INFLUENCE OF PROCESSING PARAMETERS AND SEMI-FINISHED PRODUCT ON CONSOLIDATION OF CARBON/PEEK LAMINATES

O. De Almeida[1*], E. Bessard[1], G. Bernhart[1]

[1] *Université de Toulouse ; Mines Albi, ICA (Institut Clément Ader) ; Campus Jarlard, F-81013 Albi cedex 09, France*
**olivier.dealmeida@mines-albi.fr*

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Abstract
Five millimetres thick laminates of carbon fibre PEEK matrix composite are processed with a fast thermo-compression moulding process using different parameter sets, namely temperature, pressure and consolidation time. Laminates consolidation is evaluated according to the architecture and quality of semi-finished product and process conditions.Microstructural observations show that impregnation level largely depends on the initial degradation of the matrix. Indeed, semi-finished product manufacturing can induce PEEK degradation that reduces the fluidity of the matrix and therefore impregnation.

1 Introduction

Semi-crystalline thermoplastic composites exhibit high toughness and excellent solvent resistance that make then suitable for high performance application. Among the thermoplastics, poly-ether-ether-ketone (PEEK) is a reference material for the aeronautic industry since the 80's: the unidirectional prepreg tape AS4/APC2 of Cytec Engineering Materials Inc. represents a first choice material for structural applications. However, this thermoplastic semi-finished product exhibits poor flexibility due to the high melting point of PEEK ($T_m \approx 343$°C) and complex shape composite parts are difficult to manufacture with UD prepreg tapes [1].

Carbon fabrics exhibit a convenient drapability that allows composite parts manufacturing with undevelopable geometries. But above melting temperature, thermoplastics viscosity is much higher than that of thermosets and "dry impregnation" of fibre yarns with thermoplastic resins is still not conclusive [2][3].

For these reasons, various semi-finished products have been developed during the last decade: commingled yarns used in crimp and non-crimp fabrics [4], powdered fabrics, film stacking [5]. Their specificity is to get around the difficulty of dry impregnation by reducing the distance the thermoplastic matrix has to cover to obtain a consolidated laminate. On the other hand, such products are interesting for out of autoclave processing routes that still need to be optimized.

In this study, processing behaviour of three different carbon fibre PEEK semi-finished products is evaluated using a fast thermo-compression moulding process based on induction heated dies. Thermal sensitivity of PEEK is first analysed in order to propose a process window and the quality of the semi-finished products is discussed. Laminates microstructure induced by the process conditions is then discussed for the different products.

2 PEEK processing window

Out of autoclave consolidation of PEEK laminates is a delicate issue to the extend that thermoplastics can be sensitive to oxidation. In particular, in air environment at high temperature, above its melt temperature, PEEK can exhibit a reactive behaviour leading to the formation cross-links [6][7].

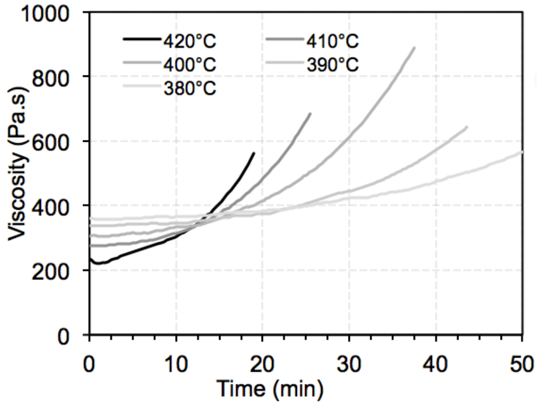

Figure 1. Time evolution of shear viscosity of PEEK for different isothermal conditions

In order to identify a processing window, measurements of the melt behaviour of a neat PEEK have been performed with a plate-plate shear viscometer. The samples were rapidly heated to an isothermal temperature condition and the viscosity was measured through time (Figure 1). The results show that in a first stage, PEEK viscosity remains constant and a classical thermal dependence is observed. But degradation of PEEK progressively occurs resulting to an increase of the PEEK viscosity that is all the more rapid that temperature is high.

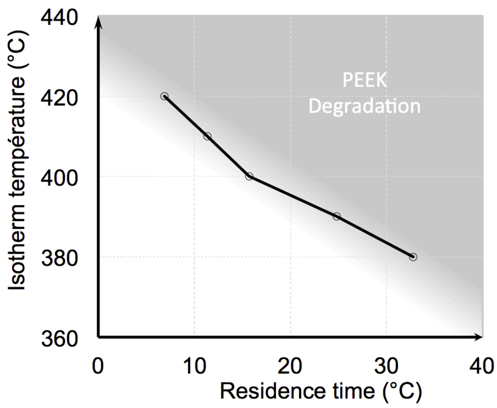

Figure 2. PEEK Processing window

The characterisation of the thermal degradation of PEEK then reveals that the use of high processing temperature for PEEK laminates consolidation is not necessarily beneficial. Low viscosity can favour impregnation but if degradation occurs before total impregnation, the advantage of fluidity can be considered as totally lost.

Considering that the advantage of low viscosity is lost from the moment where viscosity increase is of 20%, an acceptable residence time can be defined for each isothermal processing temperature. The resulting processing window is depicted in Figure 2.

3 Semi-finished products

Three different carbon / PEEK semi-finished products containing 50vol% carbon fibre were investigated, all of them based on PEEK from Victrex (151G grade).
One of the products is a Pi-Preg fabric provided by PORCHER Composites as a 2-faces powdered carbon fabric (5H Satin, 3k, 285g.m^{-2}). Powdered fabrics are manufactured by heating to melt a fabric previously sprinkled with PEEK powder. As show in Figure 3, the microstructure of this product appears as a dry fabric covered with PEEK droplets.

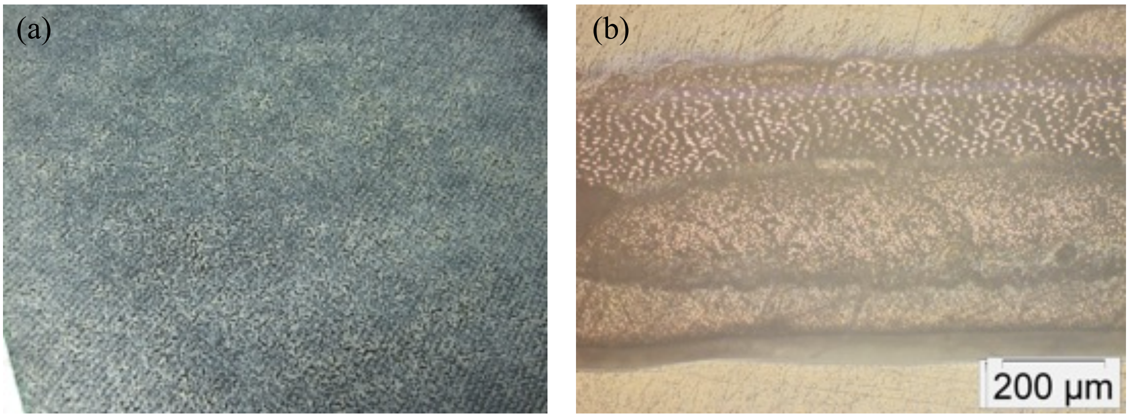

Figure 3. Powdered fabric from Porcher Composites (a) surface aspect (b) thickness microstructure

The second studied material is a commingled quadriaxial NCF consisting of a blended combination of carbon reinforcing yarns and PEEK yarns (585g.m^{-2}). PEEK fibres were obtained by melt spinning and the average diameter of PEEK filaments is 20µm. Figure 4 shows that the distribution of the filaments within the blankets is not very homogeneous. The microstructure exhibits aeras with high concentration of PEEK or carbon.

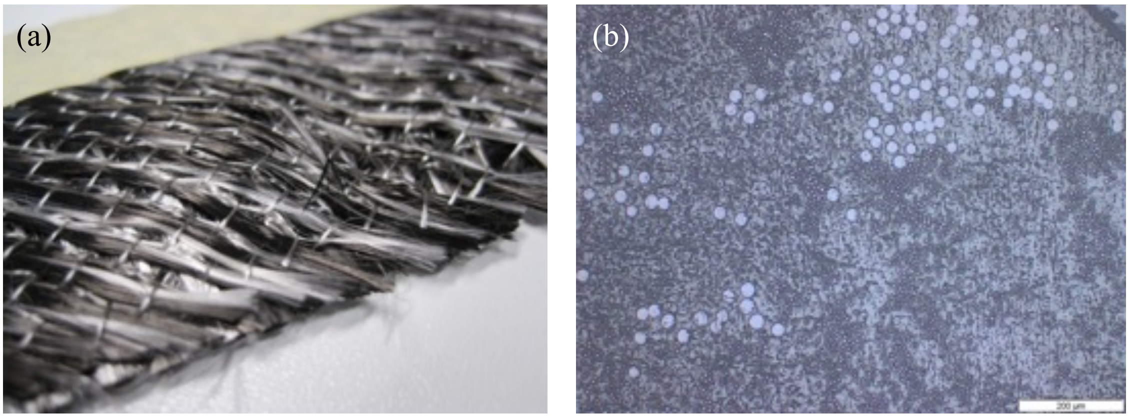

Figure 4. Commingled quadriaxial NCF (a) surface aspect (b) microstructure showing the commingling quality

A composite obtained by stacking of PEEK films and carbon fabrics (Serge 2x2, 285g.m^{-2}, 6k) was also evaluated. PEEK 38µm thick films were supplied by Victrex and the stack sequence was made laying alternatively PEEK films and carbon fabrics so as to satisfy a carbon content of 50vol%.
The three laminate configurations were compared to the reference prepreg AS4/APC2 from Cytec which fibre volume ratio is 0.6. The conventional autoclave processing cycle for AS4/APC2 consists in applying a constant pressure of 5 bars at a temperature of 400°C for 100 minutes. Nevertheless, as displayed in Figure 5, AS4/APC2 tape is already highly

impregnated before processing and shorter thermal cycle can be used to manufacture laminates in an out of autoclave configuration, using simply a vacuum bag in an oven.

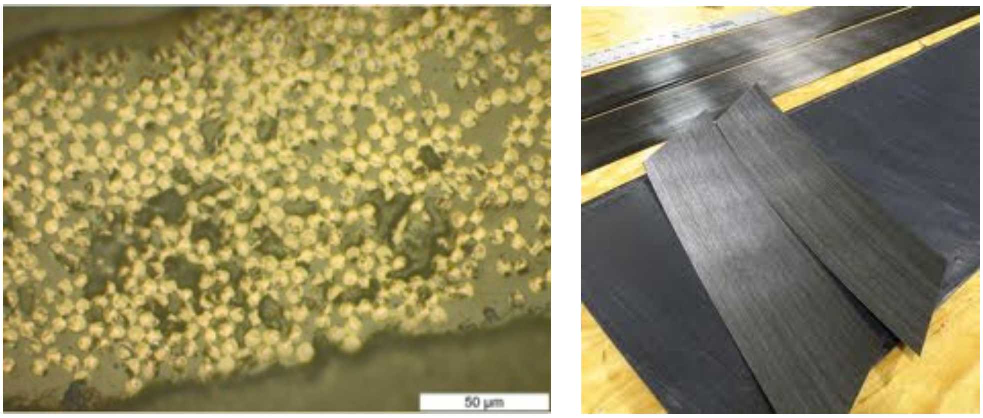

Figure 5. Semi-finished product APC2-AS4

4 Product quality

Since PEEK exhibits a high sensitivity to high processing temperatures, the initial quality of the studied semi-finished products had to be characterized. Calorimetry (DSC) measurements were performed on the different PEEK matrices and the melting temperature was used to quantify the possible initial degradation level of PEEK.

As a reference, a sealed calorimeter cap has been prepared with about 3mg of neat virgin PEEK and degradation cycles were performed on the sample. The cycles consisted in applying cooling (20°C.min-1) and heating (10°C.min-1) treatments to the sample between room temperature and 400°C (20 minutes isothermal step). The melt temperature was measured during the heating stage for 15 cycles and the evolution is plotted in Figure 6.

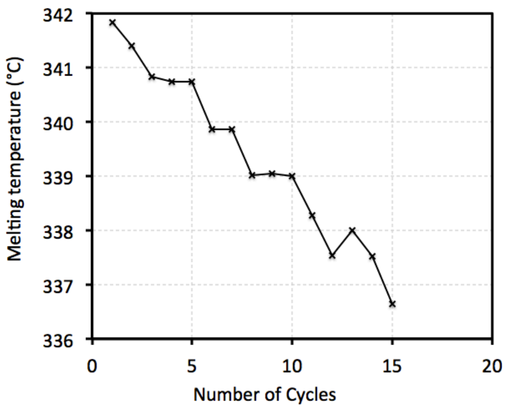

Figure 6. Influence of heating and cooling cycles on the melt temperature of PEEK

Figure 6 shows that PEEK degradation process lead to a fast decrease of the melt temperature of PEEK with cycles. After 15 cycles, the melt temperature decreases from 343°C to about 340°C, i.e. with an average rate of 0,2°C per cycle.

The same procedure was applied to the PEEK matrix of the semi-finished products and 3 cycles were performed on the samples in such a way to reduce measurements uncertainty. The melt temperature measured for the 3 different products is reported in Table 1. The values allow ranking the different matrices used in the semi-products as a function of their initial degradation level. PEEK matrix of the powdered fabric exhibits the highest melt temperature of 343,2°C that is consistent with the value of non degraded polymer. On the other hand, the melting temperature of PEEK filaments from the commingled NCF and the melting temperature of PEEK from the 38µm film are respectively 341,1°C and 340°C. This indicates that initial commingled NCF and film stacking are processed with degraded PEEK that will be damaging for fibre impregnation.

Semi-finished product	Melt temperature
Powdered fabric	342,2°C
Commingled NCF	341,1°C
Film	340,0°C

Table 1. Melt temperature of the semi-finished products PEEK matrix (average of 3 cycles)

5 Compression moulding process

Laminates were made of different number of plies so as to obtain a final fully impregnated 5mm thick reinforced composite. Thermo-compression was performed with an inductive heating mould (Cage system® technology developed by Roctool) mounted on an instrumented press. This technology allows high heating and cooling rates and therefore offers new optimization possibilities [8]. In this study, plies of 200x200mm^2 were heated to the processing temperature (resp. cooled) at a constant heating rate of 50°C.min-1 (resp. 20°C.min-1). Pressure was applied at the beginning of the isothermal temperature step and maintained until the end of cooling to avoid deconsolidation.

By using this fast thermo-compression moulding process, the exposure time to high temperature can be controlled and according to the preliminary evaluation of the processing window, different exposure time / processing temperature combinations were thus chosen to manufacture C/PEEK laminates:

- 5 minutes at 420°C,
- 10 minutes at 400°C,
- 10 minutes at 380°C,
- 20 minutes at 380°C.

These different configurations were used to evaluate the influence of processing parameters on impregnation of the powdered fabric product. The different semi-finished products are then compared so as to rank impregnability of the products.

6 Influence of processing parameters on powdered fabrics impregnation

Laminates manufactured with powdered fabrics were processed with a consolidation pressure of 8 bars. For each condition, a sample was machined in centre of the laminate and the polished specimens were observed with an optical microscope.

The microstructure resulting from the different consolidation time and temperature conditions are displayed in Figure 7. Consolidation in configuration 1 and 2 leads to a fully impregnated laminate, with a porosity level of about 2-2,5% as determined by chemical dissolution. However, consolidation quality, when performed at 380°C for only 10 minutes, turns out to be lower and numerous micro-porosities are visible.

As a consequence, processing window of powdered fabrics can be refined by adding a insufficient processing consolidation zone (Figure 8). This area illustrates the processing temperature / consolidation time couples that lead to a poor impregnation level (porosity rate of about 3%). The shape of this area is approximated in considering that high fluidity with short processing time as well as high viscosity with long processing time lead to the same impregnation level.

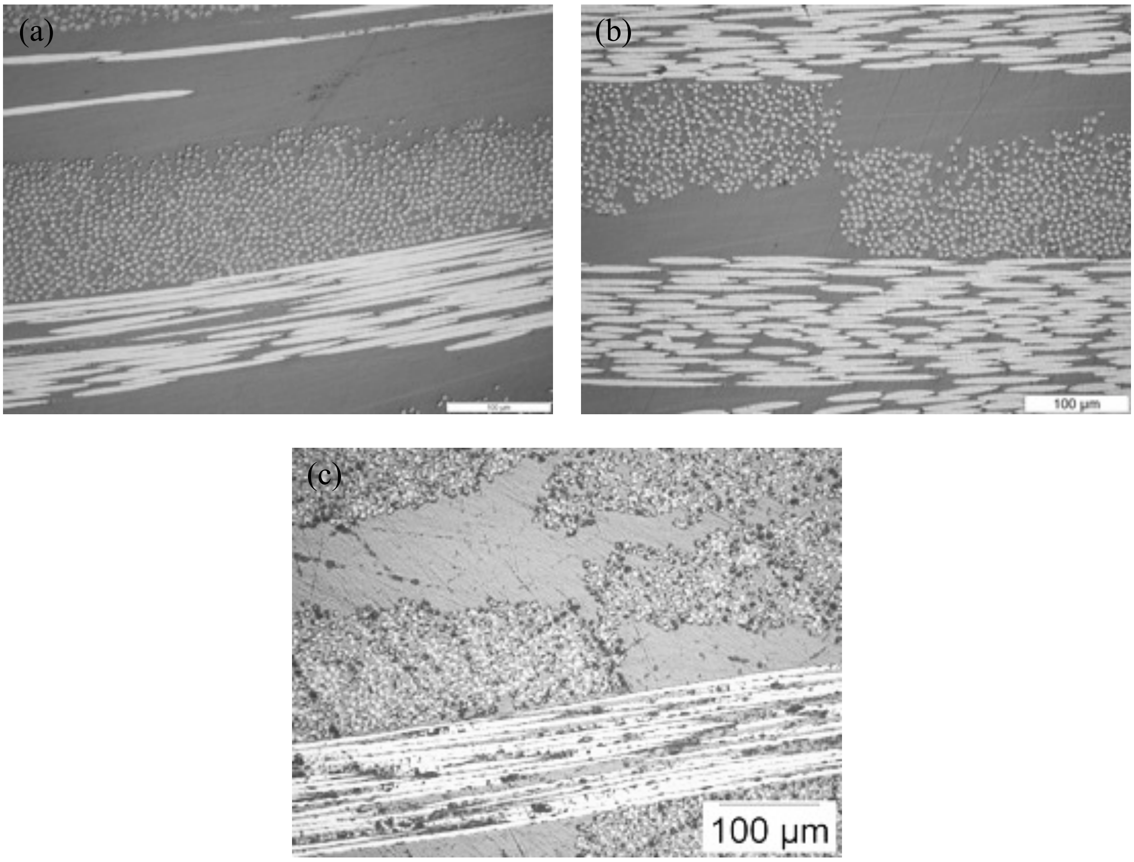

Figure 7. Microstructure of powdered fabric laminates
(a) 5 minutes at 420°C (b) 20 minutes at 380°C (c) 10 minutes at 380°C

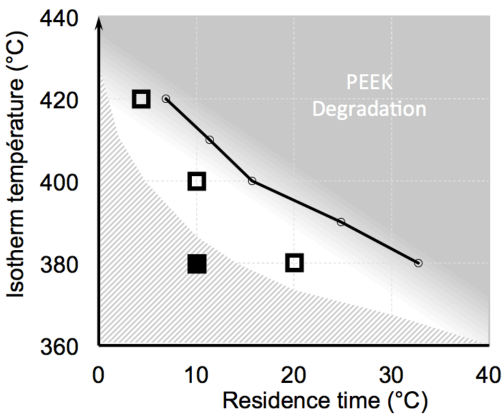

Figure 8. Processing window of PEEK powdered fabrics for a consolidation pressure of 8 bars

7 Influence of semi-finished products on impregnation

The same processing procedure has been performed to manufacture laminates from commingled NCF and from film stacking products.

Figure 9 shows the microstructure resulting from consolidation of commingled NCF laminates with a pressure of 8 bars for two extreme processing conditions. In contrary to powdered fabrics, in both cases, impregnation is incomplete and macro-porosities are observable. The microstructure consecutive to a processing condition of 5 minutes at 420°C exhibits macro-porosities in both carbon yarns and rich polymer zones while 20 minutes at

380°C lead to even worth consolidated microstructure with millimetric porosities in polymer areas.
Such particular impregnation behaviours of the commingled product cannot only be attributed to the commingling organisation since polymer distribution is supposed to favour impregnation. The initial PEEK quality may probably also have influenced the impregnability of this semi-finished product.

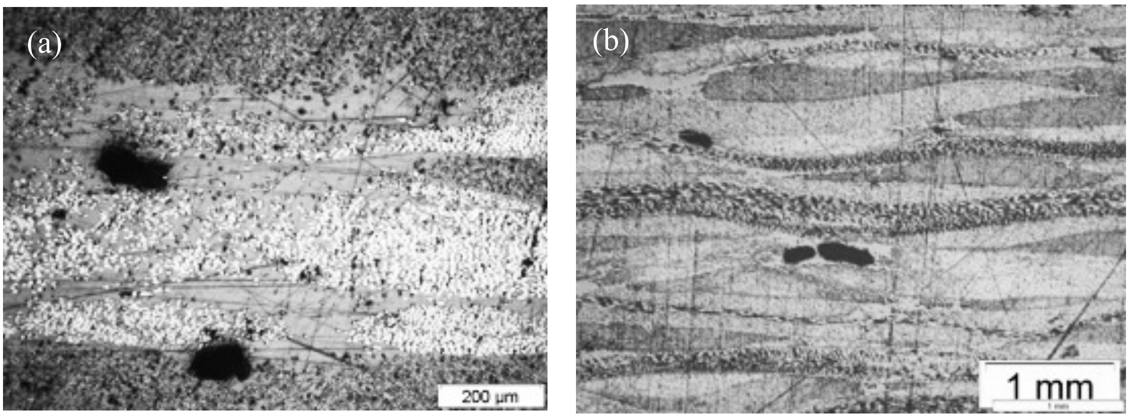

Figure 9. Microstructure of commingled NCF
(a) 5 minutes at 420°C (b) 20 minutes at 380°C

To improve consolidation quality of commingled NCF, a higher pressure is required. As shown in Figure 10, porosity can be reduced to a micrometric size by applying a pressure of 15 bars. The microstructure still exhibits a disperse micro-porosity which rate is close to 3,5%.

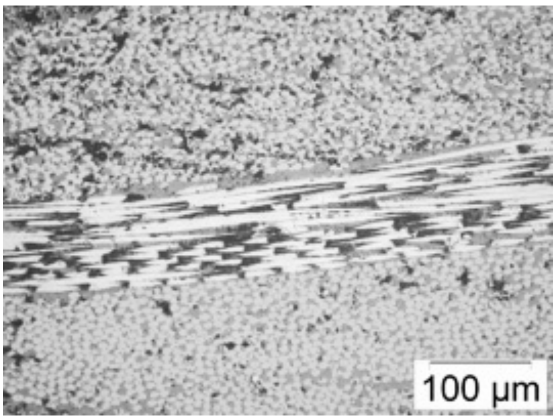

Figure 10. Microstructure of a commingled NCF laminate processed
10 minutes at 400°C with a consolidation pressure of 15 bars.

Finally, laminates manufactured from film stacking configuration were processed at 400°C for 10 minutes with an applied pressure of 7 bars. As displayed in Figure 11, the microstructure pictures exhibit enlarged areas of unimpregnated fibres depicted as large dark ellipses in the centre of the transverse yarns. To the extend that carbon fibre bundles are 6k carbon yarns, lower impregnation level could have been expected in comparison with the powdered product and to enhance the degree of consolidation, residence time and/or the molten resin fluidity and/or the pressure must be increased. Nevertheless, the advanced degradation of the PEEK films may also be responsible for some extend for this poor impregnation.

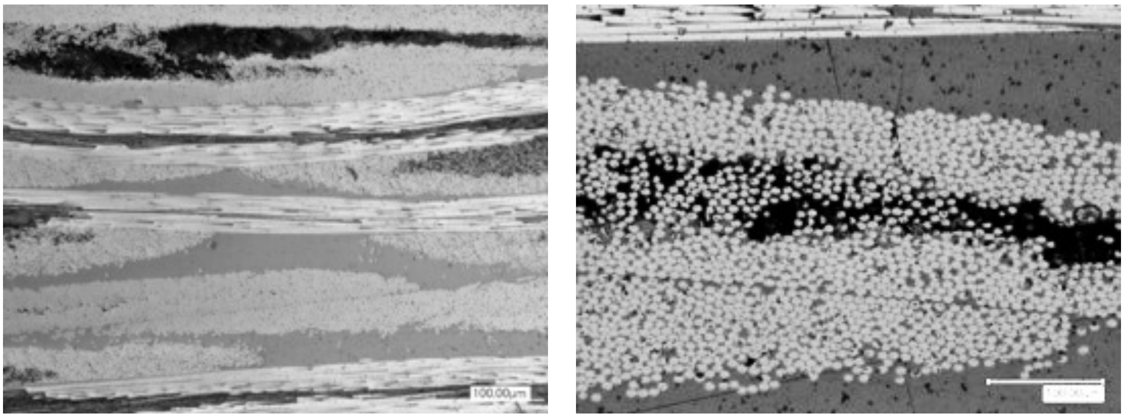

Figure 11. Film stacking microstructure after 10 minutes at 400°Cwith a consolidation pressure of 8 bars

8 Conclusions

The analysis of PEEK thermal stability shows a rapid degradation process. It induces an increase of the melt behaviour that must be taken into consideration when processing reinforced PEEK laminates. High temperature processing may favour impregnation at first but degradation may stop the PEEK percolation process within the carbon bundles for longer consolidation time.
Consolidation of different semi-finished products was evaluated as function of processing conditions. The characterization of semi-finished product matrices shows that degradation was already initiated before composite processing (i.e. during semi-product manufacturing) and as a consequence laminates exhibited distinct degrees of impregnation when manufactured with an equivalent processing parameter set.
Moreover, each semi-finished product led to different porosity type depending on the initial PEEK carbon architecture.

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