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## REVIEW ARTICLE

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# Thermoplastic matrix-based composites produced by resin transfer molding: A review

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[Correction added on 30 Apr 2022, after the first online publication: ORCID for author Gaëlle Fontaine has been added]

## Abstract

The recycling of thermoset-based composites is challenging. The replacement of thermosetting resins with thermoplastics is an initial step to address this issue, together with the use of green reinforcements. Owing to the recent development of low-viscosity thermoplastic resins, it is possible to produce thermoplastic matrix composites using the resin transfer molding (RTM) technique, which was originally conceived for the production of thermosetting matrix composites. These resins are based on cyclic esters, methyl methacrylate, and cyclic (butylene terephthalate) oligomers. This review presents the state-of-the-art works reported on the production of thermoplastic matrix composites via a thermoplastic RTM (TP-RTM) process, from the in situ polymerization of the resins through the optimization of the TP-RTM parameters for the evaluation of the composite properties.

## KEYWORDS

polymer-matrix composites, thermoplastic resin, thermoplastic resin transfer molding

## 1 | INTRODUCTION

Composite materials have been used since antiquity. For example, the Mongols produced bows made of corn, wood fibers, and animal parts glued together, and the Japanese made swords with laminated steel.<sup>[1]</sup> In contrast to metallic or ceramic materials, polymer-based composites are lightweight, and can potentially show high specific strength and environmental compatibility.<sup>[2]</sup> Nowadays, the growing interest in composite materials is justified by the demands for materials used in several branches of industry, such as in the aerospace, biomedical, electronics, construction, and packaging fields.<sup>[3]</sup>

Polymer-based composites have been extensively studied in recent decades. A good balance between the mechanical properties and processability must be achieved to allow the large-scale use of these materials in industry. Among the manufacturing composite processes,

resin transfer molding (RTM), a liquid composite molding (LCM) technique, allows for the production of large parts of composites with good impregnation of the fibers. Thermosetting and thermoplastic composites can be produced by the RTM technique by using low-viscosity resins to impregnate the reinforcement.<sup>[4]</sup> In the case of thermoplastic-based composites produced by RTM, the reagents, called “reactive thermoplastic systems,” are composed of a mixture of monomers and/or oligomers. They are associated with a catalyst, and in some cases, an additional activator, which are mixed in a chamber and subsequently injected into a mold containing the reinforcement.<sup>[3]</sup> Afterwards, the polymerization reaction takes place in the mold to form the matrix and provide the composite material in a one-step synthesis. This review focuses on reactive thermoplastic systems. To simplify the terminology, in this paper, the reactive thermoplastic systems are named by mentioning the monomer

and then its resulting polymer, for example,  $\epsilon$ -caprolactam ( $\epsilon$ -CL)/Polyamide-6 (PA-6).

The RTM technique is usually employed in the production of thermosetting matrix composites. It also has progressively tended to be used for the conception of thermoplastic-based composites, as these composites display unique properties, thereby allowing for their use where thermosetting plastics are unsuitable, for example, when a part needs to be welded or recycled, or even when the part must undergo thermoforming processes. To differentiate between the RTM technique used for thermoset resins and that used for thermoplastic resins, several authors have used the terms T-RTM or TP-RTM for thermoplastic RTM, that is, the technique focused on in this review.<sup>[2,5–7]</sup>

Although a wide range of thermosetting resins are available on the market, there are only a few commercially available reactive thermoplastic systems suitable for in situ polymerization in the TP-RTM process, namely polyacrylate matrices (Elium<sup>®</sup>, Arkema), polyamides (Bruggolen<sup>®</sup>, Brüeggemann Chemical), and polybutylene terephthalates (Cyclics CBT<sup>®</sup>, Cyclics Corporation).<sup>[5]</sup> Regarding academic research, the use of certain cyclic esters as monomers (such as  $\epsilon$ -caprolactone and L-lactide [L-LA]) in the TP-RTM process has been studied, and has shown satisfactory results for the production of biodegradable matrix-based composite materials.<sup>[6,8,9]</sup>

The purpose of this review is to present the state-of-the-art regarding the production of thermoplastic matrix composites by TP-RTM, along with recent progress and future trends in this field. With the development of new reactive thermoplastic systems, a detailed discussion on the use of thermoplastics in TP-RTM is presented, along with discussions on improving the quality of composites produced by this technique. The production of composites composed of various thermoplastic matrices is discussed, including PA-6, polyamide-12 (PA-12), poly(L-LA) (PLLA), poly(methyl methacrylate) (PMMA), poly( $\epsilon$ -caprolactone) (PCL), and poly(cyclic butylene terephthalate). In addition, the technical specifications and suppliers of the raw materials are presented. Finally, the future trends in TP-RTM (in particular, the potential copolymerization of monomers using this versatile technique) are discussed.

## 2 | RTM PROCESS

The RTM is a LCM process in which a low-viscosity resin is injected under pressure into a closed mold containing predisposed reinforcements, where polymerization occurs to form a matrix. A primal form of RTM was employed in the 1940s by the US Navy to manufacture boats from

glass fiber polymer composites.<sup>[10]</sup> To date, interest in RTM and in the optimization of this technique to obtain parts with higher mechanical performances are growing. A significant development occurred in the 1980s with the introduction of structural parts for the aeronautical, automobile, and military industries.<sup>[10]</sup> The development of new LCM machines in mid-2010 enabled a breakthrough in the use of thermoplastic resins, notably with a PA-6 matrix, in the TP-RTM process.<sup>[5]</sup>

The RTM and TP-RTM processes essentially follow five stages: reinforcement placement, mold filling, polymerization or curing (term used for thermosetting), cooling, and post-processing. The machine for these processes can be composed of one (Figure 1) or two tanks (Figure 2) where the degassing, melting (if necessary), and mixing of the reagents (resin and activator/catalyst) take place. In specific cases, such as with highly reactive systems (e.g., ( $\epsilon$ -CL)/PA-6), the TP-RTM machine can comprise different tanks and a mixing head placed between the tanks and mold,<sup>[11]</sup> where the components can be mixed under high pressure just before injection. The use of several tanks to separate the reagents is necessary in specific cases where the polymerization reaction is too rapid, as this will lead to an increase in the viscosity of the mixture and prevent the injection step. Currently, personalized industrial-scale TP-RTM machines for one or more components with a mixing head have been commercialized by Diatex (France), Tarter (Germany), Krauss Maffei (Germany), and Wolfangel (Germany). Liquid monomers and/or oligomers are injected under pressure through pipes into a mold containing the reinforcement. A press is frequently required to keep the mold parts properly joined during the injection. After the injection, the viscosity of the resin increases as the polymerization reaction occurs, until the resin is fully converted and solidified. The time from the beginning of the polymerization reaction to the complete solidification of the resin is called the polymerization time.

RTM and TP-RTM machines can be assisted by a secondary vacuum pump system placed at the exit of the mold to facilitate the impregnation of the reinforcement. This variation in the RTM process is known as vacuum-assisted resin transfer molding (VARTM). The advantages relative to conventional RTM are (i) a better finish of the composite surface, (ii) a better impregnation of the reinforcement by the matrix, and (iii) a reduction of polymerization time in certain cases.<sup>[12]</sup> However, the use of this specific technique can lead to the formation of voids in the final material. In particular, the pressure goes below atmospheric pressure, thereby inducing the sublimation or evaporation of the liquid monomer/oligomer and creating voids.<sup>[13,14]</sup> In reactive thermoplastic

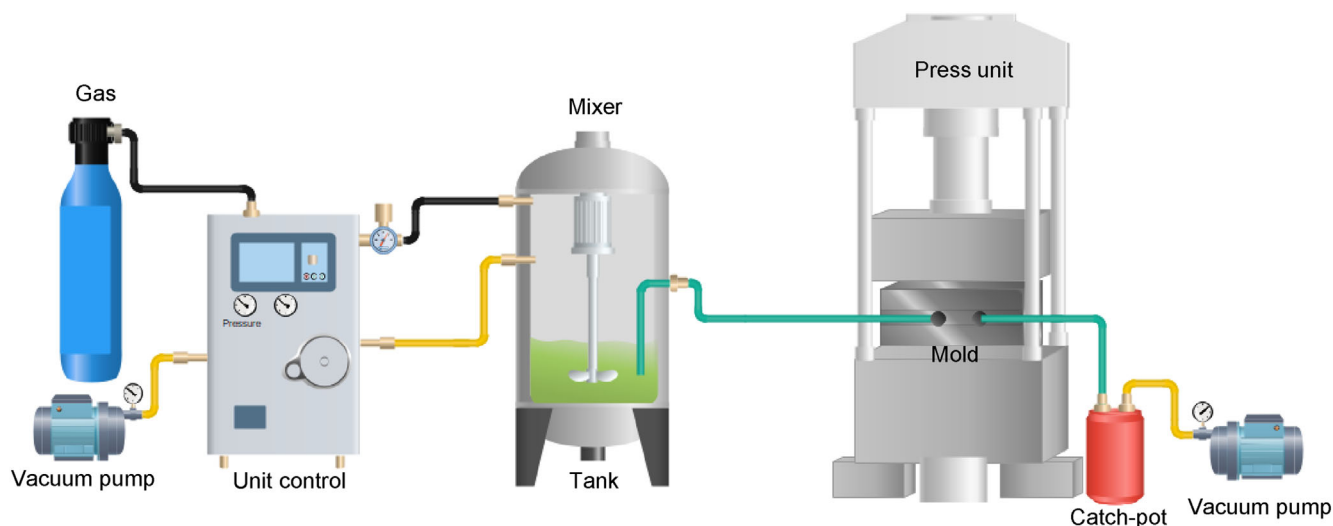


FIGURE 1 Scheme of vacuum-assisted resin transfer molding (VARTM) process for a single component machine

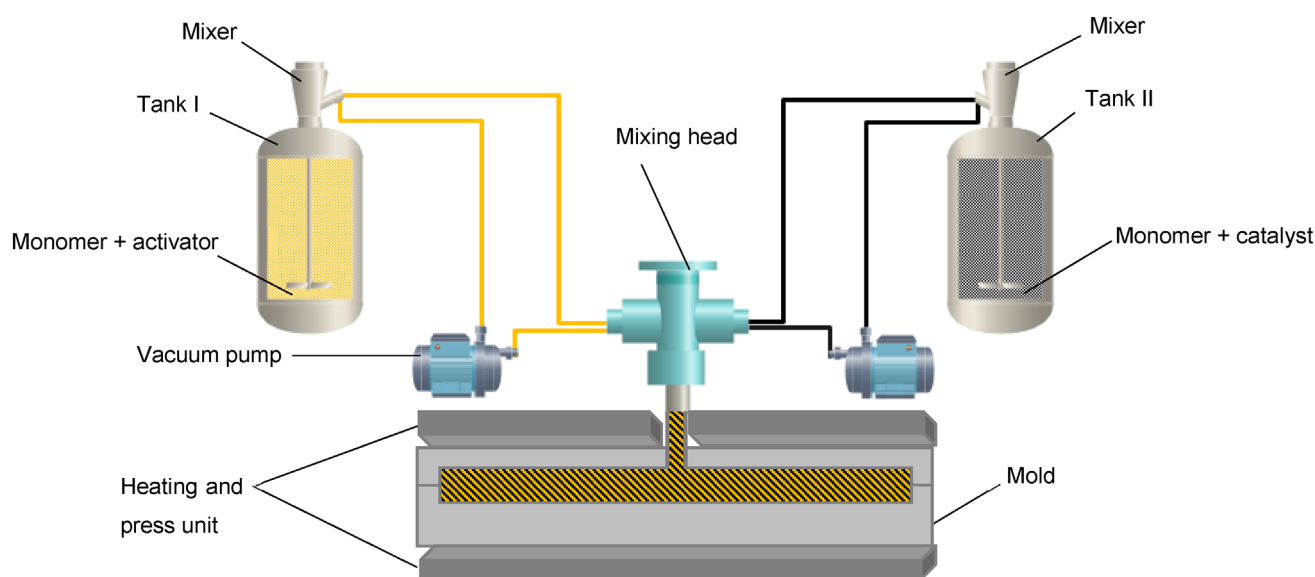


FIGURE 2 Mixing head used in thermoplastic resin transfer molding (TP-RTM) multicomponent machine for highly reactive thermoplastic systems

systems, specifically for  $\epsilon$ -CL monomers, the presence of voids is often caused by the presence of water owing to the hygroscopic nature of certain monomers, but also by the gas used during injection, which is generally nitrogen.<sup>[6,15]</sup>

The RTM and its variants have basic processing parameters, such as the tank temperature and pressure, stirring speed, injection pressure, filling time, and mold temperature. The tank temperature, stirring time, and tank pressure influence the viscosity of the resin. A higher tank temperature makes the resin more fluid, and thus, the temperature is considered as a major parameter. If the resin is sensitive to air, the melting process can take

place under a vacuum or inert atmosphere.<sup>[16]</sup> In the case of reactive thermoplastic systems, the stirring time and speed can influence the kinetics of the polymerization reaction, and consequently, the viscosity.<sup>[6]</sup> The pressure in the tank can also influence the viscosity. In the case of reactive thermoplastic systems, a high vacuum associated with a high temperature can promote vaporization or sublimation of the monomers in the tank (e.g., in the case of L-LA,  $\epsilon$ -CL, and  $\omega$ -laurolactam, which are in the solid-state at room temperature), whereas an overpressure can cause the solubilization of gases into the liquid monomer.<sup>[17,18]</sup> During the injection step, the pressure must be controlled to avoid fiber distortions related to the



permeability of the reinforcement. Usually, high pressures cause reinforcement displacements owing to a high resin flow, and the optimal injection pressure can be predicted using permeability tests and modeling simulation.<sup>[19]</sup> Ultimately, the mold temperature influences the polymerization time, as in a general manner, higher temperatures accelerate the polymerization kinetics.<sup>[20]</sup>

The advent of the finite element method has allowed for an understanding of the physical behaviors of the resin in RTM. Simulations of the resin behavior can be conducted using commercially available software exclusively developed for RTM, for example, RTM-Worx by Polyworx and PAM-RTM™ by ESI Group™. These software were designed based on thermosetting resins; therefore, the simulations for thermoplastic resins have not been fully adapted. In fact, the polymerization mechanism (most of the time ring opening polymerization [ROP] or radical polymerization) occurring during the matrix formation is not often considered in the models, but can help in the first approach. Analytical models of the polymerization, crystallization, and rheological behaviors of reactive thermoplastic systems have already been developed experimentally, that is, for  $\epsilon$ -CL/PA-6<sup>[5]</sup> and L-LA/PLLA.<sup>[21,22]</sup> However, a combination of analytical models for the resin flow in a modeling system has not yet been developed.<sup>[5]</sup>

Numerical simulations allow for a more conscious production of composites, avoiding the waste of reagents and scraps of high added value, and allowing for high reliability and tolerance of the produced parts.<sup>[12]</sup> Simulation studies and sensitivity analyses of the RTM and VARTM processes have been reported in the literature and have allowed for cost reductions, as well as better impregnation of the reinforcement by the polymer matrix.<sup>[12,23]</sup> The software serves as a first approach, and can assist the development of composite materials.

Compared with other thermoplastic composite manufacturing technologies, TP-RTM displays some advantages, as follows.<sup>[20]</sup>

- It allows for the use of different types of reinforcements, such as thick fibers, 3D structures, stitched assemblies, and braids.
- The volume of the fibers can be very well-controlled in fixed-cavity tools, resulting in composites with good mechanical properties.
- Composites with a reduced number of voids are obtained when the correct mold design is used, and with meticulous control of parameters such as the injection pressure, injection speed, and curing time.
- Parts with complex geometries can be produced.
- It provides better control of the fiber orientation and manufacturing of large parts (e.g., in the aeronautical industry), with short processing times.<sup>[10]</sup>

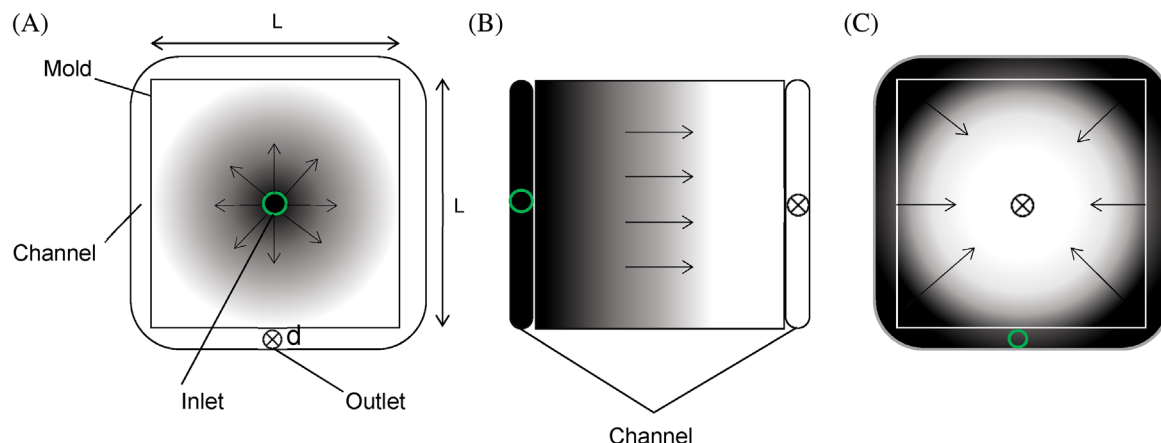
## 2.1 | Resin flow in TP-RTM

Owing to the low viscosity of the resin or liquid/melted monomers involved in TP-RTM, good impregnation of the reinforcement by the thermoplastic resin or liquid monomer can be obtained, thereby minimizing empty spaces inside the parts and improving the mechanical performance of the final composites. A perfect balance between the viscosity of the resin and permeability of the fibers allows for optimal impregnation, and reduces the filling time. The impregnation or filling time in TP-RTM is directly proportional to the resin viscosity and inversely proportional to the permeability; this limits the use of highly viscous resins. To improve the permeability and consequently decrease the impregnation time, it is possible to use a second solid phase in the core of the fibers, such as in 3D printed structures.<sup>[24]</sup> The permeability measurements are not standardized, and different procedures exist. Two experimental setups were developed by Merhi et al.<sup>[25]</sup> and Klunker et al.<sup>[19]</sup> to measure the permeability of fibers. The impregnation time of a resin or melted polymer through the fibers can be estimated using Darcy's Law,<sup>[26]</sup> assuming a Newtonian fluid in a rigid porous medium. Equation (1) describes the impregnation time for a one-dimensional flow, as follows:

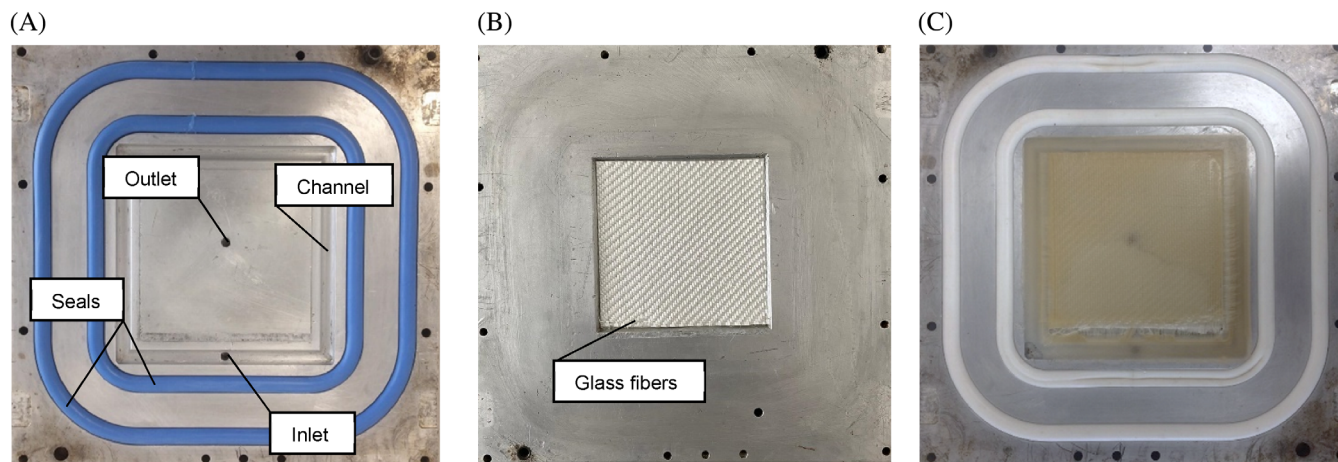
$$t_{imp} = \frac{(1 - V_f)\eta L^2}{2K\Delta p} \quad (1)$$

In the above,  $V_f$  is the fiber volume fraction,  $\eta$  is the fluid viscosity,  $L$  is the impregnation length,  $\Delta p$  is the pressure gradient, and  $K$  is the textile permeability.<sup>[27]</sup> The resin injection strategy is crucial for ensuring that the reinforcement is impregnated without air entrapment, allowing for a continuous and homogeneous flow front. For a flat panel with a single injection port, three different injection strategies can be chosen: radial injection, edge injection, and peripheral injection.<sup>[28]</sup> The direction of the flow front for each injection strategy is indicated by arrows in Figure 3.

A typical TP-RTM square plate mold is shown in Figure 4. This type of mold is adapted for radial and peripheral injections. The inlet and outlet can be switched depending on the injection strategy. In peripheral injection, the channel around the upper mold is filled with the molten monomer or resin before the



**FIGURE 3** Injection strategies for a square plate in single port with dimensions  $L \times L$ . (A) Radial injection (B) edge injection (C) peripheral injection. The flow front starts in the darkest zones in all schemes. The letter “d” corresponds to the diameter of the inlet and outlet. *Source:* Based on references 3, 28



**FIGURE 4** Configuration of TP-RTM square plate mold for peripheral injection strategy. (A) Upper mold (B) lower mold with pre-disposed glass fibers (C) upper mold filled completely

**TABLE 1** C-values for different injection strategies

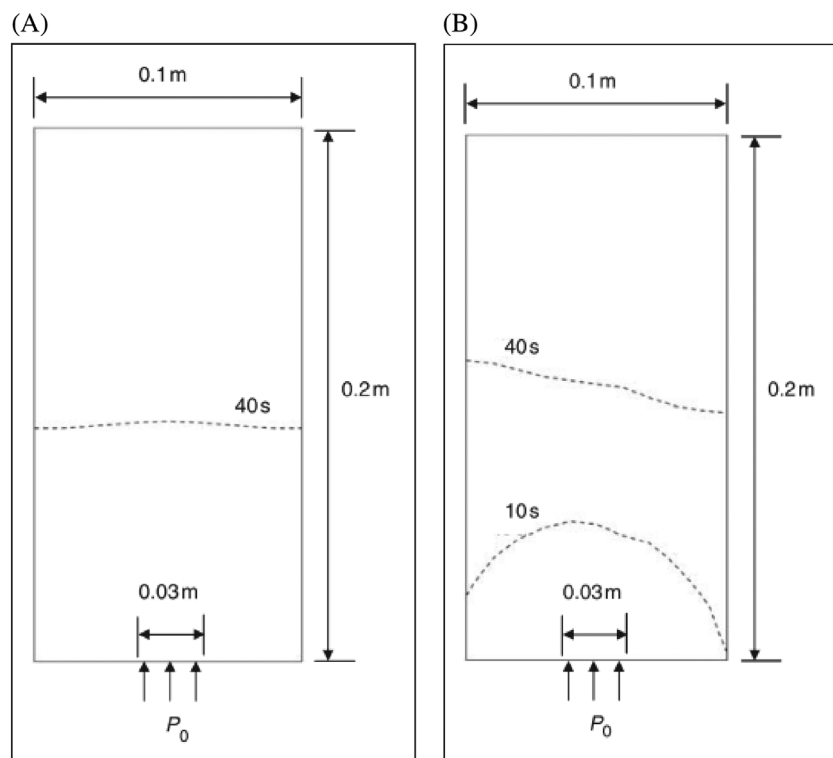
	Radial injection	Edge injection	Peripheral injection
C-value	$\frac{1}{16} \left[ \epsilon^2 + 2 \ln \left( \frac{1}{\epsilon} \right) \right]$ $\epsilon = \frac{d}{L}$	$\frac{1}{2}$	$\frac{1}{16}$

impregnation of the fibers into the lower mold. In the case of radial injection, where the inlet is localized at the center of the upper mold, the channel is filled after complete impregnation of the lower mold cavity. To keep the mold properly closed and prevent leaks, the mold disposes of the double silicone seal frequently employed in TP-RTM molds.

Depending on the injection strategy, Equation (1) can take another form (Equation (2)), where C is a constant related to the chosen injection type.<sup>[28]</sup> (see Table 1).

$$t_{imp} = C \frac{(1 - V_f) \eta L^2}{2Kp \Delta p} \quad (2)$$

The use of peripheral injection leads to the lowest impregnation times, whereas in radial injection, this time is directly related to the diameter of the inlet. However, a very fast impregnation time can cause fiber filling defects. When the resin flows too fast, the fiber bundles are not fully impregnated, resulting in void formation. The speed of resin flow must be controlled to achieve the best



**FIGURE 5** Flow front position in a 0.1 m × 0.2 m × 0.01 m resin transfer molding (RTM) mold for (a) isotropic and (B) anisotropic permeability distributions<sup>[30]</sup>

impregnation of the reinforcement without defects in the matrix.<sup>[28]</sup>

Most textile reinforcements exhibit an anisotropic nature, and the flow front is not linear. For a radial or peripheral injection strategy using anisotropic textiles, the flow front exhibits an elliptical shape, whereas for isotropic textiles, the flow front exhibits a linear shape.<sup>[29]</sup> Minaie et al. studied the permeability distribution for the edge injection strategy in anisotropic and isotropic textiles, and a numerical algorithm was proposed to predict the flow front.<sup>[30]</sup> In this study, an elliptical shape of the flow front for anisotropic textiles could clearly be established (Figure 5). The methodology used to predict the permeability distribution during the RTM process using numerical simulations can also be useful for enhancing the mold filling.

## 2.2 | Voids issues in fiber-reinforced composites produced by RTM

In the RTM process, several factors can contribute to the presence of voids in the final thermoset or thermoplastic composites. The main cause is air entrapment during resin flow, generally owing to the inhomogeneity of the textile; this creates a gradient of permeability, resulting in a variation in the resin velocity.<sup>[14,31]</sup> Owing to the multi-scale nature of reinforcements, voids can be formed at the macro-, meso-, and micro-scales (Figure 6). Macro-

voids can be observed with the naked eye in the larger zone of the preform, and meso-voids between the tows and micro-voids are formed between the fiber tow (Figure 7).<sup>[14]</sup> During the injection step, a competition between the viscous flow and capillarity flow is observed, and is governed by the resin velocity.

The void formation and characterization of capillarity flows in dual-scale engineering fabrics were studied by LeBel et al.<sup>[33,34]</sup> In addition, meso-pores and micro-pores can be observed in a thermoplastic matrix composite reinforced with carbon fibers (Figure 6).

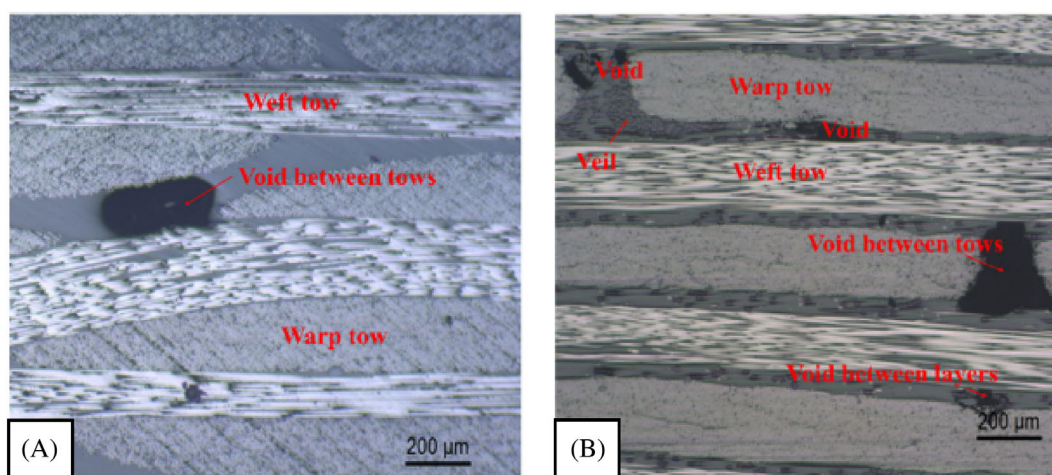
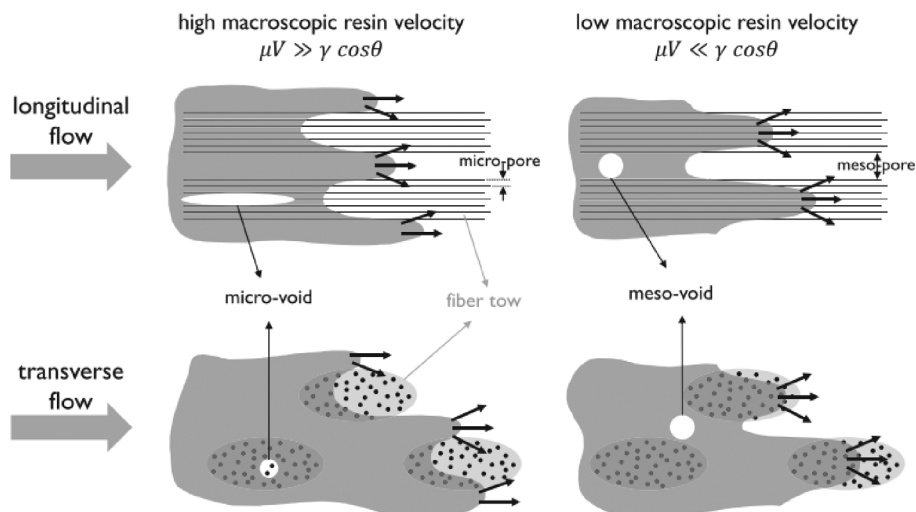
Other causes of void formation can be considered, such as gas formation owing to chemical reactions, the presence of water in the resin, and incompatibility between the fiber and resin. A detailed review of the presence of voids in fiber-reinforced polymer composites produced via LCM and their influences on the mechanical properties was reported by Mehdikhani et al.<sup>[14]</sup>

## 3 | REACTIVE THERMOPLASTIC SYSTEMS IN TP-RTM PROCESS

To produce thermoplastic composites with good mechanical properties using reactive thermoplastic systems in TP-RTM, the following are required: (i) a high conversion rate of the monomers/oligomers, (ii) a high molecular weight of the resulting polymer matrix, and (iii) no unwanted by-products.<sup>[35]</sup>

**FIGURE 6** Formation of voids during longitudinal and transverse flow in liquid composite molding. Micro-voids appear between the fiber tows governed by capillary effect, while meso- and macro-voids appears between the tows, as governed by the resin velocity.

Source: Based on reference 14



**FIGURE 7** Micrographs of cross-sections of laminates manufactured by a variant of VARTM (i.e., a vacuum-assisted process—VAP) under experiment conditions for (A) woven reinforcements and (B) non-crimp reinforcements. Source: Based on reference 32

Certain important industrial polymers are produced via ROP, such as polyethylene oxide, polyphosphazene, and polyamides like Nylon® 6 (poly( $\epsilon$ -CL)), the most significant in terms of volume.<sup>[36]</sup> Nowadays, some bio-based and biodegradable polymers are industrially produced via ROP, such as Ingeo™ (polylactide) commercialized by NatureWorks, and Capromer™ PCL from BASF. The commercial availability of these polymers shows that they can be used in a wide range of applications, particularly for packaging and biomedical applications.

The ROP of cyclic esters is commonly used for the production of thermoplastic composites using TP-RTM. ROP is an efficient synthetic route for the production of engineering plastics with specific and controllable properties (e.g., a high molecular weight) and biodegradable plastics. The ROP mechanism is based on the opening of cyclic ring-shaped molecules via the use of catalysts

comprising metal-based systems, organic molecules, or enzymes.<sup>[16]</sup> The most common ROP mechanisms are cationic, anionic, or coordination-insertion polymerization using metal-based catalysts. Ionic ROP is used for the production of polyamide matrices, whereas coordination-insertion is used to produce PCL and PLLA. Radical polymerization is another mechanism involved in the production of composites by the TP-RTM process, particularly for PMMA-based composites with peroxides as the initiator (Section 3.2.).

### 3.1 | Polyamide matrix composites produced by TP-RTM

Polyamides are widely used in the industry owing to their excellent mechanical properties, such as high strength, an excellent impact resistance, and a high abrasion



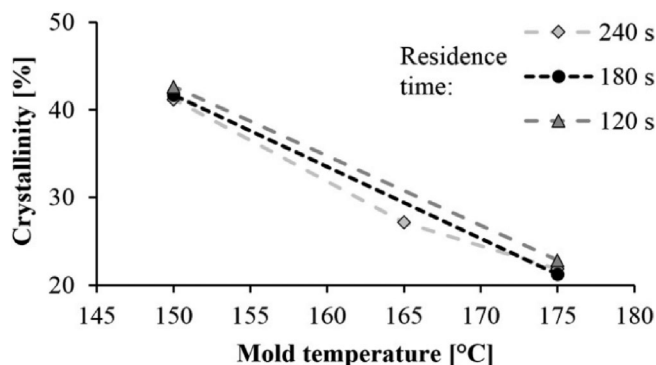


FIGURE 8 Evolution of crystallinity rate with temperature of Polyamide-6 (PA-6)-based composites<sup>[37]</sup>

resistance. Recently, research has been conducted to develop advanced polyamide-based composites using various reinforcements such as carbon fibers, glass fibers, natural fibers, carbon nanotubes, and graphene.<sup>[37]</sup>

Certain polyamides can be obtained by the anionic ROP of cyclic monomers, allowing for the formation of high-molecular-weight polymer matrices.<sup>[38]</sup> Nowadays, PA-6 is obtained via the ROP of  $\epsilon$ -CL; this has been commercially exploited by Brüggemann Chemicals.<sup>[39]</sup> In this section, the scientific works on PA-6 and PA-12 matrix composites produced by the TP-RTM process are presented.

### 3.1.1 | Polyamide-6 matrix composites

The production of PA-6 matrix composites via the anionic ROP mechanism by TP-RTM is a viable route owing to the commercial availability of the reagents, low viscosity (3–5 mPa·s) of the reactive system (monomer/activator/catalyst), and fast polymerization rate, thereby enabling its use in industry. However, some disadvantages must be considered, such as the hygroscopic nature of the monomer (which must be stored in vacuum bags or dried before use), and the corrosive nature of the activator and catalyst, which are usually hydroxide salts. Another drawback is the solid nature of the monomer, which must be melted prior to injection. However, these issues seem to be easily bypassed, as the ( $\epsilon$ -CL)/PA-6 system is the most commonly used reactive thermoplastic system in TP-RTM. According to a study by Wilhelm et al.<sup>[40]</sup> the influence of water, which could be viewed as a major problem, can be balanced by increasing the activator and catalyst concentrations. The original polymerization rate can be achieved by doubling the molar amounts of the two reagents. Thus, a careful analysis in terms of the production costs must be conducted to determine whether it is more feasible to double the

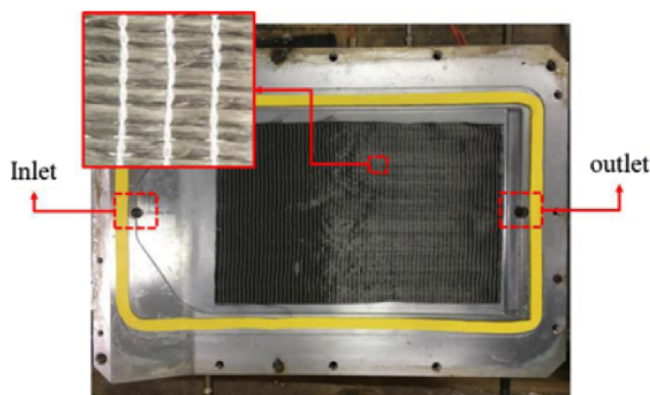


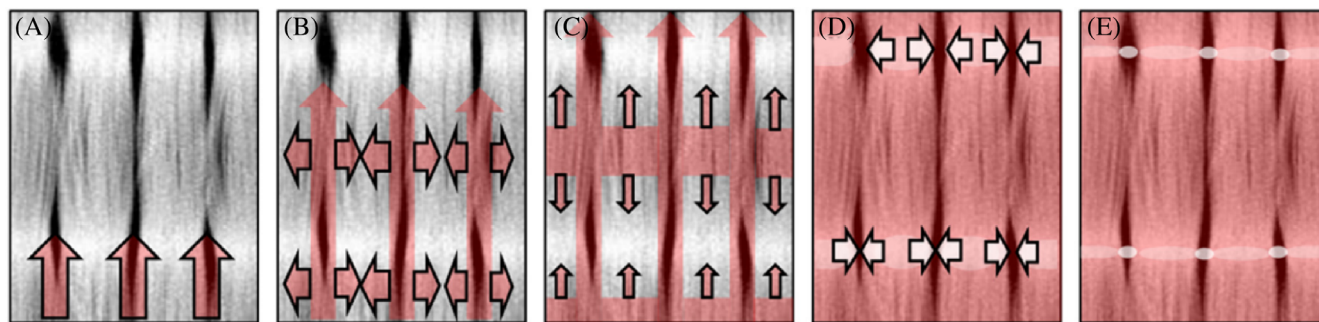
FIGURE 9 TP-RTM mold with edge injection strategy<sup>[2]</sup>

consumption of the reagents, or to store them in an inert atmosphere. The authors also demonstrated that the presence of water in the reactive system does not affect the mechanical properties of the final composite.

Semperger and Suplicz<sup>[37]</sup> investigated the effects of TP-RTM parameters on PA-6 polymerization without reinforcement. Hexamethylene-1,6-dicarbamoylcaprolactam (BRUGGOLEN<sup>®</sup>C20p) and sodium caprolactamate (BRUGGOLEN<sup>®</sup>C10) were used as the activator and catalyst, respectively, and  $\epsilon$ -CL was used as the monomer. Two different tanks were used for the melting step of the  $\epsilon$ -CL: one in which the monomer was mixed with the activator, and the other with the catalyst. The relationships between the crystallinity, mold temperature, and residence time were studied. Three mold temperatures (150, 165, and 175°C), and three polymerization times (120, 180, and 240 s) were used. A crystallinity ratio of up to 43% was obtained with the polymer processed at 150°C for 120 s. For the same polymerization time (120 s) and a temperature of 175°C, the authors observed a drop of crystallinity by 20%. The relationship between the temperature and final crystallinity of the matrix was almost linear (Figure 8), and the crystallinity decreased as the temperature increased. The authors assumed that the polymerization time did not have a significant influence on the crystallinity as the temperature increased.

Crystallinity directly influences mechanical properties. It was reported that the maximum limit bending stress and maximum flexural modulus were 61 MPa and 2.4 GPa at 150°C, respectively. At 175°C, these parameters decreased by 30% and 40%, respectively, showing that the higher crystalline phase improved the mechanical properties.

Research on PA-6 matrix composites obtained via anionic ROP of ( $\epsilon$ -CL) has shown that composites with good mechanical properties can be produced by TP-RTM.<sup>[2]</sup> Choi et al. studied the optimal polymerization



**FIGURE 10** Mechanism of void formation during injection in TP-RTM. Red areas represent the liquid and white indicates the gas. (A) Macro-flow through fibers (B) radial flow into fiber bundles (C) capillarity phenomena into intra-bundle (D) expulsion of air into inter-bundle regions (E) presence of macro and micro-voids<sup>[4]</sup>

conditions and mechanical properties of PA-6 composites reinforced with carbon fibers using the response surface method (RSM). Two mixtures in separate tanks containing an activator (BRUGGOLEN<sup>®</sup> C20p 2%)/(ε-CL) and catalyst (BRUGGOLEN<sup>®</sup> C10 2%)/(ε-CL) were injected into a heated mold at 160°C with predisposed carbon fibers. An edge injection strategy was chosen (Figure 9). The composites obtained under these experimental conditions displayed an 89% monomer conversion, and tensile strength of 300 MPa. Residual monomers greater than 5% have negative effects on mechanical properties. In addition, unreacted (ε-CL) acts as a plasticizer inside the material, and also may condense on the surface of the composite.<sup>[37]</sup> To optimize these results, the authors used RSM to predict the optimal experimental conditions. With this method, the optimal conditions were shown to be 3.8 wt% of BRUGGOLEN<sup>®</sup> C10 and 1.6% of BRUGGOLEN<sup>®</sup> C20 and an injection speed of 203 ml/min, leading to a monomer conversion of 99% and tensile strength of 497 MPa. This result shows the efficiency of RSM in optimizing the experimental conditions in the process.

Minimizing the voids in the composites is crucial for obtaining good mechanical properties, as the voids can act as stress concentrators and cause early rupture. Glass fabric reinforced PA-6 composites produced by TP-RTM were studied by Murray et al., and an investigation of the void content was performed.<sup>[4]</sup> The tank temperature was defined as 100°C, and the monomer (98 mol%)/activator (0.6 mol%) and monomer/catalyst (1.2 mol%) were mixed into separate tanks under a nitrogen atmosphere. A 52% fiber volume fraction stitched glass fiber with polyester stitching was used as the reinforcement. The mold temperature was set at 130°C, and after injection, the mixture (resin/activator/catalyst) was left for 15 min before cooling to room temperature. A conversion of 95% of the monomer was obtained using these parameters. The composite specimens were subjected to longitudinal

tensile tests, and a Young's modulus of ~41 GPa was observed, with a maximum strength of ~1.1 MPa. To measure the void content by volume and distribution, a tomography scan was conducted on the resulting composites. Approximately 1% of macro- and micro-voids were observed, which is quite low. The presence of these voids was attributed to the air trapped in the reinforcement. The authors proposed a void formation mechanism based on the difference in pressure caused by the flow front between the fiber bundles and capillarity phenomena in the inter-bundle regions (Figure 10).

Another study reporting the presence of voids in PA-6 matrix composites with PA-6-6 fibers was conducted by Gong and Yang.<sup>[41]</sup> A single-component RTM machine composed of only one tank was used, and all the reagents were mixed. The monomer (ε-CL) and catalyst were mixed into the tank at 140°C and after degassing (15 min under vacuum), the mixture was cooled down to 120°C and the activator (2,4-diisocyanate) was added. Surprisingly, the authors did not report any problems regarding the high reactivity of the reactive thermoplastic system and/or a quick increase of the viscosity (which would make the injection impossible). They reported that at 120°C, the reactive mixture did not polymerize rapidly, and that a low viscosity could be maintained long enough to allow for the injection. The mixture was then injected under nitrogen pressure. Different mold temperatures ranging from 140 to 200°C were tested, and a correlation between the void fraction and temperature was established. The highest conversion rate of 95% was reported for a mold temperature of 140°C and polymerization time of 1 h. The void fraction was measured according to ASTM D2734. It has been reported that high temperatures can increase the void fraction; indeed, at 200°C, the void matrix fraction was 2%, whereas at 140°C, it decreased to 1%. Reactions conducted at higher temperatures led to a higher polymerization rate; therefore, the viscosity of the reactive mixture increased as



well, making the air discharge more difficult. Concerning the mechanical properties, an increase of 220% in the maximal tensile strength was observed for PA-6 composites (156 MPa) compared with pure PA-6 (70 MPa). This study highlighted that the presence of voids in the PA-6 matrix increases with increasing temperature.

The void-formation mechanism is well known. One way to minimize voids is to use high pressures to impregnate all fibers and to drag the voids outside the composite plate. In addition, the temperature must be well-controlled, as higher temperatures seem to increase the void content. Another probable cause of voids is the dissolution of gases (e.g., nitrogen) in molten  $\epsilon$ -CL, depending on their use in the TP-RTM process.

In another study, PA-6 matrix composites reinforced with carbon fibers were obtained from  $\epsilon$ -CL via anionic ROP, and the polymerization was monitored in real-time with an interdigital dielectric sensor.<sup>[42]</sup> A dielectrometry method allowed for a determination of the polymerization and crystallization. Mixtures of a monomer ( $\epsilon$ -caprolactam)/activator (caprolactam-blocked isocyanate) and monomer/catalyst (sodium caprolactamate) were placed in separate tanks, and were mixed into the mold during the injection process. The curing temperatures ranged from 120 to 200°C. With the support of dielectrometry, the authors confirmed that at 160°C, polymerization and crystallization occurred simultaneously.<sup>[43]</sup> At 180°C, crystallization occurred after polymerization, and at 200°C, the polymerization occurred so quickly that the crystallization did not occur at all. The polymerized PA-6 underwent supercooling because the melting temperature of PA-6 ( $T_m = 220^\circ\text{C}$ ) was much higher than the polymerization temperature, and there was no time to adjust the crystal structure(s) between the PA-6 molecular chains. Thus, an amorphous phase was formed. The authors concluded that a curing temperature above the crystallization temperature (crystallization temperature of PA-6  $\sim 170^\circ\text{C}$ ) is not suitable for the TP-RTM process. The optimum tensile modulus (1.5 GPa) and tensile strength (57.1 MPa) were obtained at a temperature of 160°C.

In addition to the classic reinforcements already used in composite materials (such as glass and carbon fibers), nanomaterials are being used in polymer matrix composites. Specifically, carbon nanomaterials such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and graphene are also being used to produce advanced composite materials.<sup>[44]</sup> Usually employed to enhance mechanical and electrical properties, carbon nanotubes are promising in composite industry, and can be used in the TP-RTM technique. MWCNTs have an elastic modulus approaching 1 TPa and a tensile strength of 100 GPa.<sup>[45]</sup> This strength value

is more than 10-fold higher than that of any other industrial fiber. SWCNTs can exhibit a thermal conductivity of  $3500\text{ W m}^{-1}\text{ K}^{-1}$ , that is, higher than the thermal conductivity.<sup>[46]</sup> Thereby, TP-RTM has proven to be a suitable technique for the production of thermoplastic matrix composites reinforced with carbon nanotubes, as the dispersion of these nanomaterials was shown to be improved relative to those in other classic thermoforming processes. In TP-RTM, the nanomaterials must be placed together with the resin inside the tank before injection; this avoids the need to prepare the master batches commonly used in thermoforming techniques such as extrusion. The mixture and homogenization of these nanomaterials with the melted monomer can be performed in the TP-RTM tank using a homogenizer or magnetic stirrer.

The use of carbon nanomaterials in a thermoplastic matrix seems to increase the crystallinity of the matrix, improving the mechanical properties of the composite.<sup>[47]</sup> Yang et al. showed that the presence of graphene nanoparticles or graphite nanoplates can increase the degree of crystallinity in a PCL matrix.<sup>[48]</sup> Carbon nanomaterials act as a nucleation agent in the thermoplastic matrix, increasing the crystallization temperature, decreasing the size of the crystallites, and consequently increasing the crystallinity. In this context, Park et al. studied the production (via anionic ROP) of PA-6 carbon nanocomposites by TP-RTM.<sup>[49]</sup> The nanomaterials studied as additives in the PA-6 matrix were MWCNTs, graphene oxide (GO), reduced GO, exfoliated graphite nanoplatelets (xGnPs), and nanoclays. The catalyst (Addonyl<sup>®</sup> CR) and activator (Addonyl<sup>®</sup> 8120), both sodium caprolactamate-based, were placed in two different tanks, and the monomer and nanomaterials were then added (half of each into the two tanks). The two mixtures were heated above the melting temperature of caprolactam ( $T_m = 69^\circ\text{C}$ ) and dispersed for 20 min using a magnetic stirrer prior to being injected into a mold containing woven carbon fibers. Polymerization temperatures of 135, 140, and 150°C were tested, and solidification times of 255, 143, and 61 s were observed at these temperatures, respectively. Conversion rates above 97% have been reported for all PA-6 nanocomposites. An increase in the temperature in the mold can make the process faster; however, the resulting matrices display low crystallinity and, consequently, mediocre mechanical properties. The presence of nanomaterials as reinforcing agents allowed the polymerization to occur at higher temperatures, leading to an increase in productivity. The specimens were also subjected to plasma treatment, and their mechanical properties were evaluated and compared with those of PA-6 woven carbon fiber composites. The highest elastic modulus and ultimate tensile strength

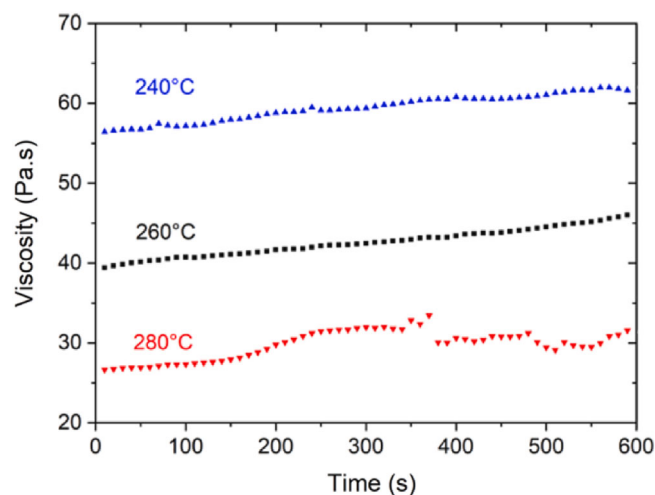


FIGURE 11 Viscosity measurements of high fluid PA6 (HFPA6)<sup>[50]</sup>

were observed in the specimens with GO and xGnP, with increases of 28% and 18% compared with PA-6 woven carbon fiber composites, respectively. After plasma treatment, increases of 4.1% and 5.4% were respectively reported for the GO and xGnP composites compared with nontreated specimens.

An innovative work done by Gomez et al. proposed the production of PA-6 matrix composites via TP-RTM using a molten polymer (melt TP-RTM) instead of the in situ polymerization of ( $\epsilon$ -CL) (reactive TP-RTM).<sup>[50]</sup> The authors reported that melt TP-RTM allows for better repeatability and well-controlled production of composites compared with reactive TP-RTM. However, the molten high fluid PA-6 (HFPA6) displays a viscosity higher than 1 Pa.s, and high injection and saturation pressures are mandatory. Viscosity measurements were conducted, and HFPA6 showed viscosities between 56 and 26 Pa.s at 240 and 280°C, respectively (Figure 11).

Composites based on glass fabric and a printed polyphenylene sulfide used as spacer were produced to create meso-channels and enhance the flow. The HFPA6 was melted at temperatures ranging from 240 to 260°C in the TP-RTM tank before being injected with pre-disposed glass fabrics and the spacer, with an injection pressure of 3.6 bar. To ensure full impregnation, an extra pressure (saturation pressure) ranging from 3.6 to 15 bar was applied after injection. The mold was then kept at 305°C for 5 min to promote the collapse of the spacer, and was subsequently cooled. Composites showing better mechanical properties and impregnation were obtained at an injection pressure of 3.6 bar and saturation pressures ranging from 10 to 15 bar, and applied for 20 min. The highest bending strength was ~472 MPa, and the flexural modulus was 19 GPa. Although the authors

provided evidence that TP-RTM can be employed with molten polymers, certain aspects must be discussed. High injection and saturation pressures (up to 15 bar) are required, increasing the dangers of the process. In addition, high temperatures are required to increase the energy consumption. At the industrial scale, the melt TP-RTM injection and saturation times are higher than those of reactive TP-RTM; this is not very relevant for continuous production. Finally, the polymer used as a spacer must display a chemical and mechanical stability at high temperatures, that is, near 280°C, to avoid its degradation and premature collapse.

Osváth et al.<sup>[51]</sup> studied the effects of post-polymerization heat on the monomer conversion and resulting molecular mass of PA-6 as prepared by an anionic ROP of  $\epsilon$ -CL in bulk. Higher monomer conversions and molecular weights were obtained for PA-6 produced without quenching than for quenched samples for the same reaction times. This study can be used to improve the properties of PA-6 based composites produced by TP-RTM.

Finally, a recent review by Toldy et al.<sup>[52]</sup> focused on the effects of the addition of various fire-retardant molecules in  $\epsilon$ -CL for the production of PA-6-based composites by TP-RTM. In most cases, the phosphorous-based organic molecules must be soluble in the monomer, which limits the panels that can be used. The studies conducted in this field highlight that the presence of these fire-retardant additives slows down or inhibits the polymerization reaction. Another strategy that has been explored for fireproof PA-6 composites is in-mold coating, where a  $\epsilon$ -CL-based flame retardant coating is deposited on the surface of the composite during the production of the composite by T-RTM, thereby ensuring good adhesion between the PA6 composite and coating. This allows for highly flame-retardant loadings in the coating, without damaging the mechanical properties of the PA6-based composites.

### 3.1.2 | Polyamide-12 matrix composites

Some studies have reported PA-12 as a matrix for composite materials produced by TP-RTM via an anionic ROP of the  $\omega$ -LL monomer.  $\omega$ -LL shows a melt shear viscosity ranging from  $4.5 \times 10^{-3}$  Pa.s at 250°C to  $8 \times 10^{-3}$  Pa.s at 200°C, which is suitable for injection in TP-RTM.<sup>[53]</sup> However,  $\omega$ -LL displays a high melt temperature of  $T_m = 154^\circ\text{C}$  relative to other monomers used in TP-RTM, such as  $\epsilon$ -CL ( $T_m = 69^\circ\text{C}$ ) or L-LA ( $T_m = 97^\circ\text{C}$ ).<sup>[22]</sup> Thus, the polymerization of  $\omega$ -LL is conducted above the melting temperature of PA-12 ( $T_m = 180\text{--}190^\circ\text{C}$ ). This temperature does not allow for

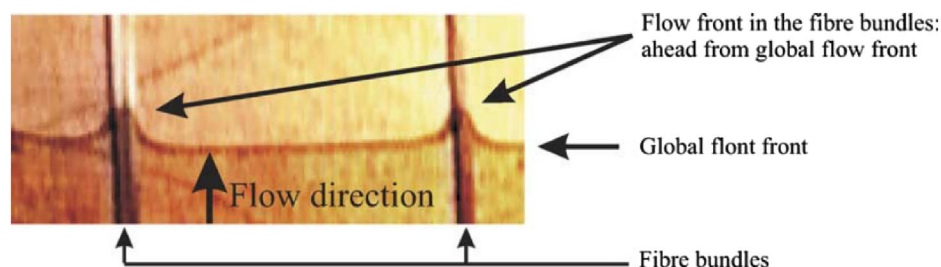


FIGURE 12 Capillarity forces observed during infiltration of molten lauro lactam in carbon fibers<sup>[54]</sup>

quick demolding (as for PA-6), as crystallization cannot occur during the polymerization reaction.<sup>[39]</sup> An additional cooling step is required for the solidification of the matrix. This can explain the low number of studies reported on the  $\omega$ -LL/PA-12 system in TP-RTM. In addition, temperatures above 200°C are required for the polymerization reaction to be initiated, making the process expensive on an industrial scale.

Zingraff et al. studied the production of PA-12 based composites reinforced with satin-weave carbon fabrics via a TP-RTM process, with an emphasis on void formation.<sup>[54]</sup> Two distinct tanks were used to avoid instant polymerization: one containing a lauro lactam monomer (heated above its melting temperature under nitrogen), and one filled with the activator mixture (carbodiimide)/catalyst (sodium-caprolactam). A mixing head was used to ensure contact between the monomer and liquid-activating system immediately prior to injection. The presence of voids and shrinkage in the PA-12 matrix during solidification was investigated, and was found to be related to the solubility of nitrogen in the monomers. The authors reported that the monomer could absorb a large amount of nitrogen, and its solubility was favored at elevated temperatures. With optimal parameters in the process, it was possible to decrease the nitrogen diffusion in the monomer, and it was shown that the number of voids is closely linked to the amount of nitrogen absorbed. A complete study of the capillarity phenomena and of the diffusion of the melted monomers through the fibers was also conducted. Molten  $\omega$ -LL spontaneously wets carbon bundles (Figure 12); therefore, this effect must be considered during the injection step, because the capillarity effects modify the resin flow, potentially causing the formation of voids. Notably, the mechanical properties of the composites were not studied.

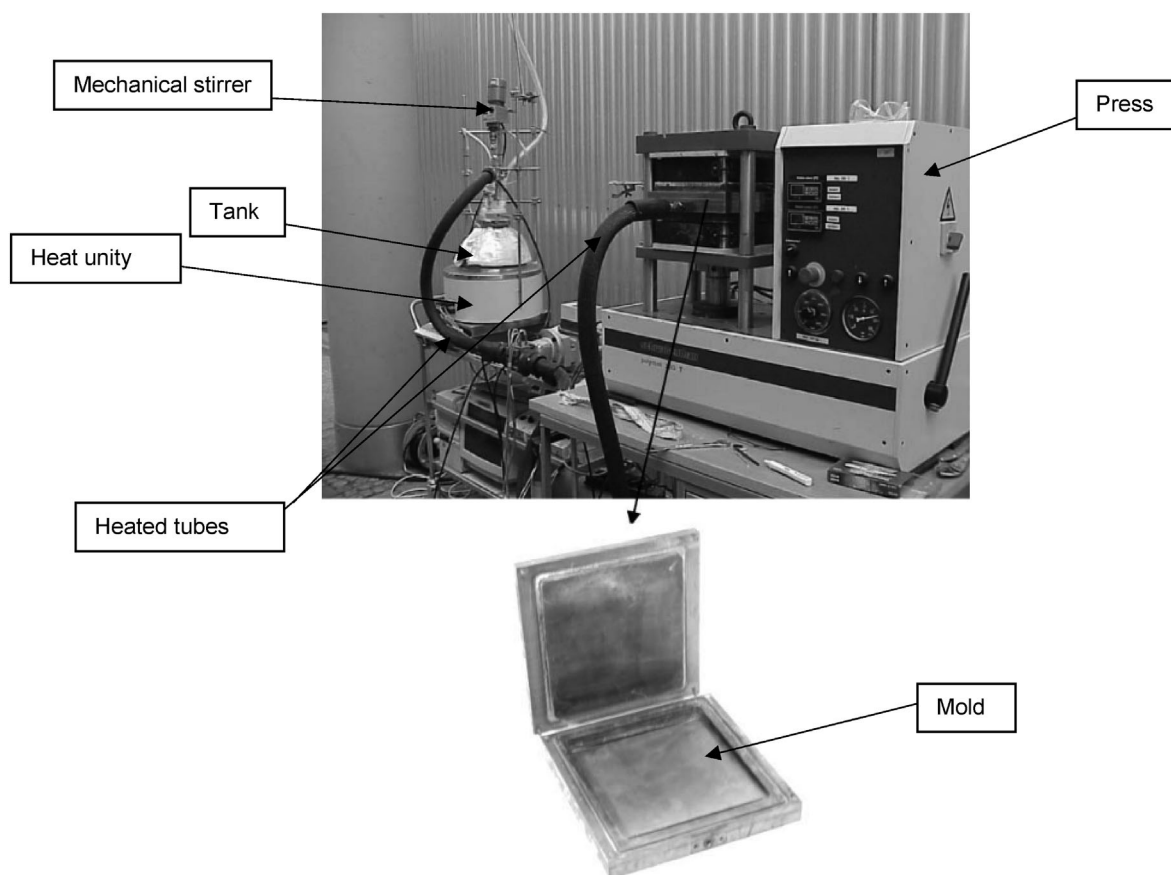
The same authors studied the production of PA-12 composites reinforced with carbon fibers.<sup>[55]</sup> In this study, the TP-RTM machine was composed of two tanks under nitrogen, where the same monomer, activator, and catalyst used in the previous work were mixed into the tanks at 180°C.<sup>[54]</sup> After injection, the mold was cooled from 200 to 50°C in 5 min. The TP-RTM process was combined with other techniques such as plate impregnation before TP-RTM, and with over-molding after TP-

RTM. After all stages of forming, the composite exhibited a tensile modulus of ~60 GPa. Thus, this study demonstrated that TP-RTM can be used as an intermediary process to produce advanced composites.

Pilot plants for the liquid injection of lauro lactam were proposed in the early 2000s. Rosso et al.<sup>[56]</sup> constructed a pilot plant (Figure 13) similar to single-component TP-RTM machines, whereas Mairtin et al.<sup>[53]</sup> proposed a multicomponent machine with a mixing head. There seems to be no consensus on single- or multicomponent RTM machines for lauro lactam/PA-12 systems.

Mairtin et al.<sup>[53]</sup> combined lauro lactam with a carbodiimide-based liquid activator system named Grilonit LA (EMS-Chemie, 2 wt%) containing both the catalyst and activator, aiming to produce carbon fiber-reinforced composites. Owing to the low viscosity of the lactam/catalyst mixture (4.5 mPa·s), a pressure of 0.4 bar was sufficient to penetrate the reinforcement. The mold was filled in only 10 s, and the mixture was kept in the mold for 8.5 min at 240°C for carbon fibers, and for 20 min at 200°C for a sandwich laminate. After completion of the polymerization, the mold was cooled to below the crystallization temperature of PA-12 ( $T_c = 150^\circ\text{C}$ ) prior to being demolded. As for the other lactams and lactone reactive systems, the anionic polymerization of lauro lactam is sensitive to water; this may decrease the monomer conversion. The authors suggested flushing the mold with nitrogen or using a vacuum pump to eliminate air and moisture entrapments. The plates exhibited a tensile strength of ~850 MPa, that is, 8% higher than a commingled carbon fiber/PA-12 composite.<sup>[57]</sup> However, the compression strength was 31% lower than the commingled material. Surprisingly, the reason suggested by the authors for the lower compression strength was the poor fiber-matrix adhesion in the PA-12 composites produced by TP-RTM relative to those produced by the commingling process. The viscosity of the lactam system seemed to be low enough to completely impregnate the fibers. Another possible reason for the unsatisfactory compression strength is the presence of voids; however, this was not mentioned in the study.

Rosso et al. compared carbon fiber laminates produced by PA-12-film stacking in an autoclave and PA-12



**FIGURE 13** Pilot plant of TP-RTM for the production of Polyamide-12 (PA-12)-based composites. This experimental set-up is similar to commercial single-component TP-RTM machines. The mold was heated and kept closed with a press unit. *Source:* figure adapted based on reference 56

laminates produced from two different laurolactam systems via TP-RTM. The first system involved *N,N*-ethylenebisstearamide as the activator and sodium hydride as the catalyst, as supplied by ATOFINA (France); the second system was based on the carbodiimide liquid activator Grilonit LA (EMS-Chemie).<sup>[56]</sup> Both reactive systems were heated at 170°C into the tank and were injected into a mold at 270°C. After 10 min, the mold was cooled with water and the plates were demolded. The flexural tests showed similar flexural strengths for both reactive systems at ~300 MPa. To evaluate the impregnation and its effects on the impact behaviors, the plates were subjected to a low-velocity impact test. The autoclave composites displayed the largest failure area relative to TP-RTM composites, and the authors justified this by using a lower fiber-matrix interface in autoclave composites. Thus, as expected, the TP-RTM composites displayed better wettability between the fibers and PA-12 matrix owing to the liquid molding technique.

After reviewing the studies reported on the polyamide matrix composites produced by TP-RTM, we can conclude that the TP-RTM process is adaptable to the

production of polyamide-based composites. Moreover, several types of reinforcements can be used in the process, including glass fibers, carbon fibers, and nanomaterials. In an industrial approach, an ( $\epsilon$ -CL)/PA-6 reactive system is more viable in terms of energy than a laurolactam/PA-12 system, owing to the high melting temperature of laurolactam compared to  $\epsilon$ -CL. Moreover, the production time for PA-12-based composites is longer than that for PA-6 matrix composites, because for PA-12, an additional cooling step is required to allow for demolding. Finally,  $\omega$ -LL monomer and activator systems are no longer commercialized by Arkema (ex-ATOFINA) and EMS-Chemie, which explains the lower interest in PA-12 composites produced via TP-RTM.

### 3.2 | Poly(methyl methacrylate) matrix composites produced by TP-RTM

PMMA has found numerous applications in optical, electronic, automotive, and biomedical devices.<sup>[58]</sup> Despite the benefits over thermoset resins already discussed,

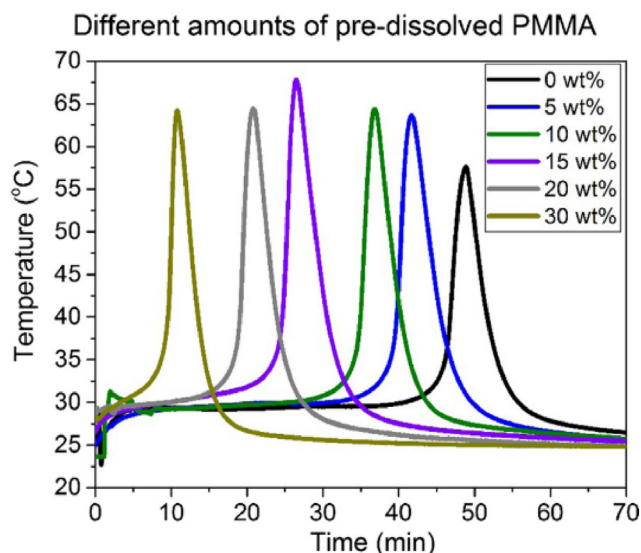


PMMA displays mechanical properties similar to those of epoxy resins, such as in regards to tensile strength.<sup>[59]</sup> This polymer can be synthesized by the radical polymerization of methyl methacrylate (MMA), with the use of a peroxide as the initiator. Recently, a MMA reactive system called Elium<sup>®</sup> was developed by Arkema for TP-RTM applications, with the resin being available with various viscosities ranging from 100 to 500 mPa·s at 25°C.<sup>[60]</sup> The short processing time gives Elium<sup>®</sup> a great advantage in the composite industry, allowing for the production of parts in a very short time. In addition, Elium<sup>®</sup> resins are liquid at room temperature, and do not require melting. Composites produced from Elium<sup>®</sup> exhibit high impact resistance but provide limited use at high temperatures, owing to the low glass transition temperature of PMMA and toxicity of MMA.<sup>[58]</sup> In addition, MMA, a toxic reagent, induces a strong scent during manufacturing.<sup>[61]</sup>

The kinetics of MMA polymerization in the VARTM process were investigated by Suzuki et al.<sup>[59]</sup> In their study, MMA, *N,N*-dimethyl-*p*-toluidine (catalyst), and benzoyl peroxide (activator) supplied by Sigma Aldrich and PMMA obtained from a commercial source (not specified) were used. The authors observed that owing to the Trommsdorff effect during MMA polymerization, the addition of pre-dissolved PMMA in the MMA increased both the temperature and viscosity rapidly. The induction time of the polymerization reaction decreased drastically from 45 min for 0 wt% pre-dissolved PMMA to 8 min for 30% pre-dissolved PMMA (Figure 14).

These results can be advantageous in mass production for reducing the number of production cycles. Even if the Trommsdorff effect enabled high-monomer conversions in free-radical polymerization, no molecular weight was reported in this work.

The ultrasonic welding of PMMA matrix composites reinforced with carbon fibers produced by TP-RTM was investigated by Bhudolia et al.<sup>[62]</sup> The MMA resin (Elium<sup>®</sup> 150) was mixed with benzoyl peroxide at a weight ratio of 100/3 into the TP-RTM tank at room temperature prior to injection under a 2-bar pressure. A binder was used between each layer of the carbon fabric to hold the layers and avoid fiber displacement during injection. The polymerization was conducted at room temperature, but no reaction was observed. A post-curing process was conducted with the mold being kept at 65°C for 45 min, and then being cooled to room temperature. After the composites were manufactured, some parts were welded using an ultrasonic welding machine. Generally, in studies investigating the weldability of thermoplastics, welded parts are compared with the adhesive assembly methods usually employed in thermosetting resins (as they cannot be welded). To compare the welding quality, the composite parts were bonded with a

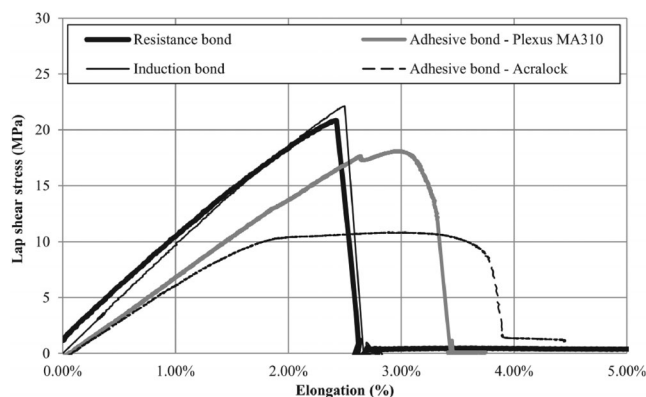


**FIGURE 14** Evolution of temperature during methyl methacrylate (MMA) polymerization for different amounts of pre-dissolved poly(MMA) (PMMA)<sup>[59]</sup>

methacrylate adhesive (SAF 30 5 by BOSTIK), and the lap shear stress was evaluated in both cases. The welded composites showed a 23% higher lap shear stress value than the bonded composites. Thus, it was demonstrated that post-processing techniques such as thermoplastic welding, which is widely used in the aerospace and automotive industries, can be applied to PMMA matrix composites produced by the TP-RTM process.

The spread of cracks in the adhesives used in the manufacture of wind turbine blades can cause part failures. Generally, adhesives are widely used in the wind industry, as wind turbines are comprised of thermosetting resins. Murray et al. investigated the fusion of PMMA matrix composites reinforced with fiber glass.<sup>[63]</sup> The composites were manufactured by the VARTM process with MMA (Elium<sup>®</sup> 188) as the resin and peroxide (2 wt%) as the initiator. The VARTM operational parameters, such as the curing time, temperature, stirring time, and nature of the initiator, were not mentioned. Acralock<sup>®</sup> and Plexus<sup>®</sup>, epoxy- and methacrylate-based adhesives, were used to join the composite parts, and the lap shear stress values were compared with those from fusion-welding thermoplastics. The adhesives showed lap shear strength values less than 10 MPa, whereas the welded parts had lap shear strengths higher than 20 MPa (Figure 15). This study confirmed the applicability of welding processes for Elium<sup>®</sup> matrix composites, showing that welding provides better shear strength than adhesives.

Another study of Bhudolia et al. investigated the flexural characteristics of PMMA matrix composites.<sup>[64]</sup> The composites produced by the TP-RTM process used an



**FIGURE 15** Elongation at break as a function of lap-shear stress for welded and bonded PMMA-based composite parts<sup>[63]</sup>

MMA resin (Elium<sup>®</sup> 280), benzoyl peroxide as the initiator, and a non-crimp carbon fabric as the reinforcement. Notably, the TP-RTM parameters were not mentioned. This study focused on comparing the flexural properties of PMMA matrix composites with those of epoxy composites. The PMMA matrix composites displayed a flexural response in terms of stiffness and strength very similar to that of epoxy composites (flexural modulus of 51.4 GPa vs. 50.9 GPa for epoxy). A morphological analysis (by scanning electron microscopy [SEM]) showed that the PMMA adhered strongly to the reinforcement.

The addition of an acrylic impact modifier to PMMA and its effect on the impact response, as evaluated by a quasi-static indentation test, was reported by Bhudolia et al.<sup>[65]</sup> A composite was manufactured by the TP-RTM process with MMA (Elium<sup>®</sup> 150) and carbon fibers. Benzoyl peroxide was used as the initiator, and Paraloid EXL 2314, a soft rubber core surrounded by a rigid polymer, was added to the resin.<sup>[66]</sup> To manufacture composites, the resin was then mixed with the initiator, and the impact modifier was added to the mold with the carbon fibers. The resin was injected at a pressure of 2 bar, and was cured at room temperature. The post-curing process was performed at 80°C for 45 min. From the indentation tests, it was concluded that the composites reinforced with the impact modifier showed an increase in the peak load. The particles of the impact modifier agent decreased the failure in the composite, because these particles absorbed the impact by dissipating energy in a thermal form.

### 3.3 | Bio-based and biodegradable polymer matrix composites produced by TP-RTM

Nowadays, the growing interest in biopolymers is justified by the demand for environmentally friendly

products, biodegradable materials, and alternative production approaches to petrochemical sources, and because they offer new possibilities in terms of functional properties. The disposal of plastic waste in the environment has severe consequences for biomes, for example, altering food chains and causing irreparable damage to fauna and flora. It was estimated that world production of polymeric resins and fibers increased enormously from the 1950s, jumping from 1.5 Mt in the 1950s to 367 Mt in 2020, with only 9% of these materials being recycled.<sup>[67,68]</sup>

<sup>1</sup> These data show that the non-biodegradable plastics from petrochemical sources must be increasingly replaced by bio-based and biodegradable polymers to reduce their environmental impacts.

#### 3.3.1 | Poly( $\epsilon$ -caprolactone) matrix composites

Downes et al.<sup>[8]</sup> described the production of composites with a biodegradable PCL matrix using a technique inspired by TP-RTM. PCL is mostly used in biomedical implants and tissue engineering owing to its biocompatibility and biodegradability, as well as in packaging and microelectronics.<sup>[69,70]</sup> In this study,<sup>[8]</sup> composites were prepared by the ROP of  $\epsilon$ -CL (Solvay Interlox, Widnes, UK), with 1,4 butane-diol as the activator, diethyl zinc as the catalyst, and glass fibers as the reinforcement (Vicryl, polyglactin 910 from Ethicon). Notably, a low-molecular-weight oligomer powdered PCL (CAPA 240 Solvay Interlox) was also added. The composite production occurred at the laboratory scale; the tank was composed of a five-necked flask equipped with a mixer, and tubes to transfer the resin into the mold. The reactive system comprising the  $\epsilon$ -caprolactone, PCL oligomer (CAPA 240), and activator was heated at 80°C under a vacuum. The catalyst (15 wt%) was added to the mixture, which was then injected under nitrogen pressure into the mold. After injection, the mold was maintained at 120°C for 18 h prior to cooling to room temperature. To compare the laminates produced via TP-RTM, PCL (CAPA 650, Solvay Interlox) powder was used to produce laminates via compression molding. The molecular weight of the PCL matrix obtained via the TP-RTM process was as high as 67,300 g.mol<sup>-1</sup>, and was similar to that of commercial PCL (CAPA 650,  $M_n = 60,600$  g.mol<sup>-1</sup>). SEM micrographs showed good impregnation of the fibers by the resin, indicating that the TP-RTM process can be used for the production of PCL matrix composites.<sup>[8]</sup> Surprisingly, the authors reported that an increase in the molecular weight of the matrix (from 33,400 to 67,300 g.mol<sup>-1</sup>), which decreases the tensile modulus. The use of Vicryl fibers did not improve the mechanical properties, as they show a low



tensile modulus. One possible reason for the low tensile modulus is the presence of voids, as these may cause an early rupture of the laminate. Unfortunately, the presence of voids was not considered in this study.

Jones et al.<sup>[9]</sup> also prepared PCL matrix composites reinforced with glass fibers using TP-RTM. An  $\epsilon$ -CL monomer was used together with PCL oligomers as the initiator (CAPA 240) and diethyl zinc as the catalyst, via two routes. In the first route, the zinc-based catalyst was dissolved in a toluene solution and mixed with the monomer at 80°C. The second route was conducted at room temperature with the addition of glycerol and boron trifluoride dimethyletherate to the mixture. The RTM process was associated with the fused deposition modeling technique, which is a rapid prototyping process. The mechanical tests performed were related to the process as a whole, and not only to the composites produced by the RTM. These synthetic routes were unusual as generally, no preformed polymers or oligomers are involved in the RTM process.

### 3.3.2 | Poly(lactic acid) matrix composites

Poly(lactic acid), also called polylactide (PLA), is a bio-based, biocompatible, biodegradable polymer used in

several sectors, such as in the biomedical, packaging, and electronic industries, and for durable consumer goods.<sup>[39]</sup> Its high compostability and in vivo biodegradability are beneficial features that highlight it among the biodegradable polymers used in the industry.<sup>[40]</sup> PLA displays mechanical properties similar to those of commodity thermoplastics such as polypropylene and polyethylene terephthalate, and has appeared as an alternative for these polymers for some applications.<sup>[71]</sup> PLA production involves lactic acid derived from the fermentation of a biomass (e.g., corn, sugar beet, sugar cane). Subsequently, the PLA can be obtained by polycondensation of lactic acid, or by ROP of the lactide monomer arising from the di-cyclization of the lactic acid.<sup>[72]</sup> The life cycle of PLA is shown in Figure 16.

Even though PLA displays acceptable mechanical properties for applications such as packaging, its brittleness prevents its use in wider range of applications. In this context, the production of PLA-based composites is of prime interest, owing to their valorization. PLA-based composite materials reinforced with fibers such as carbon fibers and natural fibers (e.g., kenaf, flax, cellulose) have been studied over the last 20 years, and a review of PLA composites was reported by Murariu and Dubois.<sup>[73]</sup> Traditionally, PLA composites are produced using two

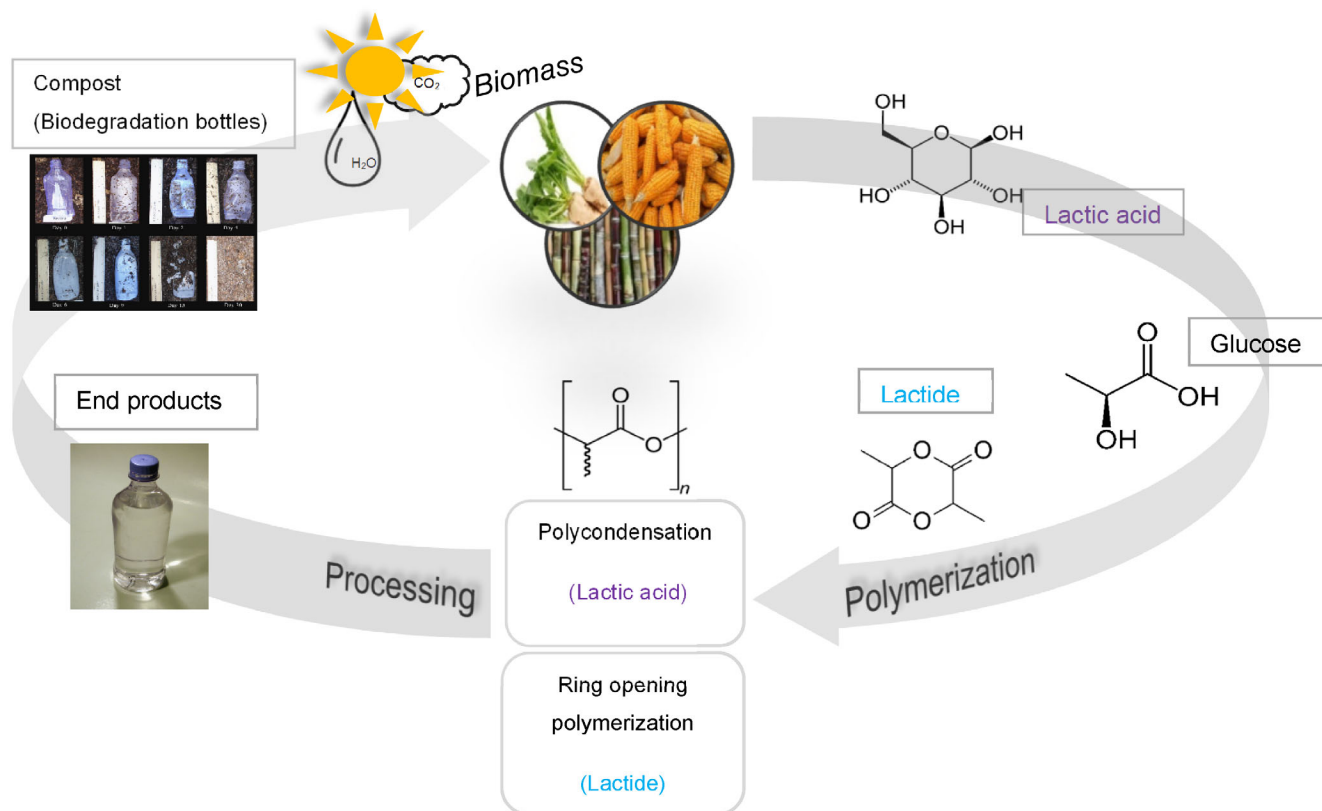


FIGURE 16 Life cycle of poly(lactic acid) (PLA) starting from glucose extracted from bio-resources. Source: Adapted from reference 73. Biodegradation of PLA bottles was reprinted from reference 74

techniques: solvent-based methods (e.g., solvent-casting) and melt-compounding (e.g., extrusion and compression molding).

The use of a TP-RTM process to produce PLLA-based composites was recently reported by Bonnet et al.<sup>[6]</sup> The composites were prepared by a coordination-insertion ROP of L-LA, conducted using tin octoate ( $\text{SnOct}_2$ ) as the catalyst and glass fabric as the reinforcement. The L-LA and catalyst were mixed together in the TP-RTM tank at 120°C under a vacuum for 30 min, allowing the monomer to melt. Nitrogen was used to inject the molten L-LA into the mold. The VARTM technique was used in this study, and the injection stage was assisted by a vacuum applied at the exit of the mold, allowing for better impregnation of the glass fabric reinforcement. The resulting PLLA-based composites display high molecular weight matrices up to 78,000  $\text{g}\cdot\text{mol}^{-1}$ , with a high monomer conversion of 97% and crystallinity ranging from 48% to 62%. The good impregnation of the fibers by the matrix was confirmed using optical microscopy. Notably, specific precautions must be taken to conduct the ROP of L-LA in the TP-RTM process. As the ROP of L-LA is sensitive to water and the monomer is highly hygroscopic, the latter must be stored under an inert atmosphere to avoid any moisture, which can decrease the degree of conversion and the molecular weight of the resulting polymer.<sup>[75]</sup> Also, the fibers must be dried prior to use, and a vacuum pump and nitrogen are needed to purge the mold before injection to eliminate residual water.

These studies on PCL and PLLA-based matrix composites show that in situ polymerization through the ROP of L-LA and  $\epsilon$ -CL monomers is possible via the TP-RTM process. Therefore, this technique should be considered for the production of novel bio-based and biodegradable composites.

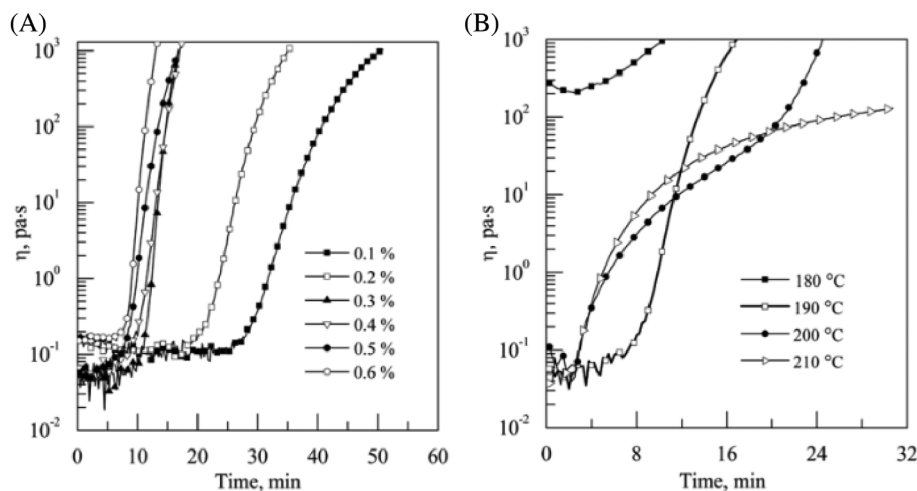
### 3.4 | Poly(butylene terephthalate) matrix composites

Poly(butylene terephthalate) (PBT) is a polyester with high strength, stiffness, and low water absorption. It is used in structural applications, the automotive industry, for packaging, and in durable goods. The production of PBT matrix composites by TP-RTM via the ROP of cyclic butylene terephthalate oligomers (CBTs) in the presence of specific catalysts has been reported in the literature. A CBT has a low processing viscosity of  $\sim 20$  mPa·s, making it suitable for the TP-RTM process.<sup>[76,77]</sup> However, CBTs are highly sensitive to water, and a drying step is needed. Another inconvenience is the high melting temperature of CBTs (up to 185°C), depending on the number of butyl groups in the oligomer mixture.<sup>[78,79]</sup>

Parton et al.<sup>[78]</sup> investigated the production of glass fiber PBT-matrix composites using the TP-RTM process. A CBT monomer (Cyclics Corporation) was associated with a tin-based catalyst (butylchlorotin dihydroxide, 0.45 wt%) to conduct the polymerization reaction. The resin was then mixed with the catalyst in a container and heated to 190°C with stirring. The viscosity of the system gradually increased, owing to the polymerization reaction. The resin was then injected into the mold at 190°C and a polymerization time of 30 min was applied. The composites produced via RTM were compared with PBT specimens fabricated via injection molding without any reinforcements. The PBT in the composite matrix showed crystallinity between 49% and 52% with large and perfect crystals, making them fragile, whereas the pure PBT showed a crystallinity rate of  $\sim 30\%$ . The authors suggested adjusting the crystallinity to decrease the brittleness of the polymer matrix.

In another study, Parton and Verpoest also studied the production of glass fiber PBT-matrix composites produced by TP-RTM.<sup>[80]</sup> The methodology used for the production of these composites was the same as in the work mentioned above.<sup>[78]</sup> Molecular weights up to 66,800  $\text{g}\cdot\text{mol}^{-1}$  were obtained with a conversion of the monomer of  $\sim 90\%$ . Compared with pure PBT, the lower crystallinity rate in the composites was attributed to the presence of the fibers. Despite this, the molecular weights obtained for the composites were close to those of commercial PBTs ( $M_w \approx 85$  kg·mol<sup>-1</sup>).

In a study of PBT matrix composites produced via VARTM, Yan et al.<sup>[6]</sup> investigated the rheological properties of CBT.<sup>[7]</sup> A relationship between the viscosity and catalyst content (butyltin tris(2-ethylhexanoate, 0.1 to 0.6 wt%) at 190°C and the variations of the viscosity at different temperatures (180 to 210°C) for the same catalyst content (0.5 wt%) were evaluated (see Figure 11). The induction time, that is, the period in which the solid monomer/oligomer was melted and mixed with the catalyst and during which the mixture exhibited a viscosity lower than 1 Pa·s (optimal for injection), decreased from 25 to 7 min with an increase in the catalyst content (from 0.1 to 0.6 wt%). The authors also reported that increasing the temperature increased the viscosity, and concurrently decreased the induction time. The longest observed induction time was 8 min at 190°C, and the authors claimed that this time is suitable for the manufacture of large-part thermoplastic laminates. At 180°C, they observed that the melt viscosity of the molten oligomer was 200 Pa·s. They indicated that the high viscosity was owing to the high molecular weight of the CBT oligomers, and because the temperature of 180°C was not sufficient to melt them completely. (Figure 17).



**FIGURE 17** Viscosity of cyclic butylene terephthalate oligomer (CBT) reactive system as function of time in different polymerization conditions. (A) Different catalyst contents at 190°C (B) different polymerization temperatures with 0.5 wt% of catalyst

For the composite production via VARTM, the CBT was melted at 190 °C under nitrogen with the catalyst (0.5 wt%) in a three-neck round bottom flask, followed by injection into a mold with pre-disposed glass fibers. The injection pressure and vacuum values were not specified. Temperatures ranging from 180 to 210°C were used to produce the composites. After the injection, the mold was heated for 1 h before being cooled to room temperature. The optimal mechanical properties were obtained for composites produced at 190°C, with a tensile strength of 549 MPa and flexural strength of 585 MPa.

#### 4 | FUTURE TRENDS OF THERMOPLASTICS SYSTEMS

Reactive thermoplastic systems can be successfully used in LCM techniques, including TP-RTM, for the production of thermoplastic matrix composites. The low viscosity of the monomers/oligomers involved in these processes leads to a high-quality impregnation of the fibers. The industrial availability of raw materials is a key factor in the manufacturing of thermoplastic-based composites using the RTM technique. In most cases, the monomers involved in reactive thermoplastic systems are cyclic and polymerized by ROP, affording high-molecular-weight matrices. Table 2 summarizes the commercial names, suppliers, viscosity, and polymerization temperatures for all reactive thermoplastic systems in TP-RTM, and the mechanical properties of the resulting matrices.

Currently,  $\epsilon$ -CL/PA-6 is the most employed reactive system in TP-RTM, owing to the good mechanical properties of the resulting composites, its industrial availability, and the low price of the monomer, catalysts, and activators. Salts of  $\epsilon$ -CL used as a catalyst and activator, generally diisocyanates and both dissolved in  $\epsilon$ -CL, were commercialized by Brüggemann Chemical (Germany) and Rhein

Chemie of Lanxess (Germany). Katchem (Czech Republic) commercialized sodium dicaprolactamato-bis-(2-methoxyethoxy)aluminate (Dilactamate<sup>®</sup>) as a solvent-based catalyst. The monomer  $\omega$ -LL and a carbodiimide-based activator (Grilonit LA), which were commercialized by EMS Chemie (Switzerland), are no longer available; this may explain the low number of studies done in the last few years. MMA-based reactive systems (Elium<sup>®</sup>) were commercialized by Arkema (France) using benzoyl peroxide as the catalyst. A CBT reactive system has been supplied by the Cyclics Corporation, under the trend name Cyclics<sup>®</sup>. Usually, these reactive systems are marketed by only one supplier owing to patent exclusivity, which can increase their prices.

The current development of eco-friendly materials suggests that the production of bio-based composites using TP-RTM should increase progressively in the coming years. The substitution of a thermosetting matrix with thermoplastic materials combined with natural fibers (ramie, hemp, sisal, kenaf, etc.) or recyclable reinforcements is an initial step in the production of green composites. An important challenge in the production of composites is the use of catalysts and activators. The use of metallic compounds such as  $\text{Sn}(\text{Oct})_2$  should be reconsidered, as even if this catalyst is approved by the US Food and Drug Administration for use in medical and food applications, it can form toxic  $\text{Sn}(\text{IV})$ -based compounds. Therefore, alternative biocompatible metal-based catalysts must be considered.

Until now, only one bio-based composite produced by TP-RTM has been reported in the literature; it was created via the ROP of L-lactide.<sup>[6]</sup> Even though L-lactide (Purac<sup>®</sup>) is commercialized at the industrial scale, one limiting factor for its use in TP-RTM could be its high cost (350 \$/kg quotation price in 2021, Corbion, Netherlands), which is 100 times higher than the price of  $\epsilon$ -CL (3\$/kg quotation price in 2021, Brüggemann Chemical, Germany).

**TABLE 2** Comparison of work temperature and viscosity for all reactive thermoplastic systems used in TP-RTM technique and mechanical properties for respective matrices

Reactive system (monomer/ Polymer)	Commercial names	Suppliers	Catalyst/ activator	Viscosity (mPa·s)	Mold temperature (°C)	Tensile strength/ tensile modulus (MPa/GPa)	References
$\epsilon$ -caprolactam/ Polyamide-6	Bruggolen <sup>®</sup>	Brüggemann Chemicals (Germany)	Sodium caprolactam salt/ carbodiimide	3–5	140–180	80/3.5	5,81,82
$\omega$ -lauro lactam/ Polyamide-12	-	Not marketed in industrial scale	Sodium caprolactam salt/ carbodiimide	4.5–8	170–205	45/1.1	53
Methyl methacrylate/Poly (methyl methacrylate)	Elium <sup>®</sup> C195 Elium <sup>®</sup> 190	Arkema (France)	Peroxide blends	100	180–200	66/3.17	64,83
Cyclic butylene terephthalate/ Poly(cyclic butylene terephthalate)	CBT <sup>®</sup>	Cyclics Corporation (USA)	Tin or titanium- based catalyst	12–33	190–240	54/2.7	84,85
$\epsilon$ -caprolactone/Poly ( $\epsilon$ -caprolactone)	Capromer <sup>™</sup> Capa <sup>®</sup> PurasorbC <sup>®</sup>	BASF (Germany) Ingevity (USA) Corbion (Netherlands)	Zinc or tin- based catalyst	nd	120	4–785/0.21–0.44	69
L-lactide/Poly(L- lactide)	Purasorb <sup>®</sup>	Corbion (Netherlands)	Tin-based catalyst	nd	185	59/3.5	6,86

Note: nd: To date, no studies on the viscosity of  $\epsilon$ -caprolactone and L-lactide have been reported.

The TP-RTM technique offers the possibility of manufacturing composites with a copolymer matrix, as in situ polymerization is possible using this technique. In this framework, the use of copolymers as matrices allows for combinations of the properties (mechanical, chemical, and thermal) of both homopolymers. Generally, the most targeted properties are the modulation of the crystallinity, an improvement of the thermal resistance, and enhancement of the mechanical properties such as toughness and ductility. By selecting new catalysts and varying the co-monomer ratios and experimental conditions, it is possible to synthesize copolymers with different architectures (block, gradient, and statistical), leading to the production of new advanced materials. Numerous copolymers have been studied in recent years, and their syntheses are well known, for example, lactam-lactam,<sup>[87]</sup> lactam-lactone,<sup>[88]</sup> and lactone-lactone.<sup>[89]</sup> The production of copolyamides via manufacturing processes such as reactive extrusion<sup>[90]</sup> and casting<sup>[91]</sup> has also been reported in literature. To date, only one academic study has been reported on using copolymers as a matrix for the production of composites via TP-RTM.<sup>[92]</sup>

The transposition of the composite synthesis from lab scale to industrial scale and adapting the copolymerization in bulk using TP-RTM remain challenges, mainly owing to the reproducibility (i.e., allowing manufacturing in a well-controlled and repeatable way). A promising future can be predicted for composites with polymeric matrices produced via the TP-RTM. This can be justified not only by the recyclability of the composite parts, but also by the enhanced properties of copolymers and beneficial post-processing features.

The replacement of thermosets with thermoplastic matrices in composites requires adaptation of the RTM process for industrial applications. New multicomponent dosing machines with mixing heads have been developed to allow for the injection of highly reactive systems, for example,  $\epsilon$ -CL/PA-6, and have been commercialized by KraussMaffei (Germany), Diatex (France), Tartler (Germany), and Wolfangel (Germany). The requirement to use high working temperatures was also an adaptation of RTM to allow for the use of solid monomers such as  $\epsilon$ -CL, L-LA, and  $\omega$ -LL at room temperature. Moreover, the problem of the water content in the reagents was partially solved with the use of a vacuum in the TP-RTM



tank, and the possibility of working under an inert atmosphere. However, water and oxygen remain the biggest issues in the ROP of cyclic esters, as they harm the reproducibility of the TP-RTM process. In that context, vacuum pumps have been used and new mold geometries have been designed to eliminate moisture.<sup>[7]</sup> In addition, an investigation of the moisture adsorption and desorption in the  $\epsilon$ -CL/PA-6 reactive system (as in fibers) has already been conducted, and should be extended to other reactive thermoplastic systems.<sup>[93]</sup> Owing to extremely low viscosity of some systems, for example,  $\epsilon$ -CL/PA-6, problems of mold sealing have arisen; nevertheless, the use of double seals can solve this problem.<sup>[7]</sup>

Mechanical, thermal, and chemical recycling are the main techniques used to recycle thermoplastic composites. Mechanical recycling is the most used technique and allows for the full recovery of the matrix and fibers, whereas thermal and chemical recycling only allow for the recovery of fibers.<sup>[94]</sup> As the technologies for recovering raw materials by grinding has been extensively investigated and is now well-established,<sup>[95–97]</sup> they can be applied to the recycling of thermoplastic composites manufactured by TP-RTM. Cousins et al. proposed a study for recycling a prototypical PMMA-based wind turbine blade produced by TP-RTM using different techniques such as pyrolysis, grinding, and dissolution.<sup>[98]</sup> In addition, they recycled wind turbine blade by thermoforming them into other products, such as skateboards. The most promising recycling technique for maintaining the good mechanical properties of recycled fibers is dissolution. The glass fibers separated by this technique generally show a tensile strength equal to that of virgin samples. Dissolution allows for a complete separation of the fibers from the matrix, but remains expensive and not eco-friendly, as solvents such as methanol and chloroform are used.<sup>[98]</sup> In terms of costs, thermoforming seems to be the most interesting technique for reprocessing large parts and giving new life to composites.

Special attention should be paid to PLA-and PCL-based composites, owing to the biodegradable nature of these polymers; thus, investigations of the recyclability and composting of such composites are of interest. Even if PLA compostability/biodegradability has already been discussed,<sup>[74,99,100]</sup> a comparison between the biodegradability of the composite matrices produced by TP-RTM and composites manufactured by more classical techniques should be performed.

## 5 | CONCLUSION

In this review, the production of thermoplastic matrix composites using TP-RTM was investigated. The use of

such composites can be expanded, as the monomers associated with the catalysts and activators display low viscosity, making them suitable for the injection step. Undoubtedly,  $\epsilon$ -CL/PA-6 is the most-used reactive system, owing to the low cost of the raw materials, short cycle time (enabling mass production), and good mechanical properties of the final composite. The use of in situ polymerization (vs. the use of preformed polymers) offers advantages such as the control of the crystallinity and molecular weights, which influence the thermomechanical properties. Accordingly, it allows for the production of composites with targeted properties for specific applications. Nevertheless, the biggest disadvantage is the high water sensitivity of the monomers, which decreases the polymerization rate and, subsequently, the molecular weight of the resulting matrices, leading to composites with poor mechanical properties.

In conclusion, the production of thermoplastic matrix composites by TP-RTM is highly advantageous, particularly because of the good impregnation of the reinforcements, and the possibility of manufacturing large parts. A promising future is expected for bio-based and biodegradable polymers in TP-RTM. In this context, studies of copolymers used as matrices should be considered in the future.

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