

Characterization of multifunctional thermoplastic composites

Saber Chelaghma, Olivier de Almeida, Philippe Marguerès, Jean-Noël Périé, Jean-Charles Passieux, Alain Vinet

▶ **To cite this version:**

Saber Chelaghma, Olivier de Almeida, Philippe Marguerès, Jean-Noël Périé, Jean-Charles Passieux, et al.. Characterization of multifunctional thermoplastic composites. JEC Composites Magazine, 2018, 55 (125), p.62-65. hal-01957044

HAL Id: hal-01957044
https://imt-mines-albi.hal.science/hal-01957044

Submitted on 23 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Characterization of multifunctional thermoplastic composites

Saber Chelaghma Ph.D., *Research Engineer*
IRT Saint Exupéry
Olivier DeAlmeida, *Assistant Professor*
IMT Mines d'Albi
Philippe Margueres, *Assistant Professor*
Jean-Noel Périé, *Associate Professor*
Toulouse University III Paul Sabatier
Jean-Charles Passieux, *Professor*
INSA Toulouse
Alain Vinet, *Research Engineer,*
Airbus SAS CR&T

Long-fibre thermoplastic composites have been the subject of research for quite some time, due to their good mechanical and chemical properties, recyclability, and adaptability to a wide range of manufacturing processes. The IRT Saint Exupēry technological research institute is currently involved in an R&D project on high-performance multifunctional thermoplastic prepreg materials, for which the research goal is to determine the effect of forming on the microstructural and mechanical properties of the composite.

The interest in organic-matrix composite materials reinforced with long fibres is growing, due to their specific mechanical properties and excellent chemical resistance. In addition, both the wide range of potential manufacturing processes and the possibilities for geometrical shapes and functional integration give access to many different applications. These materials are becoming established in a number of industrial sectors, including aerospace. Carbon/epoxy laminates are now heavily used to build the primary structures on modern aircraft (tail assemblies, the centre wing box section of the A380, the fuselages and wings of the B787 and A350, for example). Long-fibre thermoplastic composites have been studied for a long time because, besides the above-mentioned advantages, they have attractive properties in terms of recyclability and processing (easy-to-store matrix resins or prepregs with a very long shelf life and shorter cycle times, in situ consolidation, potential for automation and welding) and potential performance gains. Polyether etherketone (PEEK) is currently the benchmark matrix resin in the aerospace field. But PEEK is still rather expensive and its processing temperature is very high, so new high-performance thermoplastic matrices like polyether ketone ketone (PEKK), a matrix that has not garnered much interest since the 1990s, are being studied again. This polymer helps to significantly reduce the manufacturing cost and the processing temperatures – for PEKK 60/40, almost 40°C (104°F) less than for PEEK. However, very little research literature exists on this material.
The thermoplastic composites currently used in the aerospace industry also have very low levels of electrical conductivity (about 109 times lower than that of an aluminium alloy), due to the insulating properties of the polymer matrix. There are a number of potential ways to ensure the flow of electric charges (linked to lightning, air friction, spark jumping, etc.), including conductive coatings (paints or sprays), the incorporation of metal meshes or sheets into the stacks, or solutions based on scattering the conductive fillers (metal, carbon nanotubes, etc.) throughout the resin. The solutions based on the incorporation of metal meshes/sheets have proved themselves, even leading to commercial products (e.g. by Astroseal Products, Toray, Hexcel, Dexmet, Alcore, and ECC GmbH & Co. KG). The concept can be taken further to include integrating a conductive fabric into a ply. Various manufacturers distribute Inter Woven Wire Fabrics that are integrated into plies and adapted to the production of carbon/epoxy-laminate aircraft structures. They have been used in the fuselages of B787 aircraft, among others. Even if this type of solution is effective, it complicates the manufacturing process and significantly increases the weight of aircraft structures (for a bronze mesh, the additional weight varies from 80 to 200 grams per square metre). The integration of conductive fillers in a high-performance matrix resin shows great promise, even if it hasn't yet reached the industrial stage.
The IRT Saint Exupéry is actively involved in a research and development programme on high-performance multifunctional thermoplastic prepreg materials. A technological platform dedicated to the development of thermoplastic semi-finished products has been set up to provide support for these activities. The multifunctional thermoplastic prepregs are processed on a semi-industrial impregnation line. This flexible, modular method can process various types of tape architectures while keeping all key parameters (tow unwinding and assembly, impregnation, fusion and compaction) of the impregnation process under control. It also helps to establish the relationships among the microstructures in the semi-finished products, the process parameters, and the mechanical and functional performance of the composite laminates.
Getting from the proof-of-concept stage in the laboratory to the industrial demonstration stage is still a challenge, however, due to issues around the cost and supply of the fillers, the scaling up of the process, impregnating the semi-finished products, consolidation, controlling filler distribution, etc.). It also is advisable not just to study the effect of the manufacturing process on the disposition of the fillers, but also to assess

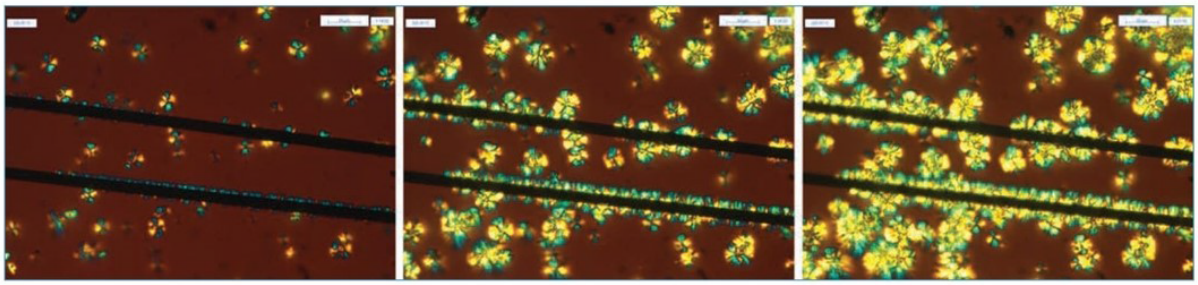


Fig. 1: Observation of PEKK crystallization in the presence of carbon fibre at a cooling rate of 1°C/min

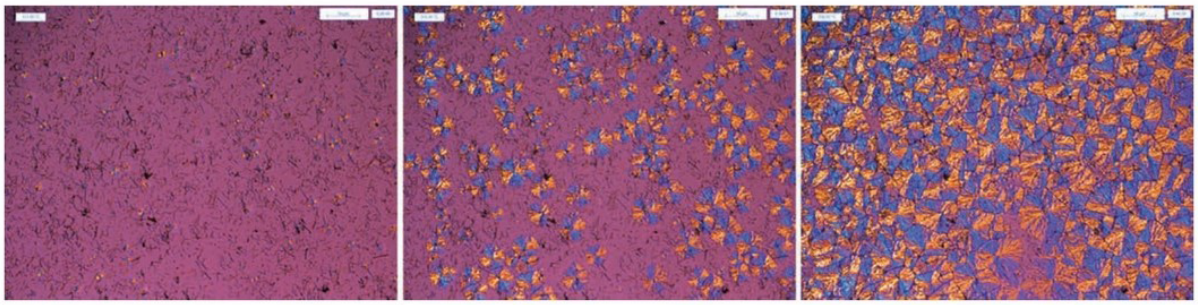


Fig. 2: Observation of PEKK crystallization in the presence of silver nanowires at a cooling rate of 1°C/min

the effect of the fillers on the composite laminate's overall end properties (and not just the electric properties). So it is essential to characterize these new materials in order to better understand, control and optimize the manufacturing processes and to succeed in in modelling and anticipating the end properties.

Characterizing the crystallization kinetics

To assess the impact of the manufacturing process and the components (in particular the functionalizing particles) on the composite properties, there was a specific focus on crystallinity, especially for PEKK, which is characterized by crystallization behaviours that are heavily dependent on the proportions of its constituent chemical entities [REF]. Just as the polymers in the PAEK family, PEKK exhibits two different crystallization mechanisms: a primary crystallization that corresponds to the stage of nucleus formation and crystal growth, and a secondary crystallization that corresponds to a perfecting of the existing crystals or a thickening of the crystalline lamellae within the crystals [REF]. To characterize these two mechanisms, two complementary experimental methods were used. In one, a hot plate was used to apply a thermal cycle and observe the crystallization process on polymer films through a polarized light microscope. This method served to characterize the nucleation rate and the crystalline growth rate (i.e., the primary crystallization) as a function of temperature. The second method uses differential scanning calorimetry (DSC) to determine the overall crystallization kinetics (primary and secondary crystallization) and the crystallinity rate. This approach makes it possible to identify the kinetics of each crystallization mechanism. To assess the influence of the carbon fibres on the crystallization mechanisms, light microscopy was used to make observations. Some fibres were inserted between two prepared PEKK films, and the assembly was heated to a temperature higher than the PEKK melt temperature in order to thoroughly impregnate the fibres. The microscopic observations of the crystallization presented in Figure 1 show that the unsized carbon fibres promote nucleation and lead to the formation of a transcrystalline zone around the fibres. This transcrystallinity is the result of a high nucleation density at the fibre/matrix interface and of the radial growth of the crystalline structures. The formation of a transcrystalline phase was observed with PEKK both for low cooling rates and for isothermal thresholds.

Higher crystallization kinetics were observed through DSC tests, whatever the conditions applied. The results also showed that the growth rate of the transcrystalline phase is identical to that of the spherulites. The acceleration of crystallization observed was therefore due uniquely to the increase in the number of nuclei at the fibre-matrix interface.

The same tests were carried out for the matrix filled with silver nanowires (AgNW). The formation of a transcrystalline phase was not observed (Figure 2), certainly due to the size of the AgNWs. The nucleation rates measured were still higher than those observed for the pure matrix. On the other hand, just as for the carbon fibres, there was no impact on the growth rate. The AgNWs apparently act as nucleating agents without leading to the formation of a transcrystalline phase around the particles. The same trend in the DSC tests was observed as for the carbon fibres, i.e. an acceleration of the crystallization kinetics as a function of the AgNW contents. This result has already been reported in the literature for other types of particles [REF]. In the case of a PEKK matrix reinforced with a 4.8% volume fraction of AgNWs, the crystallization time is divided in half compared to the pure matrix.

Ultimately, what we take away is that the carbon fibres and the AgNWs act as nucleating agents by reducing the crystallization time in a composite. The formation of a transcrystalline phase was observed in the case of unsized fibres. It should be noted, however, that this phase does not appear systematically. Depending on the cycle applied, the fibre surface treatment and the location observed, this phase is not always present.

Characterizing the composite microstructure

To understand the implementation potential of these new materials in primary aircraft structures, you need to understand their mechanical strength properties, so mechanical characterization tests were performed to assess their performance. On the materials studied, the mechanical response was not homogenous, as shown in tensile tests using stereo-digital image correlation. A study of the material health showed defects, in particular at the microstructural scale. A more precise description of the microstructure was needed to factor in these specific features, so X-ray tomography was used to characterize the composite. Due to recent developments in this technique, it can be used in combination with segmentation tools and image processing to accurately characterize the microstructure, fibre distribution, impregnation quality, and fibre content/porosity. Figure 3 shows the scans from a test carried out on a ZEISS Versa 520 tomograph at 40kV and a power of 3W, a resolution of 0.343 micrometre/voxel and a scan time of 16h.

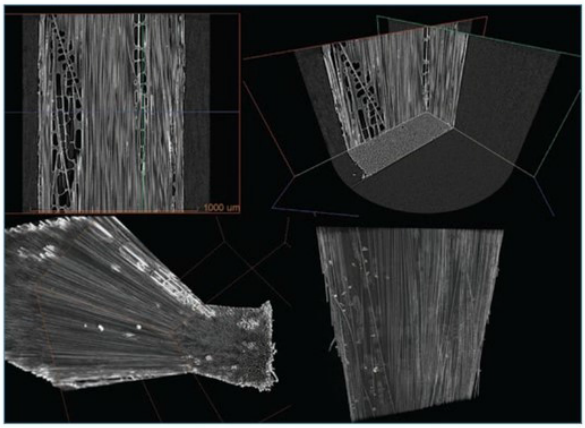


Fig. 3: X-ray tomography of a UD PEKK-matrix composite

X-ray tomography was also used to analyse the functionalized composites. Two scans using two different energies were performed in order to distinguish the fibres from the matrix, and the fibre/matrix couple from the AgNWs. The two sets of data were then combined numerically to characterize the distribution and position of the fillers.

Characterizing the micromechanical properties

The mechanical characterization of polymers at the micrometric scale is a useful tool in polymer science for several reasons. It is possible to map the local mechanical properties on the characterized specimens, using variations in the composition or a heterogeneity that is introduced, for example, by crystallization. For this study, the nanoindentation probed the material properties at a useful scale. A Berkovich three-faceted pyramidal tip was placed vertical to the surface and the load was increased at a rate of 20mN/min up to 10mN. The load applied was then reduced until partial or total relaxation of

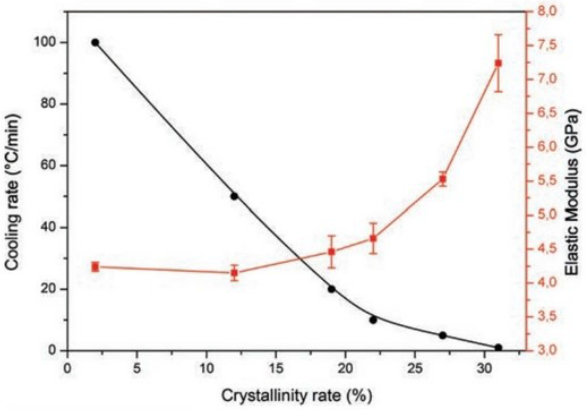


Fig. 4: Evolution of the elastic modulus as a function of the crystallinity rate

the material occurred. The curve for load as a function of the penetration depth was used to calculate the mechanical properties for hardness and elastic modulus. The specimens tested were subjected to various heat cycles in order to provide a broad range of crystallinities and crystalline morphologies. The results presented in Figure 4 show an increase in the elastic modulus as the crystallinity rate increases. The values obtained are for the stiffness of the crystalline entities (or those in the amorphous phase) and not the overall modulus of the homogenized material.

Similar tests were carried out on specimens that had been subjected to isothermal cycles. These cycles serve to generate different microstructures as a function of temperature, for the same crystallinity rate. This makes it possible to highlight the influence of spherulite size on the material's mechanical properties.

To report on the micromechanical properties brought about during the crystallization process, we propose to present the properties of the crystalline entities via a mapping of the properties that were characterized by the nanoindentation process, shown in Figure 5 for the case of an amorphous composite with much shallower penetration depths. It is possible to distinguish the matrix behaviour from that of the fibres. Tests for a crystallized matrix are ongoing.

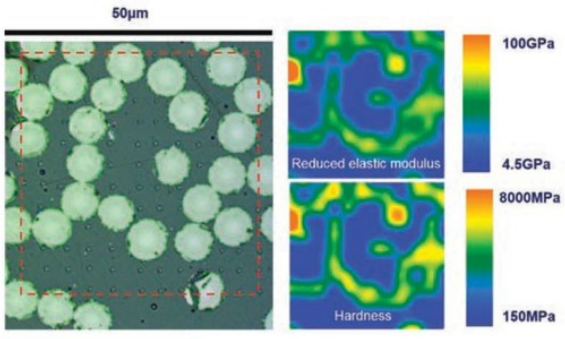


Fig. 5: Mapping of the elastic properties of an F/PEKK composite

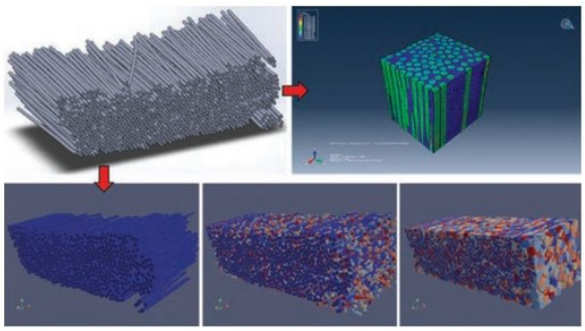


Fig. 6: Modelling approach

Perspectives: towards computational micromechanics

It is possible to use the raw tomography data to reconstruct a representative geometry for the material.
This geometry is generated from experimental data and serves to simulate the mechanical behaviour and also the crystallization process in a composite, as illustrated in Figure 6.

Using the experimental data on the crystallization mechanisms and on the effect of crystallization on the mechanical properties, it is possible to predict the properties of a composite, taking its microstructure into account.

The numerical simulations performed on 3D representative elementary volumes (REV) of a composite microstructure can be used to predict the properties of a ply, which can then be used to analyse the laminate.

This type of multiscale modelling could reduce the number, duration and cost of experimental characterization processes that extend from the specimen scale all the way to the structure. Determining the properties of the end structure using only a number of microstructure-scale characterizations and simulations (nanoindentation, push-in, pull out) is therefore a strategic scientific and industrial concern, especially in the case of thermoplastic-matrix composites that are characterized by crystallization capability. The present work contributes towards this approach. □

Acknowledgements

These results were obtained under the "COMPINNOVTP" research project. We would like to thank the Clément Ader Institute and Airbus SAS CR&T, the IRT Saint Exupéry's industrial and academic partners that sponsored this paper. We would also like to thank Fabien Amiot and Yves Gaillard for the nanoindentation tests.