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Master's Thesis

Effects of Thermal Degradation on Carbon Reinforced PEEK Composites

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The application of fibre reinforced thermoplastic composites in aerospace industry has increased drastically in the last decade. Carbon fibre/Polyether-ether-ketone (C/PEEK) is one of the highperformance thermoplastic composites and is replacing metallic and thermosetting counterparts in various aircrafts components. Parts made from such composites undergo multiple heat treatment cycles, and each cycle involves processing at temperatures above melt. At these temperatures, thermal stability is a limiting factor, which results in severe thermal degradation of the polymer, especially in oxidative environments. For this project, the thermal degradation of 8-ply unidirectional C/PEEK composites is investigated. The objectives include finding the reduction in morphological properties of PEEK polymer due to degradation over four different processing temperatures (385, 405, 425, and 445°C), and times (10, 30, 60, and 90 minutes), in two processing environments (air and nitrogen), exploring the effect of oxygen and temperature on degradation, and evaluating the mechanical performance through three-point bending. Thermal analysis through Differential Scanning Calorimetry (DSC) showed that the crystallinity reduces from 32% for an untreated laminate to 28% for the lowest heat treatment condition (385°C, 10 minutes). From there, a steady reduction is observed, with 15% at 425°C, 60 minutes, and 0% at 425°C, 90 minutes and 445°C, 90 minutes. A contour plot for polymer property reduction based on crystallinity serves as a processing guideline for C/PEEK laminates. DSC analysis through the thickness of air treated laminates showed that surface plies degrade faster than the inner plies. This effect is not observed in a nitrogen environment. This showed the effect of oxygen on the surface. Though inner plies were shielded from oxygen exposure, they still showed a higher degradation than nitrogen treated laminates, showing that diffusion of oxygen through the laminates has taken place. At 425°C and 445°C, in air, the through thickness difference is higher compared to 385°C. So, in oxygen environment, polymer degrades faster at higher temperatures than at lower temperatures. In nitrogen, at 385°C, there is almost no degradation, whereas the other three temperatures show an increased degradation. The rate of degradation in different environments and at different temperatures is characterized by computation of activation energies. The air treated laminates showed an activation energy of 126 kJ/mol, whereas, nitrogen treated laminates has 193 kJ/mol. 3-point bending tests are performed to observe matrix failure. No failure was observed at 10, 30, and 60 minutes at 385°C, but from 405°C, cracks starts to appear and cracks initiates at lower stresses with increasing heat treatment conditions.

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1.1. General Introduction

PolyEther Ether Ketone (PEEK) is a high performance semi-crystalline thermoplastic polymer. PEEK possesses a unique combination of properties, which includes excellent chemical, wear, electrical, temperature resistance, high strength to weight ratio, rigidity, and low moisture absorption. In addition to the above properties, PEEK also has general advantages of thermoplastics like short manufacturing times, the melt process-ability, capability to be fusion bonded/welded, infinite shelf life, recyclability, and inherent FST properties [1, 2]. PEEK has a higher melting temperature (~340°C) than other high performance thermoplastic polymers like PPS and PEI, thus providing a high temperature performance [3]. Such beneficial properties increased the application of PEEK in the aerospace industry over the last two decades. Typical applications include access panels, rib stiffeners, brackets, flooring and clamps [4].

In comparison to traditional aviation metals, fibre reinforced PEEK composites are 70% lighter, while maintaining equivalent or even better strength, stiffness and longevity. In comparison to thermoset based composites, which are the primary aircraft composites in use, PEEK composites lead to 75% faster manufacturing and assembly times [5]. Glass fibre reinforced PEEK clamps in the Boeing 787 improved the installation times by 30% when making the switch from metal. These non-conductive, non-corrosive clamps can provide a weight savings of at least 20%, with increased service life. Carbon fibre reinforced PEEK composite brackets have manufacturing times in minutes, while the thermoset counterpart takes several hours [6]. Thus, the use of such high-performance thermoplastic polymers in aerospace industry contributes to stronger, lighter and durable parts while simultaneously reducing manufacturing, maintenance and fuel costs.

While PEEK composites are advantageous over other materials in many ways, there are still shortcomings and challenges. One of the major challenges is the thermal stability of material during production. Processing of fibre-reinforced PEEK composites usually takes place at temperatures higher than the melting point of PEEK (360-400°C). Most thermoplastic composite parts involve a multistep manufacturing process, where the polymer is subjected to multiple heat treatments. For example, a glass reinforced PPS rib, used in a fixed wing leading edge of the Airbus A380, undergoes three heat-treatment cycles [7], as shown in Figure 1.1. During the first heat treatment, a stack of oriented fibre reinforced plies is consolidated into a flat laminate. This is done through press consolidation. The consolidated laminate is subjected to another heat treatment, where it is stamp formed into the final 3-D part. The ribs are then assembled into the wing skin through resistance welding, where the joining area is locally melted and bonded. Each step has different cycle times, and processing environments. Depending upon the reinforcement, the press consolidation press takes about 2-3 hours, in a nearly airless environment. The stamp forming cycle takes only about 5-10 minutes, in an oxygen rich environment. The welding takes about 3 minutes. In addition to this, the prepreg manufacturing may consist of a heat treatment cycle, involving melting and cooling of the polymer.



Figure 1.1 Production cycle of a fixed wing leading edge thermoplastic composite rib of Airbus A380, with three heat-treatment cycles, consolidation, stamp forming and welding. Reproduced from [7]

1.2. Problem Statement

Such multiple heat treatment cycles, with prolonged heating above the polymer's melting temperatures may result in thermal degradation of the polymer, especially in oxidative environments. Such degradation could result in decrease in polymer's morphological properties like degree of crystallinity, crystallite orientation and spherulite size. This in turn will influence the final mechanical properties such as strength and modulus. Changes in molecular structure may also lead to increase in viscosity of the polymer, deterioration of the material's capability for fusion bonding in further steps, reducing the consolidation quality in processes like stamp forming or they might serve as initiators for formation and propagation of cracks. But the extent of degradation of PEEK composites during processing, and its effect on material properties is still unknown. A clear idea about the effect of processing conditions on the quality of product is significant. This study is aimed to provide a well-defined sense about the processing window for PEEK composites.

1.3. Research Objectives

The main goal of this research is to investigate the thermo-oxidative degradation behaviour of heat treated PEEK composite laminates at processing temperatures and times, and the effect of such degradation on the material properties.

Characterisation of thermal degradation includes subjecting the laminates to a range of heat treatment conditions, and performing thermal and mechanical analysis. The heat treatment includes different time, temperature and environmental conditions. Thermal analysis is done through Differential Scanning Calorimetry (DSC) and mechanical performance is characterised through three-point bending tests.

Three sub goals are defined to achieve the primary objective, which includes the following.

- To find the reduction in morphological properties of PEEK laminates due to heat-treatment.
- To explore the effect of oxygen and temperature on degradation by conducting through thickness thermal analysis, and experiments in nitrogen environment.
- To evaluate the mechanical performance of heat-treated laminate through three-point bending.

In line with these objectives, two major research questions, with each having sub questions, are posed, with the hope of answering them by the end of the research.

- What will be the effect of time, temperature, and heat treatment environment on degradation?
 - How can we quantify these factors?
 - Will the press forming cycle before heat treatment have an effect?
 - How can we define a degradation limit above which the material cannot be manufactured into good quality product?
- How does the polymer degradation affect the mechanical performance of laminates?
 - Since fracture from static bending tests are mostly fibre dominated, what mechanical methodologies are suitable to exaggerate matrix properties?
 - Will degradation reduce mechanical properties or lead to formation of cracks?
 - How can we define a degradation limit based on mechanical property reduction?

1.4. Thesis Outline

Figure 1.2 shows the outline of this thesis. Chapter 2 provides a short report on the up to date knowledge on the degradation of PEEK and its composites. The polymer morphology, properties, thermo-oxidative degradation mechanism, its effect on some of the material properties are described. Chapter 3 presents the organization of the research undertaken, highlighting the experimental procedures, descriptions, parameters and boundary conditions. Chapter 4 encompasses the DSC analysis, presenting the changes observed in crystallisation behaviour of PEEK composites due to heat-treatment. Degradation of multi-layered PEEK laminates, effect of processing environment on degradation, and crystallisation kinetics of degraded laminates are analysed. Chapter 5 describes the three-point bending analysis, presenting the changes observed in fracture behaviour due to degradation. Chapter 6 provides a discussion on the observation and analyses, bridging gaps in understanding, attempting to explain discrepancies and unclear behaviour, followed by conclusions and recommendations on Chapter 7.



Figure 1.2 Thesis Outline

2.1. Outline

PEEK polymer and its composite has been researched extensively over the last three decades. While the thermal degradation behaviour has also been studied previously, most of the research is confined to the pure polymer and single layer composites. Thermal degradation, if any, on the multi-layered PEEK composites laminates has not been conclusively researched. This literature review gives an overview of the studies previously undertaken.

This chapter starts with a brief overview on the structure and crystallisation behaviour of PEEK and its carbon composite. Alterations in the phase transitions of PEEK polymer as a result of heat treatment at different temperature, time and environmental conditions is illustrated. It is followed by the changes in crystallisation kinetics due to this heat-treatment and a mathematical model to describe them is put forth. Finally, an overview of the effect of degradation on the properties of PEEK and its composite is provided.

2.2. Structure and properties

2.2.1. PEEK

PEEK is a semi-crystalline, colourless high performance thermoplastic polymer belonging to the class of polyaryl ether ketones. Figure 2.1 shows the molecular structure of the polymer, having aromatic rings with two ether linkages and one ketone linkage in every repeat unit. PEEK can be synthesized through two methods [8, 9, 10]. The first method involves a nucleophilic substitution process where aromatic ketone species are linked by an ether bond. The second method is through an electrophilic reaction of Friedel-Crafts acylation type. It involves linking aromatic ether species through ketone groups.



Figure 2.1 Left: Chemical structure of PEEK. Right: Semi-crystalline structure

Polymers generally contains long linear molecular chains, that can slide past each other freely at melt, and can form entangled coils. Upon rapid cooling, in polymers like acrylic and polycarbonate, these chains stay as entangled coils, and show no order, and are called amorphous. PEEK on the other hand, when slowly cooled, some chains are organized into ordered regions and are called semi-crystalline [11, 12]. The arrangement of polymer chains in a typical semi-

crystalline polymer is shown in Figure 2.1. This process of alignment of molecular chains is called crystallisation. Unlike thermosets, where the chains crosslink and form irreversible bonds, thermoplastic can be remelted and reshaped.

The microstructure and crystalline morphology of PEEK has been extensively reviewed using wide-angle X-ray scattering, Transmission Electron Microscopy, Differential Scanning Calorimetry (DSC) and density measurements [13, 14, 15, 16]. In PEEK, the crystalline phase is ordered and highly cohesive, whereas the amorphous phase is in disorder and less cohesive. Amorphous areas are more prone to stress-cracking, and are brittle due to their low mobility of molecules. So, higher crystalline areas, and thus higher crystallinity influences properties like stiffness, hardness and ductility. High values of crystallinity can be achieved only in materials with low molecular weight, because of strong entanglements, and difficulties in keeping the material above melt for longer times [17]. PEEK has an optimal degree of crystallinity between 30 and 40%. The degree of crystallinity also depends on other factors such as processing history, annealing treatments and the presence of nucleating agents such as graphite.

2.2.2. C/PEEK

Fibre reinforced PEEK belongs to a category of engineering composites. The polymer is called the matrix and the fibre is called reinforcement. Fibres are the primary load carrying element of the composite. The composite is only strong and stiff in the direction of the fibres. Unidirectional composites have predominant mechanical properties in one direction. So, this way, different fibre orientations produce optimum properties. The matrix supports the fibres, bonds them together, and transfers any applied loads to the fibres.

There are different types of fibres like glass, carbon, aramid, and basalt. Among them, carbon fibres are the most widely used reinforcing system in high performance structural composites. Carbon fibres are synthetic substances made primarily from the carbonisation of polyacrylonitrile (PAN). They have high strength to weight ratio, rigidity, corrosion resistance, fatigue resistance, and are brittle. Because of their highly anisotropic morphology, their properties are dependent on the orientation of the fibre. So, they can be specifically tailored to have maximum properties in any direction required [18, 19]. AS4 type high strength carbon fibres possess an axial tensile modulus in the range of 230 GPa and a transverse tensile modulus of 15 GPa [3]. In addition to mechanical properties, there are several other characteristics of carbon fibres that are significant for composite manufacturing. Carbon fibres have a negative coefficient of thermal expansion, which is of relevance in structures that require high dimensional stability. They have high thermal and electrical conductivity in the fibre direction.

Most material suppliers deliver Carbon/PEEK (C/PEEK) composites as pre-consolidated sheets or boards. Since thermoplastics possess the capability of melted and reshaped, this reduces the manufacturing step of impregnation. Because of the high-viscosity of PEEK, impregnation of carbon fibres is a tedious process. But there are viable different methods available, which includes solution coating, powder coating and commingled yarn weaving [20, 21, 22].

2.3. Thermal degradation of PEEK and C/PEEK

2.3.1. Thermal decomposition

Thermal degradation of polymers refers to molecular deterioration as a result of overheating. At high temperatures, the long chain backbone of polymers can break and react with one another, thus changing the properties of the polymer. The chemical reaction occurring during degradation could result in destruction of mechanical, optical and physical properties [23]. Compared to other polymers like PE, PET, PMMA, and such, PEEK has superior thermal resistance. The study of decomposition mechanism and the products of decomposition is essential to identify features and parameters that lead to thermal instability, at high temperatures.

Thermal decomposition of PEEK, analysed through pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetry/ mass spectrometry (TGA/MS) techniques showed that decomposition is a two-step process [24, 25, 26]. In the first step, random homolytic scissions (breakage of chains) of ether or carbonyl linkages occurs, resulting in phenol-end groups, as shown below. The resultant phenol-end groups, are cleaved through hydrogen abstraction method to produce phenol as the initial and major pyrolysis product. Further decomposition leads to the volatilization of phenols, leaving a carbonaceous char, which then, further oxidizes into carbon monoxide and carbon dioxide. Other volatile products during decomposition include benzene, dibenzofuran and benzoquinone, which can be formed as a result of radical recombination reactions.

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The beginning of volatile emissions can be attributed to the reduction of mechanical properties because the introduction of micro porosity in the sample can play a role in the crack initiation process. But for shorter exposure times, degradation can already be observed by the decrease in heat of fusion from DSC, before there is any emission of volatiles for the same condition in a thermogravimetry analysis (TGA) [27]. This is because the signals from such volatiles are too weak to be measured by TGA. Hence, it can be inferred that degradation cannot be measured with thermogravimetry alone. From the studies, it seems like the stability of the polymer chain is not chain-end activated, and that it is inherent to the basic chemical structure of covalent chain. Whilst much can be concluded from the mechanism of thermal decomposition of PEEK, the reactions in the melt are also needed to be studied for better control of decomposition properties.

2.3.2. Changes in melting and crystallisation due to degradation

DSC analysis of thermally degraded pure PEEK under various time, temperature and environmental conditions showed observable changes occurring during melting and recrystallisation [28]. The process results in an endothermic transition from a crystalline solid to molten crystals, losing their ordered arrangements. The lowest point of this transition is called the melting point (T_m). The amount of heat absorbed during this reaction is a direct representative of the amount of crystalline material that is capable of recrystallisation during cooling. This heat is called the heat of fusion. As evident from Figure 2.2, with increased heat treatment time and temperature conditions, there is a decrease in both melting temperature and heats of fusion. Also, this effect is only significant when the experiments were conducted in air. In nitrogen, the heats of fusion remained relatively constant, and melting temperature dropped only slightly. Like melting, during recrystallisation, with increase in exposure time and temperature, there is a decrease in recrystallisation temperature and heat of recrystallisation, in air. These data give information about the morphology of PEEK, more specifically the dependence of crystallisable material on the exposure time, temperature and environment.



Figure 2.2 Changes in melting temperature (—) and heat of fusion (---) of PEEK polymer, subjected to degradation at 380°C (o, •); 400°C ((Δ, ▲); 420°C (□, ■) Open symbols in N₂, closed symbols in air [28]

This effect is similar in single ply C/PEEK composites as well [29, 30, 31]. The heat of fusion, melting temperature and recrystallisation temperature decreases with the increase in the exposure temperature and hold time, as evident from Figure 2.3. Consequently, the ability to crystallise is decreasing as a result of high hold temperatures and times in oxidative atmospheres.



Figure 2.3 Left: Changes in melting temperature (—) and heat of fusion (---) [29]. Right: Changes in peak crystallisation temperature of single ply C/PEEK composite, subjected to degradation at $380^{\circ}C(\bullet)$; $400^{\circ}C(\blacktriangle)$; $420^{\circ}C(\blacksquare)$ in air [31]

2.3.3. Effect of environment on degradation

From previous section, it is found that degradation of PEEK and C/PEEK in air is higher than in other environments. This can be explained through two aspects. The first aspect is through the mechanism of PEEK degradation [25] and the second aspect is based on the sample surface to volume ratio.

In the first step of degradation, free radicals are formed by the energy obtained from heating. The radicals react rapidly with oxygen to form a peroxy radical. This peroxy radical then abstracts hydrogen from another polymer molecule of the same chain, forming a molecule of hydroperoxide and a second radical. This radical then undergoes the same reaction over and over until it eventually terminates. Hydroperoxides formed are unstable, and they instantly decompose into radicals by a homolytic reaction. These radicals in turn abstract hydrogen from another chain's molecules, initiating new oxidative chains. This results in the progressive branching of polymer chains, at high temperatures, resulting in crosslinking. Because of this crosslinking, the mobility of the chains is reduced, and so does their ability to arrange in order. This results in decreased crystallinity. Crosslinking also leads to an increase in molecular weight which is normally observed during degradation. For example, in nitrogen, only a 10% increase in average molecular weight of PEEK is observed after holding for 30 minutes at 440°C. Whereas, in air, 10% increase was reached just after 15 minutes at only 385°C, and 30% after 30 minutes at 400°C [27].

Another reason for increased degradation in air can be attributed to the change in rate of diffusion of air into the sample. The diffusion of air increases with increase in the sample surface to volume ratio. With large surface, there is a large oxygen diffusion zone, and thus higher degradation occurs [27]. This effect is less pronounced in nitrogen, since there is no oxygen to diffuse into the sample. Due to this crosslinking, the crystallisation parameters are very well affected.

2.3.4. Isothermal crystallisation kinetics of PEEK subjected to heat-treatment

Crystallisation of PEEK can be brought out either isothermally or non-isothermally. Effect of heat treatment on isothermal crystallisation kinetics has been studied [32, 33, 34, 28] thoroughly, but little to no research is available on non-isothermal crystallisation kinetics.

In isothermal crystallisation, PEEK is rapidly cooled from above melt to a specific temperature between glass transition (T_g) and melting point (T_m), and kept at that temperature for the material to complete crystallisation. Theoretically, isothermal crystallisation can be performed at any temperature between T_g and T_m . But close to T_g , the molecular chains cannot align themselves rapidly due to the high viscosity of the liquid phase. This therefore increases the time the nucleation embryos take to grow and form spherulites, thus decreasing the rate of crystallisation. Close to T_m , the ability of chain realignment is easier due to reduced viscosity of the melt. But the increase of free energy within the system leads to disruption of nuclei before growth can take place. This therefore increases the time taken for the polymer to nucleate and form spherulitic crystallisation. This in turn affects the degree of crystallinity [35, 36, 37]. The growth rate gradually increases from T_g , and reaches a maximum, and starts to decrease as it goes towards T_m , as shown in Figure 2.4.

In non-isothermal crystallisation the material is cooled from above melt to below glass transition at a constant rate, allowing crystallisation to occur naturally. The rate and degree of crystallisation in non-isothermal crystallisation depends on the rate of cooling.



Figure 2.4 Variation of rate of crystallisation at different isothermal crystallisation temperatures, where T_g represents the glass transition temperature and T_m represents the melting temperature [**35**]

Isothermal crystallisation kinetics of heat-treated pure PEEK can be characterized by Avrami analysis [38], which describes the phase change at constant temperature. Avrami equation is defined as shown in equation (1),

$$1 - X_t = e^{-Kt^n} \tag{1}$$

Where, X_t is the weight fraction of crystallised material at time t, K is the rate constant, and n is the Avrami exponent.

The Avrami exponent gives information about the nucleation type and crystal growth geometry, and rate constant gives information about the rate of crystal growth. It can be calculated by taking a double logarithm of the equation When heat treated PEEK is cooled to an isothermal crystallisation temperature, the Avrami exponent changes during crystallisation, specifically after 70% of the crystallisation. This means that crystallisation kinetics follows a dual crystallisation mechanism. This change suggest that the primary crystallisation corresponds to a spherulitic diffusion controlled growth with thermal nucleation, and the secondary crystallisation corresponds to rod shaped diffusion controlled growth with thermal nucleation. Figure 2.5 (Left) shows the dual crystallisation process, a competing nucleating and growth process. Figure 2.5 (Right) shows the Avrami exponents for two heat treatment conditions, in air and nitrogen.



Figure 2.5 Left: Dual crystallisation process of PEEK during cooling [35]. Right: Avrami exponents at different crystallisation temperatures, for two heat treatment conditions, in air (—) and nitrogen (---). Reproduced from [28]

The actual magnitudes of the Avrami exponents are not that large for different heat treatments, showing that the nucleation and crystal growth geometries are similar for all samples. But there is some significant variation in kinetic rate constants with different heat treatments. This can be illustrated through the Arrhenius equation [39, 40, 41], which relates the rate of crystallisation to temperature. It is given by the equation (2),

$$K = A e^{-E/RT} \tag{2}$$

Where, *K* is the rate constant, *A* is a pre-exponential factor, *E* is the activation energy (J·mol⁻¹), *R* is the universal gas constant (J·mol⁻¹·Kelvin⁻¹) and *T* = absolute temperature (Kelvin).

Arrhenius equation gives a quantitative basis of the relationship between activation energy and the rate at which a reaction proceeds. Activation energy can be defined as the minimum energy required to start a chemical reaction. Such molecular chemical reactions mark the initiation of degradation. So, if the activation energy is higher, it will be harder for reactions to occur, and thus the degradation will be lower. Plotting logarithm of K against the reciprocal of temperature, will give activation energies (E).

The activation energies obtained for different heat treatment conditions are different [28]. Higher temperatures, longer times, and air environment decreases the activation energies, as shown for few conditions in Table 2.1. The oxidative branching occurring at high temperature and high hold time in melt, results in the reduction of number of nucleation sites for crystallisation, and the rate at which the existing crystals grows. The branching also results in a lack of mobility between the chains, which in turn affects the rate and degree of crystallisation.

Heat treatment	Activation energy (kJ/mol)	
380°C, 2 min in N ₂	283	
380°C, 10 min in N ₂	248	
400°C, 10 min in N ₂	147	
380°C, 10 min in air	123	
400°C, 10 min in air	89	

Table 2.1 Activation energies at different heat treatments as found by [28]

2.3.5. Effect of degradation on crystallinity

The degree of crystallinity is influenced by the carbonyl group in the ketone linkages of PEEK, and since the initiation of degradation occurs at these carbonyl groups, the thermal stability of PEEK depends on it [42]. The decrease in activation energies increases the material's capability to undergo decomposition reactions, which results in crosslinking. This impedes the molecular mobility and significantly influence the ability of the polymer chains to order into crystalline domains, and thus the crystallinity obtained at the end of crystallisation. Short-time heated C/PEEK composites in the range of 10 ms up to 3 min, showed a significant decrease in crystallinity varying with the power and time of irradiation [30]. A large number of critical properties such as modulus, strength, hardness, resistance of stress cracking is strongly related to the crystallinity.

2.4. Effect of thermal degradation on mechanical properties

2.4.1. Bending

Mechanical Analysis of a hybrid composite made from PEEK powder in between APC-2 composite (Graphite/PEEK) [43, 44] showed that flexural strength decreases over time, over a wide range of temperatures, from 400°C to 620°C. Figure 2.6 (Left) shows the changes in flexural modulus and strength at 620°C for different hold times. There is a decrease in the flexural strength, but the large scatter in the results makes it harder to conclusively relate degradation to property reduction. But thermal degradation does generate cracks and voids within the matrix, which creates stress concentrations.

4-point bending tests on degraded unidirectional C/PEEK composite plates [45], showed no large drop in bending performance at different heat treatment conditions. Bending strength seems to be relatively constant, and dropped only for the extreme condition (440°C for 10 min) as shown Figure 2.6 (Right). Although, it should be noted that this lack of any observable difference may be due to the fact that static bending failure can be mainly fibre dominated.



Figure 2.6 Left: Flexural Strength reduction over time, at 620°C **[44]**. **Right:** Relationship between bending strength and holding time for C/PEEK composites at 380, 410, and 440°C **[45]**

2.4.2. Fracture

The fracture characterization of C/PEEK composites [45] showed degradation of the matrix even at 380°C and 20 min. Delamination at the tensile side of the bending test, with one large crack is seen, as shown in Figure 2.7 (Left). River marks are observed for 380°C and 20 min samples, which suggested that the crack propagated into the resin region. This also shows that, while there are observable damages like crack formation and propagation due to degradation of the matrix, it could not be related to the static bending test results. For 380°C and 60 min (Figure 2.7 (Right)), in addition to a large main crack, several numbers of sub cracks were observed. This means that the increase in the fabrication time had some effect on the crack propagation. The 440°C and 60 min specimens had large number of voids, and the delaminated part had a rust colour change. Exposed carbon fibres were observed, which suggested that the crack propagated through the interphase between fibre and matrix.



Figure 2.7 Fracture aspect of C/PEEK composites. Left: Heat treated at 380°C for 20 min, showing one main crack Right: Heat treated at 380°C 60 min, showing many sub cracks crack in addition to the main crack [45]

2.5. Conclusion

From the literature review, it looks like thermal degradation occurs in PEEK and C/PEEK at processing temperatures. The morphological properties such as the phase transition temperatures, crystallinity, crystallisation kinetics deteriorates, with higher heat treatment temperatures, times and in oxidative environments. As stated, most of the research is confined to pure polymer and single layer composite. One of the few researches on multi-layered C/PEEK composites showed no significant mechanical damage at higher heat treatment conditions. But changes were observed in fracture analysis. Numerous cracks, and crack propagation through resin occurred, showing that, thermal degradation, while not having great effect on static tests, did serve as source for formation of new cracks. Crack initiation is an important phenomenon in long-term loading of structural parts. But the polymer property reduction, and the effect of contributing factors to degradation of multi-layered C/PEEK composites are not well established. No comparative studies are available to correlate the polymer property reduction to mechanical or fracture behaviour of C/PEEK laminates. This seems to be the research gap.

3.1. Outline

This chapter describes the experimental set-up and conditions, process overview and the methods of evaluation and analysis to reach the objective. It starts with the description of the selected composite, and the laminate manufacturing procedure. It is followed by the heat treatment method, and the detailed look at the thermal analysis technique, Differential Scanning Calorimetry (DSC). Finally, the procedure for the mechanical analysis technique, 3-point bending, is explained. The parameters, and expected results are defined.

3.2. Materials

As mentioned in Section 2.2, most thermoplastic composites are delivered as pre-consolidated sheets. C/PEEK composites are also delivered in the same way, where the fibres are pre-impregnated in the resin by various methods [20, 21, 22]. Such form of the composite is called prepreg. For this research, the C/PEEK laminates made from unidirectional (UD) tape prepregs were used. The prepregs, specified as TC1200, from Cetex® family of thermoplastic composite materials, was delivered by TenCate Composites. These prepregs were available in two forms, UD tape and woven fabric.

To select between UD and woven fabric prepreg, preliminary experiments were performed, during the initial part of the research. Laminates were manufactured from both types, and they are subjected to heat treatment, followed by thermal and mechanical analysis. From the results and other practical considerations, UD tape was chosen to be the material of investigation. The experimental procedure and the results of those experiments are added in the Appendix-A. Some of the motives, as derived from the results of the preliminary experiments, for choosing UD tape over woven fabric prepreg includes the following.

- UD laminate degrades more than the woven fabric laminate, and UD laminate is more affected by oxygen on the surface than woven fabric.
- UD laminates are easy to slice for through thickness analysis.
- 3-point bending can show better matrix related failure in UD laminates than in woven fabric laminates because of 0/90 fibre weave.

So, the rest of the research will be focused on laminates manufactured from TenCate Cetex® TC1200 UD tapes.

UD tapes are produced by spreading untwisted fibres (tows) into flat tapes. The fibres are only in one-direction, and they have maximum properties in that direction. The process of production involves mixing the unidirectional fibres into a bath of a molten polymer, under pressure to achieve the lowest void content. TC1200 UD tape has a very low void content of <1%. Tapes are available in rolls of continuous fibres with standard 6-inch (152.4 mm) width, and a thickness of 0.13 \pm 0.02 mm as shown in Figure 3.1. UD tape prepreg has a resin content of 34% by weight. The key properties of UD tapes are provided in Appendix-B.



Figure 3.1 C/PEEK UD tape prepreg roll

3.3. Laminate Manufacturing

Structural parts are fabricated by stacking layers of prepreg materials. A single layer of prepreg material is called a ply. As mentioned above, UD plies have fibres in one direction, and so stacking different plies in different orientations gives properties and stability in any necessary direction. The stacking sequence describes the distribution of orientation of plies through the thickness of the laminate. The structural properties like stiffness and strength of the composite depends on the stacking sequence of the plies. With different stacking sequence, it is possible to achieve properties as low as fiberglass or as high as titanium. Proper orientation and total number of plies chosen is necessary for an effective design.

3.3.1. Prepreg preparation

Although this research pertains to the degradation of the matrix material, choosing appropriate fibre orientation is also necessary for mechanical analysis. Keeping that in consideration, and after the knowledge gained from preliminary experiments (Appendix-A), an 8-ply laminate is manufactured with a $[90/90/90/0]_s$ layup, as shown in Figure 3.2 (Left). The layup is symmetrical, with the plies below the midplane as a mirror image of those above the midplane. Symmetrical layups are necessary to avoid thermal warpage and twisting as they cool down after press consolidation.



Figure 3.2 Left: Layup sequence of 8-ply UD C/PEEK laminate. Right: Schematic of a single ply preparation, with four 6-inch wide UD tapes locally welded

There are six 90° plies and two 0° plies in the layup. Since the purpose of mechanical testing is to look at matrix failure, having 90° plies would magnify that effect, instead of having fibre failure. But to hold the integrity of the laminate 0° plies are also needed. Also, from the literature, it has been understood that presence of air accelerates degradation of single ply C/PEEK. This

mechanism is also expected in the laminates, and since air exposure is maximum at the surface, it is expected that the degradation of the matrix may be higher on the surface. So, 0° plies are concentrated to the center, and 90° plies are towards the surface, where the failure is expected to occur.

Eight plies of UD tape with each 24 x24 inch (610 x 610 mm) size are stacked in the mentioned layup orientation to be press formed into a laminate. Since UD tape plies are delivered in continuous rolls with 6-inch widths, each ply had to be locally welded in three lines to get the necessary width. The schematic of local welding of one ply is shown in Figure 3.2 (Right). This local consolidation of four UD tapes to one single ply is necessary so as to not let the fibres move or overlap during consolidation. Such overlap may create inter-layer thermal stresses.

3.3.2. Press consolidation

The stacked plies are then placed in between Polyimide films (0.01 mm thick), which acts as release films. It is followed by thin caul plates, which is of the same size as the stacked laminate. Caul plates transmit the pressure and temperature, and provide a smooth surface on the finished laminate. Finally, the setup is enclosed between two aluminium plates, and transferred to a flat platen press as shown in Figure 3.3 (Left)

The stacked plies are consolidated into a flat laminate between heated platens in the static press. The flat female tool is brought down and at the contact pressure (2 bar), the plies are heated to a temperature of 385° C, at the rate of 10° C/min. After it reaches the maximum temperature, the pressure is then increased to 20 bars and held for 20 minutes. Because the plies are pre-impregnated, the maximum pressure and temperature do not need to be longer than that. The part is then cooled to room temperature at the same rate, while maintaining the pressure. This press-consolidation cycle is a standard industry cycle, and it is shown in Figure 3.3 (Right) The formed laminate had a thickness of about 1.1 ± 0.1 mm.



Figure 3.3 Left: Parts of the press consolidation process of 8-ply UD C/PEEK laminate. Right: Press consolidation cycle for 8-ply UD C/PEEK laminate, with chosen industry standard temperature, time and pressure conditions. Heated to 385°C at 10°C/min, applied 20 bars of pressure, held for 20 minutes, and cooled down

3.4. Heat Treatment

The heat treatment of the consolidated laminate is a crucial step in the research methodology. To present a clear view on the degradation behaviour of C/PEEK laminates, a range of processing conditions is explored. Heat treatment is performed in two environmental conditions, air and nitrogen.

3.4.1. Air

In air, laminates are subjected to heat treatment at four temperatures (385, 405, 425, and 445°C) and four hold times (10, 30, 60, and 90 minutes). The heat treatment experiments are conducted in a high temperature convection oven. The primary advantage of this oven is that it has fans that circulate hot air around the oven faster, also it provides an excess supply of air. Although during actual processing of such composites, air supply will not be as high as in a convection oven, it is beneficiary for research purpose.

16 small laminates, each of size 150 x 150 mm, are cut from the original untreated laminate. The oven is set to the required temperature and an aluminium plate is placed inside to pre-heat it. This is to increase the heating rate once the laminates are placed in. The laminates are shielded by a thick PI film, on the bottom and in all edges, so that the exposure of air is only on the surface, as shown in Figure 3.4 (Left). A thermocouple is placed on the surface of the laminate and the ends are attached to a data acquisition instrument. This setup is then transferred to the oven and the laminates are held for required hold time. Figure 3.4 (Right) shows the heating rate for the highest temperature (445°C). The laminates heat up very quickly, and reaches the maximum temperature in under 2 minutes. This heating rate is similar in all investigated temperatures. After the heating, the laminate is taken out of the oven, and rapidly cooled to room temperature. The experiment is repeated for all 16 laminates. It should be noted that this is a secondary heat treatment, as the material underwent a heat treatment during press consolidation.



Figure 3.4 Left: Heat treatment method, laminates placed over a pre-heated aluminium plate, with its bottom and sides shielded from exposure of air. **Right:** Heating rate of the laminates. Time taken for the surface to reach maximum temperature (445°C in this case)

3.4.2. Nitrogen

While the heat treatment in air is the primary focus of research, one of the objectives also include analysing the effect of oxygen. So, heat treatments experiments were conducted in a nitrogen environment as well. Untreated laminates of size 40 x 40 mm were heat-treated in an Anton Paar Rheometer, with a constant flow of nitrogen at 385, 405, 425, and 445°C. But the hold times were only for 10, 30, and 60 minutes. It should be noted that the sample sizes are smaller, owing to the limitations of the rheometer holder size. The heating rates are similar to that of the oven treated laminates.

3.5. Differential Scanning Calorimetry

3.5.1. Theory

Differential Scanning Calorimetry (DSC) is a thermo-analytical technique, through which the change or development in a property of a sample is analysed against temperature or time. Through DSC, phase transitions like melting point, crystallisation and properties like crystallinity, kinetic behaviour can be studied. The heat-treated C/PEEK laminates are subjected to DSC analysis using a Mettler Toledo DSC 822e instrument. The samples weighing 10-20 mg, are heated in nitrogen to above melt, held for a specific amount of time and cooled down, at a constant rate. Changes in non-isothermal crystallisation behaviour during cooling with respect to the heat treatment conditions is observed.

DSC apparatus consists of a sample pan and a reference pan placed on separate bases, with separate thermocouples and heaters. Both pans are maintained at the same temperature throughout the experiment. Thermal events in the samples are usually accompanied by absorption or release of energy, which changes the temperature of the sample. But to maintain the same temperature in both reference and sample, heat supplied is varied to compensate the difference. This differential heat flow between the sample and reference is recorded against temperature. Various thermal events result as peaks in DSC curves, with areas directly proportional to the enthalpy change of the event.

For example, crystallisation during cooling from melt is an exothermic process, which makes it a concave downward curve. The curve represents the area of crystallisation. Figure 3.5 (Left) shows a typical crystallisation curve of PEEK. A crystallisation curve consists of three distinct points, onset, peak and endset. The crystallinity of the sample depends on the area under the curve. The shifts in these points indicate a change in the crystallisation process. In case of PEEK, a decrease in these points is usually accompanied with a reduced area under the curve. So, with decrease in these points, a decrease in crystallinity can be expected. For this research, the variations in the crystallisation curves are expressed and explained through the final crystallinity content and peak crystallisation temperature.

Effect of heat treatment on non-isothermal crystallisation kinetics can be studied through a term called crystallisation halftime $(t_{1/2})$. It is the time taken to complete 50% crystallisation. So, the shorter the half time, the faster is the crystallisation rate. The half time is also calculated from the crystallisation curve, as shown in Figure 3.5 (Left).

3.5.2. Procedure

The chosen DSC experimental cycle is shown in Figure 3.5 (Right). Since the DSC cycle is essentially an additional heat treatment, it is necessary to make sure that the conditions chosen (380°C and 10 min, in nitrogen) do not add to degradation, or to report that in case if it does. This is verified by testing the cycle with an untreated sample. Another factor to be considered is the

cooling rate (20°C/min). Higher cooling rates (>50°C/min) result in temperature gradients, and suppress kinetically hindered processes, such as crystallisation. Higher rates are beneficial in case of determining thermodynamic properties of unstable materials and transition temperature of metastable forms. Research [35] shows that for pure untreated PEEK, there is an observable decrease in crystallinity between cooling rate of 10°C/min and 100°C/min. As a rule of thumb, 20°C/min was chosen, as it increases productivity while still maintaining the rate to allow crystallisation.



Figure 3.5 Left: Typical DSC crystallisation curve of PEEK during cooling, with important parameters shown. Right: DSC experimental cycle, conducted in nitrogen

Three sets of DSC experiments are devised, each to analyse specific aspects of the research. The experiments include,

- Degradation behaviour of the 8-ply C/PEEK laminate, treated in air. Two samples per condition were tested.
- Evolution of degradation through thickness of the 8-ply C/PEEK laminate. One sample per condition was tested.
- Degradation behaviour of 8-ply C/PEEK laminate, treated in nitrogen. One sample per condition was tested.

3.6. Three-Point Bending

The second part of the methodology involves analysing the effect of heat treatment on the mechanical performance, through mechanical testing. The 3-point bending test is chosen as the method of investigation after exploring a few available related methods. This investigation was part of the preliminary experiments mentioned in Section 3.1, which is discussed in Appendix-C.

Before the testing, the heat-treated C/PEEK laminates are reconsolidated. This is necessary because, the laminates deform and deconsolidate during heat treatment, and because of lack of pressure to consolidate them back, they stay deconsolidated. So, reconsolidation cycle was necessary, and this leads to another heat-treatment, similar to the press-consolidation cycle.

Three-point bending tests for the heat-treated C/PEEK laminates were performed on a universal testing machine, following ASTM D790 standards. Three specimens were tested for each condition, at a cross-head speed rate of 2 mm/min. In 3-point bending test, specimens of rectangular cross section (50.8 mm x 12.7 mm), are placed on two supports (35 mm span), and is loaded by means of a loading noseP midway between the supports, as shown in Figure 3.6.



Figure 3.6 Schematic of a three-point bending test for 8-ply UD C/PEEK laminates, with specimen dimensions shown, in mm. The surface that was exposed to air during heat treatment is on the tensile (bottom) side

During bending, the top part of the specimen is in compression, and the bottom part is in tension. Because the transverse tensile strength is lower than the transverse compressive strength, failure is most likely to occur on the tensile side. As seen in literature, degradation seems to be accelerated by oxygen. So, the surface that was exposed to air during heat treatment is on the tensile side. This is also why the fibres in outer plies are transverse to the bending direction. This way, the load is completely taken by the matrix, and any failure that occurs would be matrix dominated.

Because of the two 0° fibre plies in the middle, complete failure may not be expected, even after crack formation on the outer 90° plies. So, the test procedure had to be modified, to test until the first crack occurs, instead of letting the material to fail completely or the machine to reach its limit, in terms of crosshead displacement. The active load curve is recorded against the deformation, and the experiment is manually stopped, if/when a drop in the curve is noticed. The variation in force at which the first crack appears is observed for different heat treatment conditions.

3.6.1. Microscopy

Microscopy is performed on the 8-ply UD C/PEEK laminates, subjected to bending. The bent samples are observed under a Keyence VHX-5000 digital microscope. The aim is to perform a comparative microscopic study on both cross section and surface damage of laminates subjected to different heat treatment conditions. The initiation and propagation of cracks, if any, is observed and compared for different heat treatment conditions.

4.1. Outline

DSC analysis provides information about the variations in crystallisation behaviour of heat-treated 8-ply UD C/PEEK laminates. The degradation of the polymer is quantified through the reduction in crystalline content of the laminates. This chapter starts with the results of the crystallisation curves, crystallinity and, peak crystallisation temperatures of the laminates, subjected to different heat treatment conditions. They are followed by a through thickness analysis, where the development of degradation through the laminate thickness, and the effect of oxygen is highlighted. Subsequently, the results from additional heat treatment experiments conducted in a nitrogen environment, to further clarify the effect of oxygen. Finally, non-isothermal crystallisation kinetic analysis is performed, and activation energies of air treated, and nitrogen treated samples are computed to study the effect of oxygen on rate of degradation.

4.2. Overall Degradation

4.2.1. Crystallisation

Figure 4.1 shows the crystallisation curves of 8-ply UD C/PEEK laminates, subjected to various heat treatment conditions in air. Two major variations in crystallisation curves are seen. With increasing heat treatment conditions, there is a reduction in the area under the curves and a gradual shift in the curves towards left. The reduction in the area indicates that less heat was expelled from the samples. This means that, a decrease in total crystallisation, and hence a decrease in the crystallinity is evident. The shift indicates that the crystallisation takes place at lower temperatures with increasing heat treatment conditions.

The decrease in crystallisation is so severe, that the area is almost zero for 405°C, 90 minutes, and completely zero for 425°C, 90 minutes and 445°C 90 minutes, as evident from no observed peaks. This shows that, at low temperatures, the reduction in the number of nucleation sites for crystallisation occurs slowly over increasing hold times than at higher temperatures. This is evident from the fact that at 385°C, 90 minutes, there is comparatively little decrease compared to 445°C, 90 minutes.





4.2.2. Peak crystallisation temperatures and crystallinities

From the previous section, it is found that major changes in the crystallisation curves involves a decrease in area and the shift of the curves. Figure 4.2 quantifies these two changes. The variation in crystallinity content and peak crystallisation temperature are shown. No crystallinity was observed for 425°C, 90 minutes and 445°C 90 minutes, meaning that the material's ability to crystallise is reduced to zero, due to degradation. The values of untreated laminate (0 min) are higher than all the heat treatment conditions. This shows that, even the lowest condition (385°C, 10 min) contributes to some degradation. The peak crystallisation temperature of 425°C, 60 min doesn't compare well with the general trend and the crystallinity. The reduction is lower than expected.



Figure 4.2 Left: Variation of crystallinity content of heat treated 8-ply laminate, in air, as a function of hold time. Right: Variation of peak crystallisation temperature as a function of hold time, in air. No crystallisation peaks observed for 425°C, 90min and 445°C, 90min

4.2.3. Contour plot

Crystallinity is the morphological property that affects the strength and stiffness of the polymer. The reduction in crystalline content during this heat-treatment, can be a direct representative of quality decline. A contour plot, showing the amount of crystallinity at different heat-treatment time and temperatures, provides a way to acquire a processing limit, above which the material cannot retain its properties to the required amount. That can vary with end-requirement. Figure 4.3 shows the isolines drawn based on the retention of crystallinity at different conditions. The areas under each line shows the temperature and time where the mentioned amount of crystallinity can be retained. This can serve as a guideline for processing of C/PEEK laminates.



Figure 4.3 Isolines of retention of crystallinity content of 8-ply UD C/PEEK, plotted for heat treatment hold time and temperature

4.3. Through Thickness Degradation

4.3.1. Crystallisation

The previous sections showed that heat treatment of 8-ply UD C/PEEK laminates decreases the polymer crystallisation. Degradation of polymer can be that high, that at the highest conditions, complete loss of crystallinity is observed. Literature shows that the main contributors of such accelerated degradation are high temperatures and presence of oxygen. From a research point of view, it is unclear how these factors affect degradation of multi-layered composites. Especially, if oxygen is a prime accelerant to degradation, it is necessary characterize that behaviour. In that attempt, through thickness DSC analysis is conducted to the same heat-treated samples. The aim is to compare the variation of degradation at different parts of the laminate, as a function of oxygen and temperature.

The 8-ply laminates are sliced into three parts, as shown in Figure 4.4. The first two plies, representing the top part, the last two plies representing the bottom part, and the center four plies representing the middle of the laminate. DSC analysis is performed on these parts.



Figure 4.4 8-ply laminates sliced into three parts for through thickness DSC analysis

Figure 4.5 shows the crystallisation curves during cooling, of the top, middle and bottom parts for two heat treatment conditions, 385°C, 10 min and 445°C, 10 min. It can be seen that, there is a variation in the cooling curves through thickness for both cases. The middle part has the largest area, and the highest peak crystallisation temperature, indicating the least amount of degradation, followed by the bottom. The top plies showed the lowest of these values, meaning that the degradation is highest at the top part. The variation is smaller at 385°C, 10 min compared to 445°C, 10 min. This variation conforms with other heat-treatment conditions as well.



Figure 4.5 DSC Crystallisation trace of top, middle, and bottom part of the 8-ply UD C/PEEK laminate. Left: Heat treated at 385°C, 10 min, in air. Right: 445°C, 10 min, in air

4.3.2. Peak crystallisation temperatures

Because, the through thickness analysis comprises of a large data set, degradation is expressed through only one term, peak crystallisation temperature. Evaluation of crystallinity becomes difficult in case of curves that do not possess well defined onset and endset crystallisation points, as it involves integrating the area under the curve. This makes the process slightly less precise. Also, decrease in crystallinity always corresponds with a decrease in peak crystallisation temperature, which is a single point that can be identified with greatest accuracy. So, most of the following results are expressed through that, for better understanding of the degradation behaviour.

Figure 4.6 shows the changes in peak crystallisation temperature through thickness for laminates heat treated at 445°C. The values of the untreated laminate (0 min) are also added. Because of the previous heat treatment during press consolidation, the untreated laminate shows a slight variation of peak crystallisation temperature through the thickness. But in all the heat treatment conditions (Refer Appendix-D), the degradation is higher in the top plies. No crystallisation at 445°C, 60 min, shows that, even though the top plies are completely degraded to zero crystallinity, the inner plies retain crystallinity to an extent, contributing to overall crystallinity.



Figure 4.6 Variation of peak crystallisation temperature through thickness of 8-ply UD C/PEEK laminate, heat treated at 445°C in air. No peaks observed at 445°C 90 minutes, and only middle and bottom part had peaks at 60 minutes

The higher top part degradation implies that, both temperature and oxygen contribute to it, while the degradation on the middle part should only be due to temperature. Because, the heat treatment was performed in a way that only the top surface was exposed to air. Figure 4.7 compares the variation of peak crystallisation temperature on the top part and middle part of the heat-treated laminates. As seen, at 385°C, the difference between top and middle plies is smaller even for longer times. Whereas, at high temperatures (425°C, 445°C) the difference is relatively large, even at 10 minutes. Because, the flow of air is constant for all experiments, this shows that, in an oxygen environment, the polymer degrades faster at higher temperatures.



Figure 4.7 Variation of peak crystallisation temperature of 8-ply UD C/PEEK laminates, heat treated in air. Left: Top part. No peaks observed at 60 and 90 minutes for 425°C and 445°C. Right: Middle part. No peaks observed at 90 minutes for 425°C and 445°C

Also, to confirm that the variation between outer and inner plies is due to the presence of oxygen on the surface, one control condition experiment was performed on nitrogen environment. An untreated laminate was subjected to heat treatment at 405°C, 60 minutes, in a nitrogen environment. Figure 4.8 compares the through thickness values of nitrogen treated sample to that of an air treated sample, in the same condition. As it is clear, no change through thickness is observed when treated in nitrogen, while a sizeable difference is seen in air. This proves that the increased degradation in the top plies is due to oxygen.



Figure 4.8. Variation of peak crystallisation temperature through thickness, heat treated at 405°C for 60 minutes, in nitrogen and air

4.4. In nitrogen environment

Figure 4.9 (Left) shows the peak crystallisation temperatures of the top plies of nitrogen treated samples and the middle part of the air-treated samples, for 445°C. A distinguishable difference is seen, with middle part showing higher degradation than the nitrogen treated samples. This difference is seen for the other three temperatures as well. This means that some oxygen has diffused through the surface and into the samples.

But it is unclear how deep the diffusion occurred. Because the middle part contained the middle four plies, it is unclear how deep the oxygen had diffused. This only shows that diffusion of oxygen occurs in the laminate, degrading the inner plies too. It should also be noted that at longer times, the difference is comparatively higher than in lower times.

Figure 4.9 (Right) shows the reduction in peak crystallisation temperatures of nitrogen treated samples. At higher temperatures, we see a steady decrease in peak crystallisation temperatures, while at 385°C, the decrease is not clearly distinguishable, even at longer hold times. This shows that, at lower temperatures, without presence of oxygen, only little degradation occurs over time. As temperature increases, the degradation progresses with time.



Figure 4.9 Left: Variation of peak crystallisation temperatures of middle plies of air treated and top plies of nitrogen treated samples of 8-ply UD C/PEEK laminates, at 445°C, showing the effect of diffusion of oxygen. Right: Variation of peak crystallisation temperature for nitrogen treated samples

So, such degradation in nitrogen can be considered the effect of temperature while the degradation in air, can be due to both temperature and oxygen. A contour plot similar to the one constructed for air treated samples (See Figure 4.3), will provide a way to visualize the property reduction in nitrogen, serving as a processing guideline. Such a plot is shown in Figure 4.10. It can be seen that, 20% crystallinity is retained even at 445°C and 60 minutes, when treated in air, whereas only 10% is retained, when treated in air. The plot of the air treated samples is once again added, to compare the reduction in crystallinity in both environment. Although practically difficult, processing in an airless environment controls the rate and extent of degradation to a better account.



Figure 4.10 Isolines of retention of crystallinity content of 8-ply UD C/PEEK, plotted for heat treatment hold time and temperature. Left: Heat treated in nitrogen (Effect of temperature) Right: Heat treated in air (Effect of temperature and oxygen) (Reproduced from Figure 4.3)

4.5. Kinetic analysis

4.5.1. Crystallisation halftimes (t1/2)

In addition to the characterisation of reduction in crystallinity, a study on the changes in nonisothermal crystallisation kinetics is also undertaken. Crystallisation kinetics describes the rate of nucleation and crystal growth. As seen previously, the polymer degradation causes a reduction in the overall crystallisation, and this section presents the changes observed in the rate at which crystallisation occurs, and these changes are then correlated to the degradation behaviour. Finally, activation energies are obtained for different conditions to further explain the degradation.

The crystallisation kinetics of heat treated 8-ply UD C/PEEK laminates, in air and nitrogen, are expressed through crystallisation halftimes ($t_{1/2}$). It is the time taken to complete 50% crystallisation. So, the shorter the half time, the higher is the crystallisation rate. The half time is calculated from the crystallisation curve, (see Figure 3.5 (Left)). The evolution of crystallisation over time, for different heat treatment hold times, held at 445°C, in air and nitrogen environment is shown in Figure 4.11. With increasing heat treatment hold times, the time taken to complete crystallisation increases. An untreated laminate has a crystallisation halftime of 20 seconds, while laminates heat treated at 445°C for 60 minutes in air, takes nearly 2 minutes to complete 50% crystallisation. The same laminate treated in nitrogen takes only about a minute. As degradation progresses, the rate of crystallisation decreases, and thus the crystallisation halftimes increase. So, the crystallisation half times are directly proportional to the rate of degradation.



Figure 4.11 Development of relative crystallinity with time for 8-ply UD C/PEEK laminates, heat treated for different hold times at 445°C. Left: Heat treated in air. Right: Heat treated in nitrogen. The crystallinity development for untreated laminate is also added

Plotting crystallisation halftimes against time and temperatures gives the rate at which degradation progresses over time and through temperature. Figure 4.12 shows the variation of crystallisation halftimes with hold time for different temperatures, treated in air and nitrogen. The linear regressions of different temperatures are intercepted to the crystallisation halftime of the untreated laminate. The rate of degradation is lower in nitrogen. With no oxygen available to contribute to degradation, the degradation is almost nil over time at 385°C, whereas a steady increase is

observed at higher temperatures. In presence of oxygen, even keeping for 10 minutes at 385°C, shows some degradation, which increases over time.



• 385°C • 405°C • 425°C • 445°C

Figure 4.12 Crystallisation halftimes of 8-ply UD C/PEEK laminates, for different heat treatment temperatures plotted against hold times, with linear regressions intercepted to untreated laminate. Left: Heat treated in air. Right: Heat treated in nitrogen

In addition to comparing the laminates heat treated in air and in nitrogen, the crystallisation half times are computed for the top and middle part of air treated laminates as well. The main purpose of this is to observe the different crystallisation process on the surface and centre of the laminate, when heat-treated in air. They are discussed in the Appendix-E.

4.5.2. Activation energies

The rate of degradation is different for different environment. The slopes of these curves can be used to obtain activation energies, using the Arrhenius equation. As already mentioned in Section 2.6, the Arrhenius equation connects the rate of degradation to temperature. This is also the reason for plotting crystallisation against hold times, instead of temperatures. This way, each temperature can give a slope, which can then be plotted in the Arrhenius plot to obtain the activation energy.

Plotting the logarithm of K against 1/T gives the activation energies. Figure 4.13 shows the Arrhenius plots of air treated and nitrogen treated samples. Plots from a previous internal research on pure PEEK films (0.3mm thick) are also included. The Arrhenius parameters and activation energies of top and middle plies of air-treated laminates are added in the Appendix-E.



Figure 4.13 Arrhenius plot, showing inverse of temperature against logarithm of kinetic constant, for three conditions. Pure PEEK film values are taken from literature

Table 4.1 shows the obtained activation energies for the three conditions. Air treated 8-ply laminates have an activation energy of 126 kJ/mol whereas nitrogen treated laminates have 193 kJ/mol. Pure PEEK film, treated in air, shows the highest activation energy of 289 kJ/mol. It should be noted that another study [46] showed that activation energies were lower for PEEK films of reduced thickness. For a film thickness of 0.1 mm, and analysed through thermogravimetry, the activation energy was 145 kJ/mol.

Table 4.1 Obtained activation energies of three conditions.

Condition	Activation Energy (E _a) (kJ/mol)		
8-ply C/PEEK, in air	126		
8-ply C/PEEK, in nitrogen	193		
Pure PEEK film, in air	289		

5.1. Outline

This chapter comprises the results and analysis of mechanical testing. Three-point bending tests are performed on the heat treated 8-ply UD laminates, to observe the initiation and propagation of cracks. The experiments are performed, following the procedure explained in Section 3.5. The force-displacement curves for all the conditions are presented, and the variations are emphasized and correlated to crack initiation. Stresses and displacements where the first crack appeared for different heat treated conditions are shown. Microscopy is performed on the bent samples, and the cracks and alterations on the surface of the laminates are presented. Finally, extra laminates are heat treated in vacuum environment for one condition, to compare the bending behaviour of that in air.

5.2. Force-displacement curves

Figure 5.1 shows the force-displacement curves of three samples of an untreated laminate and a laminate heat treated at 405°C and 10 min. Untreated samples underwent plastic deformation, till the machine limit was reached, with no observable drops in the force. But 405°C and 10 min laminates shows initiation of cracks which is evident from drops in the force. As seen here, within the same condition, there seems to a noticeable divergence of the force and displacement of the point of crack initiation. The impurities that were present even before the heat treatment, during heat treatment, and after the reconsolidation, maybe the cause for this deviation. They include defects like voids, foreign bodies, insufficient resin for wetting, internal cracks, and stress concentrations. Including the deviation, a general trend in formation of cracks is still observed.



Figure 5.1 Force-Displacement curves of three samples from 3-point bending of 8-ply UD C/PEEK laminates. Left: Untreated laminates, with no drops in force. Right: Heat treated at 405°C for 10 min, in air, showing drops in forces, indicating initiation of crack

Figure 5.2 shows the force-displacement curves of all the heat-treated laminates, and the untreated laminates. For clear understanding, only one characteristic sample from each condition is added.

With increase in heat treatment condition, the cracks appear faster and at lower forces. At 385°C, except at 90 min, no cracks were formed at other hold times. Even at 90 min, there was only a small drop at around 35N. Also, it was observed only in two specimens. It should be noted that, even though no cracks were observed, the maximum force reached till the end of test is lowered. Also, the experiment becomes very sensitive as the deformation increases, as evident from the fluctuations at higher displacements.

Starting from 405°C and 10 min, every sample showed a drop in the force, indicating the initiation of cracks. The gradual decrease in the point of crack formation conforms a linear trend amidst the deviation seen within the conditions, except at 445° and 90 min. In this laminate, there was already a surface crack, which was formed either during the heat treatment or the reconsolidation. Because of that, no drop was observed at lower forces. The drop at around 30N is the crack formed on the compression side. This is explained further in Section 5.4. Compared to other conditions, all 445°C specimens show a significant deviation in the slope of the curve.



Figure 5.2 Force-displacement curves from three-point bending tests of 8-ply UD C/PEEK laminates, heat treated in air. **Clockwise from top left:** 385°C, 405°C, 445°C, and 425°C

5.3. Crack initiation stresses

Figure 5.3 presents the tensile bending stresses at the point of crack initiation. Bending stresses are calculated as per equation (3).

$$\sigma = \frac{My}{I}; \quad M = \frac{Pl}{4}; \quad I = \frac{lh^3}{12}$$

Where σ is the tensile bending stress, M is the maximum bending moment, y is the vertical distance from neutral axis, I is the moment of inertia. Maximum bending moment is calculated for a simply supported beam, with a concentrated load at the centre through equation, where P is force at the point of crack initiation, 1 is the length of the specimen. Moment of Inertia is calculated for rectangular beam where h is the thickness of the specimen.

As mentioned before, even though no failure occurred at 10, 30, and 60 min at 385° C, the maximum stress tolerated by the sample till the machine limit is lowered. Also, the drop from no failure stresses of 385° C and 10 min (90 MPa) to crack initiation stress of 405° and 10 min (50 MPa) is high. At longer times and temperatures, the failure stresses are more or less close to each other, meaning that cracks initiate at stresses as low as 10 MPa, compared to a low heat treatment condition (405°C, 10 min) where the stress is at 50 MPa.



Figure 5.3 Variation of bending stress at first crack formation, with respect to hold time. Samples heat treated in air.

5.4. Microscopy

Figure 5.4 shows the cross section of the untreated laminate and a laminate heat treated at 385°C and 10 min. No inner ply matrix cracks or other significant defects were seen, and the laminates seem rather unvarying through the length. The three heat treatment conditions that didn't show drops in force-displacement curves shows a similar cross section.



Figure 5.4 Cross section of laminates after 3-point bending of 8-ply UD C/PEEK laminates. Top: Untreated laminate Bottom: Heat treated at 385°C, 10 min in air

The cross section of 405°C and 10 min showed a slight variation than an untreated sample. Figure 5.5 (Top) shows the cross section of the sample, with a small crack magnified. The crack extends to top four plies, and terminates at the 0° ply. There are no delaminations, or further propagation of crack. Figure 5.5 (Bottom) shows the cross section of 425°C, 10 min. This is also similar to 405°C and 10 min. The crack that travelled through 4 plies is clearly visible. But, two other cracks also seem to be visible, that have not propagated deeper. This gives indications about cracks originating on the surface and propagating through the matrix.



Figure 5.5 Cross section of laminates after 3-point bending of 8-ply UD C/PEEK laminates. **Top:** Heat treated at 405°C, 10 min, in air. **Bottom:** Heat treated at 425°C, 10 min in air

Figure 5.6 shows the cross section of laminates heat-treated at 425° C, 90 min. It shows a similar crack to that of 405° C, 10 min, that travels through the top four plies. But, because the crack was stopped the 0° ply, it propagates along the matrix, initiating delamination between the 4th and 5th

ply. But complete delamination is not observed. Similar behaviour is observed in other conditions where load drops in the force-displacement curves were observed.

In all observed cases, the crack initiation and propagation follow a similar pattern. Transverse matrix cracks originate on the surface, and they travel through the laminate and either terminate at the 0° ply, or initiate delamination and propagates along the interphase.



Figure 5.6 Cross section of laminates after 3-point bending of 8-ply UD C/PEEK laminates. Heat treated at 425°C, 90 min, in air

Figure 5.7 shows the cross section of 445°C 90 min. The laminate seems to be severely damaged. This is because, a surface crack was present before the test. So, this crack led to inter-ply matric cracking easily, without requiring any force. The delamination travelled through the entire length, and the exerted force seems to have transmitted through the side of the laminate, and resulted in initiation of crack at the bottom plies.



Figure 5.7 Cross section of laminates after 3-point bending of 8-ply UD C/PEEK laminates. Heat treated at 445°C, 90 min, in air

Because the degradation is maximal at the surface, visualization of the surface damage was also necessary. Figure 5.8 (Left) shows the surface of an untreated sample, and a sample heat treated at 405°C and 90 min, after bending. Compared to the untreated laminate, the heat-treated laminates show a discoloration. The laminate turned darker, which is due to the degradation of the matrix. In addition to this discoloration, the surface of degraded laminates was found to be comparatively rougher than the untreated laminate. This could also be due to the reduction of resin on the surface.

The crack at 405°C and 90 min (shown between the rectangle) runs along the entire specimen width. Because the fibres on top plies are transverse to the bending direction, the failure seems to be due to matrix cracking. Wider cracks, and cracks over the whole width are observed at higher temperatures and longer hold times. At lower temperatures and hold times, for example at 405°C and 10 min, where drops in force-displacement were seen, large cracks were not observed on the surface. Also, because the surface was not polished, it becomes difficult to distinguish between smaller cracks and scratches.



Figure 5.8 Microscopy of the surface of laminates subjected to 3-point bending. Left: Untreated laminate, showing no surface crack, and resin filled plies. Right: Heat treated at 405°C, 90 min, showing the surface crack along the entire width, and resin-less plies

5.5. In vacuum environment

DSC analysis showed that heat treatment in presence of oxygen led to accelerated degradation on the surface. From 3-point bending that cracks always initiated on the surface. So, to observe the bending behaviour of a specimen conditioned in an airless environment, one control experiment, heat treated at 405°C and 10 min in vacuum, is conducted. An untreated laminate is vacuum bagged, and heat treated in the convection oven. The procedure of vacuum-bagging is added in Appendix-F. The heat treated laminates are then reconsolidated in the press, with the same cycle as explained in Section 3.3. Samples are cut from reconsolidated laminates and are subjected to 3-point bending.

Figure 5.9 shows a representative force-displacement curve of the vacuum treated laminate, in comparison to that of air treated laminate. Unlike the air treated laminate, the vacuum treated laminate did not show any load drop till the end of experiment. But the maximum stress (force) reached was similar, with 3.4 MPa (50 N) in both cases. Also, a change in deformation is observed. Microscopy of bending of vacuum treated laminates (Figure 5.10) shows no observable cracks, compared to air treated laminates.



Figure 5.9 Force-displacement curves from three-point bending tests of 8-ply UD C/PEEK laminates, heat treated at 405°C, 10 min, in air and vacuum. Force-displacement curve of an untreated laminate is also added



Figure 5.10 Cross section of laminates after 3-point bending of 8-ply UD C/PEEK laminates, heat treated at 405°C, 10 min. Top: In vacuum. Bottom: In air

6.1. Outline

This chapter deals with the inferences made from the obtained results. Both DSC results and the 3-point bending results are discussed, where the significance of results, and how they conform to the objectives and research questions are explained. Hypotheses are put forward for discrepancies and unclear behaviour. The limitations of the results are mentioned.

6.2. Thermal Analysis

6.2.1. Reduction of crystallinity

The 8-ply UD C/PEEK laminates were subjected to heat treatment, in a convection oven, at different time and temperatures scales. Thermal analysis showed reduction of overall crystallinity and peak crystallisation temperature. This can be due to the degradation of matrix, resulting in reduction of its ability to crystallise. Reduction in the area of the cooling crystallisation curves, accompanied by shift of peaks, signified a reduction in the crystallinity of PEEK with increasing heat treatment conditions. At 425°C, 90 min and 445°C 90 min, no crystallinity was observed. At these conditions, the mobility of linear chains has decreased to an extent where the material is unable to form ordered regions at all. Comparing to the crystallinity of an untreated laminate (32%), at 385°C, all investigated hold times show only little degradation (25% at 90 min). This means that, at a constant airflow, longer hold times at lower temperatures doesn't lead to severe degradation.

It should be clear that the untreated laminate is not a completely undegraded laminate, because of the heat treatment (385°C, 20 min) it underwent during press consolidation. Although the presence of oxygen in the press is low during this cycle, compared to the convection oven, there still seems to be some degradation, because oxygen is not the only cause for degradation. It might be related to other factors, like the cooling rate during the prepreg preparation, impurities, and changes during polymerization. But generally, previous heat treatment cycles contribute to degradation. This impact should be considered during second step processing.

The contour plots showing the retention of crystallinity over different heat treatment time and temperature, can be used as a processing guideline. It gives the amount of crystallinity that can be obtained when processed at any temperature and time, in air, within the range. But this plot is limited to 8-ply UD C/PEEK laminates, as thicker or thinner laminates respond to degradation differently, in air.

6.2.2. Effect of oxygen and temperature

Through thickness analysis showed that the degradation of individual plies is not similar when treated in air. The top plies degraded more than the middle plies. The lack of this variation in nitrogen showed that this variation is due to oxygen present on the surface. So, the top ply degradation can be considered as the effect of temperature and oxygen, while the degradation in middle plies is only due to temperature, as it assumed to have been devoid of oxygen.

Having established that a variation is observed between top and middle plies, this variation is not constant in all temperatures. At 385°C for all hold times, the variation is low. This holds till 405°C and 30 min. After this, a divergence in the variation is observed, (See Figure 4.7) the top plies start degrading faster than the middle plies. So, at higher temperatures, when combined with oxygen, the degradation is faster than at lower temperatures.

Also, since only the surface of the laminate is exposed to oxygen, both the middle and bottom part should show equal degradation (having been shielded from oxygen), which is not the case here. The bottom part has degraded more than the middle part (See Figure 4.6). This is because during heat treatment, the laminate deconsolidates and deforms, owing to the large surface area (Figure 6.1), and in some cases, the PI film also detached. This could have led to the exposure of air, and thus to a higher degradation on the bottom part. This leaves the variation in the bottom part uncertain, as it is completely unclear when and how the material deforms inside the oven, so for the rest of investigation, the bottom part is not taken into consideration.



Figure 6.1 Deformation of laminates due to deconsolidation during heat treatment

6.2.2.1 Diffusion of oxygen

In an air environment, the through thickness analysis showed a variation in peak crystallisation temperature and crystallinity, through thickness of the laminates. The top plies were more degraded than the middle plies. The degradation on the top plies is the effect of temperature and oxygen, while the degradation in middle plies is the effect of temperature. But, if diffusion of oxygen through the laminate, would mean the middle plies cannot be considered as an oxygen free area, and thus, they cannot be the representative of degradation due to temperature.

When treated in nitrogen, the laminates showed lower degradation than the middle plies of air treated samples. This means that some diffusion of oxygen has taken place. But the depth of this diffusion is unclear because the samples of middle plies consisted of middle four plies, and the bottom part was also exposed to air due to deformation during heat treatment. The depth of diffusion cannot be explained with certainty. At longer times, the variation between nitrogen treated laminates and middle plies of air treated laminates increases, further confirming that diffusion takes place.

The degradation of matrix was characterized by a progressive branching of polymer chains by oxygen which resulted in crosslinking. But degradation was still observed in nitrogen environment at higher temperatures. So, it is clear that other mechanisms are involved in degradation. Other than confirming diffusion of oxygen, the nitrogen experiments showed that at 385°C, little to no degradation is observed. At 385°C, and without presence of oxygen, the material can be kept as long as 90 min and still no degradation occurs.

When treated in nitrogen, it seems like the crystallinity is retained over 70% of an untreated laminate even at 445°C for 60 min, compared to air treated when only half of that is retained. Processing in nitrogen, or more clearly, in an airless environment, controls degradation considerably. This can be taken into consideration.

6.2.3. Application of Arrhenius equation to activation energies

The main purpose of the kinetics study is to observe the rate at which degradation progresses over time and temperature for laminates treated in air and nitrogen, and to arrive at a single quantity to express the rate of degradation, through Arrhenius plots. Because of the crosslinking occurring at high temperature and high hold time in melt, the mobility of chains is reduced, the number of nucleation sites for crystallisation and the rate at which the existing crystals grows is reduced. This results in a reduced rate of crystallisation, which can also be taken as a measure of degradation.

The Arrhenius plot gives information on two aspects. The activation energy provides a broader view on how degradation proceeds in different environments. The slope of the plot gives the activation energies. The higher the activation energy, the harder it will be for reactions to occurs, and thus a lower rate of degradation. Evidently, nitrogen treated samples have higher activation energies than air treated samples.

But the activation energy of pure PEEK in air, is higher than activation energy of a C/PEEK laminate in air and nitrogen, meaning that the rate of degradation is lower. This is somewhat surprising because considering the absence of fibres, and the smaller thickness of PEEK films, pure PEEK is easily susceptible to degradation and a lower activation energy would make more sense. Although few other studies have shown different activation energies for pure PEEK.

This variation can be explained by the second aspect of the plot. The activation energies (slopes) are dependent on temperature (T) and rate of degradation (K). So, the values are highly limited by that. If the material has the same rate constant for all temperatures, the plot would be flat, leading to lower activation energies, whereas rate constants that are sensitive to temperatures, will have higher activation energies. This is the case for pure PEEK. At lower temperatures, the rate of degradation was very low, while the rate of degradation at higher temperatures was very high. The lower rate constant normalized the other values, thus leading to higher activation energies. The same goes for the laminates treated in nitrogen. At 385°C, the degradation is almost nil, whereas at higher temperatures, there is a sizeable degradation. This leads to an overall higher activation energies were obtained.

But in case of air treated samples, the rate constant is less sensitive, meaning that, changes in temperature have little effect on the rate of degradation. The degradation rate is higher in all temperatures, leading to a flatter curve, and thus lower activation energies. So, activation energies are limited by the conditions chosen. They only show the progress of degradation over the selected time and temperature conditions.

When understanding and comparing activation energies of different conditions, it should be noted that, the values are sensitive to the conditions chosen, and cannot be generically applied to other materials and conditions.

6.3. Mechanical performance

Crack initiation occurs at lower stresses with increasing heat-treatment conditions, in air. But a difference between the DSC and bending results was observed. The drop from no failure stresses of an untreated laminate to first crack initiation stress at 405°C and 10 min is high. While crystallinity is retained over 85% of an untreated laminate at 405°C and 10 min, only 40% is retained for mechanical property. This difference could be due to two reasons. One, the laminates

were subjected to a third heat treatment after DSC and before bending, to reconsolidate the laminate. That could have added to degradation. Two, the consolidation quality of the reconsolidated laminate could have been reduced (voids, impurities, etc.) due to degradation. This will not show up in DSC analysis, and hence the difference.

The microscopy showed that crack initiation occurred on the surface for all laminates. Though the surface degradation is higher than the overall degradation, at 405°C and 10 min, the top ply degradation is still comparable to the overall degradation. So, that is not the reason for this sudden drop.

A slight change in deformation mechanism for 445°C was observed. As seen from DSC, the crystallinity of laminates is lower at 445°C compared to other temperatures, which indicated the material becoming more brittle. But the force-displacement showed a change in ductile behaviour, which is unexpected. This is seen for all four hold times. Although it is hard to conclude the nature of deformation from only very little displacement. For example, at 445°C and 60 minutes, the experiment was aborted even before 1 mm of displacement. Still, this behaviour is unclear and needs further investigation.

Also, within the same heat treatment condition, a noticeable divergence in the point of crack initiation is observed. This may be due to internal defects. While this deviation was not very high, it should be noted that only three specimens were tested per condition.

The bending of vacuum treated samples showed two variations from that of an air treated sample. No cracks were observed and a change in deformation mechanism. No crack initiation could be due to the absence of oxygen on the surface. Because, while both air and vacuum treated samples reached the same maximum stress, the presence of oxygen in air treated laminate may have reduced the consolidation quality or served as the source of crack initiation on the surface. Although, this cannot be conclusively said with the results from one condition.

DSC of samples treated in a nitrogen environment (airless environment) at 405°C and 10 minutes retained crystallinity similar to that of an untreated laminate. But it is unexpected and unclear for the vacuum treated samples (airless environment) show a more ductile deformation than an untreated laminate. Considering no degradation occurred, the only difference between vacuum treated and untreated laminates is the heat treatment in vacuum pressure and the reconsolidation heat treatment. This could have led to this variation of deformation. But, again, this cannot be conclusively said with the results from one condition, and needs further investigation.

Through this project, thermo-oxidative degradation behaviour of heat-treated 8-ply UD C/PEEK composite laminates is characterized. Investigation is undertaken at four temperatures (385, 405, 425, and 445°C) and four hold times (10, 30, 60, and 90 minutes) in an oxygen environment. This section summarizes the major findings and conclusions, followed by a set of recommendations for further research.

The polymer degradation due to heat treatment is quantified by the reduction in crystallinity content. The crystallinity reduces from 32% for an untreated laminate to 28% for the lowest heat treatment condition (385°C, 10 minutes). From there, a steady reduction is observed, with 15% at 425°C and 60 minutes, and zero crystallinity for 425°C, 90 minutes and 445°C 90 minutes. The press consolidation cycle before the heat treatment, where the plies were heat-treated to 385°C for 20 minutes in a limited supply of air, also contributes to a little degradation. A single ply C/PEEK has 35% crystallinity, whereas the untreated 8-ply laminate has 32%. A contour plot for polymer property reduction based on crystallinity served as a processing guideline for C/PEEK laminates.

Temperature and oxygen together contribute to degradation. Thermal analysis through the thickness of air treated laminates and thermal analysis of nitrogen treated samples provided a way to understand the contribution of these two factors to degradation. Surface plies shows more accelerated degradation than the inner plies, and this effect is not observed in a nitrogen environment. At 385°C, in air, through thickness difference is lower compared to 425°C and 445°C. At 425°C and 445°C, the top ply degrades significantly more than the inner plies. So, in an oxygen environment, polymer degrades faster at higher temperatures than at lower temperatures. Though the inner plies are not in direct contact of air, they still showed a higher degradation than nitrogen treated samples, showing that diffusion of oxygen has taken place. This difference increases with longer times. In nitrogen, at 385°C, only little degradation is observed, whereas even 405°C shows an increased degradation. So, ideal processing temperature and conditions would then be at 385°C in an airless environment. The rate of degradation in different environment and temperature is characterized by computation of activation energies. The air treated laminates showed an activation energy of 126 kJ/mol, whereas, nitrogen treated laminates has 193 kJ/mol.

The 3-point bending tests are performed to observe matrix failure. Degradation led to initiation of cracks, at lower stresses with increasing heat-treatment conditions. But a difference between the DSC and bending results were observed. Crack initiation stresses at 405°C, 10 minutes is found to show a steep drop from the no failure stress of untreated laminates.

While this project provided useful information regarding the degradation of multi-layered UD C/PEEK laminates, both on industrial and research point of view, it also raised several questions, and there are still a lot more unanswered questions, which couldn't be solved in the timespan. They require further research, and some recommendations on various aspects of further study are as follows.

• The through thickness analysis provided a way to observe the various rates of degradation of different parts of the laminate. For this project, degradation of an 8-ply laminate, divided into three parts was investigated. A study on thicker laminates, and on individual plies could give more information, on the degradation profile.

- Through thickness analysis also showed a diffusion of oxygen taking place. That effect was not investigated in detail. A ply by ply analysis could show how deep the diffusion has taken place with respect to hold time.
- The laminates were subjected to a third heat-treatment (reconsolidation) before bending tests. Steps could be taken to avoid it, by performing heat-treatments directly before forming into final shape.
- Because of the in-depth thermal analysis, there was not enough time to investigate the effect of degradation on mechanical properties in detail. More mechanical characterization methods like, impact, hardness tests could be done.
- Bending on vacuum treated laminates seemed to show less property decline compared to air treated laminates. Further experiments on laminates treated in airless environment could prove to be useful to identify the effect of oxygen on crack initiation and propagation.

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9.1. Appendix-A: Selection of C/PEEK prepreg

C/PEEK prepregs were delivered as both unidirectional tape (UD tape) and woven fabrics (WF prepreg). Both has its advantages, but to select a material for investigation, preliminary experiments were conducted during the start of the project. 8-ply laminates are manufactured from both types, and subjected to heat treatment, and thermal analysis. This section follows those experiments, results and its analysis.

9.1.1. Laminate manufacturing

Table 9.1 shows the laminate manufacturing setup. The plies are stacked in the cross-ply orientation. The thickness of single ply woven fabric is approximately twice that of UD tape, and to have laminates of similar thickness, WF prepregs have 4 plies, and UD tape has 8 plies. The stacked plies are consolidated into two separate laminates, through press consolidation, with the consolidation conditions, as follows.

- Pressure: 15 bars
- Processing Temperature: 385°C
- Consolidation time at maximum pressure: 10 min
- Obtained Thickness 1.2±0.1 mm.

The consolidation conditions are similar to the one explained in Section 3.2.2. The maximum pressure and the time held at maximum pressure is changed, because both UD tape and WF prepreg were consolidated in a single cycle, by placing them on top of each other, separated by caul sheets. The industry standard processing pressure is 10 bars, whereas for UD tape, it is 20 bars. 15 bars was taken as a compromise.

Type of material	No. of plies	Lay-up
UD Tape	8	[0/90] _{2s}
WF Prepreg	4	[(0,90)] _{2s}

 Table 9.1 Laminate manufacturing setup for two prepregs.

9.1.2. Heat treatment

The manufactured laminates (UD tape and WF prepreg) are subjected to two heat treatment conditions, one low temperature condition $(385^{\circ}C, 10 \text{ min})$, and one high temperature condition $(445^{\circ}C, 10 \text{ min})$. An Infrared (IR) oven is used for heat treatment. The heat treatment method, is shown in Figure 9.1. The laminate is placed over a PI film, and suspended in between two IR heaters, so that heat is applied directly on the top, and through the PI film on the bottom. An atmospheric flow of air was available. The laminates are heated to the required temperatures and times, and immediately transferred to the press, and press formed again, at a pressure of 30 bars, for 1 min, at a temperature of $240^{\circ}C$ and cooled to room temperature.



Figure 9.1 Infrared heating method for the laminate, placed between two heaters, in atmospheric condition

So, this laminate undergoes only two heat treatments as a whole, unlike the procedure used in the main investigation, where after heat treatment in oven, and thermal analysis, the material is heat-treated again for reconsolidation. That step is not required here, as the material is reconsolidated right after heat treatment, before letting it cool down. This is different in the main investigation because of the practical difficulties of the IR oven. The IR oven is only capable of accepting hold times up to 15 min, and the operation of IR oven needed expert technicians. Also, the IR oven is accompanied by the press and the availability of press was very difficult. For these reasons, the main investigation, where 16 heat treatment conditions were needed, is switched to a convection oven, which is more practical and easier to operate.

9.1.3. Thermal analysis (DSC)

9.1.3.1 Overall degradation

The DSC experimental cycle is provided in Section 3.4. Figure 9.2 shows the cooling curves of the UD tape and the WF prepreg laminate, at the two heat treatment conditions. At 445°C, both UD tape and WF prepreg showed a reduction in areas of crystallisation curves, and a shift in the curve towards low temperatures. But comparing UD tape and WF prepreg, the 385°C and 10 min shows a slightly elevated curve for UD tape. This doesn't necessarily be due to degradation. The could be due to the overall resin content and fibre arrangement between the two types. But even though UD tape has an elevated curve at 385°C, the reduction at 445°C is higher than it did for WF prepreg.



Figure 9.2 DSC crystallisation trace of C/PEEK laminate, heat treated at 385°C and 445°C, for 10 minutes, in air. Left: 8-ply UD Tape. Right: 4-ply woven fabric

Figure 9.3 shows the crystallinity content of the two types at the two heat treatment conditions. As explained from the cooling curves, the crystallinity at 385°C for UD tape is higher than Woven Fabric. At 445°C, the crystallinity is lower for UD tape. This means that, the thermal degradation is higher in UD tape than at WF prepreg.



Figure 9.3 Variation of crystallinity content of heat treated C/PEEK laminates, in air

9.1.3.2 Through Thickness Degradation

One of the main objectives is to look at the development of degradation through thickness of the laminate, especially because the experiments are conducted in oxygen environment. To observe how degradation varied for both types at 445°C, laminates are slice into three parts. The method of slicing laminates for UD tape is discussed in Section 4.3. Because WF prepreg had only four plies, the top part contained only the first ply, and middle part contained the middle two plies, and the bottom part contained the last ply. The deconsolidation during the heat-treatment is higher in case of UD tape, which made the separation of plies easy. But in case of woven fabric, the deconsolidation was lower, the separation of plies was difficult, and it could not be separated with utmost reliability.

Figure 9.4 shows the cooling curves of the top, middle and bottom part of the UD tape and WF prepreg laminate, heat treated at 445°C for 10 min, in air. The UD tape shows a significant difference between top and middle part. But the difference in WF laminate is not really noticeable in the curves.



Figure 9.4 DSC Crystallisation trace of top, middle, and bottom part of C/PEEK laminate, heat treated at 445°C, for 10 min in air. Left: 8-ply UD Tape. Right: 4-ply Woven Fabric

Figure 9.5 shows the crystallinity top, middle and bottom part of the UD tape and WF prepreg laminate, heat treated at 445°C for 10 min, in air. As seen here, the crystallinity is reduced from 30% to 20% between the top and middle ply for UD Tape, which is lower than woven fabric. This means that, in UD tape, the outer plies degrade much faster than the inner plies. Presence of oxygen in the surface could be the reason for this accelerated degradation on the surface. But in Woven Fabric, this difference is comparatively lower. This means that oxygen affects degradation to a lower account than UD tape, and the degradation we see is mainly due to temperature. This could again be due to the overall resin content and fibre orientation that reduces the chemical reactions between oxygen and the PEEK molecules. Essentially, UD laminate degrades more than the woven fabric laminate, and UD laminate is more affected by oxygen on the surface than woven fabric. It should be noted that, the IR heaters were on both top and bottom of the laminate. Because of the PI film on the bottom, lower degradation is seen on the bottom than the top part.



Figure 9.5 Variation of crystallinity through thickness of UD tape and WF prepreg C/PEEK laminate, heat treated at 445°C for 10 min in air

In conclusion, because of following the reasons, UD tape is selected as the chosen prepreg for investigation.

- UD laminate degrades more than the woven fabric laminate, and UD laminate is more affected by oxygen on the surface than woven fabric.
- UD laminates are easy to separate ply by ply, for through thickness analysis.
- 3-point bending can show better matrix related failure in UD laminates than in woven fabric laminates because of 0/90 fibre weave.

9.2. Appendix-B: Properties of unidirectional tape C/PEEK prepreg

Table 9.2 Mechanical properties of unidirectional continuous fibre reinforced tape carbon PEEK prepre	eg. Produced
by TenCate Composites, specified as, Cetex TC1200 PEEK AS-4 [4].	

Mechanical Property	Result
Tensile strength (0°) (MPa)	2280
Tensile modulus (GPa)	130
Tensile strength (90°) (MPa)	86
Tensile modulus (90°) (GPa)	10
Compressive strength (MPa)	1300
Compressive modulus (GPa)	121
Interlaminar Shear strength (0°/90°) (MPa)	94

 Table 9.3 Thermal properties of unidirectional continuous fibre reinforced tape carbon PEEK prepreg. Produced by

 TenCate Composites, specified as, Cetex TC1200 PEEK AS-4 [4].

Thermal Property	Result
Resin content (by weight)	34%
Glass transition temperature (°C)	143
Melting temperature (°C)	343
Latent heat of fusion for 100% crystalline resin (J/g)	130
Service temperatures (°C)	120
Typical processing temperatures (°C)	360-400

9.3. Appendix-C: Study of mechanical testing methods for C/PEEK laminates

Before arriving into 3-point bending tests, two other methods were briefly investigated, and the results and conclusions are provided below.

9.3.1. Impact tests

An impact test could estimate the energy absorbed by the matrix before failure. The variation in this energy could be measure of degradation. The thickness of the manufactured laminates was found to be too low for standard drop weight impact testers that were available at the work place. So, initially a few simple impact testing methods were tested to qualitatively assess surface damage.

- Low-weight (5-100 g) steel balls are dropped from a height of 100 cm.
- Manual wedge hammering is performed.
- Manual Charpy Impact testers

When microscopy is performed on these laminates, no significant damage whatsoever was observed in case of the ball impact testing. With hammer, microcracking, fibre breakage, and crack growth is observed for both 385°C and 445°C laminates. The crack growth at 445°C was found to continue over many fibres before terminating, whereas, for 385°C samples, it stopped within a few fibres.

Charpy impact testing involved striking a specimen with a controlled weight pendulum swung from a set height. The specimen is supported at its two ends on an anvil and struck on the opposite face by the pendulum. The pendulum swings through during the test, the height of the swing being a measure of the amount of energy absorbed in fracturing the specimen. Laminates were fractured through technique. But it was found that the measured toughness seemed to be highly unreliable, and gave inconclusive results. The values had a large deviation, and no significant difference between 385°C and 445°C specimens were observed. So, this method is also eliminated.

9.3.2. Microhardness tests

Indentation hardness measures the resistance of a sample to material deformation due to a constant compression load from a sharp object. While hardness is a quantity that is dependent on properties like ductility, viscosity, and stiffness, all of which are expected to vary during degradation, hardness can be a good measure for observing mechanical property change due to degradation.

Hardness can be implemented for woven fabric laminate, because they have resin pockets between the $0^{\circ}/90^{\circ}$ fibre bundles, where indentations can be made. But the UD tape doesn't contain such resin pockets. Any hardness measured would be a value that combines hardness of both resin and fibres, which is not accurate measure of degradation of polymer. So, hardness tests could not be implemented for UD laminates.

But microhardness tests were conducted on Woven Fabric laminates. Through this test, static indentations of load 10 gf were made on resin pockets found between the fibre bundles on the cross-section of heat treated laminates. Vickers hardness value (HV) is calculated from the dimensions of the indent. Embedded and polished samples are used.

Resin pockets were found on the top, middle and bottom of the laminates, both at 445°C and 385°C, and indentations were made. 7-10 indentations were made for each part, based on the existing resin pocket areas. Figure 9.6 shows few of the indentations made on the top, middle and bottom part of the woven fabric laminate. Because, the indentations were made directly on the resin, the values denote only the changes in the resin property. Figure 9.7 shows the observed hardness values at different parts of the laminate, for two heat treatment conditions.



Figure 9.6 Micro indentations made on 4-ply woven fabric C/PEEK laminate, heat treated at 445°C for 10 min, in air. Left: Top part Middle: Middle part Left: Bottom part



Figure 9.7 Measured Vickers Hardness values, from micro indentation of 4-ply woven fabric C/PEEK laminate, heat treated at 385°C and 445°C for 10 min in air, with standard deviations

As seen here, the 385°C and 10 min laminate showed no difference through thickness. But there is a noticeable decrease in the hardness on the top part at 445°C. This is due to the reduction in the crystallinity. The hardness values conform to the decrease in crystallinity content.

9.4. Appendix-D: Peak crystallisation temperatures, through the thickness of UD C/PEEK laminates

DSC analysis were performed through thickness of the heat-treated laminates, in air, as explained in Section 4.3. The peak crystallisation temperatures at the three parts (top, middle, and bottom) of the laminates seem to vary, with changing temperature and holding times. This means that degradation occurs at different rate at different parts of the laminate. Figure 9.8 shows the evolution of peak crystallisation at the top, middle and bottom parts of the laminate, plotted for different temperatures and hold times.



Figure 9.8 Variation of peak crystallisation temperature through thickness of 8-ply UD C/PEEK laminate, as a function of heat treatment hold time, in air. Clockwise from top left: 385°C, 405°C, 445°C, and 425°C. No peaks observed at 90 min for 425 °C and 445°C, and only middle and bottom part had peaks at 60 min

In all temperatures and hold times, the top part shows lower peak crystallisation temperatures than the middle and bottom part. This difference is lower at 385°C and 405°C, and evidently higher at 425°c and 445°C. No crystallisation curves were observed on all parts of the laminate for 425°C, 90 min and 445°C 90 min. Whereas, at 425°C, 60 min and 445°C, 60 min, crystallisation curves were observed only for middle and bottom part. Evolution of peak crystallisation temperature, and consequently degradation over the thickness of 1.1 mm of the laminates, can be expressed alternatively, as shown in Figure 9.9. The increased effect of oxygen at higher temperatures is clearly visible through a strong drop between the top and the middle part. This starts at 405°C and 30 min, and maintains till no crystallisation is observed at 445°C, and 60 min.



Figure 9.9 Development of peak crystallisation temperatures of heat treated 8-ply UD C/PEEK laminate, as function of thickness of the laminates. 0 to 0.275mm representing the top part, 0.275 to 0.825mm, representing the middle part, and 0.825 to 1.1mm, representing the bottom part. No peaks observed at 90 min for 425°C and 445°C, and no peaks at top part at 60 min

9.5. Appendix-E: Kinetic analysis of top and middle part of heat-treated laminate, in air

Crystallisation kinetics of the top and middle part of heat treated 8-ply UD C/PEEK laminates, in air, is expressed through crystallisation halftime $(t_{1/2})$. $t_{1/2}$ is the time taken to complete 50% crystallisation. So, shorter the half time, the faster is the crystallisation rate. The half time is calculated from the crystallisation curve. (See Figure 3.5 (Left)). The evolution of crystallisation on the top part of the laminates over time, for different heat treatment temperatures and hold times is shown in Figure 9.10. The crystallisation of middle part is shown in Figure 9.11.



Figure 9.10 Development of relative crystallinity with time for the top part of 8-ply UD C/PEEK laminates, heat treated for different heat treatment hold times. **Clockwise from top left:** Heat treated at 385°C, 405°C, 445°C, and 425°C



Figure 9.11 Development of relative crystallinity with time for the middle part of 8-ply UD C/PEEK laminates, heat treated for different heat treatment hold times. Clockwise from top left: Heat treated at 385°C, 405°C, 445°C, and 425°C



Figure 9.12 Crystallisation halftimes of heat treated UD C/PEEK laminates, as function of hold times, in air, with linear regressions intercepted to untreated laminate. Left: Top part. Right: Middle part

The crystallisation half times of top and middle part, computed for each heat treatment condition, is shown in Figure 9.12. Linear regression lines are added, and intercepted to the values of an untreated laminate (19.25 seconds). It should be noted that for top part, 425°C and 445°C only has two values, since no crystallisation was observed at 60 and 90 min. Also, for 445°C, the points are not very linear, as it is for 385°C. Because of this, the linear regression is very high.

For middle part, the 445°C and 60 min does not conform well with the linear increase in the crystallisation. So, the linear regression of 445°C is also high, which led to a lower rate of degradation. Table 9.4 shows the evaluation of Arrhenius parameters for the top and middle part of 8-ply UD C/PEEK laminate. The slopes of the linear regressions of crystallisation halftimes gives the rate at which degradation proceeds for a given temperature. Plotting 1/T against ln(k) gives the Arrhenius plot, as shown in Figure 9.13, and Table 9.5 shows the evaluated activation energies.

T (Celsius)	1000/T (Kelvin ⁻¹)	Linear regression slope (k)		ln((k)
		Тор	Middle	Тор	Middle
385	0.00152	0.3115	0.0978	-1.16636	-2.3238
405	0.001475	0.9186	0.6019	-0.0849	-0.5077
425	0.001433	1.5674	0.9491	0.449418	-0.0522
445	0.001393	2.1899	1.1367	0.783856	0.12813

Table 9.4 Evaluation of Arrhenius parameters for the top and middle part of 8-ply UD C/PEEK laminates.



Figure 9.13 Arrhenius plot, showing inverse of temperature against logarithm of kinetic constant, for top and middle part of 8-ply UD C/PEEK three conditions

The rate of degradation is different for the top and middle part. Because of the complete exposure of oxygen on the top part, the rate of degradation is faster, and thus has a lower activation energy. And because of the diffusion of oxygen through the laminate, the activation energy of middle part is lower than nitrogen treated laminate (Section 4.4). As seen from the Figure 9.13, the linear regression of the middle part is higher than the top part. The limitations and further interpretations of the activation energies are explained in Section 4.5.

ConditionActivation Energy (E) (kJ/mol)Top part of 8-ply C/PEEK, in air126Middle part of 8-ply C/PEEK, in air155

 Table 9.5 Activation energies of top and middle part of 8-ply UD C/PEEK laminates.

9.6. Appendix-F: Vacuum bagging of 8-ply UD C/PEEK laminate for threepoint bending

To observe the bending of 8-ply laminates, heat-treated in vacuum, an untreated laminate (150 x 150 mm) was vacuum bagged and heated to 405°C and held for 10minutes, as this condition showed initiation of cracks in earlier experiments (Section 5.3). The laminate was placed in between two Kapton (PI) films, on top of a stainless-steel plate, which in turn is placed on top of an aluminium plate. It is covered by two layers of breather fabric. Thermocouples are attached inside, and closed with PI film, as shown in Figure 9.14. A vacuum pressure of approximately 970 mbar (atm pressure 1 bar; abs pressure 30 mbar) is applied through the vacuum inlet, and it is heated in the convection oven.



Figure 9.14 Vacuum bagging setup

The heating rate Figure 9.15 of the laminate inside the oven was very low compared to both air and nitrogen treatment. It took nearly 25 minutes to reach melting point, and 45 minutes to reach 405°C. The laminate was held for 10 minutes once it reached 405°C. The laminate was then taken out of the oven and allowed to cool to room temperature, in vacuum.



Figure 9.15 Heating rate of the laminate, inside the vacuum bag, time taken for the surface to reach 405°C