

# Stamp-Forming of Reactive-Thermoplastic Carbon Fiber/PA12 Composite Sheet

M.D. Wakeman<sup>1</sup>, L. Zingraff<sup>1</sup>, P. Blanchard<sup>2</sup>, J.-A. E. Manson<sup>1</sup>

<sup>1</sup>*Ecole Polytechnique Fédérale de Lausanne (EPFL),  
Laboratoire de Technologie des Composites et Polymères (LTC),  
CH-1015 Lausanne, Switzerland  
Email: [jan-anders.manson@epfl.ch](mailto:jan-anders.manson@epfl.ch)*

<sup>2</sup>*Ford Motor Company, Ford Research Lab,  
2101 Village Road, Mail Drop 3135,  
Dearborn, MI 48121, USA  
Email: [pblanch3@ford.com](mailto:pblanch3@ford.com)*

**SUMMARY:** Stamp-forming trials were performed on prepreg sheets of carbon fiber reinforced PA12. A thermoplastic resin transfer molding technique was used as an interim process for experimental CF/PA12 sheet production. Design of experiment techniques were used to determine statistically significant parameters prior to more detailed investigation of void content evolution. Having demonstrated the effectiveness of the stamping process, coupled impregnation and polymerization models, linked to a technical cost model, were used to establish the feasibility of a continuous reactive impregnation line to supply such a stamping process. Over-injection molding of scrap stamped composite sheet onto the formed component was shown to integrate the structural stiffness of textile composites with the added functionality and shape stiffness of flow molding techniques, giving a closed loop recycling route.

**KEYWORDS:** *Stamp-forming, reactive-thermoplastic systems, continuous impregnation line*

## 1. INTRODUCTION

In response to driving forces requiring weight reduction in automotive structures, a stamp-forming process has been developed using carbon fiber fabrics impregnated with a reactive thermoplastic material system. This approach has been developed for large manufacturing volume applications with an emphasis on reducing production costs. This was achieved by rapid, non-isothermal stamping of a novel carbon fiber reinforced polyamide material, which offers a reduction in semi-finished material costs. Carbon fiber reinforced plates were produced via thermoplastic resin transfer molding (TP-RTM). The objectives were to identify the dominating stamping parameters and to investigate the effects of 3 activator concentrations (influencing polymer viscosity) on final stamped part quality. The potential of scaling the plaque RTM production process to a continuous reactive impregnation line was then investigated with coupled impregnation, polymerization and cost models. As a trimming operation was required after stamp forming of the blank, over-injection molding of recycled material onto a stamped composite sheet was studied as a means of cost effective recycling of scrap material.

## 2. MATERIALS AND CF/APLC12 PREPEG PROCESS

---

<sup>1</sup> To whom all correspondence should be addressed

## 2.1 Material system

A reactive thermoplastic system, with in-situ polymerization of low viscosity monomer, was used to reduce fiber bed impregnation times [1]. This consists of a cyclic amide monomer (lauro lactam) that, once activated, polymerizes in the fiber bed into polyamide 12 via an anionic ring-opening reaction (APLC12). The polymerization kinetics and the final molecular weight are controlled by the type and concentration of initiator and activator, together with process temperature. Three activator concentrations of 2%, 2.7% and 4% used in this study yield theoretical molecular weights of 45k g/mol, 27k g/mol and 23k g/mol.

## 2.2 Thermoplastic RTM process

Thermoplastic resin transfer molding was used to produce the plates (56%  $V_f$ ) (Figure 1) stamped in this study [2]. The injection unit consists of two tanks/gear pumps/pipes conveying the initiator and activator (liquid system) and monomer from the tanks to the mixing head. The monomer is molten during processing while the liquid system is at room temperature; both are held under nitrogen giving a neutral environment. Immediately prior to injection, the monomer and liquid system are combined in a static mixing head. A RTM tool with a line gate was used to produce plates measuring 450mm x 550mm. For a 1mm plaque thickness, two layers of a 5-harness satin CF weave (440 g/m<sup>2</sup>) were used [0/90]<sub>s</sub>. At a tool temperature of 180°C, activated monomer was injected into the fiber bed, and heating continued to a peak temperature of 200°C, which was then held to complete polymerization. Following the polymerization phase, the tool was cooled prior to demolding. These steps were achieved in less than 60 minutes. Typical CF/APLC12 properties were: tensile stiffness and strength of 56GPa and 600MPa (ASTM D638), flexural stiffness and strength of 55GPa and 450MPa (ASTM D790), and a compressive



Figure 1 CF/APLC12 plate cross section (before heating/stamping): porosity =3.5%

strength of 155 to 260MPa, for 1 and 3mm thick plaques respectively (ASTM D3410).

### 3. STAMP-FORMING TRIALS

#### 3.1 Processing facility

Processing of the CF/APLC12 plates was performed by non-isothermal stamping. The facility (Figure 2a) consisted of a fast response medium wave 12 zone infra red oven with upper and lower pyrometer control. This was linked by a shuttle system to a fast acting hydraulic press, with typical transfer times of 2s. Trials were conducted with both a flat plaque tool and with a generic double curvature tool (Figure 2b). This incorporated a 6-zone segmented blankholder system (individually controlled temperature and pressure levels), and enabled consideration of deformation mechanisms and measurement of coupon-based mechanical properties.

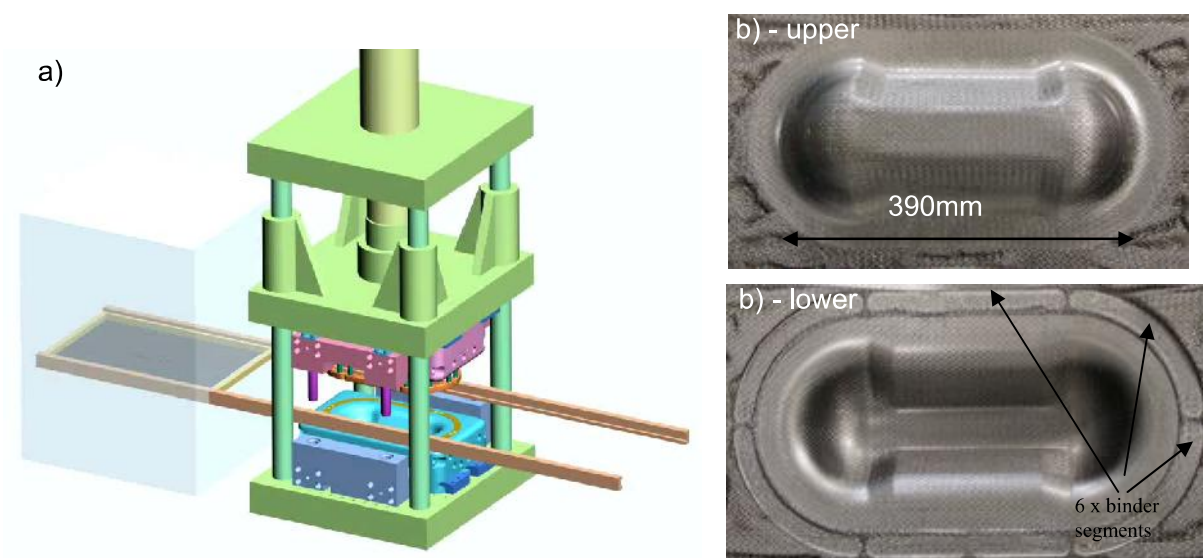


Figure 2 a) Stamp-forming cell

b) stamped CF/PA12 generic component

#### 3.2 Preheat studies

Preheat cycles, typically 120s to 280°C, were determined using thermocouples. The material exhibited limited deconsolidation (compared with commingled yarn [2]), and maximum porosity was below 10% after heating to between 180 and 280°C. Marginally increased deconsolidation occurred for higher activator levels (and hence lower viscosities). Any deconsolidation from the preheat cycle should ideally be reduced during the final stamping process.

#### 3.3 Determination of dominant stamping process parameters

The influence of material preheat temperature (200°C, 280°C), tool temperature (20°C, 120°C), stamping rate (12mm<sup>s</sup><sup>-1</sup>, 166mm<sup>s</sup><sup>-1</sup>), and time at pressure (10s, 30s) on compressive strength of 1mm thick flat plaque was investigated using a 16 run Taguchi array. Pressure was set at 40bar, after which in-plane flow of matrix material can occur. Compressive strength data was analysed. Statistically significant trends (90%) were that higher tool temperatures and increased stamping rates increased the compressive strength. Time at pressure was not statistically significant, and hence 10s was used thereafter for 1mm thick parts to give a cost effective process.

### 3.4 Effect of APLC12 activator concentration and preheat temperature

The influence of preheat temperature (180°C, 235°C, 270°C), and activator concentration (2, 2.7, 4%) was studied (9-run array). Parameters held constant were: tool temperature (120°C), stamping rate (166mm/s), pressure (40bar), and time at pressure (10s). Figure 3 shows compressive strength versus process conditions. Higher preheat temperatures increased compressive strength until a reduction at 270°C was approached (oxidative degradation). Increased activator concentrations, reducing Mw and lowering viscosities, increased compressive strength. PA12 degradation reduced properties at higher temperatures. After stamping, porosities were typically 3% for 1mm structures (Figure 4).

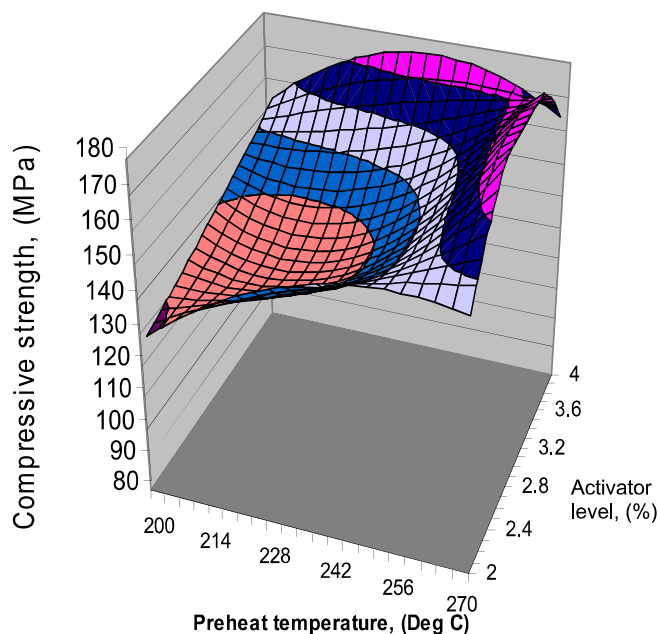


Figure 3 MLR model of CF/APLC12 study



Figure 4 CF/APLC12 stamped sheet cross-section (preheat temperature = 200°C, stamping rate = 166mm/s, 2% activator level) void content = 3.1 %

### 3.5 Over-injection molding trials

Recycled CF/APLC12 was compounded with virgin PA12 (adjusting the CF  $M_f$  to 40%) and over-molded onto a 3mm thick CF/APLC12 stamping. A standard injection cycle was used, with the CF/APLC12 stamping prewarmed ( $<T_m$ ) to facilitate in-situ fusion bonding during over-injection. Hence the intrinsic stiffness of stamped sheet was combined with the functionality and shape stiffness of injection molding, while giving a closed loop recycling route for stamping trim. Figure 5 shows the ribbed plate structure.

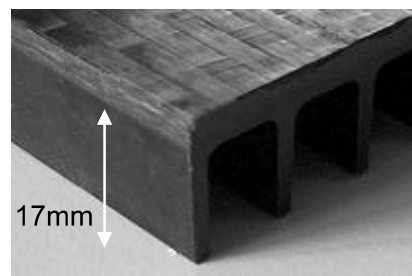


Figure 5 Over-injected stamping

## 4. CONTINUOUS REACTIVE IMPREGNATION LINE

Having demonstrated the stamp-forming of CF/APLC12 sheet produced by a batch TP-RTM process, a concept for a continuous reactive impregnation line was developed (Figure 6). Molten activated monomer would be sprayed onto fiber textiles passing continuously through an impregnation chamber and subsequently a polymerization oven, after which cooling and compaction would occur via calendaring rollers. Full preconsolidation would be of limited gain

due to preheat stage deconsolidation. A high line rate should result with low pulling forces (an impregnation die is not used) compared with an injection-pultrusion process [3]. Reduced equipment investment compared with conventional double-belt press preconsolidation processes should also occur. A model coupling impregnation mechanisms and reaction kinetics [1] of the APLC12 system was therefore developed to predict the line speeds for such a reactive impregnation line. This was then used as an input into a technical cost model [4] to estimate the final impregnated sheet cost per kg. The following approach and assumptions were taken:

- pressure applied by the spray system gives a constant driving impregnation pressure;
- material delivery rate is constant with time;
- material viscosity varies with time and the degree of polymerization;
- degree of conversion in the impregnation chamber is assumed zero (i.e. all polymerization is assumed to initiate and complete in the polymerization oven)
- time taken for the material to increase from 180°C to 245°C is assumed instantaneous.

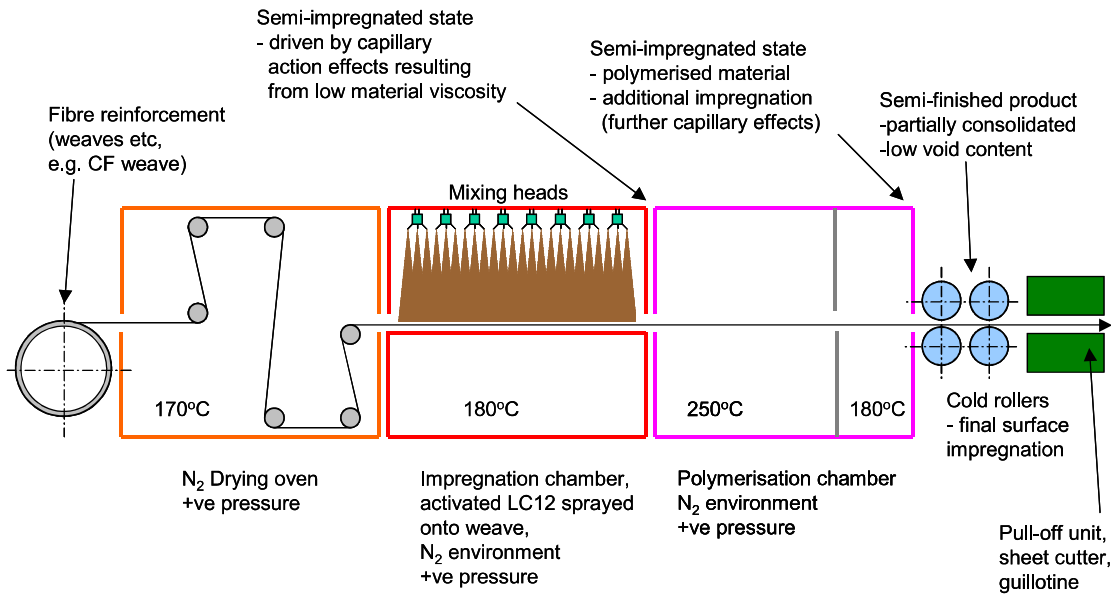


Figure 6 Continuous reactive impregnation line: textile carbon impregnated with APLC12

#### 4.1 Impregnation and polymerization

Polymerization of the sprayed activated monomer will initiate before entering the polymerization chamber. Therefore, with viscosity versus time  $\eta(t)$  a function of the degree of conversion and hence varying during impregnation, infiltration length depends on viscosity build up and hence the integral form of Darcy's law was used:

$$L^2 = \frac{2K}{(1-V_f)} (P_a + P_c) \int_0^{t_{final}} \frac{dt}{\eta(t)} \quad (1)$$

After finite difference integration, this can be rewritten as:

$$L^2 = \frac{2K}{(1-V_f)} (P_a + P_c) \sum_{i=1}^n \left( \frac{1}{2.14 \cdot \exp(-0.028T_i + (12.08 + 0.016T_i)\beta_i)} \right) \frac{t_{final}}{n} \quad (2)$$

Where:  $L$  is impregnation depth at time  $t_{final}$ ,  $K$  fiber bed permeability (Z-direction),  $P_a$  spray system pressure,  $P_c$  capillary pressure,  $V_f$  carbon fiber volume fraction,  $T_i$  temperature (in °C) at time  $i$ ; and  $\beta$  the degree of conversion at time  $i$ .

Upper and lower bounds, detailed in Table 1, were substituted in Equ. (2) to evaluate the continuous line. The upper bound transverse permeability was calculated based upon a quadratic fiber arrangement geometric approximation as  $1.7 \times 10^{-12} \text{ m}^2$ . This compared well with experimental data for the 5-harness satin weave of  $14.1 \times 10^{-12} \text{ m}^2$  for a  $V_f$  of 47% (lower bound). The capillary pressure depends on  $V_f$  and the infiltration velocity, and hence the upper and lower range of measured capillary pressures was used. An additional driving pressure results from the impingement speed of the sprayed droplets. The depth of impregnation, for a 5m long impregnation zone, was calculated numerically by a time summation of 1s steps; from zero to the time available for impregnation, with activated monomer penetration predictions in Figure 7.

Table 1 Upper and lower bound assumptions for continuous line model

Symbol and designation		Upper bound	Lower bound
L	depth of impregnation	variable of interest	variable of interest
K	fiber bed permeability in the Z-direction	$1.4 \times 10^{-11} \text{ m}^2$	$1.7 \times 10^{-12} \text{ m}^2$
$P_a$	pressure of the spray system	10,000 Pa	1,000 Pa
$P_c$	capillary pressure	1,400 Pa	500 Pa

For low line speeds (0.25 - 1 m/min), the infiltration time was sufficient for the viscosity to significantly increase, subsequently limiting the infiltration depth, as shown by the plateau. For the lower case, impregnation of a 2 mm thick textile required 6s, or at a line speed of 50 m/min, an infiltration zone length of 5 m enabled impregnation of a 2 mm thick textile. For the upper case, 2mm thick sheet could theoretically be produced above 50m/min with a 1m-impregnation zone. Hence the increasing activated monomer viscosity does not represent a significant limiting effect on line speed when infiltration is considered.

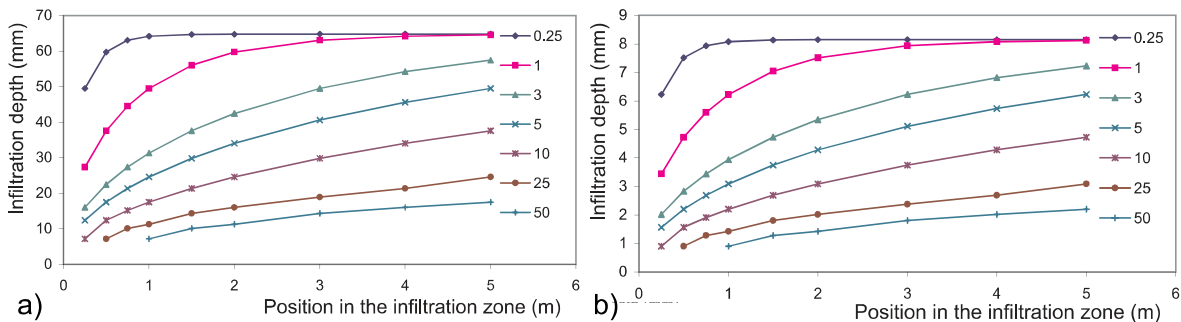


Figure 7 Depth of impregnation vs. impregnation zone position vs. line speeds (m/min); 2 wt.% of liquid system: a) Upper, b) lower bound

Following impregnation of the fiber bed, it was assumed that all polymerization occurs in the polymerization chamber at 250°C. This neglects the 10% conversion in the impregnation chamber (2 minutes at 180°C). The time required to reach 99.5% conversion (2% activator) at 250°C was 218 s, enabling the effect of line speed on polymerization zone length to be

determined. For the lower case, a line speed of 5m/min and a 2mm impregnation depth would require impregnation and polymerization chambers of 0.5m and 18m respectively; chamber length reduces further to 0.25m and 11m for a line speed of 3m/min. For the upper case the depth of impregnation did not limit line speeds in that an impregnation depth of 7mm was still possible at 50m/min for a 1m-long impregnation zone.

#### 4.4 Technical cost modeling (TCM) of the prepregging line

Based upon an X-brace concept for the Ford Thunderbird [4], the cost (excl. tax/profit) of using a continuous line at 3m/min to produce CF/APLC12 preforms (1.5m wide and 1.7 mm thick) was considered (Figure 8). Upper (2 M€) and lower (1 M€) line cost estimates were modeled. Costs were calculated for utilization-based (Ut) scenarios (i.e. cost per minute) and 1, 2 and 3 shift-

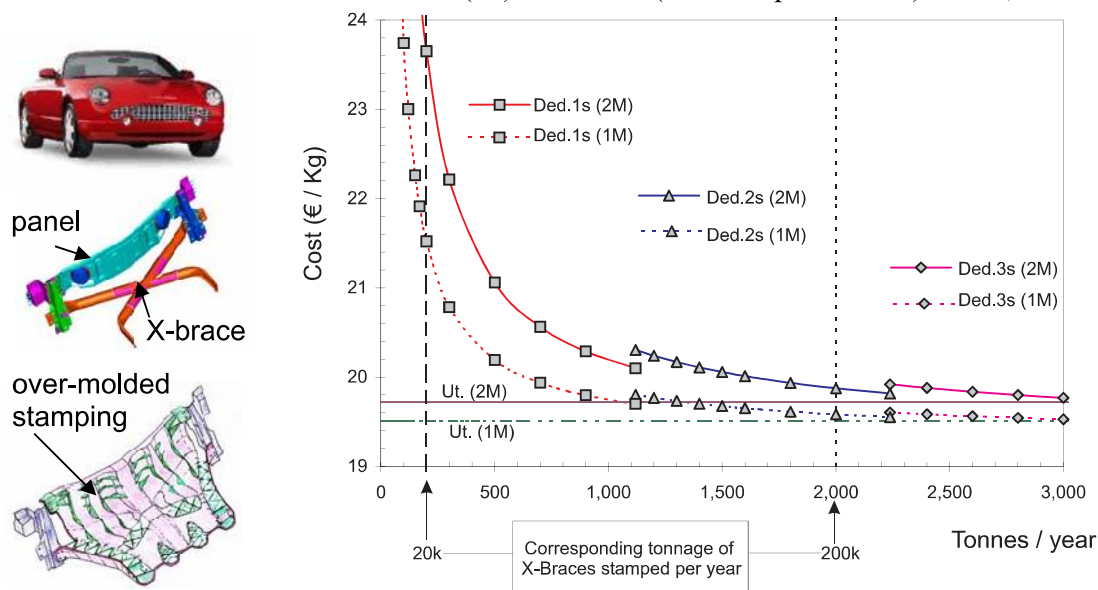


Figure 8 a) Concept application, b) CF/APLC12 prepreg cost/ kg vs. tonnes/year

based dedicated (Ded.) scenarios (line amortised over one product or client). A carbon fiber cost of €15/kg was used. For the X-brace component, a preform weight of 10kg was required to replace a steel part of 19.3kg. This required a 2.75m long CF/APLC12 preform ( $\rho = 1.43 \text{ g/cm}^3$ ). At a line speed of 3m/min, 3,700 tons/year could be produced (or 5.5 s for 1kg of preform).

For utilization-based prepreg lines (assuming full line capacity usage), equipment costs had a limited influence. With an arbitrary 30% increase for taxes and profit, the CF/APLC12 prepreg cost of 25.6 €/kg would offer a significant reduction versus commercially available materials. Where full production capacity could not be assumed, a dedicated-based scenario should be considered. Stamp-forming 20k or 200k X-brace/year would require 1 shift production to supply 200 tons/year or 2 shifts for 2000 tons/year. Prepreg costs would be (upper case, excl. tax and profit) 23.6 and 19.9 €/kg respectively.

## 5. CONCLUSIONS

Stamp-forming trials of CF/APLC12 plate, produced by a TP-RTM process, were performed to demonstrate process feasibility. To reduce prepreg cost compared with commercial products, a continuous reactive impregnation line was modeled. The line speed was predicted based upon coupled impregnation and polymerization models. For a prepreg line rate of 3m/min, a TCM was used to show the considerable cost potential of CF/APLC12.

## 6. ACKNOWLEDGEMENTS

This work was supported by Ford Motor Company and EMS-Grivory. Stamping trials were performed at a Ford facility. The authors wish to acknowledge and thank: M. Kohler, F. Demarco, F. Bonjour, P-E. Bourban, V. Michaud, D. Houston, E. Kleven, and M. DeBolt.

## 7. REFERENCES

1. Luisier, A., P.-E. Bourban, J.-A.E. Månson, "Time-Temperature-Transformation Diagram for Reactive Processing of PA12". Applied Polymer Science, 2001, 81, p.963-972.
2. Wakeman, M.D., Zingraff, L., Kohler, M., Bourban, P.-E., Månson, J.-A.E., "Stamp-forming of carbon fiber/PA12 composite preforms" ECCM10, June 3rd-7th 2002, Brugge, Belgium
3. Luisier, A., P.-E. Bourban, and J.-A.E. Månson, " Reaction injection pultrusion of PA12 composites: process and modeling", Composites: Part A 34 (2003) 583–595
4. Wakeman, M.D., Månson, J.-A.E., "Design and Manufacture of Textile Composites" Chapter 11: Cost analysis, Ed. A. Long, Woodhead, to be published summer 2004