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1 **Development of a closed-loop recycling process for short carbon fibre**
2 **polypropylene composites**

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9 **Abstract**

10 *In this study the effects of a closed-loop recycling methodology are evaluated for degradation using a*
11 *discontinuous carbon fibre polypropylene (CFPP) composite material. The process comprises two fundamental*
12 *steps, reclamation and remanufacture. The material properties are analysed over two recycling loops. For neat*
13 *polypropylene, the molecular weight analysis indicates evidence of minimal matrix degradation that does not affect*
14 *the material behaviour, as demonstrated by the shear tests. CFPP specimens show no decrease in mechanical*
15 *properties over repeated loops, the final specimens show an increase of 26 % and 43 % in ultimate tensile strength*
16 *and ultimate strain, respectively. These are attributed to cumulative matrix residue on the fibre surface after*
17 *reclamation and subsequently increased fibre-matrix adhesion. The improvement of CFPP properties and*
18 *insignificant variability in the tensile properties and molecular weight distribution of neat polypropylene validate the*
19 *potential of this proof-of-concept, closed-loop recyclable material. Future studies will investigate alternative, higher*
20 *performance matrices.*

21 **Keywords:** Recycling; Polymer-matrix composites (PMCs); Compression moulding; Discontinuous
22 reinforcement.

23 **1. Introduction**

24 The market share of carbon fibre reinforced polymer composites (CFRP) in the automotive industry is predicted to
25 grow as the high-volume manufacture sector starts to adopt CFRP as a lightweighting strategy [1]. Vehicle fuel

26 emissions are heavily regulated, US Corporate Average Fuel Economy standards limit passenger vehicle emissions
27 to 35 mpg by 2020 [2] and the European Commission set a target of 57.9 mpg by 2021 [3]. To meet these, and
28 inevitably more stringent future targets, automakers are looking at CFRP to save weight as a method of increasing
29 fuel efficiency. Decreasing vehicle fuel emissions can be achieved by structural lightweighting; a 6-8 % increase in
30 fuel economy can be achieved by a 10 % drop in vehicle weight [4].

31 The growth of CFRP applications will be accompanied by a global increase in CFRP waste. CFRP waste comes
32 from a variety of sources: testing materials from research and design, manufacturing scrap and end-of-life (EOL)
33 parts [5]; EOL components make up 60 % of all waste composites [6]. Industries which rely on high-volume
34 manufacture will be significantly deterred by the waste burden as many countries already penalise heavily for
35 landfilled waste, on top of landfill tax rates (£84.40 per tonne, excluding gate fees, as of 1st April 2016) [7]. In fact,
36 some EU countries have already banned landfilling; the most common form of waste management for CFRP [8].
37 Some industries can also be penalised for the lack of recyclable components in their products. The EOL vehicle
38 directive (ELV, 2000/53/EC) states that as of January 2015, 95 % of a passenger vehicles mass must be reused,
39 recycled or recovered [9].

40 The development of recyclable composites, and processes with which to recycle them, are therefore becoming of
41 greater interest. The term recycling here describes the reclamation of constituents from waste composites and their
42 remanufacture into useful components. Reclaimed carbon fibres (rCFs) can be a fraction of the cost of virgin CFs
43 (vCFs) and therefore the subsequent rCFRP will be at a reduced cost [10]. In the last ten years there have been
44 three comprehensive reviews of the available technologies and future outlook: Pickering in 2006 [11], Pimenta &
45 Pinho *et al.* in 2011 [12] and Oliveux *et al.* in 2015 [13].

46 Currently, the two main routes for fibre reclamation are *via* thermal processes (pyrolysis [14], micro-wave
47 pyrolysis [15], fluidised bed pyrolysis [16]) and chemical process (solvolysis [17], acid digestion [18], super-critical
48 fluid solvolysis [19]). Depending on the parameters used, rCFs from either method can retain up to 95 % of the virgin
49 tensile stiffness and strength [10,12]. CF reclamation through pyrolysis is already conducted at a commercial scale
50 [12] and rCFs are currently produced in thousands of tonnes [10]. Some solvolysis methods are able to reclaim
51 mixed monomeric material, however it is of little value compared to the virgin matrix [13]. The problem that the
52 industry faces is that the rCFs produced from these processes are in a filamentised, randomly oriented and low-
53 density-packing form [12]. In addition to being fragmented into shorter lengths because of waste size reduction for
54 transport, fibre breakage during comminution and after the reclamation process [20]. Without significant alignment,
55 high fibre volume fractions (V_f) are difficult to achieve and remanufacture results in low value material [21]. Highly

56 aligned, discontinuous fibre composites can provide comparable tensile stiffness and strength to continuous fibre
57 composites [22]. A number of technologies have been developed to align fibres, a thorough account of these was
58 conducted by Such *et al* [23]. The HiPerDiF (High-Performance Discontinuous Fibre) method, developed at the
59 University of Bristol, is a continuous hydrodynamic alignment process. It uses the sudden momentum change of a
60 fibre-water suspension directed, through a nozzle, into a narrow gap between two parallel plates to mechanically
61 align discontinuous fibres into highly aligned dry preforms. Yu *et al* showed that the HiPerDiF method can provide
62 preforms with 67 % of fibres aligned within a range of $\pm 3^\circ$ and mechanical performance comparable with those of an
63 equivalent continuous fibre composite [24]. Longana *et al* also applied the HiPerDiF method to the remanufacturing
64 of rCF achieving one of the highest mechanical performances reported in the literature for a recycled composite
65 material [25]. Longana *et al* also used the HiPerDiF method to investigate the performance of composites
66 remanufactured from short carbon fibres that have undergone multiple recycling loops [26]. However, it is evident
67 that the current thermoset material paradigm is not conducive to closed-loop composite recycling.

68 Thermoplastics offer a unique opportunity for recycling as the molecular structure can be temporarily separated
69 using heat or solvent treatment. Melt recycling causes a significant reduction in mechanical properties, due to fibre
70 breakage, and matrix degradation during processing, due to the high temperatures and shear forces required for
71 extrusion [27]. Solvent processing has been investigated in the recycling sphere before, initially as a selective sorting
72 technique for mixed plastic wastes [28–31]. Papaspyrides *et al.* used the dissolution/precipitation technique in the
73 1990s to recycle neat polypropylene (PP) wastes which showed that solvent processing did not significantly affect
74 tensile stiffness or strength [32,33].

75 In this study a proof-of-concept composite material, comprised of a thermoplastic matrix and discontinuous
76 carbon fibres, is developed to achieve full closed-loop recyclability through a dissolution/precipitation reclamation
77 technique and remanufacturing with the HiPerDiF method. The aim is to provide evidence for a shift in composite
78 materials towards adopting advanced thermoplastic composites in automotive and other advanced applications. By
79 developing reclamation and remanufacturing processes for a CFPP material, high-performance composite materials
80 become both recyclable, affordable and a realistic material option for industrial applications.

81 2. Recycling method development

82 This section details the development of a two-step (reclamation and remanufacture) closed-loop recycling
83 methodology, as outlined in Fig. 1. A process can be deemed closed-loop if, once all the initiator material has been
84 added, it requires no additional material to propagate [34]. Closed-loop processes for composites manufacturing and
85 recycling are in accordance with the Circular Economy paradigm presented by the Ellen MacArthur foundation [35]
86 and encouraged by the UK Composite Strategy (2016) [9] for new materials.

Fig. 1. The closed-loop methodology in brief; post initiation the cycle requires no additional material to propagate.

87 Discontinuous carbon fibre reinforcement and polypropylene matrix were selected as constituents due to their
88 processing advantages and intrinsic recyclability. 3 mm long fibres are the optimum length for alignment using the
89 HiPerDiF, are less prone to breakages than long fibres and are similar in form to rCFs. As a proof-of-concept study,
90 the mechanical performance of the thermoplastic used is not paramount or optimised. PP has milder processing
91 conditions in comparison to higher performance polymers such as polyamides. PP has been used in automotive
92 applications, in various formats, for many years [36–39]. The modal reinforcement for PP is typically randomly
93 oriented glass fibre due to the ease of injection moulding manufacturing and the low cost of both PP and GF. This
94 combination of materials provides low cost, high-volume parts, with a slight increase in mechanical properties.

95 In general, the methodology can be started, arbitrarily, with an initial EOL CF thermoplastic which is washed,
96 shredded and separated into its constituent fibres and matrix. Reclamation consists of matrix dissolution and fibre
97 filtration after this each constituent follows a separate reclamation path, indicated by the hashed boxes in Fig. 2.
98 Constituents are remanufactured into the same, or a similar component again, ideally requiring no additional fibre or
99 matrix. The method has been developed to minimise property degradation as the aim is to reclaim high-quality
100 constituents then remanufacture these into high-performance components after multiple cycles. In this work CFPP

Fig. 2. A flow chart outlining the experimental detail of closed-loop recycling methodology, highlighting the reclamation and re-manufacturing processes.

101 specimens (vCFPP) were manufactured from virgin constituents and mechanically tested. vCFPP specimens were
102 then washed, chopped, reclaimed and remanufactured, producing r₁CFPP specimens which were subsequently
103 mechanically tested, this process continued for a total of two loops.

104 The first part of this study evaluates the mechanical and material performance of neat PP after recycling. The
105 second part focuses on the property retention of recycled carbon fibre PP composites (rCFPP) over repeated
106 iterations.

107 2.1 Materials

108 The PP pellets were supplied by Sigma Aldrich, Table 1 and the CFs were TohoTenax C124 (standard type), Table
109 2, respectively. TohoTenax fibres come with a water-soluble sizing (3.8 % w/w) to aid dispersion. Recycling solvents
110 used were both certified ACS reagent grade xylene (xylenes mixture) and acetone sourced from Fisher scientific.

Table 1. Properties of polypropylene.

Table 2. Properties of carbon fibres.

111 3. Matrix recycling

112 3.1 Experimental

113 Virgin PP (vPP) panels were formed first, made directly from PP pellets. The virgin panel was shredded and then
114 fully dissolved in an appropriate solvent. The solvent type and volumes used were modified from the literature
115 [40,41]. A flow diagram of the experimental processes involved in the recycling methodology can be found in Fig. 2.
116 Experimental parameters used in reclamation can be found in Table 3. PP precipitates on cooling to room
117 temperature, forming a solvated powder with gelatinous properties, in xylene solvent. Non-solvent (acetone) was
118 added to encourage the precipitation of any PP still in solution and minimises residual xylene in the precipitate. Non-
119 solvent (boiling point 56 °C) was added after cooling the solution to below 50 °C. The precipitate suspension was
120 vacuum filtered using Buchner filtration apparatus. Liberal washings of non-solvent minimised the amount of residual
121 solvent. Filtered precipitate was dried in a vacuum oven (~ - 29 inHg) at 80 °C for 14 hours. Grain size of the
122 precipitate varied significantly at this stage so mechanical size reduction was used to increase the surface area and
123 homogenise grain size. Liquid nitrogen-cooled solvent traps were used to reclaim the solvent removed during drying.
124 Solvent trap collections and filtrate were combined and separated into pure solvents/non-solvents using vacuum
125 assisted fractional distillation. In the literature, solvent collection percentages for similar experiments have stated
126 solvent recovery percentages of xylene 99 % [42] and acetone 92 % [40]. Polymer yields can be found in Table 3;
127 recovery rates of ≤ 99 % can be found in the literature [30,32,33,43,44].

128 Panels were moulded in an aluminium tool with cavity dimensions: 1 mm x 100 mm x 170 mm. The compression
129 moulding cycle, conducted under vacuum conditions to remove the catalytic effects of atmospheric oxygen on the
130 degradation of polymers, is plotted in Fig. 3.

Fig. 3. Compression moulding schedule for PP and CFPP specimens.

Table 3. Reclamation parameters for each feedstock material.
Table 4. Remanufacture parameters, composite volume fractions and wastage.

132

133 3.2 *Material characterisation*134 3.2.1 *Polymer characterisation*

135 Differential scanning calorimetry (DSC) was used to examine the effect of repeated processing on the melting
 136 point (T_m) and the percentage crystallinity, calculated using equation (1).

$$\% X = [(\Delta H_m - \Delta H_c) / \Delta H_{m^o}] \cdot 100 \quad (1)$$

137 Where ΔH_m and ΔH_c are the enthalpy of fusion for the melting and crystallization transitions, ΔH_{m^o} is an enthalpy
 138 of fusion reference value for a pure crystal of the polymer. The PP ΔH_{m^o} value of 207 J g⁻¹ was used, as found in the
 139 literature [45]. All thermal ramp experiments were carried out using a TA Auto Q2000 DSC in pierced, hermetically
 140 sealed aluminium pans on samples (10 ± 3 mg), under flowing N₂ (50 cm³ min⁻¹) at a heating rate of 10 °C min⁻¹. A
 141 TA Q500 Thermal Gravimetric Analyser (TGA) was used to quantify PP degradation under the conditions of
 142 remanufacture. Isothermal analysis at 200 °C were carried out for 160 minutes in both air and N₂ atmospheres (60
 143 cm³ min⁻¹). A Perkins Elmer Spectrum 100 Fourier Transform Infrared Spectrometer was used to compare polymer
 144 functionalities between virgin and recycled polymers. The molecular weight, molecular weight distribution (MWD) and
 145 poly dispersity index (PDI) of each recyclate was determined using a gel permeation chromatograph with size
 146 exclusion chromatography (GPC/SEC). Samples were analysed using an Agilent PL220 high temperature GPC
 147 system with two Agilent PLgel Mixed D columns (300 x 7.5 mm) and a PLgel 5 µm guard column, in a TCB mobile
 148 phase (with 250 ppm BHT) at 160 °C at a rate of 1 ml min⁻¹. Samples were prepared by solubilising in 140 °C TCB
 149 overnight, in an Agilent PL-SP 260VS.

150 3.2.2 *Mechanical testing*

151 Three shear coupons and three tensile dumbbell specimens were cut from each panel. In accordance with ASTM
 152 D638, tensile tests were performed on Type IV dumbbell specimens using a Shimadzu AGS-X servo-electric tensile
 153 test machine with a 10 kN load cell and a constant cross-head displacement of 1 mm min⁻¹. Specimens were sprayed
 154 black and speckled with white dots to measure the strain with an Imetrum video-gauge system, Fig. 4a. Referring to
 155 ASTM D732, the shear strength tests were performed using a shear punch tool. 50 mm diameter discs, with a
 156 thickness of 1 mm, were punched from panels; these were given a centre-punch of 10 mm diameter to be used as a
 157 tool fixing datum. A diagram of the shear punch tool and the shear disk dimensions can be seen in Fig. 5. A servo-

158 electric tensile test machine was used in compression mode using a constant cross-head displacement speed of
159 1.25 mm min⁻¹; load was recorded using a 10 kN load cell.

160 Fig. 4. High resolution scans of: (a) a necked r₂PP dumbbell specimen with speckled pattern. (b) vCFPP specimen with speckle pattern.

161 Fig. 5. ASTM D732 Punch shear test: (a) punch assembly and (b) Shear punch disc.

161 3.3 Results and Discussion

162 3.3.1 Polymer characterisation

163 The thermal properties of PP through two recycling iterations are presented in Fig. 6. A comparison of
164 temperature ramp DSC data from vPP and r₂CFPP indicates that the crystallinity and melting temperature (T_m) of the
165 polymer are unaffected by reclamation, Fig. 6a. The isothermal TGA plot in Fig. 6b shows no degradation of vPP in
166 air at 200 °C for the first 75 minutes, then gradually drops to 85 % after 140 minutes. The r₂PP thermogram shows
167 degradation starting after 25 minutes and gradually decreasing in weight until a plateau at 50 % weight after 150
168 minutes. Isothermal analysis in flowing N₂ shows no degradation after 160 minutes of either vPP or r₂PP. This
169 confirms the catalytic effect that atmospheric oxygen has on polymer degradation and resulted in the use of vacuum
170 when moulding panels. The increase in degradation seen in the r₂PP specimen is likely due to a combination of loss
171 of thermal stability additives and significantly increased surface area of the r₂PP powder, compared to vPP pellet for
172 the same experimental conditions.

173 Number average (M_n) and weight average (M_w) molecular weights, after each iteration, are shown in Table 5.
174 The molecular weight distributions are representative of mono-disperse semi-crystalline polymers, as expected from
175 the PP used, Fig. 6c. From left to right the curve runs from low to high molecular weights. Both M_n and M_w
176 successively drop after each iteration, represented as a negative shift on the x-axis. The M_w decreases in greater
177 increments, this is represented as a narrowing of the distribution curve. After vPP there is a noticeable narrowing of
178 the curve, this is from a thinning of the low molecular weight region and the loss of a slight shoulder in the high
179 molecular weight region. This suggests that initial dissolution of the polymer is extracting small molecules into the
180 organic solvent. This could be either small PP chain fragments or, most likely, soluble additive molecules. The larger
181 chains are then fragmented into medium length chains, removing the larger weight value skew on the distribution
182 peak. There is a successive drop in M_n between r₁PP and r₂PP which suggests that some chain scission is occurring
183 during processing.

184 In Fig. 6d, The FTIR spectrum of vPP shows all of the vibrational peaks for specific functional groups expected
 185 for PP: ν_{as} (methyl group $-CH_3$) – $2970\text{ cm}^{-1}(l)$; $\nu_s(-CH_3)$ – $2910\text{ cm}^{-1}, (l)$; ν_{as} (methylene group $-CH_2-$) – 2870 cm^{-1}
 186 (m) ; $\nu_s(-CH_2-)$ – $2840\text{ cm}^{-1}, (m)$; $\delta_{as}(-CH_2-)$ – $1460\text{ cm}^{-1}, (m)$; $\delta_s(-CH_3)$ - $1370\text{ cm}^{-1}, (l)$. A peak at 1734 cm^{-1} was
 187 present in vCFPP but not in r_2 CFPP which indicates that something was removed. This peak is very close to the ν_s
 188 (carbonyl group $>C=O$) – $1735\text{ cm}^{-1}(l)$ vibration of Irganox 1010, a hindered phenol antioxidant additive typically used
 189 in commercial PP [46]. The other peaks associated with this functional group vibration are not found in vCFPP
 190 however, which could be due to: a) *swamping by the signals of other additives that were not removed by reclamation*
 191 *or b) the signal source is from a carbonyl group in an unidentified additive.* As the intensities of the main chain
 192 functional groups remain constant it can be concluded that the chain is not chemically altered during processing.

193 Fig. 6. a) DSC thermograms of vPP and r_2 PP. b) TGA thermographs of vPP and r_2 PP. c) GPC molecular weight distributions for vPP, r_1 PP and r_2 PP. d) FTIR spectra of vPP and r_2 PP.

194 Table 5. The GPC/SEC analysis of polypropylene after each recycling iteration

195 3.3.2 Mechanical Testing

196 Fig. 7. (a) Stress-strain curves for PP after each recycling loop. (b) Stress-displacement plots for PP after each recycling loop.

197 Representative stress-strain curves obtained from tensile tests of vPP to r_2 PP specimens are shown in Fig. 7a.
 198 Tensile specimens showed a typical linear-elastic region and subsequent plastic yielding expected of semi crystalline
 199 polymers. Yielding continued until ductile failure by necking ($> 100\%$) which continued until termination of the test.
 200 The latter was determined by fracture or by necking up to 20% as this was sufficient to validate necking. A typical
 201 example of the necking observed can be seen in Fig. 4. Stress-strain curves shown in Fig. 7a do not show the full
 202 extent of necking and the data is only presented to a strain preceding the ultimate tensile strength, which describes
 203 the curve maximum. The tensile stiffness (E_T), ultimate tensile strength ($X_{T_{ult}}$), ultimate tensile strain ($\epsilon_{T_{ult}}$), shear
 204 strength (S), melting point (T_m) and crystallinity values for each recycling iteration are recorded in Table 6.

205 Overall the curves show no significant deviation in shape through recycling and have almost negligible variance
 206 in the gradient of the linear elastic region. If any significant change in the polymer chain length had occurred, it would
 207 be observable in the linear elastic and plastic behaviour of the specimens. $X_{T_{ult}}$ was taken as the highest point in the
 208 stress-strain curve as tests were not continued until fracture. E_T , $X_{T_{ult}}$, $\epsilon_{T_{ult}}$, T_m and the degree of crystallinity values
 209 show no significant changes, which reinforces the notion that the polymer remains unchanged.

Table 6. The material characterisation data for PP after each recycling loop.

210 Stress-displacement curves for shear testing of specimens of vPP to r₂PP are plotted in Fig. 7b. They showed
211 typical ductile response to shear stress for semi-crystalline thermoplastics. All specimens failed in the same manner
212 with no premature failures. Specimen response to shear stress is invariable between iterations, until failure where
213 there is an observable decrease in shear strength after the last recycling iteration. The lack of variance between the
214 shear stress plots suggests that recycling had a limited effect on the shear behaviour of PP. Under shear stress the
215 polymer exhibits three distinct phenomena: 1) *an initial linear-elastic response* followed by 2) *a visco-elastic response*
216 and 3) *a final stiffening before shear failure*. The initial linear-elastic region represents elastic deformation of the
217 polymer chains. The second, visco-elastic stage represents a combination of plastic deformations and molecular
218 translation as chains start to unfurl and slide past each other. The final stage suggests a stiffening of the polymer
219 which represents the temporary alignment of unfurled and stretched polymer chains, causing the apparent increase
220 in pseudo-shear modulus; as the plot is stress as a function of deformation, and not strain, it is not the shear
221 modulus. The invariable shear plots in those stages suggests further that there is limited change in the majority of
222 polymer chains. There is a slight, but observable ($14 \% \pm 5.2 \%$), decrease in shear strength between r₁PP and r₂PP,
223 Table 6. This is attributed to the successive drop in M_n , Table 6. M_n represents the modal weight of the polymer
224 chains, therefore its reduction describes a decrease in the number of high molecular weight chains. This reflects the
225 breaking of long polymer chains into smaller, medium length chains, losing the skew of the larger value. Graphically
226 this can be observed as a narrowing of the distribution curve and a shift in the curve maximum, to a lower $\text{Log } M$ and
227 a higher $dw/d\text{Log}M$, as the number of medium length chains increases as a consequence. During loading the
228 polymer is straining, a shorter chain has less intermolecular bonds between neighbouring chains, requiring less
229 shear force for failure, resulting in a drop in the shear strength.

230 3.4 Conclusion

231 The aim of this study was to establish the degradative effects of reclamation and remanufacture on PP over
232 repeated cycles. The polymer characterisation results suggest that there is insufficient alteration to the crystalline and
233 amorphous regions of the polymer backbone to cause any observable difference in behaviour. This notion is
234 corroborated by the mechanical testing data which indicates that there is insignificant reduction in the tensile
235 properties of PP after multiple recycling loops. Loss of additives has been suggested by the FTIR results however
236 this does not seem to have a large effect on the tensile properties. A full analysis of additive composition is difficult to
237 achieve however it could be an area of future investigation.

238 4. Composite recycling

239 4.1 Experimental

240 The reclamation of fibre and matrix from CFPP specimens involves an additional filtration step, and lower
241 solution concentration than matrix reclamation from panels. Experimental parameters used in this reclamation can be
242 found in Table 3. Solution concentration reduction was required to decrease solution viscosity to optimise fibre
243 filtration and washing, a consequence of this was increased dissolution rates in comparison to the higher
244 concentrated neat PP solution. The key part of the composite recycling process is the separation of fibres from the
245 polymer solution. A bespoke filtration apparatus, heated to 200 °C, was required to provide an initial hot gravity
246 filtration step for fibre extraction prior to vacuum filtrations. This enabled fibres to be filtered from solution without
247 precipitation of matrix cooling on contact with the apparatus. Reclaimed fibres were dried in a vacuum oven (~ - 29
248 inHg) at 80 °C for 14 hours, then carded by hand to separate fibre bundles and aligned using the HiPerDiF method to
249 produce highly aligned dry fibre preforms. The water soluble sizing functions as a dispersal agent, the amount of
250 sizing remaining after alignment was tested by attempting to disperse a dry preform prior to any contact with matrix.
251 The fibres required additional stirring and sonication to achieve a homogeneous dispersal suggesting that the water
252 soluble sizing is lost after the first dispersal. Preforms were stacked in an aluminium tool along with enough recycled
253 PP precipitate to produce a specimen with 26 % CF fibre volume fraction (V_{fF}). Each specimen contained 4 preform
254 layers and 3 PP layers stacked in an ABA pattern, with preforms as the outermost layers. The compression moulding
255 cycle is plotted in Fig. 3. Experimental parameters, composite volume fractions and wastage can be found in Table 4.
256 All of the specimens were recycled, including the fracture surfaces as the combination of pull-out dominated failure
257 and the negligible amount of failed fibres in comparison to the total amount in the specimen made any influence from
258 fractured specimens insignificant. Any fractured fibres, from failure or otherwise, are accounted for in the FLD
259 analysis. For the development of a proof-of-concept material, the absolute mechanical performances were of
260 secondary importance, therefore this V_{fF} has been selected to guarantee maximum fibre impregnation. In future
261 works the impregnation and fibre wet-out will be optimised by increasing matrix melt flow and decreasing melt path
262 lengths to achieve higher volume fractions, and consequently higher mechanical properties.

263 4.2 Material Characterisation

264 4.2.1 Fibre analysis

265 Fibre length distribution (FLD) analysis was used to determine the effect of recycling on the average fibre length.
266 A portion of each preform was dispersed in water and slowly gravity filtered until an even distribution of fibres

267 remained. A portion of this distribution was scanned using an Epson 11000XL, and each fibre within a consistent
268 region of the high-resolution image was measured. A Hitachi TM3000 Scanning Electron Microscope (SEM) was
269 used (5000 V accelerating voltage) to investigate the surface quality of fibre preforms collected from each recycling
270 iteration.

271 4.2.2 Mechanical testing

272 CFPP specimens were tested for their tensile properties in accordance with ASTM D3039. Axial force was
273 provided by a Shimadzu AGS-X servo-electric tensile test machine with a 10 kN load cell and a constant cross-head
274 displacement of 1 mm min⁻¹. The gauge length of the specimens was consistently 50 mm. GFRP epoxy end tabs
275 were bonded to the specimens using cyanoacrylate adhesive. Specimens were sprayed black and speckled with
276 white dots to measure the strain with an Imetrum video-gauge system, Fig. 4b.

277 4.3 Results and Discussion

278 4.3.1 Fibre Analysis

279 The fibre length distributions (FLD) of preforms after each iteration are presented in Fig. 8. An error of ± 0.2 mm
280 was applied for the by-eye length measurement of fibres. In the vCFPP preform sample 74 % of fibres are in the
281 range of 2.8-3.4 mm; a similar value to that obtained in other studies involving 3 mm carbon fibres and the HiPerDiF
282 alignment method [26]. After the first recycling loop 42 % of fibres are in the range 2.8-3.4 mm. A combination of the
283 fibre carding and alignment stages could be causing fibre breakages. For r₂CFPP the FLD was evenly distributed
284 with 0.8-0.1 mm, 1.4-1.6 mm and 3.2-3.4 mm having the maximum 9 % of the distribution each. The alignment head
285 consists of numerous parallel plates spaced at a distance, d , much less than the length of the fibre. If d is close to the
286 average fibre length then the fibres have more space to misalign in the xy plane, resulting in poor alignment [47].
287 Minimising d therefore increases the alignment potential not only for fibres of the maximum length, in this case 3.0-
288 3.4 mm, but also for any fibres of length $> d$.

Fig. 8. Fibre length distributions of vCFPP, r₁CFPP and r₂CFPP showing percentages of fibres in effective fibre range.

289 SEM micrographs of fibres were taken from preform samples after each iteration and at multiple length scales. It can
290 be clearly seen in the magnified preform micrographs of r₂CFPP that fibres have been coated with a substance. This
291 is assumed to be PP residue left after reclamation Fig. 9c. Fibre washing methodology was kept constant for each
292 iteration therefore there is a limit to the amount of PP that can be removed. Fibres in Fig. 9c have a greater coverage
293 of coating, both in amount and fibre area; coating is along the circumference and length of fibre in r₂CFPP whereas
294 only the lengths of fibres have drops of coating on in r₁CFPP, Fig. 9b.

Fig. 9. SEM micrographs for: a) vCFPP, b) r₁CFPP and c) r₂CFPP.

4.3.2 Mechanical testing

Fig. 10. a) Stress-strain curves for CFPP specimens after each loop. b) Bar chart comparing the tensile stiffness (normalised to 26 % V_f) and ultimate tensile strength of CFPP after each recycling loop.

Representative stress-strain curves obtained from tensile tests of vCFPP to r₂CFPP specimens are shown in Fig. 10a. Tensile specimens exhibited a typical linear-elastic response followed by brittle fracture, some showing a region of increased compliance just before failure. The vCFPP and r₁CFPP failure mechanism is dominated by fibre pull-out however there is a significant decrease in the amount of fibre pull-out observed at the r₂CFPP fracture surfaces.

300

The interfacial shear strength (IFSS) between CF and PP is relatively low, typically less than 10 MPa, which results in a fibre critical length (l_c) less than or equal to the fibre length ($l = 3$ mm), as previously observed in [47]. In vCFPP the IFSS is significantly less than the tensile strength of the fibre and $l > l_c$, which causes fibre pull-out under loading. V_f , E_T , X_{Tult} and ϵ_{Tult} values are presented in Table 7. The V_f values are averaged over six specimens, the tensile stiffness $E_{T0.26}$, describes the average tensile stiffness normalised to a 26 % fibre volume fraction, following the rules of mixture. These are plotted with the X_{Tult} values in Fig. 10b.

Table 7. The mechanical performance of CFPP specimens after each recycling iteration.

Overall, the plots show a slight variation in $E_{T0.26}$ between recycling iterations, a decrease after the first followed by an increase after the second iteration. The drop in $E_{T0.26}$ between vCFPP and r₁CFPP can be attributed to fibre breakage during recycling and the increase in the frequency of fibres less than the distance between the alignment plates, d , in the HiPerDiF alignment head. The drop in $E_{T0.26}$ is not as significant as expected, following the conclusions made by Longana *et al* [26]. This is due to the decrease in d during HiPerDiF maintenance and optimisation in between studies. Kruskal-Wallis analysis suggests that statistically there is no change in the X_{Tult} and ϵ_{Tult} between vCFPP and r₁CFPP. As the FLD data show further fibre breakage between r₁CFPP and r₂CFPP it is expected that the stiffness will further decrease as more fibres will be formed with length $< d$ and thus alignment will be reduced. An increase in X_{Tult} and ϵ_{Tult} is recorded after the second recycling iteration, $E_{T0.26}$ remains statistically unchanged. The micrographs in Fig. 9c show a significant increase in the amount of PP coating on reclaimed fibres. The PP coating acts as a form of sizing that increases the adhesion between the fibre and matrix. This results in an IFSS increase and is observed as an increase in X_{Tult} and in less pull-out dominated failure. l_c is inversely proportional to IFSS, which means that even if the fibre length is slightly reduced of the recycling loops it remains above the critical length. This also results in increased specimen extension under loading, ϵ_{Tult} , as the matrix plastic

321 limit is reached before the fibre pull-out strength. The pull-out dominated failure of vCFPP and r1CFPP can be
322 attributed to the poor adhesion between the inorganic surface of carbon fibre and the organic, non-polar
323 polypropylene chains. The deposition of PP on fibres act as a sizing providing a region of increased adhesion at the
324 interface, improving overall fibre-matrix adhesion.

325 4.4 Conclusion

326 The aim of this study was to investigate the effects of the developed recycling methodology on the mechanical
327 behaviour of CFPP material. FLD analysis showed that modal fibre lengths are decreasing after each recycling
328 iteration. However, the initial invariance and subsequent improvement of mechanical performance indicates that this
329 shortening has a limited effect on material behaviour. SEM analysis of reclaimed fibres suggests the reason for
330 enhanced mechanical behaviour may be the cumulative coating of fibres with matrix material. The potential for
331 performance enhancement requires further investigation.

332 5. Overall conclusions

333 The aim of this study was to develop a closed-loop recyclable composite material and a relative recycling
334 methodology that can produce a high-performance material after multiple loops. The first objective was to understand
335 the effects of the method on neat PP matrix. The lack of significant variance in the mechanical behaviour of neat PP
336 suggested that recycling proved ineffectual and fibre impregnation was viable. The CFPP specimens showed no
337 reduction in mechanical performance but an overall increase in tensile stiffness, ultimate tensile strength and ultimate
338 strain after multiple loops.

339 The next development of the methodology will incorporate a matrix with a higher mechanical performance and
340 thus a more realistic option for the automotive market. CF-polyamide combinations are becoming a material of choice
341 for modern automotive components. The deposition of matrix on the surface of fibres is of interest as it negates the
342 need for an additional sizing step whilst providing an exact matrix specific sizing; the potential for tailorable *in-situ*
343 sizing therefore be the topic of future investigation. Subsequent studies will therefore focus on the following issues to
344 develop the methodology closer to complete its initial aim of developing a closed-loop recycling process for a
345 competitive, high-performance composite: 1) *repeat this study to develop CF-PA composite material* 2) *evaluation of*
346 *residual matrix performance as a sizing and* 3) *a comprehensive life cycle analysis of the recycling methodology and*
347 *a comparison with current reclamation and remanufacturing processes.*

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