21<sup>st</sup> International Conference on Composite Materials Xi'an, 20-25<sup>th</sup> August 2017

#### MANUFACTURING OF PRE-IMPREGNATED DISCONTINUOUS PAEK/CF COMPOSITE

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High temperature engineering thermoplastics such as the PAEK family of polymers, are now finding increased application in advanced composites structures. Polymers and polymer processing are at the heart of the manufacturing sector, with a huge number of uses. However, in many advanced applications, metals are chosen because conventional polymers either cannot deliver the required mechanical performance or are thermally vulnerable. PAEK can overcome these obstacles and are now transforming the landscape of materials usage, offering far more than just lightweight replacements for metals. Some PAEK's can operate continuously at 260°C and many are resistant to ionising radiation, corrosion, abrasion and stress-fatigue, have low toxicity, and very importantly because of their linear molecular structures - they are mechanically tough. Indeed when reinforced with carbon fibre, as part of a thermoplastic composite (TPC), their properties far outshine traditional thermoset matrix composites in terms of toughness, without loss of strength or stiffness, while significantly reducing production costs. Due to the above characteristics; unique to TPC only, these composites have found applications in most industry sectors, e.g. in aerospace: ducting, cable housings, bracketry, elevator tail sections and rudders, shear webs for localised reinforcement, seat frames and floor panels. PAEK carbon fibre moulding compounds are the latest TPC format, where material consists of short lengths of pre-impregnated discontinuous 25mm aligned carbon fibre tapes. These tapes or chips, present a major advantage over conventional prepreg sheets, in that they can flow and form to a mould, and potentially are far less labour intensive, making mass production of PAEK/ CF parts possible. The possibilities of PAEK/ CF tapes are only just starting to be explored, where the relationship between processing conditions and resulting composite properties is not yet defined. A major factor is the exposure of these compounds to extended thermal cycles during processing – which can be extremely detrimental to mechanical properties This work seeks to closely define the processing-properties relationship for these advanced materials and provide manufacturers and industry with the processing information required to control the key parameters during manufacture and thereby optimise resulting properties of moulded PAEK/ CF composites.

Keywords: discontinuous PAEK/CF composite, composite manufacturing, thermoplastic,

#### 1. INTRODUCTION

Chopped discontinuous carbon fibre reinforced composite tapes have become increasingly interesting to the aviation industry and more recently, for automotive applications as viable alternatives to established manufacturing architectures such as continuous fibre woven preforms and prepreg lay-up. This is because discontinuous fibre tapes offer the prospect of much faster and therefore cheaper, part manufacture, where a degree of flow during moulding, allows parts to simply be compression moulded, offering an alternative, cost effective, processing route for advanced composite structures where the part counts approach 10 -100,000+. There are now a range of pre-impregnated chopped discontinuous carbon fibre tapes available commercially, with typical fibre lengths of 25mm and volume fractions of >50%. The achievable composite stiffness with these materials approaches those of quasi- isotropic laminates, with competing performance in bending and impact. Consequently this class of composites are finding increasing application as a lightweight alternative to aluminium or sheet lay-up laminates, particularly for sub-structural componentry.

Interest in the discontinuous fibre-reinforced composites for airplane parts, started with thermoset composites where chopped prepreg tapes composed of aligned 12 -25mm Carbon fibre with epoxy matrices. Commercial products such as Hexcel's HexMC and Quantum's Lytex 4149 have been used within the Boeing fleet for e.g. window frames. The current trend is now a move towards Thermoplastic matrix versions. These are now gaining ground on the thermosets, because they only

require heating, forming and cooling phases to form complex-shaped parts and so offer cheaper production costs, are tougher, and are potentially, far more straight-forward to recyclable and allow the recovery of costly fibre constituents.

Perhaps the most studied and best understood of the discontinuous thermoplastic tapes systems currently available, is the Carbon fibre reinforced Nylon 6 (PM6) chopped tape moulding compounds developed in Japan, where composite mechanical properties and processing aspects have been well described [1-4]. Advanced tape systems based on the high temperature engineering polymer Polyetheretherketone (PEEK) are now in the ascendant. 12 and 25mm Carbon fibre reinforced PEEK chopped tapes are now commercially available (e.g. Tencate MC1200). These grades are of particular interest to the aviation sector as these materials promise excellent thermal and chemical resistance, high toughness, and far superior fatigue performance compared to Aluminium, whilst also demonstrating high specific stiffness and strength that can rival prepreg laminates, as well as the added advantage of rapid processabliity. However, reported work detailing the processing/mechanical properties characteristics of these PEEK/CF grades is so far, sparse in comparison to the Polyamide and epoxy systems. PEEK/CF present particular fabrication and moulding challenges because of the high melt processing temperatures required (380°C). Thermal degradation of properties in moulded parts due to prolonged exposure to elevated temperatures is a particular concern, whilst cooling rates are known to directly affect crystallinity and mechanical performance.

There have been several studies examining the relationship between processing aspects and resulting morphology - Void formation and the effect of void content on mechanical properties in moulded PEEK/CF ROS composites was the subject of a work by Levy, Landry, & Hubert [5,6] and Picher Martel etal [7]. Non-Uniform shrinkage was specified as the major cause of void formation. The work considered the effect of voids on the compressive strength of moulded panels. Other relevant studies focused on processing aspects of PEEK/CF Randomly Oriented Strand (ROS) composites include that of LeBlanc et al. [8] investigating the influence of processing pressure on void content and strand geometry plus moulding pressure on the filling of a 25 mm deep rib cavity moulded using PEEK/CF ROS composites. Short Beam shear testing was used, solely to gauge the extent of anisotropy in moulded rib sections.

Mechanical properties of PEEK/CF ROS composites were further studied by Selezneva et al. [9,10], the study focused on a commercially available grade PEEK/CF CYTEC APC-2/AS4 6.35 mm wide unidirectional slit tape with fibre volume fraction of 61%. The tape was cut to a range of lengths where variations in strand length and part thickness were assessed for their effect on tensile strength. Tensile strength in ROS composites was shown to be around a third of that of quasi-isotropic CF laminates. This is thought to be because of the reduced ability of short fibres to carry load. Aside from this, there is, little published information available regarding the mechanical characterisation of this class of composites in comparison to others. Whilst these findings are informative, composite flexural behaviour i.e. bending behaviour, is often far more representative of "real world" situations, than pure tension. Flexural loading adequately simulates the actual loading conditions the material will be subjected to in service, such a test can be very meaningful. Because flexure involves elements of tension, compression and shear, the test is a somewhat fairer method of comparing the mechanical performance of the discontinuous ROS format with rival architectures such as continuous quasi isotropic prepreg lay-ups, wherein failure is often dominated by shear delamination.

The work reported here, investigated the viability of using a commercial grade of PEEK/CF ROS composite in place of aviation grade 2014 aluminium alloy. The study compares the most pertinent properties in the application area of interest - namely flexural characteristics, notched impact performance and the stability of mechanical performance with temperature, via DMA analysis. Manufacturing variables - dwell time, moulding pressure, were assessed in the study, where samples were also subjected to CT scans and SEM examination. This study thus provides a useful addition to foregoing investigations, particularly in providing some impact and flexural data for discontinuous PEEK/ CF composites.

## 2. EXPERIMENTAL

### 2.1 Materials and Processing

The material used in this study is discontinuous PEEK/CF strand (Tencate MC1200) supplied by Royal Ten Cate (TenCate). The fibre volume content is 50%. The size of the strand is 3 x 25mm. In order to manufacture composite laminates, MC1200 was loaded into a 100 x100 mm square mould which was then heated and compression moulded on a laboratory hydraulic press (Lab Tec). The moulding temperature was 400°C and the water cooling was applied to drop the temperature down to 80°C upon completion of the compression stage moulding. To investigate the influence of processing time on the mechanical properties, a series of samples were made with the following heating times: 30, 40, 70 and 90 minutes under a moulding pressure of 13.4 MPa. To investigate the influence of pressure on mechanical properties, a series of samples were moulded under the pressure of 3.4, 4.5, 6.7, 8.9 and 13.4 MPa with same processing time, 40mins.

## 2.2 Microstructural Characterization

Characterisation of discontinuous PEEK/CF strand composites were carried out via scanning electron microscopy SEM (Hitachi S-3200N, Japan). The secondary electron images were taken under 25 KV acceleration voltages. The cross-section of discontinuous PEEK/CF composite laminates were polished and then examined with a Bruker IRScope II optical microscope. Micro-CT was used as non-distractive method to investigate the internal structure of the as-manufactured composite. The prepared samples were scanned using X-Tek Bench top CT 160 Xi (X-Tek Systems Ltd/Nikon Metrology UK Ltd, England) with a current of 95–100  $\mu$ A, voltage of 70 kV, pixel size of 3  $\mu$ m and 360° rotation.

## **2.3 Flexural Testing**

Test samples were cut from the as-moulded quasi–isotropic panels demonstrating 2D randomised fibre orientation with no preferred fibre orientation in the samples. The samples and test method followed recommendations according to ASTM D790-3. The size of testing sample was 12.5x3.2x100mm. Three point bending test was carried out on Lloyds EZ20 tensile testing machine. The span used was 52mm and the testing speed was 1.5mm/mins. 5 samples were tested for each manufacturing condition.

#### 2.4 Charpy Impact Testing

Test samples were cut from the as-moulded quasi–isotropic panels. Charpy Impact tests were performed according to standard ISO 179. Specimen size is 80 x 10 x 4mm with a machined central 2 mm V notch as specified in the standard. Tests were performed on Ceast Resil impactor junior with a 15J hammer and 62 mm span. 6 samples were tested for each manufacturing condition.

#### 2.5 Dynamic Thermal Mechanical Testing

3point bending test mode was used for the DMA investigation. Samples made under the pressure of 13.4 MPa with 30mins processing time were cut into 30x7x12mm size. The span used is 20mm and the frequency was 1Hz. The test was performed over a temperature range of 25-250°C with the heating rate of 3°C/min.

#### 2.6 Density measurement

The relative density of samples was measured according to ASTM792. The test was performed at room temperature. 3 samples were tested for each manufacturing condition.

# 3. RESULTS

### 3.1 Microstructure Characterisation of Discontinuous PEEK/CF Composite

Figure 1 shows the MC1200 and the compression moulded composite panel. As shown in Figure 2, the MC1200 raw material were characterised by SEM. The surface of the discontinuous PEEK/CF tape are covered by a uniform layer of PEEK, and cross-section images show that carbon fibres are well impregnated with PEEK. The optical microscopy image, Figure 3, illustrate the cross-section microstructure of the composites. This shows the different orientation of carbon fibre across layers. Figure 4, the Micro-CT scanning image, shows that the majority part of a typical sample and gives an indication of the void content. Whilst much of the bulk of the samples examined was void free, isolated imperfections were detected as shown on this selected CT scan slice image.



Figure 1. Discontinuous PEEK/CF tapes and the resulting compression moulded composite panels.



Figure 2. The SEM images show the surface and cross section of cut tapes.



Figure 3. The typcial cross-section OM image of discontious PEEK/CF composite



Figure 4. Typcial Micro-CT image of discontious PEEK/CF composite

# **3.2 Characterization of Mechanical Properties**

Figure 5 shows the facture images of discontious PEEK/CF composite. Debonding along the interface of carbon fibre strands and intra-laminar cracking was observed on the in-plane surface as marked by arrows. The optical microscopy image taken of the cross-section of the fractured sample clearly shows evidence of failure by delamination of the fibre tapes from the matrix as indicated by arrows.

The typical flexural stress-stain curve of PEEK/CF composite is shown in Figure 6, the materials fail gradually rather than in a catastrophic manner, which indicates the composite demonstrates high level of strain relief. The images in figure 5 strongly indicate that the stain relief mechanism at work is a tape delamination process and the debonding along the interface of carbon fibre strands.



Figure 5. The fracture of discontious PEEK/CF composite .



Figure 6. The typical flexural stress-strain curve of discontious PEEK/CF composite.

Figure 7 illustrated the influence of processing time and pressure on the flexural strength and flexural modulus. The flexural strength and modulus was found to be 400-1100MPa and 20-70GPa, respectively. However, there is no clear trend showing a significant influence of pressing pressure on the flexure strength and modulus within the range of 3.4-13.4MPa due to the a large spread in all of the measurements. This is likely due to the quasi-isotropic nature of the material and its randomised fibre orientation, and the localised volume fraction of carbon fibre. At the pressure of 13.4 MPa, the sample with 30mins processing time demonstrated the highest average flexural stress among others, approximately 1000-1200Mpa. Upon further increasing the processing time, the averaged flexural stress reduced to approximately 400-1000MPa, and processing time has no significant effect on the modulus within the frame of 40-90 mins. The flexural modulus was not greatly influenced by processing time. The averaged values vary from 20-65Gpa.



Figure 7. Influence of processing pressure and time on flexure stress and modulus

The notch charpy impact test demonstrated that the impact energy of discontinuous PEEK/CF composite is approximately 139KJ/m<sup>2</sup> which is about three times as high Al-T6 2014, as shown in Figure 7. The composites demonstrate delamination failure through the thickness of the sample and an indication of a small plastic deformation region on the polymer-rich surface region of the specimens, as marked with the white circle. The Al-T6 2014 samples demonstrated classic brittle fracture.



Figure 7 Notched Charpy impact tests results of discontinuous PEEK/CF and Al-T6 2014

There was very little density variation between samples and no discernible difference in sample density that could be attributed to changes in processing conditions used in manufacture. Density averaged at approximately 1.58kg/m<sup>3</sup>. This somewhat further supports the finding that % void content is low/similar from sample to sample, and that pressure and dwell-time over the ranges tested for, did not substantially influence the density of the mouldings.



Figure 8. The density of discontinuous PEEK/CF composite processed under various conditions.

#### **3.3 Thermal Mechanical Properties**

Figure 9 shows that the DMA curve of the composite. It shows the in-plane storage modulus of the composite is 22GPa. It drops to 12Gpa at 250°C. Below 250°C, the loss in modulus of the composite is very small at around 1GPa. This suggests that discontinuous PEEK/CF composite has good elasticity.



Figure 9 DMA curve of the discontinuous PEEK/CF composite.

#### 4. DISCUSSION AND CONCLUSIONS

Here we discuss the relevance of these results in terms of Manufacturers data, and reported flexural and impact properties for alternative forms of PEEK/CF, also a wider comment on the mechanical performance of PEEK/CF's as viable alternatives to currently used metallics such as T6 Aluminium alloy – comparing intrinsic properties of these materials, and other factors such as ease of processing. A median figure of 750MPa for flexural strength of PEEK/CF is reported here. Comparing against other product forms, for a commercial 60% VF unidirectional PEEK/CF prepreg -APC-2-PEEK/IM7 (formally made by Cytec), Manufactures data sheets gives a Axial flexural strength value of 2170MPa , and a transverse flexural strength of 103MPa. Independent researchers have reported similar values for similar products: Cogswell [11] reported the following of high strength CF versions (APC-2/AS4): axial flexural strength of 1880 MPa, and a transverse flexural strength of 137MPa. Cross-plied

uniaxials of 60% Vf PEEK/CF gave an axial flexural strength of 907MPa, whilst single-tow wovens were reported at 929MPa. Whilst a straight like-for like comparison is not possible, these figures give an insight in to the possibilities offered by PEEK/CF tape systems. Clearly MC1200 is far stronger than the transverse properties demonstrated by uniaxial PEEK/CF prepreg. Allowing for the lower 50% volume fraction in the MC1200 samples, The strength figures competes well with those made from Cross ply laminates, whilst offering a vastly simpler and cheaper manufacturing route.

Comparing the median Young's modulus in bending figures for MC1200 PEEK/CF samples (41GPa) with those for uniaxial PEEK/CF prepreg materials. The uniaxials are much stiffer in the fibre direction (~150GPa) but demonstrate drastically lower values in the transverse direction (9.7GPa), similar to the Strength figures reported above. Xycomp 1000-04 - a bi-directional (0/90) PEEK/CF made by Green Tweed has a datasheet modulus figure of 48.6GPa, not substantially different from the figures reported here.

Comparing MC1200 tapes with an aviation grade T6 aluminium alloy, some insight can be gained by looking at the relative strengths of the two types of materials. The typical yield strength for Al T6 is 270 MPa [12], whilst the measured flexural strength for the CF PEEK at 750MPa. Comparing Young's modulus figures for Al T6 are ~ 69GPa [12] vs 41GPa as measured for MC1200. Whilst the aluminium seems to demonstrate a high book value modulus, this does not however account for the effect of elevated temperatures. Comparing other factors: MC1200 is far superior in impact as reported here, and is 40% less dense than typical Al alloys. Fatigue life is another source of concern with Al alloys whilst PEEK/CF composites are known to demonstrate excellent fatigue properties, further investigation comparing Fatigue performance is the subject of on-going future work.

## ACKNOWLEDGEMENT

The authors would like to thank Royal Ten Cate (TenCate) for supplying of materials. This work was funded by the Innovate UK.

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