High Temperature-Dependent Thermal Properties of a Carbon-Fiber Epoxy Composite

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With the increased use of composite materials in aircraft structure, the need to model the detailed behavior of laminates under fire conditions has arisen. One of the main issues is to succeed in determining input data used for the fire models that are developed. Notably, it is necessary to characterise the high-temperature dependent properties of the material such as the specific heat capacity and the thermal diffusivity.

The present work is focused on the development of methods of characterising the thermal properties of laminates. The specific heat capacity and thermal diffusivity of an aeronautical carbon fibre/epoxy laminate (Isotropic T700/M21 [1]) were measured as a function of the temperature and of the decomposition degree. One of the main issues is to succeed in measuring these properties without losing the physical meaning of the measurement.

Heat of Decomposition (Non-Reversing Signal)

Specific heat capacity and heats of decomposition were determined based on the modulated signal (TM-DSC) obtained using simultaneous thermal analysis (STA) from NETZSCH (STA ***F1*** *Jupiter®*). TM-DSC measurements were performed instead of classical differential scanning calorimetry to obtain better accuracy and precision in the specific heat capacity values. It permits the separation of non-reproducible experimental artefacts from the measurement. The measurements under inert atmosphere were performed on a degraded sample to obtain a baseline and on a virgin sample during its decomposition. Using the two curves, heats of decomposition can be determined by integrating the area of decomposition peaks. Results of the non-reversing specific heat capacity and the remaining mass are presented in Figure 1.

The first peak is an exothermic peak with a heat of decomposition of $2.6 \cdot 10^5$ J/kg (315°C to 425°C) and the second one is endothermic with a heat of decomposition of $1.5 \cdot 10^5$ J/kg (425°C to 545°C). It is evident that the first peak is unusual because material decomposition is generally endothermic in an inert atmosphere. These phenomena are assigned to several processes such as bond dissociation, new bond formation and gas evaporation. Some materials can produce an exothermic reaction under an inert atmosphere [2]. Notably, PAN and bisphenol C polyacrylate (extremely flame-resistant polymers) exhibit a high exothermic decomposition reaction. Most polymers with exothermic decomposition (under nitrogen) contain either halogens or some unsaturated double or triple bonds, which can lead to char formation by cross-linking or cyclization reactions.

This explanation can be linked to the decomposition mechanism of epoxy resins presented in previous works [1, 3]. The decomposition occurs through cyclization of aliphatic chain ends and it explains the exothermic decomposition identified in our case.

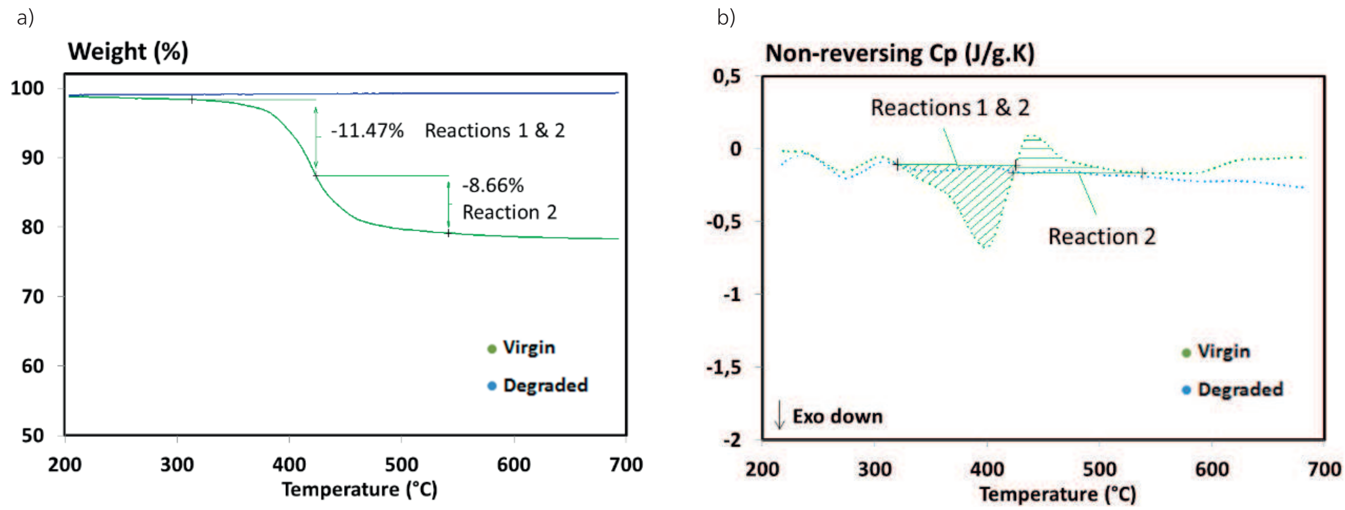

Figure 1. (a) Remaining mass and; (b) non-reversing specific heat capacity obtained during an STA test carried out under nitrogen to determine the heats of decomposition of T700/M21 [1]

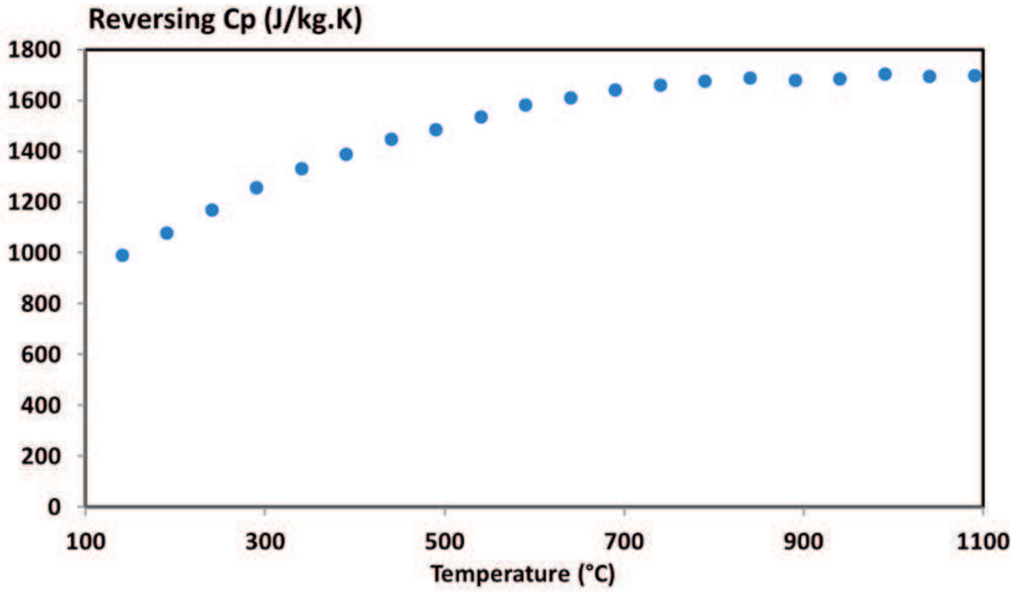

Fig. 2. Specific heat capacity of the degraded materials obtained with STA ***F1*** measurements [1]

Similar results were recently reported by McKinnon et al. [4] where a carbon fibre/epoxy composite also exhibited exothermic and endothermic reactions

Effective Specific Heat Capacity (Reversing Signal)

The specific heat capacities of the degraded materials were obtained with TM-DSC up to 1100°C. As far as we know, it is the first time such a method was applied on an anisotropic carbon fibre/epoxy laminate [1]. The reversing signal measurements obtained on the degraded materials are presented in Figure 2.

In both cases, an increasing specific heat capacity with increasing temperature is observed. The specific heat capacity of the non-degraded sample is close to the values found in literature for similar materials [6-7]. The degraded sample shows an increase in its specific heat capacity up to 1600 J/(kg·K) at 1000°C. It has been reported [8] that the specific heat capacity of carbon fiber/carbon composite can reach a value of 2020 J/(kg·K) at 1230°C.

Determination of Thermal Diffusivity

A Light Flash Apparatus from NETZSCH (LFA 467 *HyperFlash*®) was used to measure the thermal diffusivity of the sample in the through-thickness and in-plane directions. The thermal diffusivity tensor was measured up to 450°C on virgin and degraded materials. This composite has an anisotropic structure, so measurements are needed in the three main directions of the composite. However, the thermal diffusivities in the two in-plane directions are assumed to be equal for the isotropic T700/M21 laminate (assumption of homogeneous interlayers).

Test bodies were exposed to the fire test developed by Tranchard et al. [9] for 150s and 300s to get a measurement as a function of the decomposition degree – i.e., half-degraded and degraded. The thermal diffusivities of virgin, half-degraded and degraded coupons were measured as a function of temperature and their results presented in Figure 3.

The thermal diffusivity of the virgin material decreases linearly up to 350°C and then suddenly decreases sharply. This temperature (350°C) is close to the temperature of decomposition of the composite. The formation of cracks and thermal delamination seems to be responsible for this decrease. These phenomena increase the thickness of the sample (considered to be constant during the measurements) and hence the measured thermal diffusivity decreases. The half-degraded and degraded samples show a much lower thermal diffusivity at low temperatures and then a weaker dependence on the temperature. The two degraded materials have quite different thermal diffusivities due to their different thermal histories. The thermal diffusivity of the degraded sample increases slightly above 300°C, which is most probably due to further structural changes and increasing radiation within the sample. At high temperatures (>400°C), the virgin sample has a thermal diffusivity 2-3 times lower than the burnt material. This difference can be explained by differences in material thickness, decomposition state, and thus also of thermal history.

The in-plane thermal diffusivity of the virgin and half-degraded samples were measured up to 250°C (it was difficult to cut sample strips from coupons that were too degraded and thus measurement on the completely degraded sample was not possible). The results differ from the results obtained from the transverse measurement (Figure 3b). Only one direction was measured on the isotropic composite (symmetric stacking). These results show, in Figure 3, that the in-plane thermal diffusivity is approx. 15 times higher than the through-plane, which confirms the thermal anisotropy of this material. Small differences between the virgin and half-degraded samples were detected. These are attributed to heat transfer in the horizontal direction which is more or less independent of the degree of decomposition (but more investigations are necessary). On the other hand, the virgin and half-degraded materials have the same mass fraction of fibre which is not degraded [9], but differing mass fractions of resin and of carbonaceous residue.

Conclusion

The specific heat capacity, heats of decomposition and thermal diffusivity of a carbon fibre/epoxy composite were determined as a function of the temperature and of the decomposition degree. These properties and the associated protocols permit the feeding of a public database [10] necessary for providing information on a laminate exposed to fire or to high temperature. These properties are specific to a carbon fibre/epoxy composite applied to aircraft structure. As a bonus, the properties are used for such applications as modelling laminate in fire for fire safety engineering.

References

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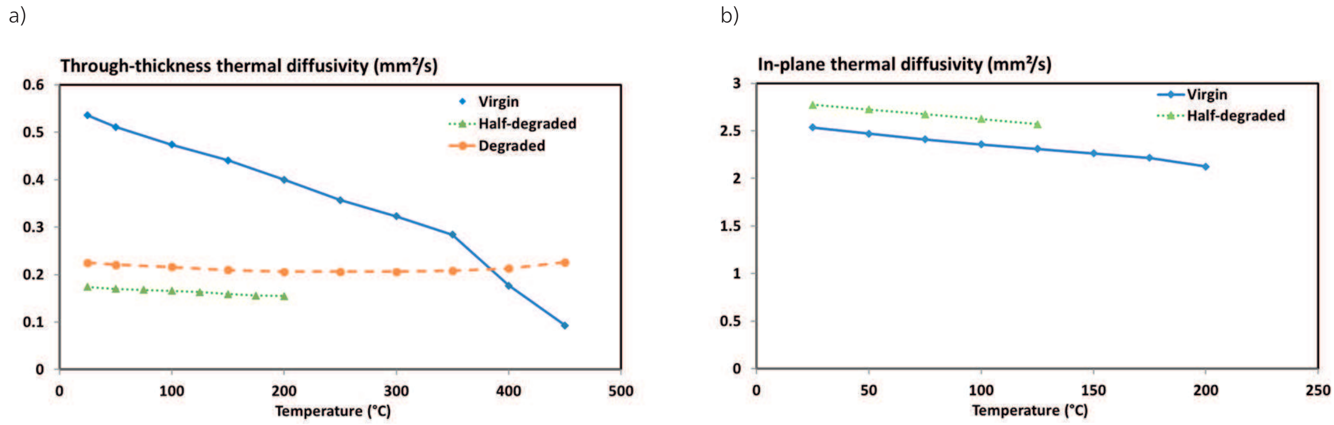

Fig 3. a) Through-thickness and; b) In-plane thermal diffusivities of the T700/M21 composite (virgin, half-degraded and degraded states) as a function of temperature [1]

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