Significantly enhanced structural integrity of adhesively bonded PPS and PEEK composite joints by rapidly UV-irradiating the substrates

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\textbf{A B S T R A C T}

A high-power UV-irradiation technique was proposed for the surface treatment of PPS and PEEK composites, aiming to achieve good adhesion with epoxy adhesives. The composite substrates were rapidly UV-irradiated for a duration of between 2–30 s, and then bonded using an aerospace film adhesive to produce joints. Tensile lap-shear strength and mode-I and mode-II fracture energies of the adhesive joints were investigated. It was observed that the application of a short-time UV-irradiation to the substrates transformed the failure mode of the specimens from adhesion failure to substrate damage in all cases. This consequently resulted in remarkable improvements in the mechanical and fracture performance of the adhesive joints. For example, the lap-shear strength increased from 11.8 MPa to 31.7 MPa upon UV-irradiating the PPS composites for 3 s, and from 8.3 MPa to 37.3 MPa by applying a 5 s UV-irradiation to the PEEK composites. Moreover, the mode-I and mode-II fracture energies significantly increased from \(\sim 0.05\) J/m\(^2\) to \(\sim 1500\) J/m\(^2\) and from \(\sim 7000\) J/m\(^2\) to \(\sim 7000\) J/m\(^2\), respectively for both of the adhesively bonded PEEK and PPS composite joints.

\textbf{1. Introduction}

Carbon fibre reinforced thermoplastic composites (TPCs) offer many advantages over thermostet composites (TSCs), including a high resistance to impact and fracture damage, the ability to be re-melted and re-shaped and a low storage cost as a result of an infinite shelf life. For this reason, they are increasingly being used to replace the metallic and TSC counterparts in a wide variety of industries, including automotive, aerospace and marine sectors. Accordingly, it becomes critical to develop effective joining methods for TPCs. To date, mechanical fastening [1–3], adhesive bonding [4–7] and welding (infusion bonding) [8,9] are the major methods for joining thermoplastics and their composite materials. Additionally, Li et al. [10–12] proposed to use a variotherm injection moulding method for joining thermoplastics to Aluminium substrates. It was reported that a lap-shear strength of 25 MPa had been obtained for hybrid Polyphenylene sulphide/Aluminium joints, showing some promise for industrial application. While each of these methods has its own strengths and weakness, adhesive bonding is unique for joining thin-walled sections or elements with a significant difference in thickness [13]. Moreover, it presents many advantages over the other methods to the structural joining of FRPs, such as the possibility of joining any pair of dissimilar materials, achieving a uniform stress-distribution along the junction between the two substrates, making light-weight constructions, and sealing the entire bonding area and hence to provide high joint strength and durability [14].

The majority of thermoplastics, including Polyether ether ketone (PEEK) and Polyphenylene sulfide (PPS), possess a low level of adhesion with epoxy adhesives due to their inherently poor reactivity, small surface energies and weak polarities [15]. Accordingly, relatively intensive surface preparation of the TPCs prior to adhesive joining is required, that could be achieved by using different methods, including acid etching [16,17], corona discharge [18,19], plasma treatment [20–22] and oxidising flame treatment [23,24]. However, there are specific limitations to each of these techniques, such as the lack of uniformity of the treated surfaces (corona discharge, plasma and oxidising flame treatments), the poor access to some small inner surfaces (corona discharge and oxidising flame treatments), the low efficiency for treating components with large surfaces (acid etching, corona discharge, plasma and oxidising flame treatments) and the acid solution is highly toxic (acid etching) etc. Ultraviolet light (UV)-irradiation was initially
2.1. Materials and sample preparation

The carbon fibre reinforced PPS and PEEK composites were produced from 8 plies of powder-coated 5-harness satin weave prepregs, supplied by TenCate Advanced Composites, the Netherlands. The stack sequence was [0°/90°]_{4S}, where 0° and 90° correspond to the warp and weft directions, respectively. They were consolidated in a hot-platen press (Joos LAP100) at 2 MPa for 30 mins. The process temperature for the PPS and PEEK composites was 320 °C and 400 °C, respectively. After the consolidation, the TPC panels were placed in a UV-irradiation chamber equipped with a LH6 MKII UV source (200 W/cm) and a Mercury D bulb for a surface treatment lasting for between 2–30 s.

In this work, the composite substrates were indicated by the type of the thermoplastic polymer followed by the duration of the UV-irradiation, e.g., PPS (None) means the non-treated PPS composites, and PPS (2sUV) indicates the PPS composite substrate that was UV-treated for 2s. The intensities of the UV spectral ranges were determined using a UV Power Puck from EIT Inc., USA. The measured intensities of UUV (395–445 nm), UVA (320–390 nm), UVB (280–320 nm) and UVC (250–260 nm) were 1979 mW/cm², 1546 mW/cm², 343 mW/cm² and 51 mW/cm², respectively. After the UV-irradiation, two sheets of TPC laminate with one layer of film adhesive in between were assembled together and then cured in an autoclave. It should be noted that a PTFE film with a thickness of 12 μm was placed at desired location above the adhesive layer to introduce crack starters in the specimens for the following fracture tests. The film adhesive used for bonding the TPCs was Scotch-WeldTM AF 163-2K from 3M Netherlands B.V. This is a structural epoxy adhesive supported by a knit carrier. The curing cycle consisted of a single dwell step at 121 °C and 3 bar gauge pressure for 90 mins, and a 730 mbar under pressure inside the vacuum bag was used throughout the curing process. The average thickness of the adhesive layer within the cured adhesive joints was 136 ± 29 μm. After the curing, specimens with desired dimensions were cut out from the cured joints for the following tests.

2.2. Analysis and testing

A X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD) was used to determine the chemical compositions of the surfaces of the non-treated and UV-treated TPCs. The surface free energies and water contact angles of the TPC surfaces were also investigated using a mobile surface analyser from KRUSS, GmbH. A single lap-shear joint test according to ISO4587, as schematically shown in Fig. 1(a) was used to determine the tensile lap-shear strength (LSS) of the adhesive joints. The test was carried out at a loading rate of 2 mm/min at ambient temperature. The specimens were attached to the testing machine using a pair of hydraulic clamps with a clamping pressure of 200 bar. To ensure the force was applied in the mid-plane of the adhesive layer during the lap-shear test, a misalignment between the upper and lower clamps was set. Three replicate tests were conducted for each set.
Adhesion Failure  
TPC substrate  
Adhesive  
TPC substrate  

Cohesion Failure  
Substrate Damage

Fig. 2. Typical failure patterns of the adhesive joints.

Table 1  
Results of the surface characterisations of the TPC surfaces, including carbon and oxygen content, O/C ratio, surface free energy (\( \gamma \)) and its polar component (\( \gamma_p \)), dispersive component (\( \gamma_d \)) and \( \gamma_p/\gamma_d \) ratio, and water contact angles (\( \theta \)).

| UV-irradiation | 0 s | 2 s | 3 s | 4 s | 5 s | 10 s | 20 s | 30 s |
|----------------|-----|-----|-----|-----|-----|------|------|------|
| **PPS**       |     |     |     |     |     |      |      |      |
| O(%)          | 11.51 | 12.29 | 13.11 | 13.84 | 14.52 | 16.38 | 17.33 | 18.25 |
| C(%)          | 76.35 | 73.96 | 72.03 | 71.05 | 70.06 | 67.60 | 66.98 | 66.01 |
| \( O/C(\%) \) | 0.15 | 0.17 | 0.18 | 0.19 | 0.21 | 0.24 | 0.26 | 0.28 |
| \( \gamma_d (mN/m) \) | 46.84 | 45.39 | 45.99 | 45.09 | 45.66 | 44.54 | 42.48 | 43.36 |
| \( \gamma_p (mN/m) \) | 1.26 | 2.56 | 3.09 | 3.68 | 4.00 | 4.94 | 5.79 | 6.19 |
| \( \gamma (mN/m) \) | 48.10 | 47.95 | 49.08 | 48.77 | 49.66 | 49.48 | 48.26 | 49.55 |
| \( \gamma_p/\gamma_d \) | 0.03 | 0.06 | 0.07 | 0.08 | 0.09 | 0.11 | 0.14 | 0.14 |
| \( \theta (\degree) \) | 85.21 | 78.49 | 76.23 | 72.47 | 72.44 | 68.13 | 66.67 | 66.40 |

| **PEEK**      |     |     |     |     |     |      |      |      |
| O(%)          | 14.93 | 15.68 | 16.49 | 18.05 | 20.04 | 22.97 | 24.04 | 25.17 |
| C(%)          | 82.67 | 80.18 | 79.23 | 77.91 | 76.75 | 73.89 | 70.39 | 69.49 |
| \( O/C(\%) \) | 0.18 | 0.20 | 0.21 | 0.23 | 0.26 | 0.31 | 0.34 | 0.36 |
| \( \gamma_d (mN/m) \) | 46.92 | 48.11 | 46.48 | 47.25 | 47.81 | 46.95 | 45.14 | 46.76 |
| \( \gamma_p (mN/m) \) | 3.64 | 4.76 | 4.98 | 5.13 | 5.87 | 6.14 | 6.31 | 6.50 |
| \( \gamma (mN/m) \) | 50.56 | 52.87 | 51.46 | 52.38 | 53.68 | 53.09 | 51.45 | 53.26 |
| \( \gamma_p/\gamma_d \) | 0.08 | 0.10 | 0.11 | 0.11 | 0.12 | 0.13 | 0.14 | 0.14 |
| \( \theta (\degree) \) | 80.22 | 78.77 | 75.09 | 73.22 | 69.84 | 67.49 | 68.37 | 67.68 |

Table 2  
Thermodynamic work of adhesion of the UV-irradiated TPC surfaces.

| UV-irradiation | 0 s | 2 s | 3 s | 4 s | 5 s | 10 s | 20 s | 30 s |
|----------------|-----|-----|-----|-----|-----|------|------|------|
| **PPS**        |     |     |     |     |     |      |      |      |
| \( W^p (mN/m) \) | 5.72 | 8.16 | 8.96 | 9.78 | 10.19 | 11.33 | 12.26 | 12.69 |
| \( W^d (mN/m) \) | 86.57 | 85.22 | 85.78 | 84.94 | 85.47 | 84.42 | 82.44 | 83.29 |
| \( W (mN/m) \) | 92.29 | 93.38 | 94.74 | 94.72 | 95.66 | 95.75 | 94.70 | 95.97 |

| **PEEK**       |     |     |     |     |     |      |      |      |
| \( W^p (mN/m) \) | 9.73 | 11.12 | 11.38 | 11.55 | 12.35 | 12.63 | 12.81 | 13.00 |
| \( W^d (mN/m) \) | 86.65 | 87.74 | 86.24 | 86.95 | 87.46 | 86.67 | 84.98 | 86.50 |
| \( W (mN/m) \) | 96.38 | 98.86 | 97.62 | 98.50 | 99.81 | 99.31 | 97.79 | 99.50 |

Table 3  
LSSs and joint stiffnesses of the PPS and PEEK composite joints with the substrates UV-irradiated for different times.

| UV-irradiation | 0 s | 2 s | 3 s | 4 s | 5 s | 10 s | 20 s | 30 s |
|----------------|-----|-----|-----|-----|-----|------|------|------|
| **PPS**        |     |     |     |     |     |      |      |      |
| LSS (MPa)      | 11.8 | 22.4 | 31.7 | 31.2 | 30.7 | 31.4 | 32.3 | 28.9 |
|                | ±0.3 | ±0.6 | ±1.5 | ±0.3 | ±1.3 | ±1.8 | ±2.2 | ±0.2 |
| Joint stiffness | 532 | 555 | 562 | 562 | 549 | 550 | 551 | 566 |
| (MPa)          | ±12 | ±16 | ±5 | ±3 | ±2 | ±8 | ±6 | ±15 |

| **PEEK**       |     |     |     |     |     |      |      |      |
| LSS (MPa)      | 8.3 | 22.9 | 26.9 | 34.1 | 37.3 | 39.0 | 37.1 | 36.9 |
|                | ±0.7 | ±0.7 | ±0.8 | ±0.7 | ±0.6 | ±1.8 | ±0.6 | ±0.8 |
| Joint stiffness | 550 | 570 | 563 | 566 | 569 | 573 | 570 | 566 |
| (MPa)          | ±19 | ±3 | ±9 | ±6 | ±23 | ±15 | ±6 | ±5 |

The mode-I and mode-II fracture energies of the adhesive joints were studied using a double cantilever beam (DCB) test and an end loaded split (ELS) test according to ISO15024 and ISO15114, respectively. The configurations of the DCB and ELS tests are schematically shown in Figs. 1(b) and (c). A constant displacement rate of 2 mm/min and 1 mm/min was used for the DCB tests and the ELS tests, respectively. During the fracture tests, a high resolution digital camera was used to monitor the length of the crack, that was synchronised with the load and displacement measurements based on the start time of the test. A 5 mm long precrack from the crack starter was generated by loading the samples under an opening mode for both of the DCB and the ELS specimens. Three replicate tests were conducted in each case. The failure surfaces of the tested specimens were imaged using a VK-X1000 microscope from KEYENCE Corporation to investigate the failure mechanisms of the adhesive joints. Fig. 2 illustrates three typical failure patterns of the adhesive joints those were identified in the current work [33,34], i.e. adhesion failure (the failure took place at the TPC/epoxy interface), cohesion failure (the failure occurred within the adhesive layer) and substrate damage (the failure progressed inside the TPC substrates).
Fig. 3. LSS (lap-shear strength) versus $W^p$ of the adhesive joints.

(a) PPS composite adhesive joints  
(b) PEEK composite adhesive joints

Fig. 4. Representative photographs and microscopy images of the failure surfaces of the lap-shear specimens of the PPS composite joints. The inset within the red box in (b) was a representative SEM image for showing the damage of the carbon fibres. The yellow arrows indicate broken carbon fibres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Composites Science and Technology 199 (2020) 108358

D. Quan et al.

3. Results and discussion

3.1. Surface characterisation

Results of the surface characterisations of the TPC surfaces are summarised in Table 1. It was found that applying a short time UV-irradiation to the TPC surfaces notably increased their oxygen contents and decreased their carbon contents for both of the PPS and PEEK composites. Consequently, the O/C ratio gradually increased from 0.15 to 0.28 for the PPS composites, and from 0.18 to 0.36 for the PEEK composites as the duration of the UV-irradiation increased up to 30 s. This was because of the high-power UV-irradiation provided sufficient energy to break the C–C/C-H species, which were associated with the development of C-O, C=O and O-C=O species to their molecular chains [31,35]. The increased amount of oxygen functional groups on the TPC surfaces subsequently affected their surface free energies. As shown in Table 1, the application of the UV-irradiation to the TPC surfaces had no obvious effects on the dispersive component ($\gamma_d$) of the surface energy, but notably increased the polar component ($\gamma_p$) of the surface energy, i.e. $\gamma_p$ increased from 1.26 mN/m to 6.19 mN/m (by 391%) for the PPS composite, and from 3.64 mN/m to 6.50 mN/m (by 79%) for the PEEK composite upon 30 s UV-irradiation. It should be noted that interactions at the interface of two phases only occur between the same type of forces, i.e. dispersive–dispersive, or polar–polar. Accordingly, a closer match between the $\gamma_d/\gamma_p$ ratios of the TPCs and the epoxy adhesive was favoured to achieve higher level of interactions at their interface. $\gamma_d$ and $\gamma_p$ of epoxy adhesives were given by Kinloch [36] to be about 5–8 mN/m and 40 mN/m, respectively, corresponding to a $\gamma_d/\gamma_p$ ratio of between 0.125–0.2. Clearly, applying the UV-irradiation to the TPCs resulted in a better match of the $\gamma_p/\gamma_d$ ratios between the TPCs and the epoxy adhesive, see Table 1. Thermodynamic work of adhesion ($W$) is defined as the reversible work that is needed.
to separate the interface from the equilibrium state of a liquid–liquid or liquid–solid phase boundary to a separation distance of infinity [37]. $W$ between the non-cured adhesive and the TPCs can be calculated as:

$$W = W^p + W^d = 2\gamma_p^p \alpha s^p 1/2 + 2\gamma_s^d \alpha s^d 1/2$$

(1)

where $W^p$ and $W^d$ are the contributions of the polar interactions and the dispersive interactions, respectively. The subscripts $p$ and $d$ denote the non-cured adhesive and the TPC substrates. The results of the calculations are presented in Table 2. Clearly, the values of $W^p$ at the adhesive/TPC interfaces significantly increased upon UV-irradiating the TPC surfaces, while $W^d$ exhibiting no obvious changes. It is noteworthy that, at the cured adhesive/TPC interfaces, the dispersive force was responsible for the temporary fluctuations of the charge distribution in the atomic/molecular structure, such as the van der Waals interactions, and the polar force generated Coulomb interactions between permanent dipoles and between permanent and induced dipoles, and subsequently generated hydrogen bonds and covalent bonds. Since hydrogen bonds and covalent bonds are much stronger than van der Waals forces, the increased values of $W^p$ resulted in significantly improved adhesive/TPC adhesion, as will be shown in Section 3.2. As expected, the increased $\gamma^p$ of the TPC surfaces significantly improved their wettabillity. As shown in Table 1, the water contact angles of the TPCs gradually decreased from 85.21° to 66.40° for the PPS composites and from 80.22° to 67.68° for the PEEK composites by UV-irradiating the TPCs for 30 s.

### 3.2. The lap-shear strength

Table 3 presents the LSSs and joint stinesses of the PPS and PEEK composite joints from the single lap-shear joint tests. It was found that the application of a short-time UV-irradiation to the PPS and PEEK composite substrates significantly increased the LSS of the adhesive joints, while the joint stiffness remaining unchanged. For the adhesive bonded PPS composite joints, the LSS increased from 11.8 MPa of the non-treated joints to 22.4 MPa by UV-irradiating the substrates for 2 s, and then to a plateau value of approximately 32 MPa upon a UV-irradiation of 3 s and above. A noticeable decrease in the LSS was observed as the treatment time increased from 20 s to 30 s, that was very likely due to the degradation of the mechanical properties of the PPS polymers due to an exposure to the UV-lights for a relatively long time. Similarly, the LSS of the PEEK composite joints gradually increased from 8.3 MPa of the non-treated joints to 37.3 MPa as the duration of the UV-irradiation increased to 5 s, and then remained more or less the same for a longer UV-irradiation up to 30 s. The plots of LSS versus $W^p$ of the adhesive joints are shown in Fig. 3. It was observed that, prior to adhesive curing, $W^p$ of about 9 mN/m and above 12 mN/m at the PPS/adhesive and PEEK/adhesive interfaces, respectively was required to achieve the plateaued LSSs of the corresponding adhesive joints.

### 3.3. Fracture behaviour of the adhesive joints

As observed in Section 3.2, the LSS of the adhesive joints plateaued at a treatment time of 3 s for the PPS composites and 5 s for the PEEK
composites. Herein, fracture test specimens underwent the same duration of UV-irradiation were also prepared and tested to evaluate the fracture response of the corresponding adhesive joints. However, the mode-I fracture energy of the adhesive bonded PEEK(5sUV) substrates was determined to be relatively low, as shown in the following section. Hence, an additional set of specimens those were UV-irradiated for 10 s, i.e. PEEK(10sUV) joints were manufactured and tested for the DCB tests.

3.3.1. Mode-I fracture behaviour

Representative load versus displacement curves from the DCB tests are shown in Fig. 6(a). It was found that the fracture loads of the DCB specimens for the non-treated TPC joints were very low, i.e. below 20 N in all cases. This was typical for the adhesively bonded PEEK and PPS joints, owing to the inherent low surface activities of the thermoplastic matrix [32,38–40]. The crack propagated in a stick-slip manner for all the UV-treated adhesive joints, indicated by the zigzag shape of the load-versus displacement curves in Fig. 6(a). In this case, only the peak loads on the load-versus displacement curves were used to calculate the mode-I fracture energies, \( G_{IC} \). Clearly, the application of a UV-irradiation to the TPCs significantly increased the fracture propagation load of the adhesive joints, that corresponded to remarkable increases in \( G_{IC} \), as shown in Fig. 6(b). One can see that the application of a 3 s UV-irradiation to the PPS composite substrates remarkably increased \( G_{IC} \) from 45 J/m\(^2\) of the PPS(None) joints to 1476 J/m\(^2\) of the PPS(3sUV) joints. However, \( G_{IC} \) of the PEEK(5sUV) joints was measured to be 281 J/m\(^2\), that was relatively low when compared to the PPS(3sUV) joints. Fortunately, this value significantly increased to

Fig. 7. Fracture surfaces of the DCB specimens of the adhesive joints. The yellow arrows indicate some bundles of delaminated and broken carbon fibres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.3.2. Mode-II fracture behaviour

Joints. Improvements in the mode-I fracture performance of the adhesive energy dissipation during the fracture process, and led to significant polymers and the carbon fibres. These phenomena contributed to the in the TPC substrates, i.e. mainly at the interface between the TPC carbon fibres, see Fig. 7. This means the crack propagation took place the majority of the surfaces were featured with bare and damaged polymers remained on the surfaces of the opposite-side substrates, and were observed. Consequently, only a small amount of thermoplastic extensive thermoplastic polymers and numerous broken carbon fibres adhesive layer attached on one side of the fracture surfaces, on which, in Fig. 6(b). For the PPS(3sUV) and PEEK(10sUV) joints, the entire 

\[ G_{IIc} \] of the PEEK(5sUV) joints, as shown in Fig. 7(b)). However, under mode-II fracture, the adhesion at the PEEK/adhesive interface of the PEEK(5sUV) joint was sufficiently high to cause damage to the substrate, and consequently resulted in remarkable improvements in the mode-II fracture behaviour. This was attributed to the different loading mode applied to the bonds at the PEEK/adhesive interface, as schematically shown in Fig. 11. During the mode-II fracture process, the bonds began to break one by one as the applied force \( F \) approached the tensile strength of the bonds. Prior to the mode-II crack propagation, the unbroken bonds were still holding the two surfaces together (as shown

1577 J/m\(^2\) as the duration of the UV-irradiation increased to 10 s. The fracture surfaces of the DCB specimens were analysed to investigate the fracture mechanisms of the adhesive joints, as shown in Fig. 7. As expected, both of the PPS(None) and PEEK(None) joints exhibited a pure adhesion failure without causing any damage to the adhesives and the TPC substrates. A number of white colour marks appeared on the adhesive layer of the PEEK(5sUV) joint, leaving corresponding white colour lines on the opposite side. These features corresponded to the peaks on the corresponding load-versus-displacement curves in Fig. 6(a), and indicate some interactions between the epoxy adhesive and the PEEK(5sUV) substrate induced by the UV-irradiation. However, no other noticeable damage was observed, and this resulted in the relatively little improvements in \( G_{IIc} \) of the PEEK(5sUV) joints, as shown in Fig. 6(b). For the PPS(3sUV) and PEEK(10sUV) joints, the entire adhesive layer attached on one side of the fracture surfaces, on which, extensive thermoplastic polymers and numerous broken carbon fibres were observed. Consequently, only a small amount of thermoplastic polymers remained on the surfaces of the opposite-side substrates, and the majority of the surfaces were featured with bare and damaged carbon fibres, see Fig. 7. This means the crack propagation took place in the TPC substrates, i.e. mainly at the interface between the TPC polymers and the carbon fibres. These phenomena contributed to the energy dissipation during the fracture process, and led to significant improvements in the mode-I fracture performance of the adhesive joints.

3.3.2. Mode-II fracture behaviour

Fig. 8 shows representative load versus displacement curves and \( R \)-curves from the ELS tests of the adhesive joints. The points in (a) are where crack initiation took place. The load increased from below 100 N to above 400 N in both cases upon applying a rapid UV-irradiation to the PPS and PEEK composite substrates, see Fig. 8(a). It should be noted that the crack propagated for a length of approximately 10 mm and then dynamically failed the entire ELS specimens during the fracture test for all the UV-treated adhesive joints. For this reason, only the fracture energies corresponding to a crack length of between 50–65 mm were obtained on the mode-II \( R \)-curves of the adhesive joints in Fig. 8(b). It was observed that the mode-II \( R \)-curves of all the UV-treated adhesive joints exhibited a ‘rising’ behaviour, indicating an extension in the length of the mode-II fracture damage zone before the dynamic failure. Herein, the fracture energies corresponding to the last points of the \( R \)-curves, corresponding to the mode-II fracture energies at the instant of the dynamic failure of the ELS specimens, were taken as the mode-II fracture energies, \( G_{IIc} \) of the adhesive joints, which are summarised in Fig. 9. It was found that \( G_{IIc} \) increased from below 300 J/m\(^2\) of the non-treated adhesive joints to 7814 J/m\(^2\) of the PPS(3sUV) joints and 6939 J/m\(^2\) of the PEEK(5sUV) joints. The significantly improved mode-II fracture performance could be correlated to the fracture mechanisms of the adhesive joints. Fig. 10 presents photographs and microscopy images of the fracture surfaces of the ELS specimens. It was observed that the mode-II fracture mode of the adhesive joints transformed from pure adhesion failure of the non-treated joints to significant substrate damage upon applying the UV-irradiation to the TPC substrates in both cases. Inter-ply delamination, i.e. the crack propagation path diverted from the mid-plane to the adjacent interlaminar during the fracture process, took place for the PPS(3sUV) joints, causing severe damage to both sides of the substrates, as shown in Fig. 10. For the PEEK(5sUV) joints, the entire adhesive layer together with a large number of damaged PEEK polymers and carbon fibres were observed on one side of the substrates, leaving obviously damaged PEEK layer and bare carbon fibres on the opposite side. Obviously, more severe damage to the substrates took place for the PPS(3sUV) joints than the PEEK(5sUV) joints, that resulted in a higher \( G_{IIc} \) of the PPS(3sUV) joints, as shown in Fig. 9.

Interestingly, the application of 5 s UV-irradiation to the PEEK composites only slightly improved the mode-I fracture behaviour of the adhesive joints (see Fig. 6), showing a clear adhesion failure of the PEEK(5sUV) joints, as shown in Fig. 7(b)). However, under mode-II fracture, the adhesion at the PEEK/adhesive interface of the PEEK(5sUV) joint was sufficiently high to cause damage to the substrate, and consequently resulted in remarkable improvements in the mode-II fracture behaviour. This was attributed to the different loading mode applied to the bonds at the PEEK/adhesive interface, as schematically shown in Fig. 11. During the mode-II fracture process, the bonds began to break one by one as the applied force \( F \) approached the tensile strength of the bonds. Prior to the mode-II crack propagation, the unbroken bonds were still holding the two surfaces together (as shown

![Load versus displacement curves](image1.png)

![Mode-II R-curves](image2.png)

**Fig. 8.** Representative load versus displacement curves and mode-II \( R \)-curves from the ELS tests of the adhesive joints. The points in (a) are where crack initiation took place.

![Mode-II fracture energies](image3.png)

**Fig. 9.** Mode-II fracture energies of the adhesive joints.
in Fig. 11(a)) and the intimate contact of the two surfaces allowed some of the broken bonds recombined to create new bonds [41]. This subsequently enhanced the overall mode-II fracture performance of the adhesive joints. However, bond recombination was unexpected during the mode-I fracture process due to its opening characteristic, as schematically shown in Fig. 11(b). The opening characteristic of the mode-I fracture also negatively affected the activation energy required to break the bonds. Fig. 12 shows the Morse potentials for the unstretched and stretched bonds [41]. It was found that stretching the bond could considerably reduce the required energy to break it. The bonds were stretched to a higher level under an opening load than a shearing load prior to the crack passing them. Accordingly, the bonds exhibited a better resistance to the mode-II fracture propagation than the mode-I fracture propagation. Moreover, it is well-known that the length of the fracture damage zone ahead of the crack tip is much longer for the mode-II fracture than the mode-I fracture [42,43], e.g., Fan et al. [43] numerically investigated the lengths of the mode-I and mode-II damage zone of a composite adhesive joint to be 0.77 mm and 9.5 mm, respectively. A significantly longer mode-II damage zone included more active bonds during the fracture process of the mode-II
fracture than the mode-I fracture. This amplified the positive influences of the bond recombination and the lower bond-stretching to the mode-II fracture energies, and subsequently resulted in the much better mode-II fracture performance than the mode-I fracture performance of the PEEK(5sUV) joints.

4. Conclusions

This work proposed to use a high-power UV-irradiation technique to rapidly prepare the surfaces of carbon fibre reinforced PPS and PEEK composites for the adhesive joining. The results of a single lap-shear joint test demonstrated that applying UV-irradiation to the PPS composites for 3 s and to the PEEK composites for 5 s was sufficient to transform the failure mode of the adhesive joints from interface failure to severe substrate damage. This consequently resulted in significant increases in the lap-shear strength of the adhesive joints, i.e. from 11.8 MPa to 31.7 MPa of the PPS composite joints, and from 8.3 MPa to 37.3 MPa of the PEEK composite joints. The application of the UV-irradiation to the substrates also led to significant substrate damage during the mode-I and II fracture process of the adhesive joints, owing to the significantly enhanced adhesion at the adhesive/substrate interface. This remarkably improved the mode-I and mode-II fracture performance of the adhesive joints. For example, applying a 3 s UV-irradiation to the PPS composites significantly increased the mode-I fracture energy of the adhesive joints from 45.1 J/m² to 1476 J/m², and the mode-II fracture energy from 225.1 J/m² to 7814 J/m². Overall, this work demonstrated that a high structure integrity of adhesively bonded PPS and PEEK composite joints could be created by rapidly UV-irradiating the surfaces of the substrates. By considering the highly effective, eco-friendly and low-cost nature of the high-power UV-irradiation method, it proved significant potential for industrial mass-production of high-performance adhesive joints of thermoplastic composites.

Acknowledgements

Dr. Dong Quan receives funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 842467. Financial support from the Irish Composites Centre is acknowledged. Special thanks to Dr. Brian Deegan (from Henkel Ireland Operations & Research Ltd., Ireland) and Mr. Lorcán Byrne (from EnBio Ltd., Ireland) for their contribution to the work through valuable technical assistance and discussions.

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