# STUDY OF THE RESIDUAL STRAINS DEVELOPED DURING PROCESS OF EPOXY AND POLYURETHANE MATRIX COMPOSITES

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**Abstract**
*Residual strains and stresses developed during the manufacturing of composite materials influence the dimensional stability and properties during service of the composite part. FBG sensors, embedded in the reinforcement, form an adequate technique to determine the strain build-up during processing of epoxy-matrix composite laminates; they also find further use for health monitoring. This work investigates the adaptability of this technique to analyze the processing of composites with a novel PU matrix system, that provides a very fast cure, suitable for high volume applications. First, the optical sensor presented good compatibility and adhesion to the PU resin, showing the feasibility for being used in this experimental study. Then, FBG sensors were incorporated into PU-matrix composites manufactured by Resin Transfer Molding (RTM). The measured strains in PU-matrix composites were compared to the results obtained with benchmark epoxy-matrix composites manufactured with the same technique. Results showed that, similarly to epoxy composites, most of the stresses build up during cool-down from the post-cure temperature and that strains measured in the PU based composites were comparable to those obtained with similar $T_g$ epoxies.*

## 1. Introduction

Reducing greenhouse gas emissions is currently a global priority. With this main target and the new governmental regulations, the automotive industries have begun a quest for an improved efficiency by reducing the weight of the vehicles [1]. This objective can be partly achieved by replacing the existing automotive materials by lighter alternatives. Fiber reinforced polymers (FRP) are nowadays used due to their outstanding mechanical properties combined with low weight [2]. Examples of these applications can be extensively found in aerospace or sport industries, where the extra cost of advanced materials is not a restrictive factor. However, the application of high performance FRP in the automotive industry has so far been hindered by the relatively high cost of these advanced materials and process cycle limitations. In order to overcome these weaknesses, and compete effectively with lightweight alloys, chemical companies have designed new resin formulations with very short curing cycles. In the EU-FP7 project HIVOCOMP, advanced polyurethane (PU) thermoset resins are evaluated; these open the possibility to combine fast-curing (a snap-cure with a proceeding low viscosity inhibition time) with high toughness and a high glass transition temperature ($T_g$ above 180°C), required for certain automotive parts which go through the paint process [3].

Resin Transfer Molding (RTM) is possibly the most adequate processing technique to exploit all the possible benefits of the fast curing thermosetting resins. The low viscosity of the PU resin allows the full impregnation of the fabric in few minutes, even for low injection pressures. At the same time, the temperature of the mold triggers the curing reaction, which is complete after ideally one or two minutes. After this step, the composite part is fully cured and can be extracted from the mold still at high temperature. This manufacturing technique is suitable for large parts of high performance FRP in very short cycle times, which could be applied to high volume applications.

The development of residual strains and stresses during manufacturing is an important issue in composite structures, which can lead to low quality parts or dimensional variability. Furthermore, these undesirable effects are even more important for fast curing systems, such as the PU investigated in the present work, where the high temperature gradients developed by the exothermic reaction can lead to very high and heterogeneous residual strains and stresses fields. Experimental methods based on the use of strain gages attached to the composite or in the mold surface have been proposed to measure the development of strains during manufacturing cycle [4,5]. However, these methods require a difficult implementation and interpretation of the results. Alternatively, fiber optic sensors can be used to measure the evolution of residual strains *in situ* during composite manufacturing. These sensors can be easily integrated in the composite at the preforming stage and applied to monitor the strains developed during the whole manufacturing process [6, 7].

In this study, Fiber Bragg Grating (FBG) sensors have been applied to measure the residual strains developed in a carbon fiber/PU composite for short curing cycle, manufactured by RTM. The measured strains in PU-matrix composites were compared to those obtained during processing of benchmark epoxy-matrix composites manufactured with a similar processing technique.

## 2. Fiber Bragg grating sensor principles

A FBG sensor consists in an optical fiber with a periodic change in the refractive index of the core along a small segment. Thus, when white light is transmitted through an optical fiber containing a FBG, a narrow-band of light is reflected back. The wavelength of the light reflected by the Bragg grating, $\lambda_B$, depends on the effective refractive index of the fiber core, $n_{\text{eff}}$ , and the grating period, $\Lambda_0$, [8].

$$\lambda_B = 2 n_{eff} \Lambda_0 \tag{1}$$

Any change in the optical fiber varying the grating period or the refractive index will then result in a shift in the Bragg wavelength, $\Delta\lambda_B$. Thus, the variation in the reflected wavelength can be related with the variation in the strain, $\Delta\varepsilon_{app}$, and temperature, $\Delta T$, applied to the optical fiber as:

$$\frac{\Delta\lambda_B}{\lambda_{B0}} = \{1 + p_e\}\Delta\varepsilon_{app} + \{\alpha_f + \xi\}\Delta T = K_\varepsilon \Delta\varepsilon_{app} + K_T \Delta T \tag{2}$$

where $K_\varepsilon$ and $K_T$ stand for the strain and temperature sensitivities of the optical sensor, $p_e$ is the strain-optic coefficient, $\alpha_f$ is the coefficient of thermal expansion of the fiber and $\xi$ is the thermo-optic coefficient. If the optical sensor is embedded in a host structure, the thermal

expansion of the structure will produce a response in the reflected wavelength. In a first approximation [6], assuming perfect bonding, the shift in the Bragg peak is given by:

$$\frac{\Delta\lambda_B}{\lambda_{B0}} = K_s\left[\Delta\varepsilon_{app} + \Delta\varepsilon_{th}\right] + \xi\Delta T = K_\varepsilon\Delta\varepsilon_{tot} + \xi\Delta T \tag{3}$$

in which $\Delta\varepsilon_{tot}$ is the total strain transferred to the optical fiber and $\Delta\varepsilon_{th}$ is the thermal strain. This last term can be approximated as the thermal expansion of the host material when the coefficient of expansion of the optical fiber is very small in comparison to that of the host material

$$\Delta\varepsilon_{th} = \alpha_H\Delta T \tag{4}$$

where $\alpha_H$ is the coefficient of thermal expansion of the host material.

The FBG sensors used in this study were supplied by Technica SA. They are optical fiber with an acrylate coating with an initial Bragg wavelength of 1528 ± 0.5 nm, and the gauge length is 10 mm. The FBG response was stabilized through a thermal annealing of 24 hours at 120 °C. The coating of the fiber in the area of the FBG was removed using sulfuric acid to ensure good adhesion and optimal strain transfer. The strain sensitivity, temperature and the thermo-optic coefficients were experimentally calibrated [9] and their values are compiled in the table below.

| $K_\varepsilon(\mu\varepsilon^{-1})$ | $K_T(\,^\circ C^{-1})$ | $\xi\,(^\circ C^{-1})$ |
|---|---|---|
| $7.7\times10^{-7}$ | $6.92\times10^{-6}$ | $6.1\times10^{-6}$ |

**Table 1.** Strain- and thermo-optic properties of the optical sensors employed in this study.

## 3. Materials and Experimental techniques

The PU resin is a thermosetting system specially developed by Huntsman within the framework of the HIVOCOMP project. This resin combines very short curing cycles with a long pot life, excellent mechanical properties and high $T_g$ [11]. Additionally, two benchmark epoxy systems were selected: (i) Epoxy XB 3585+LME 10996 (mixing ratio of 100:20 in weight) has a short curing cycle (comparable with that of the PU system) and (ii) Araldite LY 8615 + Aradur 8615 (100:50 in weight) provides a high $T_g$. Adapted process parameters were provided by Hunstman for each system and are compiled in table 2.

The compatibility between the optical fiber and the PU resin was first assessed by manufacturing single fiber composites [10]. These specimens consisted in cylinders of resin of 12 mm diameter and 40 mm length, approximately. A FBG sensor was embedded in its center (Fig. 1a) to monitor strain change during cure. Additionally, one thermocouple was employed to capture the temperature variations. The simple geometry of the specimens allowed the direct measurement of strains developed during curing the resin and the observation of possible decohesion and incompatibilities between the optical fiber and PU matrix.

**Table 2.** Resins and manufacturing parameters employed for the composite processing

| | PU | Epoxy XB 3585 + LME 10996 | Araldite LY 8615 + Aradur 8615 |
|---|---|---|---|
| **Viscosity (25 °C) [mPas]** | 270 | 5500 | 1300-1800 |
| **Pot life (25 °C) [min]** | 40 | 15 | 850-980 |
| **Degassing process** | 30 min at 25 °C | 5 min at 50 °C | 30 min at 25 °C |
| **Temperature of injection** | 25 °C | 50 °C | 25 °C |
| **Curing process** | 10 min at 90 °C | 10 min at 90 °C | 90 min at 80 °C + 60 min at 150 °C |
| **Post-curing process** | 25 min at 190 °C | 20 min at 120 °C | 60 min at 180 °C |

Unidirectional carbon fiber composites panels were manufactured with each of the three different thermosetting systems presented above. The UD fabric was ASKA 12 k CM UD 300 provided by CARBOMID (with areal density of 300 gr/m$^2$). Radial injections were carried out at constant pressure in a rectangular steel mold to manufacture carbon/epoxy laminates with a 50% fiber volume fraction and the following dimensions: 300 mm x 200 mm x 3 mm and carbon/PU laminates with the same characteristics. Six heating cartridges on each side of the mold (top and bottom) were used to apply the desired cure cycle.

The mold surfaces were treated with release agent (ACMOS 35-5015 or 19 CMS for the PU and the epoxy resins, respectively) and flexible silicone joints were used to seal it. The preform was kept 30 min under vacuum to remove the eventual entrapped air. Once the preform was placed, the mold was closed and preheated to 70°C prior to the resin injection. This initial temperature in the mold was selected in this work to delay the snap curing reaction of the PU. It allowed the adequate impregnation of the fabric for low injection pressures, however in an industrial process, the mold could initially be heated to 90°C
For each part, one thermocouple and one FBG sensor were placed between the central plies of the laminate, as shown in Fig. 1b. The optical fiber was always oriented perpendicular to the reinforcement, in order to capture the maximum strains developed during manufacturing, since the fiber dominates strains in their direction. Small incisions were performed in the silicon joint to take out both ends of the optical fiber from the mold, keeping it sealed properly.

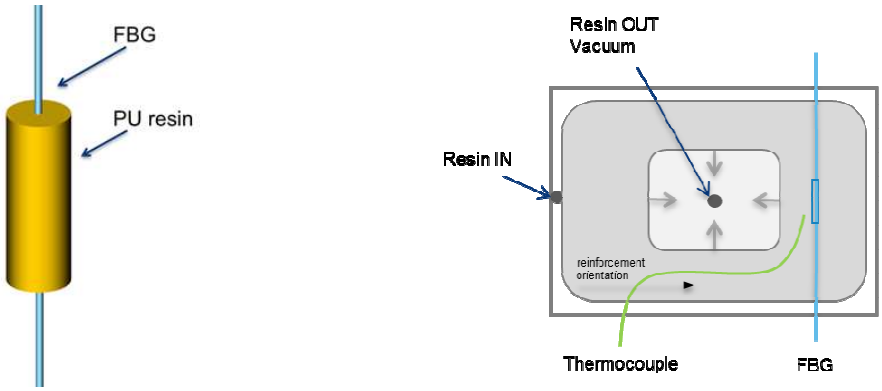


**Figure 1.** Schematic of the (a) single fiber specimens and (b) the mold and the position of the thermocouple and strain sensors.

Resin injection was carried out with a constant pressure of 1 bar above atmospheric pressure and vacuum. Once the resin started to flow out of the mold, the exit tube was blocked and the

injection pressure was maintained for three more minutes to minimize the size of the possible voids. Finally, the temperature of the mold was increased up to the curing temperature indicated in Table 2.

The composite plate was carefully removed from the mold once it was cured. The plate was positioned in an oven for the post-curing, following the temperature and time periods given by the resin suppliers (table 2). The temperature and the strain changes were monitored by the thermocouple and the FBG respectively during the post-curing process.

## 4. Results and discussion

The strains and temperatures measured during manufacturing of the Single Fiber Composite are plotted in Fig. 1. The aluminum mold was initially heated up to 70°C. The thermocouple captured a sudden drop in the temperature when the PU resin was poured into the mold. Temperature measurements showed a very sharp peak approximately two minutes after casting the resin. This sudden change in temperature was related with the exothermic curing reaction of the PU, as expected in the bulk resin sample. Shrinkage of the resin followed soon after, leading to compressive strains in the fiber. The initial curing reaction of the resin developed a compressive strain in the optical sensor of ≈-17400 με after cooling down the specimen. The post-curing process developed additional residual strains to get a final value of ≈-18500 με for the specimen at room temperature. No evidence of decohesion or incompatibility between the PU and the optical fiber was observed during the whole process, indicating that acrylate coated FBG can successfully be used in PU resins.

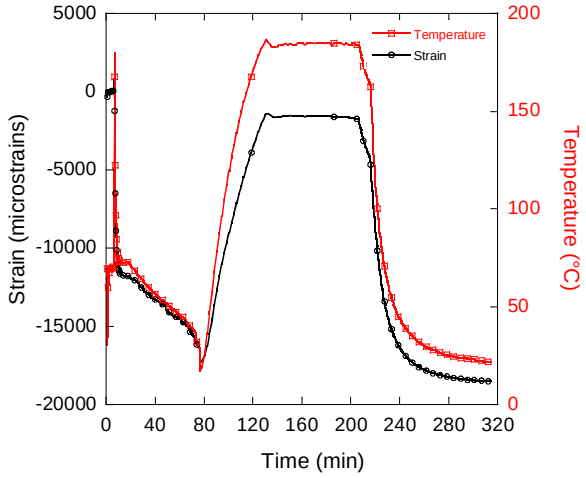


**Figure 2.** Strain and temperature evolution during the manufacturing of a PU cylinder.

Figure 3 reports one example of the transverse strain measured during VARTM processing of the carbon UD fabric with PU matrix. A rather constant strain is observed during infusion at ≈ 70 °C. During cure at 90°C, the optical sensor measured no noticeable strain development due to chemical shrinkage during the curing reaction. In the cool down stage after curing, the strains decreased to reach values of ≈-4000 με. A raise in strain was observed during the heat up for the post curing, a maximum strain of ≈ 2500 με was obtained at ≈ 190 °C. The strain measurements showed a reduction of ≈ 500 με during the time at constant temperature for the post curing. This contraction can be related with the chemical shrinkage on the PU during the post curing process. Strains become negative during the cool down due to the thermal

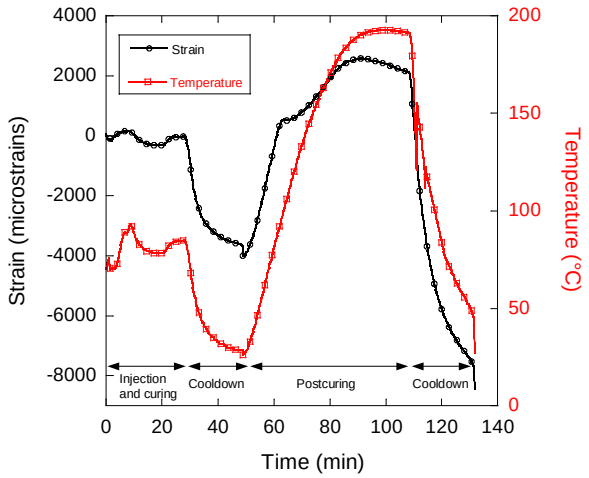


**Figure 3.** Strains and temperature evolution during the manufacturing of CF/ PU.

contraction of the PU resin. The maximum compressive strain was ≈-7500 με. Regarding the temperature curves, no evidence of the exothermic reaction was noticed in this case, as heat exchange with the bulk steel mold surrounding the preform is predominant in our experimental case.

The strains generated perpendicular to the unidirectional reinforcement in the composite manufactured with the fast curing epoxy system (XB 3585 + LME 10996) (Fig. 4) show a similar trend as the one observed in the PU matrix composite. The strain remained approximately constant during infusion of the resin. After the curing reaction, the strain decreased during cool down. After this stage, the composite showed a compressive strain of ≈-3000 με at room temperature. The evolution in the strains observed during the post curing can be explained by the thermal expansion of the resin during heating. No additional strains were detected after the post curing. This point indicates that this resin was almost fully cured after the first curing stage.

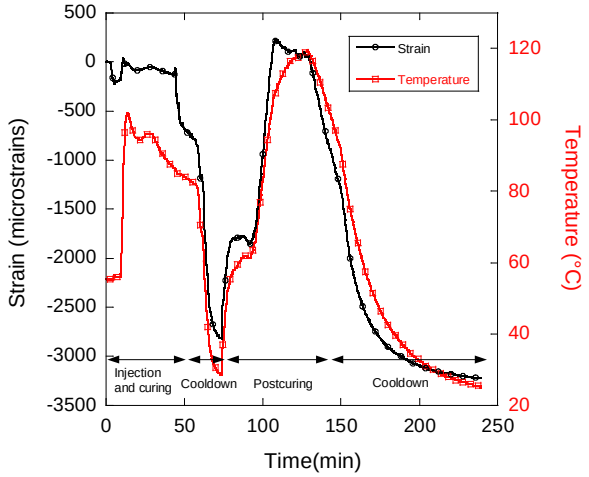


**Figure 4.** Strains and temperature evolution during the manufacturing of CF/ XB 3585.

The residual strains measured with the fast curing epoxy were lower than in the PU matrix composite. This fact is directly related to the higher temperature necessary to process the PU resin, as the post-cure was at 190 °C for the PU and 120 °C for the epoxy XB 3585. In

addition, it is worth noting that the initial viscosity of the PU resin is much lower than that of epoxy, so the shrinkage during cure is expected to be higher for PU than for epoxy, leading to additional strains. To check the influence of the resin $T_g$ and post-cure temperature, a new test with a high $T_g$ epoxy, which requires a high temperature post-cure, was carried out to compare with the strains obtained with the PU matrix. The measurement of the perpendicular strains generated in unidirectional carbon reinforced composite manufactured with Araldite LY 8615 is plotted in Fig. 5. The curing process of this resin was carried out in three main steps. The mold was maintained at 70 °C during injection of the resin. In a first curing step the temperature of the mold was increased to 80 °C during 90 min. For the second step the mold was heated up to 160 degrees and the temperature was maintained during 60 min. After this step the composite part was cooled down to room temperature and removed from the mold. The residual strain measured in after this step was ≈-6000 με. Finally the composite part was post cured at 180 °C during one hour. No noticeable additional residual strains were developed after the post curing stage. The evolution of the strains during the final cool-down allowed computing the transverse coefficient of thermal expansion (CTE) for the three composites studied (Fig. 6): $CTE_{PU} \approx 50 \cdot 10^{-6}$ °C$^{-1}$, $CTE_{XB3585} \approx 28 \cdot 10^{-6}$ °C$^{-1}$ and $CTE_{LY8615} \approx 40 \cdot 10^{-6}$ °C$^{-1}$. It is worth to notice, that the final residual strains are mainly dominated by the process temperature. The higher the postcuring temperature the larger residual strains developed. Thus, the residual strains recorded in the PU resin were not very different to those measured in the high Tg epoxy system.

## 5. Conclusions

RTM processing of composite plates with embedded fiber Bragg grating and thermocouple sensors was carried out, along with the monitoring of strains and temperature during cure and post-cure. The final residual strains were found to be dominated by temperature range of the post-cure cycle. Strains measured perpendicular to the carbon fibers show residual compressive strains of around 8000 με for the PU, 4000 με for the fast curing epoxy and 6000 με for high $T_g$ epoxy system. These differences can be attributed to the high temperature during the processing cycle, this step being required to reach a final high $T_g$. In conclusion, PU resins show a good compatibility with RTM processing for short cycle times and high resulting $T_g$. Further work is in progress to simulate the residual strain development.

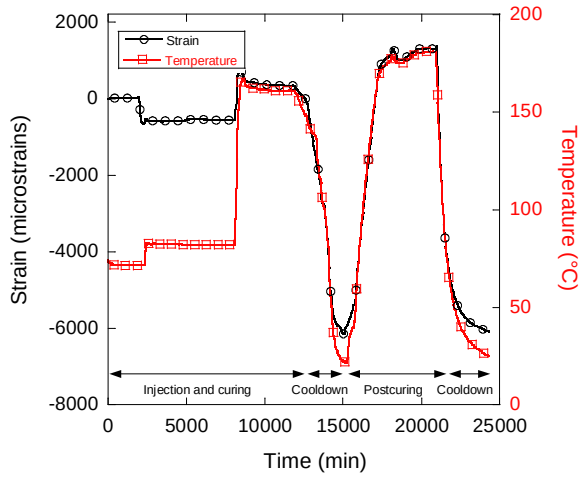


**Figure 5.** Strains and temperature evolution during the manufacturing of CF/ Araldite LY 8615.

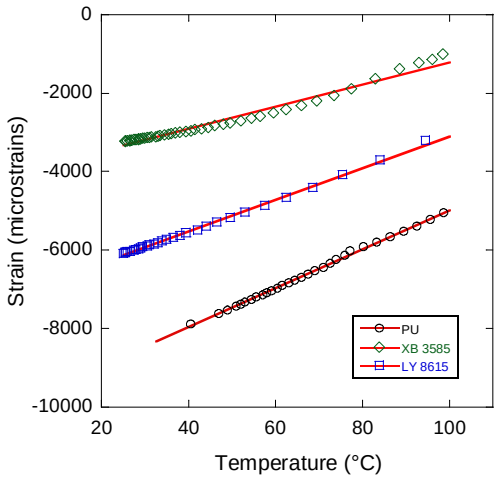


**Figure 6.** Variation of the strains with the temperature during cool-down from post-cure for the three composites studied.

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