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Natural fibre-reinforced thermoplastic composites manufactured by in-situ polymerisation infusion for marine applications: monomer selection

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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. It is clear that the selection of the resin system will significantly affect the cost, manufacturing process, mechanical properties and durability of the chosen composite material system. This report reviews the available thermoplastic monomers suitable for in-situ polymerisation during monomer infusion under flexible tooling (MIFT); and then discusses criteria for the selection of appropriate monomers based on monomer processing temperature and viscosity, polymer mechanical properties, recyclability, etc. Given the systems currently available, polymethyl methacrylate (PMMA) Elium® thermoplastic resin could be the most suitable resin/monomer for the composite production in this project. It has low processing temperature, long open window for infusion, and low moisture absorption but end-of-life recovery may be an issue. The research literature suggests that bio-based methyl methacrylate (MMA) may become available during the SeaBioComp project. Special attention is required for the recycling technology; a life cycle analysis should be performed. Polylactide (PLA) may be an alternative to Elium® as the infusible monomer, but the relatively high processing temperature may require expensive consumable materials, and there may be durability issues.

Keywords: Natural fibres; Thermoplastic; Monomer, Infusion.

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List of abbreviations

BPA	Bisphenol A
CBT	Cyclic Butylene Terephthalate
CDT	Cyclododecatriene
ETFE	Ethylene Tetrafluoroethylene
FEP	Fluorinated Ethylene Propylene
HDPE	High-density Polyethylene
LCM	Liquid Composite Moulding
LDPE	Low-density Polyethylene
MIFT	Monomer Infusion under Flexible Tooling
MMA	Methyl Methacrylate
NIP	Non-injection Point
PA6	Polyamide-6
PA12	Polyamide-12
PBT	Polybutylene Terephthalate
PC	Polycarbonate
PEK	Polyether Ketone
PET	Polyethylene Terephthalate
PLA	Polylactic Acid or Polylactide
PMMA	Polymethyl Methacrylate
PPA	Polyphthalamide
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
RIFT	Resin Infusion under Flexible Tooling
ROMP	Ring-opening Metathesis Polymerisation
ROP	Ring-opening Polymerisation
RTM	Resin Transfer Moulding
SCRIMP™	Seeman Composites Resin Infusion Molding Process
TPU	Thermoplastic Polyurethane
VARTM	Vacuum-Assisted Resin Transfer Moulding

1 Introduction

There is an increasing trend to replace conventional synthetic fibres and petrochemical resins with renewable and recyclable materials for composite production [1]. Special attention to environmental issues should be taken for composites in marine applications due to the risk of microplastic contamination of the marine ecosystem [2, 3]. Natural fibres demonstrate advantages including renewable, biodegradable, low cost, high specific strength and stiffness. Therefore, for the fibre reinforcement, natural fibres (e.g. flax, hemp, sisal, jute, coir, bamboo, etc.) have attracted much interest as alternatives to conventional glass/carbon fibres in recent years [4]. For the resin material, investigations into replacing thermoset with thermoplastic matrix in composites are growing rapidly as thermoplastic resins are recyclable and possess relatively high impact resistance [5-7].

As a form of Liquid Composite Moulding (LCM), the Resin Transfer Moulding (RTM) approach is using a matched pair of mould tools, to produce composite structures with high fibre volume fraction (high mechanical properties) [8-14]. RTM is viewed as an economic and efficient process with low styrene emission [15]. Resin Infusion under Flexible Tooling (RIFT) is a variant of vacuum-driven RTM, using a single solid mould tool and a flexible counter-face tool or membrane [16-20]. Therefore, since only a single face mould is needed, the tooling cost of RIFT is much cheaper than RTM, especially for the production of large composite structures [16].

The RIFT process involves the long-range flow of the liquid precursor that will become the polymer matrix through a porous medium defined by the reinforcement textile. In consequence, it is difficult to produce thermoplastic composites using RIFT because of the high melt viscosity of the matrix. Thus in order to meet the conditions for liquid impregnation, in-situ polymerisation of a liquid monomer (with lower viscosity at a lower temperature) could be utilised [21]. Clearly, the selection of monomers for in-situ polymerisation is of great importance for the feasibility of RIFT and the properties of the final products. Here in this report, the potential monomers are discussed and compared in terms of their viscosities, environmental sensitivities, processing temperatures, sources, product properties, recyclability, etc.

2 Resin Infusion under Flexible Tooling (RIFT)

RIFT has become a rapidly increasing production approach for large and complex composite structures [22]. For large structures (e.g. boat hulls or wind turbine blades), it is common to flood one surface of the laminate with resin in a transport mesh (a.k.a. flow medium) to expedite fill by through-thickness flow. The process is generally

referred to as Resin Infusion under Flexible Tooling with a flow medium (RIFT II), Seeman Composites Resin Infusion Molding Process (SCRIMP™), or (in North America) Vacuum-Assisted Resin Transfer Moulding (VARTM) [17]. In this report, RIFT is used as the acronym for this sample production approach. The equipment required for RIFT is only a single-part mould, a vacuum pump and some consumable materials (e.g. vacuum bag, flow media, peel ply, pipework). The key factors for the a successful RIFT process are (i) polymer rheology, (ii) reinforcement permeability, which govern the resin flow [23], and (iii) processing temperature.

2.1 POLYMER RHEOLOGY

Rheology is the science of flow and deformation of matter. For fluids, the key characteristic is viscosity: the ability of a fluid to resist a change in the arrangement of the molecules when under an applied strain or stress [24]. The polymer industry defines two forms of viscosity:

1. Dynamic viscosity (μ): the force required to overcome internal friction. The SI units are Pascal-seconds (Pa·s: identical to $1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$), although the composites industry often uses centimetre–gram–second (CGS) units: centiPoise (cP). There is a direct numerical equivalence between milliPascal-seconds and centiPoise ($1 \text{ mPa} \cdot \text{s} = 1 \text{ cP}$).
2. Kinematic viscosity (η): the ratio of the viscous force to the inertial force where the latter is a function of the fluid density (ρ). The SI units are $\text{m}^2 \cdot \text{s}^{-1}$, although the parameter is often given in centiStokes (CGS units: 1 centiStoke is $1 \text{ mm}^2/\text{s}$). Hence $\eta = \mu/\rho$.

In LCM, the process is normally modelled using Darcy's equation [25] where the volumetric flow rate (Q , units: m^3/s) of a fluid in a saturated porous medium can be expressed as:

$$Q = \frac{K \cdot A \cdot \Delta P}{\mu \cdot L} \quad (1)$$

where K is a constant of proportionality known as the permeability (units: m^2), A is the cross section of the porous medium normal to the flow direction (units: m^2), $\Delta P/L$ is the pressure gradient driving the flow (units: Pa/m) and μ is the fluid viscosity. For anisotropic media (composite systems), the equation should have tensor form.

Rudd et al [9] suggest that the most significant practical limitation on the suitability of a resin system for the LCM process is imposed by the viscosity. Note that a low viscosity indicates high flow rate whilst a high viscosity indicates low flow rate. Resins with extremely low viscosity may be unsuitable for LCM processes as they may result in high porosity or gross voidage. Resins formulated for liquid composite moulding processes typically have

an initial viscosity around 200 mPa·s. For curing thermoset resins, or for in-situ polymerisation of thermoplastic monomers, the progress of the chemical reaction causes an increase in molecular size and a consequent increase in viscosity. Becker [26] quotes an upper limit for viscosity in RTM of 800 mPa·s. Elsewhere, the non-injection point (NIP) has been defined as a viscosity of 1000 mPa·s [15]. The flow front is effectively stationary at this viscosity and the low differential pressures used in infusion processes [17].

2.2 REINFORCEMENT PERMEABILITY

Apart from the viscosity of the resin, the permeability of the reinforcement also has a huge influence on the LCM processes. Equation (1) was originally derived for the flow of water through saturated rock to feed the drinking fountains in Dijon. Even though permeability is viewed as a unique characteristic of a porous medium, it has been reported that the measured permeability is strongly dependent on the type of resin fluid [27, 28]. It can be indicated from surface tension and contact angle measurements that, the difference in permeability is due to varying interactions at the microscopic level between the fibre and the fluid [29].

The LCM process involve two types of permeation through the pore space of the reinforcement: (i) saturated (fully wetted) and (ii) unsaturated (wetting). Summerscales [27], Park and Krawczak [28] have considered the differences in permeability reported for the same fabrics between the two permeation conditions. The reported difference between unsaturated and saturated permeabilities suggests that a change in surface energy occurs during wetting and dissipates some energy. For the conventional glass or carbon fibres, Kim et al [30] and Diallo et al [31] have reported that saturated permeabilities are always lower than unsaturated permeabilities. However, other authors have reported opposite results [23, 32].

For the LCM process with natural fibre reinforcements, the permeability is more complicated. The absorption of the permeant fluid by natural fibres and the consequent fibre swelling, lead to fibre diameter increase which may be responsible for inconsistencies in permeability measurements for these reinforcements. Moreover, it was also found that the type of liquid had a significant influence on the fibre swelling ratio (wet diameter/dry diameter) [33–36]. An experimental study demonstrated that the permeability of flax fabrics showed a strong correlation to the liquid type. It was suggested that this dependence was due to liquid sorption into the natural fibre (swelling effect) [35]. Similar effects of liquid absorption and fibre swelling on permeability were also observed on jute fabrics. The average saturated permeability measured using diluted corn syrup was 23.1%–69.5% smaller than that measured using motor oil [36]. Nguyen et al [37, 38] investigated the influence of liquid absorption and fibre

swelling during RTM resin impregnation of flax fibre reinforcements and suggested a relationship between fibre swelling and permeability given by:

$$K = \frac{(1 - f_{sw}^2 \cdot V_f)^{n+1}}{A \cdot (f_{sw}^2 \cdot V_f)^n} \quad (2)$$

where K is the permeability, f_{sw} is the fibre swelling ratio, V_f is the fibre volume fraction and A and n are empirically derived constants. The progress of the resin flow front may be delayed when swelling of the fibres behind the flow front constrains liquid moving forwards or may have a favourable effect by forcing resin forwards. These opposing effects should be modelled using sink and source terms in the mass conservation equation. In consequence, the permeability value in the model may need to vary with exposure time and position in the preform. Nguyen used models with varying permeability (mass source/sink terms) to obtain better agreement with the experimental flow measurements than when using a constant permeability model. When the fibre volume increased, the effect from the mass sink became greater. Since the high fibre volume fraction is one of the main advantages of RIFT (see Section 1), different resins could lead to vastly varying effects on the fibre swelling phenomenon (permeability of the reinforcement), during the impregnation in the RIFT process. Based on the discussion above, the monomer selection is likely to have an influence on the permeability of natural fibre reinforcements, which need to be considered.

2.3 PROCESSING TEMPERATURE

The in-situ polymerisation of the thermoplastic composite usually require elevated temperature, thus the processing temperature is another crucial parameter in the RIFT, especially involving natural fibres. Special attention is needed to the compatibility of the chosen monomers with consumables that may be required in RIFT, under the process conditions required for the respective monomers (e.g., does the pipework collapse under vacuum at elevated temperature?). Table 1 summarises the commercially available consumables and their maximum working temperatures. It can be seen that some consumables can withstand up to 427 °C (material: silicone), however it is clear that these high-temperature resistant consumables will significantly increase the cost of the RIFT. Apart from the temperature effect, materials of consumables (see Table 1) may dissolve in the selected monomer; this also cannot be ignored.

Table 1 Summary of commercial consumables for RIFT, their materials and maximum working temperatures (data from Tygavac Advanced Materials [39], Easy Composites [40], Castro Composites [41] & CA Composites [42]).

Consumables	Materials	Maximum temperatures (°C)
Tape	Carrier: Polyester, PTFE, Glass fabric, Fluoropolymer, Polyamide Adhesive: Silicone, High tack silicone, Acrylic, Rubber	60, 177–204, 399
Bagging film	Nylon, Polyolefin, ETFE, Polymethylpentene, Polyimide	121–246, 426
Peel ply	Nylon, Polyester, Fibreglass, PTFE coated fibreglass. (Release coating including PTFE and Silicone)	121–288, 427
Flow medium	Polyester, HDPE, Nylon, Polypropylene	100–200
Release film	Polymethylpentene, ETFE, Fluoropolymer, FEP, Polyolefin	121–260, 315, 405
Sealant tape	Synthetic Rubber, Silicone	100–232, 400, 427
Hose/Pipe	PVC, LDPE, Silicone	50, 90, 260
Spiral	Polypropylene	60–120

PTFE: Polytetrafluoroethylene

ETFE: Ethylene tetrafluoroethylene

HDPE: High-density polyethylene

FEP: Fluorinated ethylene propylene

PVC: Polyvinyl chloride

LDPE: Low-density polyethylene

Using thermoplastic resin with relatively high processing temperature could cause detrimental thermal degradation on the properties of natural fibres (e.g. flax, hemp) and their composites, especially during long solidification time at high temperature [43]. Gassan and Bledzki [44] studied the thermal degradation of flax fibres, and found that temperatures below 170°C only slightly affect fibre properties, while significantly dropped tenacity and degree of polymerisation were observed above 170 °C. Chaishome et al [45] reported that the thermal stability of flax fibres was significantly influenced by the thermal degradation of hemicellulose and pectin. It was also suggested that during the production of a flax fibre thermoplastic composite, the mechanical properties could be improved by (i) reducing the hemicellulose and pectin content of flax fibres, (ii) decreasing the consolidation temperature and (iii) increasing the heating rate. Moreover, Chaishome and Rattanapaskorn [43] found alkaline treatment removed hemicellulose and pectin from the flax fibres and consequently, the thermal stability of flax fibres was improved. For hemp fibres, Shahzad [46] found that the thermal degradation started at around 150–200°C and prominently accelerated at around 250°C. The thermal stability of hemp fibre was also analysed by Ouajai and Shanks [47], thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results demonstrated that untreated

fibre was less thermally stable than NaOH/Na₂SO₃ treated fibre, with degradation starting at 205 °C and 240 °C for each respectively.

3 Monomers for infusion

Molten thermoplastic polymers normally have viscosities far in excess of those used for LCM. However, in recent years, the usage of in-situ polymerisation to produce thermoplastic matrix composites by RTM or RIFT has grown rapidly. Van Rijswijk and Bersee [48] have reviewed in-situ polymerisation of most polymers in this context. They classified the principal systems of potential use for in-situ polymerisation into:

1. Ring-opening polymerisation (ROP) in which ring-shaped molecules are opened into linear monomers or oligomers and connected into high molecular weight polymers in consequence. The available monomers are:
 - caprolactam (e.g. DSM Fiber Intermediates APA-6) to produce polyamide-6 (PA6).
 - laurolactam (e.g. EMS-Grivory APLC12) to produce polyamide-12 (PA12).
 - cyclic butylene terephthalate (CBT) oligomers (e.g. Cyclics Corporation) to produce polybutylene terephthalate (PBT) polyester.
 - Cyclic bisphenol-A oligomers to produce polycarbonate.
 - L-lactide to produce poly(L-lactide)
2. Vinyl polymerisation in which double bonds in monomers are opened to create free radicals which then create polymers by an addition reaction to form a long chain. The available monomer is:
 - Acrylic based methyl methacrylate (MMA) (e.g. Arkema Elium® thermoplastic resins include formulations specifically designed for RTM/RIFT manufacture of composite parts) to produce polymethyl methacrylate (PMMA).

3.1 POLYAMIDES FROM LACTAMS

3.1.1 Polyamide-6 from lactam

Anionic polymerisation of lactams is the most developed method for in-situ polymerisation of thermoplastics via ROP [48, 49]. High molecular Polyamide-6 (PA6) is produced by ROP of ϵ -caprolactam (C₆H₁₁NO, melting temperature $T_m = 69$ °C), which is usually conducted at 130–170 °C [50]. The final conversion up to 99.3% can be achieved in 3–60 min, depending on the type and amount of activator and catalyst added [48]. Pillay et al [51] polymerised carbon fabric-PA6 composite laminates through VARTM. The ϵ -caprolactam monomer showed a

low viscosity of 4.87 mPa·s at 100 °C and final polymer matrix demonstrated a conversion of ~98%. Gong et al [52] successfully produced polyamide single polymer composites with PA6 fibre and matrix using RTM, via anionic polymerisation of ϵ -caprolactam. Mechanical properties of samples produced at four temperatures (140, 160, 180, and 200 °C) were investigated. Both tensile and flexural strength reached a peak at the processing temperature of 160 °C. The conversions of monomer and the void fraction of composite were all >93% and <2.5% respectively. Delft University of Technology conducted a series of comprehensive studies on the vacuum infusion of PA6 composites. It was found that by using Hexamethylene Diisocyanate as activator and Caprolactam Magnesium Bromide as catalyst, the processing window (viscosity < 1000 mPa·s) can be up to 20 min and the viscosity remains at a low level (<100 mPa·s) during most of the injection time. The final degrees of conversion were in the range of 93–97% at processing temperatures between 130–180 °C [53]. They also optimised the infusion process by considering both polymerisation temperature [54] and choice of activator/initiator [55]. In particular, they reported the feasibility of using vacuum infused PA6 thermoplastic composites for MW-size wind turbine blades. A 10% reduction in material cost can be expected comparing to the epoxy counterparts [56].

Bio-based ϵ -caprolactam is potentially available:

1. In 2014, Genomatica (San Diego CA, USA) announced an intention to develop enzymatic pathways to produce hexamethylenediamine, adipic acid and caprolactam [57].
2. In early 2018, Genomatica and Aquafil (Trento, Italy) announced a partnership to commercialise a Genomatica process for caprolactam derived from renewable feedstocks [58, 59].
3. Lee et al (2019) have reviewed renewable routes to obtain monomeric precursors for PA66 and PA6 from food waste [60].

3.1.2 Polyamide-12 from lactam

Polyamide-12 (PA12) is produced by ROP of ω -laurolactam ($C_{12}H_{23}NO$, $T_m = 154$ °C), with similar activators and initiators as PA6. Unlike PA6 polymerisation of PA12 has to be performed above the melting temperature of the final polymer (175 °C) in order to avoid the decrease of polymerisation rate due to premature crystallisation [61]. Therefore, the processing temperatures are usually between 180–240 °C and a cooling process is required to solidify the final polymer [48]. Zingraff et al [62] investigated the RTM process of anionically polymerised PA12 (with carbon fibres). An initial viscosity of 23 mPa·s at 180 °C was reported for the molten monomer and the

polymerisation was completed at 190 °C for 1 h. By applying the optimal flow conditions, the average void content of the composites plates could reduce from 15% to less than 1%. Reactive PA12 is currently marketed by EMS Chemie, Switzerland [48].

Lauro lactam is normally derived from petrochemicals by butadiene trimerisation to cyclododecatriene (CDT) [63]. To the best of the authors' knowledge, no report of bio-based lauro lactam has been identified.

3.1.3 Polyamide-6/12 from lactams

A mixture of ϵ -caprolactam and ω -lauro lactam may be easier to process than either monomer in isolation. Rusu and Rusu [64] synthesised copolyamides with 0, 10, 30, 40 or 50% ω -lauro lactam in the monomer feed with one formulation mixed at 110 °C for one minute under a nitrogen atmosphere. The mixture was then polymerised at 160 °C for 30 min. However, the copolymer is less likely to crystallise than the homopolymers and will consequently have reduced mechanical properties (lower density so fewer bonds/m³ to react stress) and lower environmental resistance (due to greater free volume).

3.2 POLYBUTYLENE TEREPHTHALATE FROM CYCLIC BUTYLENE TEREPHTHALATE

Many researchers have reported the production thermoplastic polybutylene terephthalate (PBT) composite with cyclic butylene terephthalate (CBT) oligomer via RTM or RIFT. Commercial CBT was usually used in these studies, with the polymerisation temperature ranging from 190–260 °C [21, 65-69]. Commercial CBT is normally a mixture of oligomers with between two and seven repeat units: i.e. from the dimer to the heptamer [67, 70]. The melting point of an oligomer mixture is usually lower than the pure, discrete cyclic oligomer. CBT softens at 140 °C and melts completely at 160–190 °C, whereas the pure cyclic dimer melts at 196 °C [71] and the pure cyclic tetramer melts at 248 °C [72]. The initial melt viscosity of the oligomer mixture is 150 mPa·s at 150 °C and drops to 20–30 mPa·s at 190 °C [48, 71, 73], whereas the dynamic viscosity of conventional PBT was reported to be ~1000 Pa·s at 250°C [74]. Parton and Verpoest found the final conversions of CBT oligomers were between 92–98% when polymerised at 190 °C for 30 min.

Pang et al [75], Abt and Sanchez-Soto [76] have reviewed the polymerisation of CBT oligomers as the precursor material for thermoplastic polyesters and their composites. The properties of the final product are highly dependent on the processing temperature. When isothermally polymerised below the T_m of PBT (~225 °C), the obtained PBT will show a high degree of crystallinity, which results in brittle matrix [49, 76]. Therefore, the toughening of PBT

may be required to improve the fracture toughness of PBT composites, by adding polycaprolactone for example [67, 77].

CBT was a product of Cyclics Corporation (Schwarzheide, Germany), no reports of bio-based CBT have been identified to date.

3.3 POLYCARBONATE FROM CYCLIC BISPHENOL A OLIGOMER

The thermoplastic polycarbonate (PC) can be polymerised from macrocyclic bisphenol A (BPA, $C_{15}H_{16}O_2$, $T_m = \sim 200^\circ\text{C}$), through ring-opening metathesis polymerisation (ROMP). High molecular weight (M_w) polycarbonate (up to 300,000) with the conversion over 99% can be achieved by polymerising cyclic oligomers at 300°C for 30 min, in the presence of various basic catalysts [78].

In 1991, Salem et al successfully demonstrated that polycarbonate matrix composites (with glass fibres) can be produced by RTM [79]. It was found that at the 250°C processing temperature, melt of the cyclic BPA oligomer had a viscosity at $\sim 1\text{ Pa}\cdot\text{s}$, which is comparable with the upper limit for viscosity in RTM discussed in Section 2.1. The polymerisation was conducted at 300°C to decrease the reaction time without degrading the polymer. The final BPA polycarbonate matrix showed a high polymer content over 95% and a molecular weight up to 50000. Although some matrix voids were observed in the composites structure, these can be reduced by an additional consolidation step in a hot-press.

To the best of the authors' knowledge, no report of bio-based BPA has been found.

3.4 POLY(L-LACTIDE) FROM L-LACTIDE

Poly(lactic acid) or polylactide (PLA) is a synthetic thermoplastic polymer polymerised by direct condensation polymerisation of lactic acid ($C_3H_6O_3$), or by ROP of lactide ($C_6H_8O_4$) [80]. The monomer is produced from the fermentation of 100% natural and renewable agricultural resources, such as corn [81]. The study of the in-situ polymerisation of PLA based composites has attracted much attention, especially in particle-reinforced composites, due to the more homogeneous particle dispersion which could be achieved [82]. Zhuang et al [83] reported the production of TiO_2 / PLA nanocomposite, via in-situ polymerisation of L-lactide (one of the stereoisomeric form) conducting at 150°C for 24 h with magnetic stirring. Similarly, a graphene/PLA composite can be made utilising the same method at 170°C for 4 h [84].

In early 2019, Louisy et al [85] firstly reported the production of glass/poly(L-lactide) composites using by RTM, via in-situ ROP of L-lactide with tin octoate $\text{Sn}(\text{Oct})_2$ as the catalyst. Since the T_m of L-lactide being $\sim 110^\circ\text{C}$, in order achieve low viscosity before moulding, the monomer with the catalyst were mixed in a 120°C pot (maximum conversion being only 38% in this condition). The polymerisation in the mould was conducted at 185°C , and the resulting poly(L-lactide) matrices exhibited conversions and molar masses up to 99% and $78,000\text{ g}\cdot\text{mol}^{-1}$ respectively.

3.5 POLYMETHYL METHACRYLATE FROM ACRYLIC MONOMER METHYL METHACRYLATE

Polymethyl methacrylate (PMMA) is the vinyl polymer made by vinyl polymerisation from the monomer methyl methacrylate (MMA, $\text{C}_5\text{H}_8\text{O}_2$); simply called acrylic [48, 49]. Arkema (Paris, France) acrylic Elium[®] resin is said to be the first thermoplastic resin compatible with RTM/infusion manufacture of composite structures with mechanical properties similar to thermosetting [86]. The viscosity and processing temperature of Elium[®] resin are as low as $100\text{ mPa}\cdot\text{s}$ and room temperature 20°C respectively [87]. Due to these two main advantages, the study into using of Elium[®] resin to produce thermoplastic composites via RTM/infusion is increasing rapidly.

Raponi et al [88] have analysed the thermal, rheological, and dielectric behaviour of the polymerisation reaction of Elium[®] liquid thermoplastic resin for infusion manufacturing of composite materials. A three-step thermal cycle comprising a 25°C isothermal for 25 min, followed by an 80°C for 30 min, and finally by a 110°C isothermal for 120 min is strongly recommended when high polymerisation degrees was suggested for the full polymerisation of the resin. Bhudolia et al [89] investigated the Mode I fracture toughness of carbon fibre-Elium[®] resin composites and found excellent performance of Elium[®] against the Mode I interlaminar fracture. They also suggested optimal infusion parameters to manufacture carbon fibre-Elium[®] composites with high fibre volume fraction (up to 60%) and low void content ($<1\%$) [90]. Some researchers have successfully produced natural fibre-Elium[®] composites and tested their mechanical properties [91, 92]. In 2016, the CANOE technical platform successfully produced a 9-m thermoplastic composite boat by using RIFT of Elium[®] at room temperature [93].

A number of commercial organisations have developed proprietary processes for manufacturing bio-based MMA. Major players in global synthetic and bio-based MMA market include BASF SE, Dow Chemicals, Arkema Group, Asahi-Kasei, Mitsubishi Rayon and Evonik [94].

Besides the thermoplastic polymers discussed above which have already been studied for the infusion process, some other polymers, for example thermoplastic polyurethane (TPU), polyether ketone (PEK), polyethylene terephthalate (PET) and polyphthalamide (PPA) may also be candidates for producing thermoplastic composites via infusion due to their relatively low monomer viscosities. The key parameters of the infusion process for each polymer are summarised in Table 2. MMA emerges as the best choice for bio-based matrix which can be processed at temperatures low enough to not compromise natural fibre reinforcements.

Table 2 Key parameters for thermoplastic polymers based on the requirement of in-situ polymerisation infusion.

Polymer	Monomer viscosity (mPa·s)	Processing temperature (°C)	Bio-based monomer available?	Ref.
Polyamide-6 (PA6)	~5	130–200	Yes	[50-53]
Polyamide-12 (PA12)	23	180–240	No	[48, 62]
Polybutylene terephthalate (PBT)	20–150	180–260	No	[21, 48, 65-69, 71, 73]
Polycarbonate (PC)	1000	250–300	No	[79]
Poly lactide (PLA)	-	185	Yes	[85]
Polymethyl methacrylate (PMMA, Elium®)	100	20–100	Yes	[87]
Thermoplastic polyurethane (TPU)	800	300	No	[49]
Polyether ketone (PEK)	80	340–390	No	[95]
Polyethylene terephthalate (PET)	30	250–325	No	[96-99]
Polyphthalamide (PPA)	1000	200–290	No	[49, 100]

4 Properties of thermoplastic polymers

It is obvious that the different polymers selected will lead to various mechanical and thermal properties of the thermoplastic composites. The major mechanical and thermal properties of all thermoplastic polymer candidates are summarised in Table 3. It is clear that as high-performance polymer [48], PEK demonstrates the best overall properties (high strength, modulus and glass transition temperature T_g) among all polymers. However, the application of PEK is limited by its high price [49].

Moisture absorption is an important parameter in Table 3 as it has a great influence on composite properties. For composite mechanical properties, Davies [101] investigated the influence of seawater ageing on carbon fibre-

Elium® composites. Lower sensitivity of Elium® to seawater was suggested compared to epoxy, The Elium® polymer saturated in seawater at 60°C showed ~20% decrease in tensile strength, comparing to the virgin polymer. In addition, the fatigue performance of glass fibre-Elium® composites is comparable with that of glass fibre-epoxy with similar fibre content [102]. It should be noted however that there are various formulations of Elium available, and not all have been studied in detail yet. The water absorption effect on the mechanical properties of carbon fibre reinforced PC was studied by Tanaka et al [103]. For the CF/PC composite, water absorption was found not only in the PC resin but also in the fibre/matrix interface. For the PC resin, the tensile strength showed a decrease tendency with increasing the water absorption time, while no change was observed in tensile modulus. For the carbon fibre/PC composite, the decrease tendency was only shown when water absorption time reached 400 h. For high moisture absorption polymer, the mechanical property degradation is more serious.

Polyamides may be unsuitable for structural applications in the marine environment due to their high water absorption and the consequent depression of glass transition temperature. Prabhakaran et al [104] compared the properties of PA6 at dry and 50% RH conditions. Results demonstrated that the tensile modulus and yield strength were reduced by 65% (3.4 GPa to 1.2 GPa) and 50% (90 MPa to 45 MPa) respectively.

In terms of the thermal properties, Wright [105] plotted the fall in T_g for data from epoxy resins (from five separate published papers) as a function of moisture content and found "as a rough rule-of-thumb" that there was a drop of 20 °C for each 1% of water pick-up (data available up to 7% moisture content). For thermoplastic polymers, it was demonstrated that at saturated 1.92% water pick-up, the T_g of PMMA was depressed by ~ 20 °C [106]. By assuming water absorption will reduce the T_g for all polymers, a high water absorption could significantly reduce the T_g of the composite, which is detrimental in most marine applications.

In the context of composites intended for marine use, the hydrophilicity of the polymer is an important consideration. Colin and Verdu [107] observed three kinds of chemical groups, such that:

1. non-hydrophilic groups generally absorb less than 0.1 w/o (weight percent) of water,
2. moderately hydrophilic groups generally absorb less than 3 w/o water, and
3. strongly hydrophilic groups in the saturated state are generally limited to values lower than 10 w/o water

Although the moisture absorption of the polymer cannot directly reveal that of the composite material, other parameters (e.g. void content) also have important influences, it can still provide a general idea of the moisture absorption ability of composite materials. However, natural fibres are prone to absorb large amounts of moisture [101], the influence of fibre reinforcement in water absorption of the composite cannot be ignored.

Table 3 Overview of properties of thermoplastic polymers.

Polymer	Density (g/cm ³)	Tensile strength (MPa)	Tensile modulus (GPa)	Strain to failure (%)	T_g (°C)	T_m (°C)	Moisture absorption (%)	Ref.
PA6	1.13	85	2.0–3.8	19	40–60	219–230	6–11	[49]
PA12	1.04	50–60	1.4	300	40–50	180	1.1–1.8	[49, 100]
PBT	1.31	85	1.8–2.7	30	25–60	225	0.09	[49]
PC	1.20	60	2.2	>100	150	300	0.16	[49]
PLA	1.25	70	3.6	2.4	55–65	170–200	<2	[108–111]
Elum [®]	1.20	66	3.17	2.6	107	-	0.5	[87, 90, 93]
TPU	1.20	40	0.2–2.3	>500	-8–17	140	0.1	[49, 112]
PEK	1.30	115	3.7	20	228	-	0.07	[48, 113]
PET	1.38	69	3	13	72	255	0.5	[49]
PPA	1.18	90	2.5–3.5	6	121–138	310–330	0.36	[49, 100]

It also should be noted that due to natural fibres being hydrophilic, polymers with non-hydrophilic groups may lead to poor fibre-matrix adhesion [4]. Therefore, there may be a competing mechanism here in the monomer/polymer selection. If the polymer is too hydrophilic, high moisture absorption is likely to reduce the properties of its composites. On the other hand, a hydrophobic polymer may lead to a poor fibre-matrix interfacial strength, in consequence reduced mechanical properties of the composite. A polymer with moderately hydrophilic groups may be more suitable for natural fibre composites in marine environments.

5 Criteria for resin selection

The objective of the SeaBioComp project is to produce natural fibre bio-based thermoplastic composites with comparable mechanical properties and durability for marine applications. In order to achieve this via in-situ polymerisation infusion, there are some criteria for monomer/resin selection.

1. Essential criteria

- The viscosity of the monomer must be $< 1000 \text{ mPa}\cdot\text{s}$ (NIP) to enable the infusion process.
- The processing temperature must be $< 200 \text{ }^{\circ}\text{C}$ to reduce the cost of consumables and minimise the thermal degradation effect for natural fibres.
- Monomer/resin must be bio-based or have potential bio-based sources available.
- Low water sensitivity to maintain proper mechanical properties in marine environments.

2. Desirable criteria

- The open window for infusion should be relatively long to enable the production of a large-scale demonstrator with 3D geometry in the future.
- The cost of the monomer/resin should be relatively low.
- The embodied energy of the product is low across the entire life cycle.

Prabhakaran et al [49] reported a decision making methodology (multiple attribute decision making) in resin selection for vacuum infused of a thermoplastic wind turbine blade. They considered the viscosity, processing temperature, cost and availability of the different resin systems, including PMMA, PA6, PA12, PET, TPU, PBT, PC, PEK and PPA. Using a scoring method to evaluate, the ranking of the resin was demonstrated as: PA6 > PBT > PMMA > PPA > PA12 > PET > PC > TPU > PEK. In their conclusion, PA6 and PBT were chosen as candidate resin materials for the wind turbine blade. However based on criteria mentioned above, PA6 and PBT resin systems are not suitable for composite production in the SeaBioComp project. For PA6, it was reported that the moisture absorption could be up to 11% [49], which leads to a significant property reduction of its composites. For PBT, there is no bio-based CBT oligomer reported for the moment as mentioned in Section 3.2. For other thermoplastic polymers in Tables 1 and 2, due to their high processing temperatures, PC, TPU, PEK, PET and PPA cannot meet the essential temperature criterion. In addition, there is no known bio-based monomer available for PA12, which will exclude it from application in bio thermoplastic marine composites.

PMMA resin does not show such drawbacks; it almost perfectly meets the essential criteria. As a novel PMMA resin, although the cost of Elium[®] resin is higher [49], the low processing temperature could significantly reduce the cost of consumables for infusion. Elium[®] resin is not bio-based for the moment; nevertheless, bio-based MMA monomer is already available as mentioned in Section 3.5. Therefore, we believe bio-based Elium[®] is likely to be available in the near future. Besides essential criteria, Elium[®] offers some additional advantages. For example according to the technical data sheet, Elium[®] 188 XO (a grade of Elium[®] resin designed for natural fibres) has a processing open window of up to 60 min, a low peak exothermic temperature during polymerisation and being

recyclable (will be discussed in Section 6). In addition, Elium[®] resin is weldable [87]. A significant issue that could arise with a PMMA matrix is performance when exposed to fire. At elevated temperatures, the polymer depolymerises to produce a flammable monomer. On the night of 2 August 1973 at Douglas on the Isle of Man, Oroglas (Arkema trade name for acrylic glazing) was implicated in the rapid fire spread through the Summerland leisure centre. Fifty people were killed and 80 seriously injured.

PLA resin could be an alternative to PMMA as the matrix material. However according to Section 2.3, the process temperature of PLA (~185 °C [85]) will increase the cost of the consumables. It is also likely to result in mechanical degradation of natural fibres, so that fibre treatment may be needed to increase the thermal degradation temperature of the fibre reinforcement. Most importantly, PLA was believed to have low durability in the marine environment [101]. A study showed that the biodegradation ratios of PLA bag and bottle were ~8.4% and ~5.7% respectively after 365 days in the ocean water [114]. These drawbacks of PLA resin require further consideration.

6 Recyclability

The composites produced by ring-opening of monomers/oligomers should be processable by granulation and re-melting to produce short fibre composites of lower duty than the original continuous fibre reinforced composites. As one of the main advantages of Elium[®] resin, Arkema states two types of recycle processes on their website: (i) mechanical recycling and (ii) reactive recycling [115]. In mechanical recycling, the Elium[®] composite structures are ground down to granules; these fragments can be used to make new composite parts after being heated. In reactive recycling, the granules are heat-depolymerised into initial raw monomer at a higher temperature, which can be utilised for totally new composites. Meanwhile, the remaining carbon or glass fibres can be reused.

Cousins et al [116] comprehensively discussed four techniques for recycling glass fibre Elium[®] composites, (i) thermal decomposition, (ii) mechanical grinding, (iii) thermoforming and (iv) dissolution. The idea of thermal decomposition is to decompose the Elium[®] resin to recycle the glass fibre reinforcement, which is simple but will lose the matrix materials. Mechanical grinding is a mature technology in composite recycling and it only required low energy cost (0.29 MJ/kg_{composite}) in their study. The ground materials were made into samples for tensile testing by injection moulding. Mechanical results demonstrated higher modulus and strength compared with virgin composites with short glass fibres. In terms of thermoforming, they successfully straightened a curved spar cap under 120 °C and 5.4 kPa for 8 h. Furthermore, a prototypical skateboard was constructed with the thinner sheets planed from the straightened composite components. Glass fibre Elium[®] composites can also be recycled via

dissolution into their constituent parts. Although volatile solvent was required, both fibre reinforcements and matrix materials (~90%) can be recycled with the energy cost of 4.0 MJ/kg_{composite}.

It should be noted that some of the recycling methods discussed above may not be suitable for natural fibre Elium[®] composites, further consideration is required. It would be helpful to undertake a life cycle assessment to evaluate these recycling approaches. For example, whether the new environmental burdens arising from the reactive recycling are lower than those arising from reprocessing the ring-opened monomer systems by granulation and remelting in e.g. extrusion or injection moulding to produce short fibre composites.

For PLA resin composites, it would be interesting to investigate the feasibility of PLA fibre-PLA (self-reinforced) composites in marine environment, as it could offer great advantages in composite recycling.

7 Latent catalysts or hardeners

Catalysts or hardeners with no activity under normal (ambient) conditions, which can be activated by an external stimulus (heat, ultraviolet, etc.) to initiate chemical reactions are known as “latent” catalysts or hardeners, respectively. The catalysis is delayed until a single activation event triggers multiple subsequent catalytic reaction sites. The three principal initiation mechanisms are thermal-, photochemical- and mechano-catalysis. Mechano-catalysis is most likely to be used in the development of autonomous self-healing materials [117-119].

Subject to the identification of appropriate monomer for infusion of thermoplastic matrix composites, there could be scope for extending the open window (keeping the viscosity low until mould fill) of the system through use of a latent catalyst or harder. Although Elium[®] resin shows an open window up to 60 min, this could still be a significant advantage for the infusion of large-scale composite structure with 3D geometry.

8 Conclusion

The monomer selection for the production of natural fibre bio-based thermoplastic composites for marine applications, via in-situ polymerisation infusion has been discussed in this report. Several parameters of the thermoplastic polymer were considered including (i) monomer viscosity, (ii) processing temperature, (iii) moisture absorption, (iv) mechanical properties, (v) bio-based availability and (vi) recyclability. It was concluded that the acrylic Elium[®] resin best fits the criteria for monomer selection, thus should be the candidate thermoplastic resin. It should be noted that although Elium[®] resin is not bio-based for the moment, we believe bio-based alternatives with similar properties should be available in the market in the near future. In addition, special attention should be

given to the recycling of its composites to minimise the cost/energy required and environmental impact; life cycle assessment may be needed for evaluation. Moreover, latent catalyst could be used to further improve the open window for the infusion. Future work may focus on the influence of Elium® resin to the permeability of natural fibre reinforcements. Finally, PLA resin could be an alternative although the relatively high processing temperature and durability issues may be problematic.

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