Resin Transfer Molding Of Anionically Polymerized Polyamide 12

V. Michaud, L. Zingraff, J. Verrey, P.-E. Bourban and J.-A.E. Månson

Ecole Polytechnique Fédérale de Lausanne (EPFL)
Laboratoire de Technologie des Composites et Polymères (LTC)
CH-1015 Lausanne, Switzerland
Corresponding Author's e-mail: jan-anders.manson@epfl.ch

SUMMARY: The infiltration of Lactam12 monomer and activator system into non-crimp fabrics or satin weave carbon fabrics is presented herein, with emphasis on the specific features of this system, as compared to traditional thermoset RTM. Capillary effects are shown to be significant, and their magnitude to depend on the fiber bed architecture, volume fraction and on the matrix flow-rate. In addition, the main sources for void content in the final parts are identified. The polymerization and solidification shrinkage are quantified to account for at most 9 % in the matrix. The infiltration process is studied in details to assess the role of flow rate on the formation of voids. Optimal flow conditions are determined to minimize void content during liquid molding. Finally, as the monomer is kept under Nitrogen, diffusion and solubility of Nitrogen in the monomer are characterized, to indicate that Nitrogen bubbling during injection is a major cause of voids in the final part. The average void content is reduced from initially 17% to below 1% in flat composite plates with optimized process conditions. In parallel, complex shapes including thickness variations and hollow cores are produced, demonstrating the strong potential of this material system.

KEYWORDS: reactive thermoplastic, polyamide 12, capillary effects, void reduction

INTRODUCTION

Resin Transfer Molding is traditionally reserved to thermoset matrix composites, where it finds a wide number of applications. For thermoplastic matrices, this technique is in general not possible because of the high viscosity of the matrix. Solvent processing would be feasible but is not environmentally acceptable. The infiltration of the monomer of a given thermoplastic polymer together with an activator provides an elegant solution: the monomer viscosity is often very low (comparable to that of water or molten metals), so injection is easy and requires low pressures. The polymerization reaction then proceeds within the fiber bed [1]. Among potential systems, the Lactam 12 is anionically polymerized (APLC12) using a liquid activator and catalyst system to form Polyamide 12 (PA12). The monomer and activator system can thus be mixed in the liquid state and injected as in conventional RTM, to yield PA12 matrix composites. Although very similar in concept to thermoset RTM, the APLC12 process raises a number of specific issues. Emphasis has been placed on the definition of optimal process windows for the infiltration process, and on improving the quality of the final part, in terms of final conversion

rate, but also in terms of void content. This paper reviews recent research at LTC on infiltration of APLC12 into non-crimp fabrics or satin weave carbon preforms. After a brief description of the materials and the process, the role of capillary effects will be highlighted, as well as the strategy for void reduction, based on the analysis of matrix shrinkage, flow rate optimization and diffusion and solubility of gases in the monomer. Differences and similarities with thermoset processes, in particular with epoxy matrices, will be pointed out.

MATERIALS

The resin system consists of a cyclic Lauryllactam monomer, which polymerizes into Polyamide 12 via an anionic ring-opening reaction. The monomer is stored above its melting temperature of 154°C, under a Nitrogen flow to prevent its degradation with oxygen. The liquid activating system contains both activator (carbodiimide) and catalyst (sodium-caprolactam) in solution [2,3], and is kept at room temperature, also under Nitrogen. Stored separately in an inert atmosphere, the reactants have an infinite shelf life. The polymerization is sensitive to both the purity of the compounds and the presence of moisture, oxygen and other products such as amines and acids. The polymerization kinetics are characterized as a function of temperature and activator content together with the evolution of the viscosity of the system with time and temperature [2, 3]. With 1.5% activator content, the viscosity of the resin is measured to be initially $\eta=2.3 \ 10^{-2}$Pa·s at 180°C, and to increase slowly within the first 80s. The time for complete polymerization is about 50 min at 190°C and is reduced to 20 minutes at 210°C. A Time-Temperature-Transformation diagram is also established to help define the processing window for this system [2]. It is found that because of a phase separation between the partially converted polymer and the monomer, as well as because of the long polymerization kinetics, the infiltration and polymerization should be performed above the melting temperature of the polymer (175°C). This, in turn, implies that the mold be cooled down after polymerization is complete, in order to remove the part. The need to cycle the mold temperature up to above 180°C certainly represents an economic burden and an increase in the total cycle time compared to thermoset RTM, since thermoset parts can be de-molded hot when the vitrification time is reached.

The fabrics were all manufactured with Tenax 5N21 high tensile strength carbon fibers. This fiber was selected because its sizing does not inhibit the polymerization reaction. Commercial epoxy type sizings cannot be used, as the presence of oxygen and amino groups reduces the extent of polymerization. Two types of fabrics were investigated, a 5-harness satin weave of 440 g/m^2, and a bi-axial ±45° fabric of 626g/m^2, stitched with PA66 threads.

EXPERIMENTS

The thermoplastic liquid composite molding process consists in the following steps, which are very similar to thermoset RTM with a flow-rate controlled equipment. The molten monomer and liquid activator are pumped separately to a mixing head connected to the mold to enable injection of activated monomer. With the laboratory scale equipment available, the maximum flow rate achievable is 0.1l/min. The mold contains the reinforcement preform through which

infiltration occurs. All the process is run at a minimum of 175°C. After complete polymerization, the mold is cooled down, enabling solidification and crystallisation of the PA 12 matrix.

Two molds were used in this investigation. A small mold was developed to monitor the position of the flow front during infiltration, the inlet pressure and the mold temperature (Figure 1). APLC12 composites were thus processed at different flow rates with the two fabric types. Polished sections of the obtained plates (170 x 230 mm^2) were analysed under a microscope, and the void content was quantified by image analysis.
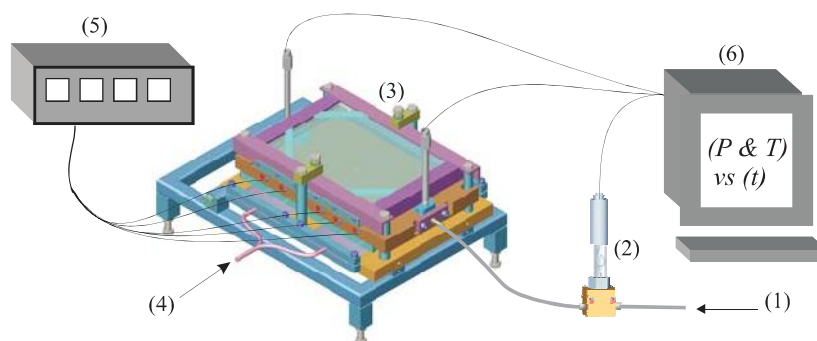

Fig. 1. Infiltration set-up, with: (1) Inlet for activated Lactam 12; (2) High accuracy pressure transducer; (3) Mold composed of a heated steel half-mold and a glass upper half-mold; (4) Compressed air inflating hoses to close the mold; (5) Heat regulation system; (6) Computer + acquisition system.

A large mold was manufactured to produce demonstration parts, which includes several features typical of a car floor-pan (hollow crossbeams, thin monolithic walls and various thicknesses) that could not be manufactured in a direct stamping operation. Figure 2 shows the bottom half of the mold. Both molds are designed to withstand temperatures up to 250°C since the polymerization of the matrix occurs at about 190°C or above. Additional details on the large mold are given in Ref. [4].

CAPILLARY PHENOMENA

A great potential of APLC12 compared to thermoset RTM is the very low viscosity of the infiltrating resin, thus reducing infiltration times or the need for high flow-rates. Also, as the infiltration is run at high temperature, it seems preferable that the resin pressure remains low in the mold, to alleviate the additional need for expensive frames or clamping equipments. This is the reason why low flow-rates are investigated. In this framework, it thus becomes relevant to investigate the magnitude of the capillary pressure drop at the flow front $\Delta P\gamma$, which is often neglected in thermoset RTM, where the inlet pressure is in general much higher than $\Delta P\gamma$ values [5]. A technique presented by Verrey *et al.* [6] is used to evaluate the capillary pressure drop in a dynamic experiment from the curve of inlet pressure increase versus time, assuming that the flow

is saturated [7]. For NCF fabric, with a volume fraction fibers of 50%, and a flow rate of 0.1l/mn, a value of $\Delta P\gamma = -13.8 \pm 3.0$kPa is obtained. The negative value indicates that the LC12 wets the reinforcement, so that flow is enhanced. Also, as the maximum inlet pressure reached during infiltration is about100kPa above the
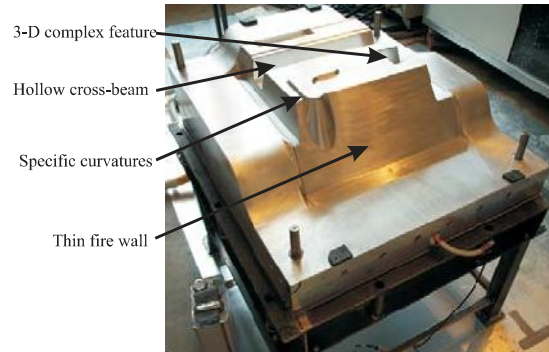

Figure 2. Lower part of the mold designed for thermoplastic components.

atmospheric pressure, $\Delta P\gamma$ represents a minimum of 14% of the pressure differential driving the flow. Similar experiments performed on NCF with an epoxy matrix have shown that effects of a similar magnitude are found for epoxy, but with an opposite sign, indicating that viscous forces tend to counteract the flow of epoxy during infiltration, although both systems are wetting according to thermodynamics [6]. This also observed directly on parts manufactured with interrupted experiments, as shown in Figure 3. When the injection is stopped, capillary forces induce a rise of resin within the bundles, leading to an unsaturated flow front. The capillary rise is of about 1 cm for the epoxy system, whereas it reaches 10 cm in the LC12 system. This indicates that the LC12 system can be injected at very low pressure, and let to infiltrate under its own capillary forces, with reasonable flow kinetics.

Similar experiments were performed with the satin weave fabric, for volume fractions of 40 to 48%, with varying flow-rates. The results are given in Figure 4, where $\Delta P\gamma$ is plotted as a function of a modified capillary number $Ca = \dfrac{Q\ \eta}{A(1-V_f)\gamma_{ma}}$, where Q is the flow-rate, A the cross-section of the fabric, η the viscosity of the matrix and γ_{ma} the surface tension of the matrix. The capillary pressure drop is still found to be negative, and increases slightly with the flow-rate, as expected from Tanner's law for dynamic wetting [7]. The magnitude is however much lower than found with the NCF fabric at a capillary number of Ca=0.0033. This was also observed with epoxy resins, and indicates that the local arrangement of bundles within the fabric plays a large role in its propensity for capillary infiltration. This should thus be checked if the process is sought to rely on capillary infiltration.

Epoxy   LC12

Saturated flow front   Unsaturated flow front

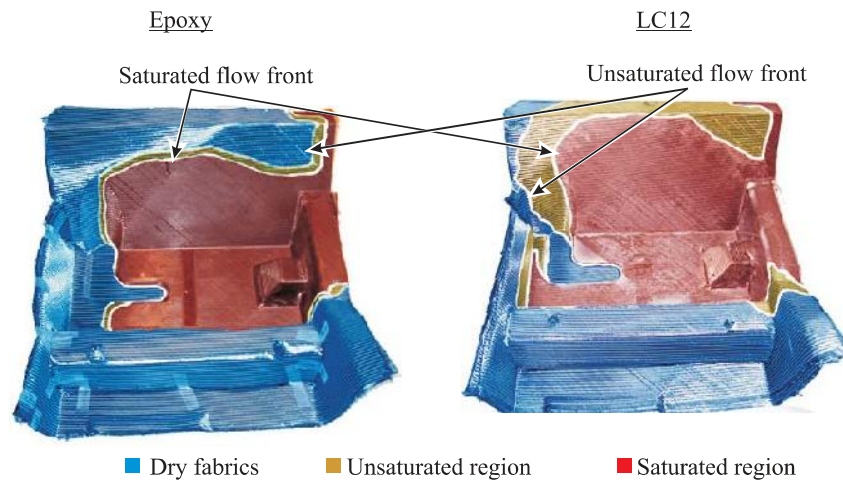■ Dry fabrics   ■ Unsaturated region   ■ Saturated region

Figure 3. Non-saturated flow front in incomplete parts with Epoxy and LC12, respectively.
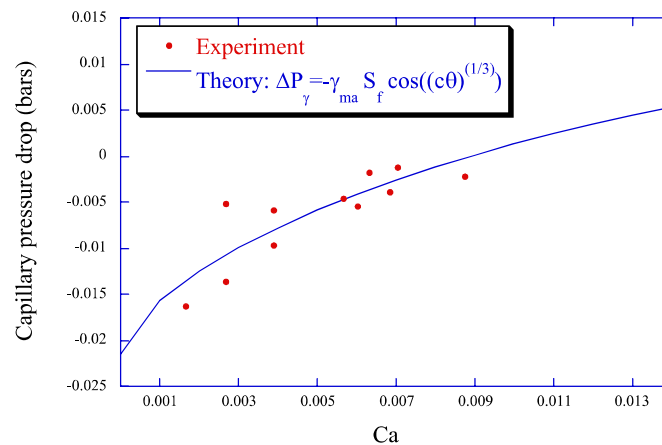

Figure 4. Capillary pressure drop as a function of Ca for the satin weave.

PART QUALITY

A necessary requirement for the APLC12 RTM process to reach a mature stage is a part quality comparable to that obtained with thermoset RTM. A first issue to address is the residual monomer content in the part. High levels of conversion are now achieved provided that the fiber sizing does not inhibit polymerization, that the preform be thoroughly flushed with Nitrogen before the infiltration, and that enough time, as indicated by the cure kinetics diagrams, is allowed for the system to polymerize before cool-down. The second issue is the residual void content in the part. Concerning this last point, a large body of knowledge has been gathered in the case of thermoset RTM [8-15], which can be quite directly applied to reactive thermoplastic processes. These studies identified the causes for void formation to include the diffusion of gases in the resin during storage, mechanical air entrapment during infiltration, nucleation of voids due to chemical reaction between the resin and the reinforcement or the release agent, leakage of the mold, inhomogeneity in the reinforcement. These phenomena result in different types of voids such as dry spots (large un-impregnated zones), macroscopic voids (entrapped air during the

infiltration process), microscopic voids (incompletely infiltrated bundles), voids created by moisture or gas liberation in the resin, or voids created by cavitation due to resin shrinkage. Following guidelines established in the literature, these points were investigated for the APLC12 system.

Matrix shrinkage

The volume evolution of LC12 upon polymerization and cooling was measured by monitoring the location of the free surface of a small amount of silicon oil placed above the molten system in a graduated test-tube [16,17]. The influence of the cooling rate and of the amount of activator were investigated. Opposite to the case of epoxy [18], no detectable shrinkage was observed during polymerization. However, shrinkage was measured during cool-down, since a fraction of the material crystallizes upon cooling below the Polyamide 12 melting temperature (174°C), while the amorphous fraction remains rubbery until the glass transition temperature (40°C). At low cooling rate (about 1.5°C/min), a volume shrinkage of 9.3% was measured, whereas at high cooling rate (about 5.5°C/min) a slightly lower value of 8.6% was obtained. By increasing the liquid activating system to LC12 ratio, a slight decrease in total shrinkage was measured, from 9 to 8.3 for an activator content ranging from 1.5 to 9 %. In summary, for most cases, the maximum void content arising from cooling shrinkage is about 9 % in the matrix, and will be reduced in the composite proportionally to the volume fraction of reinforcement. Nevertheless, care should be taken to ensure a controlled cooling of the part, as in thermoplastics molding and metal foundry practice.

Flow velocity

As observed and quantified for thermoset and model resins, the infiltration velocity, directly related to the flow rate in the present case, may influence the formation and the location of voids in the final part [13-15]. This is explained by the relative magnitude of the capillary versus viscous forces during infiltration, as represented by the capillary number Ca. Below a critical value of the capillary number, the capillary effects dominate so that the bundles are infiltrated ahead of the flow front. This may lead to gas entrapment in the inter-bundles spaces. Above the critical capillary number, the viscous forces dominate and inter-bundle flow may lead, resulting in micro-porosities inside the fiber bundles. Ideally this critical capillary number should correspond to the value at which the capillary pressure drop crosses 0 in Figure 4, at $Ca=0.009$.

A series of plates was thus manufactured with the satin weave, for different values of the flow-rate leading to capillary numbers between 0.002 and 0.01. The void content was measured, counting separately the inter-bundle void content, and the intra-bundle void content, on polished cross-sections, taken at various locations in the plate, near the inlet and in the middle. The results are given in Figure 5. First, a very large void content is observed in all cases, 6% being the minimal value observed. Secondly, a trend as predicted by the analysis of Patel *et al.* [13-15] is indeed observed. Microscopic observations support the hypothesis that inter-bundle voids dominate at low Ca, whereas intra-bundle voids dominate at high Ca. Finally, a "critical" Ca value is found at about 0.007, within the range of the value predicted above.
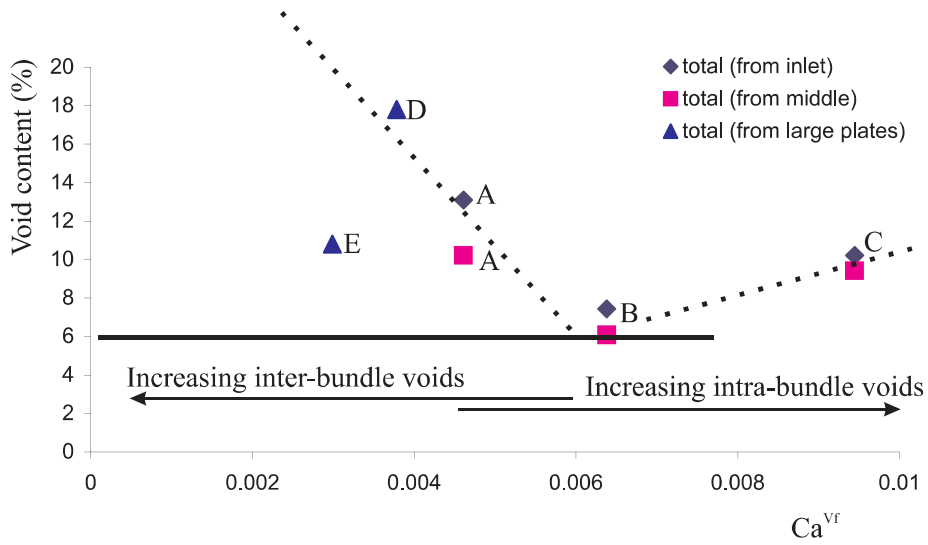
Figure 5. Void Content versus experimental Capillary number *Ca* for the satin weave.
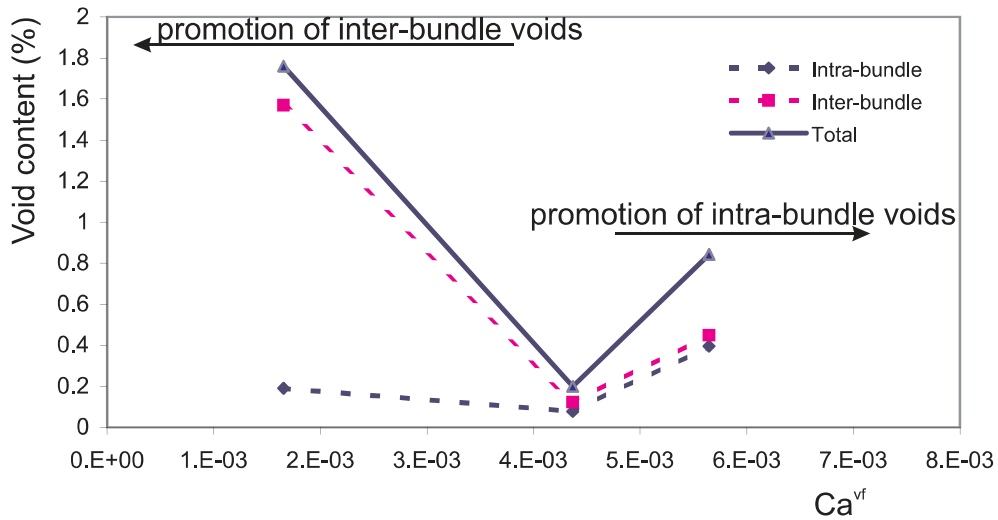

Figure 6. Void content versus experimental capillary number *Ca*, for degassed monomer and the satin weave.

Diffusion of Nitrogen

In thermoset composite molding, the resin is often degassed before injection to remove the air potentially entrapped during mixing. In APLC12 RTM, the monomer pellets are melted in the tank under Nitrogen, and the molten monomer is then kept under flowing Nitrogen, as recommended by the manufacturer to prevent its degradation. The solubility and diffusion coefficients of N_2 into the molten monomer are thus the critical parameters to evaluate this potential source of voids. Due to a lack of available data, the diffusion coefficient D of Nitrogen

in molten Lactam and the Henry's law coefficient H were experimentally determined by adapting the approach developed by Lundström for thermoset resins [10]. The D value ranges between 0.2 to $1.2.10^{-10}$ m/s^2, in a temperature range between 150 and 200°C, and the H value decreases between 4 and 0.5 10^{-5} s^2/m^2 in the same temperature range [16,17]. This indicates that if the monomer is initially free of Nitrogen, and stirred slowly, the flowing gas environment should only affect a top layer in the tank. However, since the monomer is melted under Nitrogen, a lot is initially entrapped. When the monomer is injected, its temperature raises from 175°C in the tank to up to 200°C in the mold, thereby releasing Nitrogen, since its solubility decreases with increasing temperature, at atmospheric pressure. To test this hypothesis, a special tank was designed, in which the monomer was melted and kept under vacuum. Several plates were manufactured as described earlier, but with the degassed monomer. The results of void content versus capillary number are given in Fig. 6. It is clear that this was a key factor, as the void content remains consistently below 2%, even though the same trend is observed with an optimal capillary number for best part quality.

CONCLUSION

The infiltration of APLC12 monomer and activator system into non-crimp fabrics or satin weave carbon preforms was reviewed, with emphasis on the specific features of this system, as compared to traditional thermoset RTM. The process windows for this system are now established for part production. The capillary effects are shown to enhance flow, in particular for the NCF fabrics, which are more tightly assembled. It seems thus possible to rely heavily on capillary effects to spontaneously infiltrate APLC12 into fabrics. The part quality was assessed, and it is shown that one can define optimal process parameters to minimize the void content, and that a key issue is to limit the diffusion of Nitrogen in the molten monomer before infiltration. This system thus offers a viable alternative to thermoset RTM, if thermoplastic reinforced parts are to be produced with a complex shape.

ACKNOWLEDGEMENTS

REFERENCES

1   Bourban, P.E., *Liquid Molding of Thermoplastic Composites*, in *Comprehensive Composite Materials*, A. Kelly, Editor. 2000. p. 965-977.

2   Luisier, A., Bourban, P.-E., and Månson, J.-A.E., 2001, Applied Polymer Science, (81), 963-972.

3   Luisier, A., Bourban, P.-E., and Månson, J.-A.E., 2002, Journal of Polymer Science, Part A: Polymer Chemistry, (40), 3406-3415.

4   Verrey, J., Michaud, V. and Månson, J.-A.E., "Processing of complex parts with thermoplastic RTM Techniques", 24th International SAMPE Conference, Paris, April 2003, K. Drechsler Ed. pp.553-561.

5   Michaud, V. and Mortensen, A., "Infiltration processing of fiber reinforced composites: governing phenomena", Composites part A, 32, pp.981-996, 2001.

6   Verrey, J., Michaud, V. and Månson, J.-A.E, "Capillary Effects in Liquid Composite Molding with Non-Crimp Fabrics", paper # 1658, proceedings of ICCM 14, San Diego, CA, 14-18 July 2003.

7   Berg, J., "Wettability", Surfactant Science Series, Vol.49, Marcel Dekker, INC, 1993, 531p.

8   Chen, Y.T., Davis, H.T., and Macosko, C.W., 1995, Aiche Journal, (41), 2261-2273.

9   Lundström, T.S., 1997, Composites Part A, (28A), 201-214.

10   Molnar, J.A., Trevino, L., and Lee, L.J. in Proc *44th annual conference, Composites Institute, The Society of Plastics Industry, Inc.,1989*, 1989, 1-10

11   Parnas, R.S. and Phelan, F.R. Jr, 1991, Sampe Quarterly, (23), 53-60.

12   Parnas, R.S., Salem, A.J., Sadiq, T.A.K., Wang, H.-P., and Advani, S.G., 1994, Composite Structures, (27), 93-107.

13   Patel, N. and Lee, L.J., 1995, Polymer Composites, (16), 386-399.

14   Patel, N., Lee, V., and James Lee, L., 1993, Polymer Composites, (14), 161-172.

15   Patel, N., Rohatgi,V., and Lee, L.J., 1995, Polymer Engineering and Science, (35), 837-851.

16   Zingraff, L., Bourban, P.-E., Michaud, V. and Månson, J.-A.E., "Liquid composite molding of anionically polymerized polyamide 12", paper # 1849, proceedings of ICCM 14, San Diego, CA, 14-18 July 2003.

17   Zingraff, L. "Void formation and transport during Liquid Composite Molding and Forming of reactive thermoplastic composites", EPFL PhD Thesis n°2906, 2003.

18   Eom, Y., Boogh, L., Michaud, V., Sunderland, P. and Månson, J.-A.E., "Stress initiated void formation during cure of a three-dimensionally constrained thermoset resin", Polymer Engineering and Science, Vol.41, n°3, March 2001, pp.492-503