LACTIDE IN *IN SITU* POLYMERISATION (ISP) DURING MONOMER INFUSION UNDER FLEXIBLE TOOLING (MIFT).

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ABSTRACT

Large composite marine structures normally use fibre-reinforcements in a thermoset resin and are often manufactured by resin infusion. These materials have limited options for disposal at end-of-life and are not easily recycled. Thermoplastics are too viscous to infuse even in the molten state. Thermoplastic matrix composites might be manufactured by *in situ* polymerisation (ISP) during monomer infusion under flexible tooling (MIFT). Two monomers were identified as candidates for ISP-MIFT. Fossil-based acrylic infusion monomers are commercially available, but bio-based monomers are new to the market and there is no infusion grade to date. Lactide is bio-based by default but requires processing at elevated temperatures (hence higher energy consumption with consequent environmental burdens). This paper reveals some of the constraints encountered in the development of ISP-MIFT for lactide.

Keywords: *In situ* polymerisation, Lactide, Monomer infusion

1 INTRODUCTION

In 1972, the book *The Limits to Growth* [1] suggested that the human race should seek to reduce population growth and material consumption. At the time, the population of the earth was ~3.8 billion people. Estimates of the carrying capacity of the only available planet suggest a population between two billion and four billion people dependent on the political will to solve the associated problems. The United Nations recorded the world population at 8 billion people on 15 November 2022. Sir David Attenborough has said “All of our environmental problems become easier to solve with fewer people, and harder – and ultimately impossible – to solve with ever more people”.

In 1987, Gro Harlem Brundtland defined sustainability using the phrase “Humanity has the ability to make development sustainable to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs” [2]. Figure 1 shows the growth of the world population and Earth Overshoot Day (previously calculated as days/earth used by humans), indicating that there is now an even greater gap to bridge.

International co-operation to address the problems the world faces are addressed by the Conferences of The Parties (COP) on Climate Change and on Biodiversity. All activity consumes energy and fossil fuels generate exhausts which contribute to global warming. Many activities generate waste streams which can become pollution if not mitigated at source. UNESCO state that 80% of all marine pollution is plastic waste arising from littering, improper manufacturing processes and industrial fishing [3]. The long-term ecological impact of plastic litter and microplastics in the marine environment is a growing issue that has gained considerable momentum in public perception and global media [4].

The United Nations Sustainable Development Goals (SDG) are “the blueprint to achieve a better and more sustainable future for all”. Sustainability is defined in many ways but we choose to define sustainability as a balance of technical, economic, environmental, social, and governance (TEESG) issues. The use of recyclable thermoplastic as the matrix for large marine structural composites has the potential to address SDG6 Clean Water and Sanitation, SDG8 Decent Work and Economic Growth, SDG9 Industry, Innovation and Infrastructure, and SDG12 Responsible Consumption and Production.

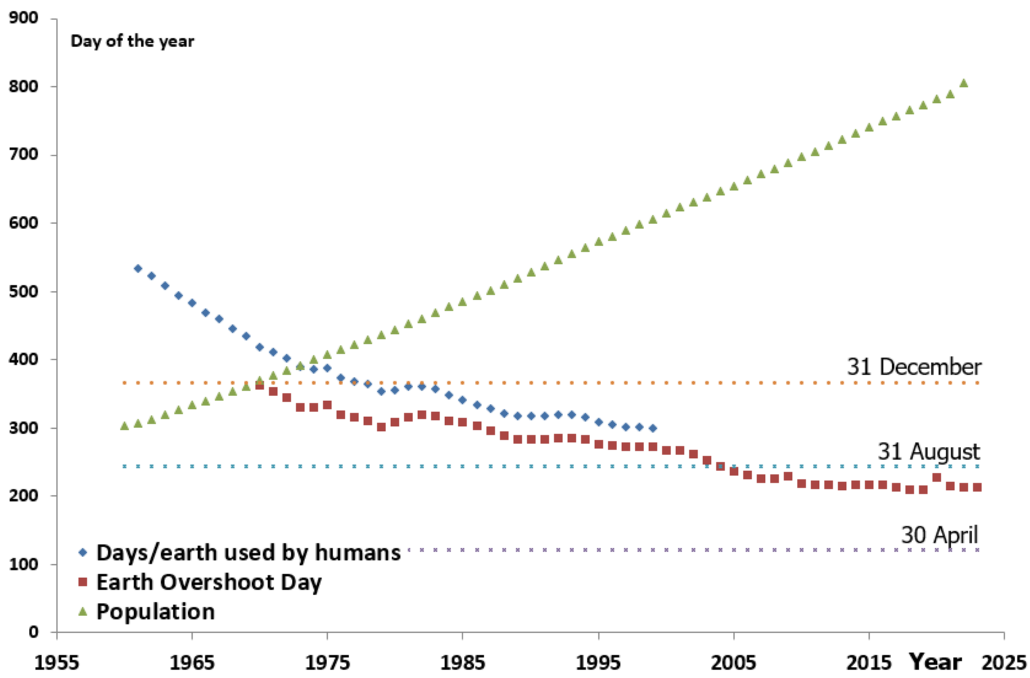

Figure 1: The World Population (y-scale x 10 million), and Earth Overshoot Day, against time

The ERDF/InterReg 2 Seas Mers Zeeën SeaBioComp project sought to develop durable biobased composites for use in the marine environment. Bio-based polymers, or polymers from renewable resources, could be a viable substitute to conventional oil-based polymers for many applications. The change might significantly reduce greenhouse gas emissions and has potential to ease end-of-life issues if the materials are biodegradable. One of the polymers of interest is poly(lactic acid), or poly(lactide) produced from the dimer. The SeaBioComp project primarily used compression moulding or fused filament additive manufacture of the polymer to produce demonstrator components. The University of Plymouth thread explored ISP-MIFT to polymerise the monomer during infusion manufacture of the polymer.

2 LARGE MARINE COMPOSITE STRUCTURES

For large composite structures, the process of choice would be Resin Infusion under Flexible Tooling (RIFT), also known as SCRIMP, VARTM or a multitude of other abbreviations (Figure 2) [5-7]. However, molten thermoplastic polymers typically have viscosities far higher than those used for the Liquid Composite Moulding (LCM) processes. Further, the melt temperatures of many thermoplastic systems are higher than the degradation temperature of the lignocellulosic fibres used in biocomposites.

3 INFUSED THERMOPLASTIC MATRIX COMPOSITES

Van Rijswijk and Bersee [8] reviewed in situ polymerisation for thermoplastics and classified the principal systems of potential use for Monomer Infusion under Flexible Tooling (MIFT). Qing et al [9] further down-selected monomers suitable for biobased composites to be used in the marine environment with natural fibre reinforcement. The parameters considered were (i) monomer viscosity, (ii) processing temperature, (iii) moisture absorption, (iv) mechanical properties, (v) bio-based availability, (vi) process open window, (vii) cost, and (viii) recyclability. Commercially available acrylic resin was the best fit to the above criteria, so chosen in the expectation that a bio-based infusion system will become available in due course. Lactide is inherently bio-based but the ISP-MIFT process is immature.

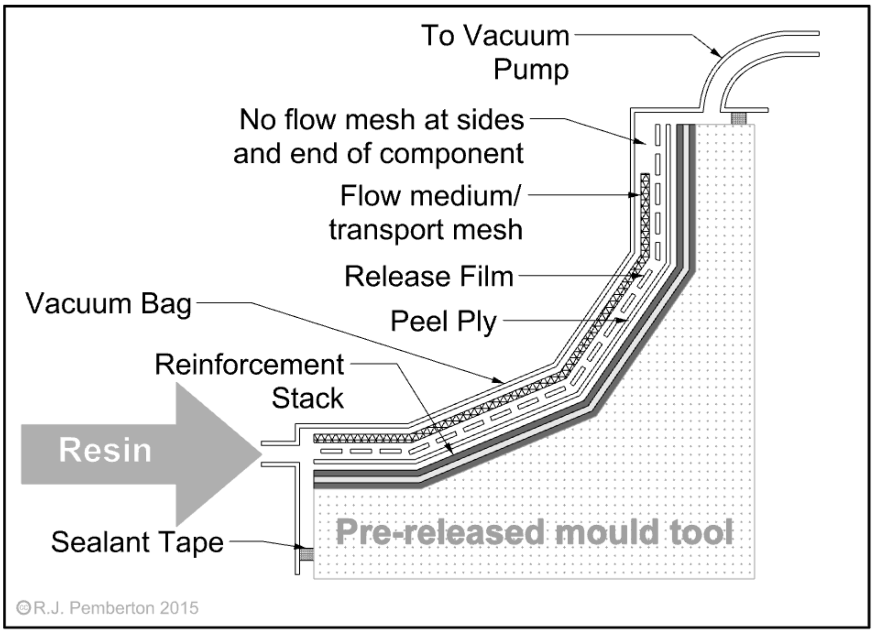

Figure 2: Resin infusion under flexible tooling with a flow medium (RIFT II).

4 LACTIDE MONOMER

Poly(lactic acid) can be manufactured by direct condensation polymerisation of lactic acid which is produced from the fermentation of 100% natural resources (*e.g.* corn or sugarcane). Lactic acid has the formula $CH_3CH(OH)COOH$ with molecular mass 90 g/mol, while the cycloaliphatic lactide dimer has the formula $C_6H_8O_4$ with molecular mass 144 g/mol. The *in situ* condensation polymerisation of lactic acid during infusion would release 20% of the mass as water, and that would become voids in the composite compromising the mechanical properties. The dimer of lactic acid (lactide) polymerises by ring-opening without releasing water.

Lactide is supplied as a white crystalline solid with a melting range of 90-100°C. The product data sheet for lactide says “preferably store below 35°C” [10, 11]. On returning from Covid-19 lockdown, the open package of lactide had gone into solution (deliquescence) in the moist air in the laboratory. A recently delivered package of lactide was labelled “packed under vacuum .. content is moisture sensitive .. use immediately after opening or keep under a nitrogen atmosphere”. Our technical team advised that “storing 20 kg under an inert gas is going to be a challenge”! [12].

5 COMPOSITE MANUFACTURE

The literature on the use of poly(lactide) in Liquid Composite Moulding (LCM) processes beyond the SeaBioComp process is limited to a single paper by Louisy et al [13]. They produced glass fibre reinforced poly(lactide) but the focus was on the degree of polymerisation rather than mechanical performance.

The constituent materials for the SeaBioComp composites subjected to mechanical testing were:

- flax natural fibre reinforcement as a 2 x 2 twill weave fabric with an areal weight of 200 g/m^2 from Easy Composites, UK,
- Elium® 188 XO from Arkema, France catalysed with 2% by weight of benzoyl peroxide (formulated with 25% H_2O), and
- L-lactide from Total Corbion, Netherlands catalysed with one-part-in-500 Tin(II) 2-ethylhexanoate, *i.e.* $Sn(Oct)_2$, of purity >92.5%.

Both catalysts were supplied by Sigma-Aldrich, Germany. The monolithic biaxial composites were made with seven layers of fabric and were subjected to vacuum degassing in the bag for 24h before infusion. Infusion was at ambient temperature (acrylic), or 170°C in an oven (lactide). The acrylic was post-cured in an oven at 80 °C for 1 h. The lactide was cured on the mould in the oven at 170°C for 3h. The fibre volume fractions achieved were ~31%.

Poly(lactide) has a glass transition temperature of 56-63°C and a melt temperature of 125-178°C [14]. This close pair of transition temperatures means the polymer can be melt processed without significant damage to lignocellulosic fibres, and can be used at ambient temperatures without creep.

6 MECHANICAL PROPERTIES

Flexural tests were conducted in three-point bending according to the ASTM D790 standard with a test span of 48 mm and a crosshead speed of 1.28 mm/min on an Instron 5582 screw-driven 100 kN universal test machine with a 5 kN load cell. For flexural modulus, flax/acrylic samples achieved 53%, while flax/PLA samples only achieved 37%, of properties predicted by rules-of-mixtures (Table 1). For flexural strength, using the Kelly-Tyson equation and only considering fibres aligned with the stress, flax/acrylic samples achieved 104%, while flax/PLA samples only achieved 62% of the predicted properties (Table 1) [15].

Table 1: Flexural properties for flax/PLA and flax/acrylic composites.
Experimental data is mean ± standard deviation (coefficient of variation) [15].

	Flexural modulus			**Flexural strength**		
Composite	Experimental (E) (GPa)	Prediction (P) (GPa)	E/P (%)	Experimental (E) (MPa)	Prediction (P) (MPa)	E/P (%)
Flax/PLA (170°C)	3.66±0.31 (8.5%)	9.86	37.1	56.98±9.58 (16.8%)	91.7	62.1
Flax/Elium (good)	4.98±0.42 (8.4%)	9.45	52.7	123.73±4.96 (4.0%)	119.3	103.7
Flax/Elium (poor)	4.32±0.29 (6.7%)	9.45	45.7	91.15±3.63 (4.0%)	119.3	76.4

The flax reinforcement fibres were used as received with no information on fibre surface treatment. The ester group in both acrylic and PLA are likely to hydrogen bond with the alcohol groups in the cellulose molecule (and other constituents of the lignocellulosic fibre) to create weak interfacial bonds. There may be scope for the development of coupling agents to produce stronger interfacial bonds.

7 DEMONSTRATOR COMPONENT

The SeaBioComp project sought to deliver a 5G telecommunication dome as a demonstrator component. The intention was to use integral fluid-heated infused composite tooling, but despite placing the order with a well-respected supplier, production of the mould tool proved to be a challenge, and it was not delivered in the time frame of the project.

The mould tool required for ISP-MIFT manufacture of poly(lactide) matrix composite demonstrator requires a state-of-the-art composite mould tool (or an unaffordable metal mould tool) for monomer infusion in the range 120-180°C. The reinforcement geometry for the demonstrator component creates low permeability volumes which are difficult to fill, and in the limit remain as dry spots. The high-temperature resin system is more viscous than is normally used for an infused tooling resin. The combination of complex geometry, with differential expansion between composites and metal heating tubes, was a further challenge.

9 LIFE CYCLE ASSESSMENT

Life Cycle Assessments (LCA) for composite material systems are constrained by system and data quality issues. A significant number of publications in the public domain need to be critically analysed to ascertain the true value of the information presented. The international standards provide for a range of functional units, goal and scope, system boundaries, and allocation between primary products and other by-/co-products such that very few LCA can be directly compared. Similarly, the availability of life cycle inventory data is such that specific materials are rarely in the databases, and the chosen proxy materials may not fully reflect the system being assessed.

Life Cycle Assessments (LCA) are available for poly(lactide) [16-22], but no previous LCA addresses ISP-MIFT production of the polymer. The inventory data for the production of lactide monomer was provided, by the Regulatory and Sustainability Manager at the supplier, but is subject to a Non-Disclosure Agreement. Initial assessments have been undertaken with the available data, but the authors are cautious about release of the information beyond the consortium [23].

9 CONCLUSIONS

The MIFT process for lactide was, and remains at, Technology Readiness Level (TRL) 1, with the SeaBioComp project possibly moving the technology to TRL2. While it may be suitable for just-in-time manufacture, storage of material under dry nitrogen presents challenges. The process temperatures are challenging for integrally-heated composite tooling, so oven-cure or metal mould tools may be appropriate. The composites do not achieve the predicted mechanical properties. The use of an appropriate coupling agent on the natural fibres could improve the composite performance.

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Interreg 2 Seas Mers Zeeën | SeaBioComp

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