THICK CARBON FIBRE REINFORCED COMPOSITE MATERIALS: INVESTIGATION OF AN INDUSTRIAL CASE-STUDY

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Abstract
In the present work, a case-study is presented, in cooperation with RI-BA Composites srl, where the industrial production of a thick composite material intended for structural application is analysed. The final product, is a bulk CFRP characterized by great dimensions and with thickness ranging between 10mm and 35mm. The object is produced via Hand-Lay- Up of pre-pregs and it is cured using vacuum bags in autoclave. Pre-pregs based on the same prepolymer are used, while the carbon fibre arrangement (both woven and unidirectional fabrics) changes along the depth of the part. The study takes into account the effect of the starting materials conditions, the time required to lay-up all the prepregs, the environmental conditions and the thermal curing cycle. A characterization of the final object, as a function of the overall thickness of the object and of the depth of the sampling will be presented.

1 Introduction

Carbon Fibre Reinforced Materials (CFRMs) are presently applied for a wide range of advanced applications such as in automotive, aerospace, construction, yachts, leisure and sport. CFRMs may have just an aesthetic role, mainly in luxury industry, but their main applications are still as structural materials where the particularly high strength to weight and stiffness to weight ratios provide the final objects with light weight and outstanding mechanical properties. CFRMs are generally produced as relatively thin objects, where layers of fibers and resin precursors, are stuck one on the other: playing on the composition of the layers, orientation of the fibers and on the stacking sequence, physical and mechanical properties can be controlled and tuned for specific applications.

When the design of the final object is particularly challenging, or the dimension is quite large, the best choice for producing CFRM is hand lay-up of pre-impregnated fabrics. In principle an infinite

stack of layer may be added to improve mechanical properties; however, when the number of layers is increased, though the composite can reach outstanding properties, in particular regarding the high strength to weight and stiffness to weight ratios, some problems arise in the manufacturing of the parts. There is no clear definition of what a thick composite material is, but Secord et al. defined[1] *"parts that have large unfavorable temperature overshoots are classified as "thick," while parts that have little or no overshoot during cure are classified as "thin"*. They claim that distinction of a CFRM into "thick" or "thin" classes depends just on how much this affects part quality. Indeed, owing to the exothermicity of the curing reaction in epoxy resins and to poor thermal conductivity across the section of single layer (due to the anisotropy of thermal conductivity in pre-pregs, which is high along the fiber axis, but definitely scarce perpendicularly to it), when thickness exceeds few millimetres overheating of the inner layers may happen, inducing thermal stresses and resin degradation in the final product and thus affecting the final object properties. When this happen, and care has to be taken in avoiding or, at least, in limiting the overheating effects, the object is considered a "*thick composite*". Additional problems might arise in the work up of big CFR objects, where not only the thickness section is increased, but the overall dimension of the final part extends over a meter scale. In this case the hand lay-up of the whole part is particularly time-requiring and the ageing of raw materials during work up might affect the kinetics of the curing reaction. Additionally the curing process, when performed at industrial scale is far form ideal laboratory condition, thus making thick composite industrial production an actual challenge.[2] In this context, the good knowledge of the thermal curing behaviour of the resin prepreg is of paramount importance to design a full production and curing cycle for a thick composite object avoiding defects that might compromise the final structural properties. Though modelling of the complex phenomena occurring in the thick composite production gives a rough estimation of what is occurring during the production of parts, the industrial reality is often far from the ideal conditions represented in the models.

In the present work, a case-study is presented, in cooperation with RI-BA Composites srl, where the industrial production of a thick part intended for primary structural application is investigated, starting form the analysis of the raw material, up to the characterization of the obtained thick and large object.

2 Materials and testing methods

The material used in this work is a commercial carbon fiber/epoxy prepreg, where the fiber is arranged either as a woven 2 twill fabric with about 600g/m^2 fiber weight per unit area or as unidirectional fibers with 300g/m^2 fiber weight per unit area, the resin content is 37wt%. Prepregs based on woven fibers will be named as PP-2T while prepregs containing unidirectional fibers will be named as PP-UD.

Images of the samples section were digitally recorded on a 3D Multifocal Microscope Hirox model HX 7700.

DSC measurements were carried out on a TA Instruments DSC 2920 Modulated apparatus equipped with and RCS cooling system. Every raw prepreg sample (10-15mg) was heated twice from -50°C to 250°C at 10°C/min in nitrogen atmosphere, with an intermediate cooling run carried out at 20°C/min. Cured samples were cut off the sample section ad different given depth and grinded to small pieces. A first pre-run was applied from room temperature (RT) to a temperature below the maximum T achieved in the curing cycle, in order to avoid further curing, then samples were heated twice from 20°C to 250°C at 10°C/min in nitrogen atmosphere, with an intermediate cooling run carried out at 20°C/min.

3 Results and Discussion

While a number of option is available for producing composite materials, lay up of commercial prepregs is an easy approach for obtaining thick and complex carbon fibre reinforced parts. Since

prepregs are tacky, they can be easily placed in moulds, even in complex shapes, and they are quite tolerant to room temperature conditions. Nevertheless, it has to be taken into account the fact that when the object to be produced is characterized by great dimensions the time required for the working up might somehow affect the properties of the crude materials. Commercial prepregs used for this case-study are made up of the same resin precursor and different types of fabric (both 2x2 twill woven, T2, and unidirectional, UD, mats). The difference between UD and T2 is not only in the fiber arrangement, but also the prepreg production technique: T2 is obtained via solvent impregnation while UD by hot melt procedure. The thermal curing of the final object is carried out using vacuum bags in autoclave. In the present case the part to be produced has a thickness between 10mm and 35mm and one dimension exceeds hundreds of cm: as a matter of fact the work up procedure might take up to three weeks from the moment prepregs are taken out of freezing cell (storage at -18°C). Hence, a first assessment of the prepreg condition as a function of time was carried out by DSC measurements.

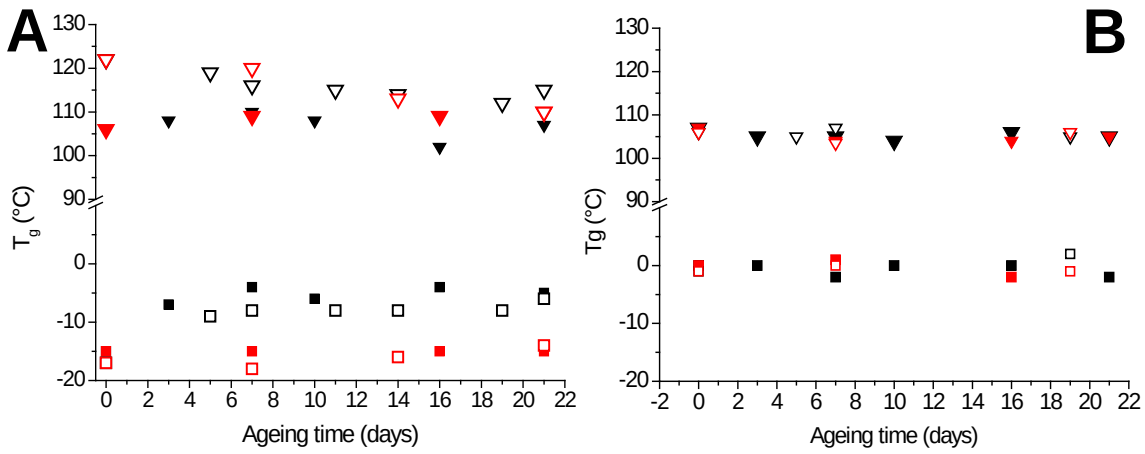

Figure 1. T_g evolution as a function of time for T2 (A) and UD (B) prepregs. Square symbols refer to I scan T_g, i.e. T_g of the crude prepreg; triangles refers to II scan T_g, i.e. T_g obtained upon curing prepregs in DSC scan conditions,. Open symbols refer to prepregs analyzed when received, filled symbols refer to materials analyzed after 4 months storage time at -18°C. Black symbols refer to materials kept at Room Temperature after taking them out of the freezing cell (-18°C), red ones refer to materials stored at 5°C during the analysis time span.

Every DSC show a low temperature T_g (below RT) and an exothermic peak in the I scan, while the second scan, upon reaching 250°C, shows only a high-T T_g. For all T2 samples the temperature of the peak maximum (T_{peak}) lie in the range 150-157°C, while UD prepregs are characterized by lower T_{peak} (145-147°C). Figure 1A-B shows the trend in the maxi shows T_g obtained during a DSC scan for crude prepregs and for the same materials upon heating up to 250°C in the instrument furnace. It is clearly observed that, irrespective of leaving the samples at RT or keeping them at 5°C, no significant differences are observed for UD prepregs, whether are they used when received or stored for 4 months in a freezing cell (-18°C). The T2 prepregs, on the contrary show an increasing trend in T_g values for the crude prepregs when kept at RT (black symbols in Figure 1). This is an indication that the uncured resin precursor tends to slowly polymerize in these conditions, i.e. in the processing condition, this phenomenon being more severe after 4 months ageing (open vs. full symbols). Figure 1 also shows that early undesired polymerization can be prevented by storing prepregs at 5°C (red symbols in Figure 1), where no changes in the T_g trend is displayed. While T_g of the crude prepreg increases when the samples are kept at RT, the corresponding T_g of the final product upon curing decreases with about the same trend. Once more 4 months ageing at -18°C worsen the situation, lowering the attainable T_g of about 8-15°C. Worth noting is that the usual shelf life of prepregs is 12months at -18°C and 4 weeks at RT. Moreover, Figure 1-A shows that

ageing has consequences also on samples kept at 5°C: though no significant change in the crude material T_g was observed, the maximum attainable T_g upon thermal treatment in the DSC furnace is even 15°C lower. Taking into account that T_g's obtained in the reported DSC scans are definitely not representative of what is the real attainable T_g in an industrial curing cycle, nevertheless the differences observed for T2 are indicative of what a good practice should imply when working with these materials in order to reach the best performances.

A first attempt was made to define a curing cycle made up of a sequence of dynamic heating steps followed by isothermal holding segments. The same curing cycle was applied to two different sequences of plies: in one case a sequence of T2 and UD was used, while in the second case only T2 layers were stack. A section of the two different thick CFRM obtained is reported in Figure 2A and B, respectively. It is easy to observe the clear stripes representing the threads from the woven fabrics: while in Figure 2A the clear stripes appear all along the sample thickness, in Figure 2B they are at the placed just at the two external sides and in the central layer. The darker part of the composite is made up of UD layers.

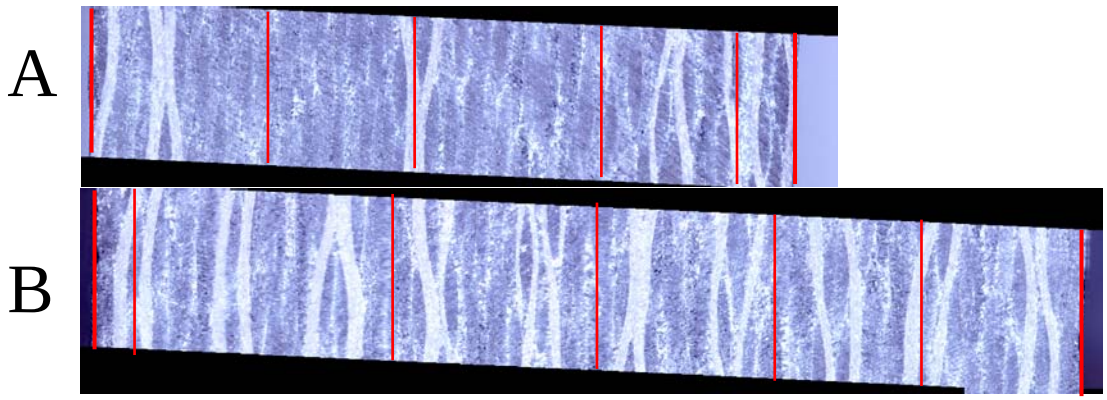

Figure 2. Section of the two different thick CFRM obtained: (A) T2+UD sample; (B) plain T2 sample. Red lines are roughly placed at the different delamination depth as reported in Figure 3.

Owing to the differences previously outlined in the starting prepregs, an attempt to characterize thermal properties of the composite was made: composites were delaminated at different depths and DSC measurements were carried out on the cured samples. Figure 3 display a profile of T_g measured across the composite section for the two obtained samples, T2 and T2+UD respectively.

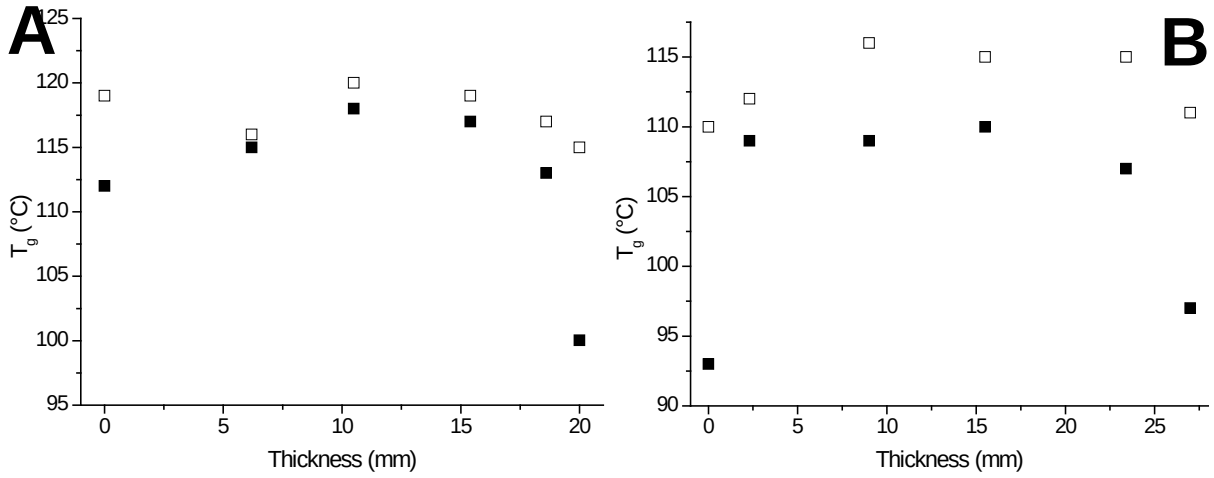

Figure 1. T_g measured across sample thickness for T2+UD (A) and T2 (B) thick laminates: (■) I scan; (□) II scan.

A gradient between the two external faces of the object is expected and, indeed, observed in the I scan for both T2+UD composite and T2 composites, as well as the bell shaped profile of T_g's. The latter behavior is mainly due, as previously stated, to the exotherm that cannot be easily dissipated from the core of the material when its thickness exceeds few mm. In this situation the heat accumulates and the curing temperature in the inner section reaches peaks higher than those planned in the cycle. Worth noting that, for T2+UD laminate, there is no significant difference when analysing samples taken in regions made up of different prepregs, as outlined in Figure 2A. The differences observed in T_g displayed at the two opposite faces, observed in both composites, depend on whether the external layer is exposed to the mould or to the bag upon curing. When comparing I and II scan T_g's, T2+UD laminate shows almost no increment in the value, accounting for an almost completeness of the curing reaction during the curing cycles in autoclave. On the contrary, the differences observed for the T2 composite in the II scan are a sign that the curing is not complete.

4 Conclusions

The industrial production of a thick and large object based on commercial prepreg was investigated in order to outline problems and critical issues. An ageing of the crude materials, when taken out of the freezing cell at -18°C, is observed when keeping prepregs at RT, while storage in the fridge at 5°C seems to help preventing this phenomenon. It appears that differences arise between twill 2x2 woven fabrics prepregs and unidirectional prepregs, probably owing to the differences in production techniques (solvent process and hot melt technique respectively) since the resin precursor is the same. When these materials are stuck in sequences to produce a thick and large composite, the mixed stacking sequence provide the best result with the achievement of an almost complete curing of the inner layers.

References

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