DEVELOPMENT AND CHARACTERISTICS OF A FULLY RECYCLED CF/PP COMPOSITE

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Abstract

A fully recycled carbon fibre reinforced polypropylene (rCF/rPP) composite material has been developed and characterised. This new, randomly oriented short fibre composite was manufactured by press forming with a fibre volume fraction of 40 %. A series of tensile tests using rectangular specimens cut in four different directions (0°, 90°, ±45°) in the composite plate were performed to confirm in-plane material isotropy. Models to predict stiffness and strength of the short fibre rCF/rPP composite were also employed and validated using experiments. To model the viscoelastic and viscoplastic responses of the composite, an inelastic material model was employed and characterised using a series of creep and recovery tests. From the creep tests, it was found that the time and stress dependence of viscoplastic strains follows a power law. The viscoelastic response of the composite was found to be linear in the investigated stress range. The material model was validated in constant stress rate tensile tests and the agreement was good, even close to the rupture stress.

1 Introduction

The increasing industrial use of carbon fibre in e.g. aircraft and wind turbines calls for strategies for their recovery and possible reuse. Carbon fibres (CF), even when trapped in composites, are valuable products worth to be recovered. The energy needed to produce pristine carbon fibres is very high, 286 MJ/kg has been reported [1]. It has been shown [2, 3] that methods to recycle carbon fibres exist that consume less than 10 % of the energy required to manufacture virgin CF. Recent results [3] demonstrate that in terms of mechanical properties, recycled carbon fibre (rCF) can compete with virgin one giving a realistic scope for recycled replacing virgin, thus realising energy saving. With carbon fibre composites, recycling technologies involving burning or chemical decomposition of the polymer matrix have been developed [3–6] in order to process carbon fibre reinforced polymer (CFRP) composite waste.

Recycling of composite materials has been considered to be difficult due to the complex structure of these materials. Various types and content of fibre reinforcement as well as very different applications are factors that make recycling complicated. Consequently, methods to recover composite materials and to reuse them are still under development.

The aim of the study is to develop and characterise a novel engineering composite material manufactured using recycled constituents. The recycled carbon fibres are converted into preforms employing papermaking principles. Polypropylene scrap is reprocessed into films.

The composite is manufactured by press forming. The elastic and inelastic composite behaviour is investigated and the models to validate the experimental results are employed. Three generations of the composite have been manufactured, however only the last generation – the most improved one is considered in the following paper.

2 Methods

2.2 Constituents

Recovered carbon fibres CFM-PYR-H-1 [7] were supplied by Hadeg Recycling GmbH, Germany. The fibres had been produced by milling of carbon fibre composites, which were obtained from production waste generated by the aircraft industry. The fibres had then been recovered using a pyrolysis process at approximately 1200 °C by the supplier. Due to the cotton-like structure (see Fig. 1 a) b)) of the recovered carbon fibres, we first reprocessed them into fibre mats with a controlled fibre distribution using a procedure developed by Szpieg et al. [8]. PURE® process scrap polypropylene was supplied by Lankhorst Indutech bv, The Netherlands, [9] in the form of tape wound onto bobbins. The mechanical and thermal properties of the reprocessed PURE® scrap were earlier characterised by Szpieg et al. [10, 11]. The polypropylene scrap material was compounded with maleic anhydride grafted polypropylene (MAPP) coupling agents in order to improve the interfacial adhesion with the recycled carbon fibres [11, 12, 13].

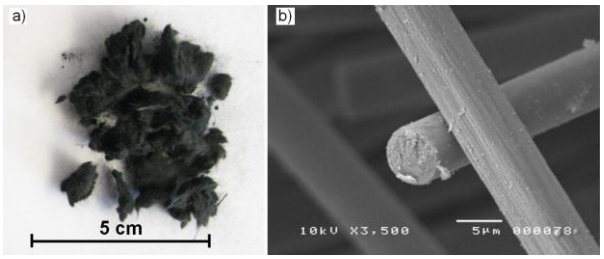

Figure 1. Recycled carbon fibres: **a)** cotton-like structure, view with the naked eye, **b)** individual fibres (x7.5k).

2.3 Preform manufacturing

The principles of papermaking [8] were employed to obtain preforms with uniformly distributed carbon fibres for subsequent composite manufacturing. As the recycled carbon fibres in their original form were difficult to process due to their entanglement, the idea was to disperse them to achieve a desired uniform fibre distribution. Here, the recovered carbon fibres were dispersed in distilled water using a mixer (see Fig. 2). The PP scrap from PURE® was reprocessed into a film using a hot press (see Fig. 3 a)).

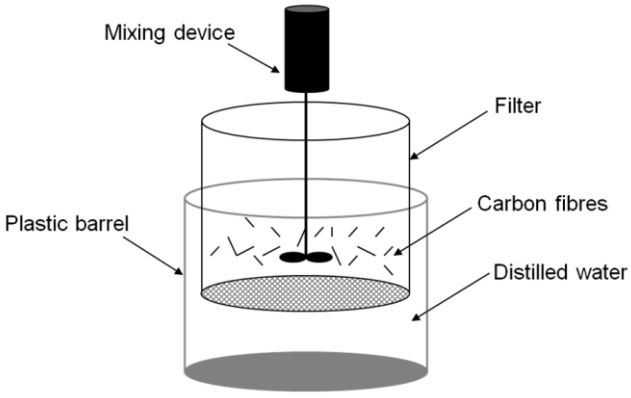

Figure 2. Dispersion of the recycled carbon fibres.

2.4 Composite manufacturing

Two recycled polypropylene (rPP) films were stacked between three recycled carbon fibre (rCF) preform layers (i.e. rCF/rPP/rCF/rPP/rCF). The stack was heated and press formed in a matched die tool (see Fig. 3 a)), also used for rPP film manufacturing, resulting in a composite plate thickness of approximately 1.20 mm. The required amounts of the constituents (rPP film and rCF preforms) were calculated to obtain a nominal fibre volume fraction of 40 %. The nominal areal weight of each rCF preform layer and each rPP film was 0.26 kg/m^2 and 0.30 kg/m^2 respectively. The following processing parameters were used: press time of seven minutes at 200 °C, an applied pressure of 13 MPa and subsequent cooling to room temperature in five minutes.

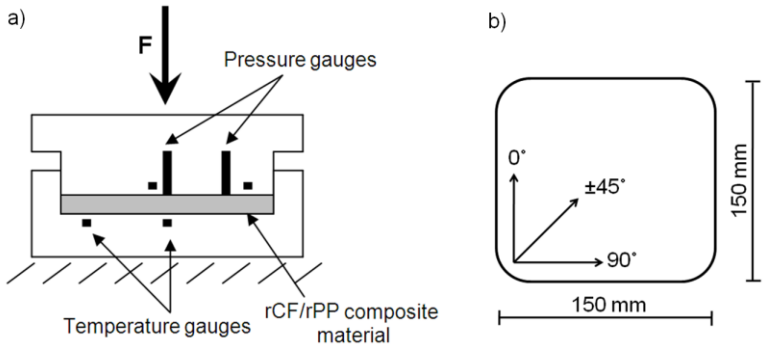

Figure 3. a) Matched die tool used to manufacture the recycled polypropylene films and the composite material, **b)** top view of manufactured plates showing the cutting directions of the samples.

2.5Material characterisation

2.5.1 Thermal degradation of the recycled polypropylene (rPP)

Thermal analysis was performed in a Perkin-Elmer DSC 7 differential scanning calorimeter (DSC) connected to a DEC computer via a TAC 7/DX thermal analysis instrument controller under nitrogen and oxygen atmospheres. In the case of thermal degradation, measurement of the oxidation induction time (OIT) provides a rapid, widely used method for evaluating the thermal stability of the polymeric materials. Approximately 3.5 mg of sample was placed in an aluminium pan, heated from 50 to 200 °C at a heating rate of 40 °C/min in a nitrogen atmosphere. As a constant temperature is obtained, the nitrogen is switched to oxygen and the time from the first exposure to oxygen until the onset of oxidation defines the OIT value. All the OIT measurements were performed at 200 °C.

2.5.2 Single fibre tensile properties and fibre length measurement

For the single fibre tensile test, 50 single fibres were manually separated from the entangled fibre batch. For the mechanical testing, fibre ends (approximately 3 mm of each end) were bonded onto a paper frame with the dimensions of 30x30 mm^2 according to the preparation procedure described in the ASTM D 3379-75 standard. The cross head speed was 1 mm/min corresponding to a strain rate of 10 %/min. The fibre diameter was measured using an Olympus Vanox-T optical microscopy equipped with an Olympus DP11 camera. The elastic modulus was calculated using the secant modulus in the strain region between 0.05 and 0.15 %. Fibre length measurement was performed using analySIS® software and the investigation was performed on approximately 150 pictures obtaining 16300 measured fibres of both processed and unprocessed fibres.

2.5.3 Stiffness and strength of the rCF composite

A series of tensile tests using rectangular shaped specimens with the dimensions of 150x10x1.2 mm were performed to investigate the mechanical properties of the rCF/rPP

composite as well as to confirm the earlier observed in-plane material isotropy [8]. The specimens were cut in four different directions (0°, 90°, ±45°) in the composite plate, see Fig. 3 b). The free length between the grips in the testing machine was 90 mm. The cross head speed was 1 mm/min corresponding to a strain rate of approximately 1 %/min. The elastic modulus was calculated using the secant modulus in the strain region between 0.05 and 0.15 %. This strain level was used expecting that damage and irreversible phenomena would not develop at these relatively low strains.

2.5.4 Inelastic properties of the rCF composite

A series of creep tests were performed to obtain the parameters in the inelastic material model [11, 12, 14, 15]. For the viscoelastic characterisation, single creep tests with duration of 40 min and a recovery of eight times the loading period were performed. In addition, a test program to identify the time dependence and stress dependence of viscoplastic strains (VP-strains) in creep tests (to obtain constants C_{VP}, M and m) described in detail in [11, 12, 14, 15] was employed. To identify the time dependence of VP-strains, a sequence of steps was selected at a fixed level of stress, each consisting of creep and strain recovery. Creep loading steps of durations t_1=3, t_2=10, t_3=20 and t_4=30 min were employed. The employed inelastic material model was used to simulate the response of the rCF/rPP composite in a constant stress rate test. A stress controlled validation test was therefore conducted. A stress rate of 1.0 MPa/min was applied until specimen failure. The duration of the test was approximately 40 minutes. Simulation was performed using a numerical integration to obtain viscoplastic and viscoelastic strains as described in [11, 12, 14, 15].

3 Results and discussion

3.1 Material degradation

The OIT results for the PP scrap material are presented in Figure 4. The figure illustrates the high stability of the material. The OIT is exceptionally long (70 min) even for 35 min of processing. This allows for both film and composite manufacturing without using any additional stabilisers.

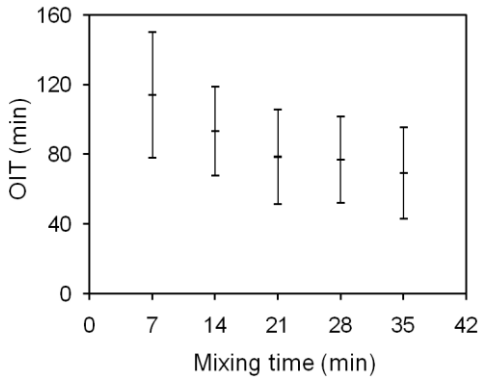

Figure 4. Oxidation induction time results for the PP scrap.

3.2 Single fibre properties fibre length distribution

The optical microscopy study resulted in an average filament diameter 7.04 μm based on three measurements. The average value of the elastic modulus of a single rCF was 93.40 (±26.88) GPa and the average value of the tensile strength was 3119 (±598) MPa. The significant scatter of the measured elastic modulus as well as the tensile strength indicates variations in the mechanical properties of the recycled carbon fibres. A typical loading curve of a single rCF is depicted in Fig. 4 a).

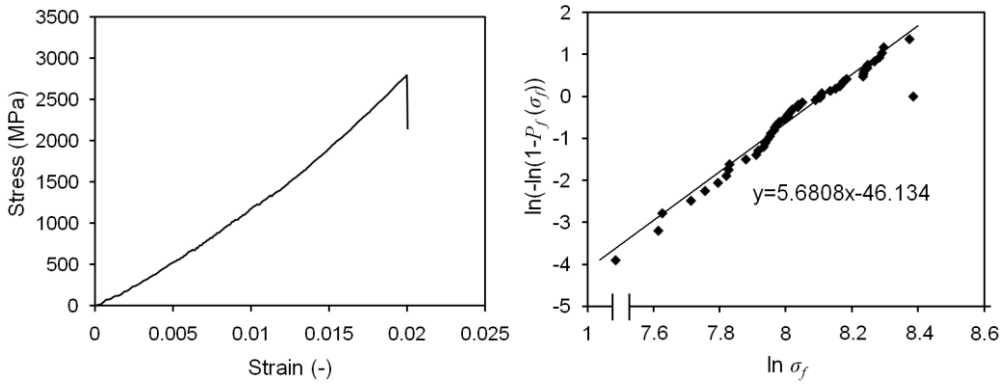

Figure 4. Single fibre properties: **a)** typical stress-strain curve of a single rCF, **b)** strength distribution of the rCF using a 10 mm gauge length .

In order to obtain the strength distribution for single fibres, the experimentally obtained tensile strengths of all fibres are considered. The results are presented in Fig. 4 b). Here, ln(-ln(1-$P_f(\sigma_f)$) is a representation of failure probability [14]. The Weibull shape parameter, β=5.68, is obtained from the slope of the data presented in Fig. 4 b) for ln(-ln(1-$P_f(\sigma_f)$) vs. ln (σ_f). The relationship between ln(-ln(1-$P_f(\sigma_f)$) and ln(σ_f) is close to linear as shown in Fig. 4 b). The scale parameter, σ_0=3365 MPa is obtained from the relation of ln(-ln(1-$P_f(\sigma_f)$) vs. ln(σ_f) [14]. Following development in [14], the fibre strength, σ_f, for the average fibre length in the rCF/rPP composite becomes σ_f=6438 MPa.
During manufacture at high pressures, as in the press forming operation employed here, fibres may break, resulting in impaired mechanical performance of the composite. Therefore, fibre length distribution was measured before (unprocessed) and after (processed) composite manufacturing to investigate the influence of the processing conditions on the fibre length. The results are presented in Figs 5 a) and 5 b). The average fibre length for unprocessed fibres and processed fibres was 0.41 mm and 0.16 mm respectively. Consequently, the average fibre length decreased dramatically during press forming.

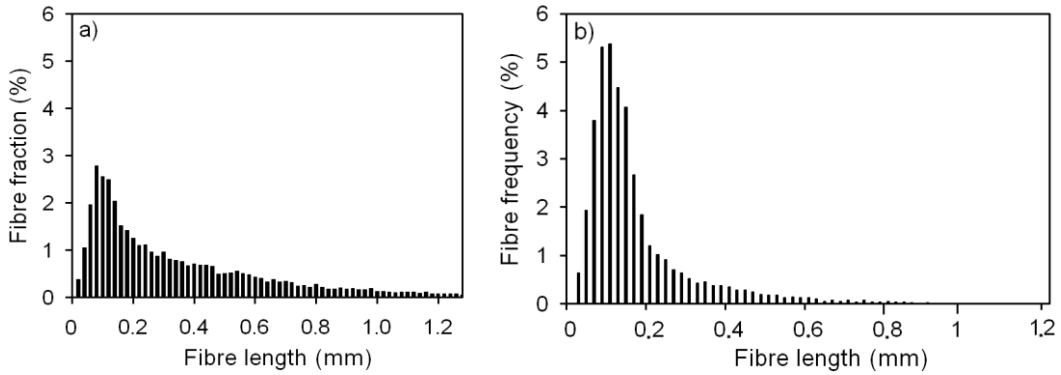

Figure 5. Fibre length distribution: **a)** before processing, **b)** after processing.

3.3 Stiffness and strength of the rCF composite
A series of tensile tests on rectangular specimens (cut in the 0°, 90° and ±45° directions) were performed to investigate the material isotropy. The results indicate that the strength and stiffness of the specimens are independent on the direction of which they have been cut in the composite plate (see Table 1). However, a few samples data at 0°) show significant scatter in strength. This scatter may be related to the material heterogeneities such as local variation in fibre concentration. However, the investigation of the fracture surfaces of those specimens did

not reveal any flaws, typically large pores or edge defects, which could explain the early failure.

Orientation	Number of samples	Stiffness [GPa]	Strength [MPa]
0˚	10	13.68 (±1.70)	77.57 (±21.70)
90˚	10	13.06 (±1.33)	63.08 (±12.35)
+45˚	4	13.53 (±0.46)	77.01 (±5.45)
-45˚	5	13.19 (±0.74)	69.04 (±4.88)

Table 1. Mechanical properties of the improved rCF/rPP composite.

3.3.1 Theoretical results

The stiffness of the rCF/rPP composite is calculated according to the development in ref. [14]. The theoretical stiffness of 11.95 GPa is in fair agreement with the experimentally determined average composite stiffness of 13.36 GPa. The predicted composite tensile strength (see Eq. (8) in ref. [14]) is σ_{uc}=69.22 MPa, assuming τ_y=12 MPa (see the study in detail in [14]). The experimentally obtained average composite tensile strength of σ_{exp}=71 MPa is in good agreement with the theoretical prediction. The experimental result for the previously investigated rCF/rPP composite [10] with v_f=30 % is also included in Fig. 6.

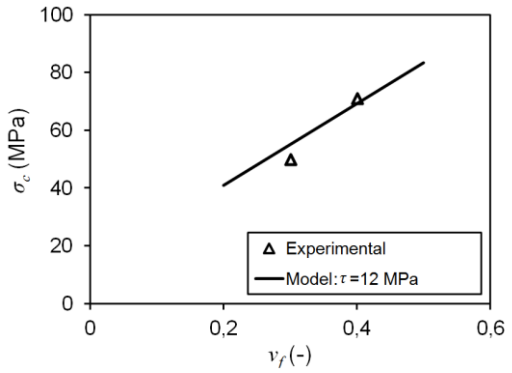

Figure 6. Experimental and modelling results of the strength of the rCF/rPP composite.

3.4 Inelastic material behavior

3.4.1 Viscoplasticity

The experimentally obtained VP-strains at different stress levels are presented in detail in [14]. The exponent *m* is constant for all stress levels, *m*=0.29. The predicted VP-strain development during creep test using the determined parameters [14] is demonstrated in Fig. 7. One can see that a moderate stress increase from 50 to 55 MPa result in a large increase in VP-strains.

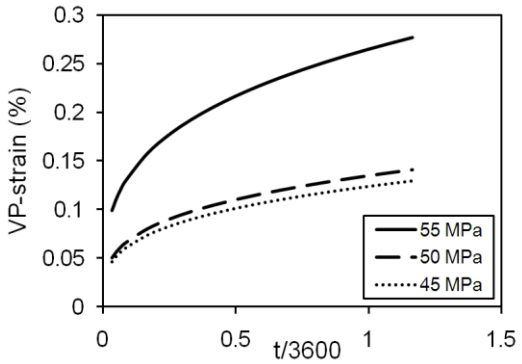

Figure 7. Predicted evolution of VP-strains with time in creep tests.

3.4.2 Viscoelasticity

In order to obtain the pure viscoelastic response, VP-strains were subtracted from the creep data (see ref. [14] for details). Viscoelastic compliances were obtained by dividing the creep strain data by the stress level. A total of 18 creep compliance responses at four different stress levels are presented in Fig. 8 a). The scatter at each stress level is much lower compared to the results found for earlier generations of the rCF/rPP composites [12, 15].

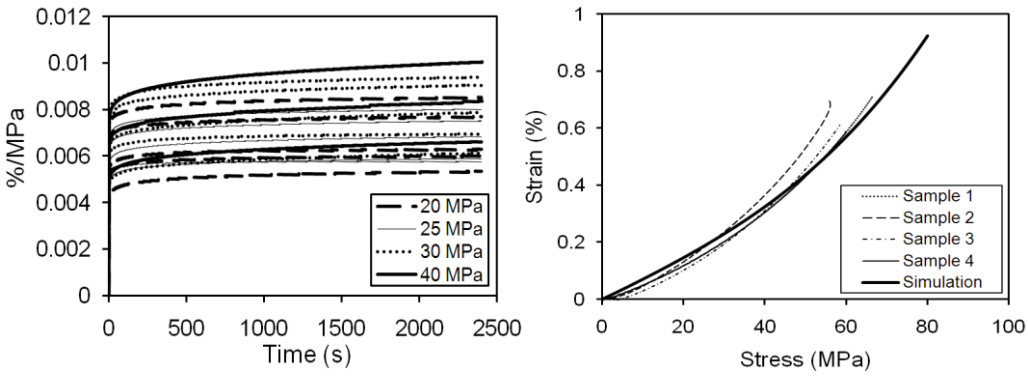

Figure 8. Viscoelastic results: **a)** creep compliance at different stress levels,
b) experimental and predicted constant stress rate loading curves at a stress rate of 1.0 MPa/min.

No systematic increase of creep compliance with increasing stress levels can be observed. Therefore, it is concluded that for the considered stress levels, the composite can be considered as viscoplastic and linear viscoelastic giving $g_1=g_2=a_\sigma=1$ and assuming that ε_0 is proportional to the stress level. The predicted stress-strain response is presented in Fig. 8 b) together with experimental data from constant stress rate tests using four specimens. The agreement is good, even close to the rupture stress.

3 Concluding remarks

In the present study, a new, fully recycled rCF/rPP composite material has been developed and characterised. The composite material was manufactured from recyclates, both matrix and fibres. Polypropylene processing scrap from PURE® was extensively studied in terms of its stability and process ability as a thermoplastic matrix material and the result indicated that the material is thermally stable, allowing for processing of about 70 min without the additional stabilizers. Polypropylene scrap material was then reprocessed into a film by press forming. The recycled carbon fibres were converted into performs using paper making principles. Fibre length distribution measurements before (unprocessed) and after (processed) composite manufacturing were performed to investigate the influence of the processing conditions on the fibre length distribution. The obtained results show a significant reduction in the avarage fibre length after press forming. Microscale models to predict stiffness and strength of the short fibre rCF/rPP composite were employed and validated using experiments. The results were found to be in good agreement with the experimental results. The tests also confirm the previously investigated in-plane material isotropy. An inelastic material model was employed and validated using series of creep and recovery test. In the creep tests, it was found that the time and stress dependence of viscoplastic strains mainly follows a power law behaviour, which makes the determination of the parameters in the viscoplasticity model relatively simple. The viscoelastic response of the composite was found to be linear in the investigated stress range. The material model was validated in constant stress rate tensile tests and the agreement was good, even close to the rupture stress.

References

[1] Suzuki T., Takahashi J. *Prediction of energy intensity of carbon fiber reinforced plastics for mass-produced passenger cars.* Proceeding of "*The Ninth Japan International SAMPE symposium"*, November-December, (2005).

[2] Carberry W. *Airplane recycling efforts benefit Boeing operators*. Boeing AERO Magazine QRT, (2008).

[3] Pimenta S., Pinho S.T. *Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook.* Waste Management, **31**, pp. 378-392, 2011.

[4] Pickering S.J. *Recycling technologies for thermoset composite materials-current status.* Compos Part A–Appl S, **37**, pp. 1206-1215, 2006.

[5] Bassam J.J., Pomykala J.A. Jr, Daniels E.J., Greminger J.L. *A process to recover carbon fibres from polymer-matrix composites in end-of-life vehicles.* JOM–J Min Met Mat S, **56**, pp. 43-47, 2007.

[6] Meyer L.O., Schulte K., Grove-Nielsen E. *CRFP-recycling following a pyrolysis route: process optimization and potentials.* J Compos Mater, **43**, pp. 1121-1132, 2009.

[7] Data sheet CFM-PYR-H-1, Hadeg Recycling GmbH, Germany, (2007).

[8] Szpieg M., Wysocki M., Asp L.E. *Reuse of polymer materials and carbon fibres in novel engineering composite materials.* Plast Rubber Compos: Macromolecular Engineering, **38**, pp. 419-425, 2009.

[9] Technical data sheet, Lankhorst Idutech bv, PURE®, (2007).

[10] Szpieg M., Wysocki M., Asp L.E. *Recycled PP aimed as a composites precursor material.* Plast Rubber Compos: Macromolecular Engineering, **38**, pp. 412-418, 2009.

[11] Szpieg M., Giannadakis K., Varna J. *Time dependent nonlinear behaviour of recycled polypropylene (rPP) in high tensile stress loading.* J Thermoplast Compos, **24(5)**, pp. 625-652, 2011.

[12] Szpieg M., Giannadakis K., Asp L.E. *Viscoelastic and viscoplastic behaviour of a fully recycled carbon fibre reinforced MAPP modified polypropylene composite.* J Compos Mater. http://jcm.sagepub.com/content/early/2011/10/20/0021998311423858. Published online, 2011.

[13] Wong K.H., Pickering S.J., Brooks R. *Recycled carbon fibre reinforced polypropylene composites: effect of coupling agents on mechanical properties.* Composites Innovation 2007 – Improved Sustainability and Environmental Performance, Organised by Net Composites, Barcelona, Spain, 4-5 October, (2007).

[14] Szpieg M., Wysocki M., Asp L.E. Mechanical performance and modelling of a fully recycled MAPP modified CF/PP composite. J Compos Mater. Published online http://jcm.sagepub.com/content/early/2011/10/22/0021998311423860, 2011.

[15] Giannadakis K., Szpieg M., Varna J. *Mechanical performance of recycled carbon fibre/PP.* Exp Mech, **51(5)**, pp. 767–777, 2011.