

# DEVELOPMENT OF A CLOSED-LOOP RECYCLING PROCESS FOR SHORT CARBON FIBRE COMPOSITES: MATRIX

Rhys J. Tapper<sup>1</sup>, Marco L. Longana<sup>2</sup>, Hana Yu<sup>3</sup>, Ian Hamerton<sup>4</sup>, Kevin D. Potter<sup>5</sup>

<sup>1</sup> Bristol Composites Institute (ACCIS), University of Bristol,  
Queen's Building, University Walk, Bristol, BS8 1TR, United Kingdom

[R.tapper@bristol.ac.uk](mailto:R.tapper@bristol.ac.uk),  
[www.bristol.ac.uk/composites](http://www.bristol.ac.uk/composites),

**Keywords:** Thermoplastics Recycling, Closed-Loop Recycling, Dissolution-precipitation,  
Compression Moulding

## ABSTRACT

In this study, the degradation effects of multiple closed-loop recycling processes evaluated for polypropylene. This is the first in a series of studies that aim to develop a fully recyclable composite material based on aligned discontinuous carbon fibre. Mechanical and material property fluctuations are analysed after three iterations. Molecular weight analysis indicates slight degradation in chain length; however, this is not reflected in material or mechanical performance. The limited variability of the tensile properties and the molecular weight distribution after multiple recycling iterations is insignificant and therefore promising for further development of the recyclable composite material by introducing fibres

## 1 INTRODUCTION

The global demand for carbon fibre reinforced polymer materials (CFRP) is growing every year. As more industries are starting to adopt CFRP material to replace conventional materials, like steel and aluminium, growth rates will continue to rise; CFRP annual growth rates of 10 % are predicted through 2020 [1]. The automotive industry has predicted significant increases in CFRP growth rate as the mass-manufactured vehicle sector starts to adopt composites as a lightweighting strategy [2]. To meet stringent vehicle fuel emissions targets, automakers are looking to composites to save weight as a method of increasing fuel efficiency [3-4]. Vehicle lightweighting is the most time and cost effective method for decreasing fuel emissions; it is reported that a 6-8 % increase in fuel economy can be achieved by a 10 % drop in vehicle weight [5].

The growth of CFRPs will be accompanied by a global increase in CFRP waste. CFRP waste comes from a variety of sources: testing materials from research and design, off-cuts, tooling and expired prepregs from manufacturing or end-of-life (EOL) parts [6]. Industries which rely on high-volume manufacture will be significantly deterred by the waste burden as some European government's already penalise heavily for landfilled waste, on top of landfill tax rates (UK: £84.40 per tonne, excluding gate fees, as of 1<sup>st</sup> April 2016) [7]. Some industries can also be penalised for the lack of recyclable components in their products. The EOL vehicle directive (ELV, 2000/53/EC) states that as of January 2015, 95 % of a passenger vehicles mass must be reused, recycled or recovered [8].

The development of recyclable composites, and processes with which to recycle them, are therefore becoming of significant interest to the industry. In the last ten years there have been three comprehensive reviews of the available technologies and future outlook: Pickering in 2006 [9], Pimenta & Pinho *et al.* in 2011 [10] and Oliveux *et al.* in 2015 [11].

The term recycling can be somewhat ambiguous; a material can be reprocessed into a variety of forms i.e. recyclates, each having a different value depending on the process and the desired application of the recyclate. This recyclate can then re-manufactured into a marketable form i.e. composite material. Low value recyclates, such as organic fillers, low molecular-weight oils and fuels are attained through tertiary recycling processes, such as mechanical grinding and incineration [11]. High-value recyclates i.e. polymers and fibres can be reclaimed from secondary recycling processes such as pyrolysis [9] and solvolysis [12]. The highest value recyclate comes from primary recycling methods which describe the direct reuse of a material in its intended application; The reuse of fibre off-cuts in the roofing panels of the BMW i3 is a prime example of this [13].

Separating composites into their high-value constituents is the fundamental aim of secondary recycling methodologies. Only pyrolysis and solvolysis methods are able to reclaim carbon fibres; in some cases property reclamation is up to 95 % of the virgin tensile stiffness and strength [10-14]. These technologies are already at an industrially applicable level and reclaimed carbon fibres (rCFs) are currently produced in thousands of tonnes [14]. The major barrier to the widespread use of rCFs in high-value applications is the lack of industrial scale alignment processes that can provide composites with high volume fractions (50-60 %  $V_f$ ) necessary to provide the mechanical performance expected of high value composites [15]. The technology for the recycling of CFs and their remanufacture into high-value components is somewhat apparent. The current issue is that thermosetting matrices cannot be reclaimed and there is currently a lack of industrially available technologies that can reclaim thermoplastic matrices along with CFs, into a high-value component. As approximately 50 % of a composite is matrix by volume, recycling of waste matrix material from high value applications is a relatively uncharted area of research.

Thermoplastics offer a unique opportunity for recycling as the molecular structure can be temporarily separated using heat or solvent treatment. Melt processing has been utilised for the recycling of thermoplastic composites for many years [16]. The problem with this method is that the mechanical performance of the recyclate is significantly reduced due to high temperatures and shear forces required for extrusion, breaking down fibres and causing matrix degradation [17-25].

## **2 EXPERIMENTAL**

### **2.1 Closed-Loop Methodology**

This study is the first step in the development of a fully closed-loop recycling process that is able to produce a recyclable composite material for high-value applications. As this is the first step in the series it investigates the effect recycling has on the matrix material.

Subsequent studies will investigate the inclusion of fibres and associated complexities. A process can be deemed closed-loop if, once all the initiator material has been added, it requires no additional material to propagate [26]. Closed-loop processes for composites manufacturing and recycling fit with the Circular Economy paradigm presented by the Ellen MacArthur foundation [27-28] and encouraged by the UK Composite Strategy (2016) [2] for new materials. This methodology aims to produce high quality constituents with the purpose of forming high performance recycled components. It has therefore been developed to minimise property degradation.

The methodology, as depicted in Fig. 1, is described as follows: Neat polypropylene (PP) pellets were formed into panels by compression moulding. The panels were cut into specimens and tested for their material properties and mechanical performance. After testing, all panel material was recycled into powder, using a non-hazardous solvent treatment process, which was then re-manufactured into a panel and re-tested. This describes one complete iteration of the methodology which was repeated three times; all performance data from each loop was recorded for comparison. The results are

presented for each panel made, in the following nomenclature: Virgin (V), Recycled 1, 2 and 3 (R1, R2 and R3).

## 2.2 Recycling Process

This process is designed to recycle thermoplastic carbon fibre composites via solvent treatment, however in this study only neat thermoplastic is used. For PP, full dissolution occurred after stirring for 3 hours. Complete dissolution can occur in concentrations as low as 15 % w/v (PP/Xylene) to minimise solvent use, however this results in a viscous solution which is not suitable for efficient fibre

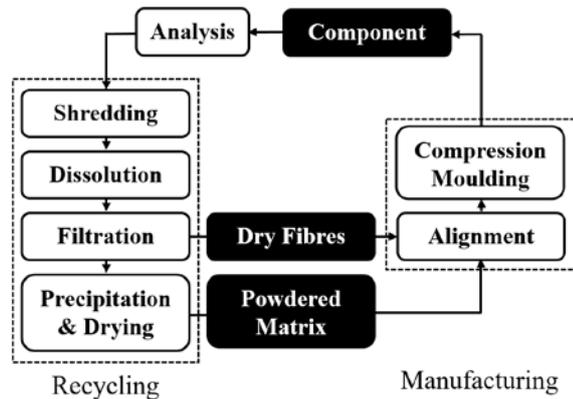


Fig. 1. A flow chart outlining the closed-loop methodology in stages. Highlighting the recycling and manufacturing processes.

filtration. PP precipitates out of solution on cooling to room temperature, forming a solvated powder with gelatinous properties. The precipitate suspension was vacuum filtered using Buchner filtration apparatus. Liberal washings of non-solvent are required to minimise the amount of residual solvent remaining. Filtered precipitate was dried in a vacuum oven, mechanical size reduction was used to increase the surface area and homogenise grain size. Liquid nitrogen-cooled solvent traps were used to reclaim the solvent removed during drying. Solvent trap collections and original solution filtrate were combined and separated into pure solvents/non-solvents using vacuum assisted fractional distillation.

## 2.3 Manufacturing Process

The manufacturing process is designed to be applicable for both neat polymer and fibre reinforced specimens. In future studies the recyclate powder and aligned dry-fibre preforms are combined in a tool and compression moulded into composite pre-preg tapes. The powder recyclate was added in layers and compacted using a hydraulic press. Panels were compression moulded at 220 °C using vacuum pressure. Three panels were made for each recycling iteration to investigate the consistency of the manufacturing process and provide averaged property values.

## 2.4 Material Characterisation

Differential scanning calorimetry (DSC) was used to examine the effect of repeated processing on the polymer melt temperature and the percentage crystallinity. The initial melting temperature was also required to design the manufacturing process. All experiments were carried out using a TA Auto Q2000 DSC with hermetically sealed aluminium sample pans. Each sample pan lid was pierced to avoid pressure build up in case residual solvents were present. All polymer sample weights were between 8-13 mg and the heating rate was 10 °C min<sup>-1</sup>. The molecular weight, molecular weight

distribution (MWD) and poly dispersity index (PDI) of each recyclate was determined using a gel permeation chromatograph with size exclusion chromatography (GPC/SEC).

## 2.5 Mechanical testing

Each panel was cut into three shear coupons and three tensile dumbbell specimens. These specimens were used to determine the shear strength, tensile stiffness, and ultimate tensile strength.

Referring to ASTM D638, tensile tests were performed on Type IV dumbbell specimens using a servo-electric tensile test machine. A punch tool of Type IV dimensions was manufactured to punch dumbbell specimens from the panel. Specimens were sprayed black and speckled with white dots to measure the strain with an Imetrum video-gauge system. Specimens were loaded at a constant cross-head displacement speed of 1 mm/min; loading was recorded using a 10 kN load cell.

Referring to ASTM D732 the shear strength tests were performed using a shear punch tool. 50 mm diameter discs were punched from panels; these were given a centre-punch of 10 mm diameter to be used as a tool fixing datum. A servo-electric tensile test machine was used in compression mode using a constant cross-head displacement speed of 1.25 mm/min; loading was recorded using a 10 kN load cell.

## 3 RESULTS AND DISCUSSION

Representative stress-strain curves obtained from tensile tests of polymer specimens from each recycling iteration, depicted as V, R1, R2 and R3, are shown in Fig. 2. Test specimens showed a linear-elastic region and subsequent plastic yielding typical of semi crystalline polymers. Yielding continued until ductile failure by necking, usually occurring at 20 % strain. Ultimate tensile strengths values used are the highest loads achieved. Overall the curves show no discernible pattern of change through recycling iteration and have almost negligible variance in the linear elastic region; suggesting that recycling had no significant effect on the crystalline or amorphous regions of the polymer macrostructure. The degree of crystallinity and melting point values shown in Table 1 correspond to the unchanged stiffness and strength results as they suggest no change in the crystalline regions through recycling. The lack of variance between the shear stress plots in Fig. 2 also reflect a lack of significant change in the polymer macrostructure after recycling. There is a slight but observable decrease in the shear strength after the second and third recycling iterations, as depicted in Table 1. The invariability of material stiffness or strength suggests this can be adequately described by an increase in voids. Panel voidage was limited in the first two panels (V, R1) but increased in the final two specimens (R2, R3). Voids decrease the total surface area involved in failure therefore decreasing the maximum shear load of the polymer.

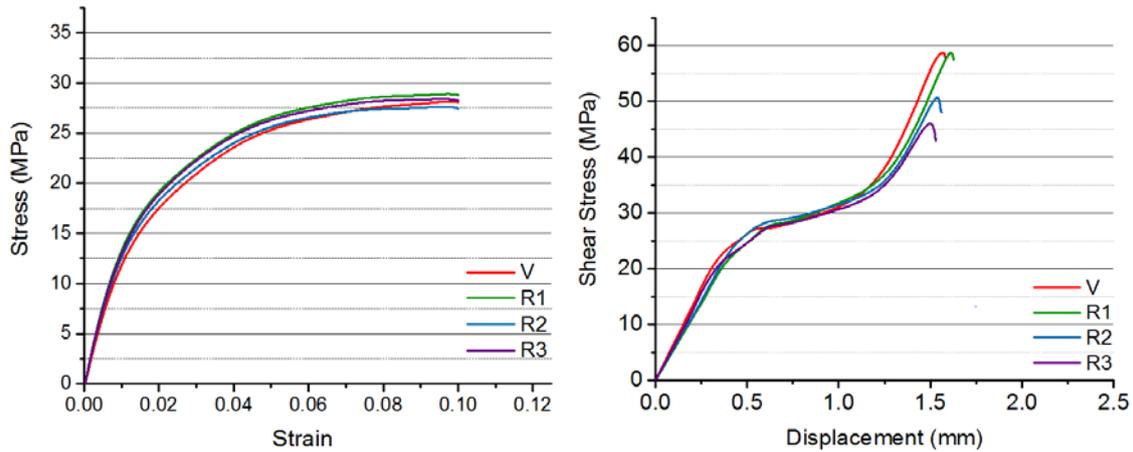


Fig. 2. Experimental Results:

Left - Representative stress-strain curves for polypropylene tensile specimens after each recycling iteration.

Right - Normalized stress-displacement plots for polypropylene shear specimens after each iteration.

Polypropylene	Tensile Stiffness (GPa) ± SD	Ultimate Tensile Strength (MPa) ± SD	Shear Strength (MPa)	Crystallinity (%)	Melting Point (°C)
Virgin	1.38 ± 0.03	27.8 ± 0.41	59.7 ± 2.30	47.3 ± 4.13	166 ± 0.56
Recycled 1	1.44 ± 0.10	27.1 ± 1.28	58.2 ± 3.20	44.9 ± 0.80	167 ± 0.57
Recycled 2	1.39 ± 0.09	27.3 ± 1.57	50.4 ± 3.23	50.6 ± 2.41	165 ± 2.89
Recycled 3	1.33 ± 0.13	27.4 ± 1.36	45.7 ± 2.41	43.7 ± 1.36	165 ± 0.21

Table 1. The mechanical performance, degree of crystallinity and melting point of polypropylene after multiple recycling iterations.

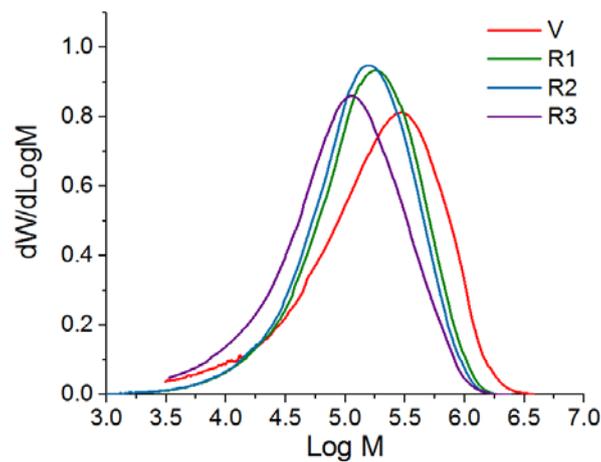


Fig. 3. Molecular weight distributions of polypropylene after each recycling iteration.

Molecular weight is inversely proportional to the degree of crystallinity therefore if the molecular weight decreases an increase in stiffness will be observed [16]. The Gaussian plots in

Fig. 3 are the molecular weight distributions of polypropylene after each recycling iteration. They are representative of a mono-disperse, semi-crystalline polymer. From left to right the curve plots from low to high molecular concentrations. After the first iteration, there is a noticeable narrowing of the curve accompanied by a thinning of the low molecular weight region and the loss of a slight shoulder in the high molecular weight region. This suggests that initial dissolution of the polymer is extracting small molecules into the organic solvent. This could be either small polypropylene fragments or, most likely, soluble additive molecules. The larger chains are then fragmented via the manufacturing process, becoming a more modal length, and thus causing the increase in the curve peak. After further recycling, there is a trend of shifting in the distribution to lower molecular weights. This can be explained by a continuation of the larger and median chain length fragmentation. Fragmentation is likely to be a mixture of main chain and branch scissions as a shift suggests a somewhat equal increase in both small and median molecular weights.

The molecular weights after each iteration, determined by GPC/SEC, are shown in Table 2. Error bounds for molecular weight readings are typically quoted at 10 %. There is a decrease in weight average molecular weight ( $M_w$ ) between V and R1 which is mirrored in the MWD. The magnitude of the decrease drops off considerably between subsequent iterations. The  $M_n$  decreases incrementally between V, R1 and R2 followed by a larger decrease after the final iteration. This is somewhat reflected in the MWD results, however the plots show an increase in  $M_n$  after the first iteration. This variation is within the quoted error bounds for measurements of this type.

	$M_n$	$M_w$	PDI
Polypropylene	(g mol <sup>-1</sup> )	(g mol <sup>-1</sup> )	
Virgin	65,750	328,450	4.87
Recycled 1	62,950	221,450	3.59
Recycled 2	59,950	195,200	3.35
Recycled 3	50,214	184,442	3.68

Table 2. The melting point and GPC/SEC analysis of polypropylene after each recycling iteration.

## 4 CONCLUSIONS

Results from this experimental work have proven this recycling methodology to be useful in reclaiming thermoplastic material properties after repeated iterations. Despite some decrease in shear strength and slight chain degradation the extent is not sufficient in causing significant reduction in properties. The retention of both tensile stiffness and ultimate tensile strength is promising and necessitates the continuation of this study to incorporate the carbon fibre reinforcement phase. Subsequent studies will focus on the following issues in pursuit of the manufacture and recycling of carbon fibre reinforced thermoplastic composites:

- 1 The qualitative and quantitative analysis of additive loss after the first iteration.
- 2 A modified manufacturing method to incorporate the impregnation of carbon fibres.
- 3 Fibre reclamation potential of the closed-loop recycling methodology.
- 4 Fibre-matrix adhesion analysis.
- 5 Comprehensive Life Cycle Analysis to determine the energy saving potential and validity of this closed-loop methodology in real terms.

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