

2020-11-30

Initial production of test samples, and optimisation of process parameters for optimal composites

Qin, Y

<https://pearl.plymouth.ac.uk/handle/10026.1/20842>

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

Project acronym: SeaBioComp

Project title: *Development and demonstrators of durable biobased composites for a marine environment.*

Project Number 2S06-006

D. 1.4.1.1

Initial production of test samples, and optimisation of process parameters for optimal composites

Due delivery date: 30/11/20

Actual first draft delivery date: 30/11/20

Organization name of lead participant for this deliverable:

University of Plymouth

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. The programme is part funded by the European Regional Development Fund.

Deliverable number:	D 1.4.1.1
Deliverable responsible:	University of Plymouth
Work package:	WP1

Author(s) – in alphabetical order (principal authors in bold)		
Name	Organisation	E-mail
Cullen, Richard	University of Plymouth	R.Cullen@plymouth.ac.uk
Graham-Jones, Jasper	University of Plymouth	jasper.graham-jones@plymouth.ac.uk
Meng, Maozhou	University of Plymouth	maozhou.meng@plymouth.ac.uk
Pemberton, Richard	University of Plymouth	richard.pemberton@plymouth.ac.uk
Qin, Yang	University of Plymouth	yang.qin@plymouth.ac.uk
Summerscales, John	University of Plymouth	J.Summerscales@plymouth.ac.uk

Document Revision History			
Version	Date	Modifications Introduced	
		Modification Reason	Modified by
V.1	30/11/20	First draft	YQ and JS - UoPlymouth
V.2	--/--/20	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

Due to the greater awareness of the environmental issues, composite researchers are increasingly interested in using “greener” materials to substitute for synthetic fibre reinforcements and petrochemical polymer matrices. Therefore, in order to minimise the ecological impact, the SeaBioComp project aims to produce natural fibre bio-based thermoplastic composites for marine applications. The University of Plymouth is developing monomer infusion under flexible tooling (MIFT) for the manufacture of bio-based composites. In Deliverable 1.1.3, the material selection identified methylmethacrylate (MMA) and lactic acid/lactide for PLA as potential matrix systems for use in the marine environment. MMA is not yet bio-based, but expected to become available as such around the end of the project. It could sensibly “drop in” as a substitute for unsaturated polyester or epoxy resins processable at ambient temperatures. The manufacture of PLA requires that the monomer feed vessel, the associated pipework and the mould tool are all heated to temperatures between 120-180°C. Deliverable D1.4.1 “Report on the development of heated mould tools, initial production of test samples, and optimisation of process parameters for optimal composites” has been split to two parts:

- D1.4.1.1 Initial production of test samples, and optimisation of process parameters for optimal composites
- D1.4.1.2 The development of heated mould tools

This report considers the process optimisation suggesting that temperatures for all stages of the PLA process will be 150°C. Process development will continue using a preliminary heating system from Jiangyin Jin Yu Electric Heating Company Limited for flat plate manufacture. In the absence of a decision on the demonstrator component some aspects of the mould tool design remain open and will be addressed in Deliverable D1.4.2 Creation of a 3D mould tool with sensible temperature uniformity. Demonstrators under consideration include scaled-down marine renewable energy turbine blades or components of floating offshore wind turbines.

Keywords: Natural fibres; Thermoplastic; Monomer, Infusion; Heated Mould Tool.

Table of Contents

Table of Contents

List of abbreviations	6
1 Initial composite sample production and testing.....	7
1.1 MATERIALS, SAMPLE PRODUCTION AND TESTING	7
1.2 RULE-OF-MIXTURE PREDICTION.....	10
1.3 RESULTS AND DISCUSSION	11
2 Optimisation of manufacture process for PLA-flax composite.....	12
2.1 SAMPLE PRODUCTION AND TESTING	12
2.2 RESULTS AND DISCUSSION	12
Summary	15
References	16

Table of Figures

Figure 1.	Schematic of the RIFT, redrawn from [2].	<u>76</u>
Figure 2	Configuration for the production of PLA-flax composites via RIFT in the oven.	<u>98</u>
Figure 3	PLA-flax and Elium [®] -flax composites for flexural testing.	<u>109</u>
Figure 4	PLA only samples (after test) from Batches P-31 (cooled in the room temperature) and P-32 (cooled in the switched-off oven).....	<u>1413</u>

List of Tables

Table 1	Monomer to catalyst ratio of each cup.	87
Table 2	Status change of the samples during the reheating process. It should be noted that all results were just an indication by hand check due to limited experimental conditions.	87
Table 3	Parameters used in rule-of-mixture equations.	11+0
Table 4	Flexural properties for PLA-flax and Elium [®] -flax composites.	12+0
Table 5	Flexural properties for PLA-only samples.	13+2
Table 6	Comparison of flexural properties between PF-170 and PF-150.	15+4

List of abbreviations

ASTM	American Society for Testing and Materials
EF-G	Elium/flax composite ~ good
EF-P	Elium/flax composite ~ poor
MIFT	Monomer infusion under flexible tooling
MMA	Methyl methacrylate
PF-150	PLA/flax composite produced at 170 °C
PF-170	PLA/flax composite produced at 150 °C
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)

1 Initial composite sample production and testing

1.1 MATERIALS, SAMPLE PRODUCTION AND TESTING

According to the discussion in the monomer selection report D.1.1.3 (now extended and published in *Polymers* [1]), MMA (Elium) and L-lactide were selected as the candidate resins for producing natural fibre reinforced thermoplastic composites via monomer infusion under flexible tooling (MIFT). MMA and L-lactide were both employed for composite production here. The MMA resin used in this work is Elium[®] 188 XO (provided by Arkema, France) catalysed with benzoyl peroxide (formulated with 25% H₂O). 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/m² (procured from Easy Composites, UK).

To produce a composite plate with the thickness of 3 mm, a mould with 7 layers of flax fabrics included (which gives a fibre volume fraction of ~31%) were firstly prepared according to the layout shown in Figure 1 below. In order to reduce the moisture content, the flax fabric was degassed under the vacuum for 24 h before the infusion.

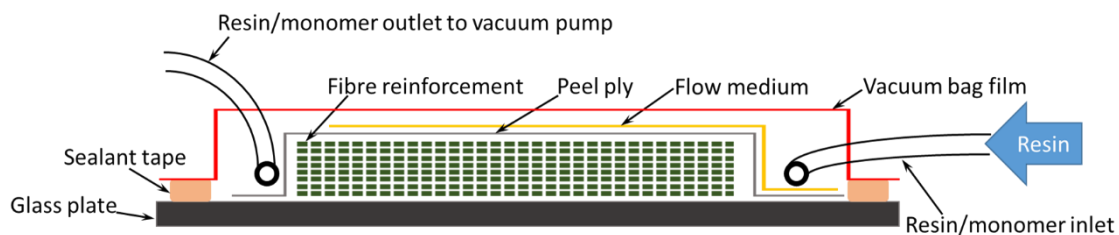


Figure 1. Schematic of the RIFT, redrawn from [2].

All development work was conducted in the Composite Manufacturing Laboratory at the University of Plymouth. The production of flax fabric composites with *in situ* polymerisation of Elium[®] MMA monomer 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. In order 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).

The *in situ* polymerisation process of L-lactide requires elevated temperature. The initial processing parameters were selected according to (i) published data [3-6], (ii) an upper limit imposed by the thermal degradation temperature of natural fibres [7-11] and (iii) preliminary trials.

The preliminary trials were based on the melting temperature of the polymer. Nine cups (marked as A-I), each with 40 grams of L-lactide monomer were prepared. The catalyst was firstly added into the melted monomer (the weight ratios of the catalyst were shown in Table 1) and stirred for 1 min. After the stirring, cups A-E were placed into an oven at 120 °C, cups F-I were moved into another oven at 170 °C. All cups with monomer/catalyst mixture were heated for 3 hours at 120 or 170 °C. Following the 3-hour heating, all cups were taken out and left in the ambient temperature for approximately 24 hours and then reheated in an oven at a starting temperature of 100 °C. The status of the polymer samples was checked manually with temperature increased; results can be seen in Table 2.

Table 1 Monomer to catalyst ratio of each cup.

	A	B	C	D	E	F	G	H	I
Monomer to catalyst ratio	No catalyst	100	200	500	1000	100	200	500	1000

Table 2 Status change of the samples during the reheating process. It should be noted that all results were just an indication by hand check due to limited experimental conditions.

T (°C)	A	B	C	D	E	F	G	H	I
100	Start to melt	-	-	Start to soften	Start to melt	-	-	-	-
110	Melted	-	-	Softer +	Melted	-	-	-	-
120	Melted	-	-	Softer ++	Melted	-	-	-	-
130	Melted	-	-	Melted	Melted	-	-	-	-
140	Melted	-	-	Melted	Melted	-	-	-	-
150	Melted	-	Start to soften	Melted	Melted	-	-	-	Start to soften
160	Melted	-	Softer +	Melted	Melted	-	-	-	Softer +
170	Melted	Start to soften	Softer ++	Melted	Melted	-	-	-	Softer ++
175	Melted	Softer +	Melted	Melted	Melted	Start to soften	-	-	Melted
180	Melted	Softer ++	Melted	Melted	Melted	Melted	Start to soften	Start to soften	Melted
185	Melted	Melted	Melted	Melted	Melted	Melted	Melted	Melted	Melted

It is clear that the polymer samples in Cups G and H show the highest melting temperature, indicating the highest monomer to polymer conversion rate and molecular weight. Therefore, along with Ref. [3-11], 170 °C for 3 h, with the monomer/catalyst ratio of 500 were selected as the processing parameters for PLA-flax composite production.

The L-lactide powder was first melted in an oven at the predetermined temperature (170 °C here). When the monomer was fully melted, the beaker containing the liquid monomer was transferred onto a magnetic stirrer, the catalyst ($\text{Sn}(\text{Oct})_2$) was added, then the mixture was stirred for 1 min. In the meantime, following the degassing of the flax fabrics, the whole mould (still under vacuum) was also pre-heated in the oven. Given the low initial viscosity of the L-lactide monomer, the infusion was started ~20 min after adding the catalyst in order to increase the viscosity. The setup can be seen in Figure 2. After the pre-designed processing duration (3 h here), the mould was taken out of the oven and the composite was cooled in the ambient temperature.

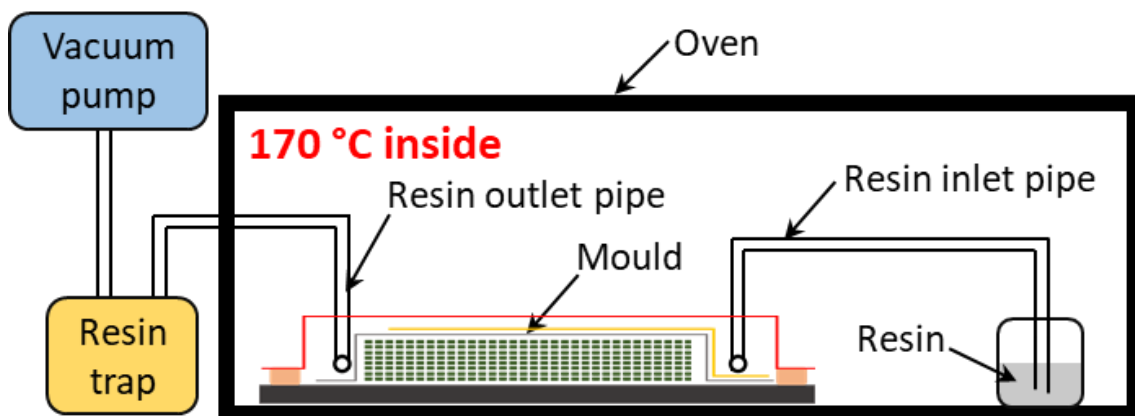


Figure 2 Configuration for the production of PLA-flax composites via RIFT in the oven.

Three batches of five mechanical test samples were prepared. Samples from Batch PF-170 were cut from the PLA-flax plate produced here (at 170 °C); batches EF-G and EF-P were Elium[®]-flax composite from relatively good permeated region (with fewer air voids) and poor permeated region (with more air voids) respectively. Pictures of the samples can be found in Figure 3 below. It is also observed that the permeation of whole PLA-flax composite plate was even worse than the relatively poor permeated region of the Elium[®]-flax plate.

The mechanical properties of the sample were investigated by three-point flexural testing. The sample geometry for flexural tests is 80 x 10 x 3 mm³ (cut from the composite plate by a laser cutter). The test span and speed in the flexural testing were 48 mm and 1.28 mm/min respectively according to ASTM D790 standard [12]. Using the Instron 5582 screw-driven 100 kN universal test machine with a 5 kN load cell, the flexural modulus was measured from the linear region (5–10 N) from the load-deflection curves.

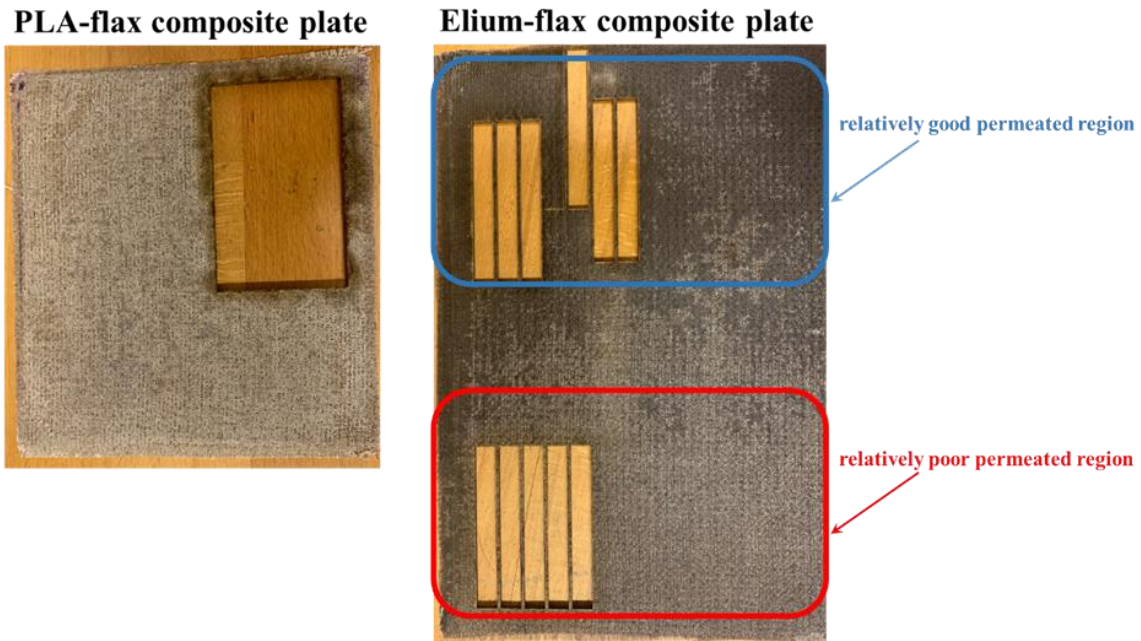


Figure 3 PLA-flax and Elium[®]-flax composites for flexural testing.

1.2 RULE-OF-MIXTURE PREDICTION

Rule-of-mixture equations [13,14] were used in this study to predict the flexural strength σ_c and modulus E_c of the composite:

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

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

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:

$$V_f = \frac{n A_F}{\rho_f t} \quad (3)$$

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

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. and [15] and Elium[®] 188 XO technical data sheet respectively). According to Ref. [16], the strength (σ_m), modulus (E_m) and strain to failure (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 [17] 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 % [18]. Considering the references above, 50 MPa, 3.5 GPa and 4% were selected for PLA in this report, to predict the performance of PLA matrix composites. The flax reinforcement utilised was ~~the Easy Composites 200 gsm 2x2a continuous~~ twill weave fabric, in consequence, η_i equalled to 1 and η_o was estimated to be ~0.48. The parameters employed for Equations (1) and (2) are summarized in Table 3. As a result, the σ_c and E_c predicted by rule-of-mixture were (i) 119.3 MPa & 9.45 GPa for Elium[®]-flax composites, and (ii) 91.7 MPa & 9.86 GPa for PLA-flax composites.

Table 3 Parameters used in rule-of-mixture equations.

Composite	V_f	σ_f	σ_{m^*}	E_f	E_m	η_i	η_o
Elium [®] -flax	31%	500 MPa	65 MPa	50 GPa	2.91 GPa	1	0.48
PLA-flax	31%	500 MPa	25 MPa	50 GPa	3.50 GPa	1	0.48

1.3 RESULTS AND DISCUSSION

The three-point flexural testing results are shown in Table 4. Composites from EF-G 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. It can be observed that the modulus and strength of Elium[®]-flax samples from batch EF-G were 35.7% and 15.3% higher than that of their counterparts from batch EF-P, respectively. Therefore, the quality of the infusion process has a significant influence on the mechanical properties of the final composite. PLA-flax samples demonstrate the poorest properties comparing with the prediction values. 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 inconsistency in permeability [19].
- (iii) The boiling temperature of the L-lactide under vacuum is lower than the processing temperature 170 °C [20]. 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, as observed in Figure 3.
- (iv) The properties of the PLA matrix from the *in situ* polymerisation of L-lactide are overestimated.

Table 4 Flexural properties for PLA-flax and Elium[®]-flax composites.

Composite batch	Flexural strength			Flexural modulus		
	Experimental	Prediction	E/P*	Experimental	Prediction	E/P*
	Mean \pm SD (MPa)	(MPa)	(%)	Mean \pm SD (GPa)	(GPa)	(%)
PF-170	56.98 \pm 9.58 (16.8%)	91.7	62.1	3.66 \pm 0.31 (8.5%)	9.86	37.1
EF-G	123.73 \pm 4.96 (4.0%)	119.3	103.7	4.98 \pm 0.42 (8.4%)	9.45	52.7
EF-P	91.15 \pm 3.63 (4.0%)	119.3	76.4	4.32 \pm 0.29 (6.7%)	9.45	45.7

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

2 Optimisation of manufacture process for PLA-flax composite

As discussed above, the poor mechanical properties of the PLA-flax composite may result from the overestimated properties of PLA matrix. It was reported by many researchers [3,4,6,21] that the *in situ* polymerisation parameters of L-lactide monomer had a significant influence on the properties of final PLA polymer. Therefore, the improvement of manufacture process is likely to result in PLA-flax composite with better quality. Here in this section, the manufacture parameters including (1) processing temperature (130–170 °C), (2) monomer to catalyst ratio (100–1000), (3) processing duration (up to 17 h) and (4) cooling rate (in the room temperature or switched-off oven) were optimised according to the flexural properties of unreinforced PLA-only samples.

2.1 SAMPLE PRODUCTION AND TESTING

The PLA-only samples were produced with the similar procedures as PLA-flax composites, but with an open silicone rubber mould. Following the stirring, the monomer with the catalyst was poured into the open mould with 80 \times 10 \times 3 mm³ cavities, which directly provide samples with dimension for flexural testing. It should be noted that unlike PLA-flax composites above, PLA-only samples were made under atmospheric pressure. The test span and speed for PLA-only samples were also 48 mm and 1.28 mm/min respectively, but the flexural modulus was measured from linear region from 2 to 4 N.

2.2 RESULTS AND DISCUSSION

The flexural testing results are summarised in Table 5. It is obvious that variation range of the flexural strength (5.1–21.6 MPa) is ~~remarkably greater~~ noticeably higher than ~~that for~~ flexural modulus (1.5–2.37 GPa), thus it is easier and clearer to compare the strength value for the evaluation of these processing parameters. As we expected, the effects of processing temperature, monomer to catalyst ratio and processing duration are not independent. In general, for better PLA properties, the monomer/catalyst ratios of 200, 500 and 1000 are suitable for processing temperatures at 130 °C, 150 °C and 170 °C respectively, indicating a lower catalyst content required for a higher temperature. The processing duration decisively affects the properties of PLA under some circumstances. It can be inferred from the results of P-14, P-15 and P-16 for

example, 1 h is not enough for the polymerisation process; 3 h is too long that may reduce the conversion rate, molecular weight or the final crystallinity of the final polymer; while a balance is likely to be achieved at 2 h processing duration which leads to better polymer properties.

Table 5 Flexural properties for PLA-only samples.

Batch	Processing temperature (°C)	Monomer to catalyst ratio	Processing duration (h)	Cooling	Flexural modulus (GPa)	Standard deviation	Flexural strength (MPa)	Standard deviation	Number of sample
P-1*	130	No catalyst	3	Room T	Properties too low to test				5
P-2	130	500	3	Room T	Properties too low to test				5
P-3	130	200	2	Room T	2.10	0.27 (12.9%)	11.24	2.00 (17.8%)	10
P-4	130	200	3	Room T	2.09	0.42 (20.1%)	11.54	2.50 (21.7%)	9
P-5	130	200	4	Room T	1.87	0.25 (13.4%)	10.30	3.06 (29.7%)	10
P-6	130	200	5	Room T	1.90	0.16 (8.4%)	10.66	1.76 (16.5%)	5
P-7	130	200	6	Room T	2.05	0.27 (13.2%)	7.18	0.20 (2.8%)	4
P-8	130	200	17	Room T	1.95	0.21 (10.8%)	8.26	1.09 (13.2%)	5
P-9	130	100	1	Room T	2.02	0.15 (7.4%)	6.17	0.50 (8.1%)	4
P-10	130	100	2	Room T	1.94	0.24 (12.4%)	6.69	0.25 (3.7%)	5
P-11	130	100	3	Room T	2.01	0.17 (8.5%)	5.41	0.50 (9.2%)	5
P-12	130	100	4	Room T	1.76	0.16 (9.1%)	6.87	0.41 (6.0%)	5
P-13	130	100	17	Room T	1.91	0.20 (10.5%)	6.35	0.74 (11.7%)	5
P-14	150	500	1	Room T	Properties too low to test				5
P-15	150	500	2	Room T	2.02	0.31 (15.3%)	21.57	7.81 (36.2%)	10
P-16	150	500	3	Room T	1.99	0.23 (11.6%)	9.16	2.67 (29.1%)	10
P-17	150	500	4	Room T	2.22	0.27 (12.2%)	9.12	2.77 (30.4%)	15
P-18	150	500	4.5	Room T	1.98	0.21 (10.6%)	14.05	4.62 (32.9%)	4
P-19	150	500	6	Room T	2.48	0.31 (12.5%)	8.21	1.44 (17.5%)	5
P-20	150	200	2	Room T	2.24	0.40 (17.9%)	8.97	2.63 (29.3%)	10
P-21	150	200	3	Room T	2.03	0.24 (11.8%)	7.62	1.31 (17.2%)	5
P-22	150	200	4	Room T	2.22	0.23 (10.4%)	6.59	1.40 (21.2%)	5
P-23	150	200	6	Room T	1.96	0.24 (12.2%)	6.39	1.27 (19.9%)	5
P-24	150	100	3	Room T	2.10	0.30 (14.3%)	6.45	2.06 (31.9%)	5
P-25	170	1000	1	Room T	Properties too low to test				5
P-26	170	1000	2	Room T	2.27	0.13 (5.7%)	10.06	1.65 (16.4%)	5
P-27	170	1000	3	Room T	1.73	0.18 (10.4%)	9.73	0.90 (9.2%)	5
P-28	170	1000	4	Room T	1.67	0.30 (18.0%)	12.23	4.63 (37.9%)	4
P-29	170	500	1	Room T	1.95	0.12 (6.2%)	6.83	1.38 (20.2%)	5
P-30	170	500	2	Room T	2.12	0.23 (10.8%)	7.09	1.29 (18.2%)	5
P-31	170	500	3	Room T	2.09	0.28 (13.4%)	8.60	3.01 (35%)	14
P-32	170	500	3	Oven	1.53	0.14 (9.2%)	4.84	0.93 (19.2%)	6
P-33	170	500	4	Room T	1.86	0.11 (5.9%)	14.64	3.06 (20.9%)	5
P-34	170	200	1	Room T	2.22	0.36 (16.2%)	5.13	1.49 (29.0%)	5
P-35	170	200	2	Room T	1.82	0.16 (8.8%)	9.00	2.64 (29.3%)	5
P-36	170	200	3	Room T	2.12	0.21 (9.9%)	7.02	1.81 (25.8%)	10
P-37	170	200	3	Oven	1.75	0.17 (9.8%)	5.08	1.66 (32.3%)	4
P-38	170	200	4	Room T	2.02	0.38 (18.8%)	6.43	0.70 (10.9%)	5

*Without catalyst, Batch P-1 are L-lactide monomer not PLA polymer samples.

Comparing P-31 to P-32 and also P-36 to P-37, PLA samples cooled in the room temperature demonstrate both higher modulus and strength compared with their counterparts cooled in the switched-off oven. It is observed that the samples cooled in the oven show lower transparency than samples cooled in the room temperature (see Figure 4), consistent with a ~~greater-reduced~~ degree of crystallinity or which may due to the micro voids generated during cooling. Further studies may include the measurement of the conversion rate from monomer to polymer, crystallinity, molecular weight, and void content for a deeper understanding of the inner mechanisms.

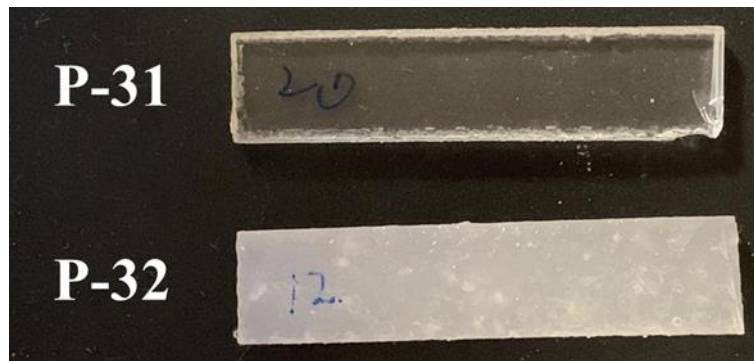


Figure 4 PLA only samples (after test) from Batches P-31 (cooled in the room temperature) and P-32 (cooled in the switched-off oven).

The manufacture parameters for PLA-flax composites in Section 1.1 were the same as Batch P-31 in Table 5. Using 8.6 MPa as σ_m and 2.09 GPa as E_m in the rule-of-mixture equations, the predicted strength and modulus for PLA-flax composites are calculated to be 80.3 MPa and 8.88 GPa, which are still significantly higher than the experimental observation in Table 4, especially the modulus. This result suggests improvement of aspects other than manufacture process (e.g. fibre-matrix adhesion) may also be required for a high quality PLA-flax composite.

Most important finding in this section, samples from Batch P-15 show the best properties of 2 GPa (modulus) and 21.6 MPa (Strength). In consequence, processing at 150 °C for 2 hours with the monomer/catalyst ratio of 500, followed by cooling at room temperature will be used as optimised parameters for PLA-flax composite production.

A PLA-flax composite plate was then produced according to the procedure in Section 1.1, but at the optimised processing parameters as for Batch P-15 PLA-only samples. The flexural properties of the PLA-flax composite samples produced here (PF-150) were tested and compared with that of PF-170. Instead of an improvement, an unexpected slight drop in both flexural strength and modulus can be seen from the result in Table 6. This observation may suggest that the properties of PLA matrix do not dominate the properties of the final PLA-flax composites. In addition, as mentioned in Section 2.1, the optimisation of PLA processing parameters was performed under atmospheric pressure without flax fabrics. Therefore, the optimised parameters may not be the optimal under the vacuum condition and with the flax fabrics ~~present~~included.

Further investigations for PLA-flax composite property improvement are still ~~undergoing~~ongoing. In addition, the manufacture procedure development will continue using a preliminary heating system from Jiangyin Jin Yu Electric Heating Company Limited for flat plate manufacture.

Table 6 Comparison of flexural properties between PF-170 and PF-150.

Composite batch	Flexural strength Mean \pm SD (MPa)	Flexural modulus Mean \pm SD (GPa)
PF-170	56.98 \pm 9.58 (16.8%)	3.66 \pm 0.31 (8.5%)
PF-150	52.85 \pm 3.67 (6.9%)	3.55 \pm 0.39 (11.0%)

Summary

The production of PMMA-flax composite via RIFT is straightforward; while PLA-flax composite is relatively complicated as it requires elevated temperature. Both PMMA-flax and PLA-flax composites demonstrate lower modulus compared with theoretical values, especially for PLA-flax, which may due to the poor fibre/matrix adhesion, fibre swelling effect, etc. By testing the PLA-only samples, the optimised processing parameters were found to be 150 °C for 2 hours with the monomer/catalyst ratio of 500, followed by cooling at room temperature. However, properties of the PLA-flax composite manufactured under the optimised parameters did not show an improvement. Further investigation is still ongoing.

References

1. Qin, Y.; Summerscales, J.; Graham-Jones, J.; Meng, M.; Pemberton, R. Monomer Selection for In Situ Polymerization Infusion Manufacture of Natural-Fiber Reinforced Thermoplastic-Matrix Marine Composites. *Polymers* **2020**, *12*, 2928.
2. Summerscales, J. *Resin infusion under flexible tooling (RIFT)*, *Encyclopedia of Composites–Second edition*; John Wiley & Sons: 2012; pp. 2648-2658.
3. Degée, P.; Dubois, P.; Jacobsen, S.; Fritz, H.G.; Jérôme, R. Beneficial effect of triphenylphosphine on the bulk polymerization of L, L-lactide promoted by 2-ethylhexanoic acid tin (II) salt. *Journal of Polymer Science Part A: Polymer Chemistry* **1999**, *37*, 2413-2420.
4. Kricheldorf, H.R.; Kreiser-Saunders, I.; Stricker, A. Polylactones 48. SnOct₂-initiated polymerizations of lactide: a mechanistic study. *Macromolecules* **2000**, *33*, 702-709.
5. Louisy, E.; Samyn, F.; Bourbigot, S.; Fontaine, G.; Bonnet, F. Preparation of glass fabric/poly (L-lactide) composites by Thermoplastic Resin Transfer Molding. *Polymers* **2019**, *11*, 339.
6. Puaux, J.P.; Banu, I.; Nagy, I.; Bozga, G. A Study of L-Lactide Ring-Opening Polymerization Kinetics. In Proceedings of Macromolecular Symposia; pp. 318-326.
7. Chaishome, J.; Brown, K.; Brooks, R.; Clifford, M. Thermal Degradation of Flax Fibres as Potential Reinforcement in Thermoplastic Composites. *Adv Mater Res* **2014**, *894*, 32-36.
8. Chaishome, J.; Rattanapaskorn, S. The influence of alkaline treatment on thermal stability of flax fibres. In Proceedings of IOP Conference Series: Materials Science and Engineering, April 2017.
9. Gassan, J.; Bledzki, A.K. Thermal degradation of flax and jute fibers. *J Appl Polym Sci* **2001**, *82*, 1417-1422.
10. Ouajai, S.; Shanks, R. Composition, structure and thermal degradation of hemp cellulose after chemical treatments. *Polym Degrad Stab* **2005**, *89*, 327-335.
11. Shahzad, A. A study in physical and mechanical properties of hemp fibres. *Adv Mater Sci Eng* **2013**, *2013*.
12. ASTM D790, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. 2010.
13. Virk, A.S.; Hall, W.; Summerscales, J. Modulus and strength prediction for natural fibre composites. *Materials Science and Technology* **2012**, *28*, 864-871.
14. Kelly, A.; Tyson, a.W. Tensile properties of fibre-reinforced metals: copper/tungsten and copper/molybdenum. *Journal of the Mechanics and Physics of Solids* **1965**, *13*, 329-350.
15. Natural Fibre Reinforcements. Available online: <https://www.easycomposites.co.uk/natural-fibre-reinforcements> (accessed on September 2020).
16. Farah, S.; Anderson, D.G.; Langer, R. Physical and mechanical properties of PLA, and their functions in widespread applications—A comprehensive review. *Advanced drug delivery reviews* **2016**, *107*, 367-392.
17. Eawwiboonthanakit, N.; Jaafar, M.; Hamid, Z.A.A.; Todo, M.; Lila, B. Tensile properties of Poly (L-lactic acid (PLLA) blends. In Proceedings of Advanced Materials Research; pp. 179-183.
18. Luminy® PLA neat resins. Available online: https://totalcorbion.4net-acc.com/media/iufhvey2/factsheet_luminy-pla-neat-resins_20190903.pdf (accessed on September 2020).
19. Summerscales, J. Composites Design and Manufacture (Plymouth University teaching support materials)-Resin Transfer Moulding (RTM). Available online: <https://ecm-academics.plymouth.ac.uk/jsummerscales/MATS347/MATS347C6%20RTM.htm> (accessed on 02 December 2020).
20. Yarkova, A.V.; Novikov, V.T.; Glotova, V.N.; Shkarin, A.A.; Borovikova, Y.S. Vacuum effect on the lactide yield. *Procedia Chemistry* **2015**, *15*, 301-307.
21. Hyon, S.-H.; Jamshidi, K.; Ikada, Y. Synthesis of polylactides with different molecular weights. *Biomaterials* **1997**, *18*, 1503-1508.