Basic characterization of the CF-PEKK prepreg and laminates for low temperature applications

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Abstract. This paper investigates a carbon fibre-reinforced polyetherketoneketone (CF-PEKK) thermoplastic composite used for low-temperature applications like hydrogen tank applications. The degree of crystallinity of the prepreg as received first and then consolidated after hot press has been investigated. The melting temperature and glass transition, as well as the melting enthalpy and degree of crystallinity, were also studied by DSC (differential scanning calorimetry). The fibre volume fraction and void content after consolidation have been measured by acid digestion and an optical microscopy image analysis. Thermomechanical analysis (TMA) was also used in order the coefficients of thermal expansion (CTE) to be determined. Tensile and compressive Dynamic Mechanical Analysis (DMA)test were performed. Storage modulus, loss modulus, and Tan δ relationship have thus been analysed. Multifrequency DMA experiments have been conducted in order to create the master curve thanks to the time-temperature superposition (TTS).

Introduction

High-performance thermoplastic matrix composite materials have been widely studied since the beginning of the 1990s, with various studies on CF-PEEK composites. However, this class of materials is not yet widely used in airframe structures. despite the increasing use of composite in Airbus A350 and Boeing 787. Only high-performance thermoplastic matrix like polyimides (TPI), polyetherimides (PEI), polyaryletherketone (PAEK), and polyetheretherketone (PEEK) are used for aircraft structures right now [1].

Despite its heightened interest in terms of potential recyclability and physico-mechanical characteristics, PEEK matrix composites require high-temperature consolidation cycles and might undergo some thermomechanical-induced distortion in large parts in terms of shape and geometry. This is why some other thermoplastic matrices of the polyetherketone family can be used to manufacture composites at temperatures lower than those required. Therefore, this study focused on one of these matrices: polyetherketoneketone (PEKK), whose processing temperature is much lower than that of PEEK. PEKK's are made from diphenylether (DPE), terephathlic acid (T) with para-phenyl links, and isophthalic acid (I) with meta-phenyl links. The presence of terephthalic/isophthalic content (T/I ratio) in PEKK leads to variations in crystallization kinetics and capabilities [2, 3, 4].

Even though the main goal of our study was to investigate the CF-PEKK matrix in low-temperature structures for storing liquid hydrogen, this paper aims to present the basic thermomechanical and chemorheological characterization of this material around room temperature. This involves utilizing various equipment and procedures, such as resin dissolution and microscopy image analysis, density determination, DSC (differential scanning calorimetry), TMA (thermomechanical analysis), and DMA (dynamic mechanical analysis). This

characterization campaign was carried out both on as-received CF-PEKK prepreg and on $[0]_6$ unidirectional laminates consolidated using a hot plate press. All along this characterization campaign, results obtained on as-received CF-PEKK unidirectional tape are compared with those obtained on consolidated laminates. Along with matrix acid digestion to find out the fibre volume content, a microstructural study of prepreg and consolidated laminate was also carried out.

Manufacturing process and materials

The CF-PEKK unidirectional prepreg used for this study was provided by Hexcel composite France. Its commercial reference or its technical datasheet are not available. This is why some basic physical characterization has been performed in the aim to enable manufacturing conditions to be chosen for future larger production and test campaigns. We have just said that for PEKK matrices the T/I ratio determines melting temperature (T_m) and therefore consolidation cycle. Considering T_m value around 339°C obtained by DSC on as-received carbon/PEKK prepreg, it can be inferred experiments that T/I is of 70/30 T/I. For all laminates, ply stacking was performed in a clean room ($T_{Cleanroom}$ = 20 °C and R.H. = 50°C) and consolidated owing a laboratory press (MIB hydro), which enable to goes up to 450 °C with a 10 MPa (100 bar) pressure. In the absence of technical data upon our prepreg, it was decided to rely on open literature to define the parameters of the prepreg consolidation cycle (temperature, time, pressure), see Table 1.

The consolidation cycle is described in Figure 1 together with mould configuration. Unidirectional $[0]_6$ laminates used in this study were consolidated on a 250x250 mm stainless steel with two layers of thermoplastic 50 µm thick polyimide film (DIATEX France) as release agents

Table 1: Manufacturing parameters from literature [2,3,4]

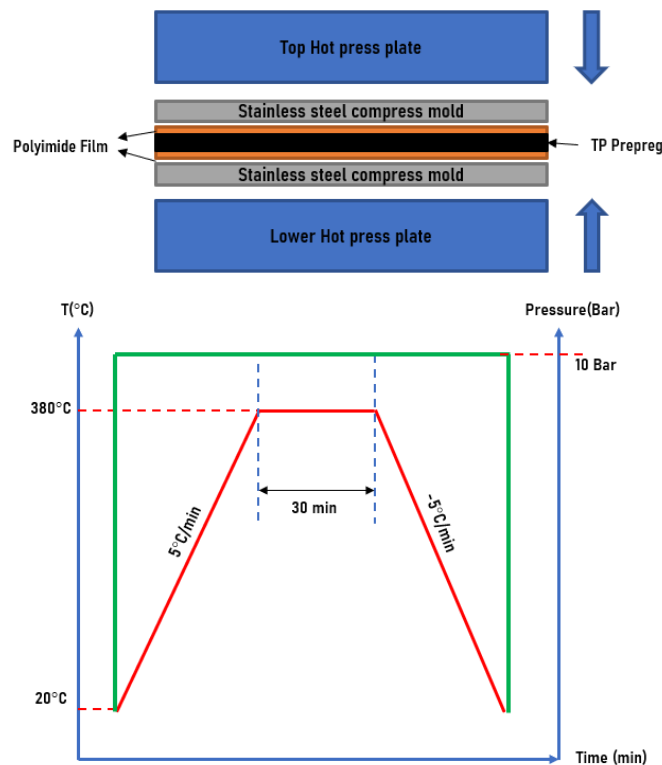| Manufacturing parameters		
Consolidation temperature	360 to 410	[°C]
Consolidation pressure	10 to 40	[Bar]
Consolidation time	10 to 30	[min]

Figure 1: Laboratory hot press

Experimental methods

Fibre volume fraction and void content

Fibre volume fraction (V_f %) was determined both on as-received CF-PEKK prepreg and on consolidated laminates by matrix acid digestion and optical microscopic image analysis, while the void content (V_v%) was determined only on consolidated $[0]_6$ laminate by optical microscopic image analysis.

Acid digestion

Matrix acid digestion was performed according to the EN 2564:2018 Standard [5]. A series of prepreg and laminated samples were immersed in a concentrated sulfuric acid solution for 5 hours at 260°C. After that stage, the resulting fibre network was filtered, dried, and weighed in order to determine the V_f%. Parallelly, the density of the specimen was measured according to Method A of ISO 1183 [6]. Lately, some fibres were observed on the sintered glass crucible to ensure that there were no PEKK particles remaining after the experiment

Image analysis

Determination of V_f % and V_v% by image analysis was performed on an Olympus BX41M Microscope together with ImageJ freeware. Prior to any microscopy observation, all specimens were polished according to the PRESI (Polishing equipment manufacturer) polishing procedure designed especially for thermoplastic matrix composites.

V_f% and V_v% were evaluated (using image J) with a conventional fibre counting approach with the maxima count function enabling to reflect the number of fibres (N_f). Knowing the average diameter of carbon fibers average diameter (d_f) can also determine with image analysis since we ignore carbon fibre reference. Therefore, V_f% can be obtained by [7,8].

$$V_f = \frac{\pi d_f^2 \times N_f / 4}{N_{image}/CF^2} \tag{1}$$

N_{image} is total the number of all pixel of a given image. CF is a conversion factor of the length of image. For instance, an image with 300 pixels per 100 μm gives CF=3.

V_v%, can be also obtained by acid digestion method and optical microscope. For acid digestion, the calculation was used the same method as the calculation of the V_f% by using rules of mixtures. For the optical microscopy, the V_v% obtained by image analysis but focused on the void area. From that procedure the V_v % can be verified.

(a)   (b)   (c)
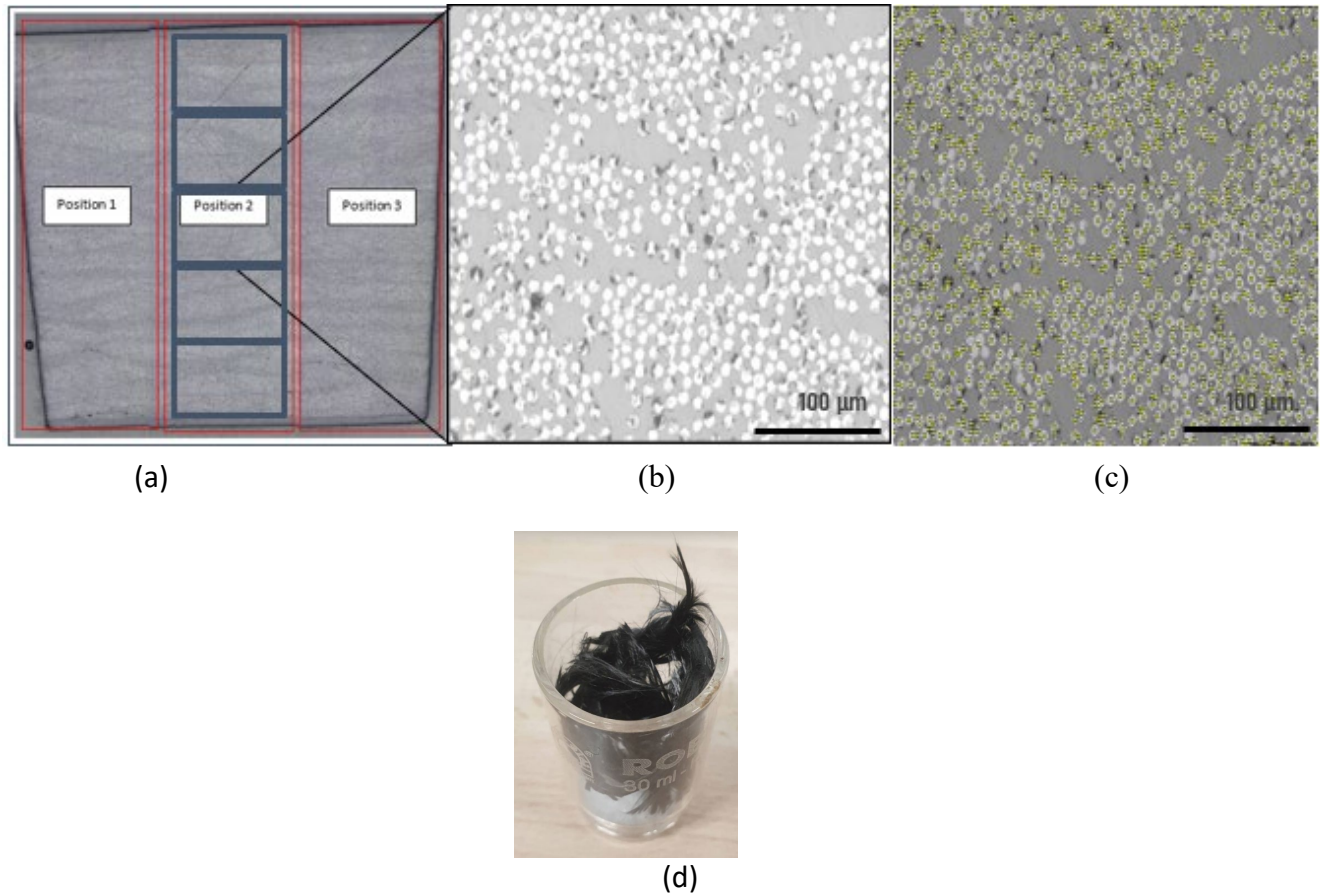

(d)

Figure 2: Acid digestion and optical microscopy analysis for fibre volume fraction and void content: (a) stitching images (b) 8-bit grey scale image conversion (c) conventional maxima method (d) carbon fibres after acid digestion of PEKK matrix.

Differential scanning calorimetry (DSC)
All measurement was carried out on a TA instrument DSC250. Prepreg samples (average mass around 15mg) were submitted to 5°C/min heat ramps from 40°C to 400 °C in a conventional scan mode. Samples extracted from consolidated composite laminates were submitted to a heat-cool-heat thermal cycle between 40°C and 400 °C with 5°C/min heating and cooling ramps. DSC thermograms enable PEKK matrix glass transition, melting and crystallization temperature to be determined, as well as the crystallization and the melting enthalpies. From these enthalpies the PEKK matrix degree of crystallization can be calculated as follows:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f^0 (1 - W_f)} \times 100\% \qquad (2)$$

In equation (2) ΔH_m represent the melting enthalpy of PEEK (J/g), ΔH_{cc} is cold crystallization enthalpy of the matrix (J/g) ΔH_f^0 is theoretical melting enthalpy of crystallization of 100% crystalline matrix (J/g) (PEEK, PEKK = 130 J/g) [9] and W_f is weight fraction of fiber has been calculated from acid digestion experiment.

Thermomechanical analysis (TMA)

Measurement of coefficient of thermal expansion (CTE) as well as glass transition temperature (T_g) were determined from thermal scans performed on a NETZSCH TMA 402 F1 in expansion

mode. $[0]_6$ is the lay-up of the specimens. The dimension of the specimens was $3\times3\times1.6$ mm (length, width, thickness). Those later range from -150 ˚C (minimum achievable temperature) to 300 ˚C heat rate was 5 ˚C /min with the contact force 1mN on the expansion probe.

DMA measurement
The thermoviscoelastic behaviour of CF-PEKK was studied using a DMA+100 Metravib equipped with a thermal chamber enabling DMA tests to be performed between -150°C up to 500°C. Here, temperature scans were carried out only between room temperature up to 300°C. Prepreg and composites samples $[0]_6$ were all tested in tensile mode with carbon fibre perpendicular to tensile force axis.

A first set of DMA tests on prepreg and consolidated composite samples were made under a constant frequency at 1 Hz, while a second set of tests used for building the CF-PEKK master curve (with WLF modelling) were performed at five different frequencies 0.01,0.03,0.1,0.5 and 1 Hz. DMA samples room temperature dimension were $50\times10\times1.6$ mm (length, width, thickness). The first set of DMA experiments enabled the changes in storage (E') and loss (E'') moduli as well as Tan δ (see eq. (3)) to be followed and Tan δ peak temperature corresponding to the main mechanical relaxation peak, manifestation of glass transition of PEKK matrix to be determined.

$$\text{Tan } \delta = \frac{E''}{E'} \tag{3}$$

The second set of DMA experiments consists in multifrequencies sweeps between room temperature and 300°C enabling to (i) build the material master curve (thanks to WLF modelling eq. (4) and (5)) and (ii) determine the activation energy of the main mechanical relaxation. For temperature lower than the PEKK matrix T_g (considered as $T_g = T_{ref} = 165.2$ °C) we have [10,11]:

$$\log a_t = \frac{E_a}{2.303 \cdot R} \cdot \left(\frac{1}{T} - \frac{1}{T_{Ref}}\right) \tag{4}$$

Where E_a denotes the activation energy and R, the ideal gas constant (8.3143 J mol^{-1} K^{-1}) and T_{ref}, the reference temperature. Here, $T_{ref} = T_g$.

For temperature higher than PEKK matrix T_g the log of the shift factor a_T of the WLF modelling is given by:

$$\log a_T = \frac{-C_1 (T - T_0)}{C_2 + (T - T_0)} \tag{5}$$

In this equation (5) Where C_1 and C_2 are constants. The parameters C_1 and C_2 may vary when the different reference temperature is chosen [11]. In our case, the $T_{ref} = T_g$.

Results and discussion
Fiber volume fraction V_f% and Void content V_v%
Obtained result in terms of V_f % and V_v% using matrix acid digestion, optical microscopy and image analysis are given in Table 2. It can be seen that a rather good agreement is obtained for consolidated laminates V_f% and V_v% between the different experimental methods and that the void content is very low. This shows the quality from a microstructural point of view of the consolidation cycle (cf. Figure 1). It is important to note that the void content in Table 2, especially the void content measured by optical microscopy, is measured directly on the images, whereas with the acid digestion method, density is required.

Table 2: V$_f$% and V$_v$%: Result of optical microscopy and image analysis and Acid digestion

Hot press	Optical microscopy		Acid digestion		Density
	Void Volume content [%]	Fiber volume fraction [%]	Void Volume content [%]	Fiber volume fraction [%]	[g/cm3]
CF-PEKK prepreg as receive [12]	5.8±0.7	55.6±1.4			
CF-PEKK consolidated	0.45 ± 0.16	55.22± 2	0.4 ± 0.2	57.3 ± 1.5	1.56± 0.01

DSC measurement

Figure 3a show a DSC scan thermogram representative of the CF-PEKK thermal behaviour during a 5°C/min heating ramp. From this thermogram three events can be spotted: (i) Glass transition at 157 °C, (ii) exothermic peak corresponding to cold crystallization at 203 °C and (iii) endothermic peak corresponding to the PEKK matrix melting at 339 °C. Cold crystallization and melting enthalpies H_{cc} and H_m were obtained by peak integration with respect to the temperature. Results given in table 3 enable the degree of crystallinity of as-received prepreg to be calculated with (eq. (2)): X_c = 4.2% ± 2% a rather low value.

Figure3b shows a typical DSC scan thermogram obtained on a sample extracted from a $[0]_6$ consolidated laminate. The heat-cool-heat cycle that the samples are submitted shows several points: (i) first heating ramp revels a T_g of 162.27 °C and the absence of cold crystallization peak, while T_m become slightly higher at 346.11°C when compared to T_m exhibited by prepreg; (ii) during cooling, a crystallization peak occurs at 264.51 °C (ΔH_c 31.127 J/g); (iii) second heat ramp shows that T_g remains around 160.34°C and that melting peak occurred at around 346.11°C with an enthalpy of 27 J/g versus 30 J/g for prepreg. As shown in table 3, values after consolidation T_g has under gone a slight increase: 157°C for prepreg versus 163 °C for consolidated laminate. It can also be noticed that T_m (Melting temperature) value increase by a few between the prepreg state and consolidated laminate one. Enthalpy values were used to evaluate the degree of crystallinity which grows from 4.2% for prepreg up to 21% for PEKK matrix in consolidated laminates showing that the strong effect of consolidation cycle.

As PEKK usually related to the presence of terephthalic/isophthalic content (T/I ratio) in PEKK leads to variations in crystallization kinetics and capabilities. Due to the lack of information on the CF-PEKK the grade of PEKK has been considered as PEKK 70/30 T/I ratio as in Choupin et al. [3,13].

Quiroga Cortés et al. also studied thermal behaviour of PEKK 60/40, 70/30, and 80/20 grades by DSC [13]. They found that PEKK 70/30 has a T_g of 159 ˚C and exhibits a melting temperature at 335 ˚C, while PEKK 60/40 has a T_g of 156 ˚C and presents a T_m at 300 ˚C. PEKK 60/40 also exhibits a cold crystallization temperature, T_{cc}, after the glass transition at T_{cc} of 241 ˚C. The crystallinity ratio is 3% for 60/40, 27% for 70/30. Where 60/40 is a quasi-amorphous polymer, and 70/30 and 80/20 are semi-crystalline polymers. This is assuming that the CF-PEKK prepreg as received has more amorphous region or act like 60/40 as [2, 3, 10, 14] mentioned. But the T_m is much higher than the typical 60/40 ratio.

Choupin et al. [3] also conducted a study using PEKK 6002 and 7002 with T/I ratios of 60/40 and 70/30, respectively. Their findings revealed that higher T/I ratios result in higher melting temperatures. From this, we assumed that our received prepreg is 70/30 T/I ratio with more amorphous region due to our T_m it is much higher than the studies of Quiroga Cortés et al [13] and Choupin [3].

It is important to note that all result of the DSC scans was conduct 4 times on each test. The values and their standard deviation are given in table 3.
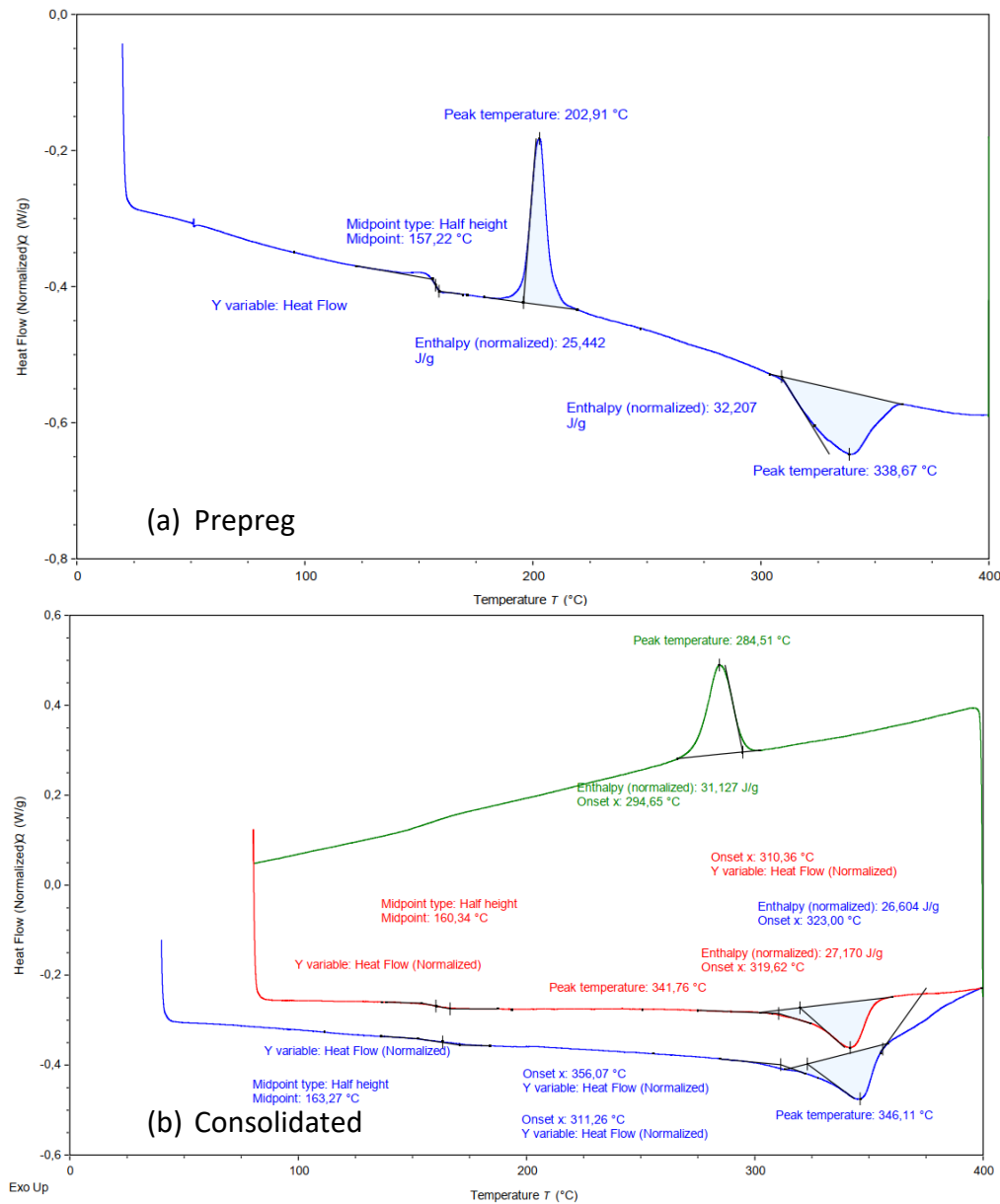
Figure 3: DSC result for CF-PEKK prepreg (a) and consolidated (b)

Table 3: Summary of DSC result for CF-PEKK prepreg and consolidated

	T_g(°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	Degree of crystallinity X_c (%)
CF-PEKK prepreg	157 ± 0.4	203 ± 0.2	339 ± 0.5	25.1 ± 0.5	30.54 ± 0.5	4.2% ± 2%
CF-PEKK consolidated	162.27± 4	N/A	346.11± 4	N/A	30.199± 1	20.67%± 0.01
	160.34± 3	N/A	341.76± 1	N/A	27.17± 1.5	21.26%± 0.01

Dilatometry (TMA)

The thermal expansion perpendicular to the lamination plane of CF-PEKK composite samples in plotted in Figure 4. As it can be seen that the expansion can be divided into three distinct zones. In the first one between -150°C to 0°C, the coefficient of thermal expansion (CTE) α_z is 20×10^{-6}°C^{-1}. Between 0°C and the thermomechanical manifestation of glass transition (here T_g =157.42 °C) $\alpha_z = 40 \times 10^{-6}$°C^{-1}. In the third zone after glass transition α_z increase up to 100×10^{-6}°C^{-1}.

Unfortunately, due to the issues with the TMA machine the CTE of the prepreg form cannot be provided here.
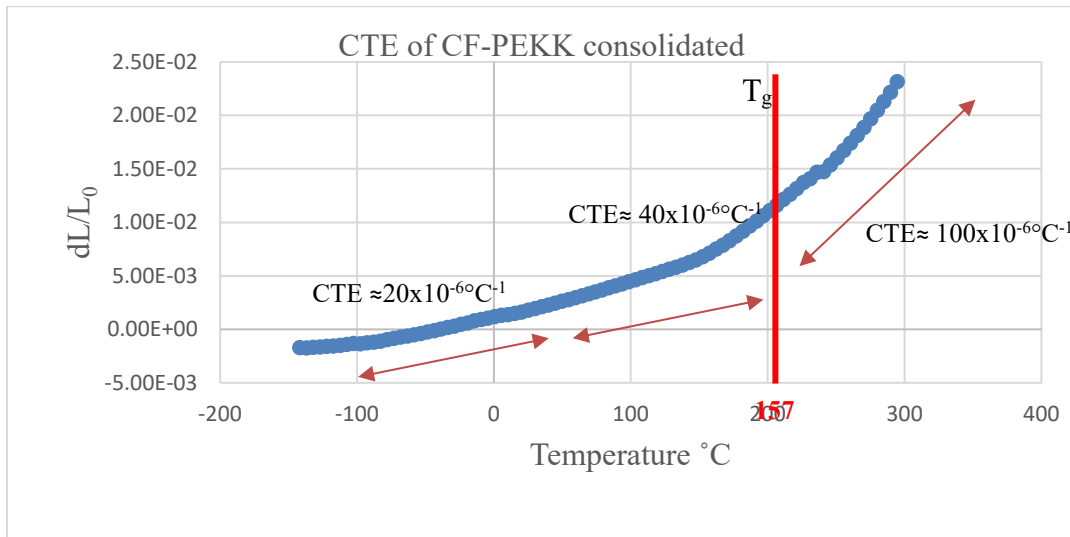

Figure 4: TMA result of CF-PEKK consolidated. Measurement perpendicular to the lamination plane.

Dynamical mechanical analysis (DMA)

Figure 5(a and b) enables the behaviour of the prepreg and consolidated laminate to be compared. As it can be seen on Tan δ (equation (3)) curves there are some differences in the main mechanical relaxation peak (or α-peak). First, T_α, the maximum temperature of α peak reach 170 ˚C for the laminate while it was 166 ˚C for the prepreg. Furthermore, the two peak magnitudes are very different showing that PEKK matrix amorphous network has undergone important changes between the two states. In addition, when paying attention to storage moduli curve E' it can be noticed that for the prepreg (figure 5a), E' undergoes an increase starting around 200 ˚C. This recalls the cold crystallization exothermic peak recorded on prepreg by DSC (figure3a). This change in E' -which does not appear for consolidated composite in figure 5b- is linked to cold crystallization.

The second part of this work with DMA was to set up a master curve for CF-PEKK consolidated composite. $[90]_6$ composite samples were submitted to multifrequency test under tension loading. Figure 6 shows the changes in E' storage modulus as function of temperature and frequency (f). Figure 7 give a view of the main mechanical relaxation peak (denoted by α-peak) as a function of frequency. Obtained result enable figures 8a and 8b to be build. They respectively show the change in Log(f) versus 1/T and the master curves for the storage E' and the Loss E'' moduli as a function of frequency. This master curve (equation (4) and (5)) gives value of C1 and C2 WLF constant (see figure8b): $C_1 = 1$ and $C_2 = 5.4$. This representation facilitates the calculation of the activation energy using equation (4), each applicable in distinct temperature ranges. The combined application of these equations yields an activation energy of approximately 2228.84 kJ/mol.
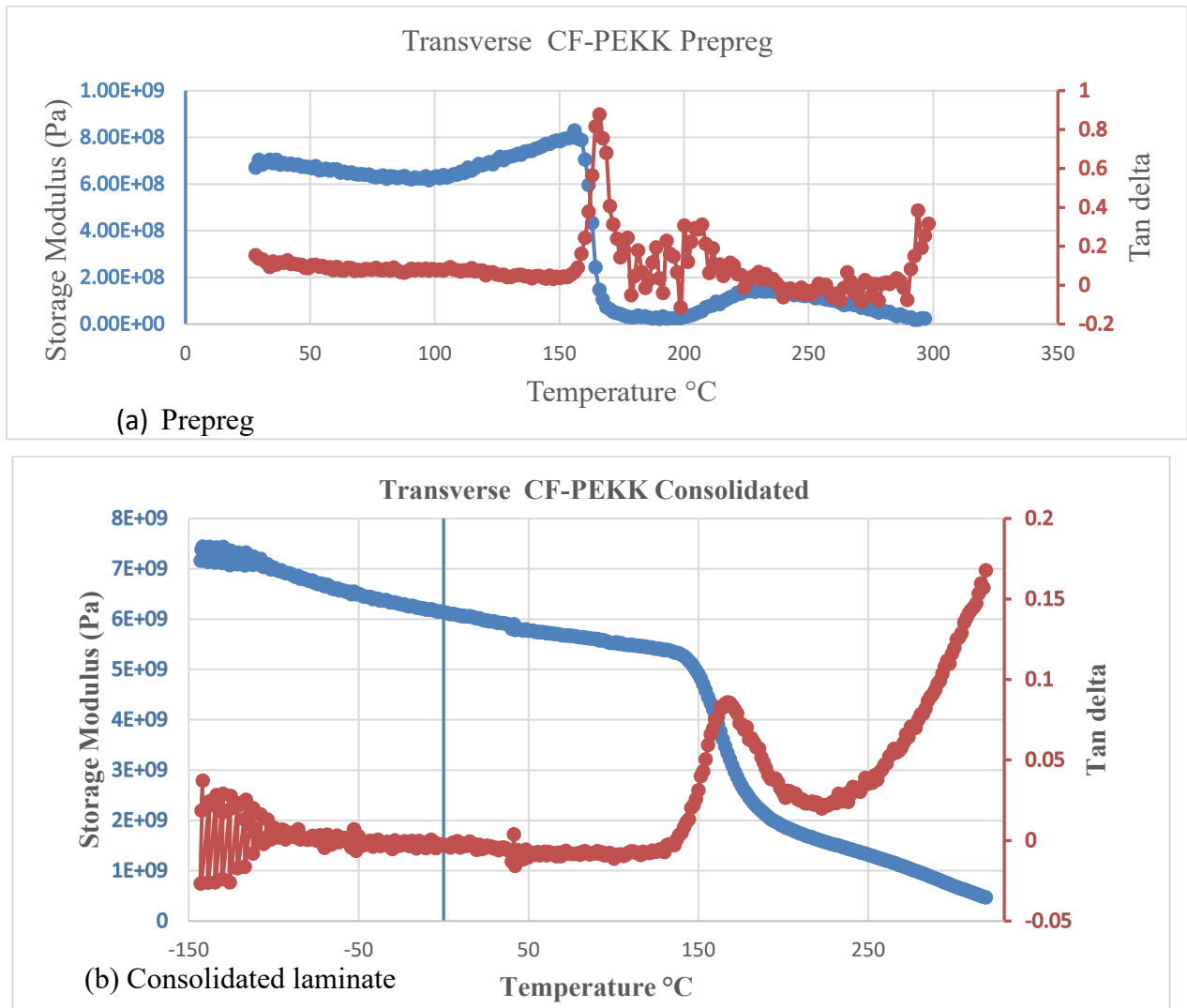
Figure 5: Dynamic mechanical scans on transverse direction for prepreg (a) and consolidated (b) CF-PEKK
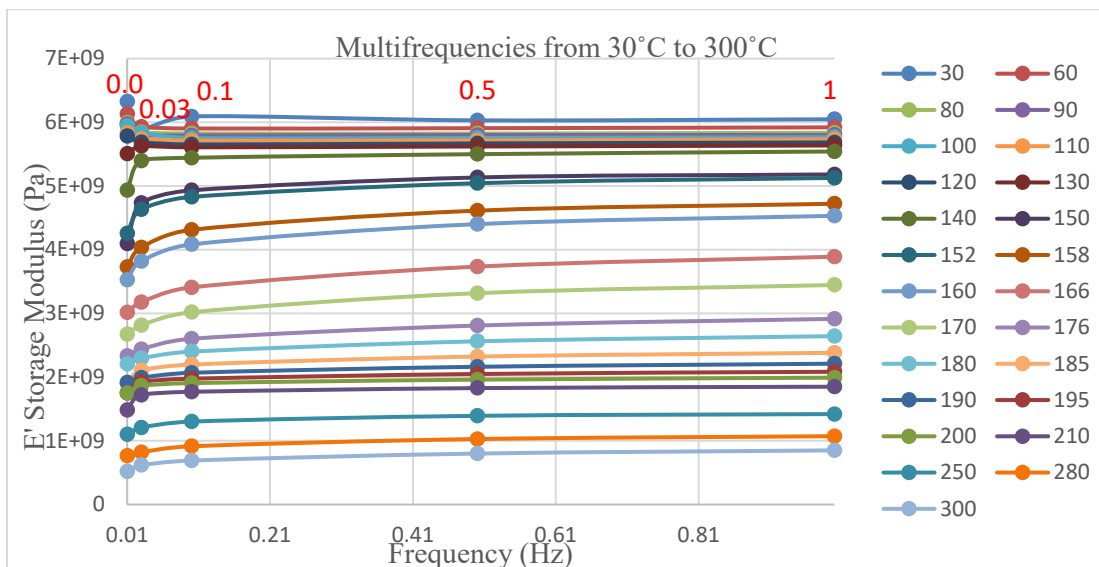

Figure 6: Multifrequency test from 30 ˚C to 300 ˚C with 5 frequencies for CF-PEKK consolidated (Transverse)
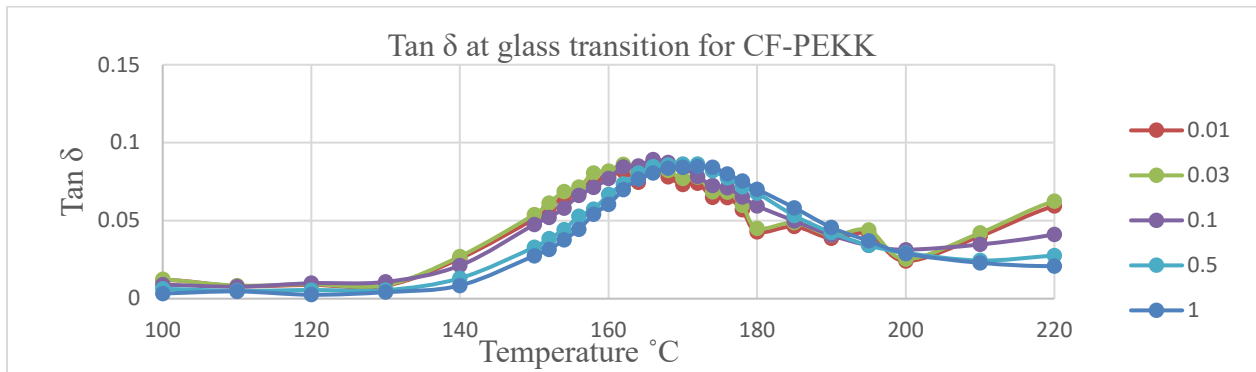
Figure 7: Tan δ at glass transition for CF-PEKK consolidated on transverse. With the shift of Tan δ through different frequencies

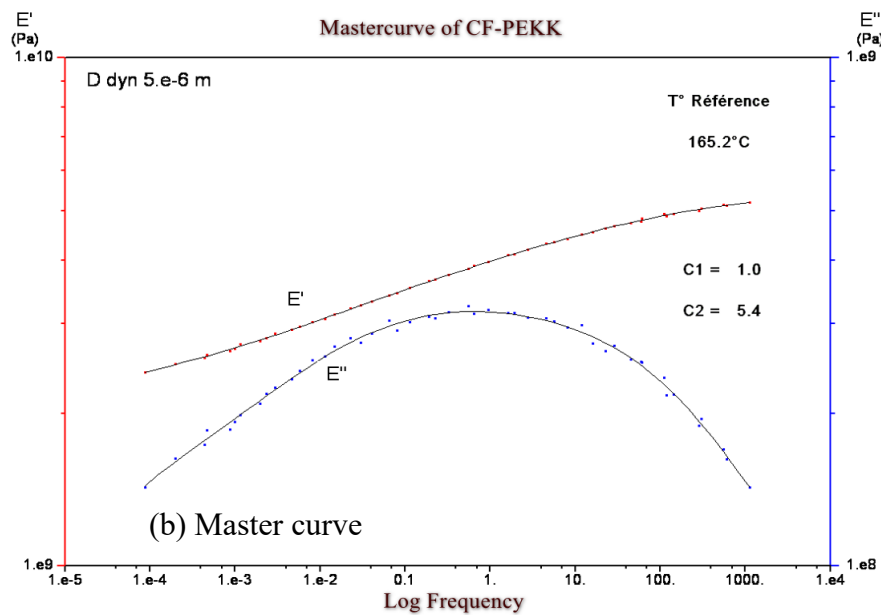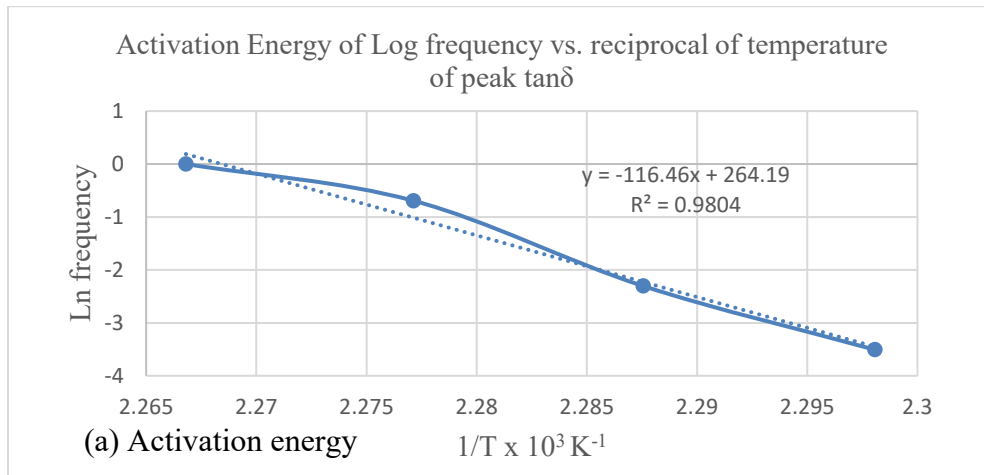*Figure 8: Activation Energy of Log frequency vs. reciprocal of temperature of peak tanδ (a) and (b) master curve storage and loss moduli at reference temperature of CF-PEKK*

Conclusion

DSC result to study the prepreg as received and after consolidated by hot press (or Hot press) has been completed and the result of DSC scans has been compared. After the hot press, fiber volume fraction and void content were investigated through acid digestion and optical microscopy. Fibre volume fraction and void content of CF-PEEK is generally matched with several researcher such as [11,16]. Thermomechanical Analysis (TMA) was also used to find the CTE Coefficients. The results are consistent with the literature [15]. Dynamic Mechanical Analysis (DMA) especially in transverse direction from low temperature also studied. Storage modulus, loss modulus and Tan δ relationship has been displayed and discussed. Multifrequency experiment has been conducted in order to construct the master curved by the Time-Temperature superposition (TTS). Williams-Landel-Ferry (WLF equation) and Arrhenius principles can be used to calculate the activation energy. This paper intents to gather the details of the CF-PEKK materials as much as possible. This important result will be used in the manufacturing process of the filament winding process and low velocity impact at low temperature for flat specimens and curved specimens The CTE in all direction will be determined. As well as the full analysis figure of DMA.

Acknowledgments

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