

MEASUREMENTS OF DIMENSIONAL VARIATIONS OF SMC COMPOSITES DURING THE CURING CYCLE

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Abstract

Sheet Moulding Compound (SMC) materials are already extensively used in the automotive industry to manufacture semi-structural parts. To succeed in the optimization of the compression moulding process, it is essential to understand the anisotropic composite material behaviour and to know its properties during cure. This study focuses on the characterization of the dimensional variations of a SMC material. A standard linear dilatometer, the PVT- α mould (volumetric dilatometer) and a new specific device called HADDOC (for Heterogeneous Anisotropic Deformation and Degree Of Cure) are used to determine the thermal expansion and chemical shrinkage coefficients. The HADDOC device allows simultaneous measurements of the through-thickness and in-plane dimensional variations during the entire curing cycle. Results were found in the same range for the cured coefficients of thermal expansion between the three used devices. Thanks to the HADDOC device and the PVT- α mould, the coefficients of thermal expansion of the material and also the coefficient of chemical shrinkage were measured and compared, leading to a good correlation between both apparatuses. The anisotropic measurement indicates that most of the shrinkage occurs in the through-thickness direction of the SMC sample.

1. Introduction

SMC materials are thermoset prepregs constituted of thermoset resin containing mineral fillers and reinforced with 25-50 mm long chopped fibres [1]. This kind of composite materials are already extensively used in the automotive industry to manufacture semi-structural parts such as front end carriers, inside hatchbacks or trunk floors. In order to design and produce structural parts, the development of new formulations with higher reactivity and/or containing a high fibre content (40-60 wt%) is ongoing. SMC process by compression moulding consists in filling the cavity of a steel mould heated to a high temperature ($\sim 150^\circ\text{C}$), then in maintaining the closed mould under pressure to ensure the curing (crosslinking reaction) and finally in ejecting the part. The control of the final dimensions and properties of the moulded part requires to understand and to know the behaviour of this anisotropic composite material, especially during cure. One of the key issues concerns the accurate determination of thermal expansion and chemical shrinkage undergone by the material during the cure. Both of these dimensional changes may induce residual stress development which can result in shape distortion defects at the part length scale (*e.g.* warpage and spring-in) and/or microcracks, fibre-matrix debonding, delamination at the microscales.

Several technics exist to determine the deformations of a cured material under a thermal cycle. Among them, one can find the use of a linear dilatometer [2]. These methods are limited to investigate the

dimensional variations only due to thermal effects. If one wants to determine the material behaviour during the whole cure, it appears necessary to capture the deformations before and during the transformation. A detailed review of the different characterization techniques allowing for the determination of the coefficients of thermal expansion (*CTE*) and of chemical shrinkage (*CCS*) of thermosetting composite materials can be found in [3]. Several methods are dedicated to the characterization of the volumetric variations of the material during cure. These techniques refer in particular to the use of plunger-type dilatometers, such as the PVT- α [4] device. In order to characterize the coefficients of thermal expansion and chemical shrinkage tensors, different techniques can be used. For example, several studies are based on the use of embedded sensors, such as strain gauges [5] or optical fibre sensors [6], or of mechanical test methods, such as TMA [7], DMA [8], compression [9] or tensile test [10]. However, several limitations can be underlined: some of these methods do not provide relevant measurements before the gel point, some are intrusive, and others do not allow for measurements along several directions. A recently developed device called PVT-HADDOC [11] allows for the measurement of composite material deformations during the whole cure cycle under representative conditions and simultaneously along two directions.

Within this context, three different apparatuses are used to characterize the dimensional variations of a SMC material. First, a standard dilatometer allows for the determination of the linear thermal expansion coefficient of the SMC in the cured state along three orthogonal axes. Then, the PVT- α device is used to determine the volumetric variations of a SMC sample during cure. Finally, simultaneous measurements of the through-thickness and in-plane dimensional variations are performed during the entire curing cycle thanks to the HADDOC device.

2. Materials & Methods

This study was focused on a high reactive SMC formulation mainly composed of a polyester-based paste (matrix) and reinforced with 28 wt% chopped glass fibres (bundles of fibres).

A Linseis L75HXLT dilatometer was used to determine the linear thermal expansion coefficients of the SMC in the cured state. The experiment consists in submitting a linear heating ramp to the sample and in recording the length changes induced by the temperature variations. The thermal cycle imposed to the samples is firstly composed of a thermal equilibrating time at 20°C for 10 min and followed by a heating ramp to 200°C at a rate of 1 or 2 K.min⁻¹.

The PVT- α mould (Fig. 1) is a homemade device [12-13] in which heat flux, surface moulding cavity temperature and volume changes are measured simultaneously during the curing cycle of thermoset resins and composites, for a given applied pressure.

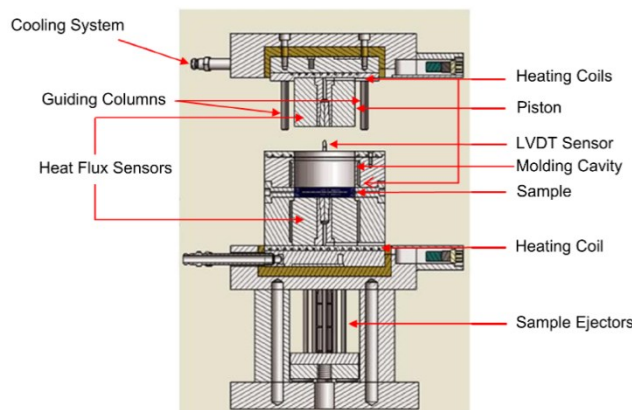


Figure 1. PVT- α mould cross section

The experiments are performed in industrial-like conditions, *i.e.* an adjustable pressure up to 10 MPa in the moulding cavity and a temperature up to 200°C. This apparatus, based on a plunger-type

dilatometer, is constituted of a cylindrical stainless steel cavity with a 50 mm internal diameter in which a 4-6 mm thick sample is positioned. This instrument is equipped with a LVDT-type displacement sensor and two heat flux sensors. The mould is designed so that heat transfer is 1D through the sample thickness. The volume change is identified by measuring the displacement through the thickness of the sample assuming that its diameter remains constant during the whole experiment (which is verified by comparing the initial and the post-cured SMC sample diameter). The thermal cycle imposed to cure SMC samples in PVT- α mould is given below:

1. Equilibrating the system at 35°C and adjusting the static pressure (2 MPa), for 10 min,
2. Heating to 180°C at a rate of 3 K.min⁻¹,
3. Isothermal step at 180°C for 15 min,
4. Cooling to 35°C at a rate of 3 K.min⁻¹.

This cycle is doubled so as to get the cured sample behaviour during a whole heating-cooling cycle. To remove the influence of thermal expansion of the PVT- α apparatus, a baseline is performed with an aluminum reference material whose properties are known.

The HADDOC device (Fig. 2) allows for the simultaneous measurement of deformation along two main directions of a sample submitted to a constant pressure level and a thermal cycle.

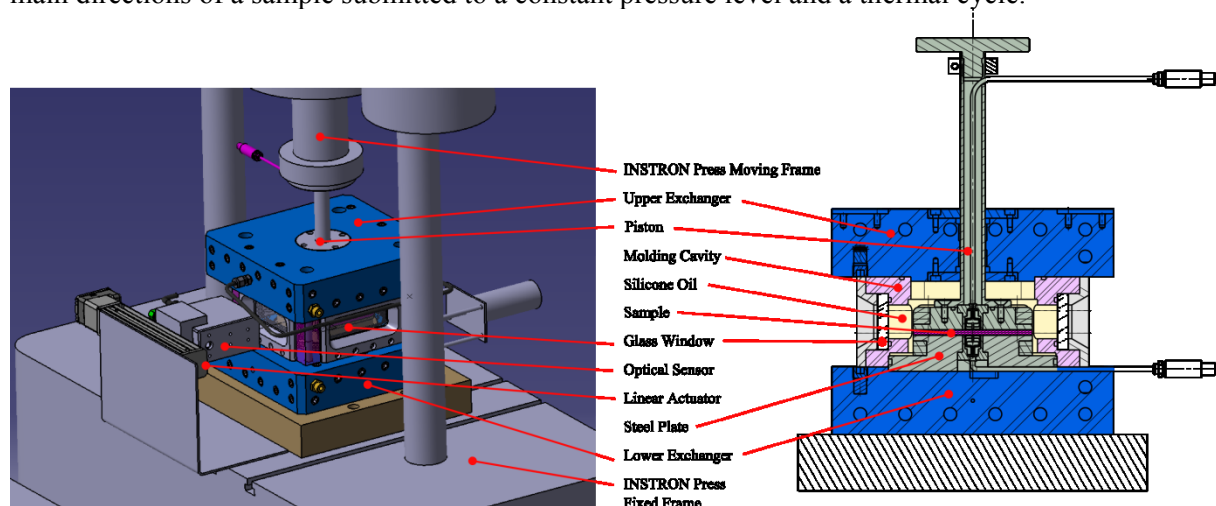


Figure 2. Global overview of the HADDOC device

The sample is placed between a piston and a stainless steel plate. These different elements are located inside of a pressurizable cavity filled with silicon oil. The whole system is placed on an Instron electrical press. By controlling the force applied by the piston through the thickness of the sample and the pressure applied by the silicone oil, it is possible to precisely control the mechanical stress state around the sample. The pressure inside the molding cavity ranges from 0.1 to 1.0 MPa. Thanks to the two heat exchangers, one can apply a thermal cycle to the sample from 20 to 200°C, with heating ramps up to 5 K.min⁻¹. The piston displacements are recorded and are directly related to the thickness evolution of the sample. A Keyence contactless profilometer is placed behind a glass window and follows the evolution of a measuring line on the lateral side of the sample with time. Two heat flux sensors are also placed on top and bottom of the sample. More details concerning this device can be found in [11]. The SMC sample was made of two stacked sheets of 105*105 mm in plane dimensions. The experiments were performed under a 0.7 MPa pressure and with the following thermal cycle:

1. Equilibrating at 30°C for 10 min,
2. Heating to 90°C at a rate of 1.5 K.min⁻¹,
3. Isothermal step at 90°C for 10 min to reach uniform temperature in the sample,
4. Heating to 100°C at a rate of 1.5 K.min⁻¹,
5. Isothermal step at 100°C for 40 min,
6. Cooling to 30°C at a rate of 1.5 K.min⁻¹.

A baseline was also performed under the same conditions to subtract the system thermal expansion recorded during the measurement done with the sample.

3. Results & discussion

3.1. Linear thermal expansion behaviour at the cured state

The linear thermal expansion behaviour of the SMC in the cured state was investigated using a standard dilatometer. Samples were cut in an industrial SMC moulded plate in the in-plane direction (along axis x and y) and in the through-thickness direction (z -axis) (Fig. 3.a). The slope of the evolution of the relative elongation ($\Delta L / L_0$) versus temperature gives the coefficient of linear thermal expansion (CTE_l) (Fig. 3.b). Along the three axis, the evolution of $\Delta L / L_0$ of the sample revealed a slope change for a temperature of around 110-120°C so that two CTE_l values can be distinguished (table 1). Global CTE_l values were also calculated on the whole temperature range (50 to 200°C) in order to get an approximate average trend.

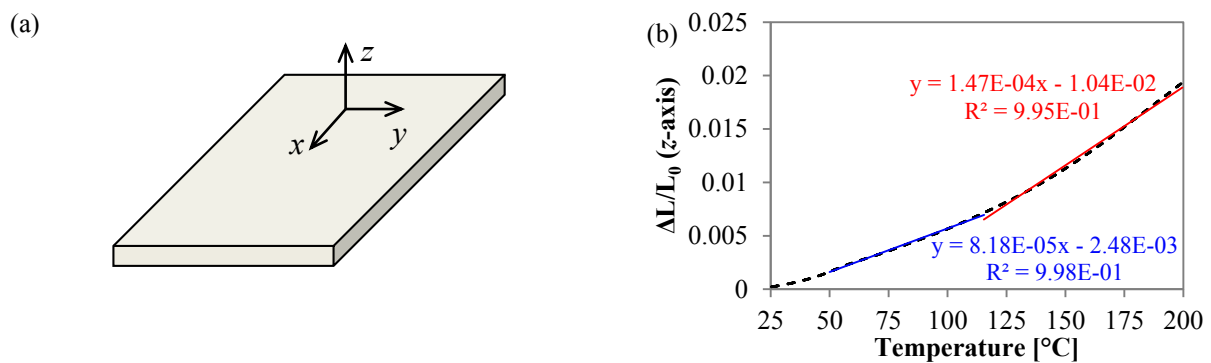


Figure 3. (a) Axes of SMC samples cutting, (b) Evolution of the relative length as a function of temperature for a SMC sample cut along z -axis (dashed line: experimental data)

Table 1. Thermal expansion coefficients in the cured state from standard dilatometry

	$CTE_l; 50-115^\circ C$ [$10^{-6} K^{-1}$]	$CTE_l; 115-200^\circ C$ [$10^{-6} K^{-1}$]	$CTE_l; 50-200^\circ C$ [$10^{-6} K^{-1}$]
x-axis	23 ± 11	12 ± 2	16 ± 6
y-axis	31 ± 2	14 ± 1	21 ± 1
z-axis	87 ± 5	153 ± 6	122 ± 6
Volumetric	141 ± 18	179 ± 9	159 ± 14

One can notice that the CTE_l change occurs in the opposite tendency between the in-plane direction and the through-thickness direction (table 1). When the temperature becomes higher than 110-120°C, $CTE_{l,z-axis}$ values show an increase whereas $CTE_{l,in-plane}$ values tend to decrease. The glass transition (T_g) phenomenon is the classical interpretation to justify a CTE_l value rise for thermoset systems [2,14-15]. Nevertheless, the glass transition cannot explain the trend observed in the in-plane direction. This behaviour is reproduced along the two axis of the plan and was not detected when paste samples was tested. The presence of the fibrous network plays certainly a role in this odd $CTE_{l,in-plane}$ diminution. The results also point out that the CTE values in the through thickness direction are three to ten times upper than those determined in the plan of the SMC plate. This significate thermal expansion anisotropy is related to the distribution of the fibers that are orientated according to the main plane of the SMC plate. The in-plane thermal expansion may therefore be constrained by the fibrous network.

In assuming that the axis x , y and z correspond to the composite main directions, an estimation of the volumetric CTE is proposed in table 1 by summing the CTE values determined in the three axis.

3.2. Volume changes through the thickness variations, thanks to the PVT- α experiment

Volume changes of SMC during the curing cycle were investigated using the PVT- α device. Fig. 4.a displays the evolution of the thickness and of the conversion degree of the SMC sample during the first heating ramp. Before the onset of the reaction (❶), the volumetric thermal expansion coefficient (CTE_v) for the uncured state (table 2) is determined since only thermal expansion contributes to the thickness increase. The chemical shrinkage phenomenon (❷) causes a severe diminution of the thickness. The thermal expansion and chemical shrinkage phenomena coexist during the reaction. Just after the step (❷), the sample thickness stabilizes (❸) as if the material was in a pseudo-glassy state, characterized by a low thermal expansion behaviour. Then, the thickness of the sample in the cured state linearly increases only due to thermal expansion (❹). For accuracy reason, CTE_v for the cured state was determined during the second heating ramp. As highlighted with standard dilatometry results, two values of thermal expansion coefficients for the cured state were identified (table 2).

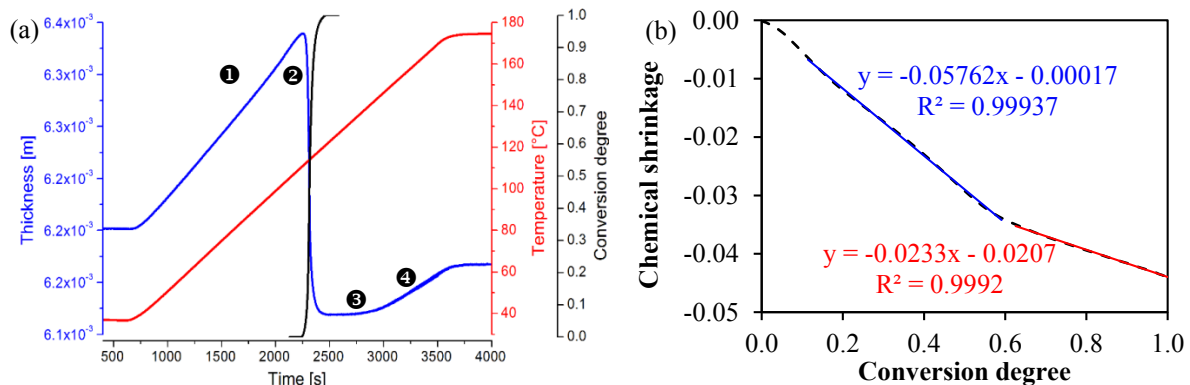


Figure 4. Variation (a) in the SMC sample thickness during the curing cycle (first heating ramp) and (b) in chemical shrinkage with conversion degree

Table 2. Volumetric thermal expansion coefficients from PVT- α measurement

	Uncured state	Cured state	
		50-115°C	115-165°C
CTE_v [$10^{-6} K^{-1}$]	404 ± 5	114 ± 7	196 ± 11

The volumetric chemical shrinkage was then deduced by subtracting the contribution linked to thermal expansion from the measured sample thickness [14,17]. The variation of the volumetric chemical shrinkage versus the conversion degree (Fig 4.b) reveals a slope change for a conversion degree of around 0.6 so that two chemical shrinkage coefficients (CCS_v) values can be distinguished. This bilinear shrinkage evolution was previously observed on thermoset systems [3,13]. If the glass transition temperature of the system is close to the imposed moulding temperature, it is known that the glass transition causes the slowing down of the crosslinking kinetics [17] and a weakening of the shrinkage is therefore expected to occur. Besides, the weakening of the chemical shrinkage may also be explained by the macroscopic manifestation of shrinkage compensation mechanism [13]. The apparent chemical shrinkage presents an amplitude of -4.4 % (Fig 4.b).

3.3. Measurements of dimensional variations into two directions (HADDOC device)

Using the PVT-HADDOC device, it was possible to follow the deformations of a sample of SMC material along two directions during the whole cure cycle (Fig. 5.a). The heat flux densities obtained from the heat flux sensors also allowed for estimating the degree of cure inside the sample.

The temperature recorded on the lower surface of the sample follows the imposed thermal cycle (blue curve on Fig 5.a).. During the isothermal step at 100°C, a temperature peak can be observed around $t = 3500$ s, which is due to the exothermic reaction. The evolution of the degree of cure indicates that the reaction totally occurs during this step. The deformations in the through-thickness direction evolve the same way as the temperature during the first steps of the curing cycle until $t = 3200$ s. Then, a decrease of the deformation appears during transformation, which is due to chemical shrinkage. The deformation remains relatively constant during the end of the isothermal step and then decreases with the temperature. The evolution of the through-thickness deformation versus temperature is plotted in Fig. 5.b. During heating (zone 1), the deformation evolves linearly with temperature. The slope of this line gives the *CTE* in the through-thickness direction in the uncured state. Then, during the isothermal step at 100°C (zone 2), the deformation drop leads to an estimation of the *CCS* in the through-thickness direction, by neglecting the thermal gradients in first approximation. Finally, the slope of the line during the cooling step (zone 3) gives the *CTE* in the totally cured state.

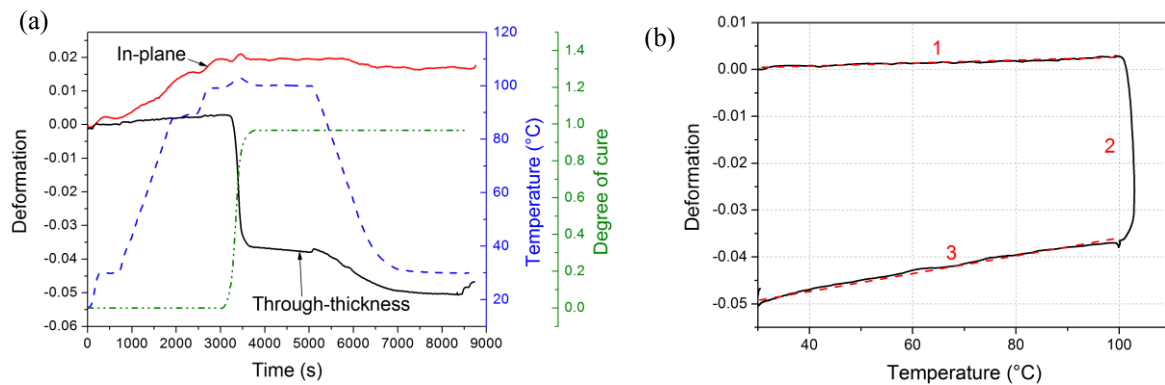


Figure 5. Evolution (a) of SMC sample deformation along two directions during the whole cure cycle and (b) of the through-thickness deformation versus temperature

The study of the in-plane deformation is carried out following the same methodology. The *CTE* and *CCS* values are summed in tables 3 and 4, where subscripts *tt*, *ip* and *v* stand for through-thickness, in-plane and volumetric, respectively. By considering the SMC material as transverse isotropic in its plane, the volumetric *CTE* and *CCS* can be obtained by applying:

$$CTE_v = CTE_{tt} + 2*CTE_{ip} \text{ and } CCS_v = CCS_{tt} + 2*CCS_{ip} \quad (1)$$

Table 3. Thermal expansion coefficients determined from HADDOC experiment

	Uncured state	Cured state
CTE_{tt} [$10^{-6} K^{-1}$]	40 ± 2	189 ± 10
CTE_{ip} [$10^{-6} K^{-1}$]	180 ± 67	38 ± 7
CTE_v [$10^{-6} K^{-1}$]	400 ± 136	266 ± 15

Table 4. Chemical shrinkage coefficients determined from HADDOC experiment

CCS_{tt} [%]	-4.0 ± 0.1
CCS_{ip} [%]	-0.2 ± 0.1
CCS_v [%]	-4.4 ± 0.3

The results in the uncured state are surprising. According to the material structure, one would have found a higher value of *CTE* in the through-thickness direction compared to the in-plane one. This is due to a slight unbalance of the pressure around the sample, which causes preferential deformations in the plane of the sample. As a consequence the apparent in-plane coefficient of thermal expansion is higher than the through thickness one. Values in the cured state are not influenced by the pressure

unbalance due to the higher stiffness of the material and, therefore, present a coherent ratio between the values in the through-thickness and the in-plane directions. The *CCS* value is much higher in the through-thickness direction compared to the in-plane one, which is due to the SMC fibrous structure.

4. Confrontation of the results and conclusion

The determination of the linear thermal expansion coefficients in the cured state along three orthogonal axes (standard dilatometry) emphasized the anisotropy between the in-plane direction and the through thickness direction. In addition, the dilatometry curves revealed a slope change for a temperature of around 110-120°C so that two CTE_i values were identified.

The investigation of the volumetric variations of a SMC sample during cure (PVT- α experiment) allowed to separate the thermal contribution from the chemical contribution and thus to identify the volumetric thermal expansion (in the uncured and cured state) and chemical shrinkage coefficients. The relative length as a function of temperature in the cured state also exhibited an inflexion point with a transition temperature around 110-120°C. The volumetric *CTE* values estimated from linear dilatometry ($141 \pm 18 \cdot 10^{-6} \text{ K}^{-1}$ and $179 \pm 9 \cdot 10^{-6} \text{ K}^{-1}$, below and above 115°C, respectively) are consistent with volumetric *CTE* values measured by means of the PVT- α mould ($114 \pm 7 \cdot 10^{-6} \text{ K}^{-1}$ and $196 \pm 11 \cdot 10^{-6} \text{ K}^{-1}$). We can thus postulate that this *CTE* variation is induced by the material response but its origin was not elucidate. Besides, the final apparent volume chemical shrinkage appeared to reach an amplitude of -4.4 %.

Simultaneous measurements of the through-thickness and in-plane dimensional variations (HADDOC device) were performed during the entire curing cycle. Despite an unexpected ratio between the contributions in the through thickness and in-plane directions in the uncured state, the resulting volumetric uncured *CTE* value ($400 \pm 136 \cdot 10^{-6} \text{ K}^{-1}$) show a good agreement with the one determined thanks to the PVT- α experiment ($404 \pm 5 \cdot 10^{-6} \text{ K}^{-1}$). As pointed out during standard dilatometry measurement, the significant thermal expansion anisotropy was confirmed with a cured thermal expansion in the through thickness directions of about ten times higher than the one in the in-plane direction. The HADDOC measurement showed also that the chemical shrinkage is also strongly anisotropic and most of the shrinkage occurs in the through-thickness direction of the SMC sample. Finally, the resulting volumetric *CCS* value ($-4.4 \pm 0.3 \%$) is totally in accordance with the apparent shrinkage evaluated from the PVT- α measurement.

A new generation of SMC material was thus extensively characterized in terms of dimensional variations using three distinctive apparatuses: a standard linear dilatometer, the PVT- α mould and the HADDOC device. The results obtained with the three different apparatuses showed a satisfactory correlation. The HADDOC device constitutes a very efficient solution to better understand the anisotropic composite material behaviour during cure and more especially for works dedicated to the development of residual stresses.

Besides, it should be noticed that the chemical shrinkage analysis (for PVT- α and HADDOC measurements) did not take into account the presence of thermal gradients through the thickness sample, coming from the strong coupling between heat transfer and reaction kinetics. A numerical approach can be considered determining precisely the *CCS* value [5]. Another forthcoming work would concern an experimental investigation about the glass transition phenomenon in order to confirm the observed change of *CTE* in the cured state and the “pseudo-glassy” step detected on the PVT- α displacement curve.

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