Processing Strategies for Recycled Carbon Fibre using In-situ Polymerizable Thermoplastics

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1. Abstract

The exponential growth of carbon fibre composite waste has led to increased efforts to develop effective recycling techniques. The degradation of conventional thermoset resins under harsh conditions damages the fibre, reducing the mechanical properties of recycled carbon fibre (rCF)-based composites. This study investigates the use of an in-situ polymerizable thermoplastic matrix for remanufacturing rCF, aiming to facilitate the recycling of second-generation composites and reduce fibre property degradation.

To identify a suitable manufacturing technique for the processing of the in-situ polymerizable thermoplastic, its polymerization kinetics and viscosity development over time and temperature are investigated. Furthermore, the compaction response and permeability of an rCF fibrous preform are determined experimentally. Eventually, a suitable manufacturing technique will be chosen by combining the characterization data using Darcy's Law, and its feasibility will be validated through composite manufacturing.

At elevated temperatures, the thermoplastic exhibits minimal viscosity and a minimum cure time of 30 minutes. The rCF non-woven requires a compaction pressure of 40 bar to achieve a volume fraction of 35%, limiting the choice of manufacturing to high-pressure techniques. Following the results, wet compression moulding is chosen as a suitable process for in-situ polymerizable thermoplastic rCF composite manufacturing.

2. Introduction

Due to the primary use of thermoset matrices, harsh conditions are required to recycle aerospace components at their end of life. In thermal recycling, high temperatures and an oxidizing atmosphere are necessary to recover carbon fibre from the composites. This removes char residuals but additionally leads to the oxidation of the fibre surface itself, reducing the mechanical properties of the recyclate [1]. After the recycling process, rCF are discontinuous and random, requiring an additional process step to manufacture a handleable preform. These preform manufacturing

techniques are inspired by the textile and paper industry. Carding is a process from the textile industry, where a set of sawtooth rollers is used to open and blend fibres into a homogeneous mat. Due to its effectiveness, carding is applied on a small industrial scale, such as from ELG Carbon Fibre Ltd. (now Gen2Carbon), United Kingdom, to manufacture their Carbiso fibre mats. The carded web is stabilized using needle punching, which reorients fibres in the through thickness direction. Existing literature indicates that the maximum achievable fibre volume fraction (V_f) for these fabric types is limited to approximately 40% and that higher volume fractions lead to increased void content and fibre breakage [2].

The damaged fibre, random orientation and limited fibre volume fraction in rCF composites lead to a reduction in mechanical properties and a performance gap of rCF to their virgin carbon fibre (vCF) counterparts. Fibre hybridization is a promising strategy to balance out the mechanical properties of two or more fibre types and presents a potential entry for rCF into the aerospace industry [3]. Wilson et al. [4] investigated the influence of hybridization on the mechanical performance of rCF-vCF hybrid composite using the Carbiso mat to replace 50% of the vCF composite with the rCF composite as the core in a sandwich-type layup. The authors showed that volume fraction and void content followed the RoM. Furthermore, they found that the damping ratio and flexural properties of the hybrid were dominated by the outermost layer, and the values reported were close to the pure vCF. Tensile testing revealed a 40% decrease in strength and modulus of the hybrid, demonstrating that the replaceable amount of vCF depends on the load case and application.

The predominant technique for the remanufacturing of rCF composites with thermoplastic is compression moulding (CM). Multiple studies manufacture hybrid rCF preforms using TP fibres or films, which are consolidated in a heated press [5-7]. Lopes et al. [7] compared these two CM techniques and investigated their influence on physical, mechanical and thermal composite properties. The TP-fibre-based composite showed a higher flexural modulus, which was explained by a better dispersion and fibre impregnation due to the intermingling. Brahma et al. [8] used an in-situ polymerizable nylon for vacuum-assisted resin transfer moulding (RTM) and compared its influence on the mechanical properties at multiple fibre volume fractions to CM with TP-fibres. For the compression moulded samples, the authors observed a strong decrease in mechanical performance by increasing the V_f from 40% to 50%, whereas the RTM samples continuously improved. This was attributed to the lower viscosity of the RTM-TP and the resulting better impregnation of the fibres.

In this work, we aim to reprocess a carded rCF non-woven with an in-situ polymerizable thermoplastic in a suitable process to achieve aerospace-grade physical properties. This will be done by characterizing the polymerization kinetics and viscosity development of the in-situ polymerizable thermoplastic as functions of time, temperature and degree of conversion using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and rheology experiments. The dry rCF fabric will be analyzed in compaction behaviour, and transverse permeability and benchmarked against a vCF twill weave. By combining the results of the characterization experiments, a simple model based on Darcy's Law will be developed to determine infusion times of different liquid moulding processes.

3. Materials and Methodology

3.1. Materials

The in-situ polymerizable thermoplastic used in this study is the Elium 188O from Arkema, France [9]. The Elium material family is based on a reactive methyl methacrylate (MMA) monomer blend mixed with additives, suitable for liquid moulding processes and room temperature curing. Other Elium types and their polymerization kinetics have already been investigated in the literature [10, 11].

Two different carbon fibre fabrics are investigated: the Carbiso SM500 rCF fabric from ELG and a 200 gsm vCF twill weave from Texonic. The Carbiso SM500 is a carded fabric based on a rCF recovered through pyrolysis. The twill weave vCF is based on the 3k HexTow AS4 carbon fibre.

3.2. In-situ polymerizable thermoplastic characterization

Thermogravimetric analysis (TGA) is used to identify the degradation temperature as well as the mass loss of the Elium 188O during degassing and staging. For this, the sample mass is measured during a temperature ramp. The degradation temperature (T_d) is the temperature at which a significant mass loss initiates. Additionally, isothermal TGA tests will be conducted to identify the amount of gas evaporation during degassing and staging. T_d is used as a temperature limit for differential scanning calorimetry (DSC) experiments. In a DSC experiment, the heat flow in and out of a sample is measured over time or temperature. The polymerization conversion rate is proportional to the heat emitted throughout the reaction [12]. Temperature ramps are applied to determine the total heat of reaction and define the state of full conversion. Isothermal DSC scans at RT, at 50 °C, and at 80 °C are conducted to identify the degree of conversion achieved at these temperatures and define a necessary post cure. All tests are carried out three times to ensure the accuracy of the results.

The quality of the composites manufactured through liquid moulding depends on the full penetration and wet out of the fabric reinforcement. To estimate the time and pressure necessary for the Elium 188O to achieve this, the initial viscosity and its evolution over time must be considered. This is determined using isothermal rheology experiments at equal temperature levels compared to the DSC tests. This allows us to formulate a relationship between viscosity and degree of conversion, temperature, and time. An Anton Paar rheometer with a parallel plate setup is used in an oscillating test type. Since a shear-thinning behaviour of the TP resins is expected, a shear-sweep is conducted before the viscosity experiments to define a suitable oscillating frequency and amplitude within the linear visco-elastic region of the TP.

3.3. Preform Characterization

The ratio between compaction pressure and fibre volume fraction is essential for a thorough design of liquid moulding processes. It directly relates to the necessary tool forces and the achievable mechanical performance of the composite. Additionally, the fabric compaction data can be combined with permeability measurements to determine infusion times at process conditions. Thus, both fabrics are analyzed in terms of compaction and permeability.

The compaction experiments are conducted on an MTS Insight electromechanical press equipped with a 5 kN load cell and a flat plate mould using dry fibre preforms and the compaction profile presented by Yong et al. [13]. The profile consists of a compaction phase with defined speed, a dwell phase with a defined time to allow for relaxation and a decompaction phase with the same speed as during compaction. The displacement is measured using a linear variable differential transformer (LVDT). The resin penetration of the fabric in the wet CM occurs through thickness, which is why this study considers only the transverse permeability. Experiments are conducted at 20%, 30% and 40% V_f using a custom test rig at the McGill Structures and Composite Materials laboratory (SCML). In these experiments, silicon oil flows through a cavity which holds the sample. The fabric permeability K can be determined by measuring the pressure loss of the silicon oil over the cavity ΔP, the volume flow of the oil Q, the cavity depth h and area A, and applying Darcy's law:

$$K = Q\frac{\mu\, h}{A\ \Delta P} \tag{1}$$

where μ is the oil viscosity. As the rCF and vCF are co-moulded in a one-shot CM process, both materials are tested in compaction and permeability to investigate the effect of hybridization on these properties.

4. Results and Discussion

The TGA experiments show a degradation temperature of 230 °C for the Arkema Elium 188O thermoplastic, which was taken as input for the following DSC tests. Considering the total heat of reaction and the isothermal DSC experiments, the polymerization rate was plotted as a function of degree of polymerization, as shown in Fig. 1, left. All temperatures show a two-peak conversion, which aligns with findings in the literature [12]. The first peak can be explained by a free radical polymerization driven by the catalyst. With advancing polymerization, the polymer chains start to increase viscosity, which limits the chain movement and leads to a sharp increase in polymerization, visible as the higher second peak. This phenomenon is called the Trommsdorf- or gel effect. With increasing temperature, the reaction rate increases. Additionally, it can be observed that RT processing achieves a degree of conversion of 82%, whereas higher temperatures, such as 80 °C, led to full conversion. Thus, a post cure is necessary for temperatures below 80 °C.

Based on these results, a two-step semi-empirical Arrhenius type autocatalytic model, a phenomenological polymerization model, as shown in Eq. (2), with the conversion rate $\frac{d\alpha}{dt}$, the pre-exponential constants A_1 and A_2, activation energies E_1 and E_2, the reaction orders n_1, n_2, m_1 and m_2 and the degree of conversion α was chosen to describe the reaction. The data was fitted to the model by applying the least squares method in a MATLAB script. The parameter values are shown in Table 1. Based on fitting approaches from the literature, the second pre-exponential factor A_2 was defined as a function of temperature to improve the model fit [14].

$$\frac{d\alpha}{dt} = A_1 \exp\left(\frac{-E_1}{RT}\right)\alpha^{n_1}(1-\alpha)^{m_1} + A_2(T)\exp\left(\frac{-E_2}{RT}\right)\alpha^{n_2}(\alpha_{max}(T)-\alpha)^{m_2} \tag{2}$$

Table 1. Parameter values for the 2-step Arrhenius type autocatalytic model describing the polymerization reaction of the Arkema Elium 188O

A_1	$E_1\left[\frac{J}{mol}\right]$	n_1	m_1	A_2	$E_2\left[\frac{J}{mol}\right]$	n_2	m_2
887.4	37970	0.2614	3.181	4.655-0.0119*T	3887	4.962	1.834

The viscosity was measured with an isothermal experiment at RT as well as in a temperature ramp from RT to 200 °C, just below the degradation temperature. Fig. 1, right, shows the development of viscosity at RT over time. An initial viscosity of 250 Pa*s can be observed. After 3000 seconds, the viscosity exceeds 1000 Pa*s, followed by a sharp increase similar to the viscosity behaviour at gelation of thermoset polymers. Fig. 1, right, furthermore shows the degree of conversion over time. It can be observed that this increase in viscosity aligns well with the second peak in degree of conversion caused by the Trommsdorf-effect. The temperature ramp shows an initial viscosity decrease to 100 Pa*s around 50 °C, which can facilitate infusion. Still, the increased temperature accelerates polymerization, which reduces pot life and working time.

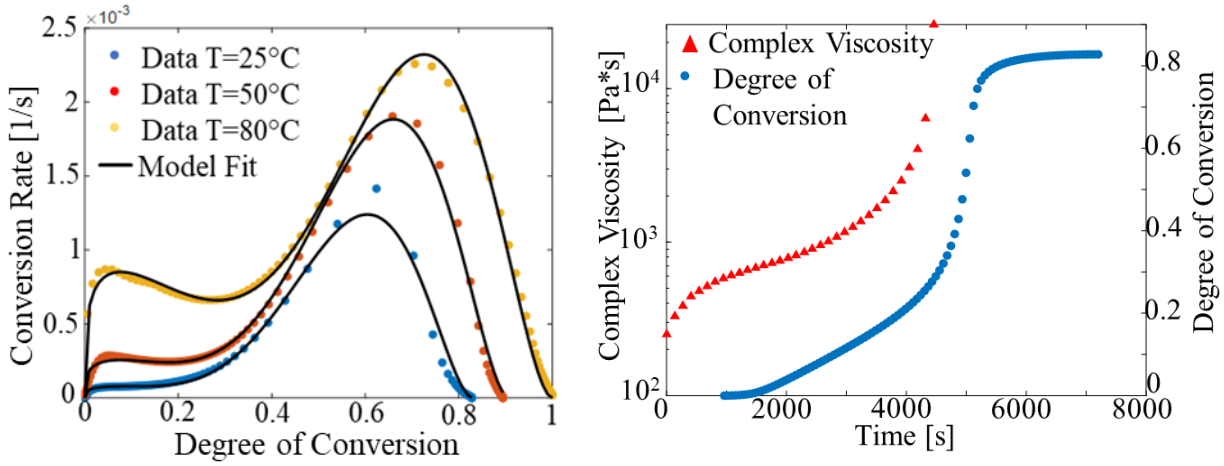

Figure 1. Arkema Elium 188O polymerization kinetics (left), viscosity development (right) Arkema

The results of the permeability experiments are shown in Fig. 2, left. The Carbiso SM500 shows a permeability in the range of 1.1E-12 to 2.4E-12 m^2 from 20% to 40% fibre volume fraction. With increasing fibre volume fraction, the permeability decreases, which can be explained by the reduction in porosity. It can be observed that the scatter of the results is much higher in lower fibre volume fractions compared to higher ones. This aligns with findings from Yong et al. [13]. The authors argued that this was due to the decreasing influence of nesting at an increasing number of plies to reach an increasing fibre volume fraction at constant cavity height. Since the number of plies was kept constant in this experiment, this argument would be invalid. However, it can be

hypothesized that the increasing pressure at higher V_f leads to a uniform nesting behaviour across the different samples, which would decrease the scatter in results.

From the force-displacement data recorded during the compaction experiments, a relationship between pressure and fibre volume fraction can be established using specimen area, weight and density. This relationship is shown in Fig. 2, right. It can be observed that low pressures, as occurring in processes such as vacuum infusion, reach a maximum volume fraction of 14%. To achieve competitive volume fractions, higher pressures of above 20 bar are necessary, which are well within the range of compression moulding processes.

To contextualize the characteristics of the rCF fabric, its transverse permeability and compaction behaviour were benchmarked to the corresponding values of a vCF twill weave. The permeability of a twill weave at various fibre volume fractions, sourced from the literature [15], is shown in Fig. 2, left. It can be observed that the permeability of the twill weave is within the same order of magnitude as the rCF, albeit at higher volume fractions. This occurs despite the fundamentally different fibre architectures. While a virgin tow possesses a highly dense fibre packing, restricting possible resin flow through the tow itself, the weave pattern allows for transverse resin flow through macroscopic gaps in the fabric. At low V_f, the random fibre orientation of the rCF fabric facilitates transverse flow. A higher V_f, however, leads to the previously discussed reduction in porosity, limiting the resin flow and promoting the formation of voids. Compaction experiments on a 200 gsm twill weave from Texonic were performed and the results are shown in Fig. 2, right. Due to the fibre orientation in the vCF fabric, a V_f of 50% and above can be achieved without significant application of pressure. Conversely, this nested structure leads to a significantly steeper increase in pressure compared to the rCF, when the V_f is further enhanced.

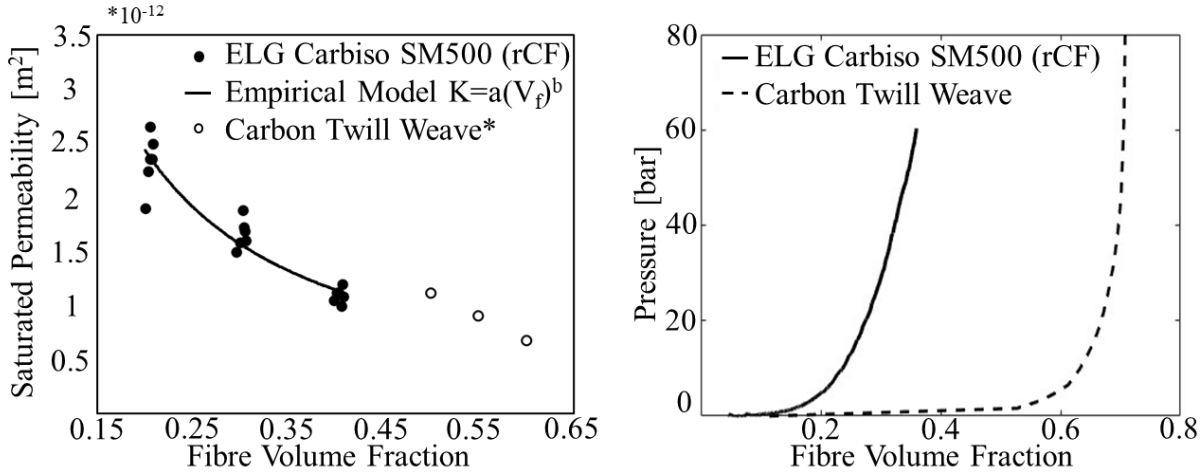

*Figure 2. Comparison of the fabric permeability (left) and the compaction response (right) of the Carbiso SM500 rCF and a Texonic carbon twill weave. *Transverse permeability data taken from Yoo et al. [15]*

The characterization results of the Elium thermoplastic and ELG rCF fabric can be used for a simple comparison of vacuum infusion and wet compression moulding for the manufacturing of a 2ply rCF Carbiso SM500 composite, as shown in Table 2. Vacuum infusion is limited to a maximum pressure of 1 bar, whereas compression moulding can apply pressures of up to 100 bar,

leading to a higher V_f but lower permeability. By increasing the temperature of the mould, the viscosity can be decreased, further facilitating infusion in CM. Using Darcy's Law, the infusion time of both processes can be calculated. This includes multiple simplifications on the resin and the fabric side, which is why the results should be taken only as guidance. Resin flow in a wet compression moulding process is highly complex, and a complete modelling would exceed the scope of this study. For both processes, the fabric is assumed to be a homogeneous and isotropic porous medium with a constant volume fraction throughout the infusion. The resin flow is assumed to be laminar, steady-state, fully saturated, and with constant viscosity. The pressure on the resin is assumed to be equal to the pressure on the fabric and constant throughout the infusion. For the vacuum infusion process, the infusion time can be calculated to approximately 6 hours, exceeding a possible process window of the thermoplastic when compared to the viscosity development in Fig. 1. The infusion time of the wet compression moulding process can be calculated to 115 seconds, being well within a suitable viscosity window while achieving higher V_f.

Table 2. Comparison of vacuum infusion and wet compression moulding for the manufacturing of a 2ply rCF composite based on Darcy's Law

Process	Temperature [°C]	Viscosity [Pa*s]	Pressure [bar]	Permeability [E-12 m²]	Part thickness [mm]	V_f	Infusion Time [s]
Vacuum Infusion	RT	500	1	3.25	12	14	21600
Wet Compression Moulding	50	200	40	1.1	5	35	115

This process setup was validated in a compression moulding experiment, and a flat plate was manufactured as shown in Fig. 3. A 100 mm-by-100 mm mould, typically utilized for conventional thermoplastics, was employed. A 2-ply layup was used, with the Elium thermoplastic resin applied between the rCF layers. The resulting composite exhibited no visible dry spots or voids on the top and bottom surfaces, indicating an effective impregnation of the rCF fabric. The dry spots in the top left and bottom corners were attributed to resin flash escaping through the mould's edges during the compression cycle. A thickness of the panel of 2.15 mm and a fibre weight fraction of 48.8% was measured, indicating a V_f of 35%.

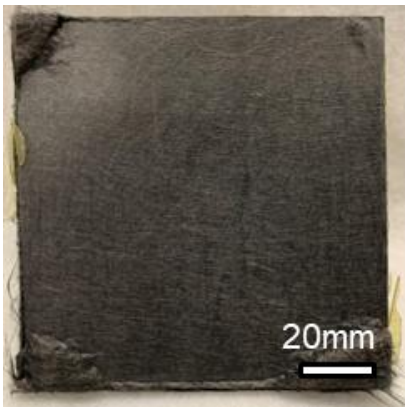

Figure 3. ELG Carbiso rCF thermoplastic composite manufactured through wet compression moulding

5. Conclusion

This study investigated the feasibility of liquid moulding processes for the remanufacturing of recycled carbon fibre preforms with an in-situ polymerizable thermoplastic. By combining polymerization kinetics and viscosity data of the thermoplastic with the permeability and compaction response of the rCF fabric, a theoretical infusion time for different processing scenarios was calculated based on Darcy's Law. The analysis identified that compression moulding promises the best results in terms of processing time and composite properties, due to the high pressures available. With a compaction pressure of 40 bar, a V_f of 35% in a composite manufacturing validation experiment was achieved.

This study provides the foundation for future research on fibre hybridization of rCF preforms with vCF fabrics. The results will be used to optimize a wet compression moulding process for rCF thermoplastic composite manufacturing. rCF, vCF and hybrid composites will be manufactured and compared in quality and mechanical performance to quantify the hybrid effect of vCF and rCF hybridization.

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7. References

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