Influence of calcium carbonate on RTM and RTM light processing and properties of molded composites

André C. Garay¹, Vicente Heck¹, Ademir J. Zattera², Jeferson A. Souza³ and Sandro C. Amico¹

Abstract
In the RTM light composite manufacturing process, inorganic fillers are commonly added to the resin to reduce cost and alter the final composite properties, especially rigidity, even though they also adversely affect processability. The aim of this study is to evaluate resin characteristics, reinforcement permeability, and mechanical properties of the composite and analyze the detrimental effects when a variable amount of calcium carbonate (CaCO₃) is added to the resin. The addition of calcium carbonate increased the viscosity and gel time of the resin and considerably decreased the permeability of the reinforcement and therefore the expected process productivity. Besides, Barcol hardness, short-beam strength, and elastic modulus increased for higher CaCO₃ content, whereas Izod impact, flexural, and tensile strengths decreased. Besides, the coarser CaCO₃ filler particles managed to penetrate only partially into the fiber-rich layer of the combination mat used, which comprised of a PP flow media core and glass fibers at the surface.

Keywords
resin transfer molding, resin flow, filler, RTM light

Introduction
There is a wide variety of techniques available to manufacture polymer matrix composites. The family of processes called liquid composite molding (LCM) is numerous and includes RTM (resin transfer molding) and RTM light, sometimes called L-RTM.¹ RTM and its variants have been widely used in aeronautic, automotive, nautical, energy, civil, and sports goods.¹–³ RTM consists of injecting a pre-catalyzed thermosetting resin into a mold where a preform of dried fibrous material, typically carbon fiber or glass, has been previously placed.⁴

RTM light is a vacuum-assisted RTM with low-pressure resin injection system. A peripheral vacuum is used for clamping, whereas positive pumping pressure, combined with a controlled cavity vacuum, produces consistent parts. In RTM light, at least one side of the mold is made of a fairly flexible material, e.g., a plastic or composite which is more flexible than the near-rigid mold of conventional RTM. The mold is normally translucent, enabling monitoring of the progress of the resin within the mold.¹

One of the main advantages of RTM light is that the mold can be closed and the fibrous preform can be compacted under a compaction-force which is less than that required in RTM, leading to cost and time savings.⁵ Literature on RTM light is recent and scarce, mostly focusing on the simulation aspects of the transient behavior of the flow due to the non-rigid mold

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cavity, which can lead to fiber volume fraction variation and ultimately to poor filling time predictions.\(^6\),\(^7\) The numerical effort strives to avoid dry spots, bubble entrapment, and curing during infusion, and also optimize surface quality.\(^3\)

Unsaturated polyester resins are the common choice for RTM light-molded glass fiber-reinforced parts. Inorganic fillers are often added to polyester, the most common being calcium carbonate (CaCO\(_3\)). The addition of these fillers directly influences viscosity, density, and gel time of the resin, as well as permeability of the reinforcement. During processing, the multiphase resin system (neat resin/filler) replaces the air/vacuum phase, as the flow front propagates. In fact, the main characteristic of the LCM family is that the flow of resin occurs through usually long dry paths, requiring detailed study of the flow behavior. In addition, the dual geometrical characteristic of multi-scale reinforcements and variable local mold compaction alters fiber volume fraction, which leads to capillary pressure and permeability variations.\(^8\) Surely, analysis of the flow pattern when suspensions (resin + dispersed solid particles) are used instead of neat resins becomes even more complex.\(^9\),\(^10\)

If the filling stage of the RTM process does not occur in a proper way, for instance due to a highly viscous fluid, problems arise, which may include dry spots, low productivity, and poor mechanical properties of the part, sometimes even leading to premature failure. For instance, a highly uneven flow front during filling of multi-scale (heterogeneous) reinforcements can lead to void formation in the processed material, which results in poor mechanical properties.\(^11\) In fact, void content, mechanical properties, and cost of the final composites are also affected by the presence of the filler. For instance, composite stiffness was reported to increase when the filler content is increased, whereas the composite strength remained nearly constant.\(^12\)

Considering the lack of comprehensive scientific studies related to the RTM light process and its importance in the current composite manufacturing scenario, the aim of this study is to investigate resin characteristics, reinforcement permeability, and mechanical properties of the final composite when a variable amount of calcium carbonate (CaCO\(_3\)) is added to an unsaturated polyester resin.

### Materials and methods

#### Materials

The following materials were used in the experiments:

1. Orthophthalic polyester resin (density 1.19 g/cm\(^3\) – UCEFLEX UC 5518 – Elekeiroz).

2. Initiator BUTANOX M-50 (methyl-ethyl-ketone peroxide, P-MEK) – used at 1% in relation to the resin volume.

3. Combination mat (E-glass fiber mats with a polypropylene (PP) flow media core) – 350/250/350 g/m\(^2\), manufactured by Owens Corning.

4. Calcium carbonate (CaCO\(_3\)) was used as the filler. Density was evaluated with a gas pycnometer (Multipicnometer Model MVP-1 – Quantachrome) as 2.82\(\pm\)0.01 g/cm\(^3\) and mean diameter was found using a CILAS 1180 Liquid equipment as 18.22 \(\mu\)m.

The nomenclature adopted here for the different experiments carried out is shown in Table 1. The polyester and the calcium carbonate were called (P) and (C), respectively. The resin systems or suspensions studied were called: P100/C0, P100/C5, P100/C10, P100/C15, and P100/C20, the numbers referring to the volume fraction of polyester and calcium carbonate present in each case.

#### Methods

Viscosity measurements, in the 15–30°C range, were carried out on the various resin systems studied using a Brookfield HBDV-II + C/P viscometer (S40 and S51 spindles) operating at 30–100 RPM (192–384 N/m\(^2\), respectively).

Differential scanning calorimetry (DSC) was used to evaluate the curing behavior of the various polyester/P-MEK systems, with and without the filler. DSC analysis (model Q20) was carried out from 20°C to 250°C, with a heating rate of 10°C/min. The gel time and maximum curing temperature of these resin systems were determined using Society of the Plastics Industry (SPI) Table 1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Resin</th>
<th>CaCO(_3)</th>
<th>Glass fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100/C0</td>
<td>89.7</td>
<td>–</td>
<td>10.3</td>
</tr>
<tr>
<td>P100/C5</td>
<td>85.8</td>
<td>4.3</td>
<td>9.9</td>
</tr>
<tr>
<td>P100/C10</td>
<td>81.7</td>
<td>8.2</td>
<td>10.1</td>
</tr>
<tr>
<td>P100/C15</td>
<td>78.5</td>
<td>11.7</td>
<td>9.8</td>
</tr>
<tr>
<td>P100/C20</td>
<td>75.4</td>
<td>15.1</td>
<td>9.5</td>
</tr>
<tr>
<td>P100/C0-L(^a)</td>
<td>91.1</td>
<td>–</td>
<td>8.9</td>
</tr>
<tr>
<td>P100/C5-L(^a)</td>
<td>86.5</td>
<td>4.4</td>
<td>9.1</td>
</tr>
<tr>
<td>P100/C10-L(^a)</td>
<td>83.1</td>
<td>8.3</td>
<td>8.6</td>
</tr>
<tr>
<td>P100/C15-L(^a)</td>
<td>79.6</td>
<td>11.9</td>
<td>8.5</td>
</tr>
<tr>
<td>P100/C20-L(^a)</td>
<td>76.1</td>
<td>15.2</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Note: \(^a\)L means produced by RTM light.
and ASTM standards. Thermogravimetric analysis (TGA) of the resin, the CaCO$_3$, and the fiberglass were separately carried out in a TA instruments model 2050 analyzer. The tests were performed under nitrogen atmosphere, with a heating rate of 20°C/min, from 25°C to 1000°C.

The RTM equipment consisted of a stainless steel mold (inner cavity: 320 × 150 × 3.6 mm$^3$) with a glass top that allowed visualization of the fluid flow. A digital camera was used to capture the position of the flow-front throughout the experiment. More details on the methodology used for determining permeability of fibrous reinforcements in traditional RTM can be found in the literature.$^{13,14}$ The effect of using a CaCO$_3$-filled resin on the estimation of permeability of the reinforcement was investigated through RTM experiments conducted using P100/C0, P100/C5, P100/C10, P100/C15, and P100/C20 systems as the impregnating fluid. A constant injection pressure was used, preset at 0.15 bar, and one layer of the E-glass fiber mat was pre-placed in the mold prior to injection, yielding a constant fiber volume fraction of 10% throughout the RTM experiments.

RTM light was also used in this study. The mold used for that is schematically shown in Figure 1, being designed to produce 3 mm thick trays. The vacuum pressure applied over the flange area, between the outer wing and the inner seals, was pre-set at 0.5 bar, whereas the vacuum pressure applied to the central cavity was 0.3 bar. The positive pressure inside the resin pot was pre-set to 0.3 bar to aid filling. For these moldings, a single layer of the combination mat was again used, which was impregnated using P100/C0-L, P100/C5-L, P100/C10-L, P100/C15-L, or P100/C20-L resin systems.

Density of the P100/C0-L, P100/C5-L, P100/C10-L, P100/C15-L, and P100/20-L RTM light composite samples was determined using the Archimedes method. With these results, it was possible to estimate the void content of the composite samples using ASTM D2734. ASTM D5630 was used to help in the evaluation of the distribution of calcium carbonate/glass fiber in the various regions of the composite plaque by monitoring the amount of residue at 560 ± 25°C with the aid of a muffle-furnace. This test was applied to all RTM light-molded parts, taking rectangular samples (25 × 15 mm$^2$) every 100 mm, following a straight line between the vacuum port and the injection ports (right and left directions), at the central region of the part.

Specimens for the mechanical testing were obtained exclusively from composites molded using the RTM light process. The mechanical tests included: Barcol hardness (in a Bareiss BS 61 II equipment, ASTM D2583), Izod impact (in a Ceast Impactor II machine, 5.4 J hammer, ASTM D256), short-beam (ASTM D2344), flexural (ASTM D790), and tensile (ASTM D3039). The last three tests were carried out at room temperature using an EMIC LD2000 equipment, with a 30 kN load cell. Surface morphology of the P100/C20-L composite was studied using a JEOL model 6060 scanning electron microscope operating at 10.0 keV with magnifications 27x, 70x, 190x, and 450x, after following a standard grinding/polishing protocol.

**Results and discussion**

Viscosity of the various resin systems were found to decrease with temperature (Figure 2). This is expected
since the average kinetic energy of the molecules decreases and the intermolecular forces become more effective at lower temperature, leading to higher viscosity. In addition, viscosity was found to increase with the addition of CaCO$_3$ to the resin. The presence of CaCO$_3$ increases the friction between the molecular layers, which is a consequence of inter-particle collisions,\textsuperscript{15} thereby decreasing fluidity of the fluid.

The results of the DSC analysis are shown in Table 2. It can be observed that the overall enthalpy of the curing reaction decreases with the addition of CaCO$_3$ to the resin. A great part of this reduction occurs simply because the real amount of resin in the resin system decreases with the addition of CaCO$_3$. However, when the amount of resin is corrected, i.e., as in the column called ‘J/g$_{\text{resin}}$’ in Table 2, enthalpy is still found to decrease with the amount of CaCO$_3$. The small fluctuations found at lower CaCO$_3$ content may be explained by the considerably small sample used for the DSC analysis (around 6 mg), which may not be fully representative of the bulk sample.

Following the SPI test methods, exothermic curves were obtained for each resin system and the compiled results are shown in Table 2. Gel temperature and maximum curing temperature decreased whereas gel time increased with the addition of the inorganic filler. In other words, increasing the content of CaCO$_3$ in the resin decreases the reactivity of the system. This may be expected since the filler has a high coefficient of thermal conductivity (0.24–0.30 W/K.m) in comparison to polyester (0.15–0.24 W/K.m) and acts as a kind of a physical reaction inhibitor.

The results of the RTM infiltration experiments (Figure 3) have shown that the higher the content of CaCO$_3$ in the resin, the lower the permeability and the longer the time required to fill the mold. The presence of CaCO$_3$ particles between the fibers reduces the overall porosity of the reinforcement and thus hinders the

![Figure 2. Variation of viscosity with the CaCO$_3$ content at different temperatures.](image)

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\Delta H$</th>
<th>Gel time (min)</th>
<th>Gel temperature ($^\circ$C)</th>
<th>Maximum curing temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100/C0-L</td>
<td>421.8</td>
<td>13.5</td>
<td>110.0</td>
<td>165</td>
</tr>
<tr>
<td>P100/C5-L</td>
<td>400.6</td>
<td>13.2</td>
<td>105.5</td>
<td>155</td>
</tr>
<tr>
<td>P100/C10-L</td>
<td>354.9</td>
<td>17.2</td>
<td>105.0</td>
<td>153</td>
</tr>
<tr>
<td>P100/C15-L</td>
<td>283.6</td>
<td>18.2</td>
<td>104.5</td>
<td>150</td>
</tr>
<tr>
<td>P100/C20-L</td>
<td>247.8</td>
<td>20.7</td>
<td>95.0</td>
<td>134</td>
</tr>
</tbody>
</table>
flow of resin. It is important to mention that the increase in viscosity of the resin system itself is not supposed to affect the determination of permeability, since a corrected viscosity value was used for each system when applying Darcy's Law.

Flow in a fibrous reinforcement is usually classified into macro-flow (flow through the spaces between fiber bundles) and micro-flow (within the bundles). The fibrous reinforcement discussed in this study is a glass mat comprised of non-continuous randomly oriented thin fiber bundles and the presence of the filler is expected to slow down both macro- and micro-flows. Indeed, particles are expected to be found between and within fiber bundles.

The TGA results are shown in Figure 4. The degradation of polyester occurred in three stages, as reported in the literature: (1) loss of water via dehydration, showing 8% mass loss in the 120–275°C temperature range; (2) rupture of polyester and polystyrene chains to form a primary char with a mass loss of 80% in the 275–460°C range, and (3) char oxidation, contributing to 8% mass loss in the 460–600°C range, leaving 4% residual char at 800°C. On the other hand, glass fibers do not show considerable weight loss in this temperature range, whereas calcium carbonate starts decomposing into calcium oxide (CaO) and carbon dioxide (CO₂) at c.a. 650–700°C. For PP, degradation becomes evident with increasing temperature and at 450°C, for example, it already shows severe degradation, losing between 16% and 25% in mass.

The results of the TGA analysis have allowed the use of the muffle-furnace for further investigation. Figure 5 shows the distribution of residue (mainly glass fibers + CaCO₃) in the composite along the infiltration path. Taking into account, the random fluctuation observed in both central and edge regions, particularly in the former, and the nearly horizontal linear fitting trend lines obtained, the amount of CaCO₃/glass fiber can be considered uniform in each sample.

Density of the cured neat resin was 1.18 ± 0.01, whereas the P100/C0-L, P100/C5-L, P100/C10-L, P100/C15, and P100/C20-L resin systems yielded density values, as given in Table 3. Thus, as expected, density increased with the addition of CaCO₃ since CaCO₃ (2.82 g/cm³) is denser than the polyester resin (1.18 g/cm³). This will ultimately lead to an increase in the density of the composite, which is a drawback regarding the use of these fillers since many industrial sectors, such as automotive, usually seek materials of medium performance and low weight. Calcium carbonate or any common inorganic filler that could be added to the resin causes an increase in density, but it has to be born in mind that the leading factor driving their use is the achievement of parts with higher stiffness at lower cost, which is a characteristic that can be easily obtained with low-cost ceramic fillers.

The results of void content (%V_v) of these composites are shown in Table 3. The addition of a varied amount of CaCO₃ in the resin showed a negligible influence on void content, which may be credited to the use of vacuum in the molding process, which reduces void content.

These results indicate that accumulation of calcium carbonate closer to the injection port, i.e., filtering of CaCO₃ in the fibrous medium, did not occur regardless of the amount of calcium carbonate in the suspension.
Figure 4. TGA results for polyester resin, PP, glass fiber, and calcium carbonate.

Figure 5. Residue content vs. position in the mold (RTM light) obtained for the composites produced with the various resin systems.

Table 3. Density, void content, Barcol hardness and Izod impact strength results obtained for the composites

<table>
<thead>
<tr>
<th></th>
<th>P100/C0-L</th>
<th>P100/C5-L</th>
<th>P100/C10-L</th>
<th>P100/C15-L</th>
<th>P100/C20-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.23 (±0.01)</td>
<td>1.33 (±0.01)</td>
<td>1.39 (±0.01)</td>
<td>1.44 (±0.01)</td>
<td>1.52 (±0.01)</td>
</tr>
<tr>
<td>Void content (%Vv)</td>
<td>0.98</td>
<td>1.02</td>
<td>0.98</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Barcol hardness</td>
<td>49 (±4)</td>
<td>52 (±4)</td>
<td>54 (±4)</td>
<td>55 (±4)</td>
<td>56 (±3.0)</td>
</tr>
<tr>
<td>Impact strength (kJ/m²)</td>
<td>50.0 (±4.0)</td>
<td>39.4 (±5.0)</td>
<td>35.0 (±3.9)</td>
<td>34.5 (±3.1)</td>
<td>33.9 (±2.2)</td>
</tr>
</tbody>
</table>
In Fernberg et al., particle (with the median diameter of $8 \mu m$) filtering in the reinforcement $(V_f = 50\%)$ did not occur, which is in agreement with the results of this study. It is important to mention that the glass fiber weight fraction itself is not uniform along the mold due to the nature of this reinforcement and also because only one layer was used. It can thus be considered that the fiberglass and the CaCO$_3$ are evenly distributed.

Regarding the mechanical properties of the RTM light-molded composites, Barcol hardness showed an increasing trend with the addition of CaCO$_3$ (Table 3). This was expected because CaCO$_3$ is an inorganic material with high hardness that when incorporated into the resin makes the composite harder, and also because the volume fraction of glass fibers on the surface of the composite (which comes in contact with the indenter) is quite low. Comparison of the impact strength of the composite produced with the neat resin with those produced with the filled resin systems (Table 3) shows that the composite becomes more fragile for higher CaCO$_3$ content, absorbing less energy on impact and showing a more brittle fracture behavior.

The results of short-beam testing of the composites can be seen in Figure 6(a). An abrupt increase in short-beam strength was noticed when CaCO$_3$ was added to the neat resin (comparing P100/C0-L and P90/C10-L). This was followed by a decrease in strength for higher filler content. Interestingly, Park et al. also found a maximum for ILSS (inter-laminar shear strength, i.e., short-beam strength) when adding MoSi$_2$ to a phenolic resin in carbon–carbon composites, in their case around 12% in weight. The reported increase in ILSS was credited to the effect of increasing the degree of adhesion at interfaces among the three elements, i.e., fiber, matrix, and filler, and, in addition, ILSS was found to correlate well with the London dispersive component of the surface free energy of the composites. The existence of an optimum amount of filler that maximizes short-beam strength is perhaps associated to unwanted inter-particle interactions that become significant at higher filler content and poorer wetting of the particles.

The results of flexural strength of the composites are given in Figure 6(b). As expected, the material loses strength with the incorporation of the CaCO$_3$ since this filler does not show good adhesion to the matrix in comparison with the fiber/matrix adhesion, which is promoted in the latter with the use of coupling agents. Instead, the presence of the filler yields stress concentration sites that lead to premature failure. The same explanation applies to tensile strength, which also decreased with the addition of CaCO$_3$ (Figure 7a).

On the other hand, the incorporation of CaCO$_3$ into the matrix increased the tensile modulus of the composite (Figure 7b), since each particle acts locally in helping the matrix to resist deformation. It is important to bear in mind that this is a very important characteristic of this material considering its potential application in bumpers, roofs and mudguards of buses, and bonnets of tractors.

Micrographs were taken of the polished cross-sectional surface of the P100/C20-L composite (Figure 8). Figure 8(a) shows, from right to left, the flow medium filled with resin and then the layer of glass-fibers at the surface of the composite and the reinforcement heterogeneity can be readily noticed. At higher magnification (Figure 8b), the PP fibers can be easily found on the right. At even higher magnification (Figure 8(c)–(d)), the calcium carbonate becomes apparent (neither circular nor elliptical geometries). During composite molding, the CaCO$_3$ is carried by the resin, which flows through the middle layer and then infiltrates (through-the-thickness) toward the glass layer at the surface. Although the overall glass content of the composite is around 10% (considering the whole composite

**Figure 6.** Short-beam strength (a) and flexural strength (b) of the various composites.
volume), the fiber fraction near the surface is much higher and, because of that, the coarser filler particles manage to penetrate only partially into this fiber-rich layer, becoming eventually trapped, as seen in Figure 8(d).

**Conclusions**

The use of CaCO$_3$ in polymer composites with the primary objective of reducing cost is a common practice in various sectors, including the Brazilian automotive composite industry. Even though the incorporation of this or other inorganic fillers in resins used in the RTM light process has steadily grown there are only a few scientific studies on this subject.

The results of this study showed that CaCO$_3$ impacted processability and properties of the composite, including: (1) increase in gel time, (2) decrease in gel temperature and maximum curing temperature, (3) increase in viscosity of the suspensions, exceeding the desired range for RTM processing at higher filler loading, and (4) severe decrease in permeability (fourfold) and increase in filling time for a 20% CaCO$_3$ addition. These variations may lead to great difficulties regarding mold filling and processability in liquid molding processes such as RTM light. Nevertheless, in-plane
particle filtering, or clogging, was not found in the combination mat used, partly because of the short-fiber random mat reinforcement, with a low fiber volume fraction (both typical of RTM light-molded parts), but mainly because the main flow in RTM light occurred preferably within the flow media core, which has considerably high pore sizes and permeability.

With the incorporation of CaCO₃, some composite properties improved, such as hardness, short-beam strength, and elastic modulus. However, this was associated with the decrease in impact, tensile, and flexural strength. Some of these variations were significant even for a low filler content (5% in weight) and cannot be disregarded for design purposes.

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References
