Exploration of irreversible residual stresses in a carbon/epoxy composite

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Abstract. Residual stresses in composite material may rise from several sources; difference in thermal straining between fibre and matrix, chemical shrinkage of the matrix material. The presented paper explores an irreversible Eigen-strain in the material which is shown to change and be removed by a thermal treatment above the Tg of the matrix material. This has been observed though TMA measurements of a carbon/epoxy unidirectional sample. The local Eigen-strain is translated into stresses using a visco-elastic constitutive relation. Further exploration indicates that cooling rate influence the generation of residual stresses in the material.

1. Introduction
Residual stresses in composite materials have been investigated by many researchers throughout the past decades and their effect on the mechanical performance. Some of the consequences of residual stresses may be geometrical distortions and altered fatigue endurance.

The build-up of these stresses are rather well understood and may rise due to thermal and chemical straining in the material which often take place during the manufacturing process of the material. This has been investigated by several authors. Hahn [1], Bogetti et al [2] and White et al [3], [4] were among the first to formulate the ground laying theory of residual stresses buildup by the curing process.

Later authors like Baran et al. [5] applied the theory to study residual/cure stresses in pultruded rods, which may be used e.g. in wind turbine blade applications.

The complexity in modelling residual stress build–up increases due to the directional dependence from the fiber [6]. Some material properties show to be highly temperature-depended. In most cases, properties in the fiber direction show less dependence compare to the transverse directions and may often be approximated to be temperature-independed. However, the properties transverse to the fibers are dominated the matrix properties which typically are highly temperature-depended with transition at the glass transitions temperature (Tg). Examples hereof is the modulus, coefficient of thermal expansion, etc.

The thermal expansion in the transverse direction of a fully cured carbon fiber/epoxy composite can be measured using a Thermo Mechanical Analyzer (TMA) and during the first heating material relaxation is observed slightly before the Tg of the epoxy material (see Figure 1). Moreover, it is noticed that during cooling the material contracts in a bi-linear manner with transition at Tg. Further heating and cooling of the sample follows the same bi-linear behavior. This further shows that the sample ends up a slightly contracted shape.
This permanent contraction (or eigen-strain) has also been observed by other researchers in the past \[7\] and \[8\] and has been explained by some type of material relaxation possibly originating from residual stresses in the material. However, further details on this relaxation seems to be missing to support the argumentation that this is true.

In this paper, the authors attempt to investigate this permanent contraction behavior by applying a visco-elastic model, where the thermal dependence on several properties are taken into account. The model takes a starting point, where the material has reached the state of fully cured and to be cooled rapidly to room temperature. After a holding period at room temperature the material is heated to examine if this sudden contraction can be observed in the model.

In case the model results can confirm that during cooling stresses are build up in the material and later relaxed upon a second heating, it may be a contribution to the understanding the residual stresses in composite material and their ability to relax at elevated temperatures and further support other researchers explanation of this phenomenon.

### 2. Material

The material used in this study is a carbon fiber epoxy composite, which has been cured at 100°C and then rapidly cooled to room temperature. Properties of the material used in the later modelling is as stated in Table 1.

| Model parameter | Value, \[Comment\] | \[Comment\] |
|-----------------|-------------------------|-------------------------|
| $T_g$           | 80 [°C]                 | $T_g$ of the epoxy matrix |
| $T_i$           | 100 [°C]                | Stress free temperature |
| $\nu_{23}$      | 0.35 [-]                | Poissons ratio |
| $CTE_{subT_g}$  | $100 \cdot 10^{-6}$ [1/°C] | Coefficient of thermal expansion below $T_g$ |
| $CTE_{supT_g}$  | $200 \cdot 10^{-6}$ [1/°C] | Coefficient of thermal expansion above $T_g$ |

The visco-elastic behavior of the material is measured by a series of DMA tests and shown in the next section.

#### 2.1. Generation of a master curve
The stiffness behavior is both time and temperature depended as argued earlier [9]. Therefore, a number of stress relaxation measurements are performed at a number of isothermal temperatures to create a “master curve” for the modulus (see Figure 2).

A Prony-series is then fitted to the master curve data from which the visco-elastic behaviour of the material described in equation (1) [10].

\[
E(t) = E_0 + \sum_{i=1}^{3} E_i e^{-\frac{t}{\tau_{Ri}}} \\
\tau = \frac{t}{a_T}
\]  

The fitted values obtained are stated in Table 2 and the model is plotted together with data in right side graph of Figure 2.

| Model parameter | Value, (MPa) | Model parameter | Value, (s) |
|-----------------|--------------|-----------------|------------|
| \(E_0\)         | 35.0         | \(\tau_{R1}\)  | 1.579 \(10^4\) |
| \(E_1\)         | 490.9        | \(\tau_{R2}\)  | 1.908 \(10^7\) |
| \(E_2\)         | 1039         | \(\tau_{R3}\)  | 4.200 \(10^9\) |
| \(E_3\)         | 914.2        |                 |            |

The time-temperature shift \((a_T)\) is modelled using a WLF type equation (2) and similar fitted to data (see Table 3) [10].

\[
\log(a_T) = \frac{-C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}}
\]
Table 3. Model parameters for the time-temperature shift model

| Model parameter | Value, Comment |
|-----------------|---------------|
| $T_{ref}$       | 20 °C, Reference temperature for the master curve |
| $C_1$           | 1002          |
| $C_2$           | 7582 °C       |

The WLF equation is known to be valid for polymers above its $T_g$ [10] and an Arhenius equation is normally used to express the shift function below $T_g$. According to data presented in the middle graph of Figure 2 the WLF equations seems to match the data reasonably well for the entire temperature range. However, the obtained values for the coefficients $C_1$ and $C_2$ are far from their typical values when $T_{ref}$ is set equal to $T_g$. Therefore the use of equation-2 should merely be considered as good fitting functions for the data presented.

3. Model

A thermo-mechanical model is made in the multi-physics finite element packages Comsol®. The model starts by being in thermal equilibrium at 100°C and then cooled rapidly at the outer edge to mimic the experimental cooling process of the sample. This rapid cooling is simulated to occur over a period of 10s and then hold at 20°C for a period of 900s. Lastly, the sample edge is heated slowly back to 100°C. Symmetry condition are utilized at $x=0$ and $y=0$, which means that displacement and heat fluxes normal to these edges are zero. The material includes the visco-elastic behavior as described earlier and temperature depended coefficient of thermal expansion. The model is meshed with second order triangular elements (see Figure 3). The imposed boundary temperature is seen in the graph of Figure 3.

Figure 3. The cylindrical composite sample is modelled as a 2D quarter circle where symmetries are utilized and plane-stress is assumed. The temperature boundary condition applied is shown on the right side graph.

The model has a radius of 2.5mm (R=2.5mm) and a thickness of 2mm. Moreover, plane stress is assumed. Lastly the model presented here is a homogenized representation of the material.
4. Results
The initial rapid cooling of the model leads to rather large temperature differences between outer boundary and center in the magnitude of 50°C (see top graph of Figure 4). This temperature gradient results in thermal stresses in the material, where the outer boundary comes in tension and the center is in compression. As the stresses are relaxed and thermal equilibrium is obtained, the stress state is to some extent reversed such that the boundary comes in a state of cylindrical compression and the center in radial tension (see bottom graph of Figure 4). It is however worth noticing that residual stresses remain in the sample after completing the cooling process and thermal equilibrium is obtained.

![Temperature and Stress Graphs](image)

Figure 4. Top graph) the temperature response at the model boundary and in the center. Bottom graph) the stress response at the boundary and in the center. Notice that residual stress remains in the model after the rapid cooling.

It is then speculated if these residual stresses can cause this sudden contraction in the material which are argued earlier and reported by other researchers. It should however be mentioned that the residual stress buildup is a consequence of the cooling rate and the visco-elastic material behavior.
Figure 5. Left graph) subsequent “slow” heating of the model. Right graph) elastic and thermal strain in the center. Notice that stress relaxation occurs when the temperature approach Tg and further that an eigen strain is present in the model at 20C.

Heating the model at a slower rate to above its Tg should then allow the induces stresses to relax. This is also observed to some extend in the results presented at right side graph in Figure 5, where both the elastic and thermal strain are presented. The thermal strain displays a bi-linear behaviour which is explained by the difference in coefficient of thermal expansion below and above Tg. Moreover, it is seen that some stress relaxation takes place slightly before reaching Tg and are displayed through a small contraction.

The eigen-strain obtained by the model at 20C is evaluated to 0.05% on the other hand the eigen-strain obtained from the TMA measurement is (~0.30%). Therefore it is still questionably if the sudden contraction observed is purely due to relaxation of residual stresses or if other effects add to phenomenon.

5. Conclusion

The sudden contraction of a fully cured carbon/epoxy composite cylinder when heated to near Tg is analyzed using a thermo-mechanical model to replicate the experimental measurement. It was found that rapid cooling and visco-elastic relaxation lead to residual stress in the material at room temperature. Upon a slow reheating of the model, residual stress relaxation does to some extent explain the contraction near Tg but the magnitude of contraction was much less than observed from the TMA measurement.

At this stage, it is not clear if the disagreement between model and experimental data is due to lack in precision in the material data (i.e. Prony-series) or if some other phenomenon not accounted for may contribute to this sudden contraction under investigation.
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