2021-11-18

Optimisation of tool design and RIFT process

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Project acronym: SeaBioComp
Project title: Development and demonstrators of durable biobased composites for a marine environment.
Project Number 2S06-006

D 1.4.3
Optimisation of tool design and RIFT process

Due delivery date: 30/06/21
Actual first draft delivery date: 21/11/21

Organization name of lead participant for this deliverable:
University ofPlymouth

Dissemination level		
PU	Public	
CO	Confidential , only for members of the consortium	X

SeaBioComp is an Interreg 2 Seas 2014-2020 project covering England, France, the Netherlands and Belgium.

Deliverable number:	D 1.4.3
Deliverable responsible:	University of Plymouth
Work package:	WP1

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Document Revision History			
Version	Date	Modifications Introduced	
		Modification Reason	Modified by
V.1	31/10/21	First draft	YQ and JS - UoPlymouth
V.2	18/11/21	Final version w/ modifications by WP1 members	YQ and JS - UoPlymouth
V.3	DD/MM/YY		
V.4	DD/MM/YY		
V.5	DD/MM/YY		
V.6	DD/MM/YY		

Abstract

In Report D 1.1.3, two monomers: methyl methacrylate (Elium®) and L-lactide were selected for in-situ polymerisation infusion manufacturing of natural-fibre reinforced thermoplastic-matrix marine composites, by considering the processing temperature and viscosity, polymer mechanical properties, recyclability, etc.

In this report, the composite production procedures are reported and the tooling and processing parameters are optimised towards better mechanical properties.

The Elium® was straightforward to use (room temperature infusion) with similar processing to conventional thermoset epoxy and unsaturated polyester resins, and its composite showed relatively high mechanical performance, especially following post-curing.

The processing of L-lactide is far more complicated as there is no infusion processing standard given that the material is not marketed as an infusion monomer by the supplier. The effects of the processing parameters and vacuum level have been investigated, but while composite plates have been produced, the measured mechanical performance of PLA matrix composite fall short of the estimated values from rules-of-mixture predictions.

Keywords: acrylic, lactide, monomer infusion, bio-based matrix, process parameters, tooling

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1 Introduction

Following the monomer selection and heated mould tool development studies in Reports D 1.1.3 and D 1.4.1, the next research phase addresses composite sample production. The methyl methacrylate (MMA) Elium® has been used by many researchers as the monomer for the production of polymethyl methacrylate (PMMA) matrix composites. Bhudolia et al. [1] studied Elium® reinforced carbon fibre composites and reported a 72% increase Mode I fracture toughness relative to carbon fibre-epoxy composites. Obande et al. [2] compared the mechanical and thermomechanical performance between Elium® and epoxy glass fibre composites and found that acrylic composites showed equivalent modulus, 33% higher tensile strength and 19% increase in fracture toughness against their counterparts with epoxy resin. Moreover, some researchers have successfully produced natural fibre-Elium® composites and tested their mechanical properties [3, 4]. The study of the in-situ polymerisation (ISP) infusion manufacture of polylactic acid (PLA) matrix composite using L-lactide monomer has just started. In 2019, Louisy et al. [5] firstly produced PLA-glass composite via ISP vacuum infusion of the L-lactide monomer, and optical microscopy analysis of the samples showed a good impregnation of the reinforcement by the matrix. However, no mechanical properties for the PLA-glass composites were reported.

In this report, both PMMA and PLA matrix composites were produced via ISP vacuum infusion and their flexural properties and interlaminar shear strength were investigated. The processing parameters were also discussed and optimised according to the mechanical properties.

2 Materials and sample production and testing

According to the discussion in the monomer selection Report D.1.1.3, MMA (Elium®) and L-lactide were selected for producing natural fibre reinforced thermoplastic composites via monomer infusion under flexible tooling (MIFT). The MMA resin used in this work is Elium® 188 XO (provided by Arkema, France) catalysed with benzoyl peroxide (formulated with 25% H_2O). The L-lactide (purchased from Total Corbion, Netherlands) was catalysed with Tin(II) 2-ethylhexanoate (Sn(Oct)2; purity: 92.5–100.0%). Both catalysts were supplied by Sigma-Aldrich, Germany. The natural fibre reinforcement was a 2 x 2 twill weave flax fabric with areal weight of 200 g/m^2 (procured from Easy Composites, UK). The glass reinforcement used was a 300 g/m^2 plain weave fabric.

To produce a composite plate with the thickness of 3 mm, a mould was firstly prepared according to the layout shown in Figure 1 below. For flax composite production, in order to reduce the moisture content, the flax fabric was degassed under the vacuum for 24 h before the infusion.

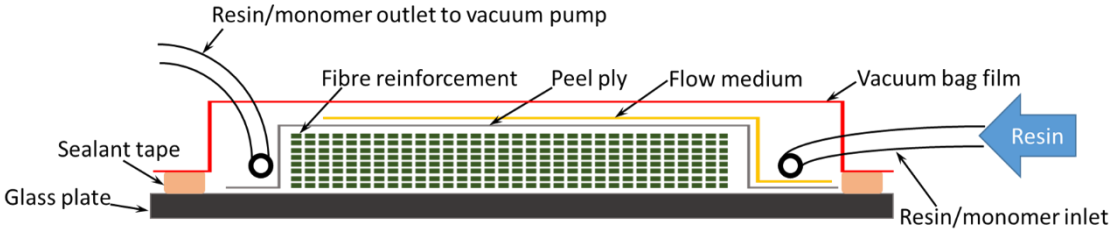

Figure 1 Schematic of the RIFT, redrawn from [6].

The production of Elium® composites via ISP followed the standard RIFT method for thermoset resin at ambient temperature. The benzoyl peroxide catalyst was added into Elium® resin at 2% weight ratio and then fully mixed manually. For improved mechanical properties, following the curing of resin, the mould with the composite plate was post-cured in an oven at 80 °C for 1 h (recommended by the Elium® 188 XO technical data sheet).

Report D 1.4.1.1 studied the influence of processing temperature and duration, monomer/catalyst, cooling method on the mechanical properties of 100% pure PLA matrix samples and the optimised processing parameters were found to be 150°C for 2 hours with the monomer/catalyst ratio (M/C) of 500, followed by cooling at room temperature. Therefore, the parameters above were applied in this study for the production of PLA matrix composite from L-lactide. As the processing of L-lactide monomer requires elevated temperature, heated mould tool shown in Figure 2 has been utilised, detailed information can be found in Report D 1.4.1.2. The L-lactide powder was first melted at 150°C using a heating loop. When the monomer was fully melted, the catalyst (Sn(Oct)2) was added, then the mixture was stirred for 1 min. In the meantime, following the degassing of the flax fabrics, the whole mould

under vacuum was pre-heated, also at 150 °C. Given the low initial viscosity of the L-lactide monomer, the infusion was started ~10 min after adding the catalyst in order to increase the viscosity. After the pre-designed 2-h processing duration, the mould was taken out from the heating blankets and the composite was cooled in the ambient temperature.

All the flax reinforced composites were cut by laser cutter, while glass fabric composites were cut by diamond cutter or water jet. The sample geometry for three-point flexural testing is 80 x 10 x 3 mm^3, with the test span at 48 mm and test speed at 1.28 mm/min according to ASTM D790 standard [7]. For interlaminar shear strength (ILSS) testing samples, the geometry is 30 x 15 x 3 mm^3 with the test span at 14 mm and the test speed at 1 mm/min according to ISO 14130 and 14125 standards [8]. The mechanical tests were performed on an INSTRON universal testing machine.

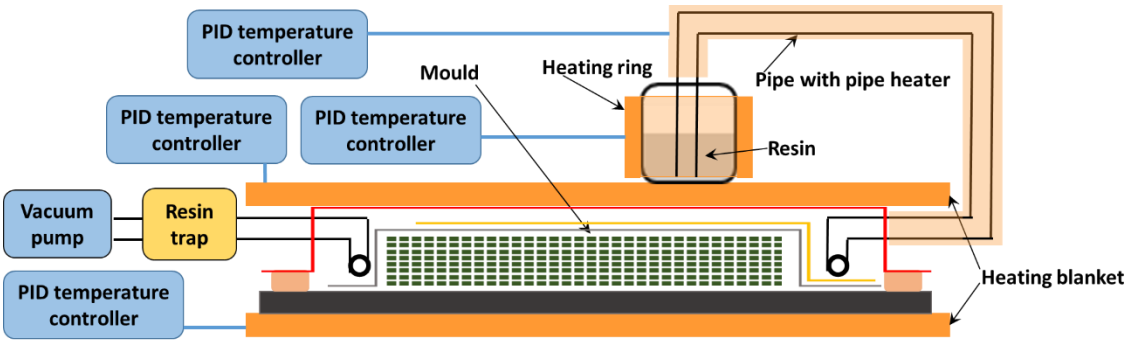

Figure 2 Schematic of the heating of the mould.

3 Rules-of-mixture

To evaluate if the produced composite possesses the expected mechanical properties, rule-of-mixture equations [9, 10] were utilised to predict the theoretical flexural strength σ_c and modulus E_c of the composite:

$$E_c = \eta_l \eta_o V_f E_f + (1 - V_f) E_m \quad \textbf{(1)}$$

$$\sigma_c = \eta_l \eta_o V_f \sigma_f + (1 - V_f) \sigma_{m*} \quad \textbf{(2)}$$

Here, V_f is the fibre volume fraction; σ_f and σ_{m*} represent the strength of the fibre and the stress in the matrix at the failure strain of the fibre respectively; E_f and E_m are the modulus of the fibre and matrix; η_l is the fibre length distribution factor and η_o is the fibre orientation distribution factor. The V_f and σ_{m*} were estimated by:

$$V_f = \frac{nA_F}{\rho_f t} \quad \textbf{(3)}$$

$$\sigma_{m*} = \sigma_m \frac{\varepsilon_f}{\varepsilon_m} \quad (4)$$

where n is the number of fabric layers, A_F and ρ_f represent the areal weight of the fabric and density of the fibre respectively, t is the thickness of the laminate, σ_m is the strength of the matrix, ε_f and ε_m represent the strain to failure value for fibre and matrix respectively.

The properties of the flax fabric and Elium® matrix can be found on the suppliers' datasheet (Ref. [11] and Elium® 188 XO technical data sheet respectively). For glass fabric, strength (σ_m), modulus (E_m) and strain to failure (ε_m) applied in the equations were 3000 MPa, 70 GPa and 2.5% respectively [11]. According to Ref. [12], the σ_m, E_m and ε_m of the PLLA all vary widely in the range of 15.5-150 MPa, 2.7-4.14 GPa and 3-10%. Eawwiboonthanakit et al [13] tested the tensile properties of 100% pure PLLA and found σ_m, E_m and ε_m were 56.6 MPa, 2.59 GPa and 3.38% respectively. The supplier of the L-lactide monomer, Total Corbion, also provides multiple grades of PLA resin, whose E values are 3.5 GPa, σ values are between 40 MPa and 50 MPa and ε_m is less than 5 % [2]. Considering the references above, 50 MPa, 3.5 GPa and 4% were selected for PLA in the estimation of the performance of PLA matrix composites in this report. The flax and glass reinforcements utilised were continuous twill and plain

weave fabrics respectively, in consequence, η_1 equalled to 1 and η_0 was estimated to be ~0.48 for both of them. The parameters employed for Equations (1) and (2) as well as the prediction results are summarised in Table 1.

4 PMMA matrix composites

The influence of post-curing was studied using Elium®-glass composites. Three composite plates EG1 (no post-cured), EG2 (post-cured), EG3 (post-cured) were made. Two and three samples from each composite plate were used for the flexural and ILSS tests respectively, the testing results are shown in Tables 2 and 3.

Little or no difference in flexural modulus between post-cured and no post-cured samples is found; while for the flexural strength, post-curing seems to result in an improvement. It can be observed that the experimental strength values are comparable to the predicted value 760.5 MPa (ranging from 73% to 87%). Unexpectedly, the predicted modulus value is slightly lower than experimental results. This may result from the underestimated V_f value in Table 1.

In ILSS tests, it should be noted that composite samples did not show the acceptable shear modes of failure [8]. However, the relatively consistent values may still indicate a good bonding between fibre and matrix within Elium®-glass composites. In addition, it can be observed that the post-cured composites show slightly higher ILSS than the counterparts without post-curing.

Following the study of Elium®-glass composites, Elium®-flax composites were also produced with post-curing, five and four samples were cut for the flexural and ILSS tests respectively. As shown in Table 4 below, Elium®-flax composites show comparable strength to the prediction value, but the modulus was 47% lower, which may be due to the poor fibre-matrix bonding, as the flax fabrics were not pre-treated to increase fibre-matrix adhesion. Compared with Elium®-glass, the ILSS of Elium®-flax composites decreased by 60% which may also suggest relatively poor fibre/matrix bonding.

5 PLA matrix composites

According to the mechanical properties of 100 % pure PLA samples, 150 °C for 2 hours with the M/C of 500, followed by cooling at room temperature should be the optimised processing parameters for PLA-flax composites production. However, the resulting composites showed poor mechanical properties, therefore another two processing parameters at 130°C and 170°C (both cooled at room temperature) were also studied, and the results are shown in Table 5. Unexpectedly, the composites produced at 170°C demonstrate the best mechanical performance. However, their overall properties are still not satisfying, especially the ILSS.
It is speculated here the poor properties could be attributed to four causes:

(i) Fibre-matrix adhesion is poor.

(ii) The fibre swelling due to the interaction between monomer/oligomer with the reinforcement, which leads to the inconsistence in permeability [14].

(iii) The properties of the PLA matrix from the *in situ* polymerisation of L-lactide are overestimated.

(iv) The boiling temperature of the L-lactide under vacuum is lower than the processing temperature 170°C [15]. Although the polymerisation already starts before infusing the resin into the vacuum mould, it may still lead to the low permeation and more voids within the composite.

According to Cause (iv) above, we assume that the vacuum level may need to be reduced in order for better composite properties. As the glass reinforced PLA composite is easier to manufacture (produced at 150°C, 2h, M/C=500), it was used to study the influence of vacuum level and the result can be seen in Table 6. Firstly, water jet cut method is likely to induce less initial damage to the composites and therefore provide better flexural properties. Secondly, it can be seen that PLA-glass samples produced under ¾ vacuum shows the best flexural properties but no increase is found for ILSS. More importantly, all samples in Table 6 demonstrate extremely poor flexural strength and ILSS, which would significantly limit their practical engineering applications. Further study of the whole PLA composite processing procedure (including the vacuum effect) towards better mechanical performance is still on going.

6 Tooling for demonstrator components

It is proposed that a 5G telecommunications dome, which fits within a 1 metre edge cube, should be the demonstrator component/functional unit for the Life Cycle Assessment (LCA) of in situ polymerisation (ISP) monomer infusion under flexible tooling (MIFT). The LCA will compare glass and natural fibre reinforcements and synthetic (unsaturated polyester and/or epoxy) thermoset resins and acrylic (Elium®) and lactide monomer-infused thermoplastic matrix composites. The analysis will use a common mould tool for all components during data acquisition to inform the LCA.

The system requirements for lactide infusion are the critical case given the higher temperature processes required to produce the bio-based matrix composites by ISP MIFT. Operating at the highest temperatures investigated for lactide composite production may require expensive aluminium tooling (and not be affordable with the current project budgets). High temperature epoxy resin mould tools would appear to be a sensible compromise if process temperatures are kept low. Higher temperatures will inevitably require higher energy inputs and contribute to greater global warming potential, which is contrary to the sustainability ethic of the SeaBioComp project.

7 Summary

The ISP vacuum infusion production of PMMA matrix composite using Elium® monomer was straightforward and the composite showed relatively high mechanical properties, especially following post-curing. However, PLA matrix composite was relatively complicated to manufacture and their properties (ILSS in particular) were not satisfying even at optimised processing parameters including vacuum level. Further studies for mechanical improvement is required for the practical engineering application of PLA composites produced via ISP infusion.

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Table 1 Parameters used in rule-of-mixture equations and the predicted strength and modulus for composites.

Composite	V_f	σ_f	σ_{m*}	E_f	E_m	η_l	η_o	σ_c	E_c
Elium®-flax	31%	500 MPa	65 MPa	50 GPa	2.91 GPa	1	0.48	119.3 MPa	9.45 GPa
PLA-flax	31%	500 MPa	25 MPa	50 GPa	3.50 GPa	1	0.48	91.7 MPa	9.86 GPa
Elium®-glass	50%	3000 MPa	81 MPa	70 GPa	2.91 GPa	1	0.48	760.5 MPa	18.25 GPa
PLA-glass	50%	3000 MPa	31 MPa	70 GPa	3.50 GPa	1	0.48	735.5 MPa	18.55 GPa

Table 2 Flexural properties for Elium®-glass composites.

	Sample	σ_c			E_c		
		Experimental (MPa)	Prediction (MPa)	E/P* (%)	Experimental (GPa)	Prediction (GPa)	E/P* (%)
Without post-curing	EG1[1]	593.1	760.5	73.3	19.13	18.25	114.2
	EG1[2]	521.3			22.57		
Post cured	EG2[1]	584.3	760.5	76.5	19.82	18.25	109.3
	EG2[2]	579.8			20.08		
Post cured	EG3[1]	652.4	760.5	86.8	19.17	18.25	108.2
	EG3[2]	667.1			20.33		

*E/P represents the ratio between experimental value and prediction.

Table 3 ILSS results for Elium®-glass composites.

	Sample	ILSS (MPa)	Mean ± SD (MPa)
Without post curing	EG1[1]	37.88	37.29±1.47 (3.9%)
	EG1[2]	38.37	
	EG1[3]	35.62	
Post cured	EG2[1]	40.53	41.91±1.25 (3.0%)
	EG2[2]	42.96	
	EG2[3]	42.25	
Post cured	EG3[1]	41.05	40.16±0.81 (2.0%)
	EG3[2]	39.46	
	EG3[3]	39.98	

Table 4 Flexural properties and ILSS for Elium®-flax composites.

σ_c			E_c			ILSS
Experimental Mean±SD (MPa)	Prediction (MPa)	E/P* (%)	Experimental Mean±SD (GPa)	Prediction (GPa)	E/P* (%)	Experimental Mean±SD (MPa)
123.73±4.96	119.3	103.7	4.98±0.42	9.45	52.7	16.60±0.71

*E/P represents the ratio between experimental value and prediction.

Table 5 Flexural properties and ILSS for PLA-flax composites at different processing parameters.

Processing parameters	σ_c			E_c			ILSS
	Experimental Mean±SD (MPa)	Prediction (MPa)	E/P* (%)	Experimental Mean±SD (GPa)	Prediction (GPa)	E/P* (%)	Experimental Mean±SD (MPa)
130 °C, 3h, M/C=200	48.86±2.72	91.7	53.3	6.38±0.61	9.86	64.7	3.82±0.28
150 °C, 2h, M/C=500	47.64±1.31	91.7	51.9	6.24±0.33	9.86	63.3	4.20±0.16
170 °C, 3h, M/C=500	53.37±3.06	91.7	58.2	7.24±0.51	9.86	73.4	4.59±0.54

*E/P represents the ratio between experimental value and prediction.

Table 6 Flexural properties and ILSS for PLA-glass composites at different vacuum levels and sample cutting methods.

Vacuum level (in the vacuum bag)	Cut method	σ_c			E_c			ILSS
		Experimental Mean±SD (MPa)	Prediction (MPa)	E/P* (%)	Experimental Mean±SD (GPa)	Prediction (GPa)	E/P* (%)	Experimental Mean±SD (GPa)
Full vacuum	Diamond cutter	79.81±8.39	735.5	10.9	8.22±0.68	18.55	44.3	4.39±0.41
¾ vacuum	Water jet	101.55±4.88	735.5	13.8	14.48±1.27	18.55	78.1	3.76±0.17
½ vacuum	Water jet	90.78±1.95	735.5	12.3	12.96±0.86	18.55	69.9	3.58±0.26
½ vacuum	Diamond cutter	89.35±3.35	735.5	12.1	9.59±1.43	18.55	51.7	3.64±0.23
¼ vacuum	Water jet	90.87±6.08	735.5	12.4	13.88±1.06	18.55	74.8	3.80±0.28

*E/P represents the ratio between experimental value and prediction.