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ARTICLE

Rapid surface functionalization of carbon fibres using microwave irradiation in an ionic liquid.

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The modification of carbon fibre surfaces has been achieved using a novel combination of low power microwave irradiation (20 W) in both an ionic liquid (1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide) and an organic solvent (1,2-dichlorobenzene). The use of the ionic liquid was superior to the organic solvent in this application, resulting in a higher density of surface grafted material. As a consequence, carbon fibres treated in ionic liquid displayed improved interfacial adhesion in composite material (+28% relative to untreated fibres) compared to those treated in organic solvent (+18%). The methodology presented herein can be easily scaled up to industrially relevant quantities and represent a drastic reduction in both reaction time (30 min from 24 hrs) and energy consumption, compared to previously reported procedures. This work opens the door to potential energy and time saving strategies which can be applied to carbon fibre manufacture for high performance carbon fibre reinforced composites.

Introduction

The manufacture of carbon fibres is an energy intensive process. The energy costs of carbon fibre constitutes almost 30% of the production costs, requiring high temperatures for carbonisation (up to 2000 °C) and large energy input for surface treatment processes. The latter treatment constitutes the carbon fibre being passed through a warmed (35 °C) aqueous solution of ammonium bicarbonate. During this process both high currents and potentials are applied to the fibre encouraging surface oxidation and installation of oxygenated species (typically phenol, carboxyl, carbonyl, etc.).^[1-2] The rationale behind this process is that these functional groups encourage crosslinking from the fibre surface to epoxy groups within a polymeric matrix that the fibres are used to reinforce.^[3]

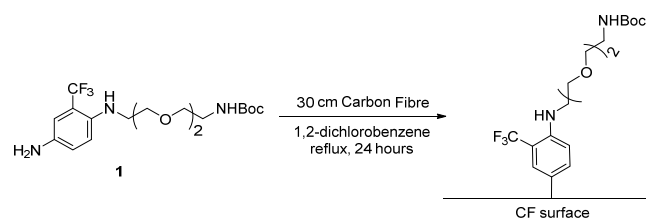
In our previous work we have shown that the introduction of novel reactive species (typically a primary amine) at low concentrations can have profound beneficial effects on interfacial shear strength (IFSS) due to covalent cross linking from the fibre to resin.^[4]

In the context of small molecule organic synthesis,^[5-7] reaction rate has been shown to dramatically increase when a reaction is carried out under microwave irradiation and/or in ionic liquids (ILs). This is thought to be due to the more effective stabilisation of intermediates in ILs and the sharper heating profiles provided by microwave irradiation.^[8-9]

Similarly the use of microwave irradiation has been explored in the production of carbon fibres both as a carbonisation technology and as a means to introduce chemical functionality

on the fibre surface (via plasma generation).^[10-11] Conversely, the combined use of ILs with carbon fibre has shown very limited cross-over, though there are a few notable reports mostly concerned with using ILs as solvents or co-solvents in the wet-spinning process of carbon fibre precursor polymers.^[12-13] Therefore, the utilisation of microwave heating in ionic liquids for the application of surface grafting was an obvious choice due to their existing relevance to the carbon fibre industry and the gap in the existing literature.

In our previous work on the use of phenyl-diazo compounds to functionalise the surface of carbon fibre, we used a very high concentration of our intended grafting molecule, 2 g of **1** per 30 cm of carbon fibre tow (24K) (Scheme 1).^[4] We later showed that fibres treated using only 25% of this concentration (0.5 g of **1** per 30 cm tow) equalled the performance of the fibre functionalised at the highest concentration, when assessed by the Single Fibre Fragmentation Test (SFFT).^[14]



Scheme 1 Previously used methodology to attach small molecules to the surface of carbon fibre.

While this decrease in reagent concentration allowed for the more economical use of **1**, the attachment strategy still required

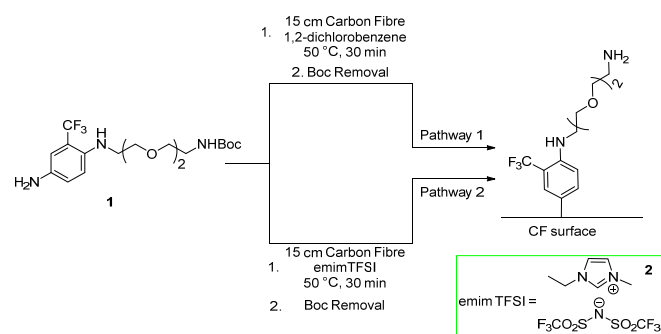
the use of extended heating times making high throughput of surface grafting a major limitation and prohibited translation to an industrial setting.

The goal of this study was to effect surface functionalisation of carbon fibres using an energy economic strategy. Ideally, the treated fibres would possess similar key performance properties (tensile strength and modulus) while still showing excellent interfacial interaction characteristics.

Herein we present the enhancement of surface functionalisation by small molecules in ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimTFSI) under microwave irradiation. The functionalised fibres show excellent reactivity in an epoxy resin with negligible sacrifice to critical performance parameters. We compare this to a typical organic solvent used in our previous grafting reactions (*ortho*-1,2-dichlorobenzene, 1,2-DCB) under the same conditions.

Results and Discussion

To extend on our previous work, here we chose the lowest viable concentration of grafting material to perform this study.^[14] Two fibre grafting procedures were designed: Pathway 1 (Scheme 2 - blue), was adapted from the original methodology by changing the heating source from a benchtop oil bath to a microwave reactor (CEM scientific). Pathway 2 (Scheme 2 - green), used the same microwave methodology as Pathway 1, replacing the solvent with an ionic liquid (emimTFSI, **2**). The reactions were designed such that the effect of microwave irradiation could be assessed independently to the effect of the IL solvent. In both cases the reaction time was reduced from 24 hours (in previous work), to 30 minutes, and the temperature reduced from 70 °C to 50 °C. If surface modification and enhanced interface performance are successful at these values, they represent a major advancement in throughput and a significant reduction in energy consumption, respectively.



Scheme 2 Two reaction design for enhancing the surface grafting reaction under modified conditions.

After carrying out these procedures, the fibres were washed with 250 mL of multiple solvents to ensure the removal of unreacted material (refer to Supplementary Information for details). Additionally, in the case of pathway 2, a control experiment was performed whereby fibres were heated with microwave irradiation in emimTFSI for 30 minutes, followed by the same washing procedure. The control fibres were then submitted for

X-ray Photoelectron Spectroscopy (XPS) analysis which showed that the IL could be successfully removed by washing from the surface (characterised by a lack of fluorine, data not shown) and thus, any fluorine found on the treated fibre samples could be attributed to the successful grafting of **1**.

Both emimTFSI and *o*-DCB treated samples however, had a similar fluorine content (Table 1, 3.3 % and 2.8% respectively) by XPS analysis. Additionally, an increase in nitrogen and oxygen content were detected for each of the treated samples, suggesting successful grafting of the fluorinated compound **1**.

Table 1 XPS analysis of untreated fibres, and those functionalised in emimTFSI, and 1,2-dichlorobenzene.

Element	Untreated	emimTFSI	1,2-DCB
C	96%	89.7%	90.8%
N	1.7%	3.0%	2.6%
O	2.1%	3.9%	3.7%
F	0%	3.3%	2.8%

As is consistent with our previous work, detection of the surface bound molecules using IR and Raman spectroscopy proved fruitless.^[4, 14, 17, 18] This is primarily due to the very small amount of molecule being grafted onto the surface of the carbon fibres. In each case the spectra provided from these analytical techniques focus on carbon bond vibration or hybridisation, and any molecule(s) added to the surface of the fibre tend to be swamped by the heterogeneous carbonaceous nature of the fibre surface. Evidence of surface modification is typically indicated by improved interfacial adhesion, which was also carried out in this study (see below).

Electron microscope images of the treated fibres showed similar morphology between the control fibres (A) and those functionalised in 1,2-DCB (C) with longitudinal striations (Figure 1). Interestingly, the fibres functionalised in emimTFSI (B) lack the definition of striations as the control sample, which may have implications on critical fibre performance parameters and interfacial adhesion.

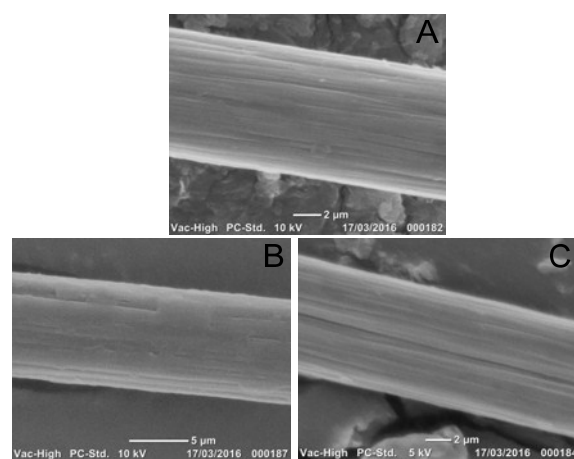


Figure 1 – SEM images of functionalised fibres A. Control; B. emimTFSI functionalised; C. 1,2-DCB functionalised.

Following this we determined the physical properties of the treated fibres to ensure that our treatments had no detrimental effects on key performance parameters (tensile strength and modulus). Only very minor changes in both tensile strength and modulus resulted from the combined IL and microwave treatment (<5% in each case). Conversely, both properties showed more substantial decreases, almost double that of the IL, when performed in 1,2-dichlorobenzene under microwave irradiation.

It is important to note that while both treated samples displayed some minor property degradation as a result of this treatment, these fibres are still eminently suitable for application in reinforcing lightweight composite materials. The treated fibre properties, including those functionalised in 1,2-dichlorobenzene, which resulted in the most pronounced decrease in performance, are still comparable to industry standard carbon fibres such as Toray T300, and DowAksa A-38 which are used in a myriad of applications.[†]

Table 2 Physical characterisation of control fibres and those functionalised in emimTFSI, and 1,2-dichlorobenzene

Fibre	Tensile Strength (GPa) ^a	Decrease relative to control	Young's Modulus (GPa) ^a	Decrease relative to control
Control	3.62±0.06	-	246.3±1.00	-
emimTFSI	3.46±0.04	-4.4%	240.4±0.63	-2.4%
1,2-DCB	3.36±0.05	-7.1%	235.3±1.8	-4.5%

^a This data was obtained from a minimum of 75 individual filaments tested on a TexTechno Favimat+.

Next we examined the effect of these appended molecules on the adhesion at the fibre-to-matrix interface, as described previously.^[14] This is of major importance as the performance of carbon fibre composites depends heavily on the interaction between the carbon fibre and the reinforcing polymer, in this case, epoxy.^[15]

Evaluation of interfacial adhesion is conducted by first making a single fibre composite, followed by stretching the sample along the fibre axis until fragment saturation occurs. By measuring the average fragment size and understanding the way single fibres fail, an IFSS value can be calculated, an increase in which is indicative of crosslinking occurring between the resin and fibre surface. Such tests showed large increases in interfacial shear strength for both of our samples. When compared to an untreated sample of carbon fibre, substantial increases of 28% and 19% for emimTFSI and 1, 2-dichlorobenzene, respectively, were noted (Table 3). This is an outstanding result considering the reduction in reaction time and energy consumption for this process.

Having demonstrated the viability of using microwave irradiation and ionic liquids as a suitable means to rapidly functionalise carbon fibres, our attention turned to examining the role of the solvent and microwave irradiation in the success of the reaction.

Table 3 Interfacial Shear Strength of control and treated fibres.

Fibre	IFSS (MPa) ^a	Error (MPa)	Increase relative to control
Control	32	±0.8	-
emimTFSI	41	±1.1	+28%
1,2-DCB	38	±2.6	+18%

^a A minimum of 5 single fibre composites were used in this evaluation each giving between 20-50 fibre fragments, see ESI for procedure.

To understand the enhanced grafting reactivity observed as a result of microwave irradiation and the ionic liquid solvent, there are several considerations to be made. Firstly, carbon fibres are a conductive material and therefore, when placed in an electromagnetic field, could cause a current to be generated within and on the fibre surface. This is analogous to the electrochemical deposition of diazonium groups on the surface of carbonaceous materials, one of the most common surface functionalisation strategies used.^[16] This effect may be supplemented by the thermal breakdown of the *in situ* generated diazonium groups which we have previously used for our surface grafting strategy.^[4]

A second effect, potentially complementing the first, is the different diffusion rate of **1** through each solvent. The functionalisation strategy described in this and our previous work is diffusion limited, in that only molecules able to diffuse to the surface of the fibre from the bulk solution are able to be grafted.^[14, 17-18]

Therefore, we carried out pulsed field gradient nuclear magnetic resonance (PFG-NMR) experiments to determine the diffusion coefficients in both emimTFSI and 1, 2-dichlorobenzene of amine **1** as a surrogate to the unstable phenyl-diazo species generated *in situ* for each reaction protocol.

Using ¹⁹F PFG NMR we determined the diffusion coefficient for **1** in 1,2-dichlorobenzene to be $(3.3 \pm 0.1) \times 10^{-10} \text{ m}^2/\text{s}$ at 20 °C, approximately one order of magnitude higher than in emimTFSI $(1.6 \pm 0.1 \times 10^{-11} \text{ m}^2/\text{s})$ at the same temperature. This result was expected as the ionic liquid is substantially more viscous than the molecular solvent.

This result seems counterintuitive to the data observed for surface functionalisation as the faster diffusing molecules gave a less profound effect at the interface. While the rate of diffusion can have significant ramifications in reaction rate and success, in this instance we assume that the difference in diffusion is being outweighed by other factors.

Therefore, the only meaningful difference between the two procedures is the ability of each solvent to absorb microwave irradiation. Ionic liquids are known for enhancing reaction rate, especially under microwave conditions.^[19-20] Thus we presume a similar effect has occurred in this case whereby the energy provided by the microwave irradiation is more efficiently transferred in the ionic liquid when compared to the organic solvent. This effect was recently investigated by Kiefer *et al.*^[21] who used femtosecond time-resolved coherent anti-Stokes

Raman scattering (CARS) to examine the energy transfer in imidazolium ionic liquids, specifically emimTFSI. That study determined that vibrational energy transfer in ionic liquids is governed by interionic interactions. This is especially relevant to this study as the *in situ* generated phenyl-diazo species is charged, and thus may participate in energy transfer via interionic interactions whereas this would not occur in 1,2-dichlorobenzene. This would lead to more efficient grafting to the surface of the fibre in the ionic liquid, compared to the organic solvent, as is consistent with our observations.

Due to the great customisability of ionic liquids with respect to their polarity, viscosity, and conductivity etc. the results from this preliminary investigation have enormous potential to be optimised. An exhaustive investigation of ionic liquids and their grafting potential is far beyond the scope of this work, we are examining this and will report it in due course.

Conclusions

In conclusion we have shown for the first time the ability to surface functionalise carbon fibres using microwave irradiation and ionic liquids, resulting in substantially improved interfacial effects. This work represents a major decrease in energy consumption compared to industry standards, and a vastly reduced reaction time compared to previously reported procedures. This methodology is easily scaled up to industrially relevant sizes. While an initial outlay would be required for the acquisition of the ionic liquids, current carbon fibre manufacturing design allows for recovery of solvents during the wet chemical treatments. Indeed, ionic liquids can easily be removed from the fibres by filtration (or roller system) and reused. Due to their negligible vapour pressure, they would be well suited to recovery, as loss to the atmosphere would be minimised.

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† Data sheets on these commercially available carbon fibres are freely available online.

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