the solution turns a deep red, this suggest that the IL is an active solvent and likely interacting with the PAN, interactions of PAN with the dissolving solvent are common and known to directly impact the polymers properties[15,25,28,29]. It should be noted that an initial weight loss in the region 0-100° C is likely due to water loss, this is more obvious in the samples containing the RC additive and likely suggest that the water uptake of these samples is impacted by the addition of the additive.

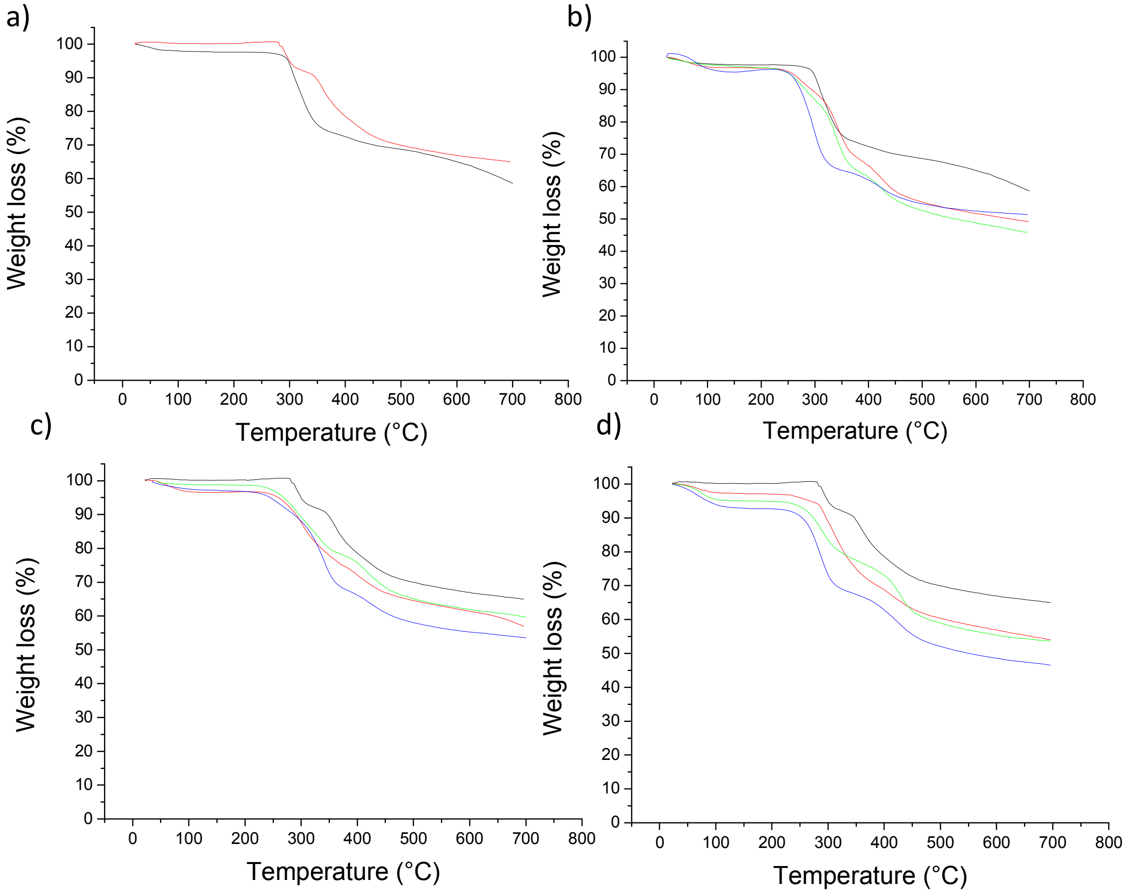

Figure 3: TGA traces of the various PAN composites where and a) 100% PAN dissolved in 70: 30 v/v DMSO: [BMIM]CI (black) and 30: 70 v/v DMSO: BMIMCI (red) b) PAN:CA composites dissolved in 70: 30 v/v DMSO: [BMIM]CI c) PAN:CA composites dissolved in 30: 70 v/v DMSO: BMIMCI, d) PAN:RC composites dissolved in 30: 70 v/v DMSO: [BMIM]CI where black is 100% PAN, red is 90% PAN: 10% additive, green, is 80% PAN: 20% additive blue is 70% PAN: 30% additive

Next, we explored the structure of the composites prepared in this study using FTIR[30]. Figure 4a shows a comparison of 100% PAN dissolved in the co solvent solutions 70: 30 v/v DMSO: [BMIM]CI and 30: 70v/v DMSO:[BMIM]CI. Figure 4b and c shows the FTIR spectra for composites of varying PAN: CA dissolved using 70: 30 v/v DMSO: [BMIM]CI and 30: 70v/v DMSO:[BMIM]CI respectively. Figure 4d shows the PAN: RC composites dissolved in 30: 70 v/v DMSO: [BMIM]CI. For clarity we show only the hydroxyl region 3000-4000 cm $^{-1}$ and the amide region 1500 cm^{-1}-1700cm^{-1}, as these are the regions, which give the most information about the structure of the composites (full spectra given in supplementary information). The appearance of the low frequency component of the C = O vibration at 1580 cm^{-1} for PAN dissolved in 70: 30 v/v DMSO: [BMIM]CI has been previously observed for PAN dissolved in DMSO[31] and suggests short conjugated chains exist. The absence of this band in the PAN dissolved using 30: 70 v/v DMSO: [BMIM]CI suggests the absence of an C=O groups. This sample also showed the single sharp exothermic peak indicative of a well ordered system. Differences were also observed in the hydroxyl region for the PAN dissolved in the different co-solvent solutions. These differences can be attributed to differences N – H and C = O stretching vibrations manifested by differences in the inter and intra molecular hydrogen bonds likely due to different degrees of order in the coagulated PAN and or different complexes as a result of the different dissolving solvents. Differences are also observed for the PAN:CA composites as a function of dissolving solvent. The appearance of the peak at 1580 cm $^{-1}$ is observed for the PAN:CA composites containing 20 and 30wt% PAN dissolved in 30: 70 v/v DMSO: [BMIM]CI, Figure 4c (this peak is present for all PAN:CA composites dissolved in 70: 30 v/v DMSO: [BMIM]CI Figure 4b). This suggests that for this system as the cellulose acetate is added the chains are becoming shorter ie the system is more disordered. A similar trend is observed for the cotton containing composites with the appearance of the lower frequency amide peak at the higher cotton amounts. It is not surprising that the addition of an additive increases the disorder in the system. The increase in the intensity of the peak in the hydroxyl region, particularly noticeable for the PAN:RC composites is likely due to the incorporation of the natural polymer which has a significant peak in this region.

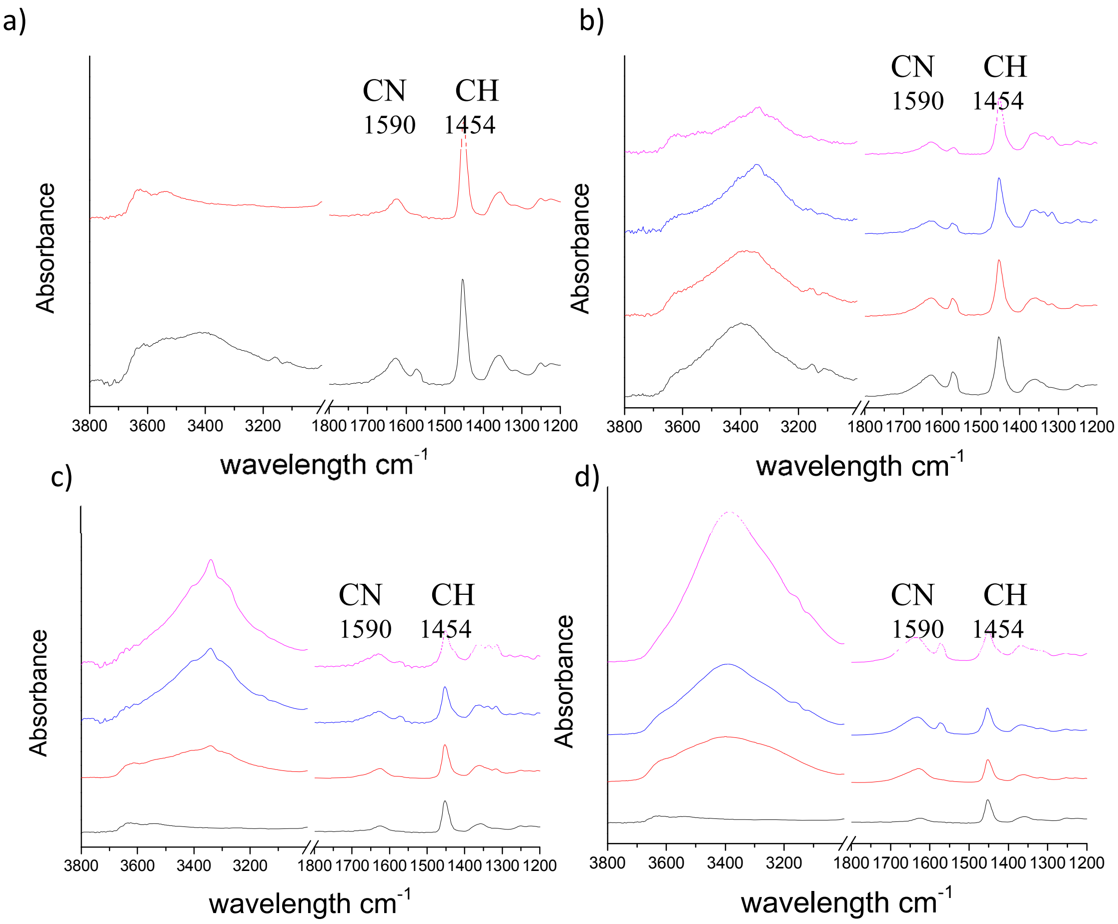

Figure 4: FTIR spectra of the various PAN composites where a) 100%PAN dissolved in black 70: 30 v/v DMSO: [BMIMC]I, red, 30: 70 v/v DMSO: [BMIM]CI, b) PAN:CA composites dissolved in 70: 30 v/v DMSO: [BMIM]CI c) PAN:CA composites dissolved in 30: 70 v/v DMSO: [BMIM]CI, d) PAN:RC composites dissolved in 30: 70 v/v DMSO: [BMIM]CI where black is 100% PAN, red is 90% PAN: 10% additive, green, is 80% PAN: 20% additive blue is 70% PAN: 30% additive

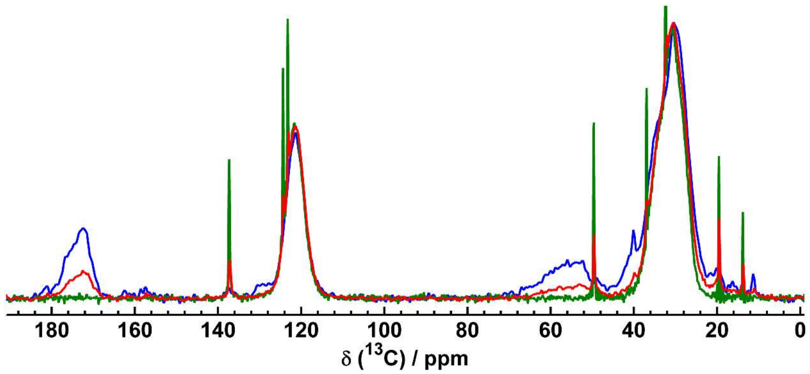

Figure 5: ^{13}C solid state NMR spectra of PAN dissolved in 100% DMSO (blue), 70: 30 v/v DMSO: [BMIM]CI (red), 30: 70 v/v DMSO: [BMIM]CI (green).

To further explore the role of the solvent on the structure of the coagulated PAN we used solid state ^{13}C MAS NMR to examine the PAN[32,33], dissolved in 70: 30 v/v DMSO: [BMIM]CI and the PAN dissolved in 30: 70 v/v DMSO: [BMIM]CI, we also include the PAN dissolved in 100% DMSO illustrated in Figure 5. Small differences are seen in the CH region (20-60 ppm) for the different PAN samples this is the backbone region, no significant difference is seen for the C-N region (120ppm). An important difference is seen in the carbonyl region (175 ppm) most notable the absence of the carbonyl peak for the PAN dissolved in the higher IL co solvent, 30: 70 v/v DMSO: [BMIM]CI. A carbonyl peak is observed for the PAN dissolved in 100% DMSO and to a lesser extent in the PAN dissolved in 70: 30 v/v DMSO: [BMIM]CI. This clearly shows the role the solvent plays in the polymer properties of PAN. It has previously been reported that PAN will interact with the solvent and in the case of DMSO or propylene carbonate can form polymer –solvent complexes[15,24], the presence of the carbonyl peak for the DMSO and the 70: 30 v/v DMSO: [BMIM]CI can likely be explained by these polymer-solvent complexes. The PAN “as received” spectrum (supporting information) shows no evidence of the carbonyl peak again supporting the likelihood of polymer-solvent complexes contributing to this peak. The absence of the carbonyl peaks in the high IL solvent combined with the higher carbon yield is a promising result for the use of ILs for the processing of PAN. A limitation of ILs is however their high viscosities, often higher than traditional solvents commonly used for PAN, the presence of “IL” peaks in the ^{13}C spectra is clear for the sample dissolved in 30: 70 v/v DMSO: [BMIM]CI. It should be noted that FTIR did not detect the presence of IL peaks, here the coagulate used was water, the solubility of the IL used in this study, [BMIM]CI, in water is excellent therefore, to better understand the restrictions of coagulating the PAN from the IL co solvents the diffusivity of water in these two co solvents was measured using pulse filed gradient NMR. We selected 5wt% water as this represents the initial coagulation conditions, as the coagulation process proceeds the water content in the polymer would increase and it is less likely to be diffusion limited. The diffusion of water in the 70: 30 v/v DMSO: [BMIM]CI was measured to by 1.2 e^{-10} m^2/s whereas the water diffusion in the 30: 70 v/v DMSO: [BMIM]CI was significantly slower, measured to be 3.4 e^{-12} m^2/s. This slower diffusion rate will directly influence coagulation and complete removal of the IL.

Conclusions

We describe the use of ionic liquid co solvents for the dissolution of PAN and PAN – natural polymer composites. We show that the PAN and its composites can be dissolved by the ionic liquid and electrospun into fibers. The thermal properties and structure of the PAN and PAN composites were shown to be influenced by the dissolving solvent, the solid state NMR clearly showed that the high IL content co solvent produced a PAN fiber which did not have a carbonyl group present, indicating structurally a different PAN fiber.

The use of both natural polymer additives blended with PAN and ionic liquids as the dissolving solvent presents as an environmentally friendly approach to the development of carbon fiber. Future work will be aimed at exploring the wet spinning characteristics as well as understanding what new PAN-IL complexes result and how these are infleunced by the choice of IL and the impact this has on the properties of the PAN fiber.

Notes and references

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† Electronic Supplementary Information (ESI) available: [FTiR spectra]. See DOI: 10.1039/b000000x/

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