Application of calcium carbonate in resin transfer molding process: An experimental investigation

Anwendung von Calciumkarbonat beim Harz-Injektionsverfahren: Eine experimentelle Untersuchung

I. R. de Oliveira¹, S. C. Amico², A. G. B. de Lima¹, W. M. P. B. de Lima¹

The resin transfer molding (RTM) process is used to manufacture advanced composite materials made of continuous glass or carbon fibers embedded in a thermoset polymer matrix. In this process, a fabric preform is prepared, and is then placed into a mold cavity. After the preform is compacted between the mold parts, thermoset polymer is transferred from an injection machine to the mold cavity through injection gate(s). Resin flows through the porous fabric, and eventually flows out through the ventilation port(s). After the resin cure process (cross-linking of the polymer), the mold is opened and the part is removed. The objective of this study is to verify the application of calcium carbonate mixed in resin in the RTM process. Several rectilinear infiltration experiments were conducted using glass fiber mat molded in a RTM system with cavity dimensions of 320 × 150 × 3.6 mm, room temperature, maximum injection pressure 0.202 bar and different content of CaCO₃ (10 and 40%) and particle size (mesh opening 38 and 75 μm). The results show that the use of filled resin with CaCO₃ influences the preform impregnation during the RTM molding, changing the filling time and flow front position, however it is possible to make composite with a good quality and low cost.

Keywords: Resin transfer molding (RTM) / resin / filling time / pressure / experimental

Schlüsselwörter: Harz-Injektionsverfahren (RTM) / Harz / Füllzeit / Druck / Experiment

1 Introduction

Liquid composite molding (LCM) processes are used to manufacture composite materials by injecting liquid thermoset resin into a mold cavity in which a reinforcing fabric preform has previously been placed. The following are the most commonly used liquid composite molding processes: resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM), Seeman’s composites resin infusion molding process (SCRPIM), injection compression molding, reinforced reaction injection molding (RRIM), and structural reaction injection molding (SRIM) [1].

Resin transfer molding and other manufacturing processes of composite materials have not yet been completely automated due to the variations in raw material and in their preparation. Process monitoring plays a crucial role in the resin transfer molding process as it significantly affects the repeatability of the process cycle and the quality of parts produced.

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Monitoring the resin flow allows engineers to detect whether the flow front propagates as it was designed to or not, and hence if any undesired void remains within the mold cavity. For a good by resin transfer molding, it is necessary to know and control different processes parameters such as viscosity, injection pressure, volumetric fraction of fiber, temperature and permeability of the medium. The injection pressure and temperature gradient are the main factors [2], so their optimizations are desirable for a correct filling of the mold and high productivity. Nowadays, resin transfer molding is used by many industrial sectors such as automotive, aerospace, civil and sporting equipment [3].

Polymeric composites are constituted by two different phases, the dispersed phase (referred as reinforcing fibers or particulate) and the matrix phase (thermoset or thermoplastic polymer). The composite properties differ depending on the combinations of the two components, the matrix type, type and shape of the reinforcement, the processing method applied, among others.

The resin transfer molding process has the following major advantages: (i) manufacture of near-net-shaped composite parts; (ii) good surface finish and close dimensional tolerances; and (iii) good mechanical properties when a high content of continuous reinforcing fibers is compacted in the mold cavity. Besides its advantages, resin transfer molding has the following major disadvantages that need to be overcome, incomplete mold filling caused by inconsistencies in material (fabric preform and resin), and inconsistencies in the labor of cutting of preform and its placement into the mold cavity; and typically high cost and long cycle time compared with the metal industry [1]. In many cases, the resin is injected together with solid particles, such as calcium carbonate, in an attempt to improve the mechanical properties of the composite and optimize the process [4]. Several authors have carried out experimental investigation in resin transfer molding [5–9].

Lebrun et al. report that the use of heated resin transfer molding moulds filled with a resin at ambient temperature has been proved to be effective in lowering the overall cycle time by reducing the filling and cure cycle times [5]. Gourichon et al. in their research related to resin transfer molding process noted that a impregnation of fiber clusters may lead to local incomplete saturation of fabrics, mechanical softening, early failure, or part rejection because of high voids content [6]. A new experimental method has been proposed to measure the air volume entrapped within the wetted part of the fabric at any given time and to quantify air entrapment kinetics. An important observation is that the whole unsaturation grows linearly with time for 1D flow. The modified capillary number has been correlated to the amount of air entrapped during the injection process. However, results of this study show that it cannot account for void mobilization and elimination. A critical pressure for the onset of void mobilization has been identified for one fluid/preform combination.

Haider et al. reports a study about the effects of controlled material and processing parameters on the pressure variations, process cycle times and ultimately on the surface quality of resin transfer molding molded components [7]. Taguchi experimental design techniques were employed to design test matrices and an optimization analysis was performed. According to authors a resin with low profile additives (LPA) was used to reduce cure shrinkage and improve surface quality of the composite parts. However, little is known about the behaviour of low profile resins during resin transfer molding manufacturing and their ultimate effects on the surface quality of molded plaques.

Simon and Advani have realized an experimental study about resin transfer molding process [8]. The goal was to develop a library of experimental flow visualization and pressure measurement data. A mold was constructed, providing a moderately complex three-dimensional mold cavity. The cavity shape is a thin-shelled, five-sided box, having a base and four sides. The mold was built to provide flexibility, including multiple injection, pressure measurement, and venting sites. A wide variety of experiments were completed, varying a number of important processing parameters. All experiments were isothermal, both mold and fluid being held at room temperature. Several examples of the experiments completed are described, and organized into two case studies. The first case study demonstrates how three experiments were used in an initial investigation into the ‘racetracking’ phenomenon. The second study investigates the effect of preform fiber volume fraction on fluid injection pressure.

Sanches et al. describe a new flux limiter fixed mesh technique for the calculation of the incubation time and the fluid fraction in mold filling simulation of thin cavities containing a fiber reinforcement.
The results about the resin flow front and incubation time profile throughout the mold can be an important simulation tool with low computation cost because it can be applied to bidimensional isothermal simulations and allow an optimized resin transfer molding process design.

Lefevre et al. report an experimental investigation of the particle filtration during the injection of a composite part [11]. The experimental investigations revealed two distinguished behaviours. In the first case, filler concentration along the composite part strongly decreases showing an important retention of the particles by the fibrous preform. In the second case, filler concentration along the composite part was merely varying compared to the first case mentioned but with a characteristic U-shape curve.

Lefevre et al. have investigated a molding process through an efficient coupling between a filtration model, that has been previously described, and a flow model (Darcy’s law) [12]. It can be seen that the filtration model previously proposed has been coupled to a flow solver to simulate the molding of a resin-filled composite part. This coupling allows to quite precisely predict such molding.

Oliveira et al. report a theoretical and experimental study of the resin transfer molding process [13]. Experiments and simulations of a rectilinear infiltration of polyester resin (filled and non filled with CaCO₃) in a mold with glass fiber preform and dimensions 320 × 150 × 3.6 mm were performed. Numerical results of the filling time and fluid front position over time were assessed by comparison with experimental data and good accuracy was obtained. It was verified that the CaCO₃ content affect resin velocity during filling, the permeability of the reinforcement and resin viscosity, thus the filling time is affected strongly.

Oliveira et al. have investigated the effect caused by the use of CaCO₃ filled resin on the characteristics of the resin transfer molding process [14]. Several experiments were conducted using glass fiber mat and polyester resin molded in a resin transfer molding system with cavity dimensions of 320 × 150 × 3.6 mm. Experiments were carried out at room temperature, maximum injection pressure of 0.202 bar and different content of CaCO₃ (10 and 40%) and particle size (38 and 75 µm mesh size). Table 1 summarizes informations about the different cases and materials.

All experiments were performed by the Group of Composite and Nanocomposite Materials in the Laboratory of Polymeric Materials, Department of Materials Engineering, Federal University of Rio Grande do Sul (GCOMP/LAPOL/UFRGS), Porto Alegre – RS, (Brazil).

Before to be mixed with the polyester resin, particles of CaCO₃ were submitted to sieving in sieve with mesh sizes 38 and 75 µm. After sieving particles size distribution of the CaCO₃ was performed by means of a laser granulometer model CILAS 1180 liquid.

The resin transfer molding experiments were performed in the equipment illustrated in Fig. 1.

Fig. 2 shows the glass fiber mat and Fig. 3 shows the preform inserted in the mold. Details about the equipment and experimental procedure can be found in the related Refs. [15–17].

Table 1. Experimental condition used in this work

<table>
<thead>
<tr>
<th>Case</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh opening [µm]</td>
<td>38</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyester resin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃ content [%]</td>
<td>10</td>
<td>40</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>1260</td>
<td>1430</td>
<td>1260</td>
<td>1430</td>
</tr>
<tr>
<td>Preform</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volumetric fraction [%]</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>Glass fiber mat [g/m²]</td>
<td>450</td>
<td>450</td>
<td>450</td>
<td>450</td>
</tr>
</tbody>
</table>

Therefore, in complement for these cited researches the objective of this study is to verify the effect of the calcium carbonate mixed in resin in the resin transfer molding process. Herein, the analysis of the CaCO₃ content and particle size are performed.
In the experiments with rectilinear infiltration, after the injection pressure ($P_{\text{inj}}$) is constant, and with on the time ($t_{\text{ff}}$) required to the flow front achieve a specific position ($x_{\text{ff}}$) inside the mold, the permeability of the porous media can be obtained using the Eq. (1), as follows:

$$x_{\text{ff}}^2 = \frac{2KP_{\text{inj}}}{\varepsilon \mu} t_{\text{ff}}$$

where $\varepsilon$ is the resin volume fraction ($\varepsilon = 1 - V_f$), $V_f$ is the fiber volumetric fraction, $\mu$ is the fluid viscosity and $K$ is the fibrous media’s permeability.

The fiber volume fraction inside the mold can be calculated using the Eq. (2), as follows:

$$V_f = \left( \frac{G}{\rho h n} \right)$$

Figure 1. Photo of the RTM experimental apparatus from LACOMP/UFRGS (Brazil): (a) pressure vessel, (b) strengthened glass top mold, (c) steel lower mold, (d) pressure controller, (e) pressure transducers, (f) data acquisition system and (g) camera

Figure 2. Glass fiber mat

Figure 3. Preform inserted into the mold
where $G$ is the fiber weight, $\rho$ is the fiber’s specific mass, $h$ is the mold thickness and $n$ is the fiber mat’s stacked quantity.

Mobility is defined as being a fluid ratio of the effective permeability and viscosity. Can be represented as follows (Eq. (3)):

$$\gamma = \frac{\kappa}{\mu} \quad (3)$$

Thus, the mobility of the mixture (resin + CaCO$_3$ particles) is given by $\gamma_m = k_m/\mu_m$. As the effective permeability, mobility also depends on the fluid saturation.

### 3 Results and discussion

In the experiments with CaCO$_3$ two different average particle sizes were used. Table 2 and 3 illustrate the values of particle size of the CaCO$_3$ in distributed band. CaCO$_3$ exists in a large concentration of particles around 10–80 $\mu$m with their respective percentage of 53.3%, Table 2. The sample shows an average size of 15.83 $\mu$m.

It can be clearly seen by the particle size distribution, the greater concentration of particles occurred in 10–80 $\mu$m (66%), Table 3. The sample shows an average particle size of 21.78 $\mu$m.

The results obtained from the experiments are presented in Table 4. With the increase of the CaCO$_3$ content of 10% to 40%, higher permeability, viscosity and mold filling time are found.

It is important to obtain information on the size of the particles, since, as mentioned in the literature review, the particle size distribution can influence the mechanical properties of the composites. Figs. 4–7 show the position of the flow front as a function of time for the cases of injection of resin with 10 and 40% CaCO$_3$ with their respective granulometries (38 $\mu$m and 75 $\mu$m mesh size). In these figures, it becomes clear that the filling time of the mold is smaller for the particle size of 75 $\mu$m. With these results, it is understandable that, with the excess fine particles the average size of the air bubbles decreases, finer particles, creating smaller voids be-

| Table 2. Distribution of CaCO$_3$ particle size (Sample 1) |
|-----------------|-----------------|-----------------|
| Sample | Diameter $[\mu$m] | Average diameter $[\mu$m] |
| CaCO$_3$ | $<$1 $\leq \Phi < 10$ $10 \leq \Phi \leq 80$ | 15.83 |
| 8% | 38.7% | 53.3% |

| Table 3. Distribution of CaCO$_3$ particle size (Sample 2) |
|-----------------|-----------------|-----------------|
| Sample | Diameter $[\mu$m] | Average diameter $[\mu$m] |
| CaCO$_3$ | $<$1 $\leq \Phi < 10$ $10 \leq \Phi \leq 80$ | 21.78 |
| 6% | 28% | 66% |

| Table 4. Data obtained for each experiment carried out with calcium carbonate |
|-----------------|-----------------|
| Parameters | Mesh size $38 \mu$m $75 \mu$m |
| CaCO$_3$ content [% mass/mass] | 10 | 40 | 10 | 40 |
| Set pressure [bar] | 0.25 | 0.25 | 0.25 | 0.25 |
| Maximum injection pressure [bar] | 0.229 | 0.203 | 0.202 | 0.200 |
| Experimental permeability $[x \times 10^{-10} \text{m}^2]$ | 1.48 | 1.82 | 1.00 | 2.21 |
| Filling time [s] | 550 | 390 | 625 | 570 |
| Viscosity $[\text{cP}]$ | 962 | 2113 | 962 | 2113 |

Figure 4. Advancement of the resin flow front during infiltration rectilinear (CaCO$_3$ content 10%, $P_{set} = 0.25$ bar, $V_f = 30\%$ and mesh opening 38 $\mu$m)
between them, which results in smaller pores that difficult the resin flow.

Figs. 8 and 9 show the flow front position as a function of mold filling time for cases presented in Table 1, respectively. It can be noted that with 10%
CaCO₃ in the resin, it flows more easily than 40% CaCO₃, due to the slope. Because the higher the slope, the greater the permeability and therefore the less time filling the middle fibrous.

Results of measurements of permeability for the cases of granulometries 38 and 75 µm with constant pressure (0.25 bar) are shown in Figs. 10 and 11. Observing these results, it is noted that the permeability obtained for the case of 40% CaCO₃ is higher compared to those without screening and is similar to that reported by [16] for the case of mesh size 75 µm, approximately $2.8 \times 10^{-10}$ m². It can be noted clearly the difference between the permeability with and without screening, Table 5.

The fluid mobility versus CaCO₃ content is documented in Figs. 12 and 13. With using the sieve size 75 µm, CaCO₃ particles mixed with the resin has increased mobility in relation to the case when sieve size 38 µm is used. The smaller the particle size the smaller the phase mobility and displacement efficiency of the mixture (resin + CaCO₃), since the in-
4 Conclusions

In this paper an experimental study of rectilinear mold-filling process by a fluid mixture (polyester resin plus particles of CaCO₃) so called resin transfer molding process (RTM) has been performed. Herein, the effect of particle granulometry and content of the CaCO₃ in the porous media permeability, phase mobility, flow front position, and filling time were evaluated.

From the obtained results it can be concluded that the use of CaCO₃ in the polyester resin:

- Retards the flow of the fluid phase, into the fibrous media, consequently, difficulty to fill the mold during resin transfer molding process is greatly increased.
- Alter the porous media permeability and both viscosity and mobility of the fluid phase.
- Affect filling time. By increasing the CaCO₃ content into the resin, was verified an increase in the filling time.

Porous media permeability has varied from 1.770 to 2.300 × 10⁻¹⁰ m², while phase mobility has varied from 0.843 × 10⁻¹⁰ to 1.830 × 10⁻¹⁰ m²/cP in the experimental conditions established.

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5 References


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