INNOVATIVE WELDING OF CF/EPOXY AND CF/PEEK COMPOSITES

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ABSTRACT

Thermoplastic composites (TPCs) are very attractive to several industries as a result of their cost-effective manufacturing and assembling. One of the most cost-effective manufacturing techniques for TPCs is press forming. In the aerospace industry, press forming is widely used for the high-volume production of small- to medium-sized TPC parts. An example of which are the TPC (mostly C/PEEK) clips used to connect structural elements in the fuselage of the new composite passenger aircrafts. The manufacturing of bigger components relies on the use of thermoset composites (mostly C/epoxy) which currently show cost advantages as compared to TPCs for such applications. C/PEEK clips are currently assembled to the C/epoxy fuselage structure via mechanical fastening. Nevertheless, the ability of TPCs to be welded with little surface preparation and short assembly times poses the question of whether welding could be also used for such C/PEEK – C/epoxy dissimilar composite combinations.
The research presented in this paper proposes an innovative procedure to effectively weld C/PEEK and C/epoxy composites. Firstly, the C/epoxy composite was made "weldable" by co-curing a very thin layer of thermoplastic PEI resin onto the C/epoxy laminate. During the curing cycle, the PEI resin and the components of the epoxy resin system partially dissolved into each other generating a graded interphase between the original epoxy and PEI resins. Subsequently, the C/PEEK composite adherend was welded onto the PEI-rich surface of the "weldable" C/epoxy adherend, exploiting the compatibility between PEI and PEEK. Thermal degradation of the C/epoxy adherend during the welding process was avoided via ultrashort heating times enabled by the ultrasonic welding technology. In this fully experimental research work, mechanical testing was used to comparatively evaluate the quality of the welds. Cross-section scanning electron microscopy was used to assess the size and morphology of the PEI/epoxy interphase before and after the welding process.

1 INTRODUCTION

Owing to their cost-effectiveness in manufacturing, thermoplastic composites (TPCs) are increasingly found in engineering applications. An example of that are the thousands of press-formed TPC clips (mostly made out of carbon fibre reinforced poly-ether-ether-ketone, C/PEEK) used as structural connections in the fuselage of the modern composite (mostly made out carbon fibre reinforced epoxy, C/epoxy) passenger aircrafts, such as Airbus A350 and Boeing 787. Currently, dissimilar composite parts are assembled through mechanical fastening, which is the preferred assembling method for aircraft metallic structures. Mechanical fastening is however not a composite-friendly joining technique owing to stress concentrations and the necessity to drill holes for fastener installation. TPCs are well known for their ability to be welded or fusion bonded in a fast and energy efficient manner and several welding processes have already been industrialised for this type of materials [1][2]. An interesting question

is whether it is possible to also apply welding to dissimilar composite (i.e thermoplastic and thermoset) combinations as a composite-friendly alternative to current assembling procedures.

In parallel with the wider use of thermoplastic composites, the effort to develop welding strategies for dissimilar composites has increased in the last years. A common approach to make thermoset composites "weldable" entails adding a thermoplastic-rich "coupling" layer to the welding surface through a co-curing process [3]. Compatible thermoplastic and thermoset resin systems are known to inter-diffuse during the co-curing cycle resulting in a graded interphase [4][5]. Such interphase, composed of a polymer blend with gradually varying composition, is regarded as a strong and reliable connection between the two materials. Polyetherimide (PEI) is a high-performance amorphous thermoplastic resin known to be compatible with epoxy [6]. PEI is also fully compatible with PEEK [7], which makes of it an interesting coupling material for the welding of epoxy and PEEK based composites. The glass transition and recommended processing temperatures of PEI, 215°C and 350°C respectively, are however relatively high. Consequently, the use of PEI as coupling material for the welding of epoxy-based composite introduces the risk of thermal degradation of the epoxy resin during the welding process. One way of circumventing this issue entails increasing the thickness of the coupling layer above a certain critical value (e.g. 250 µm for induction welding of C/epoxy-PEI-C/PEI as reported in [8]). Increasing the thickness of the coupling layer, however, increases the extra weight added to the structure and increases secondary bending moments in the loaded joint. Another way entails using coupling thermoplastic polymers with low-processing temperatures. This approach however typically implies placing a low-performance thermoplastic polymer at the highly-loaded joint interface.

The fully experimental research work presented in this paper focuses on welding C/epoxy to C/PEEK composites through a 50 µm-thin PEI coupling layer. In order to prevent thermal degradation with such a thin coupling layer ultra-short heating times are used during the welding process, shown as a promising approach by our previous research [9]. Ultra-short heating times around 500 ms are enabled by the use of ultrasonic welding, which is a much faster welding technique than other popular welding techniques for thermoplastic composites such as induction or resistance welding [10]. Within this research the following aspects were investigated: morphology and size of the interphase between epoxy and PEI, effect of the welding process on the interphase and on the C/epoxy adherends, and strength of the welded joints relative to reference joints.

2 EXPERIMENTAL

2.1 Materials and manufacturing of composite laminates

The thermoset composite used in this study was carbon fibre reinforced epoxy (Hexply M18-1, Hexcel), hereafter referred to as C/epoxy. M18-1 is an 180°C epoxy resin system toughened with 20% PEI [6]. It contains TGMDA (tetraglycidyl ether methane diphenyl aniline) and MBDA (4,4-Methylenbis-(2,6-diethylanilin)), MBIMA(4,4-Methylenbis-(2-isopropyl-6-methylanilin) and DDS (4,4-Diaminodiphenylsulfone) as curing agents [6]. The thermoplastic composite used was carbon fibre reinforced poly-ether-ether-ketone (Cetex, Ten Cate Advanced Materials), hereafter referred to as C/PEEK. PEEK is a semicrystalline thermoplastic polymer with a glass transition temperature of 143°C and a melting temperature of 343°C. Polyetherimide (PEI) film (Ultem 1000, Sabic) was used as coupling layer for the C/epoxy laminates and as energy director for the welding process.

Carbon fabric reinforcement (1/4 twill weave) pre-impregnated with M18-1 epoxy resin (43% vol.) was used to manufacture the C/epoxy composite laminates through an autoclave curing cycle. Eight pre-preg layers were laid-up

in a $[0/90]_{4S}$ configuration. A 50 µm-thick PEI coupling layer was laid on top of the last pre-preg layer. This stack was subsequently vacuum bagged an cured in an autoclave following a two-hour curing plateau at 180°C and 6 bar pressure. The thickness of the cured C/epoxy-PEI (i.e. C/epoxy with co-cured PEI coupling layer) laminate was around 2 mm. An aluminium caul plate was used to ensure good surface finish on both sides of the laminate. Carbon fabric reinforcement (5 harness satin weave) powder-impregnated with PEEK resin (50% vol.) was used to manufacture the C/PEEK laminates in a hot platen press. Six pre-preg layers were laid up in a $[0/90]_{3S}$ configuration for a nominal final thickness around 2 mm. The press consolidation cycle featured a consolidation temperature of 385°C, consolidation pressure of 10 bar and 20 min consolidation time.

2.2 Welding equipment and welding process

A Rinco Dynamic-3000 microprocessor-controlled ultrasonic welder operated at 20 kHz frequency and maximum power of 3 kW was used for this research. Composite adherends of dimensions 25 mm x 100 mm were welded in a single lap configuration with an overlap length of 12.7 mm. These adherends were water-jet cut to the right dimensions from the C/epoxy-PEI and the C/PEEK laminates. A custom-designed welding jig was used to ensure proper clamping and parallelism of the adherends throughout the welding process. A 40 mm-diameter titanium cylindrical sonotrode was used to achieve welding of the entire overlap in a single step. Figure 1 shows the ultrasonic welding setup.

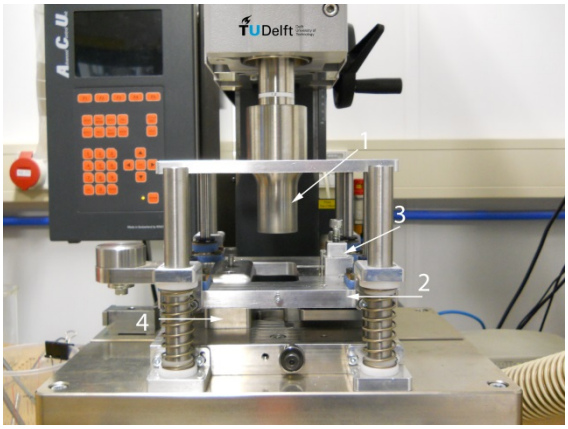

Figure 1. Ultrasonic welding setup: (1) sonotrode, (2) moving platform for top clamp, (3) top clamp, (4) bottom clamp.

Two different types of dissimilar-material welded joints were created in this study, C/epoxy-PEI welded to C/PEEK and C/epoxy-PEI welded to C/epoxy-PEI. Mono-material welded joints, i.e. C/PEEK welded to C/PEEK were also manufactured for comparison purposes. For all these welded joints a 250 µm-thick flat PEI energy director was used to concentrate heat generation at the welding interface. Flat energy directors are neat resin films with an area slightly larger than the overlap which are placed between the adherends prior to the welding process [11]. Displacement-controlled welding was used and the optimum displacement for each material combination (i.e. net displacement of the sonotrode that results in maximum lap shear strength) was graphically determined from the power and displacement data provided by the ultrasonic welder for calibration welds [12]. The different steps in the welding process were hence as follows: (1) A welding force of 2000 N and a 73.4 µm peak-to-peak vibration amplitude were applied until the optimal displacement was reached as a result of melting and squeeze flow of the energy director; (2) Subsequently the vibration was stopped and a force of 1000 N was applied for 4 s to achieve consolidation of the welded joint during cooling. A combination of high welding force and high vibration amplitude

were used in order to attain ultra-short heating times to prevent thermal degradation of the C/epoxy material [9]. Table 1 lists all the different types of samples considered in this study together with the optimum displacement values and the corresponding heating times. It must be noted that two different reference joints were used in this study, the already mentioned C/PEEK-C/PEEK welded samples and co-cured C/epoxy joints with a PEI layer in between the two adherends.

Joint type	**Adherend 1**	**Adherend 2**	**Optimal displacement (mm)**	**Average vibration time ± stdev (ms)**	**Joining process**
C/epoxy-PEI-C/PEEK	C/epoxy-PEI	C/PEEK	0.16	421±48	Welding
C/epoxy-PEI-C/epoxy	C/epoxy-PEI	C/epoxy-PEI	0.16	479±57	Flat ED (PEI)
C/PEEK-C/PEEK*	C/PEEK	C/PEEK	0.22	550±37	WF= 2000 N A= 73.4 µm
C/epoxy-PEI-C/epoxy*	C/epoxy	C/epoxy	-	-	Co-curing

Table 1. Different types of joints investigated in this research (*Reference joints). ED = energy director, WF= welding force, A=amplitude.

2.3 Testing and analysis

The welded and reference joints were mechanically tested following the ASTM D 1002 standard in a Zwick 250 kN universal test bench with a cross-head speed of 0.13 mm/min. Five coupons were tested per each type of joint and for every coupon the apparent lap shear strength was calculated as the maximum load divided by the overlap area. Optical and scanning electron cross sectional microscopy were used to investigate the internal structure of the adherends and of the welded joints. In order to resolve the microstructure of the epoxy-PEI interphase the microscopy samples were etched with NMP (N-Methyl-2-pyrrolidone). The etching process entailed dripping 1 ml of NMP on the surface of the polished microscopy sample, followed by rinsing with distilled water and drying with compressed air.

3 RESULTS AND DISCUSSION

3.1 Epoxy- PEI interphase

To investigate the interphase formed between epoxy and PEI during the curing process, cross section micrographic analysis of samples obtained from the C/epoxy laminate with the PEI coupling layer was performed with the following results. Optical microscopy of non-etched samples did not show any significant differences in appearance between the PEI and epoxy resins. Optical microscopy of etched samples allowed differentiation between the PEI layer and the epoxy resin but did not evidence the presence of an interphase between the two resins. It is interesting to mention that a scratch-like texture appeared on the PEI layer after the etching process. Finally, SEM (scanning electron microscope) inspection of the etched cross sections revealed the presence of an interphase with distinct morphological features between the pure epoxy resin and the pure PEI resin (Figures 2 and 3).

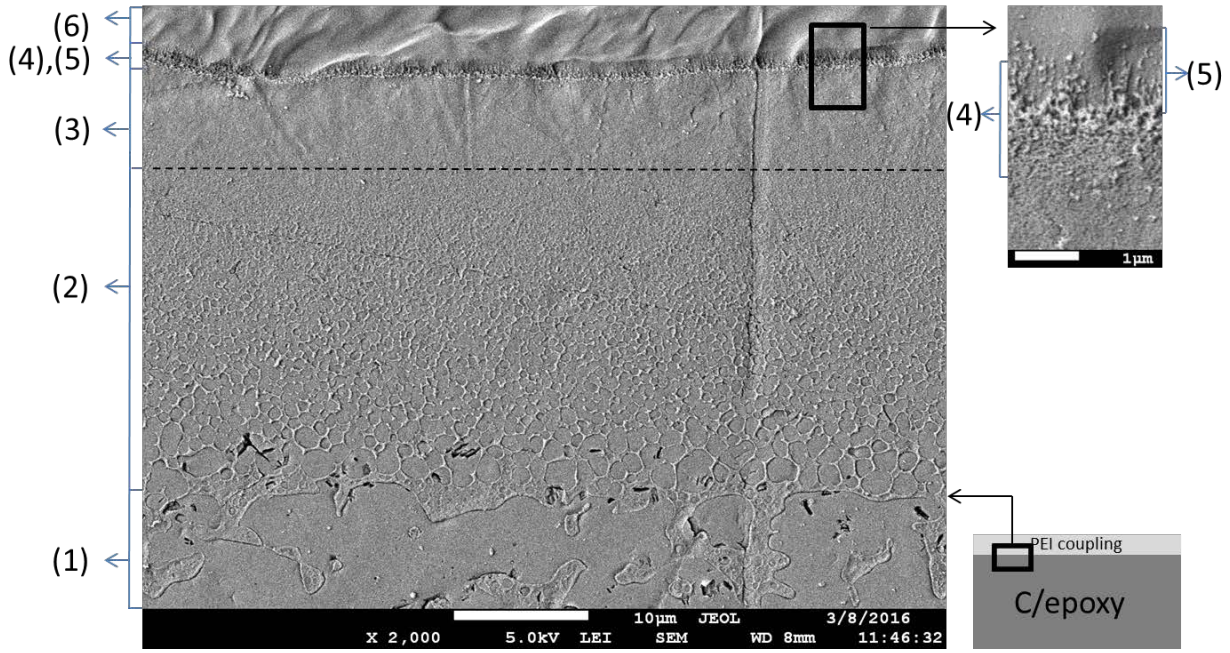

Figure 2. SEM image of the epoxy-PEI interphase. The dotted line indicates approximate location of epoxy-PEI interface prior to co-curing process. Number in between brackets indicate regions within the interphase.

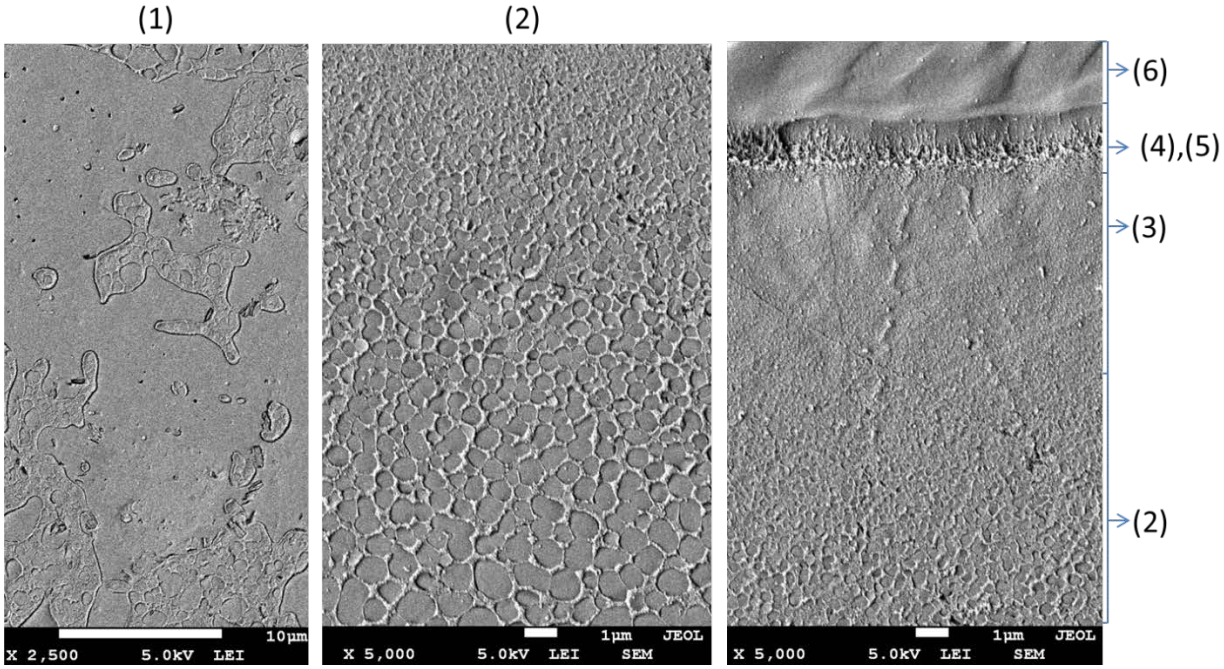

Figure 3. SEM details of different morphologies in epoxy-PEI interphase. Number in between brackets indicate regions within the interphase.

The overview in Figure 2 and details in Figure 3 show that six different regions can be distinguished in the C/epoxy-PEI cross section (from bottom to top):

(1) Epoxy resin with a co-continuous morphology typical of thermoplastic toughened epoxy systems [4].
(2) Epoxy with increasing PEI content resulting from the diffusion of PEI from the coupling layer into the epoxy matrix characterized by epoxy spheres dispersed in a PEI matrix, which is a typical nucleation-and-growth morphology [4]. The size of the epoxy spheres decreases as the PEI content increases moving upwards in the SEM images.
(3) PEI with very small epoxy domains that shows a light scratch-like texture which resembles the heavier texture found in the pure PEI layer.
(4) Epoxy diffusion front with an increased epoxy content that locally increases the size of the epoxy spheres.
(5) Darker band that could potentially result from faster diffusion of the hardener into PEI.
(6) Pure PEI characterised by a heavy scratch-like texture caused by etching.

It should be noted that the total thickness of regions (3), (4), (5) and (6) amounted to approximately 50 µm, i.e. the original thickness of the PEI coupling layer. Consequently, it could be thought that regions (3), (4) and (5) resulted from the diffusion of epoxy in the PEI coupling layer. Region (2) resulted, however, from the diffusion of PEI into the epoxy resin.

The qualitative results of the SEM analysis indicate hence that during the curing cycle diffusion of PEI into epoxy and vice-versa occurred resulting in a graded interphase, regions (2) to (5), in which the original epoxy matrix evolved into pure PEI. The relatively smooth morphology transitions from regions (1) to (3) seem to indicate that a gradual increase in the PEI content occurred in those regions. The epoxy diffusion front in region (4) potentially involves a local anomaly to that gradual concentration change. The thickness of the total interphase varies and seems to be influenced by the presence of fibre bundles, which are thought to act as a physical barrier to the diffusion process. The minimum thickness measured for the total interphase on the SEM cross sections was 30 µm. Of this, approximately 2/3 corresponded to region (2) and 1/3 to regions (3), (4) and (5). It should be noted that this interphase is 10 times thinner than the one reported in literature between PEI and A-stage DGEBA-MCDEA epoxy (DDS curing agent) [4]. Reasons for this discrepancy could be a lower diffusion speed of the B-stage epoxy used in the present study, lower diffusion speed caused by the presence of PEI as a toughening element in the original epoxy resin, and finally the fibre reinforcement acting as a physical barrier to diffusion, as mentioned before.

3.2 Welded joints

Despite the fact that the PEI coupling layer was much thinner than that used in previous studies [8][9], no visible signs of thermal degradation could be found in the C/epoxy adherends after welding. Figure 4 shows representative cross section micrographs of a C/epoxy-PEI-C/PEEK welded joint in which no porosity, resulting from sublimation of the epoxy resin when exposed to high temperature, can be observed. Regarding the post-welded epoxy-PEI interphase, SEM observation indicated that the interphase was either unaffected or only slightly affected by the welding process. The way in which the welding process majorly affected the interphase was by displacing its outermost regions (namely regions (4) and (5) through (local) melting and squeeze flow of the PEI coupling layer together with the energy director. Less frequently, the welding process was also found to affect deeper regions in the interphase. As an example, Figure 5 shows an area of a C/epoxy-PEI-C/PEEK welded overlap were regions (3), (4) and (5) were displaced.

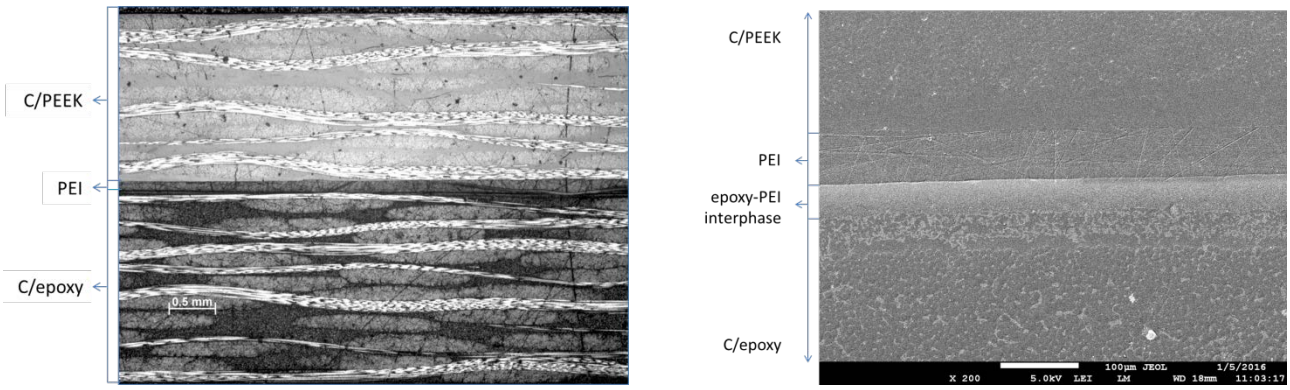

Figure 4. Cross section optical micrograph of etched C/epoxy-PEI-C/PEEK welded sample (left) and SEM detail of the welded joint (right).

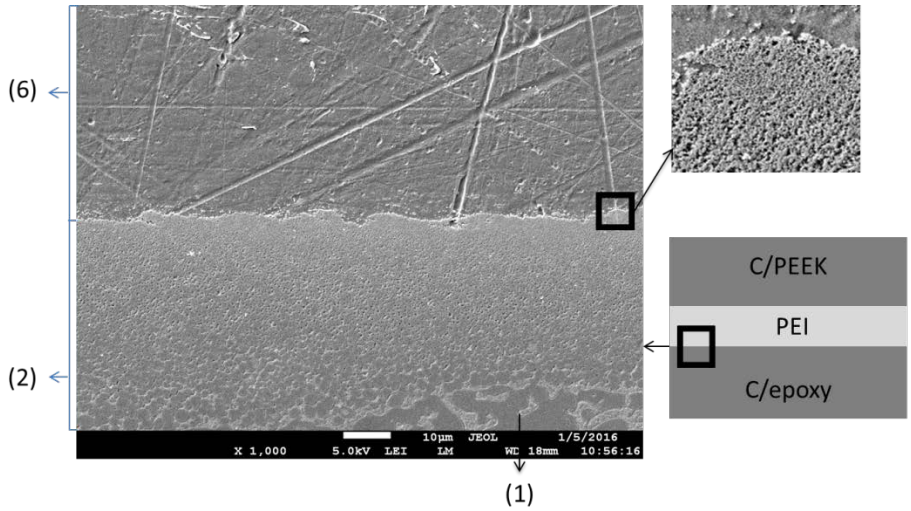

Figure 5. SEM image of post-welded interphase in C/epoxy-PEI-C/PEEK welded sample. Regions (3), (4) and (5) have been displaced by melting and flow of the PEI coupling layer during welding.

Mechanical testing of the welded and of the reference joints yielded the apparent lap shear strength (LSS) values listed in Table 2. The C/epoxy-PEI-C/PEEK welded joints resulted in an average 28.6 MPa LSS with 8% scatter (coefficient of variation). The C/epoxy-PEI-C/epoxy welded joints resulted in a somewhat lower average LSS, amounting to 23.6 MPa with 4% scatter. Both types of joints majorly underwent failure in the first layer of the C/epoxy composite underneath the coupling layer. SEM inspection of the fractured samples seemed to indicate that failure did not preferentially occur at the epoxy-PEI interphase (see Figure 6), although further research is needed to fully confirm this statement. The lower LSS in the C/epoxy-PEI-C/epoxy welded joints is believed to result from adherends with different mechanical properties, which are found to influence the stresses at the weld line and hence the results of the lap shear test [13]. The LSS yielded by the C/epoxy-PEI-C/epoxy co-cured reference samples (26.5 MPa, 3% scatter) was close to the one yielded by the corresponding welded joints, which once more indicates that the welding process does not negatively influence the strength of the

C/epoxy adherends or that of the interphase. The somewhat lower LSS of the welded joints is attributed to the presence of a small unwelded area in the middle of the overlap. This unwelded area, present in mostly all the welded joints in this study is believed to result from insufficient healing due to the short heating times and the relatively lower temperatures in the middle of the overlap [14]. This issue could be remediated by adequately modifying the energy director. Finally, the LSS yielded by the C/PEKK-C/PEEK welded joints was 43MPa with 10% scatter, featuring C/PEEK first-ply failure. The fact that this value was significantly higher than the one corresponding to the C/epoxy-PEI-C/PEEK joints could be attributed to different stresses at the weld line and by the higher ductility of the C/PEEK composite.

Joint reference	LSS (MPa)	Standard deviation (MPa)	Notes
C/epoxy-PEI-C/PEEK	28.6	2.3	Welded joint
C/epoxy-PEI-C/epoxy	23.6	0.9	Welded joint
C/epoxy-PEI-C/epoxy	26.5	0.7	Co-cured in autoclave
C/PEEK-C/PEEK	42.4	4.5	Welded

Table 2. Apparent lap shear strength values for welded and reference samples

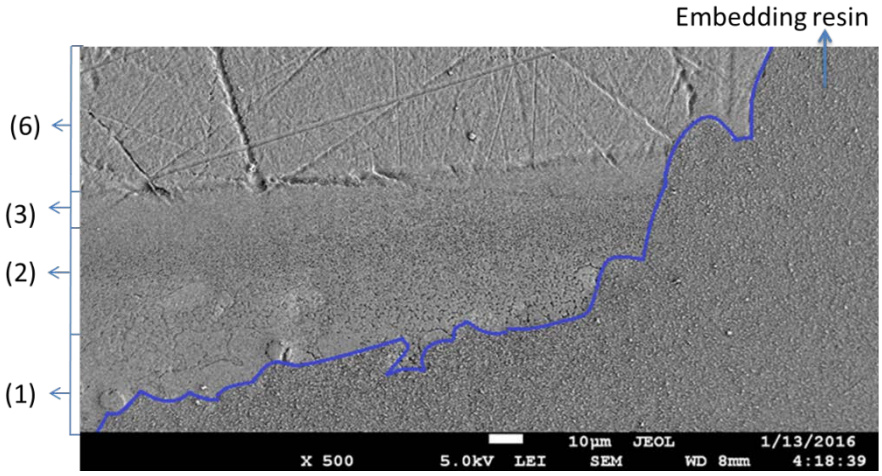

Figure 10. SEM image of a crack path in a C/epoxy-PEI-C/PEEK welded sample (outlined in blue). Numbers in between brackets refer to regions in the epoxy-PEI interphase.

4 CONCLUSIONS

This paper presents a procedure for the welding of dissimilar composites, i.e. C/epoxy and C/PEEK composites. The main features of this procedure are: (i) a 50 µm-thick PEI film was used as a coupling layer to obtain weldable C/epoxy laminates in which the epoxy matrix gradually evolved into the PEI thermoplastic polymer on the surface

to be welded and (ii) ultrasonic welding was used to enable high-temperature welding without thermal degradation of the CF/epoxy material. The main conclusions concerning this welding procedure are as follows:

- Co-curing of a PEI film on the welding surface of the C/epoxy laminates used in this study resulted in a graded interphase in which the original PEI content in the PEI-toughened epoxy resin gradually increased until pure PEI was obtained on the surface. This gradual increase of PEI content could be qualitatively assessed through morphological changes in the resin revealed by SEM inspection of etched samples. On one hand, partial diffusion of the PEI film into the epoxy resin caused the original co-continuous morphology in the epoxy resin to evolve into a PEI-richer morphology consisting of epoxy spheres dispersed in PEI matrix. The size of these epoxy spheres gradually decreased as the PEI content increased towards the surface. On the other hand, diffusion of the epoxy monomer and hardener into the PEI film resulted in an increased content of epoxy, and hence increased sphere size, that seemed to locally interrupt the graded nature of the interphase next to the pure PEI surface.
- The epoxy-PEI interphase had a minimum total thickness of 30 μm and it was mostly found between the outermost layer of reinforcing fibres in the C/epoxy composite and the PEI coupling layer. Of this thickness, approximately 2/3 corresponded to the area where PEI diffused into the epoxy resin and the other 1/3 to the area where epoxy diffused into the PEI layer. The lower thickness of the interphase as compared to literature studies on diffusion of PEI in A-stage epoxies was attributed to the lower reactivity of the B-staged epoxy in the pre-preg system used in this study together with the fibre reinforcement acting as a physical barrier for the diffusion process.
- Owing to melting and flow of the PEI coupling layer during the welding process, the area of the interphase corresponding to epoxy diffusion into the PEI coupling layer, i.e. the outermost regions of the interphase, was found to disappear in some areas of the welding overlap. However, the rest of the interphase as well as the C/epoxy composite were not visibly affected by the welding process.
- During static single lap shear testing, the C/epoxy-PEI-C/PEEK welded samples predominantly failed within the first layer of the C/epoxy composite and seemingly away from the epoxy-PEI interphase. The average lap shear strength yielded by the C/epoxy-PEI-C/PEEK samples was 28.6 MPa, which is comparable to strength values reported for high-performance adhesives.
- When the same process was applied to weld two C/epoxy adherends the resulting average single lap shear strength was 24.8 MPa, which is quite similar to the 26.5 MPa yielded by C/epoxy co-cured joints. This indicated that, apart from not causing any significant visible damage, the welding process did not negatively affect the mechanical properties of the C/epoxy adherends or of the interphase.

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