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ABSTRACT

The use of high performance thermoplastic composite structure in aerospace has seen a great increase in the past decade. Thermoplastic composites present many advantages over thermoset composites in term of processing and performance. Their fast processing time, infinite shelf life and recyclability lead to a decrease in the manufacturing costs compared to traditional autoclaved thermoset composites. Also, their high toughness and fatigue resistance, high temperature performance, chemical resistance and low flammability make them good candidates to replace metallic or thermoset composite aerospace structures. Among the several manufacturing techniques available, autoclave processing of thermoplastic composite is a simple technique allowing the co-consolidation of semi-complex composite structures. In this study, the effect of the autoclave process parameters (processing temperature, temperature cooling rate and consolidation pressure) on the crystallinity, the panel quality and mechanical performances of PEEK/carbon composite panels was investigated. The neat resin crystallinity was first examined by Differential Scanning Calorimetry (DSC) under different cooling rates. Tensile, in-plane shear, and interlaminar shear tests were performed to assess the panel mechanical performance under different processing conditions. Panel quality was defined by observing the panel consolidation and void content via microscopy and X-ray tomography. From these results, the sensitivity of the material performance to the process parameters was determined and the optimal autoclave processing windows of PEEK/carbon tape material was established.

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INTRODUCTION

First developed in the 1980's, the use of high performance thermoplastic (TP) composites increased significantly in the past decades and it expanded to a large range of applications from automotive and oil industry to aerospace. TP composites present many advantages over thermoset composites in term of processing (fast processing time, infinite shelf life) and performance (high toughness and fatigue resistance, high temperature performance, chemical resistance and low flammability). The main high performance TP matrices used in aerospace applications are Poly-Ether-Imide (PEI), Poly-Phenylene-Sulfide (PPS), Poly-Ether-Ether-Ketone (PEEK) and Poly-Ether-Ketone-Ketone (PEKK). Despite its high material and processing costs, PEEK remains a material of choice for its high mechanical performance, high crystallinity, high service temperature and high resistance to solvents. In aerospace industry, TP composites found their main applications in aircraft interiors for non-structural applications such as seats, hatches, table flaps, clips or brackets and structural ones like pressure and non-pressure floors. The use of TP composites for aerospace primary structures slowly arose ten years ago with the conception of the glass/PPS J-nose leading edge developed by Airbus and Stork Fokker for the A340-600 and extended for the A380 [1]; but the initial material cost and the lack of material database compared to thermoset matrices still limited their application to a wider range of composite structures.

In this study, the processing of PEEK/carbon panels by autoclave was investigated. Manufacturing thermoplastic composite parts by autoclave is similar in principle to the manufacturing of thermoset components. The main difference in the process parameters is the use of higher processing temperature (>300°C) and higher consolidation pressure (0.6 – 2 MPa) to ensure a good impregnation of the fibre and a low porosity. Also, high temperature resistant auxiliary materials (vacuum bag, sealant, ect) have to be used in order to handle the processing temperatures. Few studies investigated autoclave processing of thermoplastic composites. Manson and Seferis [2] and Lystrup and Andersen [3] investigated the influence of the processing parameters on the CF/PEEK part quality (void content and consolidation, mechanical properties). The effect of the consolidation pressure, temperature, holding time, and cooling rate was examined. It was observed that high processing temperature combined with high consolidation pressure led to a better consolidation and a lower void content. The dimensional stability of thermoplastic angled-composite was also investigated by Salomi *et al.* [4].

In this work, the effects of the autoclave temperature and consolidation pressure on the panel quality and panel mechanical performance were examined. The quality of the panel consolidation and the void content were observed by optical microscope and X-ray tomography. Tensile, in-plane shear and interlaminar shear tests were performed to determine the panel mechanical performance under different processing conditions. From these results, the sensitivity of the material performance to the process parameters was determined and the optimal autoclave processing windows of PEEK/carbon tape material was established.

EXPERIMENTS

Material

A commercial PEEK/carbon tape (CETEX Thermo-Lite TC1200 PEEK AS-4) supplied by TenCate was used in this work. The tape fibre volume content is 59% with a fibre areal weight of 146 g/m^2. The ply thickness is 0.14 mm. The PEEK matrix glass transition temperature (T_g) is 143°C and its melting temperature (T_m) is 343°C. The typical processing temperature is around 380°C [5].

Autoclave Processing

Composite plates were moulded on a 1.9 cm thick aluminum mould. Prior to autoclave processing, the mould was sealed with two layers of mould sealant (Sealer GP from Zyvax) and coated with four layers of release agent (Composite Shield from Zyvax). The TP plies were then directly laid on the aluminum tool. Fibreglass peel ply and breather material were placed above the laminate. A combination of low temperature and high temperature sealing tapes were positioned on the mould perimeter and high temperature bagging material was used to finalize the vacuum bag. Three thermocouples were positioned along the length of the mould on the composite surface. The autoclave temperature was then controlled based on the average temperature measured by the three thermocouples.

Consolidation temperature and pressure are two key processing parameters influencing the quality and the performance of thermoplastic composite. Two levels of temperature (380°C and 400°C) and three levels of pressure (90 psi, 120 psi and 150 psi) were tested for a total of six processing conditions. Figure 1 shows a typical autoclave cycle. The autoclave was set to heat up at a rate of 2°C/min and cool down at rate of 15°C/min. The consolidation temperature was maintained for 60 minutes. The consolidation pressure was applied during the heating step just before the composite part reached its glass transition temperature and was released during the cooling step at a temperature below T_g. The vacuum was maintained during the entire cycle.

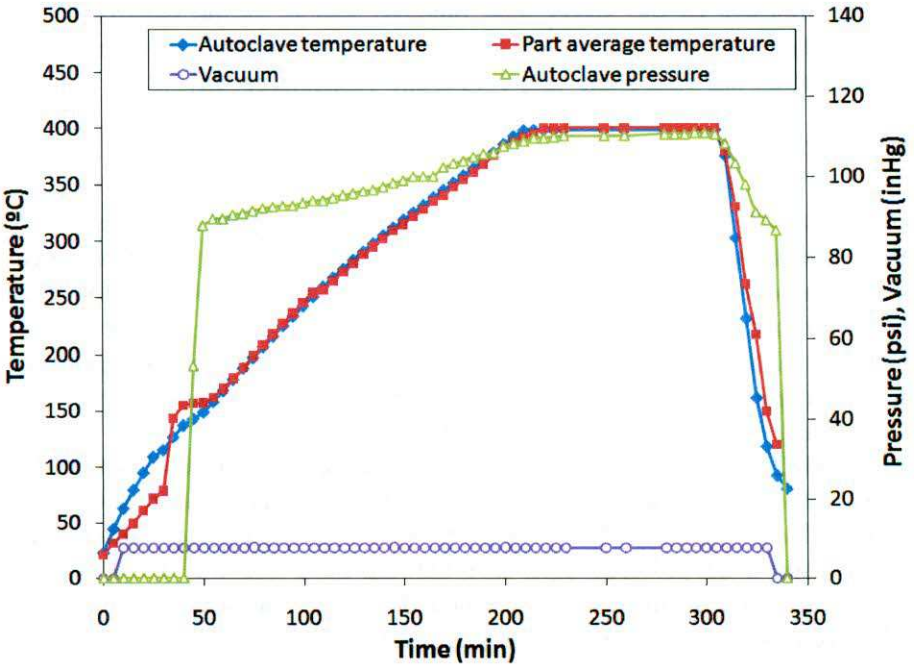


Figure 1: Autoclave cure cycle at 400ºC and 120 psi

Material Characterization

CRYSTALLINITY

The crystallinity levels of PEEK neat resin were measured by Differential Scanning Calorimetry (DSC). Dynamic tests were performed at different cooling rates. PEEK sample was first melted at 380ºC for 10 minutes to eliminate any existing crystals and cooled down to room temperature at various cooling rates (1, 2, 5, 10, 12, 14, 16, 18 and 20ºC/min). The crystallization occurs at the cool down between T_m and T_g temperatures. The measured heat H_c generated during the crystallization is related to the crystallinity level by the following equation:

$$X_{mc} = \frac{H_c}{H_u} \tag{1}$$

where X_{mc} is the weight fraction crystallinity and H_u is the total ultimate heat of reaction if 100% of crystals were formed. For PEEK resin, H_u is equal to 130 J/g [6].

The weight fraction crystallinity X_{mc} can be then linked to the volume fraction crystallinity X_{vc} as follows:

$$X_{vc} = \frac{X_{mc}\rho_a}{\rho_c - X_{mc}(\rho_c - \rho_a)} \tag{2}$$

where ρ_a is the density of the amorphous material and ρ_c is the density of the crystalline material. For PEEK material, the values of the amorphous density and the crystalline density are 1.26 g/cm^3 and 1.40 g/cm^3 respectively [6].

MECHANICAL TESTS

Tensile tests at 0°, in-plane shear tests and interlaminar shear (ILS) tests were performed to assess the influence of the processing conditions on the mechanical properties of the composite panels. Three laminates were moulded for each processing conditions. The laminate layups were defined based on the ASTM standards D3039, D3518 and D2344 [7-10]. The layup and the test specimen dimensions are specified in TABLE I. Aluminum tab were used for the tensile specimen at [0°] as recommended by the ASTM standard.

An Instron 5582 testing machine was used with a load cell of 100 kN with the traction fixture. For the tensile and in-plane shear tests, the cross head speed was fixed to 2 mm/min. Composite's ILS properties were measured using a three-point bending fixture and a 25 kN load cell. The loading nose and the radial support diameters are 6 mm and 3 mm respectively and the cross head speed was set to 1 mm/min. Between five to ten samples were tested for each mechanical test.

PANEL QUALITY

The panel quality was defined by the material consolidation and was observed by microscopy and X-ray tomography. For each processing condition, samples were cut from the middle and the side of the manufactured panels and then polished. The cross sections in the longitudinal and transverse direction of the fibres were then observed under optical microscope.

One sample of the two extreme processing conditions (380°C/90psi and 400°C/150psi) were also observed by X-ray tomography to visualise their internal structure and the quality of the consolidation. The samples were scanned using a HMXST 225 micro-ct from X-Tek with no filter at a resolution of 9 µm/pixel with an x-ray voltage of 64 kV and an intensity of 133 µA. 8 images per position were acquired and averaged to one scan.

TABLE I: SPECIMEN LAYUP AND DIMENSIONS

	Tests	**Layup**	**Length (mm)**	**Width (mm)**	**Thickness (mm)**
Laminate 1	Tension [0°]	$[0]_{15}$	250	25	2
	DMA	$[0]_{15}$	55	7	2
Laminate 2	ILS	$[0]_{36}$	40	12	5
Laminate 3	In-plane Shear	$[+45/-45]_{4S}$	250	25	2.24

RESULTS AND DISCUSSION

Crystallinity

Figure 2 presents PEEK final volume fraction crystallinity, X_{vc}, for the different cooling rates, calculated using equation (1) and (2). It can be noticed that PEEK final crystallinity remains stable under a wide range of cooling conditions (31.6 ± 1.2 %), which is valuable in case of unexpected changes in autoclave processing conditions.

The crystallinity kinetics was investigated for the autoclave cooling rates, from 10°C/min to 20°C/min, typically used in industry. The Avrami equation was used to model the rate of crystal formation with time and temperature under non-isothermal conditions:

$$X_{vcr} = \frac{X_{vc}}{X_{vc\infty}} = 1 - exp(-Kt^n) \tag{3}$$

where X_{vcr} is the relative crystalliniy, $X_{vc\infty}$ is the final crystalinity, t is the time, K is a rate constant value and n is the Avrami exponent. A data fitting software was used to determined the Avrami parameters K and n from the experimental data. The values of K and n are presented in Figure 3 and Figure 4 respectively. These values were not constant but they evolved rather linearly with the cooling rates and can be expressed as reported on the graphs. Using Avrami equation (3), the evolution of the crystallinity can be predicted for the typical autoclave cooling rates and compared to the experimental values measured by DSC (Figure 5). The experimental and calculated crystallinity compared well, validating the use of the Avrami equation to compute the crystallinity level under different cooling rates. This empirical model can be then used to predict the evolution of PEEK crystallinity under different autoclave temperature cycles and cooling rates.

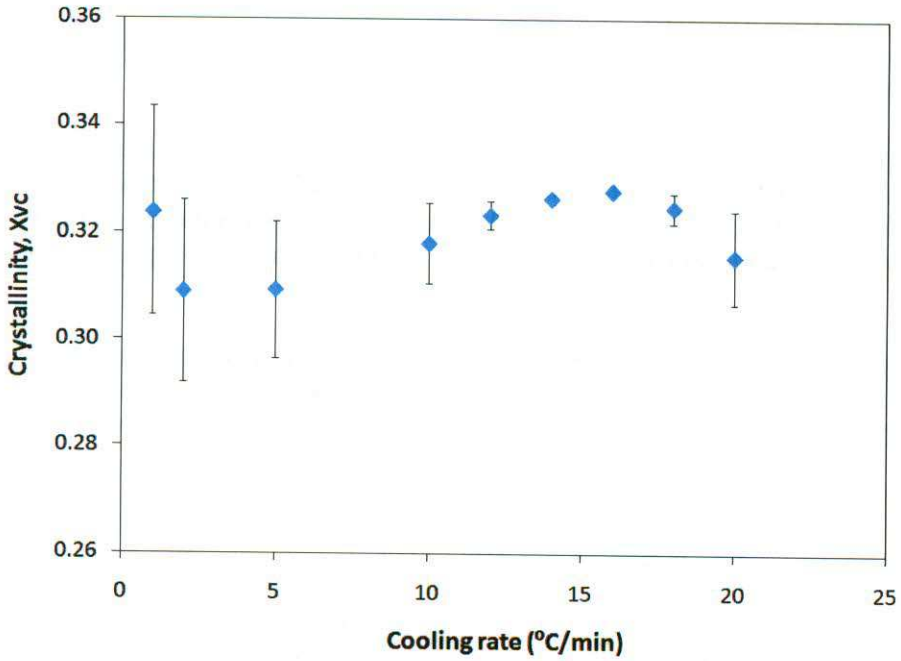


Figure 2: Volume fraction crystallinity as a function of the temperature cooling rate

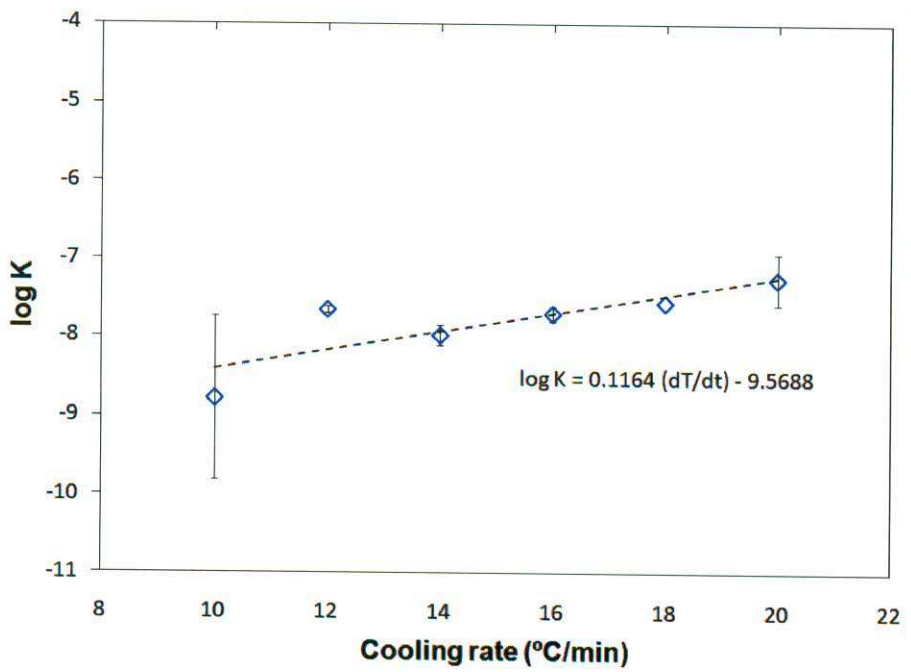


Figure 3: Variation of the rate constant K with the cooling rate

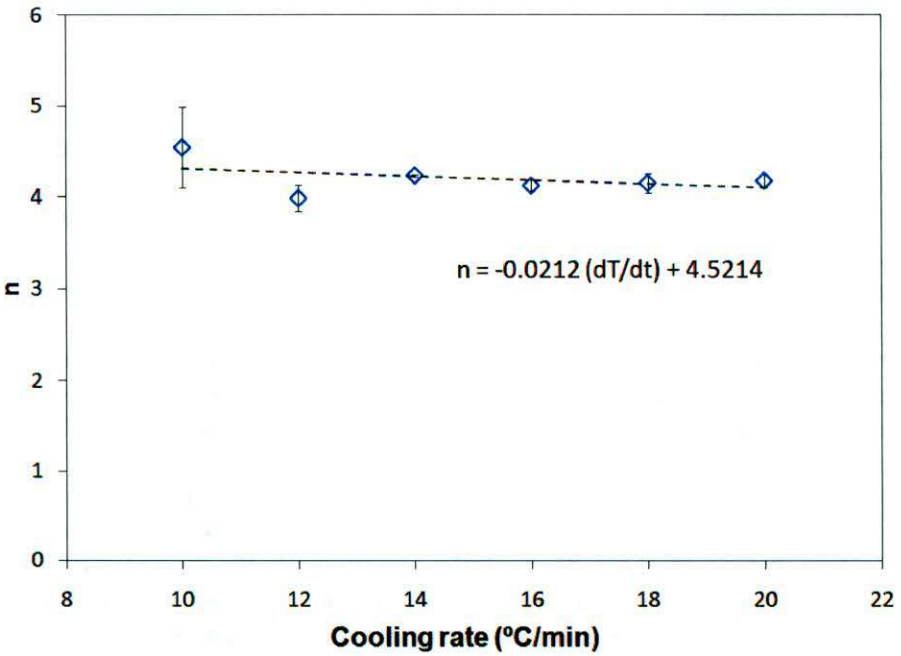


Figure 4: Variation of the Avrami's exponent *n* with the cooling rate

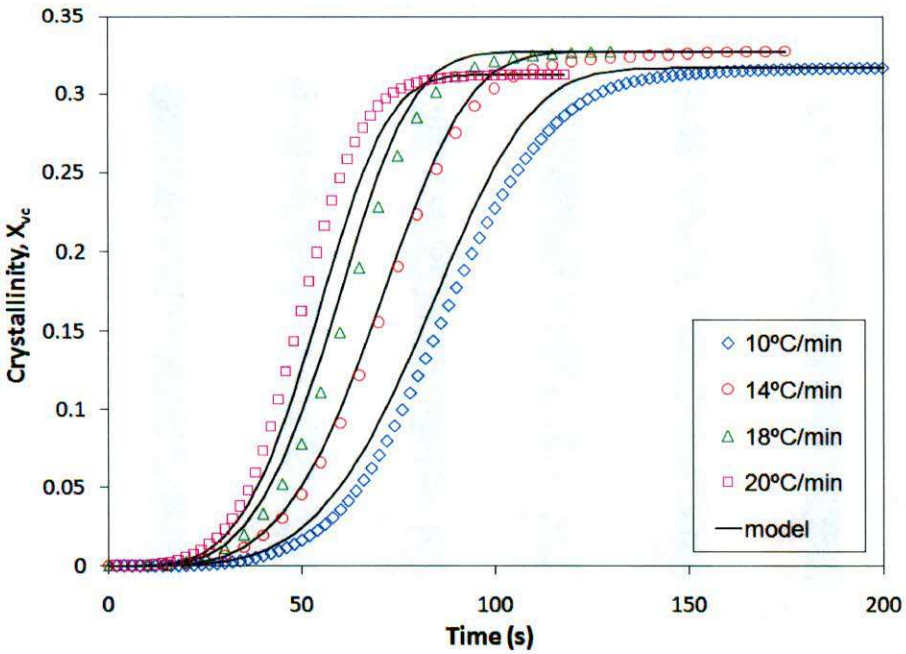


Figure 5: Evolution of the measured and modelled crystallinity with time

Mechanical Performances

TENSILE AND IN-PLANE SHEAR PROPERTIES

Figure 6 and Figure 7 present the Young's and shear moduli and the tensile and shear strengths, respectively, for the six tested processing conditions. From Figure 6, the Young's modulus and the shear modulus do not seem affected by the tested processing conditions. The average Young's modulus was found to be E=131.51 ± 3.43 GPa and the average shear modulus was G = 18.35 ± 1.63 GPa. The Young's modulus is in agreement with the tensile modulus of 141 GPa given by the manufacturer material data sheet [5]. The influence of the processing conditions is more noticeable on the material tensile strength as seen in Figure 7. The tensile strength increases with the increase in consolidation pressure and temperature. This might be due to a better consolidation of the material or a better alignment of the fibres in the laminate with the pressure. For the tensile tests, it should be mentioned that about half of the samples reached the limit of the 100 kN load cell without breaking. Therefore, the reported tensile strengths correspond to the lower limits of the material properties. The manufacturing conditions do not seem to have an influence on the shear strength. This means that a good consolidation and a low porosity level were achieved for the range of processing parameters tested.

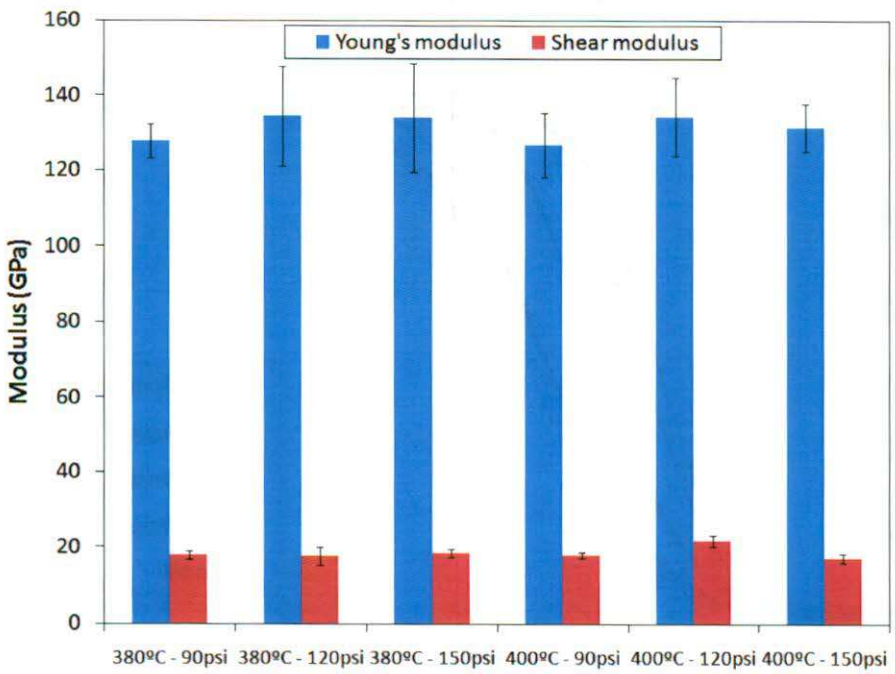


Figure 6: Young's modulus and shear modulus of PEEK/carbon samples manufactured under different processing conditions

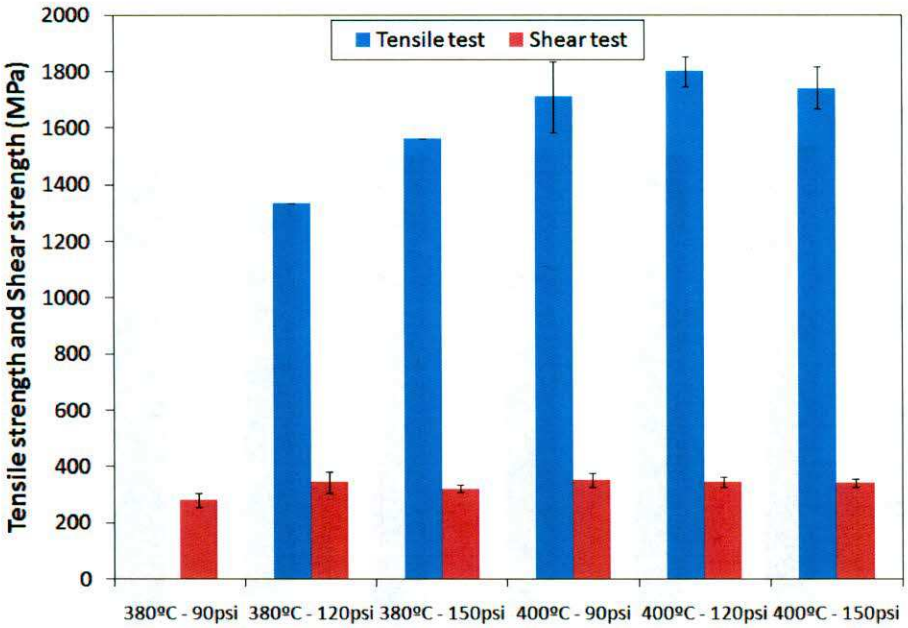


Figure 7: Tensile strength and shear strength of PEEK/carbon samples manufactured under different processing conditions

INTERLAMINAR SHEAR PROPERTIES

Figure 8 shows the variation of the interlaminar shear strength (ILSS) with the manufacturing temperature and consolidation pressure. Similarly to the Young's and shear moduli and the shear strength, the interlaminar shear properties were not affected by the tested processing parameters. An average short beam strength of 92.36 ± 1.05 MPa was measured. This value is in agreement with the SBS of 88.9 MPa given by the manufacturer [5]. Mid-plane interlaminar shear failure mode was observed for most of the samples.

ILSS is known to be very sensitive to void content and a decrease in ILS is usually observed for a void content above 1% [11-14]. As the ILSS values vary less than 3% for the six processing conditions tested, it can be assumed that the void content within the samples is low with a variation inferior to 1% from one condition to another.

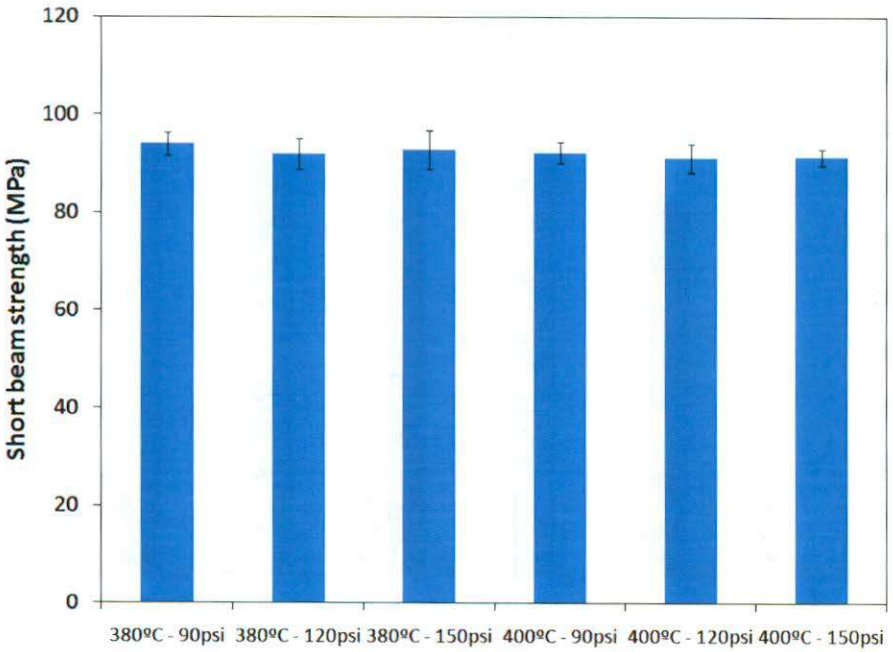


Figure 8: Short beam strength of PEEK/carbon samples manufactured under different processing condition

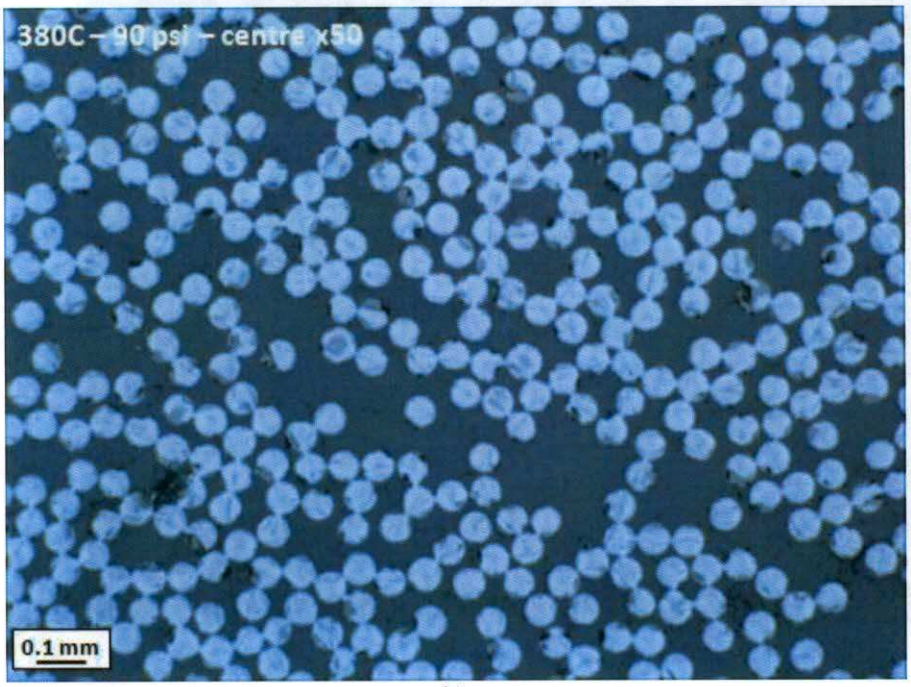
Consolidation and Void Content

The assumption of a low void content and a good consolidation was verified by observing manufactured samples under optical microscopy and X-ray tomography (micro-CT). Figure 9 and Figure 10 show the micrograph at a magnitude of x10 and x50 for the two ultimate processing conditions (380°C/90psi and 400°C/150psi). A good consolidation of the samples was observed with a good fibre distribution and no significant resin rich area at the interface between the plies. No macro-porosities were observed. Similar observations were obtained for all the other sets of pressure and temperature conditions. No effect of the pressure on the quality of consolidation was observed which is in correlation with the results from the mechanical tests.

Figure 11 shows the X-ray micrographs in the middle of the samples manufactured at 380°C/90 psi (Figure 11-a) and 400°C/150psi (Figure 11-b). By visualising the scans through the sample thicknesses, no major defects were detected and a good consolidation was observed. No difference in consolidation was observed between the two processing conditions. By analysing the images, very small regions were detected and isolated at the ply interface that could correspond to the presence of voids or resin pocket. These regions, parallel to the fibres alignment, are highlighted in red in Figure 11. More X-ray scans will be needed to distinguish the resin rich area from the voids. These observations are in

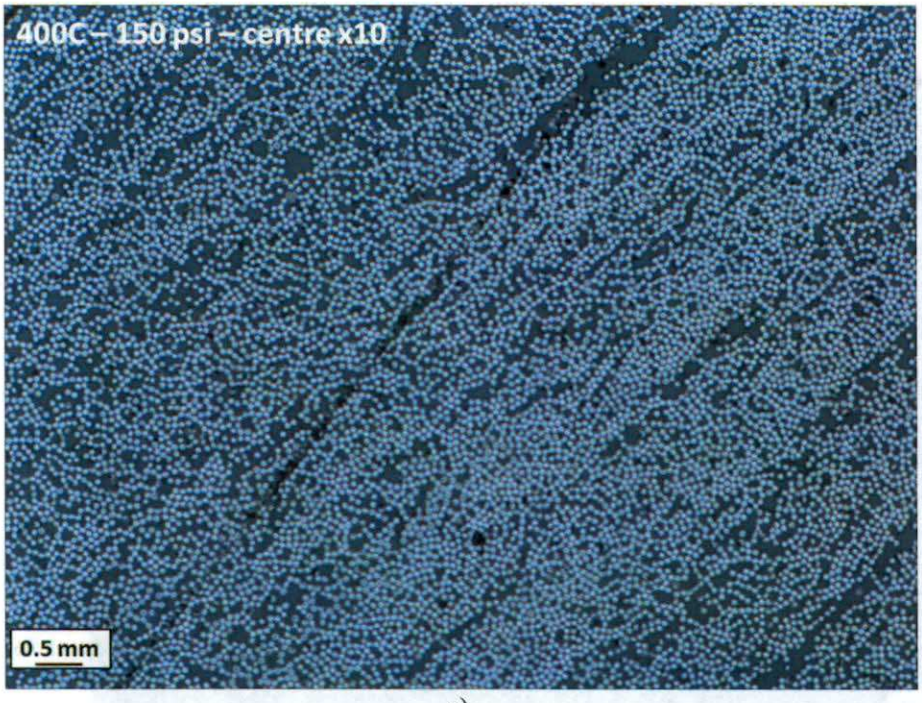
agreement with the observations done by microscope and the results of the mechanical tests.

a)

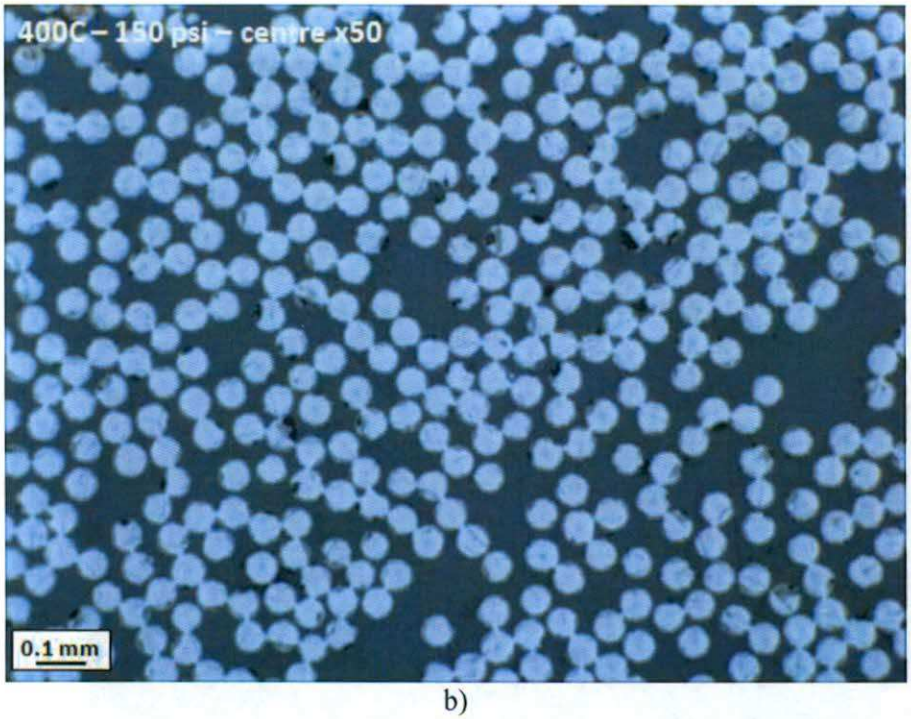


b)

Figure 9: Micrographs of PEEK/carbon sample processed at 380°C and 90 psi: a) magnification x10 and b) magnification x50

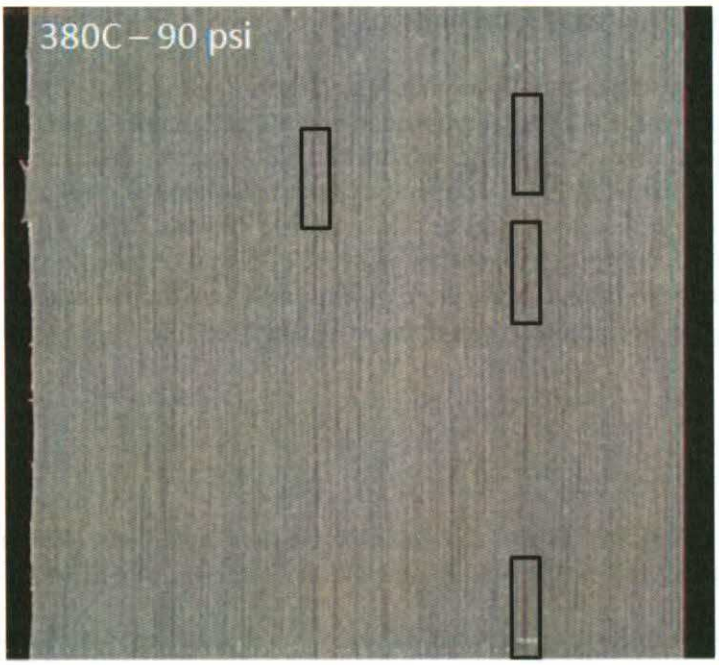


a)

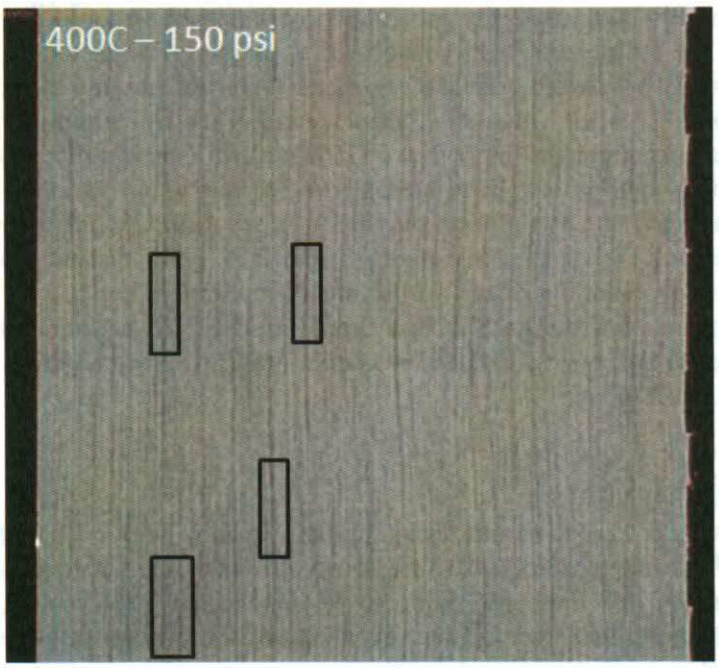


b)

Figure 10: Micrographs of PEEK/carbon sample processed at 400ºC and 150 psi: a) magnification x10 and b) magnitude x50



a)



b)

Figure 11: X-ray micrographs of PEEK/carbon samples: a) manufactured at 380°C and 90 psi and b) manufactured at 400°C and 150 psi

Optimal Autoclave Processing Parameters

This study demonstrates that good mechanical performance and consolidation quality can be achieved for PEEK/carbon composite parts manufactured under a large range of autoclave processing conditions. This means that similar final properties can be achieved at lower temperature and consolidation pressure leading to lower processing costs. In that case, the optimal process cycle would be a temperature of 380°C with a consolidation pressure of 90 psi. Also, the stability of PEEK/carbon composite over a large range of processing conditions means that an unexpected change in the process parameters will not affect the final properties of the part.

CONCLUSION

In this study, the effects of the autoclave processing conditions (cooling rate, temperature and pressure) on the quality and the performance of PEEK/AS4 were investigated.

The cooling rate was found to have an effect on the crystallinity kinetics of PEEK but a negligible influence of the final amount of crystallinity. A simple crystallinity kinetics model was developed based on the Avrami equation to predict the evolution of the PEEK crystallinity as a function of the applied cooling rate.

The effect of the temperature and consolidation pressure on the tensile, shear and interlaminar shear properties was also examined. Their effect was negligible on the Young's modulus, shear modulus, shear strength and interlaminar shear strength. Only the tensile strength increased of 25% with an increase in temperature and pressure. A high interlaminar shear strength with a maximum variation of 3% was measured leading to the assumption that a good consolidation with a low void content was achieved for each processing conditions. This assumption was validated by optical observations of the sample and X-ray tomography.

This study demonstrates the stability and flexibility of PEEK/carbon composite material in the tested processing window to obtain good mechanical performance and consolidation quality.

ACKNOWLEDGEMENT

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