INVESTIGATION OF THE RELAXED SHAPE OF PARTLY CURED THERMOSET COMPOSITE MATERIALS

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ABSTRACT

The objective is to obtain further insight into the behaviour of curing resins by performing a sequence of cure steps at different types of mechanical constraints. Curing is performed either flat or constrained on a curved mould. Two different materials produced by RTM are studied, one is neat resin and one is a composite reinforced with glass fibres. The plates will initially be in-mould cured to a degree of cure of approximately 83%. The plates are then divided into 5 specimens of neat resin and 5 composite specimens, who are post cured to four different degrees of cure, e.g. 83, 88, 92, 95 and 100%. After the first post cure follows a second post cure on a curved mould at a temperature of 120°C, which is above the current glass transition temperature of the specimens with a degree of cure of 83 to 95%. The specimens are expected to be curved after demoulding at room temperature due to frozen deformations. During a third free-standing post cure (heat treatment) above the ultimate glass transition temperature the specimens will return to their relaxed shape that depend on the mechanical constraints during the previous cure steps. The experimental results are compared to the SICOMP cure model.

1. INTRODUCTION

Cure simulation is an important tool during product development of complex composites parts with high shape tolerances, for instance to evaluate and find potential manufacturing problems. Or as a guide during the compensation process of the mould surface for manufacturing induced shape distortions. A composite material is not stress free after manufacturing and the manufacturing induced residual stresses will affect the in-service behaviour. For that reason cure simulations are important input to a subsequent analysis of load response and strength of a part.

The most accurate models for cure simulation of residual stresses are based on linear or non-linear thermal-chemical-rheological complex viscoelastic constitutive models [1, 2, 3]. Despite their supposed accuracy, these models have not found a widespread use as they are very complex to use and require a lot of material characterization. A simpler approach that give reasonable good predictions of residual stresses and shape distortions are Cure Hardening Instantaneously Linear Elastic, CHILE, models [4]. The CHILE approach mange to handle the important rubber to glass transition (vitrification) during in-mould cure of a thermsoset and are therefore extensively used. There are however several conditions where the tradition method is known to give poor results, for instance during glass to rubber transition during a multi-step cure cycles. However the SICOMP cure model [5, 6], which is a special form of the CHILE model derived from linear visco-elasticity handle both rubber to glass and glass to rubber transition and is therefore usefully for multi-step cure cycles. Previous results have showed that SICOMP cure model works for material and process conditions typical for RTM and prepreg.

The objective of this work is to obtain further insight into the behaviour of curing resins subjected to multi-step cure cycles by performing a sequence of cure experiment using

different types of mechanical constraints. The experimental results are compared to the SICOMP cure model.

2. EXPERIMENTS

One neat epoxy and one composite plate have been manufactured by RTM (Resin Transfer Moulding) at a high level of thermal and dimensional control. Different cure temperatures have been used to obtain different degree of cure after first post cure.

2.1. Materials

The resin used in this study was the cold curing epoxy laminate system ®Araldite LY5052 / Hardener HY5052, which is suitable for resin transfer moulding at a wide range of in-mould cure temperatures. The mix ratio used was 100 to 38 parts by weight [7]. An 8 harness satin glass weave, Hexcel 7781-127, was chosen as reinforcement. The surface weight is 300 g/m^2 with 53 % of the fibres in the warp direction [8].

2.2. Manufacturing

The injection equipment used to manufacture plates was a heated pressure pot positioned on a scale [9]. The RTM-mould used in this study was made of aluminium with a mould cavity of 350 x 250 x 1.5 mm, see Figure 1. The mould consists of two rigid mould halves with water channels connected to a water heater used for accurate temperature control during the entire cure cycle.

Figure 1. RTM mould and composite specimens after cutting-

For the composite plate the injection strategy was edge injection perpendicular to the length of the plate. An inlet and outlet hose connects into the upper side of the mould and a channel distributes resin. The composite plate consists of 4 layers of reinforcement, which corresponds to a fibre fraction of 31% by volume. The resin and hardener were mixed thoroughly and degassed at 40°C for 10 minutes. Prior to injection, the tool was heated to 50°C. The injection pressure was around 0.5 bar, which

was kept until the resin reached gelation. The plates were in-mould cured at 50°C for 24 hours, which is sufficiently long for the epoxy to approach the maximum degree of cure at 50°C. After complete in-mould cure the specimens were cooled in the mould from the in-mould cure temperature to room temperature in approximately 30 minutes by flushing cold water through the channels in the mould. After demoulding each plate (neat epoxy and composite) was divided into 5 specimens with dimensions of 222 x 25 x 1.5 mm. The specimens were post cured in an oven according to Table 1, which resulted in neat resin and composite specimens with different degree of cure.

Table 1 In-mould cure and first post cure.

Cure schedule	In-mould cure + First post cure	Degree of cure*	Glass transition temperature**
1	50°C/24h	83%	80°C
2	50°C/24h +60°C/20h	88%	94°C
3	50°C/24h +80°C/15h	92%	107°C
4	50°C/24h +100°C/12h	95%	117°C
5	50°C/24h +120°C/2h	100%	136°C

* Degree of cure after post cure 1 estimated from Ref. (6)

* Glass transition temperature that corresponds to the degree of cure [6].

Next the specimens was formed at room temperature between two cylinders where the inner radius was 136 mm, see Figure 2. Then followed a second post cure where all the specimen and cylinders were placed in an oven and cured at 120°C for 2 hours and then taken from the oven and cooled in room temperature. In Figure 3 the transitions region for the epoxy have been illustrated from information found in the product data sheet [7]. Point 1 to 5 in Figure 3 represents the starting point of the second post cure for the five cure schedules in Table 1. From Figure 3 it is clear that the second post cure temperature is above the current glass transition temperature for all specimens except for specimens cured with cure schedule 5, already cured at 120°C. A cure temperature above the glass transition temperature, T_g means a glass to rubber transition during heating and a rubbery glass transition during the isothermal cure at 120°C. At the end of the second post cure all specimens are fully cured but have different thermal history. When the specimens had reached room temperature they were released from the cylinders and the free curvature was measured, see Figure 4.

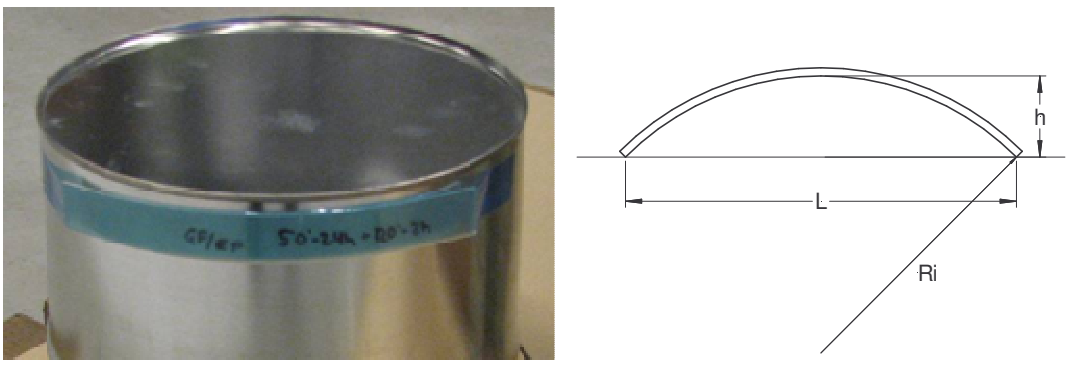

Figure 2. Forming of the specimens before the second post cure at 120°C, *Ri* = 136mm.

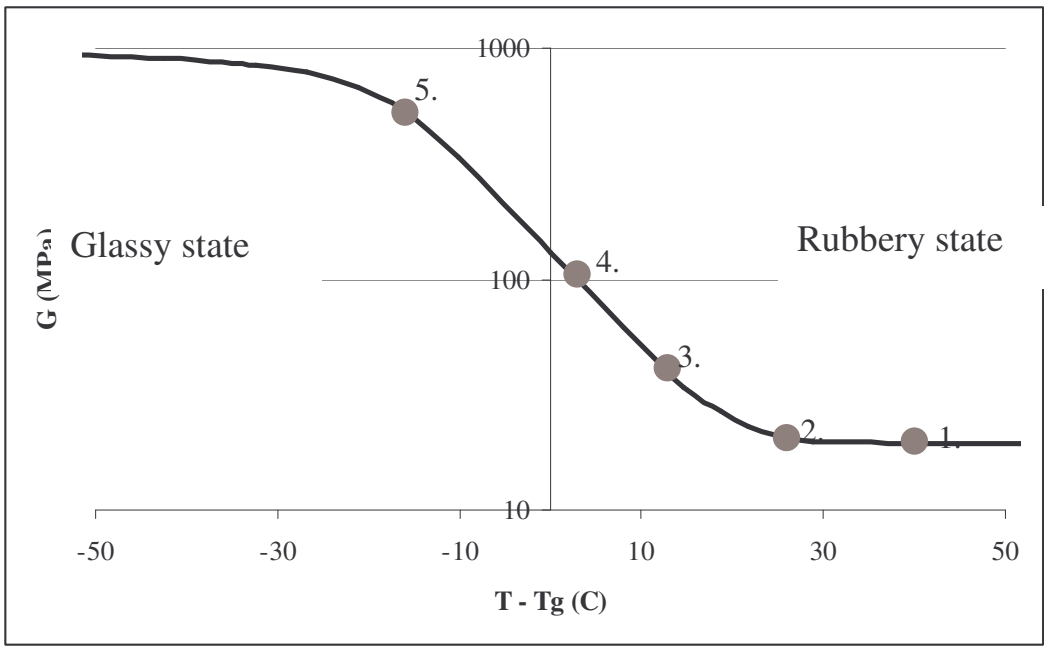

Figure 3. Illustration of the starting point of Post cure 2, T = 120°C.

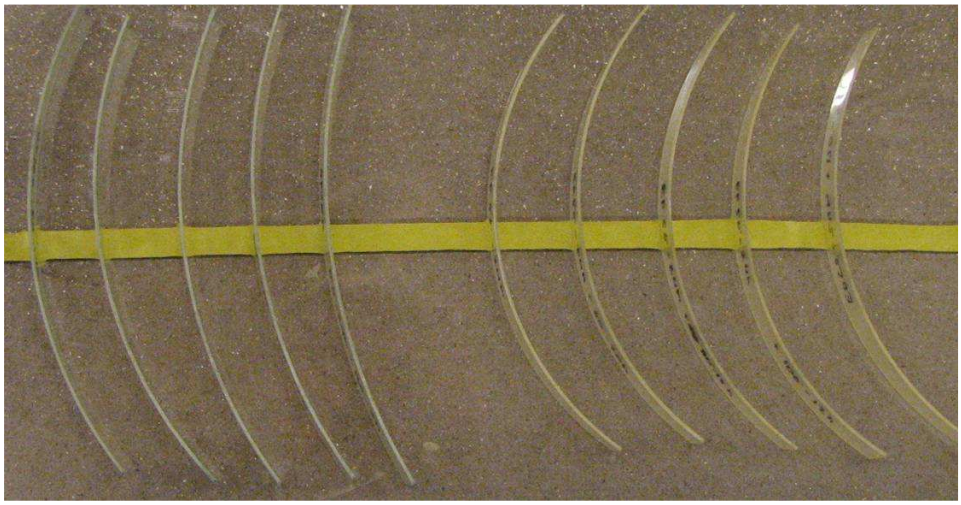

Figure 4. Shape after second post cure (neat resin to the right).

Finally all specimens were subjected to a third post-cure (or heat treatment) free-standing at 150ºC for 2h and cooled to room temperature. 150ºC is well above the ultimate glass transition temperature, $T_{g\infty}$, as defined by Aronhime and Gillham [10], for this material. After cooling in air at room temperature the free curvature was measured one more time. The curvature was in both cases measured by importing a scanned picture of the specimens into the AutoSketch software from Autodesk. Figure 5 show the free relaxed shape of the specimens at room temperature.

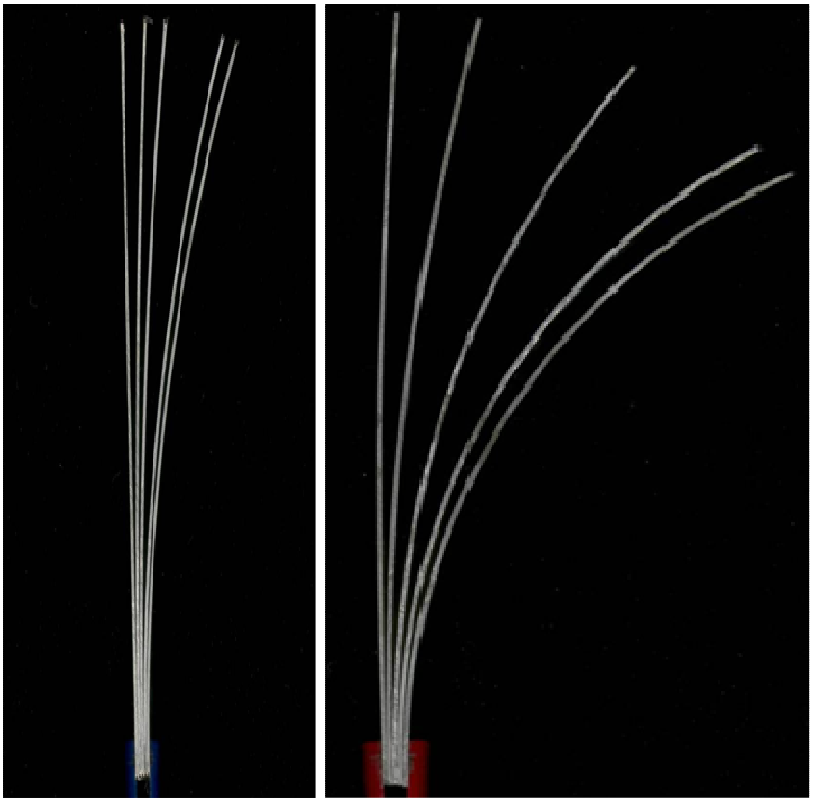

Figure 5. Relaxed shape after third post cure (neat resin to the right).

3. SICOMP CURE MODEL

A detailed description of the cure model can be found in Ref. (5). In this section we neglect the effect of thermal expansion and cure shrinkage and focus of the effect of the different mechanical constraints used during the experiments.

In rubbery state ($T > T_g$) the polymer is relaxed but in the glassy state ($T < T_g$) the polymer is not relaxed and the load response is dependent of the history. The bending moment in glassy and rubbery state can be found by,

$$M = \begin{cases} I\int_0^t E_r \frac{\partial \rho}{\partial t} dt & ,\mathrm{T} > \mathrm{Tg} \\ I\int_0^{t_{vit}} E_r \frac{\partial \rho}{\partial t} dt + I\int_{t_{vit}}^t E_g \frac{\partial \rho}{\partial t} dt & ,\mathrm{T} < \mathrm{Tg} \end{cases} \quad (1)$$

where the last rubbery-glassy vitrification ($T = T_g$) occurred at $t = t_{vit}$. I, E_r, E_g and ρ are the second moment of area, stiffness in the rubbery state, stiffness in the glassy state and the curvature ($1/R$ in Figure 2), respectively. On incremental form the bending moment within a material state is,

$$\Delta M = M(t+\Delta t) - M(t) = \begin{cases} I\int_t^{t+\Delta t} E_r \frac{\partial \rho}{\partial t} dt & ,\mathrm{T} > \mathrm{Tg} \\ I\int_t^{t+\Delta t} E_g \frac{\partial \rho}{\partial t} dt & ,\mathrm{T} < \mathrm{Tg} \end{cases} \quad (2)$$

At a rubbery-glassy transition (vitrification) where $t_{vit}=t$ and $\Delta t \to 0$ the resulting change in bending moment is,

$$\Delta M = 0 \quad (3)$$

and at a glassy to rubbery transition where $\Delta t \to 0$ the increment in bending moment is,

$$\Delta M = I \int_{t_{vit}}^{t} (E_r - E_g) \frac{\partial \rho}{\partial t} dt \qquad (4)$$

Before the second post cure the specimen was constrained to a curvature of ρ_0 in the glassy state, which result in a bending moment of $M_1 = E_g I \rho_0$ according to Eqn. (2), illustrated in Figure 6. During the heat up to the second post cure temperature a glass to rubber transition occur for all specimens cured with cure schedule 1 to 4 and the bending moment change to $M_2 = E_g I \rho_0 + (E_r - E_g) I \rho_0 = E_r I \rho_0$ according to Eqn. (4).

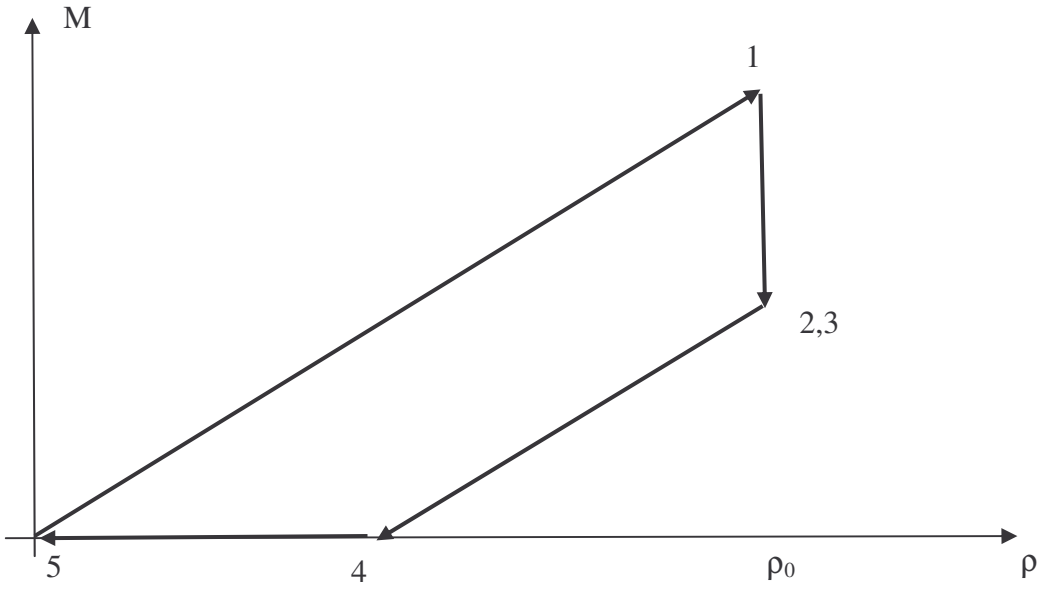

Figure 6 Illustration of loading and unloading during post cure.

Then follows a rubber to glass transition when the cure move forwards which not change the bending moment $M_3 = M_2 = E_r I \rho_0$ according to Eqn. (3). When the mechanical constrain is released the specimens are unloaded in glassy state and the bending moment becomes zero but a frozen curvature is left, which can be calculated by $M_4 = E_r I \rho_0 + E_g I \Delta \rho = 0$ using Eqn. (2), which results in a frozen curvature of,

$$\rho_4 = \rho_0 + \Delta \rho = \frac{(E_g - E_r)}{E_g} \rho_0 \qquad (5)$$

During the third post cure (or heat treatment) the specimens are relaxed by heating into the rubbery state without mechanical constrains which results in a release of the frozen deformations,

$$\rho_5 = \rho_4 + \Delta \rho = 0 \qquad (6)$$

3.1. Material properties

The stiffness of the polymer in glassy state, E_g is 3GPa [7] and in the rubbery state the stiffness, E_r is approximately 1% of E_g.

The stiffness of E-glass fibres is 76 GPa [11]. From the volume fraction of 31%, the [0/90] lay-up, the stiffness of the resin and fibres, using self-consistent field micro mechanics [12] and three-dimensional laminate theory [13] the longitudinal stiffness of the composite in glassy state and in the rubbery state were estimated to 16.3GPa and 12.5 GPa, respectively.

4. RESULTS

4.1. Experimental results

The measured curvature at room temperature after the second constrained post cure and after the free-standing third post cure (or heat treatment) is presented in Table 1.

Table 2 Curvature after post cure 2 (constrained) and 3 (relaxed)

	Curvature, $\rho = 1/R$ (m)*			
	Neat resin		**Composite**	
Cure schedule	**Post cure 2**	**Post cure 3**	**Post cure 2**	**Post cure 3**
1	7.52	5.43	5.21	2.21
2	7.46	5.15	5.05	1.99
3	7.41	3.39	4.48	0.81
4	7.46	1.39	4.35	0.40
5	7.41	0.53	3.83	0.00
$1/R_0$**	7.35	-	7.35	-

* R is defined in Figure 2

** R_0 corresponds to the inner radius of the mould used during Post cure 2.

4.2. Model results

The cure model and the material properties in the previous section result in the predicted curvatures after the second and third post cure in Table 3.

Table 3 Curvature after post cure 2 (constrained) and 3 (relaxed)

	Curvature, $\rho = 1/R$ (m)			
	Neat resin		**Composite**	
Cure schedule	**Post cure 2**	**Post cure 3**	**Post cure 2**	**Post cure 3**
1 -4*	7.27	0	1.71	0
5	0	0	0	0

* *According to Eqn. (5) and Eqn. (6).*

5. DISCUSSION

5.1. Neat resin specimens

The experimental results show almost no effect of the unloading after the constrained second post cure and the curvature is closed to the curvature of the mould. This is also predicted by the model and is an effect of the large difference between the stiffness in glassy and rubbery state. However, the model simplifies the glass transition as a step, which means that the specimens cured with schedule 5 is assumed to never enter the rubbery state and relax during the second post cure (illustrated in Figure 3). For that reason the predicted curvature for cure schedule 5 is zero after the second post cure. From the experimental result it is clear that cure schedule 5 results in the same curvature as the rest, which means that even if the material only reach the beginning of the transition region stress relaxation occur. During the third post cure (or heat

treatment) the specimens are relaxed and the model predicts that the curvature will vanish independent of the previous cure history. This do not corresponds to the experimental results where only cure schedule 5 shows the same behaviour as the model. From the experimental result is it clear that a lower degree of cure at the beginning of second constrained post cure result in a larger curvature after relaxation, which the current model do not handle. However, this effect might be a result of that the stiffness in rubbery state is dependent of the degree of cure and therefore the rubbery stiffness is different during loading and unloading. In the current model the stiffness is assumed to be constant within each state.

5.2. Composite specimens

Also the composite specimens showed a frozen curvature after the constrained second post cure. But the curvature decrease with increased degree of cure at the beginning of the second post cure, which was not the case for the neat resin. The model predicts the same curvature for cure schedule 1 to 4, which is much less that in the experiments. As for the neat resin specimens the relaxed curvature after the third free-standing post cure (or heat treatment) is larger for specimens with lower degree of cure at the beginning of second constrained post cure.

The poor correspondence between experimental result and the model might be explained by damage found close to the surface subjected to compression, see Figure 7. The cracks did probably occur when the material was transferred into the rubbery state during the constrained second post cure.

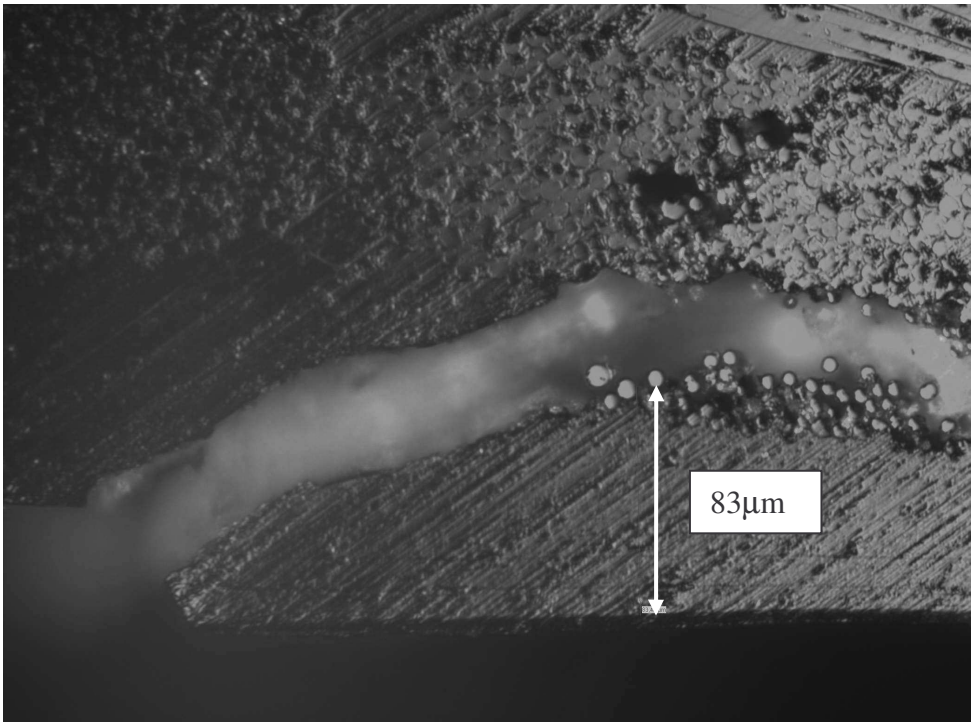

Figure 7 Crack at the surface subjected to compression during the constrained second post cure.

6. CONCLUSIONS

It has previous been showed that the SICOMP cure model works for material and process conditions typical for RTM and prepreg. The objective of this work was to obtain further insight into the behaviour of curing resins by using non typical multi-step cure cycles and mechanical constraints. The results showed that the free relaxed shape

of both the resin and composite specimens is affected by how much of the degree of cure that is developed during the constrained post cure. This effect is not yet included in the current model. For the composite specimens the correspondence between experimental result and model predictions was poor, which might be explained by damage developed during the constrained post cure.

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