On avoiding thermal degradation during welding of high-performance

thermoplastic composites to thermoset composites

Irene Fernandez Villegas^{1*}, Pablo Vizcaino Rubio¹

¹Structural Integrity and Composites Delft University of Technology Kluyverweg 1, 2629HS Delft, The Netherlands

*Corresponding author: Irene Fernandez Villegas, <u>I.FernandezVillegas@tudelft.nl</u>, T: +31152789745, F: +31152781151

Abstract

One of the major constraints in welding thermoplastic and thermoset composites is thermal degradation of the thermoset resin under the high temperatures required to achieve fusion bonding of the thermoplastic resin. This paper presents a procedure to successfully prevent thermal degradation of the thermoset resin during high-temperature welding of thermoplastic to thermoset composites. The procedure is based on reducing the heating time to fractions of a second during the welding process. In order to achieve such short heating times, which are much too short for commercial welding techniques such as resistance or induction welding, ultrasonic welding is used in this work. A particularly challenging scenario is analysed by considering welding of carbon-fibre reinforced polyether-ether-ketone, with a melting temperature of 340°C, to carbon-fibre reinforced epoxy with a glass transition temperature of 157°C.

Keywords: A. Thermoplastic resin; A. Thermosetting resin; A. Polymer-matrix composites (PMCs);E. Joints/joining.

1. Introduction

Thermoplastic composites (TPC) are very attractive to several industries as a result of their costeffective manufacturing and cost-effective assembling through welding. One of the most cost-effective manufacturing techniques applied to thermoplastic composites is press forming. Flat pre-consolidated thermoplastic composite laminates can be press formed into near to net-shape parts in several minutes [1]. In the aerospace industry, press forming is widely used for the manufacturing of small, e.g. clips or cleats used as structural connecting elements in the fuselage, to medium-sized, e.g. ribs or stiffeners, thermoplastic composite parts. An example of this are the several thousands of thermoplastic composite clips used for the fuselages of the new composite passenger aircrafts, Airbus A350 and Boeing 787 [2]. The manufacturing of bigger components such as fuselage or wing sections or panels relies, however, on the use of, more traditional, thermoset composites (TSC), which currently show cost advantages as compared to thermoplastic composites. The usage of both thermoplastic and thermoset composites for optimal manufacturing of different parts in the aircraft requires assembling of dissimilar TPC/TSC structures, which nowadays is solved through mechanical fastening [2]. However, the ability of thermoplastic composites to be welded with little surface preparation and short assembling times, makes it interesting to investigate whether thermoplastic and thermoset composites can be welded together using current welding techniques for thermoplastic composites. Reliable thermoplastic to thermoset composite welding processes could be expected to offer a significant reduction in assembly times, assembly costs and weight reduction as compared to mechanical fastening.

The two main challenges in welding of TPC/TSC structures are, firstly, adhesion between the thermoplastic and thermoset composites and, secondly, thermal degradation of the thermoset composite when subjected to the relatively high temperatures generated during the welding process. Regarding the adhesion between thermoset and thermoplastic composites, researchers seem to agree on the necessity of coating the thermoset composite with a thermoplastic-rich layer through a co-curing process in order to achieve sufficient adhesion between the thermoset and the thermoset are then either welded together or welded to thermoplastic composite parts by locally melting the thermoplastic/thermoplastic interface. Adhesion between the thermoset composite and the thermoset and the thermoset and the thermoset composite and the thermoset composite and the thermoset composite and the thermoplastic-rich coating layer can be based on micro- and/or macro-mechanical interlocking. Micro-

mechanical interlocking entails the migration of thermoset pre-polymer molecules into the thermoplastic to create a semi-interpenetrating network. Semi-interpenetrating networks have been successfully created between compatible thermosetting and amorphous thermoplastic polymers, such as epoxy with polysulfone (PS) or polyethersulphone (PES), and bismaleimide (BMI) with PS, PES or polyetherimide (PEI) [4]. In these cases, the amorphous nature of the thermoplastic polymers and, therefore, their low resistance to solvents allow the uncured components of the thermoset component to migrate through the interface. Moreover, Hou et al state in [5] that there are combinations of semi-crystalline thermoplastics and thermosets with matching solubilities, such as polyvinilidene fluoride (PVDF) and epoxy, which can as well create semi-interpenetrating networks. Macro-mechanical interlocking can be created through the co-curing of a composite hybrid layer partially impregnated with thermoplastic resin onto the thermoset composite laminate, as proposed by Jacaruso et al in [6].

Regarding thermal degradation of the thermoset composite during welding, a possible solution entails the selection of a thermoplastic/thermoset combination such that the welding temperature is lower or similar to the glass transition temperature of the thermoset resin. Such is the case of PVDF to epoxy welding. PVDF has a melting temperature of 170°C and therefore, it allows the welding process to be performed at a temperature that does not cause severe overheating of epoxy composites cured either at 177°C or 127°C [5,7]. This method, however, greatly limits the nature of thermoplastic composites that can be welded to thermoset composites.

An option to avoid degradation in high-temperature welding of thermoplastic and thermoset composites is reducing the temperature the thermoset resin is exposed to during the welding process. Van Toren proposes in a patent application [8] two approaches to ensure that a thermoset composite coated with a thermoplastic-rich layer does not reach its maximum operating temperature during welding. One of the approaches proposed is based on the usage of heat sinks either within the thermoplastic coating or externally applied to it. The other approach relies on, as quoted from [8], "the thermoplastic coating having a heat capacity per unit length larger than the heat applied to the assembly per unit length". From the perspective of the authors of the present paper, this last approach would entail increasing the heat capacity of the thermoplastic coating layer, by either modifying its

nature, and/or by increasing its thickness. Preferred welding processes proposed in this patent application are induction, resistance and laser welding. No experimental results to support these approaches to prevent degradation are, however, presented in this document. Ageorges et al. also showed in [9] that, by using a glass-fibre reinforced hybrid coating layer co-cured with the thermoset composite adherend, resistance welds between carbon fibre CF/PEI and CF/epoxy (+hybrid coating layer) composites with lap shear strength levels between 20 and 25 MPa could be obtained. Even though thermal degradation of the epoxy resin was not experimentally assessed in that paper, the strength levels obtained, considered as acceptable by the authors, might indicate however that no significant degradation took place. From our viewpoint, the usage of glass, and hence thermally insulating, fibres in the thermoplastic coating of the CF/epoxy adherends contributed to shielding the epoxy resin from the relatively high temperatures developed during welding. However, this method introduces a foreign material at the welding interface that typically has a lower strength to failure than the adherends themselves.

Our alternative approach to preventing degradation during high-temperature welding of thermoplastic and thermoset composites is primarily based on significantly reducing the heating time during the welding process. Several welding techniques applicable to thermoplastic composites are known to be capable of very short heating times, between a few tenths of a second and a few seconds, such as ultrasonic, laser or microwave welding, as opposed to other, more mature, welding techniques such as induction or resistance welding with heating times in the order of minutes [10]. Very short heating times during the welding process result in: (a) a very short time for heat to be transferred through the thermoplastic coating layer used to generate adhesion with the thermoset composite adherend, which will decrease the temperature at which the thermoset composite adherend is exposed to; and (b) a very short time for degradation mechanisms to occur in the thermoset composite adherend, which if short enough, could potentially hinder the occurrence of any degradation [11]. An approximate quantification of the influence of heating time on the temperature beneath the thermoplastic coating layer, and thus on the surface of the CF/epoxy adherend closest to the welding interface, can be obtained through the one-dimensional heat transfer model proposed by Holmes and Gillespie in [12] for resistance welding of carbon-fibre (CF) reinforced polyether-ether ketone (PEEK) composites. The model considers that a neat PEEK layer is placed between the heating element and the thermoplastic substrates (for the original resistance welding process considered by the authors), which makes it suitable for an approximate analysis of temperatures developed during welding of adherends with thermoplastic coating layers. Resulting from this model, Figure 1 shows that, for heating times under 1 s, temperatures below 200°C can be obtained beneath the PEEK coating layer when the temperature at the welding interface is 400°C. A similar temperature reduction is achieved by increasing the thickness of the thermoplastic coating layer above 2 mm in a typical resistance welding process with 90 kW/m² input power at the welding interface (Figure 2). However, for thin-walled aircraft structures a 2 mm-thick coating can be expected to severely weaken the joint through high secondary bending moments. Alternatively, fast welding processes, with heating times below1 second, can offer a feasible alternative to prevent degradation while maintaining coating thicknesses of at least one order of magnitude lower than the thickness of the adherends. It must be noted, however, that the graphs shown in Figures 1 and 2 are based on the material properties for CF/PEEK and PEEK provided in [12] and, therefore, they just offer an approximate result for thermoplastic to thermoset welding.

This paper presents the results of a fully experimental study focused on prevention of thermal degradation during welding of CF/PEEK to CF/epoxy composites through very short heating times. Very short heating times are achieved in this study through the use of ultrasonic welding, which is widely acknowledged as one of the most appropriate welding processes for thermoplastic composites [3] and it is capable of heating times well below 1 sec [13] Two sets of welding parameters with significantly different average heating times, namely 460 and 830 ms, were used in order to assess the effect of heating time on degradation during ultrasonic welding hereafter. Direct ultrasonic welding of CF/PEEK onto CF/epoxy, i.e. with no PEEK coating on top of the CF/epoxy adherend, was performed as well in order to investigate the sole effect of short heating times on hindering the degradation reactions in the epoxy resin. Degradation assessment was based on the analysis of the

fracture surfaces of the CF/PEEK to CF/epoxy welded joints through fractography and infrared spectroscopy.

2. Experimental

2.1 Materials and sample preparation

The materials used in this study were 5-harness satin CF/PEEK from Ten Cate Advanced Composites, The Netherlands, and Hexply 913 unidirectional CF/epoxy from Hexcel. Stacks of powderimpregnated CF/PEEK with a [0/90]₃₈ stacking sequence were consolidated in a hot-platen press at 385°C and 10 bar for 20 min. The CF/PEEK consolidated laminates had a nominal thickness of 1.92 mm. The unidirectional CF/epoxy tapes were laid up using an in-house built automated tape layer on a [0]₁₁ configuration. Taking into account that the main goal of this study was to investigate thermal degradation caused by the welding process, this unidirectional layup, although not structurally optimum, was chosen for simplified manufacturing. According to the specifications of the manufacturer, the CF/epoxy laminates were cured in an autoclave at 125°C and 6 bar for 60 min. A stainless steel caul plate was used to ensure a flat surface on the side of the vacuum bag. The final thickness of the laminates was 1.7 mm. The glass transition temperature of the CF/epoxy laminates was 157°C, as measured via differential scanning calorimetry (Sapphire DSC Perkin Elmer). Thermogravimetric analysis (Pyris Diamond TGA, Perkin Elmer) showed 5% weight loss at 370°C (heating rate 20°C/min) for this CF/epoxy composite.

A 0.25 mm thick neat PEEK film (Victrex, UK) was cocured to one of the sides of some of these CF/epoxy laminates. The surface of the PEEK film directly in contact with the CF/epoxy prepreg was degreased and subsequently subjected to ultraviolet (UV) ozone cleaning prior to the laying-up process. UV ozone cleaning is known to be an effective room-temperature method to remove a variety of contaminants from surfaces through a photosensitized process in which the contaminant molecules are dissociated by the absorption of short wavelength UV light [14].

CF/PEEK and CF/epoxy adherends, 25.4 mm-wide and 101.6 mm-long, were water-jet cut out of the composite laminates. The adherends were cut so that their longer side coincided with the main apparent orientation of the fibres in the CF/PEEK laminates and with the 0° orientation of the fibres in the CF/PEEK laminates.

2.2 Welding process

Single-lap welded joints with the two different types of overlaps sketched in Figure 3 were considered in this study. One of them was a direct weld between the CF/PEEK and the CF/epoxy adherends, i.e. with no PEEK coating layer cocured onto the CF/epoxy adherend. The other type consisted of a CF/PEEK adherend indirectly welded onto a CF/adherend through a co-cured PEEK coating layer. In both cases 0.25 mm-thick flat energy directors were used. A flat energy director is a neat layer of matrix resin, PEEK in this case, that is placed at the welding interface prior to the welding process. It concentrates heat generation at the welding interface through combined surface friction, i.e. friction between energy director and adherends moving relative to each other, and viscoelastic friction, i.e. friction among adjacent polymer molecules in the energy director when subjected to cyclic strain, and provides 100% welded areas [13].

Individual CF/PEEK and CF/epoxy adherends were welded in a single lap shear configuration with a 12.7 mm long overlap. A Rinco Dynamic 3000 microprocessor-controlled ultrasonic welder with 3000 W maximum power and able to deliver 3000 N force was used for this purpose. An in-house designed clamping jig was used to ensure no shifting of the samples and to allow vertical movement, and hence no bending, of the top adherend during the welding process (see Figure 4). A 30 mm x 15 mm rectangular sonotrode with 1:2.75 amplification and a 1:1 booster were used. With this booster/sonotrode configuration, nine different amplitude values ranging from 72 to 120 µm could be selected for the welding process. Adherends and flat energy directors were degreased prior to the welding process. At least five samples were welded per joint type (see Figure 3) and set of welding parameters.

Displacement-controlled welding was used in this study since it was been shown to provide consistent weld quality [13,15]. Consequently, the amount of time during which the vibration was applied to the welding stack, i.e. the heating time, was indirectly controlled through the displacement of the sonotrode. The optimum displacement, i.e. displacement that ensures melting of the thermoplastic resin in the first layer of the adherends without significant bulk heating [13], was determined through the power and displacement data provided by the ultrasonic welder following the procedure explained in [15]. It must be noted that the optimum displacement values used in this work were obtained for CF/PEEK to CF/PEEK welds. However, when applied to CF/PEEK to CF/epoxy welding, they also provided welds within the optimum stage of the welding process as defined by the power and displacement curves [15].

Two different combinations of welding force and vibration amplitude, i.e. the welding parameters that control heat generation rates at the welding interface [13], were chosen in this study (see Table 1). Increasing the welding force and/or the amplitude is known to cause a decrease in the heating time needed for an optimum weld as well as to increase the dissipated power [13]. Therefore, the shortest heating time (indirectly controlled through the displacement of the sonotrode in this study) is achieved when maximum force and maximum amplitude for a certain booster/sonotrode configuration are selected, but at the cost of high power requirements. In order to stay within the power limit of the ultrasonic welder, a 1500 N force (4.7 MPa welding pressure)/90 µm peak-to-peak amplitude combination was chosen in this study to achieve an average short heating time of 460 ms (0.10 mm optimum displacement obtained following procedure in [15]) with an average maximum power consumption of 2100 W. On the other hand, force and amplitude were reduced to the minimum operative values of the machine with the booster/sonotrode configuration used, i.e. 300 N force (0.9 MPa welding pressure)/ 72 µm peak-to-peak amplitude, to increase the heating time to an average of 830 ms (0.08 mm optimum displacement obtained following procedure in [15]) and average maximum power consumption of 1500 W. The 1500 N force / 90 µm amplitude / 0.10 mm displacement conditions are referred to as "short-heating-time conditions" hereafter. Likewise, the $300 \text{ N} / 72 \,\mu\text{m}$ amplitude / $0.08 \,\text{mm}$ displacement conditions are referred to as "long-heating-time

conditions" hereafter. Please note that the optimum displacement values for these two force/amplitude combinations were slightly different, which is believed to result from the impact of force and amplitude on heat generation, heat transfer and energy director squeeze-out rates, and is consistent with the results presented in [15] for displacement-controlled ultrasonic welding of thermoplastic composites.

2.3 Analysis and testing

Welded samples were either mechanically tested following ASTM D 1002 standard [16] in a Zwick 250 KN universal testing machine with offset grips to minimise specimen bending (1.3 mm/min crosshead speed) or manually broken open when adhesion was poor. Degradation on the welding surface of the CF/epoxy adherend was assessed through fractography and Fourier Transform Infrared Spectroscopy (FTIR, Spectrum 100 Spectrometer, Perkin Elmer). In order to better interpret the FTIR spectra of the welded samples, the following references were established. Firstly, the reference spectrum for non-thermally degraded CF/epoxy material was obtained from as-manufactured CF/epoxy samples. Secondly, reference spectra for thermally degraded CF/epoxy material were obtained from CF/epoxy samples exposed to 200°C in an oven for 4, 20 and 60 min, with the aim of capturing different stages in the thermal degradation process. It must be noted that neither the exposure temperature nor the exposure times held any relationship with temperatures and exposure times expected during the welding process. However, they served the purpose of causing different degrees of detectable thermal degradation in the CF/epoxy material and hence providing useful reference spectra to assess thermal degradation in the welded samples. Samples exposed to 200°C for 4 min did not show any visual damage but samples exposed for 20 and 60 min showed bumps on their surfaces indicating the occurrence of delamination. The spectra of the samples exposed to 200°C were similar and presented clear differences with the spectrum of the as-manufactured material. Figure 5 shows the absorbance peaks for the degraded and non-degraded reference cases within the 3200 to 1500 cm⁻¹ wavelength range. Main observations are :

- i. All four cases showed the peaks corresponding to the CH_2 and CH_3 bonds located between 2965 and 2870 cm⁻¹ wavelength [17], indicating that the backbone of the epoxy polymer did not undergo major damage after oven exposure.
- Thermally degraded samples did not show a clear peak at 2165 cm⁻¹ wavelength
 corresponding to CN bonds [17], probably caused by breakage of amine-based crosslinks.
- iii. In the wavelength region between 1740 and 1590 cm⁻¹ thermally degraded samples showed a shift towards lower wavelengths of the original 1740 and the 1610 cm⁻¹ peaks. Likewise they showed a clear peak at 1665 cm⁻¹ which was not so obvious in the spectrum of the as-manufactured material. Since the carbonyl group, C=O, has absorption peaks in that region [17], these changes could potentially be related to oxidation phenomena.

No temperature measurements were performed in this study since thermocouples directly placed at the welding interface were found to cause significant disturbance in the temperature distribution. This disturbance is attributed to local changes in the strain field and, hence, in the viscoelastic heating rate within the flat energy director at the thermocouple locations. Moreover, non-intrusive temperature measure techniques, such as infrared thermography, could not be applied due to lack of accessibility (it must be noted that the welding stack is sandwiched between the sonotrode and the base of the welding jig throughout the welding process). However, the way in which the process parameters were defined ensured that, in any of the cases investigated in this paper, the energy director was fully melted and able to flow before the end of the vibration phase. Consequently, it could be assumed that the maximum temperature reached at the welding interface, which might vary for different force/amplitude combinations owing to differences in heat generation rates, was, in any case, equal or above the melting temperature of PEEK.

3. Results and discussion

3.1 Direct welding of CF/PEEK onto CF/epoxy

Welding of CF/PEEK adherends directly onto CF/epoxy adherends provided samples with a low degree of adhesion that could be separated manually. Figure 6 shows representative CF/epoxy fracture

surfaces for direct welding under the long- and short-heating time conditions used in this study (see Table 1), respectively. As indicated in this Figure, the fracture surfaces are delimited by the two longitudinal edges of the welding overlap (i.e. edges on the longest side of the adherends) and the two transverse edges of the overlap (i.e. edges on the shortest side of the adherends). One of the two transverse overlap edges, the transverse external edge, coincides with the end of the adherend, and the other one, transverse internal edge, connects the overlap with the rest of the adherend. CF/epoxy fracture surfaces from direct welding (see Figure 6) showed smooth resin-rich areas, with a similar appearance to the material outside of the welding overlap, as well as visibly damaged areas (indicated by arrows in Figure 6). In the case of long-heating-time conditions, fracture surfaces showed a relatively big damaged area characterised by visibly dry carbon fibres and detached fibre bundles at the longitudinal edges of the overlap. In the case of short-heating-time conditions, damage in the form of dry fibres could as well be observed but it covered a much more limited area. Some detached fibre bundles were found at the longitudinal overlap edges as well as some longitudinal cracks within the adherend. Finally, fracture surfaces showed a non-uniform appearance with more visible damage at the longitudinal and transverse external edges of the overlap than at the transverse internal edge of the overlap

The non-uniform appearance of the fracture surfaces in Figure 6 is consistent with the fact that, during the welding process, heat is generated at a faster rate at the edges of the welding overlap [18]. The fact that the transverse internal edge of the overlap seemed less affected than the rest is attributed to a more effective heat transfer from that edge to the relatively colder adherend outside of the welding area . A closer look into areas of visibly dry fibres (see Figure 7) revealed different degrees of visible damage ranging from carbon fibres partially covered with resin (relatively colder areas closer to transverse internal overlap edge) to completely dry and disconnected fibres (relatively hotter areas closer to the transverse external overlap edge). This type of damage, present on both long- and short-heating-time fracture surfaces, is believed to have a thermal source and it is attributed to partial or total sublimation of the epoxy resin during welding. The combination of thermal damage and the mechanical vibration exerted in the adherends during welding causes the fibre bundles to detach along the longitudinal

overlap edges. Furthermore, the higher stresses generated at the welding interface by the higher force and higher amplitude used to achieve the short heating time [18] combined with the thermal exposure are believed to cause the longitudinal cracks observed in Figure 6(right).

With regards to the visibly undamaged, smooth resin-rich areas, on both fracture surfaces, FTIR analysis on those areas yielded the absorbance spectra plotted in Figure 8. The analysis of the FTIR spectra of the welded samples compared to the reference spectra from as-manufactured samples and samples heated at 200°C for 4 min led to the following main observations:

- i. The spectra for the long-heating-time and the short-heating-time samples were alike, despite the existence of obvious differences on the appearance of the fracture surfaces.
- ii. Similarly to the thermally degraded reference (exposed to 200°C for 4 min), both welded samples showed no C-N peak, indicating potential breakage of amine crosslinks.
- iii. However, as opposed to the thermally degraded reference, the welded samples showed no shift in the 1740 and 1610 cm⁻¹peaks and no 1665 cm⁻¹ peak. This could be due to hindering of the oxidation phenomena related to thermal degradation owing to the fact that during the welding process the CF/epoxy surface was heated in direct contact with the CF/PEEK adherend and therefore with limited exposure to air.

From these results it follows that not even the short-heating-time conditions used in this study did result in a fast enough process to prevent thermal degradation of the epoxy resin during direct CF/PEEK to CF/epoxy welding. Even though the short-heating-time conditions caused less visible thermal damage on the surface of the CF/epoxy adherends, characterised by resin-poor areas, FTIR indicated the presence of overall thermal degradation for both the short- and long-heating time conditions.

3.2 Indirect welding of CF/PEEK onto CF/epoxy through a co-cured PEEK coating layer

Welding of CF/PEEK adherends onto CF/epoxy adherends through a co-cured PEEK coating layer resulted in stronger welds that had to be pulled apart through mechanical testing in order to access the fracture surfaces. Figure 9 shows representative CF/epoxy surfaces resulting from indirect welding in

both the long-heating-time and the short-heating-time conditions used in this study (Table 1). In the long-heating-time case, fracture surfaces showed damage in the CF/epoxy material along the transverse external overlap edge and also in the middle of the overlap (marked by arrows in Figure 9). The remaining areas had a smooth resin-rich appearance with some occasional resin-rich residues (marked by arrows in Figure 9), probably resulting from the PEEK coating removed from the CF/epoxy surface during testing due to insufficient adhesion. In the short-heating-time case, fracture surfaces had a smooth resin-rich appearance with also some resin-rich residues (marked by arrows in Figure 9) and no visual signs of damage. A closer look into the damaged areas on the long-heating-time fracture surface (see Figure 10) revealed the presence of dry carbon fibres at the transverse external overlap edge, which, as discussed in the previous section could be interpreted as a sign of thermal degradation. The middle of the overlap showed, however, resin-rich interlaminar damage, which is in turn believed to result from mechanical testing rather than thermal degradation, since the latter was found to be characterised by resin-poor surfaces as discussed previously.

FTIR spectra of the smooth resin-rich areas on the CF/epoxy fracture surfaces from the welded samples (Figure 11) led to the following observations:

- i. Both welded samples showed the C-N peak at 2165 cm⁻¹ similarly to the as-manufactured sample but opposite to the thermally-degraded reference sample
- Likewise the welded samples did not show a shift in the 1740 cm⁻¹ peak or a peak at 1665 cm⁻¹ wavelength. Similarly to the PEEK spectrum, they showed peaks at 1650 and 1600 cm⁻¹, which thus are believed to be aromatic peaks from PEEK residues left on the surface of the CF/epoxy by the co-cured coating layer, rather than from any thermal degradation.

According to these results, the 0.25 mm-thick PEEK coating layer succeeded in preventing any observable or measurable thermal degradation on the CF/epoxy adherends when the short-heating-time conditions were used. By using the PEEK coating layer, the location at which heat generation occurred during the welding process was moved away from the surface of the CF/epoxy adherend to the interface between the PEEK coating and the energy director (as well as the interface between the

energy director and the CF/PEEK substrate), i.e. to those locations where surface friction can occur [13,19,20]. Consequently, the temperature at which the surface of the CF/epoxy substrate was exposed to during the welding process was dependent on the heat conducted through the PEEK coating layer during a very limited amount of time and, hence, it was expected to be significantly lower than the temperature at the welding interface (see Figure 1). The importance of short heating times to prevent degradation was demonstrated by the fact that for the long-heating-time conditions some initial degradation could already be observed at the hottest edge of the overlap in the form of dry and disconnected fibres on the CF/epoxy substrate. This initial degradation, which is believed to be responsible for the initiation of interlaminar failure in the CF/epoxy during mechanical testing of the welded samples, was however very localised as proven by the FTIR analysis. Given the significant gap in terms of force and amplitude between the two sets of welding parameters considered in this study (welding force ranging from 300 to 1500 N and welding amplitude ranging from 72 to 90 μ m), these results indicate the potential existence of a relatively wide processing window, i.e. combinations of processing parameters providing welds without thermal degradation of the CF/epoxy adherend, for the welding of this particular material combination.

As a step further in this research, CF/epoxy adherends with a 0.25 mm-thick co-cured PEEK coating layer that featured improved adhesion between the PEEK coating layer and the CF/epoxy adherends were welded to CF/PEEK samples under the short-heating-time conditions (Table 1) and mechanically tested afterwards. As illustrated by representative fracture surfaces in Figure 12, failure primarily occurred at the CF/PEEK substrate. The change of location of failure from the CF/epoxy-PEEK interface (see Figure 10) to the CF/PEEK adherend (Figure 12) shows that improved adhesion was indeed achieved and hence the CF/epoxy-PEEK interface was no longer the weakest interface. More importantly to the topic discussed in this paper, the change of location of failure confirms the lack of any thermal damage caused by the welding process that could induce failure at or next to the CF/epoxy adherend.

4. Conclusion

A fully experimental study focused on prevention of degradation during high-temperature welding of CF/PEEK ($T_m=340^{\circ}C$) and CF/epoxy ($T_g=157^{\circ}C$) composites was presented in this paper. A novel approach to prevent degradation of the CF/epoxy composite during the welding process based on the usage of very short heating times was followed. FTIR and fractography analysis were performed on the fracture surfaces of welded and subsequently tested samples in order to determine the occurrence of thermal degradation of the CF/epoxy composite.

The major conclusion of this work is that, in high-temperature welding of thermoplastic and thermoset composites, keeping the heating time well under 1 second is of vital importance to prevent thermal degradation of the thermoset composite. Such short heating times, only offered by ultra-fast welding techniques such as ultrasonic welding, are able to turn a thin thermoplastic coating layer into the most efficient heat shield and hence can provide a solution for the welding of virtually any thermoset/thermoplastic composite material combination.

5. References

- Offringa A. Thermoplastics in aerospace, a stepping stone approach. In: Bersee HEN and NinoG (eds) CETEX thermoplastic composites: from scratch to flight. Delft, The Netherlands, Delft University of Technology, 2006.
- Deters A., Miaris A., Sohnes G. Serial production of thermoplastic CFRP parts for the Airbus A350XB. In: Proceedings of the ITECH Conference, Bremen, October 2012.
- Ageorges C., Ye L., Hou M. Advances in fusion bonding techniques for joining thermoplastic matrix composites: a review. Composites Part A 2001; 32: 839-857.
- 4. Don R.C., Gillespie J.W.Jr., McKnight S.H. Bonding techniques for high performance thermoplastic compositions. United States Patent No. 5643390, 1997.
- Hou M., Beehag A., Yuan Q. Welding techniques for polymer or polymer composite components. International patent WO2003/011573, 2003.
- Jacaruso G.J., Davis G.C., McIntire A.J. Method of making thermoplastic adhesive strip for bonding thermoset composite structures. United States Patent No. 5264059, 1993.

- Hou M. Thermoplastic adhesive for thermosetting components. Materials Science Forums 2012; 706-709: 2963-2973.
- 8. Van Toren M. Method for bonding a thermoplastic polymer to a thermosetting polymer component. International Patent Application No. WO2012/161569A1, 2012.
- Ageorges C., Ye L. Resistance welding of thermosetting composite/thermoplastic composite joints. Composites Part A 2001; 32: 1603-1612.
- Yousefpour A., Hojjati M., Immarigeon J.-P. Fusion bonding/welding of thermoplastic composites. Journal of Thermoplastic Composite Materials 2004; 17: 303-339.
- Wetzel E.D., Ron R.C., Gillespie J.W.Jr. Modelling thermal degradation during thermoplastic fusion bonding of thermoset composites. In: Proceedings of the 52nd Annual Technical Conference, ANTEC'94, 1994.
- Holmes S.T., Gillespie J.W. Jr. Thermal analysis for resistance welding of large-scale TPC joints. Proceedings of the American Society for Composites, 1992.
- Villegas I.F. In-situ monitoring of ultrasonic welding of thermoplastic composites through power and displacement data. Journal of Thermoplastic Composite Materials 2015; 28(1): 66-85.
- Vig J.R. UV/Ozone cleaning of surfaces. Journal of Vacuum Science and Technology A 1985; 3(3): 1027-1033.
- 15. Villegas I.F. Strength development versus process data in ultrasonic welding of thermoplastic composites with flat energy directors and its application to the definition of optimum processing parameters. Composites Part A 2014; 65: 27-37.
- 16. ASTM Standard D1002. Apparent shear strength of single-lap-joint adhesively bonded metal specimens by tensile loading (metal-to-metal). 2005.
- Braun U., Brademann-Jock K., Stark W. Cure monitoring of epoxy films by heatable in situ FTIR analysis. Correlation to composite parts. Journal of Applied Polymer Science 2014; DOI: 10.1002/APP. 39832.

- Levy A., Le Corre S., Villegas I.F. Modelling of the heating phenomena in ultrasonic welding of thermoplastic composites with flat energy directors. Journal of Materials Processing Technology 2014; 214: 1361-1371.
- Zhang, Z., Wang, X., Luo, Y., Wang, L. Study on heating process of ultrasonic welding for thermoplastics. Journal of Thermoplastic Composite Materials 2009; 25: 647–654.
- Villegas I.F., Valle Grande B., Bersee H.E.N., Benedictus R. A comparative evaluation between flat and traditional energy directors for ultrasonic welding of CF/PPS thermoplastic composites. Composite Interfaces 2014; DOI: 10.1080/09276440.2015.1053753.



Figure 1. Temperature beneath a 0.25 mm-thick PEEK coating layer (applied on a CF/PEEK adherend) for different heating times (i.e. different heat inputs) when the temperature at the welding interface is 400°C (based on Holmes & Gillespie 1D heat transfer model [12]).



Figure 2. Temperature beneath a PEEK coating layer with variable thickness (applied on a CF/PEEK adherend) for a typical resistance welding process with 90 kW/m² constant input power. The temperature at the welding interface is considered to be 400° C (based on Holmes & Gillespie 1D heat transfer model [12]).



Figure 3. Schematic of the overlap for direct welding (left) and indirect welding (right) of CF/PEEK onto CF/epoxy adherends with flat energy director (ED) (thickness of CF/epoxy adherend = 1.70 mm, thickness of CF/PEEK adherend = 1.92 mm, thickness of PEEK coating = 0.25 mm, thickness of PEEK energy director = 0.25 mm, sketch not to scale).



Figure 4. Ultrasonic welder and welding jig used in this study: (1) sonotrode, (2) sliding platform for top adherend, (3) clamp for top adherend, (4) clamp for bottom adherend.



Figure 5. FTIR reference spectra for as-manufactured CF/epoxy samples and samples exposed to 200°C for 4, 20 and 60 min.



Figure 6. CF/epoxy fracture surfaces after direct welding under long-heating-time conditions (left) and shortheating-time conditions (right). Figure on the left shows names used for the different edges of the welding overlap (delimited by white horizontal line). Different types of damage can be observed: (1) Visibly dry fibres; (2) Visibly dry fibres and fibre bundles detachment; (3) longitudinal cracks.



Figure 7. SEM details of damaged areas on CF/epoxy fracture surface (direct welding, long-heating-time conditions). Left detail shows some resin still present on and between the carbon fibres. Right detail shows total absence of resin connecting the carbon fibres.



Figure 8. FTIR spectra for CF/epoxy samples subjected to direct welding under both long and short welding times and reference spectra for as-manufactured CF/epoxy samples and samples exposed to 200°C for 4 min.



Figure 9. CF/epoxy fracture surfaces after indirect welding under long-heating-time conditions (left) and under short-heating-time conditions (right). Interesting features that can be observed on these fracture surfaces are: (1) damage on transverse external overlap edge; (2) damage in the middle of the overlap; (3) potential resin residues from PEEK coating. White horizontal line delimits welding overlap.



Figure 10. SEM details of damaged areas on CF/epoxy fracture surface (indirect welding, long-heating-time conditions). Left detail shows dry carbon fibres (thermal damage). Right detail shows resin-rich interlaminar damage (damaged caused by mechanical testing).



Figure 11. FTIR spectra for CF/epoxy samples subjected to indirect welding under both long- and short-heatingtime conditions and reference spectra for as-manufactured CF/epoxy samples and samples exposed to 200°C for 4 min.



Figure 12. Fracture surfaces of a CF/PEEK to CF/epoxy indirect weld with improved adhesion between the CF/epoxy and the PEEK coating layer co-cured to it, consequently failure mostly occurs in the CF/PEEK composite substrate (right).

Reference	Welding force (N)	Peak-to-peak amplitude (µm)	Optimum displacement (mm)	Average heating time (ms)	Average maximum power (kW)
Short heating time	1500	90	0.10	460	2.1
Long heating time	300	72	0.08	830	1.5

Table 1. Summary of ultrasonic welding conditions used in this study