# Characterisation of Crystallinity at the Interface of Ultrasonically Welded Carbon Fibre PPS Joints

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## Abstract

The influence of ultrasonic welding on the crystallinity degree at the welding interface of carbon fibre reinforced polyphenylene sulphide (CF/PPS) joints was investigated. Two sets of welding force and vibration amplitude were used, (1000N, 86.2µm) and (300N, 52.8µm), representing short and long welding times, respectively. The evolution of temperature with time at the centre of the joint overlap was recorded using thermocouples while the crystallinity degree of PPS was measured using differential scanning calorimetry (DSC). The cooling rate dependency of crystallinity was determined through fast scanning calorimetry (FSC) measurements. It was found that high force and high amplitude resulted in faster cooling rates and predominantly amorphous PPS, while low force and low amplitude resulted in slower cooling rates and yielded PPS of moderate crystallinity. It is suggested that the capability of PPS to crystallize despite the very fast cooling rates could be attributed to strain-induced crystallization during the welding process.

## 1 Introduction

Aerospace industry requirements of lightweight structures and cost-driven manufacturing have created the need for fast and cost-efficient joining processes. Welding of thermoplastic composites is a joining method with fast production cycles and minimal labour work. One of the most promising welding techniques is ultrasonic welding (USW), which is classified as a friction welding technique, converting high frequency (typically 20-40 kHz) and low amplitude mechanical vibrations into heat via friction. The produced vibrations are transverse to the weld interface and cause surface and intermolecular friction in the materials to be welded, which result in heat generation. In order to concentrate the heat generation between the adherends, energy directors (ED), which are made of the same polymer as the adherends' matrix, are placed at the welding interface [1] - [3]. The lower compressive stiffness of the energy directors compared to the composite adherends result in higher cyclic strains in the EDs during the welding process which, in turn, promote heat generation [2] - [4]. Ultrasonic welding is a very fast process, it does not require a foreign material in the interface and it produces excellent quality joints [1].

Most of the efforts so far, have been directed at investigating the heating mechanisms and the factors affecting the ultrasonic welding process and the weld strength. Benatar and Gutowski [5] studied the heating mechanism in ultrasonic welding of carbon fibre PEEK composites, dividing the mechanism into five steps, (i) mechanics and vibration, (ii) viscoelastic heating, (iii) heat transfer, (iv) flow and wetting, and (v) intermolecular diffusion. The heating and bonding mechanisms in ultrasonic welding of neat polystyrene were investigated and it was suggested that the most rapid heating occurred at the proximity of the welding interface [6]. Furthermore Levy et al. [7] showed that the heat initiated mainly due to friction dissipation between the energy director and the substrate in ultrasonic welding of CF/PEI composites. Amplitude of vibration and hold time were recognised as key factors affecting the weld performance [8] - [10], while higher force resulted in shorter welding times and lower welding energies [11]. Villegas demonstrated that power and displacement data can be related to weld strength and can be used for the in-situ monitoring of the welding process. Furthermore, increasing welding force and increasing vibration amplitude were found to significantly shorten the vibration times [1] [2].

The cycle times of the ultrasonic welding process are extremely fast (only a few seconds), hence, the cooling rates at the welding interface during ultrasonic welding are expected to be very high. Considering that the high-performance thermoplastics such as PEEK, PEKK and PPS are semi-crystalline polymers, the speed of the ultrasonic welding process could have an effect on the properties of the polymer at the welding interface. In particular, when such semi-crystalline polymers are cooled very fast from the melt down to room temperature they can become predominantly amorphous or reach low levels of crystallinity degree, as it has already been reported [12] - [18]. Kenny and Maffezzoli [13] reported that quenching the PPS matrix system at cooling rates above 1.67 °C/s can yield an amorphous structure, while in a later study [14] the same authors reported that PPS was quenched at a cooling rate of 6.67 °C/s. Cebe and Chung [19] observed that cooling rates of 3.3 °C/s did not yield an amorphous PPS since the polymer was still able to crystallize during cooling. Furthermore, Ferrara et al. [20] suggested a dual-mechanism for PPS melt crystallization which resulted in a minimum crystallinity of 8% independently of the processing conditions. In recent years, the crystallization of different resin systems at very fast

cooling rates has been investigated by many researchers using fast scanning calorimetry [17] [18] [21] - [29]. A study on the crystallization of PPS using fast scanning calorimetry (FSC) revealed that PPS could not crystallize at cooling rates equal or higher than 20 °C/s [17]. Similarly, Furushima et al [28] investigated the crystallization and melting kinetics of PPS at very high scanning rates, and found that a 30 °C/s cooling rate was sufficient to yield amorphous PPS. It is worth to mention that the cooling rates required to quench PPS were found to be lower in the older studies (at 80s and 90s) compared to the ones reported nowadays. Possibly, the different grades of PPS available nowadays are capable of crystallizing faster. Furthermore, the limited capabilities of the thermal testing techniques used in the older studies did not allow for experiments to be conducted at temperatures close to the actual temperature of maximum crystallization rate. Regarding other relevant semi-crystalline polymers, cooling rates higher than 100 °C/s resulted in a neat PEEK matrix with very low crystallinity levels, as shown in separate studies [16] [21] [30].

It has been well studied and documented that the semi-crystalline nature of thermoplastic matrix systems can influence properties such as stiffness, shear strength, fibre/matrix interfacial strength, fracture toughness and chemical resistance. Talbott et al. [16] studied the mechanical properties of PEEK and found that decreasing crystallinity led to a lower elastic modulus, lower tensile strength and lower shear strength for neat PEEK. Similar observations on the beneficial effect of crystallinity on the tensile properties of PPS and its composites have been made in past studies [17] [31]. Crystallinity has also been reported to have a positive influence on the interfacial shear strength of carbon fibre reinforced PPS and carbon fibre reinforced PEEK [14] [32]. On the contrary, a decrease in crystallinity has been demonstrated to cause an increase in Mode-I interlaminar fracture toughness of PEEK and PPS composites [16] [33] [34]. Along similar lines, in a previous study it was suggested that increasing crystallinity caused a reduction in fracture toughness of PEEK [35]. Furthermore, the fracture toughness of the weld interface of carbon fibre reinforced PPS tapes welded on carbon fabric PPS laminates, was shown to become substantially lower upon annealing [36]. In addition, it is well known that highperformance semi-crystalline thermoplastics possess excellent chemical resistance and low moisture absorption [31] [37] - [40], properties that are heavily influenced by the semi-crystalline structure of these polymers [38] [39] [41].

Hence, considering the very fast welding times of the ultrasonic welding process and given the influence of crystallinity on the final properties of polymers and fibre reinforced polymers, the investigation of the polymer state at the interface of ultrasonically welded thermoplastic composites joints is of significant importance. This article presents a characterisation of crystallinity at the interface of ultrasonically welded carbon fibre PPS joints, having two main objectives. First, to study the influence of the ultrasonic welding process parameters on the degree of crystallinity at the welding interface of CF/PPS joints and, second, to determine whether it is possible to obtain a semi-crystalline welding interface by appropriately modifying the process parameters. In order to determine the crystallinity degree and the average crystallite size of the matrix at the welding interface, differential scanning calorimetry (DSC) and Wide-Angle X-ray diffraction (WAXD) measurements on energy director films removed from the welding interface after the welding process, were performed. The temperature profile at the centre of the joint overlap was measured, using thermocouples embedded in energy directors. The dependence of the crystallinity degree on the cooling rate, as well as the critical cooling rate at which the matrix crystallization is suppressed, were determined using fast scanning calorimetry. The conventional DSC technique could not be used to study the thermal transitions of polymers at very high heating and cooling rates (applicable to the ultrasonic welding process) due to its limited capabilities [27] [29], therefore the FSC technique was employed.

### 2 Experimental Procedure

# 2.1 Materials

The material used in this study was Cetex® woven (five harness satin) carbon fibre reinforced polyphenylene sulphide composite (CF/PPS) supplied by Ten Cate Advanced Composites, The Netherlands. Laminates measuring 580 mm x 580 mm were built from six powder-impregnated CF/PPS layers with a stacking sequence of [(0°/90°)<sub>3</sub>]<sub>s</sub>, with a nominal 50% fibre volume content. The laminates were consolidated using a hot platen press at 320 °C and 1 MPa pressure for 20 min and subsequently cooled down at a cooling rate of 15 °C/min. The stainless steel moulds used in the press consolidation process were first cleaned with acetone, then degreased with PFQD degreasing agent (from Socomore) and finally coated with Marbocote 227CEE release agent. The final thickness of the consolidated laminates was 1.9 mm. Welding adherends and test specimens were cut from the consolidated laminates using a water-cooled diamond blade. Flat ED films were consolidated by placing three 0.08 mm-thick amorphous PPS films between two stainless steel moulds in a hot platen press at 270 °C and

1 MPa pressure for 20 min. The ED films were cooled down at 15 °C/min and had a final thickness of 0.24 mm.

# 2.2 Ultrasonic Welding

All the joints in this study were manufactured using a 20 kHz Rinco 3000 microprocessor-controlled ultrasonic welder with maximum power output of 3000 W (Rinco Ultrasonics, Romanshorn, Switzerland) in a single-lap configuration. Figure 1 depicts the ultrasonic welder and the welding jig, which consists of a clamp for the bottom adherend, a clamp for the top adherend, and a sliding platform which allows vertical movement of the top adherend. The welding jig also prevented shifting of the adherends during the welding process. The diameter of the cylindrical titanium sonotrode was 40 mm. The adherends and the energy director were always degreased prior to welding using a degreasing agent (PFQD). The energy director was fixed on the bottom adherend prior to the welding process using an adhesive tape.

The ultrasonic welding process consists of two phases, the vibration phase during which heat is generated via friction and the matrix only starts to melt and flow, and the solidification phase during which the weld is cooled down under constant pressure, achieving consolidation. The USW machine provides output curves of dissipated power and vertical displacement with respect to vibration time, after each weld. It is possible to control the ultrasonic welding process through the vibration time, the dissipated energy or the vertical displacement of the sonotrode. However, it is known that controlling the process through the vertical displacement (called "travel" hereafter) of the sonotrode, can produce consistently high-strength welds [1]. Therefore, the process in this study was "displacement-controlled", i.e. the vibration phase was terminated after the sonotrode travelled a certain distance (called "optimum travel"). The procedure that was followed in order to determine the optimum travel values has been described in previous work [1]. The optimum travel values used per experiment are provided in the sections 2.3 and 2.4.2. As it was previously mentioned in the introduction section, increasing the welding force as well as the vibration amplitude result in shorter vibration times which could, possibly, influence the heat generation during the welding process and, evidently, have an effect on the cooling rates that PPS experiences. Hence, the influence of the ultrasonic welding process on PPS crystallinity at the welding interface was investigated with respect to the welding force and the vibration amplitude.



**Figure 1.** Utrasonic welder and welding jig. (1) sonotrode, (2) sliding support for top clamp, (3) top clamp, (4) bottom clamp.

Two different sets of force and peak-to-peak vibration amplitude, (1000 N, 86.2  $\mu$ m) and (300 N, 51.8  $\mu$ m), were used to study the effect of the process parameters on crystallinity of PPS at the welding interface. The first set represents the fast process (vibration times around 400 ms) while the second set represents the slower process (vibration times around 1500 ms). The solidification phase was characterised by the solidification time which was 4000 ms, and the solidification force which remained constant, and equal to the welding force, for all the welded joints produced in this study.

# 2.3 Temperature Measurements

The temperature at the centre of the overlap was measured in order to obtain the temperature profile of the ultrasonic welding process during the vibration phase and the solidification phase. Embedding a thermocouple inside the energy director was proven to be the most effective method to measure the temperature at the welding interface. Machining a groove on the adherend surface and then inserting a thermocouple inside the groove was also considered, however, the edges of the groove would act as heat concentrators and interfere with the welding process. In addition, a thermal camera could not be used because the weldline view was blocked from the welding set-up itself.

K-type thermocouples with a diameter of 0.1 mm were placed between four films of amorphous PPS. Prior to press consolidation, the thermocouples were manually fixed on the PPS films using a Rinco handheld ultrasonic welder. Figure 2 illustrates a schematic representation of manufacturing of EDs with embedded thermocouples. Two stainless steel moulds were used as the bottom and top moulds (cleaned following the procedure described in 2.1). A silicon layer of 1.95 mm thickness was placed in between the top mould and the PPS films stack for achieving a more uniform pressure distribution (the presence of the thermocouples caused a non-uniform pressure distribution). The silicon layer was sandwiched between two 25  $\mu$ m-thick polyimide (Kapton, from Dupont) films (called "Kapton films" hereafter), to prevent contact with the EDs which, in turn, would cause contamination of the product. The stack was consolidated in a hot platen press following the same cycle used for the consolidation of EDs (described in section 2.1), having a final thickness of 0.32 mm, instead of 0.24 mm, to ensure that the thermocouples were located in the centre of the energy directors. It is worth noting here, that by using a thicker ED for the temperature measurements (0.32 mm instead of 0.24 mm) slightly lower cyclic strains would occur as it was shown by Palardy and Villegas [3].



Figure 2. Schematic of manufacturing of energy directors with embedded thermocouples. Dimensions are not to scale.

The ED with the embedded thermocouple (ETC) was fixed on the bottom substrate using an adhesive tape, ensuring that the thermocouple tip was located at the centre of the overlap (Figure 3). The optimum travel for both sets of parameters was 0.22 mm. The temperature was recorded during ultrasonic welding using a Thermocouple Data Logger, TC-08, from Pico Technology, at a frequency of 10Hz. It must be noted, that the sampling rate (1 measurement recorded per 100 ms) in conjunction with the very rapid cycle times of USW (typically 4-5 s) might have limited the precision of the measurements. The specimen series welded using a force of 1000 N and a peak-to-peak vibration amplitude of 86.2 µm are denoted by ETC\_F ("F" stands for fast process), while the specimen series welded using a force of 300 N and peak-to-peak vibration amplitude of 51.8 µm are denoted by ETC\_S ("S" stands for slow process). In total, two ETC\_F specimens, three ETC\_S specimens, and two Kapton\_ETC\_S specimens were tested. Table 1 presents the welding conditions and the number of measurements per series.

Table 1. Welding conditions and number of measurements per series.

Specimen Series	Number of measurements	Welding Force (N)	Vibration Amplitude (µm)	Travel (mm)
ETC_F	2	1000	86.2	0.22
ETC_S	3	300	51.8	0.22
Kapton_ETC_S	2	300	51.8	0.22



**Figure 3.** ED with embedded thermocouple prior to ultrasonic welding, positioned in such way to measure the temperature at the centre of the overlap (highlighted area). The arrow in the picture points at the tip of the thermocouple (location of the temperature measurements).

In order to calculate the cooling rates, the temperature at which the crystallization rate is maximum needs to be known. The maximum crystallization rate of a semi-crystalline polymer occurs at a temperature approximately around the midpoint of the glass transition temperature (Tg) and the equilibrium melting temperature [31] [42] [43]. Close to the Tg, the molecular movement is sluggish while close to the melting temperature the crystal nucleation rate and the growth rate are very low, hence, the rate of crystallization is very slow close to both temperatures; at the midpoint between the two temperatures, the balance between the chain mobility and the nucleation rate results in the fastest crystallization rate. Chung and Cebe [44] reported that the fastest crystallization rate at 160 °C, thus, we assumed that in this study the maximum crystallization rate of PPS occurred between 160 °C and 190 °C.

# 2.4 Crystallinity Assessment

## 2.4.1 Fast Scanning Calorimetry

The FSC experiments were performed using a Mettler Flash DSC 1 calorimeter, which is a chip-based fast scanning device with power compensation. The chip sensor had an active area of 500 µm and the thickness of the membrane was approximately 2 µm. The maximum heating and cooling rates can reach up to 20 000 °C/s and 5 000 °C/s, respectively. The specimens were prepared from a piece of ED under a microscope and placed in the centre of the chip sensor as illustrated in Figure 4. The specimen was purged with dry nitrogen gas at a flow rate of 10 mL/min. A good thermal contact between the specimen and the sensor was achieved by, first, melting the specimen on the sensor by heating it up to 320 °C at a 10 °C/s heating rate and, subsequently, consolidating the specimen on the sensor by cooling it down to room temperature at 1000 °C/s. As a result, the preparation procedure does not allow measurements of an "as-received" specimen using the FSC technique. Hence, after the first heating/cooling cycle that was required to melt and consolidate the specimen on the sensor, a second cycle with very slow cooling equal to 0.16 °C/s was performed, in order to obtain a semi-crystalline structure of PPS. The effect of cooling rate on the crystallinity of PPS was investigated by selecting eight cooling rates, between 0.16 and 50 °C/s (Table 2). The rate of the heating scans was 1000 °C/s in order to prevent reorganisation of crystals which can occur upon heating [26] [27]. The mass of the specimens (per sensor) ranged between 250 - 500 ng. Such low masses cannot be weighed using common balances (which normally have a readability of 0.01 mg), thus, an alternative approach has been adopted in literature. In particular, the heat capacity or the melting enthalpy can be used to estimate the specimen mass [18] [21] [27]. In this study, the melting enthalpy was used to estimate the specimen mass, m<sub>FSC</sub>, using the following equation:

$$\mathbf{m}_{FSC} = \frac{\Delta \mathbf{H}_{FSC}}{\Delta \mathbf{H}_{DSC}} * \mathbf{m}_{FSC} \tag{1}$$

Where:

- ΔH<sub>FSC</sub>, (in J) is the measured melting enthalpy determined from the melting peak of PPS previously crystallized at 0.16 °C/s, using FSC.
- ΔH<sub>DSC</sub> (in J) is the measured melting enthalpy determined from the melting peak of PPS previously crystallized at 0.16 °C/s, using Standard DSC.
- m<sub>DSC</sub> is the mass of the specimen used in the standard DSC.

The degree of crystallinity, Xc, was calculated using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_f^o} * 100 \ (\%) \tag{2}$$

Where  $\Delta H_m$  is the measured specific melting enthalpy in J/g and  $\Delta H_f^o$  is the specific melting enthalpy of an ideal crystal ( $\Delta H_f^o = 112 \text{ J/g } [45]$ ).



Figure 4. Example of a PPS granule placed at the centre of the chip sensor.

Table 2. Number of FSC measurements per cooling rate.

Cooling Rate (°C /s)	0.16	0.33	1	1.6	5	10	20	50
Number of Measurements	4	2	1	1	3	4	2	2

#### 2.4.2. Standard DSC and WAXD Analysis

Removing material from the welding interface of a consolidated welded joint is necessary to perform DSC or WAXD experiments, however, it requires meticulous attention in order to prevent material from the welding interface from being mixed with material from the adjacent plies (i.e. 1<sup>st</sup> ply of the adherend). For example, PPS in powder form could be obtained by grinding the cross-section of the joint but it is impossible to determine whether the powder originated from the welding interface or from the resin rich areas of the adherends. Therefore, an alternative and quite simple method was used. Prior to welding, two 25 µm-thick Kapton films were fixed with tape one to each adherend and, subsequently, the ED was sandwiched between the Kapton films and fixed with an adhesive tape as well (Figure 5). The ultrasonic welding interface after the completion of the welding process, due to the Kapton films. The optimum travel values for the two sets of parameters, (1000 N, 86.2 µm) and (300 N, 51.8 µm), were 0.15 mm and 0.13 mm, respectively. The ED films removed after welding with high force and high vibration amplitude are denoted by ED\_F. The details of the preparation conditions of the ED films removed from

the welding interface (called "removed EDs" hereafter) are summarised in Table 3. In addition, in order to study the effect of the initial state of PPS (amorphous or semi-crystalline) on the final crystallinity of PPS, EDs made of amorphous PPS were prepared by cutting three amorphous PPS films (0.08 mm thick each) into sections of 30 mm x 30 mm and stacking them together by spot welding the four corners using a Rinco handheld ultrasonic welder. The final thickness of the amorphous EDs was 0.24 mm. The amorphous ED films were placed between the two adherends and welded using the 20 kHz Rinco 3000 ultrasonic welder (Figure 1). After the completion of ultrasonic welding, the EDs were removed from the welding interface following the same procedure described in this section (Figure 5). If there is any effect of the initial state of PPS on its crystallinity degree at the welding interface, the effect would be more pronounced and easier to study at slower cooling rates which were expected to be obtained by using low welding force and low vibration amplitude. Hence, the amorphous EDs were welded using a welding force of 300 N and a vibration amplitude of 51.8 µm, and are denoted by AMR\_ED\_S. It is important to note though, that the removed ED films were not fully representative of an ED of a consolidated welded joint produced without the interference of Kapton films. The presence of Kapton films might have an influence on the heat generation and heat transfer as the ED is in contact with the Kapton films and not with the composite adherends. On these grounds, energy directors with embedded thermocouples were placed between two Kapton films following the corresponding procedures described in sections 2.3 and 2.4.2 regarding temperature measurements and the use of Kapton films. Two specimens produced using low welding force and low vibration amplitude were tested, denoted by Kapton ETC S. The potential implications of using Kapton films are addressed in the discussion section.



**Figure 5.** Schematic of specimen prepared for removing the energy directors from the welding interface in order to perform direct crystallinity measurements. Dimensions are not to scale.

Specimen Series	Welding Force (N)	Vibration Amplitude (µm)	Travel (mm)	ED state prior to welding
ED_F	1000	86.2	0.15	Semi-crystalline
ED_S	300	51.8	0.13	Semi-crystalline
AMR_ED_S	300	51.8	0.13	Amorphous

Table 3. Preparation conditions of removed EDs.

Standard DSC measurements on ED films in their initial state (after press consolidation and prior to ultrasonic welding, hereafter called "ED\_Ref") and on the specimens presented in Table 3 were carried out in a Sapphire DSC from Perkin Elmer. The melting peak temperature and heat of fusion were calibrated prior to the experiments following indium standards. Three measurements per series were performed: the specimens were heated from 25 °C to 310 °C at 10 °C/min, in a nitrogen atmosphere, and the degree of crystallinity was determined from the heating run and calculated using the following equation:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_f^o} * 100 \quad (\%)$$
(3)

Where  $\Delta H_m$  is the measured specific melting enthalpy in J/g,  $\Delta H_c$  is the specific energy associated with the cold crystallization peak in J/g, and  $\Delta H_f^o$  is the specific melting enthalpy of an ideal crystal ( $\Delta H_f^o = 112 \text{ J/g} [45]$ ).

Valuable information about the state of PPS can also be obtained via measuring the change in the specific heat capacity ( $\Delta C_p$ ) in the glass transition region: a higher amount of the specific heat capacity could mean a higher amorphous content.  $\Delta C_p$  was measured using the Perkin Elmer software.

An X-ray powder diffractometer from Bruker was used for the WAXD measurements (one per series) on amorphous PPS (80 µm thick), ED\_Ref (250 µm thick), ED\_F (70 µm thick) and ED\_S (90 µm thick). The samples were in the shape of films. There was no WAXD measurement on AMR\_ED\_S due to lack of samples at the time the WAXD tests were performed. The diffractograms were [46] [47] obtained using a Cobalt radiation source. The average crystallite size, D, was estimated using the Scherrer equation [46] [47]:

$$D = K\lambda / (\beta \cos \theta) \quad (\dot{A}) \tag{4}$$

Where K is a shape factor (approximately 0.9 [46] - [48],  $\lambda$  is the X-ray wavelength (1.789 Å for Cobalt),  $\beta$  is the full-width at the half maximum intensity of the diffraction peak and  $\theta$  is the Bragg angle. It is noted, that although WAXD is not the most accurate method to measure crystal size (Small-Angle X-Ray Scattering would measure with a higher precision [49], the results shown in this paper can still be considered reliable and acceptable because they still have the correct order of magnitude and they are mainly used for comparison purposes.

#### 3 Results

## 3.1 Temperature measurements

Figure 6 shows the temperature evolution during ultrasonic welding for one specimen per series. As it can be seen the time-temperature relationship was non-linear, therefore it was considered inaccurate to calculate and provide a global cooling rate. Instead, the temperature region between the equilibrium melting temperature of PPS (between 298-330 °C [31]) and 160 °C was divided into smaller temperature regions, in which the time-temperature relationship was assumed guasi-linear, allowing the cooling rates to be calculated. For all series, the cooling rates decreased continuously with increasing time, and the lowest cooling rate was calculated between 190 °C and 160 °C; in this temperature region, the cooling rate for ETC F was 41.0 ± 8.4 °C/s, for ETC S was 16.9 ± 5.9 °C/s and for Kapton ETC S it was 10.9 ± 2.1 °C/s. Therefore, although a global cooling rate could not be used due to the non-linearity between time and temperature, it can be said that the rates at which PPS was cooling down from the equilibrium melting temperature to 190 °C, were higher than the abovementioned cooling rates. Between 160 °C and 120 °C the cooling rates decreased even further, reaching  $3.9 \pm 0.1$  °C/s and  $3.5 \pm 1.0$  °C/s for ETC\_S and Kapton\_ETC\_S, respectively. The cooling rate of ETC\_F on the other hand was much faster, being measured around 19 ± 3.6 °C/s. An additional point to be made from these calculations is the relatively large experimental errors in most of the cooling rates which is addressed in the discussion section.



**Figure 6.** Temperature evolution during ultrasonic welding of ETC\_F, ETC\_S and Kapton\_ETC\_S. Only one specimen per series is illustrated for clarity purposes.

## 3.2 FSC measurements

Figure 7 shows FSC heating curves for PPS previously subjected at different cooling rates (ranging from 0.16 °C/s to 50 °C/s). In this figure, all the measurements were carried out using the same chip sensor. Four main observations regarding the melting peaks can be made from this graph. Increasing cooling rates seems (i) to result in smaller melting peaks, (ii) to shift the melting peaks to lower temperatures and (iii) to broaden the melting peaks, which were characterised by a "shoulder" shifting to lower temperatures with increasing cooling rates (above 0.33 °C/s). Finally, (iv) PPS previously cooled at 20 °C/s showed a very weak signal, exhibiting an almost negligible melting peak. Further increase of the cooling rate (at 50 °C/s) resulted in no melting peak indicating a completely amorphous structure. In addition, all heating curves exhibited a smaller endothermic signal at lower temperatures, very close to the glass transition; this phenomenon could be attributed to the enthalpy relaxation occurring during the previous cooling and/or heating curve, as it was suggested by Furushima et al. [28]. This smaller endothermic peak shifted to lower temperatures with increases in the preceding cooling rates.



**Figure 7.** FSC heating curves of PPS (1000 °C/s) performed after cooling from 320 °C to RT at eight different cooling rates using the same chip sensor.

The dependency of the crystallinity degree on cooling rate is illustrated in Figure 8. As it was already indicated by the smaller melting peaks in Figure 7, higher cooling rates resulted in lower crystallinity values.





The highest degree of crystallinity, 28.9 %, was measured for the lowest cooling rate, 0.16 °C/s. The reduction of crystallinity degree was relatively gradual up to 1.6 °C/s, where the degree of crystallinity was 22.2 %. A further increase in cooling rate, though, caused a substantial decrease in crystallinity: at

a cooling rate of 5 °C/s the crystallinity degree was 11.3 % while at a cooling rate of 10 °C/s the degree of crystallinity was only 3.6 %. However, it must be noted that the standard deviation for the last two values was quite large, especially for the latter. Finally, the critical cooling rate at which crystallization was suppressed was 20 °C/s, a result which is in close agreement with previous studies [17] [28]. Such cooling rate yielded almost amorphous PPS, exhibiting a crystallinity degree of only 0.5 %.

## 3.3 DSC and WAXD analysis of removed EDs

Figure 9 shows two energy directors that were removed from the welding interface after welding under different conditions, where clear differences in terms of transparency can be observed. A welding force of 1000 N and a vibration amplitude of 86.2 µm produced a predominantly transparent film, with some small opaque areas (Figure 9). Contrarily, a welding force of 300 N and a vibration amplitude of 51.8 µm produced an opaque film with some randomly distributed small transparent areas (Figure 9).



**Figure 9.** Energy directors removed after welding at 1000 N, 86.2 μm (left) and at 300 N, 51.8 μm (right). High force and high vibration amplitude produced a predominantly transparent film, while low force and low vibration amplitude produced an opaque film. A black background was used in order to facilitate observation of the films.

Transparency can provide evidence of amorphous structure while opacity of semi-crystalline structure. However, this is just a first indication since the difference in appearance could also be related to the larger thickness of the opaque film. Furthermore, it is well known that even a semi-crystalline polymer can be transparent if the crystallites are too small to scatter visible light [50] Hence, further investigation was conducted through DSC and WAXD measurements. Figure 10 illustrates heating curves of standard DSC measurements carried out on removed EDs and on ED\_Ref. Three measurements per ED film were performed but only one measurement per ED film is shown in Figure 10 for clarity purposes. As the DSC graph demonstrates, only the ED\_Ref specimen did not exhibit an exothermal peak while the other three specimens exhibited an exothermal peak around 128 °C, due to cold crystallization, with the ED F specimen showing the most pronounced one. Cold crystallization occurs above the glass transition temperature during heating from the glassy state; it was an indication of a partial crystallization during the previous specimen cooling due to a too fast cooling rate with respect to crystallization kinetics. The enthalpy associated to the cold crystallization is related to the PPS fraction which did not have time to crystallize during cooling prior to the DSC heating scan. In addition, the change of the specific heat capacity ( $\Delta C_P$ ) at the glass transition (around 90 °C) was larger for ED\_F (0.17 ± 0.01 J/(g\*°C))) compared to ED\_S (0.1 J/(g\*°C)), indicating that ED\_F specimens had a larger amorphous phase fraction compared to ED\_S. It is noted that for ED\_F, the  $\Delta C_P$  value was an average of three measurements while for ED\_S the specific heat capacity "step" was detectable in only one measurement. It was not possible to detect the corresponding specific heat capacity "steps" in the other ED\_S and AMR\_ED\_S specimens, despite the use of higher heating rates (20 °C/min) or the 1<sup>st</sup> derivative of the heat flow.





Figure 11 shows the same heating curves as Figure 10 but focusing only on the melting peaks of the four specimens (illustrating only the temperature range between 180 °C and 300 °C). Only one endotherm peak corresponding to the melting of PPS crystals was observed per specimen. In addition, the melting peak temperature was found to be approximately 280 °C ( $\pm$ 1 °C) in all series. The average crystallinity degree values were calculated using equation (3) and are outlined in Figure 12. The crystallinity degree of ED\_Ref was 26 % and exhibited a coefficient of variation (CoV) of 6.2 %. With

respect to ED\_Ref, low welding force and low vibration amplitude were capable of producing ED films of moderate crystallinity, 14.6 % for ED\_S and 17.2 % for AMR\_ED\_S.



**Figure 11.** Standard DSC measurements on energy director prior to ultrasonic welding (reference, i.e. after press consolidation and before welding) and on energy directors removed from the welding interface under different welding conditions. The graph focuses on the melting peaks of the four specimens. The curves are vertically shifted for better clarity.



**Figure 12.** Crystallinity degree of PPS ED films calculated from Standard DSC measurements. Low welding force and low vibration amplitude produced ED films of moderate crystallinity while high welding force and high vibration amplitude produced predominantly amorphous ED films.

On the contrary, high welding force and high vibration amplitude produced a predominantly amorphous PPS, showing a crystallinity degree of only 2.4 %. An additional point to be made for Figure 12 is the large scatter of crystallinity degree of ED\_S and ED\_F, showing CoV equal to 26.7 % and 45.8 %, respectively. The large experimental error on the crystallinity values could probably be a result of non-

uniform crystallization of the ED films during cooling, however, this was not in line with the low experimental error of AMR\_ED\_S (CoV equal to 4.4 %). Figure 13 demonstrates the diffraction patterns of four specimens. The intensity of each curve was normalised with respect to the corresponding intensity of the major diffraction peak, (200, 111), and plotted against the diffraction angle, 20. The amorphous PPS curve was normalised with respect to the intensity of ED\_Ref, in order to obtain a clear and readable diffractogram. It can be seen that ED\_Ref exhibited narrower diffraction peaks compared to the removed EDs, with ED\_F showing the most considerable peak broadening. The latter showed two less distinct peaks within the 20 range of 22° to 25° and one broad peak within the 20 range of 28° to 34°, compared to the ED\_Ref and ED\_S which showed four distinct diffraction peaks within the 20 range of 28° to 34°.



**Figure 13.** WAXD diffraction patterns showing the effect of the welding process parameters. The intensity of the ED films was normalised with respect to the intensity of the main diffraction peak (200, 111).

The amorphous PPS material exhibited a broad peak at 22°, characteristic of the diffraction peak of an amorphous material. Equation (3) was used to estimate the order of magnitude of the average crystallite size of the crystalline phase of PPS, and it was found that the average crystallite sizes of ED\_Ref, ED\_S and ED\_F were 115.6 Å, 41.3 Å and 25.6 Å, respectively. In addition, the positions of the four main PPS diffraction peaks were identified and labelled in the graph [48], and were found to not be influenced by the welding conditions, remaining the same for all specimens.

#### 4 Discussion

In this section, first, a brief analysis of the most probable mechanism responsible for the temperature profile at the centre of the joint overlap is presented, followed by the discussion concerning the influence of the ultrasonic welding parameters on the degree of crystallinity of PPS at the welding interface. Furthermore, the additional features of the thermograms and the WAXD diffractogram of sections 3.1 and 3.2 are addressed.

The temperature profile of ED PPS during the ultrasonic welding process in Figure 6 showed that lowering the welding force and the vibration amplitude decreased the cooling rates significantly. The reasons for the slower cooling rates of ETC\_S can be found, mainly, in the slower heat generation,  $\dot{Q}$ , due to the lower vibration amplitude [6] [7] which is given in the equation:

$$\dot{Q} = \omega^* \varepsilon^{2*} E^{\gamma/2} \tag{3}$$

Where  $\varepsilon$  is the strain amplitude,  $\omega$  is the frequency and E<sup>''</sup> is the loss modulus. Due to the high thermal conductivity of carbon fibres, heat dissipation occurs, through the composite substrates, increasing their temperature as well. As a result, the slower heat generation would, possibly, cause a larger heat affected zone within the substrates and, essentially, cause a less effective heat transfer leading to a slower cooling of the welding interface. Regarding the relatively large experimental errors of the cooling rates, one possible reason could be the low sampling rate (1 measurement point per 100 ms). Especially for the ETC\_F specimens the experimental error was larger since there were less measurement points.

The standard DSC measurements on the removed EDs showed that the process parameters had a substantial impact on the crystallinity degree. Welding using a force of 300 N and a vibration amplitude of 51.8 µm yielded PPS of moderate crystallinity at the welding interface while a welding force of 1000 N and a vibration amplitude of 86.2 µm resulted in predominantly amorphous PPS (Figure 12). Although the DSC measurements are sensitive to chain reorganisation during heating, it is not expected that it would have such a significant impact on the measured crystallinity degree of ED\_S and AMR\_ED\_S, that would result in such a large difference with the crystallinity degree of ED\_F. This statement is supported by the enthalpy associated to the cold crystallization peaks of the three series presented in

Figure 10: this enthalpy for ED\_F was much larger than the corresponding areas of ED\_S and AMR ED S, indicating that a higher crystallinity degree was obtained during cooling using low welding force and low vibration amplitude. Similarly, the lower value of the specific heat capacity of ED\_S associated to glass transition (about 41 % lower than that of ED\_F) suggests a higher crystallinity degree: the lower  $\Delta Cp$  value is a result of a constrained chain mobility due to the presence of crystals and a smaller amorphous phase content of ED\_S. The DSC analysis was complemented by the WAXD analysis which showed that the diffraction pattern of ED F was different than the diffraction pattern of fully amorphous PPS (Figure 13) while the relatively well-defined diffraction peaks of ED S confirm the presence of a PPS crystalline phase in specimens welded under low welding force and low vibration amplitude. ED F showed two very broad diffraction peaks, suggesting lower crystal perfection and lower crystallinity degree than ED S. With respect to the average crystallite size of PPS, it was found that the very high cooling rates of the USW process caused a reduction in the average crystallite size of PPS. Further evidence supporting the notion of less perfect crystals can also be found in Figure 7 where it is shown that increasing cooling rates resulted in broader melting peaks, which were also shifted to lower temperatures. The appearance of broader melting peaks is an indication of a wider distribution of lamella thickness [51], while it is well known that, under fast cooling, less perfect and/or smaller crystals are being formed at lower melt-crystallization temperatures which, in turn, result in lower melting temperatures [19].

As it was mentioned in section 3.1, the time-temperature relationship was non-linear, however, by dividing the temperature region between the equilibrium melting temperature and 160 °C into smaller temperature regions, it was demonstrated that the cooling rates of all series, independently of welding force and vibration amplitude, were approximately 11 °C/s or higher. Figure 8 showed that increasing cooling rates resulted in lower crystallinity degree values. The polymer chains need time to disentangle from the melt and organise themselves to form crystalline domains, therefore, a fast cooling rate will result in a lower crystallinity degree. Cooling rates of 10 °C/s and 20 °C/s resulted in crystallinity degrees of only 3.6 % and 0.5 %, respectively. The results of the FSC measurements, in conjunction with the measured cooling rates from the temperature measurements, suggest that PPS at the welding interface should be predominantly amorphous regardless of the welding parameters. However, the standard DSC and WAXD measurements were not in line with the FSC measurements, as Figure 12 and Figure 13

illustrated. A few potential factors responsible for the disagreement between Figure 8 and Figure 12 (and Figure 13) are critically discussed in the following paragraphs.

## Effect of temperature measurements

As it was mentioned in section 2.3, the EDs used to obtain the temperature profile at the welding interface were thicker than the EDs removed from the welding interface. However, considering the lower cyclic strains that occur in thicker EDs due to their higher stiffness [3], it is expected that the thinnest EDs (i.e. the EDs removed from the welding interface) should exhibit, if not the same, even faster heating and cooling rates. Therefore, it is safe to assume that the higher thickness of ETC\_S and ETC\_F did not render the measured cooling rates higher than the rates encountered in ED\_S and ED\_F. With respect to the effect of the sampling rate (1 measurement recorded per 100 ms) on the measurement precision, most certainly some temperature values were not recorded, especially during heating, and during cooling from very high temperatures (e.g. from 400 °C to 300 °C). However, at the temperature range between 190 °C and 160 °C the rates had decreased significantly (less than 20 °C/s), allowing for sufficient measurement points to be recorded (at least 5 points per 10 °C) and to calculate the cooling rates in good approximation.

# Effect of Kapton films

One possible reason for this disagreement could be the use of Kapton films in obtaining the ED\_S and ED\_F specimens, from which the DSC and WAXD measurements were acquired. In particular, the removed EDs were not fully representative of an ED of a consolidated welded joint produced without the interference of Kapton films. Normally, the ED is in contact with the CF/PPS substrates while in our approach, the ED was in contact with the Kapton films which could, potentially, cause different heating and cooling. Kapton\_ETC\_S exhibited a lower cooling rate than ETC\_S, 10.9 °C/s compared to 16.9 °C/s, respectively. The differences in the cooling rates between ETC\_S and Kapton\_ETC\_S could be attributed to the thermal insulation properties of Kapton and to the differences in friction between the Kapton - ED interface and CF/PPS - ED interface. On these grounds, it can be argued that the presence of Kapton films altered the heat generation and heat transfer at the overlap, nonetheless, 10.9 °C/s is still a very high cooling rate and incapable of producing PPS of moderate crystallinity (as a reminder, a

cooling rate of 10 °C/s resulted in a crystallinity degree of 3.6 %).

# Annealing effect

It is well known that annealing of semi-crystalline thermoplastics (i.e. heating above Tg) leads to increased crystallinity degree and crystal perfection [52]. The changes in the crystalline regions can already occur in the first few minutes of annealing. In addition, the highest the annealing temperature, the shortest the annealing time required. Cold crystallization of PPS occurs around 120 – 130 °C which is usually the lowest annealing temperature of PPS; below that temperature the chain mobility is too low and it would require lengthy annealing times to achieve changes in crystallinity and crystal perfection. ETC\_F was quenched down to 120 °C (in almost 2 seconds) while ETC\_S and Kapton\_ETC\_S cooled down slower, in 10.3 and 11.4 seconds, respectively. Hence, an annealing effect could be possible, enhancing the crystallinity degree of ED\_S and contributing to the growth of the average crystallite size. However, the studies reporting the effect of annealing on PPS, have investigated times in the order of a few minutes [52] [53]. Performing experiments to isolate the effect of annealing in non-isothermal conditions for such short times is extremely complex and technically challenging. Recognising the absence of experimental proof due to technical complexities, we suggest that annealing had a negligible effect on the crystallinity degree of ED\_S due to the very short "annealing" time.

# Crystal seed effect

Another possible reason for the semi-crystalline structure of ED\_S could be the presence of remnant crystals in the melt. Although the temperature reached values much higher than the melting temperature of PPS (Figure 6), which ensured that the temperature was high enough to melt the crystals, the material remained a very short time in the melt, which could have caused PPS to partially maintain its chain conformation. Hence, there is always a possibility that some of the crystals, which pre-existed in the initial state of the ED (as received from press consolidation), did not melt or melted partially and, therefore, acted as nucleation sites during cooling (crystal seed effect). However, AMR\_ED\_S had a crystallinity degree of 17.2 %, hence, if the remnant crystals were the main reason for the fast crystallization of PPS then AMR\_ED\_S should have had a much lower crystallinity degree (as the PPS energy director was amorphous in its initial state). Therefore, the (potential) presence of remnant

crystals is not considered to have had a major impact on the crystallization of PPS at the welding interface.

#### Strain-induced crystallization

One major difference between the crystallization of PPS during FSC tests and during ultrasonic welding is that the former proceeds in quiescent conditions while the latter encounters very high strain rates. The vibration frequency used in the ultrasonic welding process was 20 kHz, therefore, very high strain rates could be achieved instantaneously. When a polymer is in the melt state, the molecular chains are entangled and interpenetrated, having a random coil conformation. In quiescent conditions, the crystallization is only driven by chain mobility and supercooling level. If the kinetics of cooling is higher than the crystallization one, crystallization is prevented, leading to an amorphous PPS solid. However, under high strain the molecular chains can be oriented. The formation of nuclei is favoured which, in conjunction with the increase of nucleation density, accelerate crystallization [54], considering the same cooling conditions as in quiescent conditions. The effect of high strain rates on polymer crystallization has also been reported by several researchers [54] - [57], reinforcing our suggestion that strain-induced crystallization could explain the crystallization of PPS despite the very fast cooling rates. Nonetheless, the strain rates are linked to the time available for the molecular chains to form crystals. Although ED\_F encountered higher strain rates than ED\_S (and AMR\_ED\_S) due to the higher vibration amplitude (86.2 μm vs 51.8 μm), PPS in ED F was almost amorphous, exhibiting a very low degree of crystallinity (2.4 %). A plausible explanation could be the shorter time of melted PPS under high strain rates for ED\_F. The crystallization rate of a polymer can be accelerated due to high strain rates, however, it is likely that a very short time in the melt is not sufficient for strain-induced crystallization to occur [54]; for a melted polymer, a given time under high strain rates is required to observe an effect on crystallization kinetics. Zhang et al [57] also suggested that the crystallization rate of PPS increased with increasing shear time. Therefore, it appears that the time under high strain rates for melted PPS in ED F was not long enough to significantly increase the crystallization rate, while the low welding force and the low vibration amplitude favoured the conditions for strain-induced crystallization to occur by decreasing the cooling rates and allowing more time in the melt.

#### 5 Conclusions

This article presented an investigation of the crystallinity at the interface of ultrasonically welded CF/PPS joints by studying the influence of welding force and vibration amplitude on the degree of crystallinity at the welding interface. The results of our work can be summarised in the following conclusions:

- Temperature measurements at the centre of the overlap of ultrasonically welded CF/PPS joints revealed that low welding force (300 N) and low vibration amplitude (51.8 µm) decreased the cooling rates from 41 °C/s to 16.9 °C/s, compared to high welding force (1000 N) and high vibration amplitude (86.2 µm). The lower cooling rates were attributed to the slower heat generation under 300 N and 51.8 µm. It is suggested that the slower heat generation possibly caused a larger heat affected zone, resulting in a less effective heat transfer.
- The FSC experiments showed that the degree of crystallinity of PPS decreased with increasing cooling rates. Furthermore, it was shown that, in quiescent conditions, the critical cooling rate at which PPS crystallization was suppressed was 20 °C/s, exhibiting a degree of crystallinity of only 0.5 %.
- DSC and WAXD measurements performed on energy director films that were removed from the welding interface, showed that the ultrasonic welding process parameters had a significant impact on the crystallinity degree of PPS and its crystal perfection. High welding force (1000 N) and high vibration amplitude (86.2 µm) produced predominantly amorphous PPS and imperfect crystals, while low welding force (300 N) and low vibration amplitude (51.8 µm) were capable of increasing the crystallinity to moderate levels as well as the crystal perfection. Although the crystallinity degree and the crystal perfection were not as high as in the initial state of the PPS energy directors (i.e. prior to ultrasonic welding), it was clear from the DSC thermograms and the WAXD diffractogram that PPS had obtained a semi-crystalline structure. A possible explanation for the PPS capability to crystallize despite the very high cooling rates at the centre of the overlap, is the significantly high strain rates involved in the ultrasonic welding process which are suggested to have induced PPS crystallization. The orientation of the molecular chains in the melt due to high strain rates could have facilitated crystal formation and

accelerated PPS crystallization. Hence, it was shown that by appropriately modifying the welding force and the vibration amplitude it was possible to obtain a semi-crystalline welding interface.

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