

POLYBENZIMIDAZOLE CARBON FIBRE COMPOSITE – UTILISING A HIGH PERFORMANCE THERMOPLASTIC

Thomas R. Pozegic^{1*}, Putu Suwarta¹, Michael R. Wisnom¹, Ian Hamerton¹

¹Advanced Composites Centre for Innovation and Science, Department of Aerospace Engineering, University of Bristol, Bristol, BS8 1TR.

*Email: t.pozegic@bristol.ac.uk

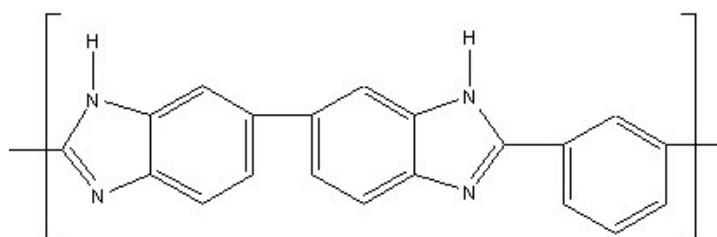
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ABSTRACT

Polybenzimidazole (PBI) is an amorphous thermoplastic with the highest tensile and compressive strength of any unfilled polymer [1] (160 MPa and 340 MPa, respectively [2]) and is currently being exploited for its high temperature performance in fire resistant clothing [1]. Unfortunately, given its high glass transition temperature [2, 3], poor flow characteristics –does not melt - incorporating PBI as a matrix in a fibrous composite has proven challenging. Current efforts require highly polar and aprotic solvents such as dimethylacetamide, to dissolve the polymer. Such solvents are toxic and have high boiling points, thus making industrial scale-up and removal of such polymer difficult. In this study, we consider using a ‘greener’ alternative to these solvents, called ionic liquids, and demonstrate their capabilities of fabricating a PBI – carbon fibre composite. We will study the thermal properties of the PBI to determine any residue by-products of the synthesis that could form unwanted voids in the composites. Following this, a fabrication procedure shall be demonstrated to cast a PBI polymer film on the carbon fibre concluding with a mechanical tensile test to demonstrate consolidation.

1 INTRODUCTION

Polybenzimidazole is a heterocyclic thermally stable polymer (Figure 1.) that possesses both proton donor (-NH-) and proton acceptor (-N=) hydrogen-bonding sites [4]. The PBI molecule is structurally similar to a polyimide molecule, thus has similar properties, except that the five-member ring is altered [5]. PBIs are of interest due to their high temperature properties; glass transition point (~427 °C [2, 3]), good thermal stability (decomposition temperature of 500 – 600 °C [3]) and excellent chemical resistance [1] (dissolvable in high



polar and aprotic solvents) and mechanical properties.

Figure 1. The highly aromatic structure of polybenzimidazole

PBI is commercially prepared from the polycondensation of tetraaminobiphenyl (TAB) with diphenylisophthalate (DPIP). Initially, the DPIP melts and solubilises the TAB. As the temperature increases, polymerisation initiates with the generation of the by-products of

phenol and water, forming a friable foam. Following this, the foam is crushed and the polymer molecular weight is increased in the solid state. [6]

PBI has the capability of absorbing 15 – 18 wt% water [1] due to the intermolecular hydrogen bonding between N and N-H groups in the imidazole ring, leading to approximately 2.5 water molecules per repeat unit [7]. Interestingly, Brooks *et al.* [7] claims the high compressive strength of PBI was due to the water being present in the molecular chains of PBI, helping to redistribute the compressive load and prevent buckling of the PBI chains. [1]

The disadvantages of employing PBI are the expense and difficulties in processing. Current methodologies typically involve solution processing *via* an organic solvent/ionic liquid or heat pressing. For solution processing, PBI requires aprotic solvents (*e.g.* dimethylacetamide [3], dimethylsulfoxide [8] or *n*-methylpyrrolidone (NMP)[9] *etc.*) which have high boiling points, requiring aggressive conditions to remove. In contrast processing *via* a heat press requires high temperatures and pressures to sinter the polymer into a film or composite. Furthermore, the poor flow characteristics create difficulties for the polymer to permeate the carbon fibre fabric.

Subsequently, recent work has considered ionic liquids as a ‘green’ alternative to solvents [8, 10], as they do not require high temperatures, nor a vacuum to remove (soluble in water), are non-toxic and can be regenerated. Recent work studying the molecular interactions by Xing *et al.* [8] identified 1-ethyl-3-methylimidazolium [EMIM]OAc amongst other ionic liquids for dissolving PBI as the acetate anions break up the interchain bonding in PBI molecules leading to the lowest interaction energy (ΔE_{int}) compared to the other ionic liquids tested.

To fabricate high quality polymer films *via* a solution or thermal process requires knowledge of the behaviour of the polymer prior and during fabrication. In this work, PBI was thermally characterised with the assistance of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and hyphenated thermal analysis (TGA/DSC, gas chromatography, mass spectrometry). By thermally characterising the polymer film, the fabrication process can be modified to remove chemical species that would otherwise form voids. The polymer-ionic solution was cast on carbon fibre (CF) to create PBI-CF composites, which were analysed by FTIR and mechanically assessed *via* tensile testing.

2 METHODOLOGY

2.1 Materials

Plain weave, non-crimp carbon fibre (areal density, 320 gsm) with a polymer sizing was supplied by SGL. The polybenzimidazole was obtained from PBI Performance Products, Inc. and the ionic liquid, 1-Ethyl-3-methylimidazolium acetate from Sigma-Aldrich.

2.2 DSC

DSC was conducted using a TAI Q20 with sample masses of 5 – 10 mg placed in hermetically sealed aluminium (Tzero) pans. The methodology involved an initial isothermal step of 40 °C at 5 mins, following a ramp of 10 K/min to 500 °C with an isothermal stage of 5 mins.

Modulated DSC (MDSC) was performed on a TAI Q200 with a modulation temperature and time of ± 1 °K and 60 s, respectively; ramp rate of 3 K/min with a start temperature of

35 °C and an end temperature of 350 °C. Samples masses were between 5 – 10 mg and were placed in hermetically-sealed aluminium (Tzero) pans.

2.3 TGA

TGA was conducted on a TAI Q500 using samples of masses between 19 – 28 mg in a platinum pan in an air atmosphere with a starting temperature of 25 °C, concluding with a final temperature of 500 °C at a heating rate of 10 K/min.

2.4 Evolved Gas Analysis

The evolved gas analysis carried out using a Netzsch TG 209 F1 Libra coupled to an Agilent 7890A gas chromatograph (GC) and the Agilent 5975 MSD. The evolved gases were injected over a heated transfer line (up to 300 °C) into the heated JAS valve box of the Agilent GC. The helium carrier gas (20 ml/min) drove the evolved gases over a specific sample loop and transferred to a heated column. The single components of the gas mixture travel through the column and leave it in dependence of the interactions with the column material and were subsequently detected in the Agilent mass selective detector.

Samples (1 – 2 mg) were transferred into an alumina crucible and placed in the thermobalance. The temperature range was from room temperature to 1000 °C under a helium atmosphere (flow rate of 65 ml/min).

2.5 PBI-CF Fabrication

After drying the polymer in a vacuum oven at 100 °C for 24 hours, 20 wt% of PBI in [EMIM]OAc was magnetically stirred on a hot plate for 24 hours (see Figure 2 for methodology). To avoid coagulation of the PBI-[EMIM]OAc and prevent it from infiltrating the carbon fibre, the cavity which held the carbon fibre was pre-heated to 100 °C. After 30 mins, distilled water (~ five times the volume of the PBI-[EMIM]OAc) was added and left for 4 days. After draining, the sample was dried in a vacuum oven for 48 hours. The sample was heat pressed at 200 °C (ramp at 15 K/min) under 50 MPa pressure with a dwell time of 1 hour. The targeted fibre volume was 60% for a single ply composite.

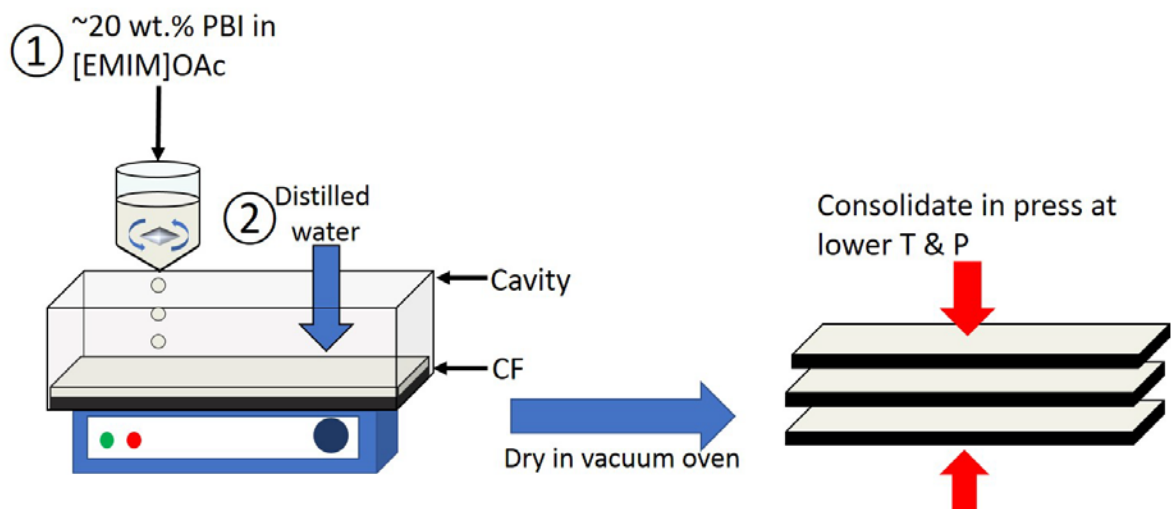


Figure 2. Fabrication of PBI-CF using EMIM[OAc]

2.6 FTIR

FTIR (PerkinElmer Spectrum 100) was conducted on neat polymer samples and the PBI-CF samples using attenuated total reflectance for a wavenumber range of 600 to 4000 cm^{-1} .

2.7 Tensile Testing

Tensile tests were conducted using an Instron 8872 with a 25 kN load operating at 0.5 mm/min. Strain data was recorded over a gauge length of 80 mm using a Imetrum video gauge system, tracking four dots applied to the specimen face.

3 RESULTS

3.1 Analysis of PBI

MDSC was carried out on the PBI sample whereby the temperature was modulated with respect to time enabling kinetic (non-reversing) and heat capacity (reversing) signals to be obtained. Typically, reversing signals include glass transition (T_g), melting. Whereas, non-reversing encapsulates oxidation, curing, relaxation and cold crystallisation (glass crystal transition below the melting temperature) [11]. The subsequent 'total', non-reversing and reversing signals are displayed in Figure 3. Both non-reversing and total signals are characterised by two endothermic events, whereas the reversing is characterised by two exothermic events. Endothermic events are typically a melting process, whereas an exothermic event is characteristic of a crystallisation process.

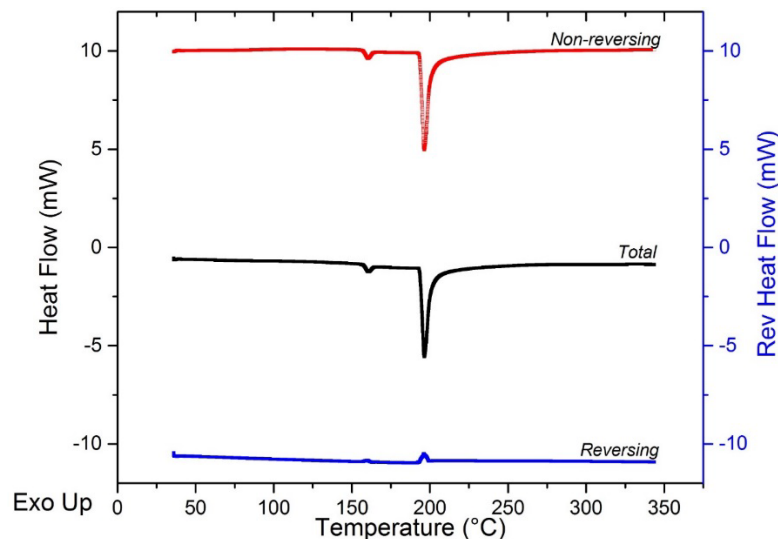


Figure 3. The total, reversing and non-reversing signals of the PBI from the MDSC.

The 'total' heat flow is characterised by two endothermal events of different magnitudes. The first begins at ~ 157 °C, whilst the second, smaller endothermic peak begins at ~ 193 °C. These are expected to be the melting of lower molecular weight molecules within the PBI (from smaller chains). The second signal has the characteristic of a pure melt. Similarly to the total heat flow, the non-reversing heat flow signal shows the same characteristics, with two endothermic melting thermal events of different magnitudes. The reversing heat flow signal

is characterised by two thermal events, an exothermic event beginning at ~157 °C, with the other at ~193 °C. These are expected to be crystallisation signals. It should also be noted the rising baseline beyond ~200 °C, alluding to the possibility of a change in heat capacity. The exothermic events coincide with the endothermic events seen for the ‘non-reversing’ and ‘total’ signals seen in Figure 2. Therefore, these crystallisation signal observed could be crystallisation in the melt as a consequence of the re-ordering of the molecules within the PBI.

Using non-modulated DSC, the PBI polymer was subjected to repeated (twice) thermal cycles. The purpose of this is to understand whether the polymer can be thermally treated to remove foreign species. The results are presented in Figure 4. Evidently, repeating the process has led to a more stable polymer as the thermal characteristics observed in the MDSC were not present. Given the high thermal stability of the polymer, these events could be foreign species within the material that would need to be removed prior to pure resin or composite fabrication. If they are foreign species, the thermal events observed are that of the foreign species and not associated with the PBI polymer.

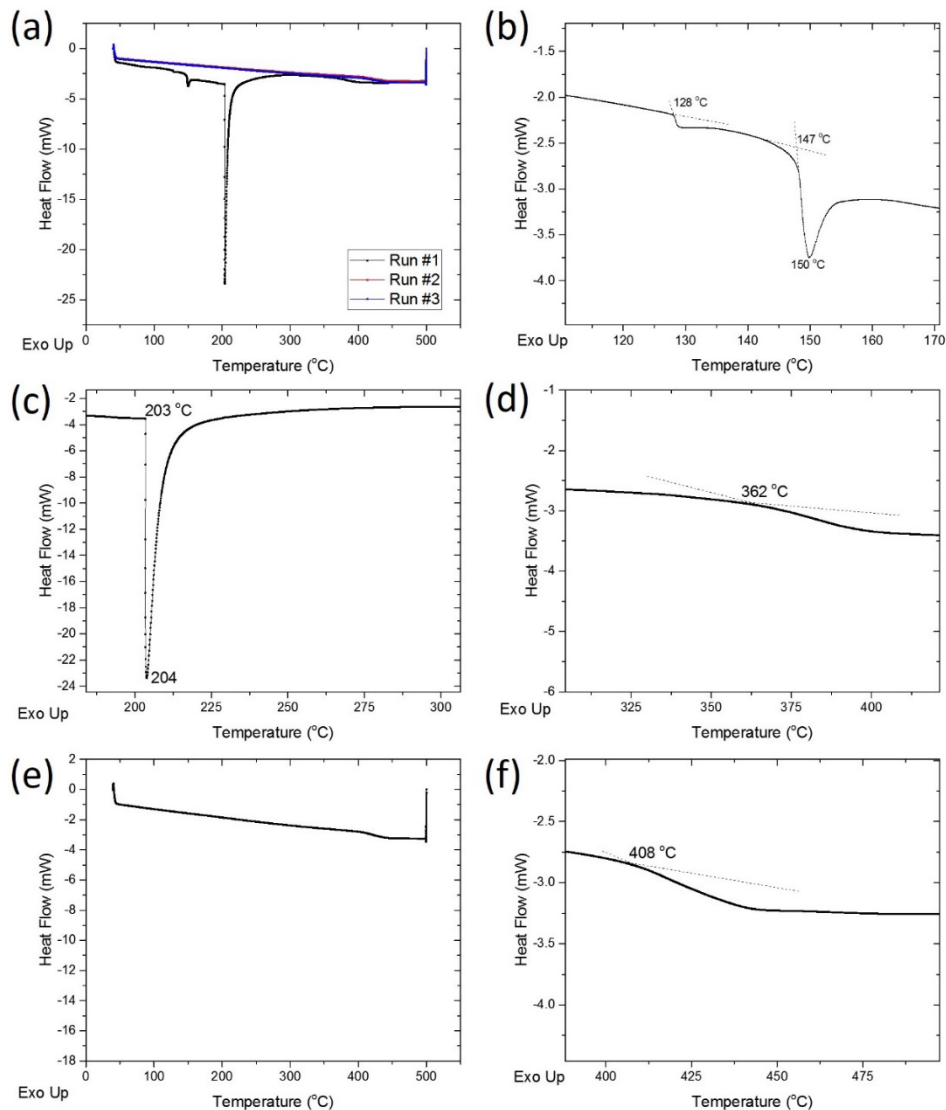


Figure 4. (a) Repeated runs on the same samples using DSC, (b-d) First run of the PBI sample using DSC, (e-f) second run on a polymer specimen that was received a heating cycle

The peaks of the first run are analysed in Figure 4 (b-d). At ~ 128 °C (b) and ~ 362 °C (d), there are arguable changes in the heat capacity, potentially being the glass transition points (T_g). Whereas at ~ 147 °C (b) and ~ 203 °C (c) there are endothermic melting events.

Figure 4 (e,f) displays the analysis of the peaks after the repeated run. Evidently the endothermic melting events are not present, however the small change in baseline at 408 °C is still present, suggesting that this change in heat capacity. The glass transition temperature of polybenzimidazole is expected to be 400 – 427 °C [2, 3]. The glass transition temperature is expected to be dependent on the heating rate.

TGA was performed twice on the same samples and the results are shown in Figure 5. As can be seen for the first run (black curve), there are two temperature regions where there is a reduction in mass. The first, begins from room temperature to ~ 150 °C and the second at ~ 375 °C. The first temperature reduction is expected to be a consequence of moisture, whilst the second is expected to be phenol and other gaseous products that exist as by-products of the synthesis of PBI. As expected, the reduction in mass in the second run (red curve) are suppressed, but they exist in approximately the same temperature range. Moisture vapour condensing on the sample is not expected for the 'open' specimen pan. The total mass loss on the second run is 3.5% compared to 8% on the first run.

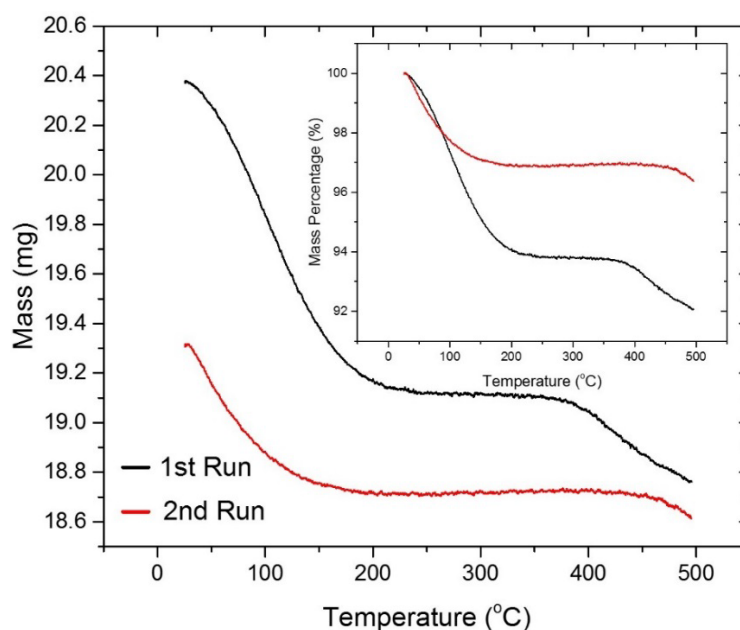


Figure 5. Reduction in mass with increasing temperature performed twice on the same specimen. Inset: Mass percentage reduction with temperature.

The TG-GC-MS results performed are presented in Figures 5, 6 and Table 1. Figure 5 depicts the TG and total ion chromatogram (TIC) of the PBI specimen. The sample exhibited three mass loss steps of 7.2%, 2.8% and 19.1% with DTG peaks at 128 °C, 469 °C, 604 °C and 725 °C. DSC suggests two main endothermic events were detected.

Evolved compounds were condensed at -50 °C in the cryo trap and after completion of the TG run, analysed by GS-MS. However, not all released compounds could be condensed at -50 °C. This caused increased intensity of TIC during the TG run were NH_3 , HCN and CO_2 . All other compounds were separated on the column after the completion of the TG run. The

corresponding TIC is shown in Figure 7. Mass spectra were compared to the NIST database; Table 1 displays the database hits with high hit quality.

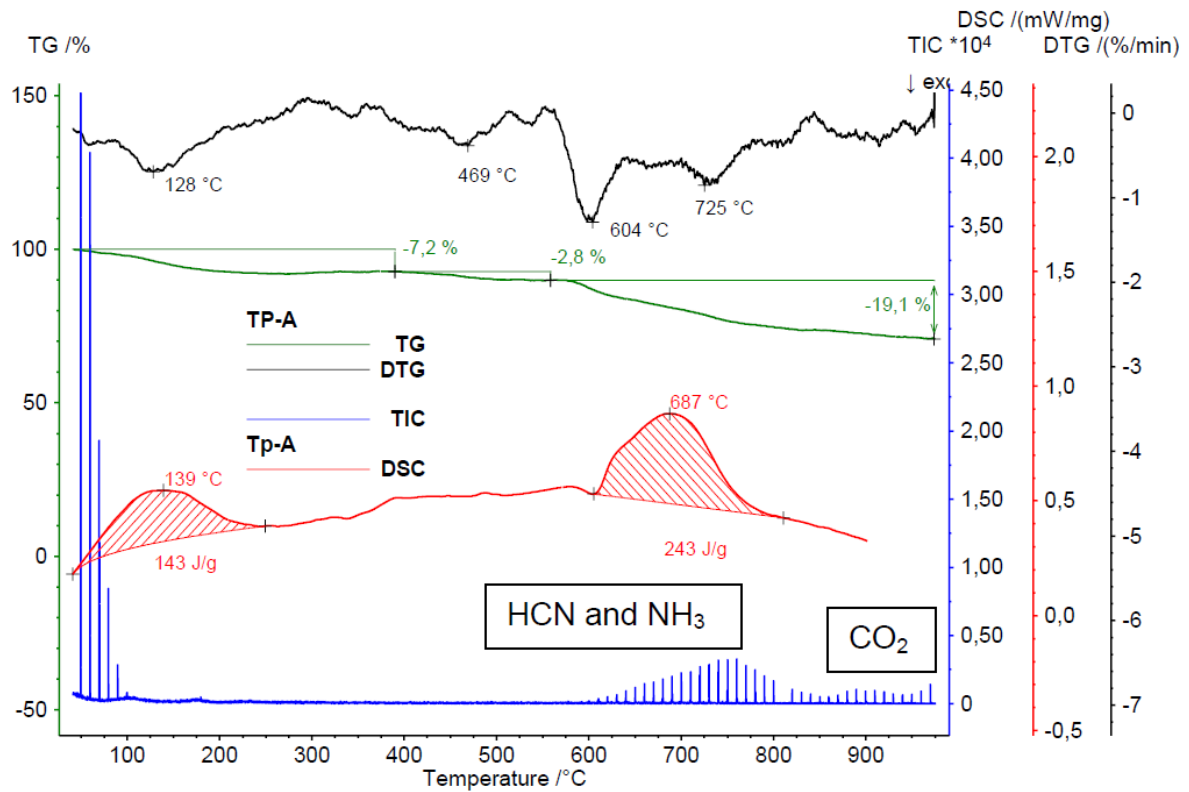


Figure 6. Temperature-dependent mass change (TG, green), DSC (red), mass-loss rate (DTG, black) and total ion chromatogram (TIC, blue) of the polybenzimidazole.

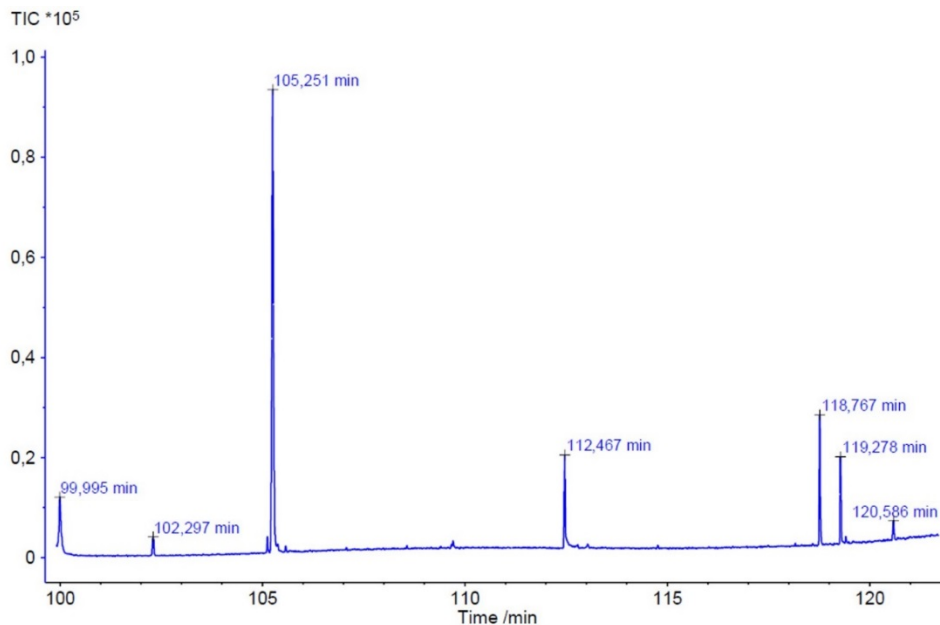


Figure 7. Total ion chromatogram (TIC, blue) after heating the cryo trap.

Table 1. Mass spectral data compared with the NIST database.

Retention time	Database Hit	Hit Quality
102.297	column material	
105.251	Phenol	96
112.467	1H-Indazole	94
	Benzonitrile, 4-amino-	91
	1H-Benzimidazole	91
118.767	Phenol, 4,4'-methylenebis-	94
	Phenol, 2-[(4-hydroxyphenyl)methyl]-	90
119.284	4,4'-Ethylidenediphenol	91
	s-Indacene, 1,2,3,5,6,7-hexahydro-1,1,7,7-tetramethyl-	80

The TGA results typically describe three main reductions in mass; room temperature to ~150 °C, ~400 °C and ~500 °C. The initial loss, can be attributed to moisture, as expected. Ehlers *et al.* [12] studied the decomposition of polybenzimidazole and explained that the benzimidazole with its carbon nitrogen bond, is the cause of the water absorption. The possibility of an oxygen containing group being emitted is present as a result of oxygen being contained in polymer, which is not eliminated even under normal drying conditions [12]. Thermal degradation through a decarboxylation step has been postulated earlier for polyamides and polyimides and seems to explain the formation of carbon dioxide in PBI [13].

Benzene and phenol are expected; phenol is a by-product of the synthesis of PBI. At 500 – 600 °C, ammonia and hydrogen cyanide are detected. These products are formed from the decomposition of the aromatic rings which crosslink to an essentially carbonaceous polymeric structure [12]; other reports suggest the presence of ammonia and hydrogen cyanide [12].

Friedman *et al.* [14, 15], studied the gasses resulting from a time-of-flight experiment and noted the presence of small amounts of benzene, aniline, benzonitrile, phenylene diamine, aminobenzonitrile, acrylonitrile and phthalonitrile. Benzene is expected given the aromatic structure of the polymer (arising from single bond scissions).

Elhers *et al.* [12] summarised by stating that “although the major products during the initial temperature steps are H₂O, CO₂ and CO, the major volatile products are H₂, HCN and NH₃, leading to crosslinking and some fragmentation of the aromatic and heterocyclic ring”.

3.2 PBI – CF Composite

After heat pressing the PBI-CF composite it was noted that there was some residue that was forced out of the mould. FTIR (Figure 8), reveals that although there was no clear [EMIM]OAc signal (Figure 8c), it is expected that there was a small quantity present prior to heat pressing, which then decomposed at the elevated heat press temperature, thus explaining why there is no clear [EMIM]OAc signal. As can be seen in Figure 8d, water is present, reinforcing the theory that there was still [EMIM]OAc left as it is hygroscopic and difficult to remove from the ionic liquid.

Observations of the composites showed a relatively well consolidated composite. However, it is believed that when the heat press removed the [EMIM]OAc, it also removed a small quantity of PBI, leaving the composite dry in areas.

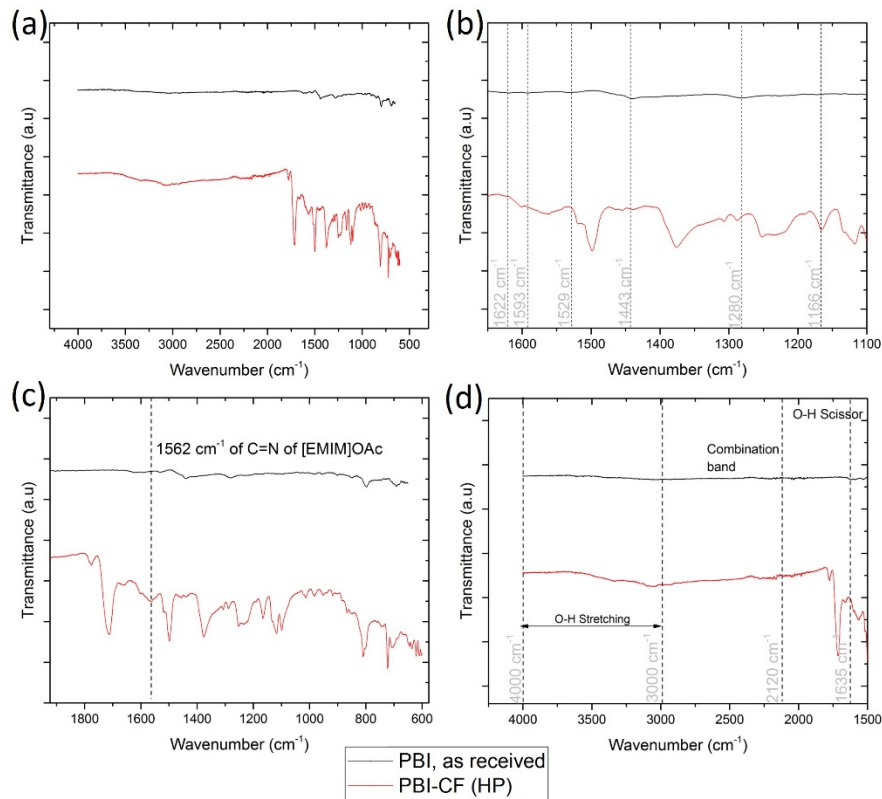


Figure 8. FTIR results of the as received and the PBI-CF. (a) Full spectra, (b) Characteristic signals of PBI, (c) C=N signal of [EMIM]OAc and (d) H₂O characteristic signals.

An example of a stress-strain curves (2 samples tested) is shown in Figure 7. Failure was mixed mode, occurring across multiple areas, suggesting the possibility that there are multiple dry areas. The elastic modulus was measured as (33.99 ± 3.51) GPa. Nonlinearity in the curve at $\sim 0.4\%$ strain is expected to be the consequence of the small undulations in the composite.

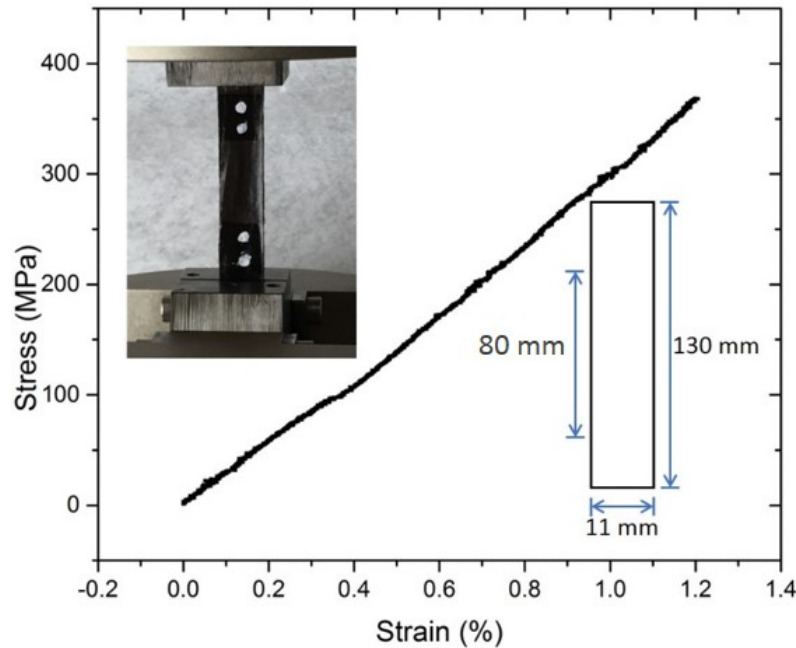


Figure 7. Tensile test conducted on PBI-CF specimens. This displays the inertial, elastic region.

4 CONCLUSION

Evidently, there are signals from foreign species present in the polymer that would need to be removed prior to the fabrication of the polymer/composite sample. The hyphenated evolved gas analysis suggests that there is a presence of phenol in the polymer and moisture. Phenol was expected given it is a by-product of the polymer synthesis and moisture has been expected given the propensity of the PBI to form hydrogen bonds [12].

Phenol can be removed by washing the PBI pellets with distilled water (phenol is moderately soluble in water so around 8 g will dissolve in 100 g/100 ml or water) or a very mildly alkaline solution (*e.g.* potassium carbonate in water). This should remove the phenol (as the phenolate ion which is soluble in water). Water will then be extracted using a separator funnel. The PBI can then be stored in a desiccator. For moisture, the PBI pellets can be dried in a vacuum oven after removing the phenol and then stored in a desiccator until processing.

The evolved gas analysis also suggests boundaries to the upper temperature if a heat press method is considered. This avoids the issue of releasing HCN and benzene. Subsequently, any heat press methodology will be limited by a maximum temperature of 400 °C.

PBI was successfully dissolved in the ionic liquid [EMIM]OAc with casting on the carbon fibre to form a composite looking encouraging, however, further work needs to be done to remove [EMIM]OAc before heat pressing. The composite produced has alluded to the possibility that [EMIM]OAc (with moisture) was present, which then degraded during the heat press procedure. In addition, the pressure displaced the solution (with a small quantity of PBI), leaving areas of the composite dried.

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REFERENCES

- [1] T.-S. Chung, "A Critical Review of Polybenzimidazoles," *Journal of Macromolecular Science, Part C*, vol. 37, pp. 277-301, 1997/05/01 1997.
- [2] yasojima, "Properties of PBI (Polybenzimidazole) Celazole SCM7000 ", ed, Accessed October 2016.
- [3] H. M. S. Iqbal, S. Bhowmik, and R. Benedictus, "Process optimization of solvent based polybenzimidazole adhesive for aerospace applications," *International Journal of Adhesion and Adhesives*, vol. 48, pp. 188-193, 1// 2014.
- [4] A. Sannigrahi, D. Arunbabu, R. M. Sankar, and T. Jana, "Aggregation Behavior of Polybenzimidazole in Aprotic Polar Solvent," *Macromolecules*, vol. 40, pp. 2844-2851, 2007/04/17 2007.
- [5] A. B. Strong, *Fundamentals of Composites Manufacturing: Materials, Methods and Applications*, 2nd ed.: Society of Manufacturing Engineers, 2008.
- [6] E. J. Powers and G. A. Serad, "History and Development of Polybenzimidazoles," in *High Performance Polymers: Their Origin and Development: Proceedings of the Symposium on the History of High Performance Polymers at the American Chemical Society Meeting held in New York, April 15-18, 1986*, R. B. Seymour and G. S. Kirshenbaum, Eds., ed Dordrecht: Springer Netherlands, 1986, pp. 355-373.
- [7] N. W. Brooks, R. A. Duckett, J. Rose, I. M. Ward, and J. Clements, "An n.m.r. study of absorbed water in polybenzimidazole," *Polymer*, vol. 34, pp. 4038-4042, 1993/01/01 1993.
- [8] D. Y. Xing, S. Y. Chan, and T.-S. Chung, "Molecular interactions between polybenzimidazole and [EMIM]OAc, and derived ultrafiltration membranes for protein separation," *Green Chemistry*, vol. 14, pp. 1405-1412, 2012.
- [9] G. S. Copeland, M. Gruender, J. M. Petit, and J. C. Moore, "Thermal Resistant Coatings Using PBI Resin," *Society for the Advancement of Materials and Process Engineering (SAMPE) Conference, Baltimore, MD. , 2012*.
- [10] D. Y. Xing, S. Y. Chan, and T.-S. Chung, "The ionic liquid [EMIM]OAc as a solvent to fabricate stable polybenzimidazole membranes for organic solvent nanofiltration," *Green Chemistry*, vol. 16, pp. 1383-1392, 2014.
- [11] Y. Leng, *Materials Characterization: Introduction to Microscopic and Spectroscopic Methods*: John Wiley & Sons, 2009.
- [12] G. F. L. Ehlers and K. R. Fisch, "Studies of Thermal Breakdown of Polybenzimidazole," *Thermal Analysis: Organic and Macromolecular Chemistry*, vol. 3, 1971.
- [13] G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, *Journal of Polymer Science A-1*, vol. 8, p. 3511, 1970.
- [14] H. L. Friedman, G. A. Griffith, and H. W. Goldstein, *ML-TDR-64-274, Part III*, 1967.
- [15] H. L. Friedman, H. W. Goldstein, and G. A. Griffith, *AFML-TR-68-111, Part II*, 1969.