Thermal conductivity of thermosetting composite materials

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Abstract
In this work the thermal conductivity, λ, of composite materials is investigated. The experimental results are from the experimental transient hot wire method and the experimental transient plate source method. The measurements are carried out on pure RTM6 epoxy resin and glass fibre and carbon fibre composites. The material is investigated both in its fully cured, pristine shape as well as during curing, consolidation and degradation. The λ-values for pure epoxy, glass fibre composite and material during degradation has been determined.

1 Introduction
The present work is investigating the thermal conductivity, λ, of thermosetting composite materials. The polymer used is RTM6 epoxy from Hexcel and the measurements are carried out on pure resin as well as on resin reinforced with glass and carbon fibres. λ is a very important parameter when calculating cure and fire behaviour. Variations in λ throughout a cure or a fire simulation could affect the outcome significantly. Therefore it is important to investigate how λ is affected by degree of cure, material state and degree of thermal degradation which varies in both cure and fire situations. Methods are available for measuring λ in composites in the transverse fibre direction but not in fibre direction of a composite.

2 Method
The Transient Plate Source (TPS) by the company Hot-Disk AB, Figure 1, and The Hot-Wire method [1], Figure 2 has been used for experimental determination of λ. Both methods involve a sensor that is clamped between two samples of the material to be studied. The sensor is acting both as a heat source and as a resistance thermometer. The measured temperature increase is depending on the supplied power and the heat conducted away by the surrounding material. By using theoretical models λ can then be calculated. The difference between the methods is that for the TPS method, the sensor is a circular disc containing a thin metal spiral while for the hot-wire method, the sensor is simply a thin metal wire with electrodes attached to it. This implies that the TPS method measures in all directions which is suitable when the materials are isotropic while the hot-wire method only measures in the transverse direction to the wire. By keeping the wire straight and approximating it with an infinitely long sensor this yields a measurement in only two dimensions. By embedding the wire in a unidirectional laminate aligned with the fibres enables measuring λ transverse to the fibres.

Figure 1. TPS method sensor.

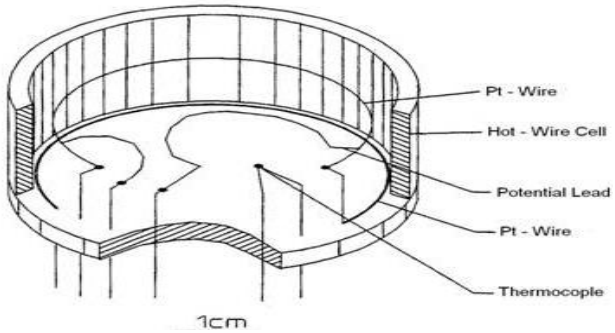

Figure 2. Schematic image of Hot-Wire method setup.

3 Results

3.1 Fully cured, pristine material.

Pure RTM6 is examined between room temperature, RT, and 150°C (~300-450K) and show a linear behavior of λ vs. temperature, see Figure 3.

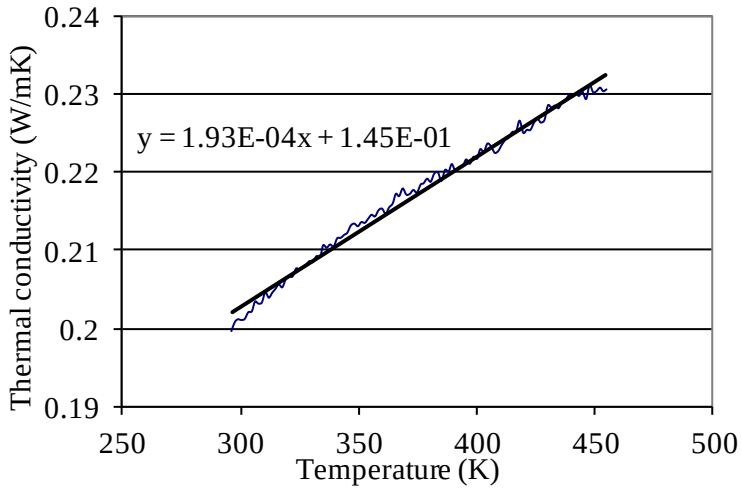

Figure 3. Thermal conductivity of pure RTM6 epoxy vs. temperature

The glass fibre laminates investigated are manufactured using filament winding in order to get unidirectional laminates of very high fibre volume fraction, 66%. The hot wire is positioned along the fibres so that it measures λ transverse to the fibres. A number of measurements are done for varying temperatures and the results are found in Figure 4, where λ shows a linear behavior. By comparing values in Figure 3 with values in Figure 4 one notice that λ of the composite transverse to the fibre direction is approximately in the middle between the values for glass, ~1 W/mK, and the polymer which seems reasonable.

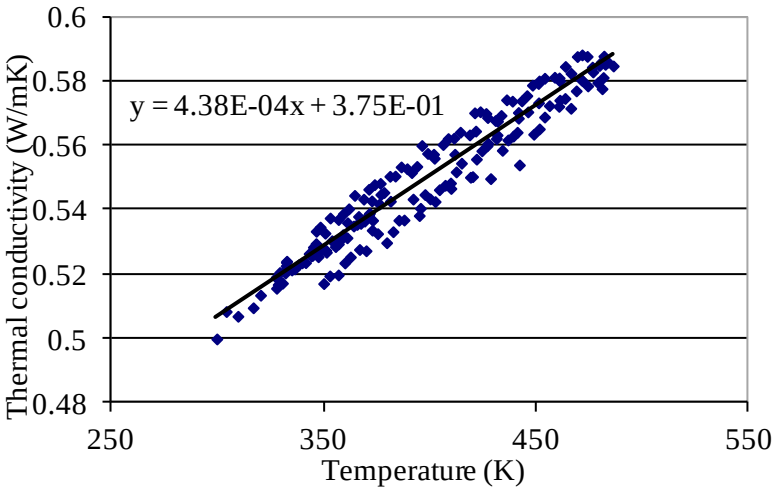

Figure 4. Thermal conductivity transverse to the fibres of unidirectional glass fibre laminates.

Determination of λ for carbon fibre laminates with the Hot-wire method is complicated by the fact that carbon fibres are electric conductors and the hot wire needs to be electrically insulated. Different methods for insulating the wire are therefore tested e.g. insulating paint, PTFE hose and plastic sheets. Our experience is however that when the temperature increases the wire sinks into the surrounding material and the contact conditions are changed which in turn affects the measured λ. This makes the results difficult to interpret and the experimental uncertainty becomes very large. One conclusion that can be drawn, despite experimental uncertainties, is that λ transverse to fibre direction at room temperature is between 0.54 and 0.60 W/mK. This is slightly higher than λ observed for glass fibre laminates, ~0.50 W/mK.

3.2 Modeling of fully cured, pristine material.

Theoretical models for calculating λ transverse to the fibres are available in the literature [2,3]. A number of these models are compared to the measured values for the glass fibre laminates. The models require λ of both the matrix material and of the fibres in the transverse direction. The values for the matrix material is taken from Figure 3 and the value for the glass fibres is assumed to be constant and equal to 0.93 [4]. In Figure 5 it is seen that the measurement has a stronger temperature dependency than the models. There are models that match the experimental λ-value at room temperature and other models that match the experimental values at 450 K.

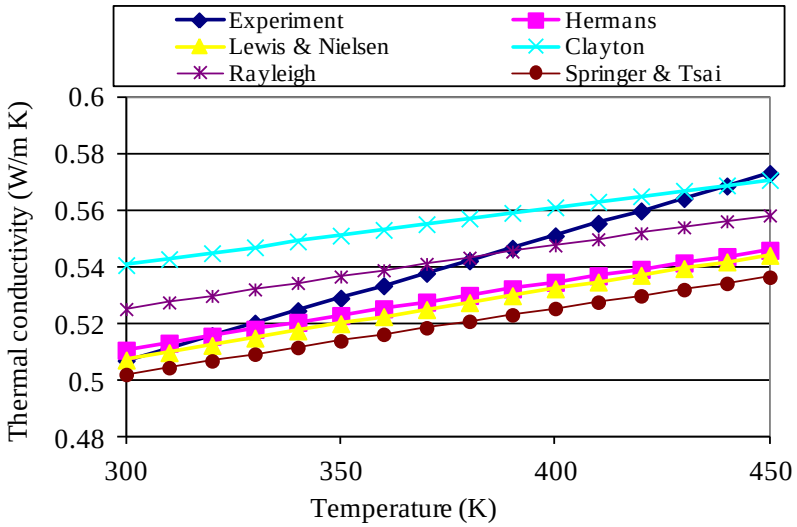

Figure 5. Thermal conductivity for a glass fibre laminate both measured and calculated using five different theoretical models.

3.3 Degrading material.

Composite material will degrade when subjected to high temperatures. The degradation changes λ which in turn affects the spreading velocity of temperature. In this work the thermal degradation is quantified as remaining resin content (RRC) which can be measured using thermogravimetric analysis (TGA). The degradation is carried out at 300°C for approximately 12 hours. The TGA measurement is conducted in a nitrogen environment to resemble the oxygen low conditions inside a laminate. Three samples of the same type of glass fibre laminates as above are tested with TGA with a good repeatability, the results are found in Figure 6 together with a fourth degree polynomial fitted to the experimental data.

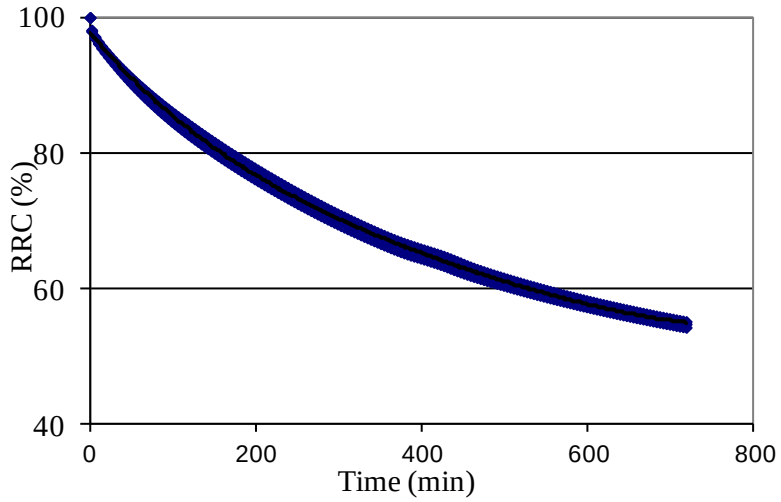

Figure 6. RRC of RTM6 as a function of time at 573K

Measurement of λ is carried out using the same thermal history as in the TGA measurements, i.e. 573K or 300°C. In Figure 7, λ is plotted against RRC for two glass fibre laminates. By studying Figure 7 it is observed that λ is decreasing quite linearly down to an RRC of 75% and is fairly constant after that point. There are some anomalies at ~80% RRC and at ~67% RRC, these are probably caused by disturbances of the measurement equipment.

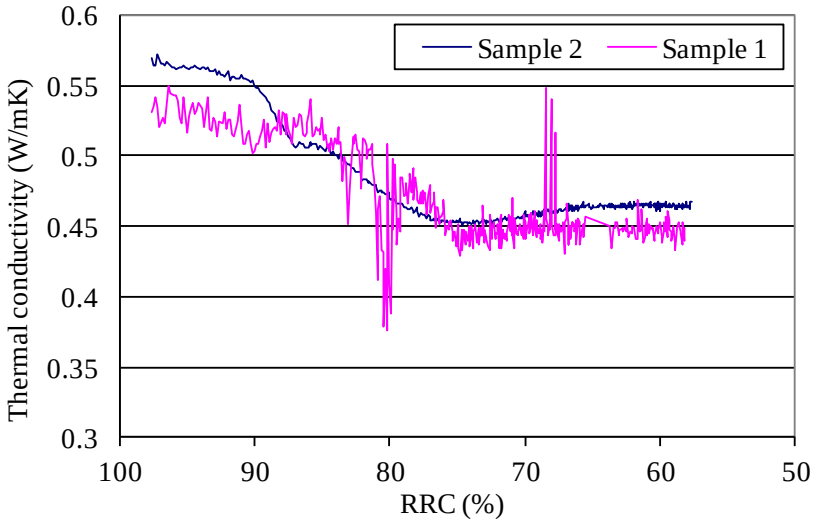

Figure 7. Thermal conductivity of a glass fibre laminate vs. RRC.

In Figure 8 the data points above 75% RRC are used to fit a linear model. However, one needs to bear in mind that this model is only valid above 75% RRC. Below 75 % RRC λ seems to be constant. The reason for this behavior needs further investigations.

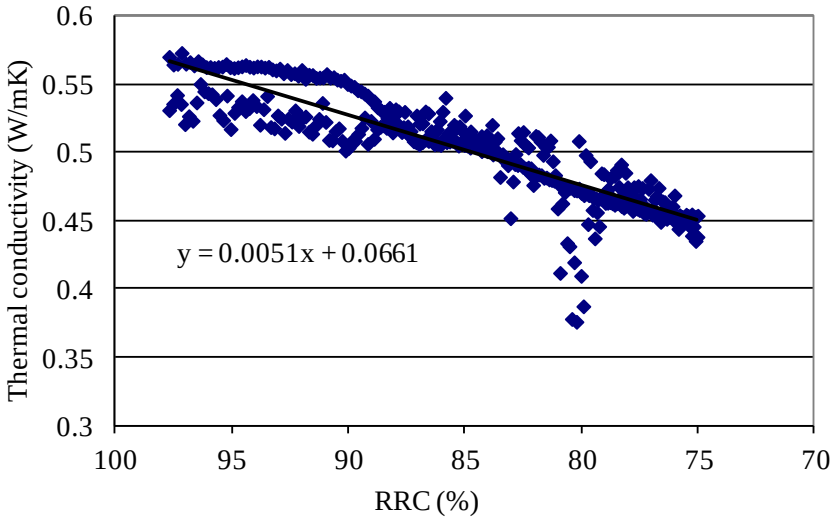

Figure 8. Linear regression to measurements above 75% RRC.

3.4 Material under consolidation.

Heat transport during consolidation and curing of a composite layup, sometimes conducted at elevated temperature and under non iso-thermal conditions, is of great importance for the final properties of the composite. Therefore λ is measured in a stack of uncured carbon fibre prepreg during compression in a servohydraulic tensile testing machine. The material is Hexply M21, a unidirectional carbon fibre prepreg with a dry surface weight of 268 g/m^2 containing AS7-12K with a fibre density of 1790 kg/m^3. The layup is unidirectional and the measurements are carried out transverse to the fibres. Two measurements are carried out, one at room temperature and one at 50°C. The pressure is increased stepwise and the distance between the pressure plates is allowed to stabilize before the measurement. The pressures in the experiment vary between 0.5 bar and 5 bar. The fibre volume fraction is calculated from the distance between the pressure plates, the number of layers and the dry surface weight of the prepreg. In Figure 9 λ is plotted against the fibre volume fraction.

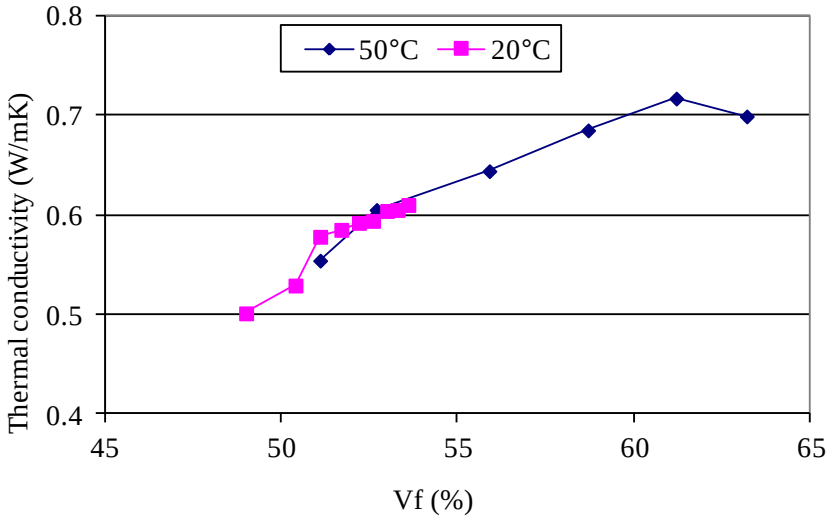

Figure 9. Thermal conductivity of prepreg stack as a function of fibre volume fraction.

The experiments show that λ increases quite significantly during the consolidation, between 40 and 50 %. It should be noted that these results should not be compared to the other results of this work since a different epoxy is used. The reason of the increase in λ is the higher fibre volume fraction since the fibres have a higher λ than the polymer. A reduction of pores and air pockets is also assumed to increase λ.

3.5 Material during curing.

The thermal conductivity of a curing material is interesting for simulations of the curing process. For example when thick laminates are cured, exothermal effects of the curing reaction yield temperature peaks inside the material. In order to predict these peaks, any variations in λ during the cure are important. The measurement was carried out by embedding the hot wire in a dry stack of glass fibres, filling the stack with resin using vacuum infusion and then curing it in an oven. λ is measured through the entire procedure. Two measurements are made with different cure schedules; these can be viewed in Figure 10 and Figure 11. The degree of cure plotted in the figures have been calculated using the cure kinetic model of RTM6 proposed by [5].

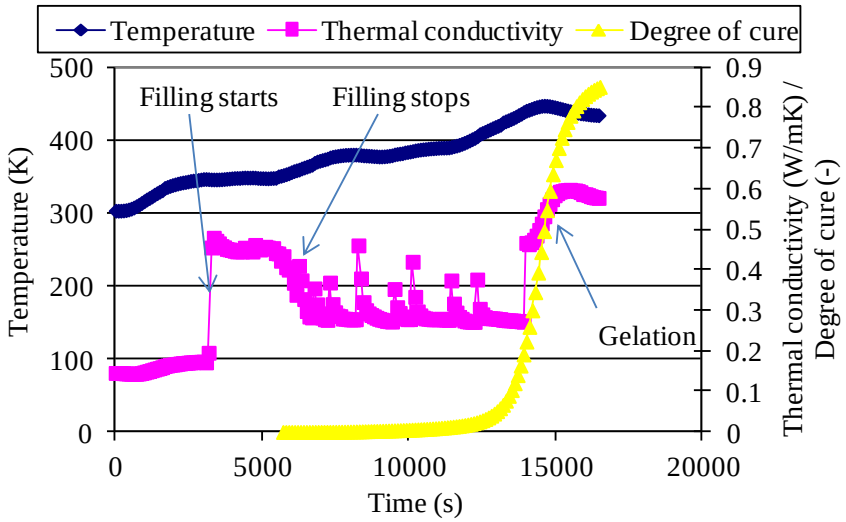

Figure 10. Thermal conductivity, temperature and degree of cure during a curing procedure of glass fibre/RTM6 laminate

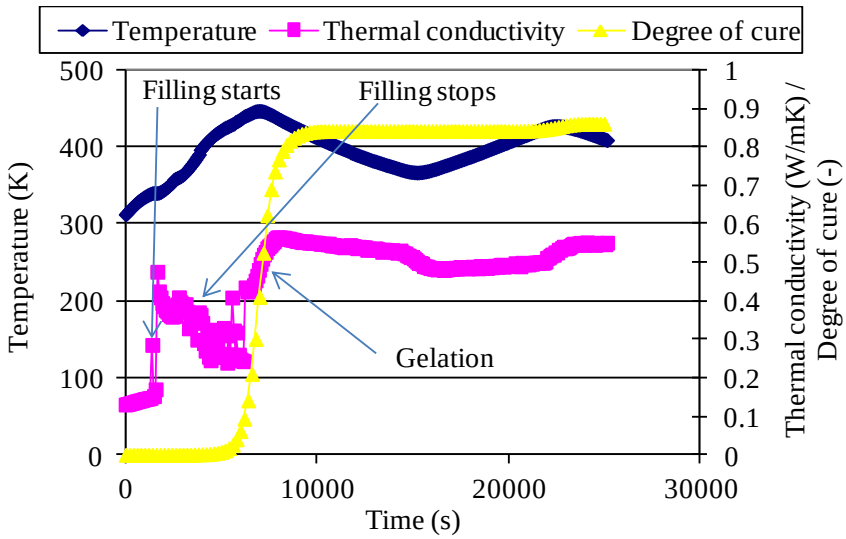

Figure 11. Thermal conductivity, temperature and degree of cure during a curing procedure of glass fibre/RTM6 laminate

The measurements are not detailed enough to build any models of λ based on degree of cure but there are some interesting effects that can be observed. First there is a significant increase of λ as the fibres are wetted, marked in the graphs with "Filling starts". Second there is also a small drop in λ when the filling stops. This drop has to do with the fact that the resin is not moving as it is during the filling. Finally λ increase significantly again when the resin cures. This is probably related to both the curing process and that the resin solidifies at the point of gelation. It should be noted that there is no visible change of λ as the resin goes from a rubbery state to a glassy state during the temperature decrease in Figure 11. The gradients of λ after about 9000 s in Figure 11 can be explained by the temperature changes.

4 Discussion and conclusions

During the project the complexities of λ measurements have become clear. Especially for anisotropic materials the measurements require a lot of effort to produce reliable results. However, reliable values of λ of pure RTM6 have been produced for different temperatures. Also the measurements of λ of the glass fibre laminates are considered to be accurate. The measurements on pure RTM6 and glass fibre laminates enable a comparison of different models of λ transverse to the fibres. The models all show reasonable results even if none of the models could match the temperature dependency of λ.

Another important observation is the dependency of λ to degree of degradation or RRC. It shows a relatively linear behavior for RRC above 75% and an almost constant value below 75%.

During consolidation λ increases with increasing fibre volume content. This was more or less expected but the measurement gives a good view of the magnitude of the increase.

The measurements during cure are complex and the results are a bit difficult to interpret. The results are not detailed enough to build a model of λ vs degree of cure. Some important trends in the results can however be noticed. For instance, there is a significant increase in λ when the resin solidifies and cures but there is no noticeable effect when it goes from rubbery to glassy state.

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