Intégrité du PEEK dans les semi-produits composites et son impact sur l'imprégnation

Integrity of PEEK in composite semi-finished products and its impact on impregnation

FEUILLERAT Lisa[1], DE ALMEIDA Olivier[1], FONTANIER Jean-Charles[2], SCHMIDT Fabrice[1]

1 : Institut Clément Ader, Université de Toulouse, CNRS, Mines Albi, UPS, INSA, ISAE-SUPAERO, Campus Jarlard, 81013 Albi, France
e-mail : lisa.feuillerat@mines-albi.fr, olivier.dealmeida@mines-albi.fr, fabrice.schmidt@mines-albi.fr

2 : Institut Français du Textile et de l'Habillement
14 Rue des Reculettes, 75013 Paris
e-mail : jcfontanier@ifth.org

Résumé

Le niveau de dégradation des matrices de différents semi-produits carbone/poly (éther éther cétone) (PEEK) ainsi que son impact sur la qualité de la consolidation ont été étudiés. La spectrophotométrie infrarouge à transformée de Fourier ainsi que l'analyse calorimétrique ont mis en évidence la dégradation initiale des semi-produits. Les mesures FTIR ont permis de détecter l'apparition de bandes d'absorption des liaisons C-H et des liaisons O-H, respectivement associées aux alcanes non aromatiques et à des produits de dégradation tels que les phénols et l'acide benzoïque. Les thermogrammes DSC ont montré une diminution de la température de fusion de la matrice PEEK au cours de traitements cycliques à 400°C, pour l'ensemble des semi-produits, mais avec une cinétique différente. Les mesures de porosité sur les plaques consolidées ont permis de classer les différents semi-produits et de corréler la porosité à leur niveau de dégradation. Ainsi, les premiers résultats tendraient à montrer que les semi-produits tels que les non-tissés comêlés craqués présentent un niveau de dégradation élevé tandis que les tissus poudrés affichent une dégradation plus faible. Le comportement observé serait lié aux conditions sévères de fabrication des non-tissés comêlés craqués qui génèreraient une dégradation initiale.

Abstract

The degradation of different semi-finished products carbon/poly (ether ether ketone) (PEEK) and its impact on consolidation quality have been studied. Fourier Transform Infrared spectrophotometry (FTIR) in ATR mode and calorimetric analyses have demonstrated initial degradation of semi-finished. FTIR measurements have allowed to detect spectral modifications, with the appearance of C-H and O-H absorption bands attributed to non-aromatic alkanes and degradation products such as phenols and benzoic acid respectively. DSC thermograms have shown important modifications of melting temperature during cyclic treatments at 400°C for all of the semi-finished matrices. The melting temperature decrease with the number of cycle and this decrease is different between the semi-finished products. The porosity measurements of consolidated parts have allowed to classify the different semi-finished products and correlate this to degradation. The first results seems to demonstrate that semi-finished product such as the stretch-broken commingled have an important degree of degradation whereas the powdered fabric have a small one. This behaviour may be due to extreme conditions of NCF spinning which initiate degradation.

Mots Clés : PEEK, dégradation, semi-produits, consolidation
Keywords : PEEK, degradation, semi-finished product, consolidation

1. Introduction

Long fibre reinforced thermostable thermoplastic composites have several advantages, such as high thermo-mechanical properties, high chemical resistance and the possibility of hot stamping and welding assemblies after consolidation, contrary to thermoset composites.

Processing such composites is however a particular issue due to the high melting temperature and high viscosity of thermoplastic matrices. Indeed, at the molten state, high molar mass macromolecules exhibit a non-Newtonian viscosity that is 100 to 1000 times higher than uncured thermosets [1], [2]. Conventional Liquid infusion route (RTM or LRI) is no longer possible with polymerized thermoplastic polymers and infusion of reinforcing yarns as described by Darcy's law requires the application of high pressure. The consequence is slow impregnation behaviour and non-negligible solid-fluid interaction effects during composites consolidation [1], [3].

Faced with this problematic, alternative composite products have been developed and various combinations of reinforcement and matrices are now available. The main proposed solutions are commingled fabrics, films stacking, powdered yarns or fabrics, or co-woven fabrics. The common point between these different solutions is that the polymer is placed around or within the fibre yarns in order to accelerate impregnation and thermoplastic laminates consolidation. Even so, high pressure is needed to fully consolidate such semi-finished materials and autoclave manufacturing is no longer efficient.

Among thermoplastic matrices, semi-crystalline poly-ether-ether-ketone (PEEK) is of particular interest because of its glass transition temperature of 143°C and a service temperature up to 200°C. A temperature of 380 to 400°C is however required to process PEEK composites, and this organic polymer may suffer degradation during each transformation operation.

Several authors reported PEEK degradation above the melting temperature, such as Day et al. [4]–[7] which have shown that degradation of PEEK results simultaneously in chain cleavage and formation of crosslinks between adjacent aryl groups of polymer chains. These mechanisms of degradation have been then described in details by Patel et al. [8].

They also showed that PEEK was relatively stable in a non-oxidative environment at 400°C for periods up to 6h, but that glass transition temperature and crystallisation behaviour were rapidly affected under air conditions. Different types of characterisation have been used by the authors to describe and confirm the degradation: FTIR and UV-visible spectrophotometry, steric exclusion chromatography (SEC), viscosimetry in solution, differential scanning calorimetry (DSC) and mechanical tests [9]–[13].

Philips et al. [14] also confirmed the dominating effect of crosslinking on viscosity and correlated the thermal exposure to air with the compression moulding processing of AS4/APC-2 composites. They concluded on the definition of an out-of-autoclave processing limit of carbon/PEEK composites regarding the thermal stability of the matrix.

Nevertheless, even if these studies on PEEK thermal stability propose some guidelines for out-of-autoclave manufacturing of PEEK composites, the authors always assume that the matrix is non-degraded with stable properties before composite processing. This assumption is pertinent when using neat PEEK or pre-impregnated materials made by solvent impregnation (AS4/APC-2 tapes), but the fabrication of complex semi-finished materials requires several transformation operations that may influence the viscous behaviour of the matrix and affect the processability of the materials.

This study thus proposes to analyse the polymer integrity depending on PEEK based semi-finished product organisation and to assess the consequence of degradation on the consolidation of the

products. For that purpose, different matrices of semi-finished products with the same initial PEEK grade have been investigated and compared to the PEEK reference grade. In order to estimate the degree of degradation of the composite materials, the matrices of semi-finished products have been analysed by differential scanning calorimetry and FTIR spectrophotometry measurements. Filaments diameters have been measured for comparison purpose. Then, the semi-finished products have been consolidated by thermo-compression moulding and the quality of consolidation have been assessed by porosity measurements.

2. Materials and methods

1.1 Material

The PEEK polymer used as a reference in this study is a Victrex grade 150 provided as a coarse powder (150P). This polymer is characterized by a glass transition of 143°C and a melting temperature of 343°C as mentioned in the material's technical data sheet and confirmed by DSC measurements.

Fig. 1. Powdered carbon/PEEK fabric. (a) Macroscopic view; (b) and (c) cross-section microstructure of the powdered fabric.

Four different carbon/PEEK semi-finished products were investigated, all of them based on this same PEEK grade from Victrex. In order to characterize the microstructure of the materials, pieces of the different semi-finished products have been embedded with an ultra-fluid resin, polished and observed with an optical microscope.

The first material is a 2-faces powdered carbon fabric (PF). The powdered fabric has a satin weave with an areal weight of $285 g.m^{-2}$. Powdered fabrics are manufactured by heating to melt fine PEEK powder previously sprinkled on a dry fabric. When melted, the polymer droplets coalesce so as to form drops at the surface of the fabrics (Fig. 1).

At the same time, gravity and capillary effects induce a slight migration of the polymer at the surface of the reinforcing yarns. After cooling, the polymer locally rigidifies the resulting semi-finished composite product but the heterogeneous distribution of the drops on the fabric surfaces preserves the global suppleness of the fabric. Powdered fabrics have thus a better drapability than the equivalent pre-impregnated products.

The second material under study is a commingled quadriaxial Non Crimp Fabric (NCF1). This product has been manufactured by combining together aligned AS4 carbon and PEEK yarns so as to obtain a global commingled structure. Then, the four unidirectional layers were stitched together with a PEEK yarn (sewing filaments). Each ply has an areal weight of $145 g.m^{-2}$ and two stacking directions references are available: [0/45/90/-45] and [0/-45/90/45]. The NCF weaving structure improves the drapability in comparison with the unidirectional pre-impregnated tape. However, as shown in Fig. 2, the commingling level remains poor since no reorganisation of PEEK and carbon filaments were performed before the weaving operation. The commingled filaments and the sewing filaments are named NCF1-C and NCF1-S respectively.
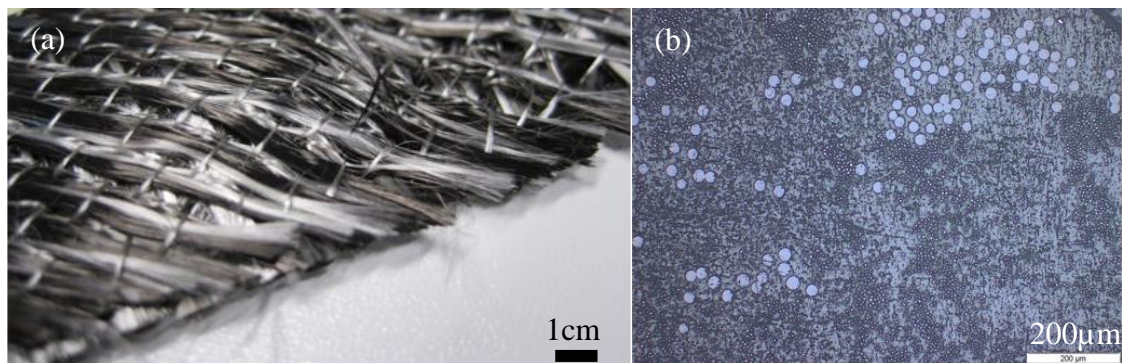
Fig. 2. Continuous AS4/PEEK NCF1. (a) Macroscopic view; (b) Cross-section microstructure of a NCF unidirectional ply. The white disks with a diameter of about 25µm are the PEEK filaments and the carbon filaments are the grey small disks (diameter of 7µm).

The third material is also a commingled quadriaxial NCF of AS4/PEEK that differs from the previous one as the yarns used in this semi-finished product are made of discontinuous filaments of PEEK and carbon. This material is made of stretch-broken commingled yarns. These commingled yarns are obtained by combining stretch-broken 12K or 24K carbon fibre slivers, typically 40 to 200 mm, with similarly broken fragments of thermoplastic filaments. As shown in Fig. 3, the commingling level is better than in the previous NCF (NCF1). The two stacking directions references available are [0/45/90/-45] and [0/-45/90/45]. These relatively long, overlapping fibre lengths preserve the integrity of the NCF during manipulations and improve the flexibility and the drapability of the fabric. This stretch-broken NCF is named NCF2 in this study. The commingled filaments and the sewing filaments are named NCF2-C and NCF2-S respectively.

The fourth material is a commingled fabric of AS4/PEEK with discontinuous filaments of PEEK and carbon as in the stretch-broken NCF2. These commingled yarns are exactly the same as in the stretch-broken NCF2 (Fig. 3). The only difference is that filaments are surrounded with a helical PEEK filament of the same grade to allow weaving operations. The commingled fabric has a satin weave with a total areal weight of 469g.m^{-2}. This stretch-broken fabric is named SBF in this study. The commingled filaments and the helical filaments are named SBF-C and SBF-H respectively. The SBF-C and NCF2-C are the same filaments whereas SBF-H and NC2-S are different.
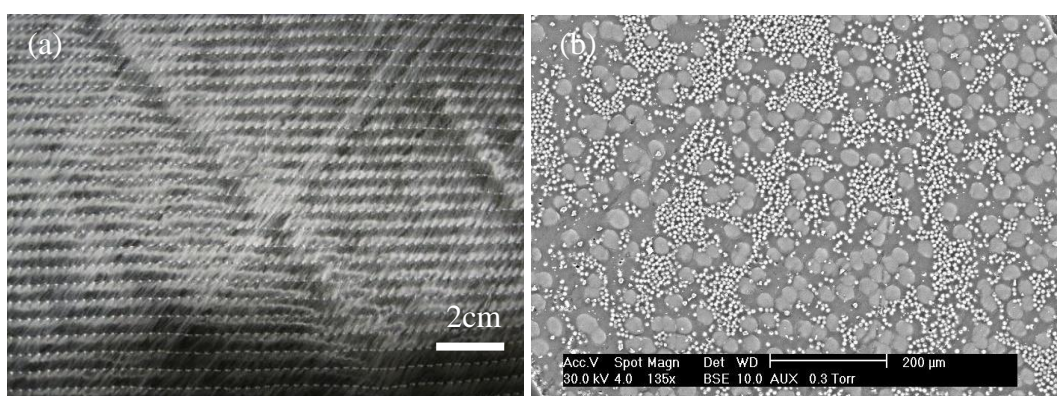

Fig. 3. (a) Macroscopic view of a stretch-broken AS4/PEEK NCF2; (b) Cross-section microstructure of a commingled yarn in stretch-broken NCF2 and fabric. The grey disks with a diameter of about 20µm are the PEEK filaments and the carbon filaments are the white small disks (diameter of 7µm).

Finally, the film-stacking technique has also been compared to the semi-finished products route by adding to the materials list two casted films with two different thicknesses 38 and 100µm. The main characteristics of the six studied PEEK semi-finished products are summarized in Tab. 1.

Tab. 1– Structural morphology and characteristic sizes of PEEK matrix
in the different semi-finished products.

Semi-finished product	Shape	Size
Powdered fabric (PF)	Drops	200µm to 1mm wide and 200µm thick
Continuous NCF (NCF1)	Cylindrical continuous spun filaments (NCF1-C) and sewing filaments (NCF1-S)	Diameter of 25µm (commingled filaments)
Stretch-broken NCF (NCF2)	Stretch-broken spun filaments (NCF2-C) and sewing filaments (NCF2-S)	Diameter of 20µm – 40 to 200mm long (commingled filaments)
Stretch-broken fabric (SBF)	Stretch-broken spun filaments (SBF-C) and helical filaments (SBF-H)	Diameter of 20µm – 40 to 200mm long (commingled filaments)
Film (Film-38)	Continuous film	38µm thick
Film (Film-100)	Continuous film	100µm thick

1.2 Experimental

FTIR, calorimetry, and diameter measurements have been carried out on the sole matrix previously separated from the composite reinforcement.

The changes in molecular structure were followed by FTIR spectrophotometry in attenuated total reflection (ATR) mode in the wavelength range from 400 to 4000 cm^{-1} using a Nicolet 6700 instrument from Thermo Scientific. The spectra are the results of 16 recordings with a resolution of 4 cm^{-1}. The results have been normalised by using the absorption band at 1653 cm^{-1} as a reference.

Calorimetry measurements were performed with a Perkin Elmer DSC8500 using an intracooler IC2. For all experiments, aluminium sealed pans filled with 4mg +/-1mg of PEEK were used. The samples were subjected to 15 heating and cooling cycles. The applied treatment consisted in holding the sample at 400°C during 20min to cause degradation, then in cooling it at a constant rate of 20°C/min to induce PEEK crystallization in identical conditions and finally in heating it at 10°C/min. During this last stage of the thermal treatment, the melting temperature (T_m) was measured. T_m has been taken from the maximum of the melting peak.

Matrices filaments were observed under Scanning Electron Microscopy (SEM) using a Hitachi TM3030Plus Tabletop SEM. The diameters of 20 different filaments were measured and averaged for obtaining a representative diameter for each composite product.

Consolidation of carbon/PEEK composites was performed on a thermo-compression moulding pilot process equipped with the 3iTech® technology developed by Roctool. The thermo-compression pilot plant consists of a vertical compression press with a capacity of 100T, a 200kW induction generator, a cooling unit that can deliver water at a flow rate of 150 L.min^{-1} and an inductive mould designed by Roctool. All the equipment are controlled from an operating panel that coordinates the actions and centralizes the data (mainly mould temperatures and applied press load) from the different equipment.

The 3iTech® mould used in this study is a plane mould designed for composite laminates manufacturing with a moulding surface of 400x400mm². This moulding process was used to manufacture 200x200mm² composite plates of each reference. The thermo-compression cycle applied consisted in a heating phase at 42°C.min^{-1} until 400°C, an isotherm stage at this temperature

during 10min under a pressure of 9bars, and finally in a cooling stage at 20°C/min. The porosity of all composites was then assessed from thickness measurements taken at 13 identical locations on the plates after consolidation (Eq.1).

$$X_v = 1 - \frac{A_{ini}\, N_{layer} \left(\dfrac{m_{s\,fibre}}{\rho_{fibre}} + \dfrac{m_{s\,matrix}}{\rho_{matrix}} \right)}{A_{plate}\, th_{plate}} \qquad \text{(Eq.1)}$$

In Eq. 1, X_v is the void radio [-], A_{ini} and A_{plate} are the initial and final areas of the plate respectively [m²], N_{layer} is the number of layers of semi-finished product [-], $m_{s\,fibre}$ and $m_{s\,matrix}$ are the fibre and matrix surface densities respectively, ρ_{fibre} and ρ_{matrix} are the fibre and matrix densities respectively and th_{plate} is the average thickness of the plate after consolidation.

3. Results and discussion

The comparison of the different PEEK semi-finished spectra is presented in Fig. 4. Only the spectral window from 2700 to 3800 cm⁻¹ is shown, because the biggest changes were observed in this range. The alkane and hydroxyl zones are between 2700 and 2950 cm⁻¹ and between 3000 and 3700cm⁻¹ respectively. Two major changes in the FTIR spectrum are observed for all of the semi-finished products except the powdered fabric compared to the PEEK reference. On the one hand, in the hydroxyl zone between 3400 and 3700 cm⁻¹, it can be seen the appearance of two IR absorption bands centred at 3650 and 3525 cm⁻¹. They are attributed to the stretching vibrations of the O-H bonds of phenols and benzoic acid respectively [9], [10]. On the other hand, between 2700 and 3000 cm⁻¹, it is observed the appearance of two IR absorption bands centred at 2915 and 2850 cm⁻¹. They are attributed to the stretching vibrations of the C-H bonds of non-aromatic alkanes. These FTIR measurements show that aliphatic groups increase and products of degradation appear, which indicate that probably ring opening reactions and thermolysis have occurred during fabrication of the different semi-finished products except for the powdered fabric. Indeed, the powdered fabric has the same spectra as the PEEK reference. FTIR spectra of NCF products also show that sewing filaments are more degraded than commingled filaments. The behaviour of stretch-broken products, i.e. fabric (SBF-C) and NCF2-C, has been associated with the behaviour of NCF2-C because they have the same matrix.
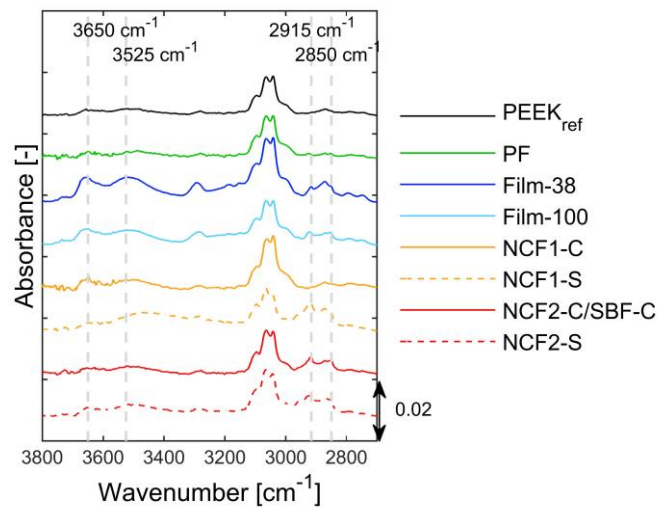

Fig. 4. FTIR spectra for the different semi-finished products.

The melting temperatures measured on DSC scans are presented in Fig. 5 as a function of heat treatment cycle. If neutral atmosphere slows down the degradation process, its effects can still be observed in a non-oxidative environment. In particular, Day et al. have noticed that degradation can occur in a nitrogen atmosphere which consequences are a decrease of the crystallisation temperature, the melting temperature and the enthalpies of crystallization and fusion [6]. Here melting temperature measurements from DSC (Fig. 5) on the different semi-finished products show that with increasing number of cycle the melting point decrease linearly except for the PEEK reference. Zhang et al. suggested that crosslinking occurs in the melted part of PEEK which can hinder crystallisation and cause this decrease of melting temperature [15]. Initial degradation of the different semi-finished products may be responsible of this phenomena already visible in the first cycle. The two NCF and fabric (associated with NCF2 which have the same matrix) that appeared to be degraded in the FTIR spectra, show a rapid decrease of T_m. The decreased thermal stability while number of cycle at 400°C increase may be due to initial degradation which was observed in the FTIR spectra.
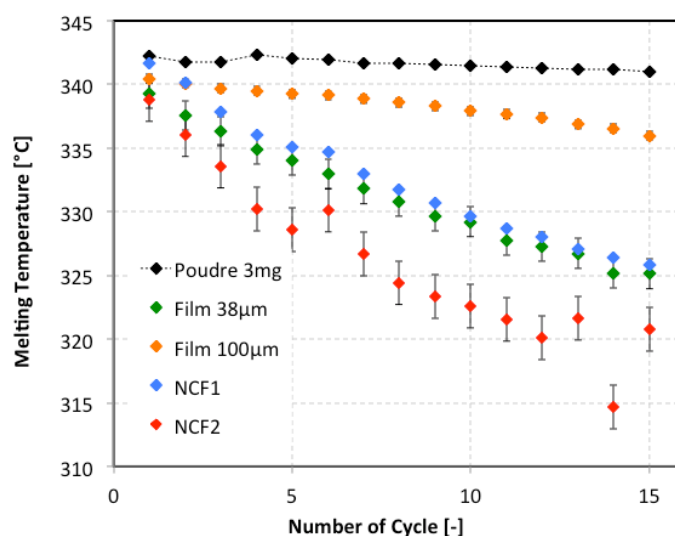

Fig. 5. Melting temperature as a function of number of cycle for the different semi-finished products ("Poudre 3mg" corresponding to PEEK reference).

Diameters measurements (Fig. 6) show that filament of fabric (SBF-C) and NCF2 have the same diameter as expected, because it is the same fabrication. Filaments diameters of NCF2, sewing (NCF2-S) and from the ply (NCF2-C) are smaller than those of NCF1. This difference may explain that NCF2 is more degraded from its fabrication, as seen in FTIR and DSC analyses, than NCF1.

Porosity measurements (Fig. 7) show that powdered fabric (PF) has the smallest void ratio whereas NCF2, which corresponds to stretch-broken NCF, has the most important void ratio. In this way, powdered fabric has the best consolidation behaviour while theoretically it is the worse configuration for impregnation. On the contrary, commingled products are difficult to consolidate while this configuration is supposed to enhance impregnation. The good consolidation behaviour of powdered fabric may be due to almost unmodified PEEK integrity during its fabrication whereas extreme conditions of filaments spinning or film extrusion lead to initial degradation of matrices. The more important porosity of NCF2 than NCF1 may be due to stretch-broken filaments in NCF2 that are indeed more degraded as seen before. The stretch-broken fabric (SBF) is probably better consolidated than the NCF2 because of the favourable weaving pattern that enhances impregnation.
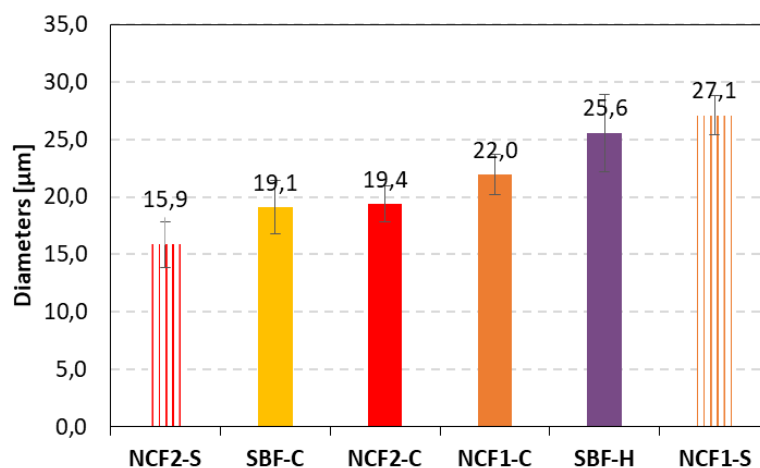
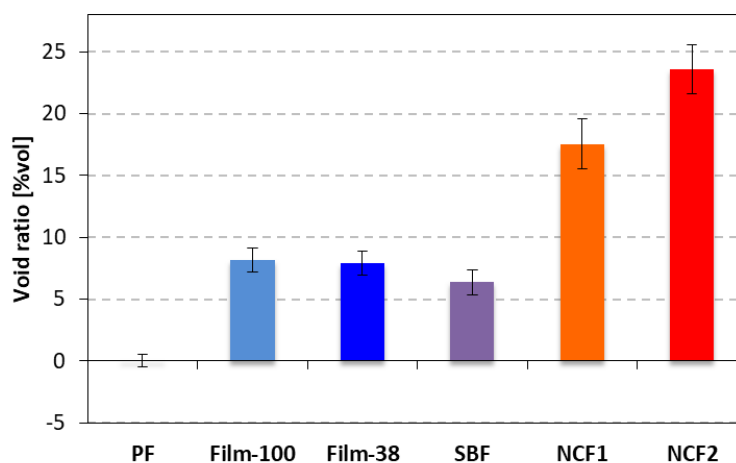*Fig. 6. Diameters measurements of the different semi-finished products.*

Fig. 7. Void ratio of the different semi-finished products.

4.   Conclusions

The degree of degradation of different PEEK matrices semi-finished products has been studied. The analysis at the molecular scale, by FTIR spectrophotometry, has allowed identifying some spectrum modifications for the different semi-finished products except for the powdered product. This phenomena is probably caused by open ring reactions and thermolysis during fabrication. The analysis by DSC has shown a decrease of the melting temperature for the different semi-finished products whereas no modification has been observed for the PEEK reference. This behaviour may be due to crosslinking that reduces considerably the molecular mobility causing the decrease of crystallinity. These physico-chemical characterisations confirm that initial degradation is caused by the fabrication process of the different semi-finished products. The consolidation behaviour of the different semi-finished have been compared through porosity measurements. The most degraded semi-finished product appears to be the non-crimp commingled fabric whereas the less degraded is the powdered fabric. This classification corresponds to the initial degradation observed by FTIR and DSC analyses.

References

[1]   M. Hou, L. Ye, H. J. Leeb, and Y. W. Maib, "Manufacture of a Carbon-Fabric-Reinforced Polyetherimide (CF / PEI) Composite Material," *Compos. Sci. Technol.*, vol. 58, pp. 181–190, 1998.

[2]   E. Bessard, "Matériaux composites structuraux à base de PEEK élaborés par thermo-compression dynamique relation procédé-propriétés," 2012.

[3]   A. K. Kadiyala, J. Bijwe, and P. Kalappa, "Investigations on influence of nano and micron sized particles of SiC on performance properties of PEEK coatings," *Surf. Coatings Technol.*, vol. 334, pp. 124–133, 2018.

[4]   M. Day, D. Sally, D. M. Wiles, and D. Chemistry, "Thermal Degradation of Poly(aryl-Ether-Ether-Ketone) : Experimental Evaluation of Crosslinking Reactions," *J. Appl. Polym. Sci.*, vol. 40, no. 30271, pp. 1615–1625, 1990.

[5]   M. Day, J. D. Cooney, and D. M. Wiles, "The thermal degradation of poly(aryl-ether-ether-ketone) (PEEK) as monitored by pyrolysis-GC/MS and TG/MS," *J. Anal. Appl. Pyrolysis*, vol. 18, no. 31856, pp. 163–173, 1990.

[6]   M. Day, T. Suprunchuk, J. D. Cooney, and D. M. Wiles, "Thermal Degradation of Poly(aryl-Ether-Ether-Ketone) (PEEK): A Differential Scanning Calorimetry Study," *J. Appl. Polym. Sci.*, vol. 36, no. 28274, pp. 1097–1106, 1988.

[7]   M. Day, J. D. Cooney, and D. M. Wiles, "The thermal stability of poly(aryl-ether ether-ketone) as assessed by thermogravimetry," *J. Appl. Polym. Sci.*, vol. 38, no. 29850, pp. 323–337, 1989.

[8]   P. Patel, R. T. Hull, R. E. Lyon, and S. I. Stoliarov, "Investigation of the Thermal Decomposition and Flammability of PEEK and its Carbon and Glass-Fibre Composites," *Polym. Degrad. Stab.*, vol. 96, pp. 12–22, 2010.

[9]   K. C. Cole and I. G. Casella, "Fourier transform infra-red spectroscopic study of thermal degradation in poly(ether ether ketone)-carbon composites," *Polymer (Guildf).*, vol. 34, no. 4, pp. 740–745, 1993.

[10]   E. Courvoisier, Y. Bicaba, and X. Colin, "Multi-scale and multi-technique analysis of the thermal degradation of poly(ether ether ketone)," *Polym. Degrad. Stab.*, vol. 151, pp. 65–79, 2018.

[11]   A. Jonas and R. Legras, "Thermal stability and crystallization of poly(aryl ether ether ketone)," *Polymer (Guildf).*, vol. 32, no. 15, pp. 2691–2706, 1991.

[12]   V. Mylläri, T. P. Ruoko, J. Vuorinen, and H. Lemmetyinen, "Characterization of thermally aged polyetheretherketone fibres - Mechanical, thermal, rheological and chemical property changes," *Polym. Degrad. Stab.*, vol. 120, pp. 419–426, 2015.

[13]   K. L. White, L. Jin, N. Ferrer, M. Wong, T. Bremner, and H. J. Sue, "Rheological and thermal behaviors of commercial poly(aryletherketone)s," *Polym. Eng. Sci.*, vol. 53, no. 3, pp. 651–661, 2013.

[14]   R. Phillips, T. Glauser, and J. A. E. Månson, "Thermal stability of PEEK/carbon fiber in air and its influence on consolidation," *Polym. Compos.*, vol. 18, no. 4, pp. 500–508, 1997.

[15]   Z. Zhang and H. Zeng, "Effects of thermal treatment on poly(ether ether ketone)," *Polymer (Guildf).*, vol. 34, no. 17, pp. 3648–3652, 1993.