



Reactive Processing of Acrylic-Based Thermoplastic Composites: A Mini-Review

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The demand for thermoplastic composites is continuously increasing because these materials offer many advantages over their thermoset counterparts, such as high toughness, long storage time, easy repairing and recycling, and ability to be thermoformed and heat-welded. However, the manufacturing of thermoplastic composite parts using liquid composite moulding techniques (e.g. resin transfer moulding, vacuum assisted resin transfer moulding ...) is often tricky in the case of melt processing where high temperature and pressure should be chosen to impregnate the fibre reinforcement because of the high melt viscosity of thermoplastics. These issues may be overcome by means of reactive processing where a fibrous preform is first impregnated by a low viscosity mono- or oligomeric precursor and the polymerization of the thermoplastic matrix then occurs *in-situ*. This article draws a state of the art on the manufacturing characteristics of continuous fibre reinforced acrylic-based reactive thermoplastics (e.g. polymethylmethacrylate (PMMA) such as Elium®), which are becoming more and more popular compared to other fast curing thermosets and thermoplastics for *in-situ* polymerization. Techniques for the *in-situ* polymerization of methylmethacrylate monomers, characterization and modelling of the rheological properties and polymerization kinetics, and some manufacturing related issues such as polymerization shrinkage are reviewed. Particular features of the use of reactive PMMA in different manufacturing techniques of continuous fibre reinforced composites and potential industrial applications are also introduced. Finally, some perspectives for the academic research and industrial development are proposed.

Keywords: thermoplastic composites, composites manufacturing, reactive processing, *in-situ* polymerization, acrylic

INTRODUCTION

Thermoplastic Composites (TPCs) provide some competitive advantages over thermoset counterparts such as better toughness and impact resistance, recyclability, weldability and reshapability, etc. (Mitschang, 2012; Stavrov and Bersee, 2005; Steenkamer and Sullivan, 1998; Krawczak and Maffezzoli, 2020). Today, thermoplastic composites account for 40–50% of polymer matrix composites and this share is steadily increasing (JEC Observer, Current trends in the global composites industry 2021–2026). Currently, the most popular form of thermoplastic composites is discontinuous glass fibre reinforced thermoplastics for injection moulding, whereas most of structural composites reinforced by continuous fibres are still thermoset ones.

In the case of continuous fibre reinforced thermoplastic composites, the standard material is prepreg or semipreg where fibre reinforcement has already been impregnated by matrix material before the manufacturing of structural parts. These semi-products such as prepreg or semipreg should be submitted to another step of manufacturing process such as thermoforming or automated tape layup (a.k.a. automated fibre placement) to obtain final composite parts (Gutowski et al., 1987; Chow, 2002). Hence, the total cost of manufacturing process is higher than that of direct manufacturing routes such as liquid composite moulding processes of thermoset composites. The main reason for the need of semi-product preparation is high viscosity of thermoplastic melt which makes the impregnation process difficult (Wang and Gutowski, 1991; Taketa et al., 2020). The issue of high viscosity of thermoplastic melt poses a problem in semi-production fabrication as well. Therefore, some special methods are often employed to obtain prepreg sheets. The most representative one is the use of a pre-mixed form of reinforcing fibres and solid state matrix material such as powder impregnated fabric, commingled yarn and film stacking, which is consolidated under heat and pressure (van Rijswijk and Bersee, 2007). Meanwhile, the direct impregnation of thermoplastic melt into fibre reinforcement via hot melt method is also employed for thermoplastic prepreg fabrication. Nevertheless, the residue of solvent used to decrease the viscosity of thermoplastic melt can be a technical issue. For instance, the evaporation of N-methylpyrrolidinone (NMP) during the melting process of polyetherimide (PEI) prepreg is a typical problem in hot melt method for high molecular weight polymer prepreg manufacturing (Hou et al., 1998; Mairtin et al., 2001). Moreover, due to the high viscosity of thermoplastic matrix, a high processing temperature is required to manufacture complex parts without process-induced defects such as imperfect impregnation or wrinkle formation. In particular, for high performance polymers such as polyphenylenesulfide (PPS) which have a high melting point, all the steps of prepreg and final part manufacturing require high temperature for melting, leading to an increase in the number of cross-links, and hence resulting in a more brittle matrix (Chen et al., 2021). This high processing temperature related to the high viscosity and high melting point of thermoplastic melt can be even crucial in the case of natural fibre reinforced composites because natural fibres such as flax and hemp fibres begin to thermally degrade at a temperature range between 170 and 200°C (Kim and Park, 2017).

All the aforementioned problems related with melt processing can be substantially addressed by the reactive processing of TPCs (van Rijswijk and Bersee, 2007). During the impregnation process, a low viscosity mono or oligomeric precursor flows into the pores between fibres and the precursor is subsequently polymerized *in-situ* in the mould. Therefore, this kind of reactive processing methods are analogous to Liquid Composite Moulding (LCM) processes such as Resin Transfer Moulding (RTM) and Vacuum Infusion (VI) or Vacuum Assisted Resin Transfer Moulding (VARTM) of thermoset composites where fibre reinforcement is impregnated by low viscosity

monomer and the resin is cured inside the mould (Bodaghi et al., 2020; Matadi Boumbimba et al., 2017; Obande and Bradaigh, 2021). In general, this reactive processing requires a high process temperature for *in-situ* polymerization, however and is not adapted for large part manufacturing (e.g. wind turbine blade, boat hull, etc.) where mould heating is relatively tricky, and for natural fibre reinforced composites manufacturing where the process temperature cannot exceed the temperature of thermal degradation of fibres.

Recently, acrylic resin for reactive processing such as Elium® (Arkema) is attracting great attention by virtue of its low process temperature (even room temperature) and recyclability. It has great potentiality for the manufacturing of large structures such as wind turbine blade and yacht which are generally produced at room temperature. Moreover, the recycling of those structures at the end of life cycle is a big issue nowadays. Hence, recyclable thermoplastic composites can be an excellent alternative to the conventional thermoset composites.

During the last few years, many research papers have been published about the characterization of Elium® and its composites (Obande and Bradaigh, 2021). Conversely, the research on the processing science is still in its infancy even if some industrial developments are on-going. In this mini-review, we make a critical review on some important topics related to the processing of reactive acrylic composites, such as rheology, polymerization kinetics and manufacturing issues (shrinkage, volatile generation, etc.). Even if the main focus of this mini-review is made on LCM processes, other manufacturing routes, such as filament winding (e.g. high pressure vessel manufacturing) and pultrusion, are also considered. In the end, we propose some perspectives about the future research.

PROGRESS IN *IN-SITU* POLYMERIZATION AND ACRYLIC RESINS (ELIUM®)

During the last two decades, a number of precursors for reactive thermoplastics have been developed. In the beginning, some precursors of reactive thermoplastic materials have been developed to obtain thermoplastic polymers via *in-situ* polymerization such as cyclic butylene terephthalate (Bank et al., 2004; Parton and Verpoest, 2005), caprolactam (van Rijswijk et al., 2009), and laurolactam (Mairtin et al., 2001; Zingraff et al., 2005), and more recently L-lactide (Louisy et al., 2019; Miranda Campos et al., 2022). Representative polymers for reactive processing are Polybutyleneterephthalate (PBT), thermoplastic polyurethanes (TPU), polyamides including Polyamide-6 (PA-6) and Polyamide-12 (PA-12) (van Rijswijk and Bersee, 2007). A crucial disadvantage of such thermoplastic systems is the requirement of high processing temperature, for example above 150°C for PA-6 and PA-12, 180°C for PBT and 270°C for TPU to achieve a viscosity of a few *Pa.s* (Figure 1). Qin et al. made a review of the processing temperature and the corresponding viscosity of commercially available thermoplastic monomers for *in-situ* polymerization, including several bio-based monomers suitable for reactive processing of polymers such as PA-6 and polylactide (PLA), and reported a similar conclusion (Qin et al., 2020).

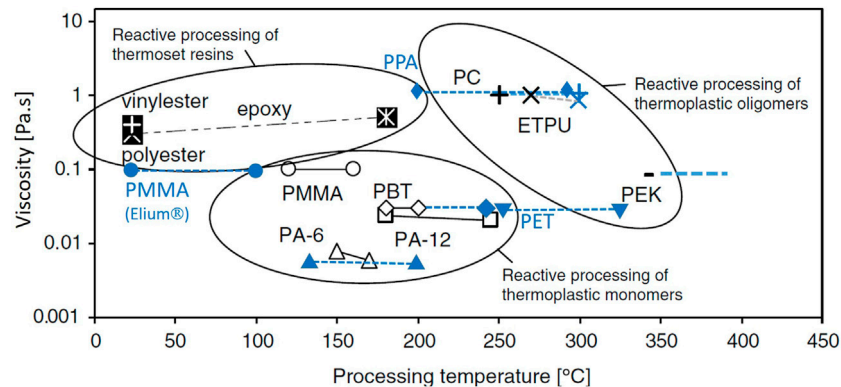


FIGURE 1 | Processing temperature and viscosity ranges of various polymers suitable for reactive processing (adapted from (van Rijswijk and Bersee, 2007), plotted in black and white, and (Qin et al., 2020), plotted in blue).

TABLE 1 | Benchmarking of E-glass fibre/acrylic against E-glass fibre/epoxy vacuum-infused laminates and corresponding matrix resins—Tensile, bending, shear, mode I interlaminar fracture toughness and thermomechanical properties (adapted from Obando et al., 2019 and Obando and Bradaigh, 2021).

Property (Measured)		Glass fibre/acrylic (Elium [®] 188 O)	Glass fibre/epoxy (SR 1710/SD 7820)	
Tensile properties (transverse)	Strength (MPa)	73 ± 3.9	54 ± 4.1	
	Modulus (GPa)	13 ± 0.6	13 ± 0.5	
	Failure strain (%)	1.2 ± 0.3	2.1 ± 0.2	
Bending properties (longitudinal)	Strength (MPa)	879 ± 49	869 ± 42	
	Modulus (GPa)	40 ± 1.7	38 ± 2.3	
	Failure strain (%)	3.3 ± 0.4	3.4 ± 0.6	
Bending properties (transverse)	Strength (MPa)	91 ± 5.4	94 ± 7.2	
	Modulus (GPa)	11 ± 0.2	12 ± 0.4	
	Failure strain (%)	1.7 ± 0.3	2.0 ± 0.2	
Short beam shear properties	Strength (MPa)	58 ± 1.7	57 ± 1.0	
Fracture toughness properties (Mode I)	G _{IC-Init.} (J/m ²)	556	466	
	G _{IC-Prop.} (J/m ²)	1,814	1,574	
Thermo-mechanical properties (DMA)	T _g , tan delta (°C)	106	119	
	Height of tan delta peak	0.76	0.45	
	Storage modulus at onset (GPa)	40	38	
Property (from technical datasheets or literature)		Range for different Elium [®] resin grades	Acrylic matrix – Elium [®] 188 O (Arkema)	Epoxy matrix – SR 1710/SD7820 (Sicomin)
Tensile properties	Strength (MPa)	66–76	66	78
	Modulus (GPa)	3.17–3.3	3.2	3.8
	Failure strain (%)	2.8–6	2.8	2.6
Bending properties	Strength (MPa)	111–130	111	117
	Modulus (GPa)	2.91–3.25	2.9	2.8
Glass transition temperature (°C)		116.2–123.4	120	127

The only material for *in situ* polymerization at room temperature which is available in the market is Elium® (Gardiner, 2015) (Qin et al., 2020) (Miranda Campos et al., 2022). Elium® acrylic resin is a mixture of 2-Propenoic acid, 2-methyl-, methyl ester or methylmethacrylate monomer (MMA) and acrylic copolymers. The combination of the resin with a compatible initiator system such as a benzoyl peroxide allows for the conversion of MMA to its polymer PMMA under diffusion-controlled reactions in a free radical polymerization. They provide the same mechanical properties as compared to epoxy resins (Table 1).

The resin with a viscosity of around 10 mPa.s allows to impregnate all the empty pores between the dry fibre reinforcement in its net shape in a closed mould such as RTM/VARTM. Moreover, some of its variants can be cured at ambient temperatures (Elium, 2022). TPCs with an acrylic polymer such as polymethylmethacrylate (PMMA) are more cost-efficient than the aforementioned first-generation reactive resins and have comparable tensile modulus to those of epoxy (Liu and Wagner, 2007). The synthesis of PMMA can be carried out by bulk free radical vinyl polymerization of the

methylmethacrylate monomer (MMA). The use of benzoyl peroxide in the presence of an amine will generate the radicals under milder conditions (i.e. at room temperature). In other words, this type of polymerization reaction does not require an additional heat source for the initiation of the reaction (Goseki and Ishizone, 2014).

The properties of Elium[®] acrylic-based composites have been studied by many authors. Obande *et al.* have summarized the published literature on comparative performance of acrylic composites reinforced with flax, glass, carbon and vegetal fibres against comparable epoxy composites (Obande *et al.*, 2019). The authors have also made a comprehensive benchmark of E-glass fibre/acrylic against E-glass fibre/epoxy laminates showing that the former exhibited comparable and marginally superior mechanical performance and even significantly higher fracture toughness (+15–19%) and tensile transverse strength (+33%) than its counterpart (Table 1).

RESEARCH TREND ABOUT ELIUM[®]

By searching for “Elium[®]” in Scopus, 75 papers contain this term in their title, abstract, or keywords. From the analysis of 75 papers published since 2016 in more than 10 journals and three conference proceedings, it is observed that most of the research papers are related to impact properties of Elium[®] based FRP composites. These recent advances have already reported remarkable enhancement, especially in the impact response (up to 40% increase in the impact energy absorption (Bhudolia *et al.*, 2021)) and structural integrity (21% lower loss (Bhudolia *et al.*, 2020a)) of Elium[®] based composites in comparison with their epoxy counterparts. The importance of moulding methods for *in-situ* polymerization of Elium[®] based composites has recently been dealt with only in fewer than five papers per year. The same trend is observed with respect to the polymerization (Han *et al.*, 2020), weldability (Bhudolia *et al.*, 2020b), and recycling of Elium[®] based FRP composites (Bel Haj Frej *et al.*, 2021; Khalili *et al.*, 2021).

As the key advantage of reactive thermoplastic monomer is *in-situ* polymerization, the characterization of polymerization and its modelling have been the main research topics with respect to the manufacturing process. Indeed, the polymerization kinetics has been a classic research topic for many decades and a wide span of literature exists about this subject. There are new challenges, however, when the process cycle time should be reduced to less than two or 3 mins, as needed for mass production of automotive vehicles, and adapted materials should be developed (Henning *et al.*, 2019). For example, the polymerization of highly reactive acrylic resins starts while the mould is still being filled (Han *et al.*, 2020). Moreover, it is indispensable to develop a reliable simulation tool for fully automated and reproducible composites manufacturing processes (Chai *et al.*, 2021).

Polymerization of the methylmethacrylate monomer (MMA) into its polymer PMMA is carried out by free-radical addition polymerization. The free-radical polymerization of MMA occurs in a bulk state, consisting of only monomers, polymer, and

initiators. The final product is, therefore, of high purity as there is no other additive contaminant (Mills *et al.*, 2020).

The mechanism of bulk free radical polymerization of MMA has been well reported in the literature (Oadian, 2004; Mita and Horie, 1987; Biondi *et al.*, 2010). The analysis of polymerization is critical not only for the optimization of process cycle time but also for the minimization of residual stress generated during the manufacturing process. In particular, the exothermic reaction heat generation during the conversion of MMA into PMMA is relatively great (57 kJ/mol, three times greater than typical epoxy resins) and the corresponding residual stress induced during the polymerization can be more pronounced in the manufacturing of thick products (Han *et al.*, 2020; de Andrade Raponi *et al.*, 2018a; Murray *et al.*, 2019).

The optimisation of MMA polymerization depends on many variables in the production process such as temperature history, processing time, part size, and may help to reduce the amount of scrap associated with cost and environmental implications without compromising the performance of composite components (Terrazas-Moreno *et al.*, 2008; Asteasuain *et al.*, 2006; Flores-Tlacuahuac and Biegler, 2008; Flores-Tlacuahuac and Biegler, 2007; Rivera-Toledo *et al.*, 2006). Nevertheless, the most important parameter is the temperature history. To distribute heat generation under a controlled temperature history, and subsequently reduce the occurrence of thermal runaway, one possible scenario is to use different initiators by simultaneously triggering initiator scission at different times (Cioffi *et al.*, 2001; Cioffi *et al.*, 2004; Pojman *et al.*, 1995; Pojman *et al.*, 1995; Ray *et al.*, 1995; Ram *et al.*, 1996; Garg *et al.*, 1999). In addition, the initiator content and thermal history of a reacting system are very important parameters to achieve the optimum condition for MMA polymerization.

With respect to the development of mathematical models for polymerization kinetics, there have been several works in the literature (Zoller *et al.*, 2015; Suzuki *et al.*, 2018; Charlier *et al.*, 2018) based on the previous works about free radical bulk polymerization (Achilias, 2007; Barner-Kowollik *et al.*, 2005; Russell *et al.*, 1988; Buback, 1990). Based on the model by Zoller *et al.* (2015) software PREDICI was developed (Zoller *et al.*, 2016) and used to optimize the acrylic resin polymerization kinetics during the pultrusion process (Zoller *et al.*, 2019). In another model developed by de Andrade Raponi *et al.* (de Andrade Raponi *et al.*, 2018a; 2018b), the type (for example, dibenzoyl peroxide or other peroxide systems) and content of initiators were also considered.

As stated above, most of works in the literature have focused on the analysis and characterization of polymerization kinetics so far, even if there are many other important issues related to the manufacturing. In the subsequent section, some important other subjects to address in terms of manufacturing will be stated.

FUTURE RESEARCH OUTLOOK

Rheology

Because the low viscosity of monomers is a key to the use of Elium[®], the characterization of its viscosity has been performed at

its monomer state. In some manufacturing processes where a very short process cycle time is required (e.g. mass production in the automotive sector), however, the polymerization of monomer and the impregnation of reinforcement by the resin take place simultaneously. The monomer of Elium[®] has the viscosity around 0.1 Pa·s which is equivalent with that of thermoset counterparts. Nevertheless, its viscosity increases greatly, as the polymerization proceeds, even if its degree of conversion is still low for example, about 10% (Suzuki et al., 2018; Miranda Campos et al., 2022). Hence, it is important to establish a mathematical relation (for example, in a function of Arrhenius) among the temperature, the degree of conversion and the viscosity of Elium[®] as has been done for thermoset resins. Moreover, the non-Newtonian behaviour, namely, the relation between the viscosity and the shear rate, should also be investigated.

- As a matter of fact, this task is not easy because the polymerization of Elium[®] takes place instantly and the corresponding change of viscosity is also fast. Nevertheless, the viscosity characterization in terms of temperature and conversion degree has been addressed for other types of fast curing thermoset resin such as dicyclopentadiene (DCPD) and epoxy in the literature (Ng et al., 1994; Rhode et al., 2015). Hence, this subject can be dealt with by adopting or adapting the characterization methods used for such materials.

Different Polymerization Strategies

Up to now, the most common method for polymerization of Elium[®] is the thermally activated free radical polymerization process. To further decrease the polymerization cycle time, however, the photopolymerization method is also considered, for example in the COMPOFAST project (<https://www.jecomposites.com/news/lancement-du-projet-compofast/>). Indeed, the photopolymerization process where small molecules (i.e. monomers) are converted into large molecules (i.e. polymers) under a light (in general, ultra violet light) is very adaptable to additive manufacturing by virtue of its instant polymerization (Bagheri and Jin 2019). Therefore, the research in the photopolymerization of Elium[®] should be performed as its industrial application has already been exploited.

Polymerization Shrinkage

In general, polymer is submitted to a reduction of volume (viz. shrinkage) during its conversion from monomers, which is a different mechanism from thermal expansion or contraction.

The most detrimental effect caused by shrinkage stress in the production of polymer-matrix composite parts is debonding at the fibre/resin interface, which results in gap formation and matrix microleakage. These initial defects are detrimental to the stiffness and strength of polymer composites and also can accelerate environmental degradation which acts as sites for macrocracks nucleation (Hsissou et al., 2021; Schricker, 2017).

A more crucial issue for reactive polymer is the residual stress formed during the polymerization, however, because the shrinkage tends to be great for highly reactive resin such as Elium[®]. The residual stress can lead to the deformation of final

product such as warpage or spring-in, as well as the reduction of the strength and service life. In general, common PMMA has a relatively low shrinkage rate, e.g. 0.8% (Obande et al., 2019). On the contrary, Elium[®] has a much greater shrinkage (e.g. up to 10%) due to its fast polymerization process. Therefore, the influence of its polymerization shrinkage and the corresponding remedies should be investigated.

Diverse Manufacturing Processes and Applications

Elium[®] can be employed for diverse manufacturing processes such as liquid composite moulding processes (resin transfer moulding, vacuum infusion, compression RTM, etc.) (Bhudolia et al., 2020a; Bhudolia et al., 2021; Han et al., 2020), pultrusion (Zoller et al., 2019), filament winding, and welding (Bhudolia et al., 2020b; Gohel et al., 2020) and different grades are available for each manufacturing process. Moreover, new sheet moulding compound of Elium[®] has also been developed to replace the conventional thermoset SMC. Some industrial demonstrators such as boat hull, wind turbine blade and hydrogen tank were fabricated to demonstrate the manufacturing feasibility (Arkema, 2022). The current state of the art is still at a low TRL (Technology Readiness Level) and many issues such as process modelling and optimization, product durability and economic viability assessment, are yet to be addressed.

In particular, the interface adhesion mechanism during additive manufacturing and welding processes should be deeply investigated. In general, the establishment of interlaminar strength at the interface of thermoplastic matrix is modelled by the combination of the establishment of intimate contact and the polymer molecular interdiffusion across the contact interface, a.k.a. autohesion or reptation (Lee and Springer, 1987). In some manufacturing processes of Elium[®] such as additive manufacturing, however, the interfacial adhesion strength is built during the *in-situ* polymerization process. Hence, the corresponding mechanism is totally different and new modelling approaches will be needed.

Recycling

One of the most interesting advantages of Elium[®] is its recyclability. Some recycling technologies for Elium[®] have already developed. In particular, the mechanical recycling methods of flax/Elium[®] (Allagui et al., 2021) as well as carbon/Elium[®] and glass/Elium[®] (Gérard and Lafranche, 2018) have been investigated. In the case of mechanical recycling, however, recycled materials are complemented with virgin materials to obtain good mechanical properties. On the contrary, the technical feasibility for the chemical recycling method where Elium[®] can be recovered as monomers up to 100% by depolymerization has already been exploited (Arkema, 2022). Nevertheless, the fibres are submitted to severe degradation leading to significant reduction of mechanical properties. Recently, a physico-chemical recycling method by dissolution where both the matrix and the fibres can be recovered while keeping the fibre length has been developed (Gérard, 2022). As a result, more

intensive work on the process optimization, the characterization of the properties of recycled products and the analysis of life cycle should be performed.

CONCLUSION AND OUTLOOK

Elium[®] acrylic resin has been the subject of much study since its products were marketed and sold in 2014. For developing the Elium[®] acrylic resin, a mixture of 2-Propenic acid, 2-methyl-, methyl ester or methyl methacrylate monomer (MMA) and acrylic copolymers are used. Here a free radical polymerization is used to convert MMA to its polymer PMMA.

Owing to its low viscosity in a monomer state, the impregnation is relatively easy and the common manufacturing processes for thermoset counterparts can be employed. Moreover, on account of its fast polymerization process, the process cycle time can be greatly reduced compared with the conventional thermoset and thermoplastic composites manufacturing methods. Its room temperature process capacity and full recyclability are particularly advantageous in the design of large structures such as wind turbine blades and boat hull which have been manufactured by thermoset matrix composites.

So far, most of research efforts have been made for the characterization of material properties. With respect to the manufacturing characteristics, only a few research articles about the analysis of polymerization kinetics have been published in the literature and the scientific research about the other aspects such as rheology and process modelling is still in its infancy. In fact, the industrial research and development are

ahead the academic research as can be proven by some industrial projects and demonstrators. Nevertheless, there is still a far way to go for a widespread adoption of Elium[®] based composites in different industrial sectors. There remain a number of topics to address such as chemorheology, modelling, process-induced issues (e.g. polymerization shrinkage, volatile generation) and recycling.

AUTHOR CONTRIBUTIONS

MB: Conceptualization, Methodology, Formal analysis, Investigation, Writing-original draft. CP: Investigation, Writing, Review and Editing. PK: Investigation, Supervision, Resources, Review and Editing, Project administration.

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