Sacrificial component fabrication for optimised production of micro-vascular polymer composite

B Dalton¹,², D Dixon¹,²,³, A McIlhagger¹,²,³, E Archer¹,²,³

¹ School of Engineering, University of Ulster, Shore Road, Newtownabbey, Co. Antrim BT370QB, UK.
² ECRE Engineering Composites Research Centre, University of Ulster, Shore Road, Newtownabbey, Co. Antrim BT370QB, UK.
³ ERI Engineering Research Institute, University of Ulster, Shore Road, Newtownabbey, Co. Antrim BT370QB, UK.

bm.dalton@ulster.ac.uk

Abstract. Smart functional materials are a viable future goal for advanced applications in aerospace, space and medical applications. In this work micro-vascular polymer composite systems have been developed using sacrificial fibres produced from catalyst loaded Poly(lactic acid). The sacrificial fibres have been produced via a published technique which treated PLA in a solvent catalyst mixture of 60% Trifluoroethanol, 40% H₂O dispersed with 10 wt% tin (II) oxalate catalyst. A second process of polymer extrusion of PLA using graded fill contents of tin (II) oxalate has also been developed for the up scaled production of fibres as an alternative to solution treatment. Thermal analysis (TGA) was used to compare sacrificial fibre specimens. PLA fibres produced via the polymer extrusion method outperformed solution treated fibres displaying a lower degradation onset temperature (average 25°C lower), higher degradation rates (observed through a derivative curve comparison) and lower residual catalyst content (0.67% solvent treated fibre against 0.16% extruded fibre). The continuous extrusion process is solvent free and is suitable for high volume production. This work has been carried out to fully understand the fabrication issues with sacrificial components.

1. Introduction

“Smart materials” is a term now used to describe materials with an additional functionality which are able to react to their environment. With composites the dominant areas are self-healing, thermal control, sensory/damage detection, and electrical/magnetic utilization. The definition of a smart material is “one in which a key material property is altered in a controlled fashion in response to the introduction of pre-determined external stimulus” [1]. Self-healing materials were first researched at in the 1990s. Much of the work since has been heavily dominated by R&D, with industrial applications relatively confined. Much of the inspiration for early works was influenced by organic biological systems. This inspiration still dominates the ideology behind smart autonomous materials.

Traditional methods of repairing polymer composites are both basic and time consuming. Added to the repair process, the input of inspection and detection and the process becomes a costly, non-value added affair. Techniques of welding, patching and in-situ curing are all employed currently. These methods are useful, and may never be fully superseded [2]. While intelligent polymer composite materials have been viewed by many industries, major interest has come from the aerospace sector.
Many of the features promised by smart materials can apply directly to aircraft applications. These may include structurally integrated batteries for energy storage, structural profile morphology for aerodynamic application in wing skins, electrical and magnetic surface signatures for signal and transmitting, integrated sensors for detection and monitoring, thermal control and, of course, self-healing capabilities [3].

There are limited techniques for achieving vascular networks for functional fluid delivery. Hollow glass fibre tubes which are pre-impregnated with epoxy have been used. Known as discrete channel arrays, the glass pipettes were incorporated into glass and carbon fibre polymer composites with limited success. After mechanical testing to induce ‘healing’, samples with completed heal cycles showed no more mechanical recovery than control samples with unfilled fibres [4]. Micro-machining and etching are achievable via various methods also but again with limited success and lengthy integrated process. The latest and most promising technique for creating a vascular network within a composite is that of the incorporation and subsequent thermal removal of sacrificial fibres.

2. Methods and materials

2.1. List of materials
PLA monofilament of 500 µm diameter was used as received from Monofil Technik UK. The catalyst tin (II) oxalate and solvent Trifluoroethanol were used as received from Sigma-Aldrich UK. The epoxy Huntsman epoxy system; Araldite LY 564 with Aradure 2954 cure agent was used for both carbon fibre and epoxy optical samples.

2.2. Tools and analysis
TGA was performed on a TA Instruments Q100 Series machine. For Scanning Electron Microscopy, an FEI Quanta 200 was employed. An Olympus SZ-PT was used for optical imaging of incorporated PLA fibres and post vapourisation evacuated chambers. Vascular fluid behaviour was also studied via optical microscope for imaging and video footage. Carbon fibre composite components were produced on a 500 mm² (bottom) aluminium tool piece, with 390 mm² caul plate, sealed with Nylon 800G vacuum bagging material from Aerovac systems, giving composite components averaging 350 mm². Both vascular (study) and non-vascular (reference) composite components were consolidated via Resin Transfer Moulding (RTM). An Edwards RTM system was employed for the transfer moulding configured with a Walther Pilot degassing system type MD6 12 HZM. Vaporisation of sacrificial components VaSc (post consolidation) was carried out via two methods. A vacuum bagging technique was employed as well as a sealed vessel vacuum. 800G Nylon vacuum bagging was used (suited for larger more complex geometrical components). Also a Pyrex 10 lt vacuum vessel was used for smaller components. A Magnum Venus Plastech 240 v twin port vacuum system was used for VaSC experiments. For alternative fibre production methods, (polymer extrusion with catalyst filler) a Thermo Scientific Haake Polylab OS RheoDrive 7 (drive system) with Haake RheoMex OS ptw16 (barrel) was used.

2.3. Fibre treatment (solvent)
The fibre treatment method previously used to prepare vascular composites is not fully described in literature [5]. For the initial experiments 500 µm PLA monofilament was rolled into loose coils and supported within a 3 litre Pyrex beaker on a steel wire nest. The beaker, wire nest, flea and thermometer were all solvent cleaned to minimise contamination in the catalyst solution. The beaker was placed onto a heater plate/stirrer [Figure 1]. A mixture containing 60% trifluoroethanol, (TFE) and 40% H₂O dispersed with 10wt % tin (II) oxalate was mechanically stirred for 30 minutes to evenly disperse the catalyst. All catalyst mixtures were measured via weight on a digital scale and the solution was then poured into the beaker fully submerging the suspended monofilament. The hot plate was set to 37°C and regulated via a thermostat. To keep the catalyst suspended during the 24 hour soak a medium speed stir setting was selected. All fibre treatment was performed in a fume cabinet.
and with appropriate personal protective equipment due to the corrosive properties of trifluoroethanol. After a 24 hour soak time at 37°C the fibre bundles were removed from the solution and suspended within the fume cabinet to air dry for a further 24 hours. Evaporation of the trifluoroethanol/catalyst mixture (discussed in results section) was minimised in by inclosing the mixture within a sealed vessel.

Figure 1. Solution treatment of PLA fibres on hot plate.

2.4. New fibre production method
For primary experiments to determine the polymer melt/catalyst compatibility, PLA material (in fibre form) was re-melted in a glass beaker at 100°C. Tin (II) oxalate was added to the polymer melt and dispersed roughly by stirring. Several oven runs were necessary due to the rapid cooling of the PLA when removed from heat. Crude fibre like structures could then be hand drawn into various lengths and diameters producing structures which could be tested for vaporisation efficiency. PLA/catalyst structures were suspended in a matrix material of Huntsman epoxy (Araldite LY 564 with Aradure 2954 hardener) and room cured for 24 hours before a post cure oven cycle of 2 hours at 120°C. The resulting sacrificial structures could then be trimmed to expose fibre ends and put through a fibre removal cycle. Prepared components were sealed in a Pyrex vacuum vessel and run at 180°C for a 20 hour oven cycle under vacuum. The process left a vascular epoxy sample with visible cleared channel architecture.

Following this, fibres were produced via a polymer extrusion method using Tin (II) oxalate (a powder) as a filler/additive in the extrusion process on a Thermo Scientific Hakke PolyLab OS RheoDrive 7 (drive system) with Rheomex OS PTW16 barrel. The extrusion of a thermoplastic monofilament [6] becomes more temperamental when incorporating a powder filler [7,8]. The same monofilament from solvent treatment was used as a polymer feed. Using the same PLA material as a base would allow for a closer comparison of the two end products. PLA fibre reels were mounted on spindle mounts and six fibre ends were fed into the barrel. A slow screw speed ensured the fibres would be taken into the barrel and catalyst material was added using a screw-driven force feeder with 7 different feed rates ranging from <0.5% to 5.0%. A water tank cooled the fibre upon exiting the die.

With these extruded fibres, vascular components were developed in two forms; carbon fibre reinforced vascular structures, and plain epoxy vascular. Carbon fibre reinforced samples were developed to determine the mechanical implications of vasculature on a load bearing structure, and epoxy samples were developed for optical analysis, to view the void architecture. Vaporisation of sacrificial components (VaSC) techniques follow the reported literature method [4].
sacrificial components were thermally evacuated through an oven cycle of 20 hours at 180°C under vacuum.

3. Results and discussion

3.1. Fibre treatment (solvent)
Untreated PLA monofilament is a rigid transparent material (Figure 2a), whereas solvent treated fibres turned white and were more ductile (Figure 2c). Long exposure times to the PLA solvent trifluoroethanol swells the fibre allowing the tin catalyst to absorb but over exposure (treatment times above 24 hours or at temperatures higher than 37°C) dissolved the PLA fibres into a white paste like material. As an initial indicator a uniformed white fibre may be a sign of a successful treatment but upon closer inspection fibres were not uniformly discoloured throughout their entire lengths. Observable clear patches (Figure 2b) would suggest areas where catalyst treatment has not fully occurred.

3.2. Fibre extrusion
The first identified issue with extruded fibres was a significantly more brittle material when compared to solution treated fibres. This is a result of two factors. Firstly the thermal and mechanical (shear) action experienced through the extrusion process where the molten poly(lactic acid) is subjected to barrel temperatures of >200°C. The result of these events contribute to a loss in mechanical properties for the extruded fibre. Secondly the catalyst powder fill content has a direct effect on the polymer during cooling [7, 8]. This can be confirmed by the fact that higher fill content fibres are more brittle than low fill content fibres. From results there is an optimum fill content (0.5% - 1.0%) after which, higher levels of catalyst become a hindrance in the evacuation of chambers (Figure 3) resulting in lower percentage clearance. High levels of residual catalyst materials contribute to ‘plugging’ and can reduce the fibre removal efficiency. These results correlate with findings from TGA and SEM, where there is a direct relation between fill content and residual materials. However there were different methods employed for the calculation of channel clearance. For solvent treated fibre components, the percentage channel clearance was calculated from the amount of channels which appeared to be fully cleared. The problem with this method is that some channels may have been 95% clear, with a 5% plug, which will render the entire channel inoperative; as this will affect the overall fibre removal efficiency percentage extruded components were quantified via optical microscope analysis of clear epoxy samples where the entire channel could be viewed. Total areal percentages could then be ascertained giving a more accurate value. 0.5% and 1.0% fill rate fibres perform as well as solution treated fibres and so must be forwarded as the most ideal candidates for further development.

![Fig 2. (a) Untreated PLA fibres appearing clear and transparent.](image-url)
3.3. Vaporisation of sacrificial components
Sample coupons of both carbon fibre and plain epoxy samples were initially developed with 10 micro-channels per sample. Each sample was prepared using the same process and fibres removed via the same technique. Vascular samples were then individually tested for channel content and fluids were driven through each channel; if the channel was clear fluids could travel through the component. If there were blockages the fluid would not travel. The percentage of cleared channels was then recorded (Figure 3). Much higher efficiency for fibre removal was observed for the epoxy only samples versus the samples containing carbon fibre/epoxy. The vaporisation capability for the sacrificial fibres must be considered equal as all fibres came from the same treatment process and components also experienced identical fibre removal conditions. This would suggest the presence of carbon fibre materials may in some way hinder the evacuation of chambers. Another possibility is that carbon fibre samples have increased 'plugging' due to increased crimping of sacrificial fibres in the presence of carbon.

Cross sections of vascular carbon fibre samples were observed in Figure 4b. Whilst structural patterns were not perfect there has been a good average areal displacement of the channels. Also noted is the increased crimp in vascular samples (Figure 4b) when compared to non-vascular (Figure 4c) due to the presence of the carbon fibres. Sacrificial components displace carbon fibres in the layup. Upon removal of sacrificial fibres the carbon fibres remain displaced. It is not yet known if this crimping
has an effect on the mechanical properties of the component. Optical/epoxy samples were developed to observe the internal void architecture of vascular components. Channels were highly visible allowing for the mapping of 'plugs' and rough estimates of fibre removal efficiency. Channel architectures including a double braid (Figure 5a) triple braid (Figure 5b) and quadruple braid (Figure 5c) have been realized.

![Figure 3. Fibre removal (%) for extruded components of varying fill content.](image)

4. Thermogravimetric analysis
Thermogravimetric analysis was performed on poly(lactic acid) PLA materials. The samples were prepared to compare PLA fibres developed through the solvent treatment method against those prepared through polymer extrusion with catalyst filler. The thermal degradation characteristics of treated PLA materials will have a serious implication on the efficiency of fibre removal as the most important event of thermal degradation of solvent treated fibres from literature is the onset of mass loss [5].

![Figure 4. (a) Carbon fibre cross section pre VaSC showing PLA fibre ends.](image)

![Figure 4. (b) Vascular sample showing displacement of carbon.](image)

![Figure 4. (c) Virgin sample with no fibre displacement.](image)

The lowest reported onset of thermal degradation from literature for PLA has been 180°C. The lowest degradation onset temperature achieved with extruded materials in this study was 200°C (Figure 6) with maximum onset of ~300°C. For all runs untreated PLA gave similar results and are
comparable to literature. Extruded samples with higher fill content (>1.0%) degraded at lower temperatures however, with a large remaining volume of catalyst filler (tin II oxalate) which degrades at much higher temperatures. The remaining measured catalyst materials relate directly to the percentage fill rates used during production. Also noted from both literature graphs and experimental graphs is the initial weight drop off at ~100°C. This drop is exclusive to solvent treated materials and not observed for extruded materials (seen in all graphs; green curves). It is presumed that this drop off may be the vaporisation/escape of trapped trifluoroethanol (TFE) within the PLA. TFE has a boiling point of 74°C, however trapped materials may take longer to evacuate.

![Figure 5. (a) Epoxy specimen with double braid configuration.](image)

![Figure 5. (b) Epoxy specimen with triple braid configuration.](image)

![Figure 5. (c) Epoxy specimen with quadruple braid configuration.](image)

![Figure 6. Mass loss onset for extruded PLA with catalyst fill.](image)

4.1. Degradation profile
After preliminary runs secondary runs were performed on specimens with the most potential for further trials (0.5% fill rate extrusions); multiple runs were completed on 0.5% samples and solvent treated samples [fig.8]; 1%, 3% and 5% specimens were also run for reference. Mass loss onset for some specimens remain similar in run 2, however, 0.5% fill rate samples experience an earlier onset of mass loss though rates of degradation remain similar for both runs. The remaining specimens with higher fill content (3%, 5%) experience earlier mass loss onset but with significantly larger volumes of residual catalyst materials. Specimens with 1% fill rate display attractive qualities of early onset and low residual catalyst content.
4.2. Residual materials
Whilst 1% fill rate specimens display improved onset temperatures when compared to 0.5% fill rate samples there is significantly less residual catalyst in 0.5% samples (0.16%) when compared to both 1% fill rate samples (0.67%) and solvent treated samples (0.67%) (Figure 9). This data corroborates scanning electron microscopy SEM images taken from interior channel walls of vascular components created using fibres from both solvent treatment methods and extrusion methods.

4.3. Derivative
In Figures 10, a sharp derivative peaks represent rapid rates of degradation. 0.5% fill rate samples were compared to 5% fill rate samples (lowest, highest) to determine the effect of catalyst content on degradation rates. It is clear from results that are direct relations between fill content and degradation rates. Higher fill rates (5%) (Figure 10b) degrade faster than low fill (0.5%) (Figure 10a). The
difference is clear in the overlay (Figure 10c). Although faster degradation may be an attractive quality, the higher levels of residue in high fill samples is much more of a concern.

5. Conclusions
“Smart functional” polymer composites have been realised. In this study Micro-vascular components have been developed from fibres produced via a solution treatment method previously described in literature, and a novel method of polymer extrusion using a catalyst filler. Solvent treatment of polylactic produced soft and ductile fibres making them ideal for weaving/handling, however, the treatment process is highly critical to the outcome of the sacrificial component. Treatment times are long (24 hours) and solution mixture/temperature must be kept constant (TFE and water has different rates of evaporation). Variability in the catalyst adhesion was found to be an issue which could cause poorly treated areas, ultimately resulting in plugging and channel clearing issues. It is difficult to determine the final catalyst percentage or indeed control catalyst content through solution treatment methods; polymer extrusion on the other hand is a well established versatile process. Components may be produced in a variety of geometrical profiles or indeed injection moulded into more advanced sacrificial components and fibres may be produced with varying levels of catalyst fill. Moreover, if this fill content is optimised, components can be produced yielding less residual materials post
evacuation (0.16% for 5% samples against 0.67% for solution treated fibres), have higher channel clearing efficiency (observed through TGA) and cleaner internal channel walls (observed through SEM) than those developed through solution treatment style).

TGA degradation profiles show extruded components with earlier onset temperatures, higher rates of degradation and lower residual catalyst content post degradation. The most promising specimens being the lower fill content materials (0.5% - 1.0%).

![Figure 10. (c) Comparative derivative signal overlay for low fill against high fill specimens.](Image)

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