

## Rapid surface activation of carbon fibre reinforced PEEK and PPS composites by high-power UV-irradiation for the adhesive joining of dissimilar materials

Quan, Dong; Deegan, Brian; Byrne, Lorcán; Scarselli, Gennaro; Ivanković, Alojz; Murphy, Neal

**DOI**

[10.1016/j.compositesa.2020.105976](https://doi.org/10.1016/j.compositesa.2020.105976)

**Publication date**

2020

**Document Version**

Final published version

**Published in**

Composites Part A: Applied Science and Manufacturing

**Citation (APA)**

Quan, D., Deegan, B., Byrne, L., Scarselli, G., Ivanković, A., & Murphy, N. (2020). Rapid surface activation of carbon fibre reinforced PEEK and PPS composites by high-power UV-irradiation for the adhesive joining of dissimilar materials. *Composites Part A: Applied Science and Manufacturing*, 137, Article 105976. <https://doi.org/10.1016/j.compositesa.2020.105976>

**Important note**

To cite this publication, please use the final published version (if applicable). Please check the document version above.

**Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

**Takedown policy**

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.



# Rapid surface activation of carbon fibre reinforced PEEK and PPS composites by high-power UV-irradiation for the adhesive joining of dissimilar materials

Dong Quan<sup>a,\*</sup>, Brian Deegan<sup>b</sup>, Lorcán Byrne<sup>c</sup>, Gennaro Scarselli<sup>d</sup>, Alojz Ivanković<sup>e</sup>, Neal Murphy<sup>e,\*</sup>

<sup>a</sup> Structural Integrity & Composites Group, Faculty of Aerospace Engineering, Delft University of Technology, Netherlands

<sup>b</sup> Adhesives Research, Henkel Ireland Operations & Research Ltd., Ireland

<sup>c</sup> EnBio Ltd., Ireland

<sup>d</sup> Department of Engineering for Innovation, University of Salento, Italy

<sup>e</sup> School of Mechanical and Materials Engineering, University College Dublin, Ireland



## ARTICLE INFO

### Keywords:

Thermoplastic composites  
B: Strength  
E: Joints/joining  
E: Surface treatments

## ABSTRACT

Carbon fibre reinforced poly-etherether-ketone (PEEK) and poly-phenylene-sulfide (PPS) composites were rapidly surface-treated by high-power UV light, and then adhesively bonded to aluminium 2024-T3 and carbon fibre/epoxy composites. The results of a single lap-shear joint test demonstrated that a UV-treatment lasting for 5 s was sufficient to prevent joint failure occurring at the composite/adhesive interfaces in all cases, e.g. it increased the failure strength of the PPS composite/aluminium joints from 11.1 MPa to 37.5 MPa. Moreover, the composite/adhesive interfaces performed well upon an exposure of the joints to an environment of high humidity and temperature for 8 weeks. Additionally, an investigation lasting for 6 months showed no degradation of the surface functionalisation from UV-irradiation. Overall, this work highlights high-power UV-irradiation a very promising method for surface preparation of thermoplastic composites (TPCs) for adhesive joining, i.e. TPC adhesive joints with excellent structural integrity can be obtained by using this rapid, eco-friendly and low-cost surface-treatment method.

## 1. Introduction

Carbon fibre reinforced polymers (CFRPs) are increasingly used in a wide variety of industries, including automotive, aerospace and wind energy sectors, due to their light weight, good structural performance, and excellent environmental resistance. This introduces the challenge of joining CFRPs, to both themselves and other dissimilar materials, such as steel and aluminium. Over the last three decades, extensive research has been performed to develop structural CFRP joints using various joining technologies. While mechanical fastening, adhesive bonding and welding (infusion bonding) represent the three major technologies [1–4] for joining polymers and their composite materials, other methodologies, such as a variotherm injection moulding method [5–7], have also demonstrated some promise. Among different joining methods, adhesive bonding offers many advantages over the others for the structural joining of CFRPs [8], such as the possibility of making light-weight constructions, the ability to join any pair of dissimilar

materials with a relatively uniform stress-distribution along the junction between the two substrates, and the possibility to seal the entire bonding area and hence to provide high joint strength and durability. Moreover, adhesive joining is the only applicable method for joining thin-walled sections or elements with a significant difference in thickness [2]. Notwithstanding, there are also disadvantages of adhesive joining, the foremost being the requirement to perform an appropriate surface treatment before bonding, particularly for substrates with relatively low surface energies, such as thermoplastic composites (TPCs) and aluminium [9,10].

Kinloch et al. [11–15] were the first to perform systematic investigations on the joining of TPCs using structural adhesives, and reported that obtaining high-strength adhesive joints for TPCs was far more difficult than for thermosetting composites (TSCs). This was due to the inherently low reactivity, small surface energies and weak polarities of the thermoplastics, that led to a poor compatibility between the TPCs and the adhesives, typically based on epoxies [4]. Kinloch

\* Corresponding authors.

E-mail addresses: [d.quan-1@tudelft.nl](mailto:d.quan-1@tudelft.nl) (D. Quan), [neal.murphy@ucd.ie](mailto:neal.murphy@ucd.ie) (N. Murphy).

et al. [12–14] also revealed that, to ensure a sufficiently good adhesive/composite interfacial strength, a simple abrasion/solvent-wiping treatment was all that was needed for the TSCs, while more intensive surface treatments were necessary in the case of TPCs. Considering the significant advantages of TPCs, such as a greater resistance to fracture and impact damage (owing to the significantly higher toughness of thermoplastics than that of thermosets) and the ability to be recycled, exploring efficient and low-cost surface treatment methods for TPCs becomes critical. Various techniques, including corona discharge [16,17], plasma treatment [18,19], acid etches [20,21] and oxidising flame treatment [22,23], have been employed to increase the surface energy and functional groups of thermoplastics for adhesive joining, with different levels of success achieved. However, there are still many limitations to these techniques, such as the lack of uniformity of the treated surfaces, the difficulty in accessing the inner surface of complex parts and the low efficiency of treating large surfaces. Ultraviolet light (UV) irradiation is another method that has been used for cleaning and functionalising polymer surfaces [24]. In the 1990s, Mathieson and Bradley [25] first used UV-irradiation to treat poly-ethylene (PE) and poly-etherether-ketone (PEEK) polymers for the adhesive bonding, and observed significant increases in the joint strength, i.e. the maximum value of the lap shear strength increased from approximately zero to 10 MPa for the PE joints, and from 2.3 MPa to 13 MPa for the PEEK joints. Since then, extensive research employed the UV-irradiation technique to enhance the adhesion at the interface of dissimilar materials, such as copper/epoxy [26], graphene/copper [27], rubber/polyurethane [28], PMMA/copper, PMMA/gold [29] and silicon/gold [30]. Nevertheless, the studies on the application of UV-irradiation specifically for adhesive joining of TPCs are still very limited. Recently, Shi [31] et al. used UV-irradiated PEEK film as an adhesive for the co-cured joining of carbon fibre/epoxy composites. It was revealed that the mode-I fracture energy significantly increased from 380 J/m<sup>2</sup> for the non-modified joints (without PEEK films as adhesives) to 820 J/m<sup>2</sup> for the joints bonded by PEEK films that were UV-irradiated for 15 min. It should be noted that the mode-I fracture energy was essentially zero if a non-treated PEEK film was used as an adhesive for the co-cured bonding. This observation demonstrated that applying UV-irradiation on the PEEK polymers can achieve strong adhesion at the PEEK/epoxy interface. Obviously, UV-irradiation is an attractive method to prepare the surfaces of TPCs for adhesive joining, and an investigation into the structural performance of adhesive joints between UV-irradiated TPCs and dissimilar materials is desirable, but has not yet been performed. Moreover, the use of high-power UV light for rapid surface preparation of TPCs is appealing for industrial manufacturing. The aim and main novelty of this work was to investigate the structural integrity of adhesive joints between TPCs and other dissimilar materials with the bonding surfaces of the TPC substrates irradiated by a high-power UV light source. Carbon fibre reinforced PEEK and PPS composites were UV-irradiated for a short period of between 5 and 20 s, and then adhesively bonded to dissimilar aerospace-grade materials, i.e. aluminium alloy 2024-T3 and TSCs based on epoxies, using a verified aerospace adhesive. The lap-shear strengths of the adhesive joints were measured, and the corresponding failure mechanisms were investigated. The performance of the adhesive joints upon humidity ageing and the stability of the surface functionalisation after the UV-treatment were also investigated.

## 2. Experimental

### 2.1. Materials

The carbon fibre/PEEK composites (PEEKc) and carbon fibre/PPS composites (PPSc) were manufactured based on 7 plies of Tencate Cetex TC1200 and Tencate Cetex TC1100 prepregs from Toray Advanced Composites, UK, respectively. The reinforcements were 5-harness weave carbon fibre (T300JB 3 K) fabrics in both cases. The

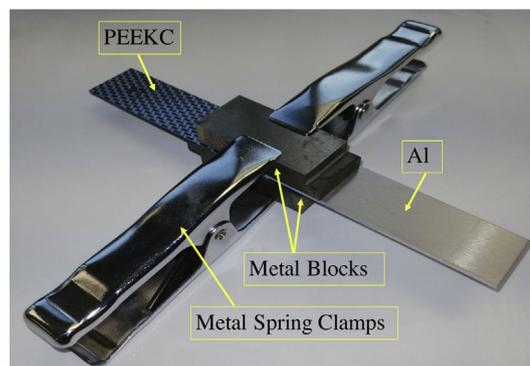


Fig. 1. Assembled lap-shear joints for curing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Carbon and oxygen content, surface free energies and water contact angles ( $\theta$ ) of the UV-irradiated TPC surfaces. The values in the brackets indicate the duration of the UV-irradiation.

TPCs	C (%)	O (%)	$\gamma_d$ (mN/m)	$\gamma_p$ (mN/m)	$\gamma$ (mN/m)	$\theta$ (°)
PEEKc(Control)	81.12	14.53	44.72	3.93	48.65	75.70
PEEKc(5s)	78.84	18.45	44.90	4.49	49.39	73.03
PEEKc(10s)	76.84	19.71	44.39	5.74	50.12	71.07
PEEKc(20s)	73.47	22.39	44.83	6.75	51.58	68.37
PPSc(Control)	75.56	10.30	48.44	1.52	49.97	82.25
PPSc(5s)	71.04	12.75	46.00	3.75	49.75	75.53
PPSc(10s)	69.66	13.89	43.53	4.24	47.78	73.66
PPSc(20s)	68.88	15.44	41.94	6.11	48.05	71.60

carbon fibre/epoxy composites (EpoxyC) based on 4 plies of Hexply 8552/5H, consisting of 5-harness carbon fibre (AS4) weave pre-impregnated with an epoxy resin, were manufactured and supplied by Bombardier Aerospace, Belfast. A layer of wet peel-ply (Hysol EA9895 from Henkel) was co-cured on the surface the EpoxyC to create a bonding surface. The aluminium (Al) substrates, made from alloy 2024-T3, were Q-Panel AR-14 from Q-Lab Corporation. The bonding surfaces of the Al substrates were treated using a CoBlast technique developed by ENBIO, Ireland [32]. This is a novel, green, ambient temperature blast coating technique, that can achieve an equivalent bonded tensile strength to those of commercially available state-of-the-art solutions, as will be shown in Section 3.2. The epoxy adhesive was an aerospace-grade film adhesive, Hysol EA9696, from Henkel. The adhesive was supported with a mesh, that aids in handling the film adhesive and also in controlling the bond-line thickness of the joint.

### 2.2. Preparation and testing of the adhesive joints

An in-house UV-irradiation system in Henkel, Ireland was used to treat the bonding surface of the PEEKc and PPSc substrates. The UV source was Light Hammer 6, from Heraeus Noblelight, UK. The intensity of the UV light can be controlled by placing the substrates at different distances to the UV lamp. In the current work, the distance between the substrates and the lamp was fixed, and the intensity of the UV light at such a distance was measured using a UV Power Puck from EIT Inc., USA. The measured intensities of UVV (395–445 nm), UVA (320–390 nm), UVB (280–320 nm) and UVC (250–260 nm) were 1590 mW/cm<sup>2</sup>, 1180 mW/cm<sup>2</sup>, 267 mW/cm<sup>2</sup> and 36 mW/cm<sup>2</sup>, respectively. The TPC substrates were treated for a short duration of 5 s, 10 s and 20 s. In this paper, the UV-treated TPCs will be referred to as the composite type followed by the duration of the UV-treatment. For example, PEEKc(5s) represents a PEEKc substrate that was UV-treated for 5 s. After that, the surface free energies and water contact angles of

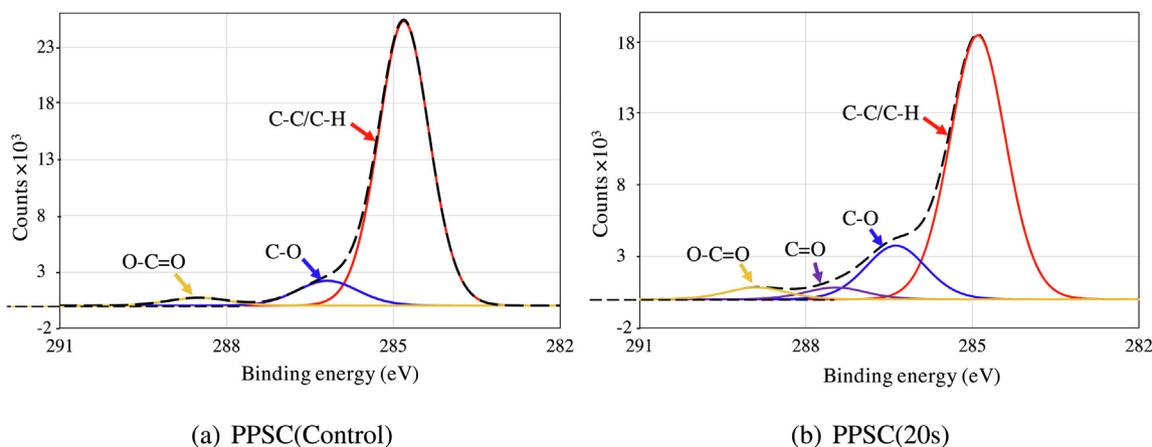


Fig. 2. Typical results of a narrow XPS scan of the carbon peak for: (a) the control PPSC; and (b) the PPSC treated by UV-light for 20 s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

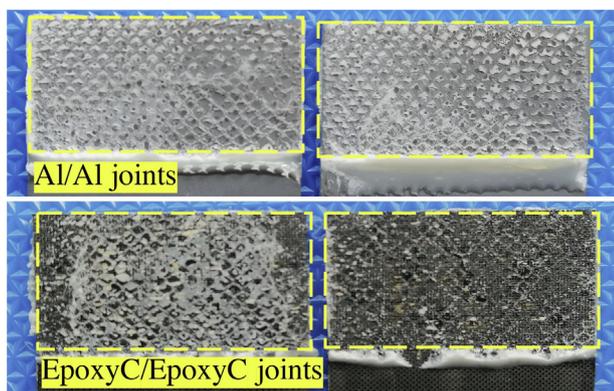


Fig. 3. Photos of the failure surfaces of the Al/Al and EpoxyC/EpoxyC adhesive joints. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the PEEKC and PPSC substrates were investigated using a mobile surface analyser from KRÜSS, GmbH. The chemical composition and functional groups on the treated surfaces were analysed using a X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD), equipped with an Al K $\alpha$  (1486.7 eV) X-ray source. The UV-treated TPC substrates were stored in sealed plastic bags (air-allowed) at room temperature in a laboratory atmosphere for subsequent bonding.

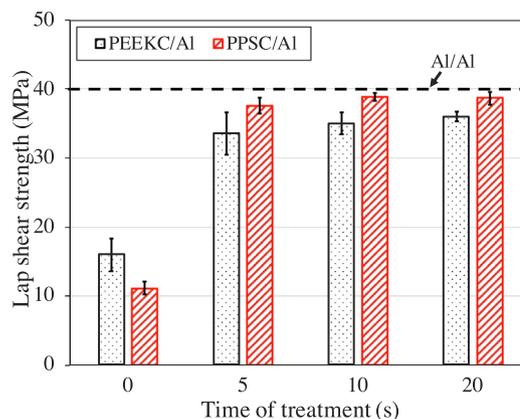


Fig. 5. Lap-shear strengths of the TPC/Al adhesive joints. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this work, a single lap-shear joint test was used to measure the tensile lap-shear strength (LSS) of the adhesive joints. To produce the adhesive joints, a pair of substrates with a length of 102 mm and a width of 25 mm was firstly assembled by inserting a piece of non-cured film adhesive in between, with an overlap of 12.5 mm. A uniform pressure of approximately 350 kPa was then applied to the bonding

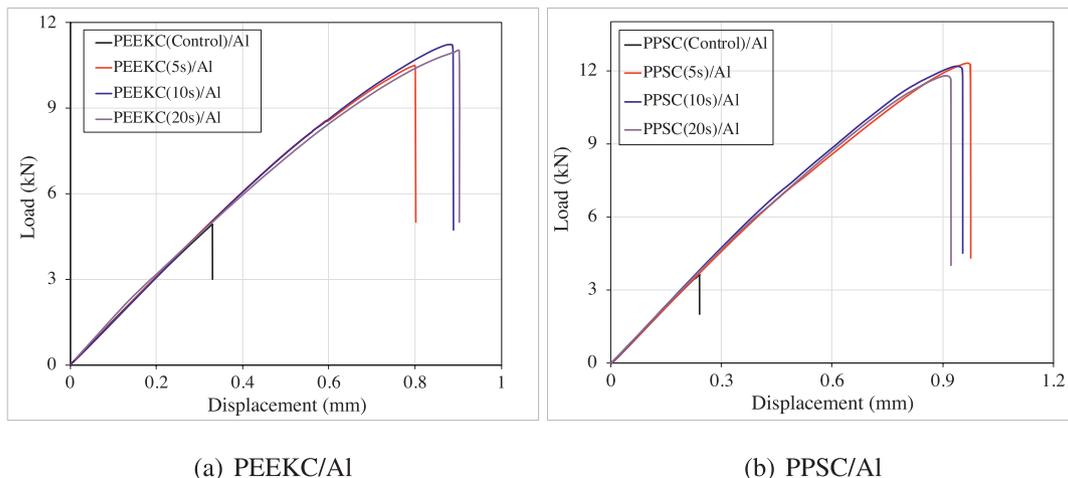
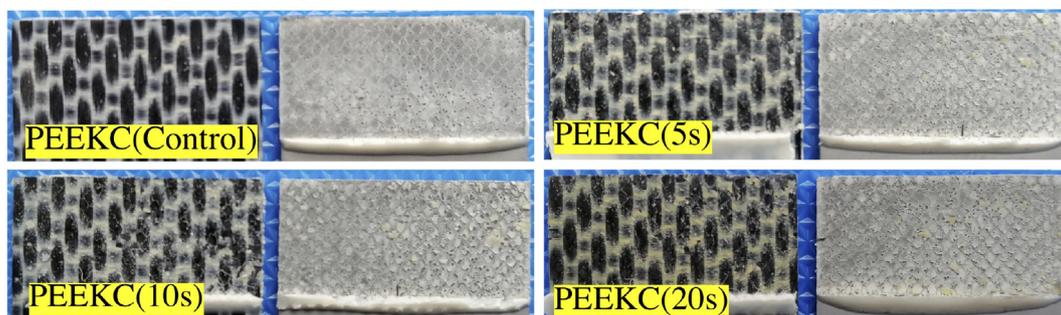
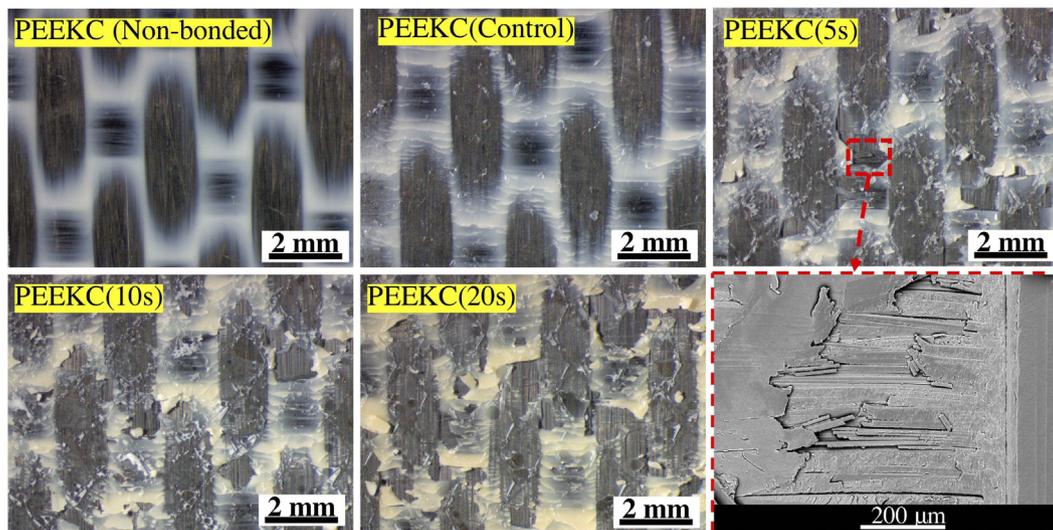


Fig. 4. Representative load versus displacement curves of the TPC/Al adhesive joints. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



(a)



(b)

**Fig. 6.** (a) Typical photographs of the failure surfaces of the PEEKC/Al joints, and (b) Corresponding microscopy images of the failure surfaces of the PEEKC sides, with the non-bonded PEEKC surface as a reference. The insert image in (b) shows damaged carbon fibres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

area of the adhesive joints by clamping steel blocks on either side of the joining area with two spring clamps, as shown in Fig. 1. The assembled joints were then placed in an air-circulated oven for curing. The curing cycle consisted of a 0.5-h ramp from room temperature to 120 °C followed by a 1.5-h hold, or dwell, at 120 °C. After curing schedule, the specimens were allowed to cool down naturally to room temperature inside the oven for approximately 4 h. Different combinations of substrates, including Al/Al, EpoxyC/EpoxyC, TPC/Al and TPC/EpoxyC, were bonded and tested in this work. The first group of UV-treated TPC substrates were bonded within 24 h after the UV-treatment. After the curing, these adhesive joints were either tested within 24 h (to evaluate the effects of the UV-treatment on the joining strength) or placed in a humidity controlled environment (to investigate the effects of humidity ageing on the joining strength). The humidity controlled environment was obtained by placing an air tight container with sodium chloride/water solution (35 g sodium chloride in every 100 ml water) inside an oven [33,34] at a temperature of 56 °C. The humidity inside the container was monitored to be 80–90% RH during the entire ageing process, which lasted for 8 weeks. The samples were taken out of the container after being aged for different times and then tested immediately after they cooled down to room temperature in the air, which took about 30 min. The second group of the UV-treated TPC substrates were used to study the post-treatment stability of the surface functionalisation of the TPCs. These substrates were bonded and tested at

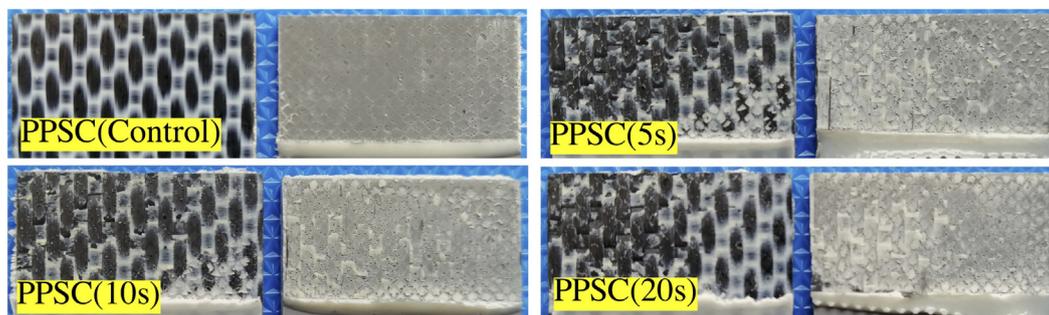
different times after the UV-treatment, with the time between the UV-treatment and bonding being 1–168 days.

The single joint lap shear test was performed according to ISO4587. Two mild-steel shims were bonded on both ends of the lap-shear adhesive joints using an adhesive (Loctite 480 from Henkel) to make sure the applied force was in the plane of the adhesive layer during the tensile test. The adhesive joints were then tested using a universal testing machine (Instron 5982 with a 50 kN load cell) at a constant loading rate of 2 mm/min at ambient temperature. The specimens were fixed to the machine using a pair of hydraulic clamps with a clamping pressure of 180 bar, that was trialed to be sufficient to avoid slippage during the test. At least three replicate tests were conducted for each set of substrate combinations.

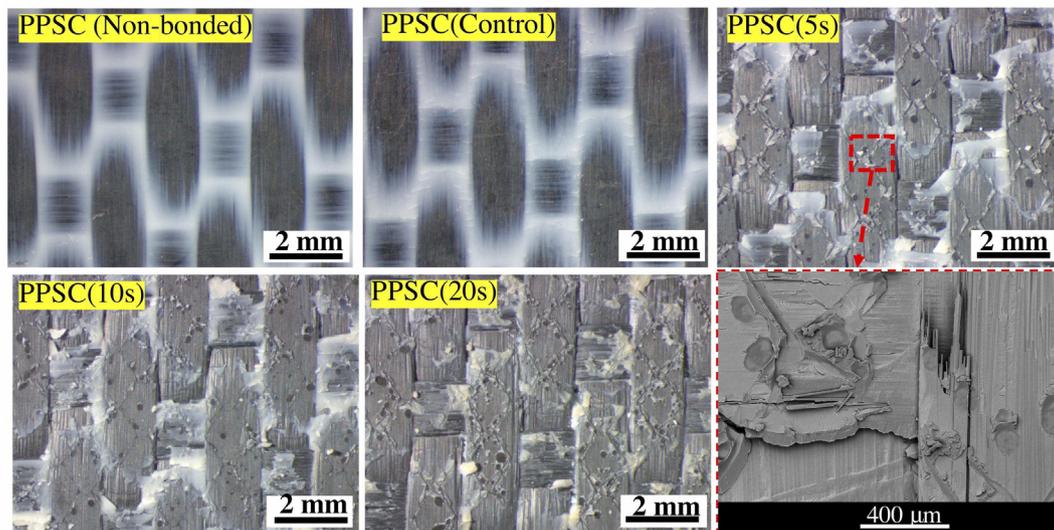
### 3. Results and discussion

#### 3.1. Characterisation of the UV-irradiated surfaces

The amount of carbon and oxygen atoms on the surfaces of the UV-treated and non-treated TPCs from the XPS analysis is given in Table 1. It was found that the UV-irradiation decreased the carbon content and increased the oxygen content for both the PEEKCs and the PPSCs. This resulted from the breakage of the C–C/C–H bonds, followed by the generation of additional carbon–oxygen functionalities [14,15,25].

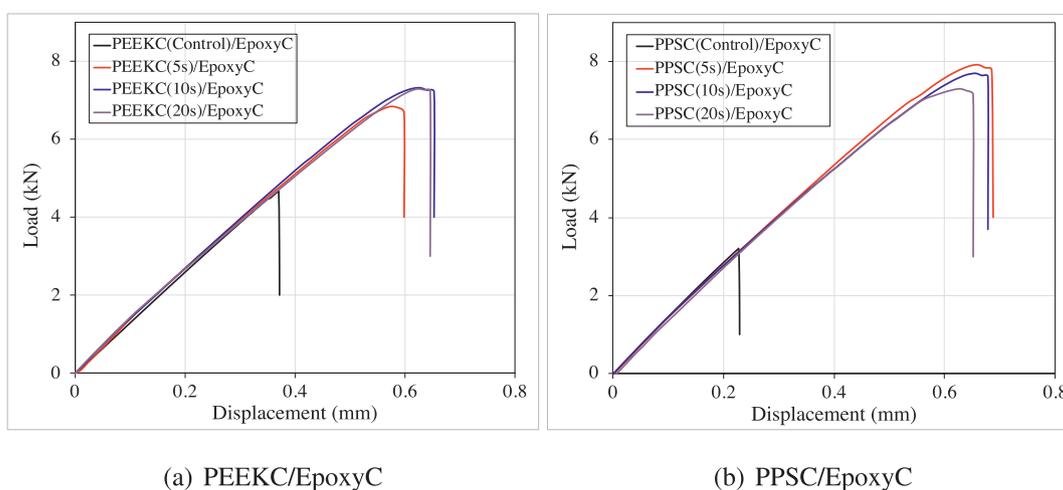


(a)



(b)

Fig. 7. (a) Typical photographs of the failure surfaces of the PPSC/Al joints, and (b) Corresponding microscopy images of the failure surfaces of the PPSC sides, with the non-bonded PPSC surface as a reference. The insert image in (b) shows damaged carbon fibres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



(a) PEEKC/EpoxyC

(b) PPSC/EpoxyC

Fig. 8. Representative load versus displacement curves of the TPC/EpoxyC adhesive joints. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2 shows typical results of a narrow XPS scan of the carbon peak for the control PPSC and the PPSC treated by UV light for 20 s. It is clear that the intensity of the C–C/C–H species dropped considerably, while the intensities of the C–O species notably increased as a result of the

UV-irradiation. Moreover, an additional peak was observed on the curves for the UV-irradiated TPCs, which was due to the development of the C=O species [14,15,25]. The changes in the chemical composition of the TPC surfaces subsequently affected the surface free

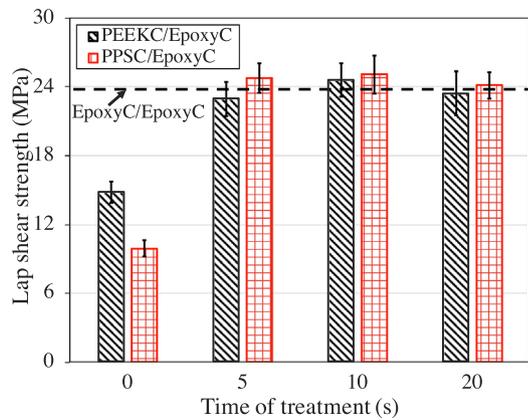


Fig. 9. Lap-shear strengths of the TPC/EpoxyC joints. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

energies, as shown in Table 1. The surface free energy ( $\gamma$ ) of an item is the sum of two components, namely the dispersive ( $\gamma_d$ ) and polar components ( $\gamma_p$ ). It was found that the dispersive force remained more or less the same for the PEEKCs, but decreased for the PPSCs due to the UV-irradiation. The polar force significantly increased for both the PEEKCs and the PPSCs, i.e. a 20s-treatment increased  $\gamma_p$  from 3.93 mN/m for the control PEEKC to 6.75 mN/m, and from 1.52 mN/m for the control PPSC to 6.11 mN/m. Noteworthily, the dispersive force is responsible for the temporary fluctuations of the charge distribution in the atoms/molecules, such as the van der Waals interactions, and the polar force generates Coulomb interactions between permanent dipoles and between permanent and induced dipoles, e.g. hydrogen bonds. Since hydrogen bonds are far stronger than van der Waals interactions, a higher polar force for both sides of the interface is desirable to achieve good adhesion. As a result of the changes in the chemical composition and surface free energies of the TPC surfaces, the wettability of the TPC surfaces considerably increased after the UV-irradiation, evidenced by the decrease of the water contact angles, as shown in Table 1. All these observations were beneficial for enhancing the adhesion between the TPC substrates and the epoxy adhesive.

### 3.2. The Al/Al and EpoxyC/EpoxyC adhesive joints

The Al/Al and EpoxyC/EpoxyC adhesive joints were tested to

evaluate the quality of the surface preparation for the Al and EpoxyC substrates. The LSSs of the Al/Al joints and the EpoxyC/EpoxyC joints were measured to be  $40.0 \pm 1.4$  MPa and  $23.7 \pm 1.1$  MPa, respectively. Photos of typical failure surfaces of the Al/Al and EpoxyC/EpoxyC adhesive joints are shown in Fig. 3. For the Al/Al joints, both sides of the failure surfaces were covered with a layer of white coloured adhesive, indicating a cohesive failure inside the adhesive layer. This demonstrated a strong bonding between the adhesive and the blast-coated Al substrates, that resulted in the high lap-shear strength of the Al/Al adhesive joints. Moreover, this set of tests measured the failure strength of the adhesive layer to be around 40.0 MPa. For the EpoxyC/EpoxyC joints, almost all of the adhesive remained on one side of the failure surfaces, with the opposite side showing a bare surface. This was caused by an interfacial failure between the EpoxyC substrates (i.e. the surface of the wet peel-ply) and the adhesive layer, which took place at a lap shear strength of around 23.7 MPa.

### 3.3. The TPC/Al adhesive joints

Fig. 4 shows representative load versus displacement curves from the lap shear tests of the TPC/Al adhesive joints. It was found that the application of the UV-treatment to the TPC substrates had no effects on the stiffness of the adhesive joints, i.e. the stiffness of the lap shear joints varied between 616–632 MPa for all the TPC/Al joints. However, it significantly increased the failure load of the TPC/Al joints in all cases. For example, the failure load increased from around 4.5 kN for the non-treated PEEKC/Al joints to around 11 kN for all the UV-treated PEEKC/Al joints. Moreover, the curves were linear for the non-treated TPC/Al joints, while a nonlinear section before the failure point was observed on the curves of the UV-treated joints, as shown in Fig. 4. It indicated that pure elastic deformation took place before the failure of the non-treated joints, and additional plastic deformation and damage occurred for the UV-treated joints. This was confirmed by performing a microscopy analysis of the failure surfaces of the adhesive joints, as discussed below. The LSSs of the adhesive joints between the TPC substrates and the Al substrates are summarised in Fig. 5. The dashed line indicates the mean LSS of the Al/Al joints, as a reference. A value of 16.0 MPa was measured for the LSS of the control PEEKC/Al joints, i.e. without UV-treatment on the PEEKC substrates. This value significantly increased to around 35 MPa in all cases after the surface of the PEEKCs were UV-treated. The LSS of the control PPSC/Al joints was measured to be 11.1 MPa, which remarkably increased to approximately 39 MPa after a UV-irradiation was applied to the PPSC surface. The LSS slightly

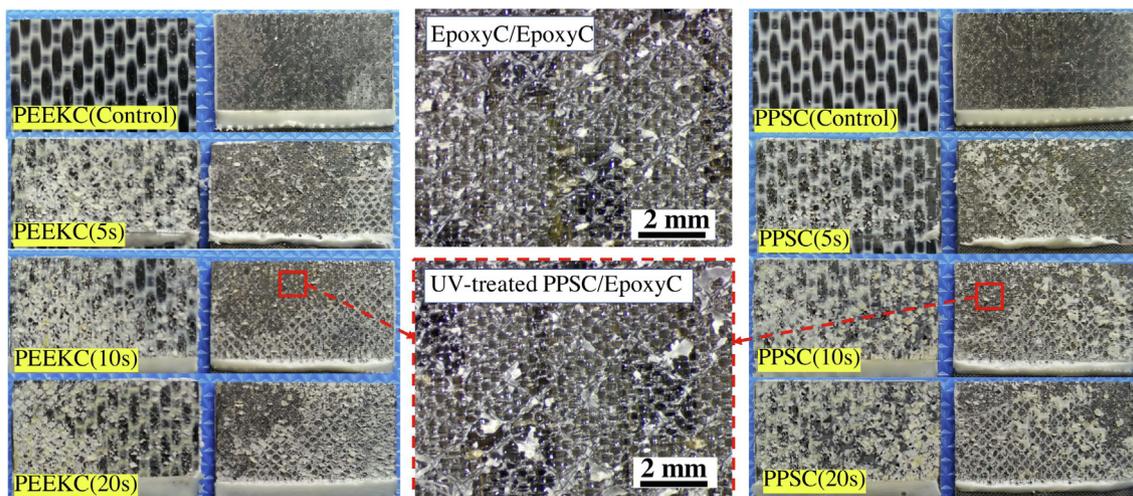
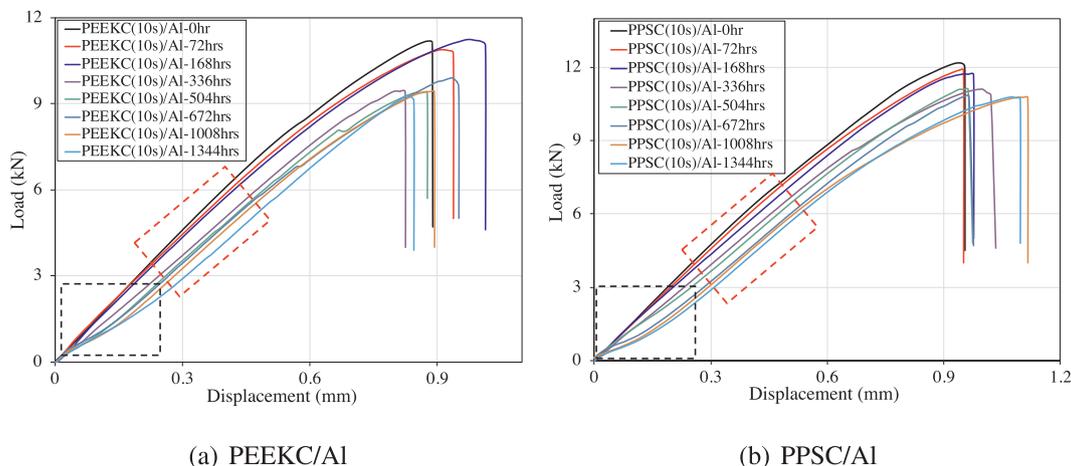
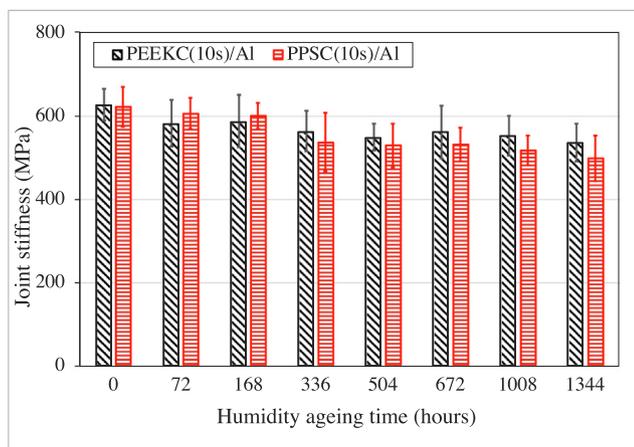


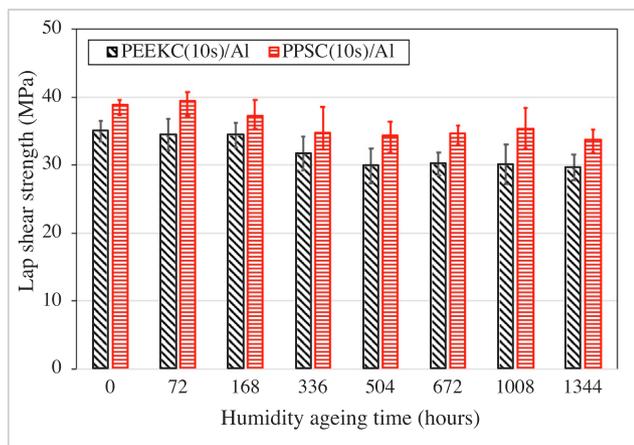
Fig. 10. Photographs of the failure surfaces of the PEEKC/EpoxyC joints (on the left) and the PPSC/EpoxyC joints (on the right). The figures in the middle are typical images for the adhesive-sparse side of the failure surface of the EpoxyC/EpoxyC joints (see Fig. 3) and for the interfacial failure region of the TPC/EpoxyC joints close to the EpoxyC substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 11.** Representative load versus displacement curves of the TPC/Al adhesive joints aged for different time. The black dashed boxes indicate the location of a softening region resulting from the ageing, and the red dashed boxes indicate the linear section for the stiffness calculation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



(a) Joint stiffness



(b) Lap shear strength

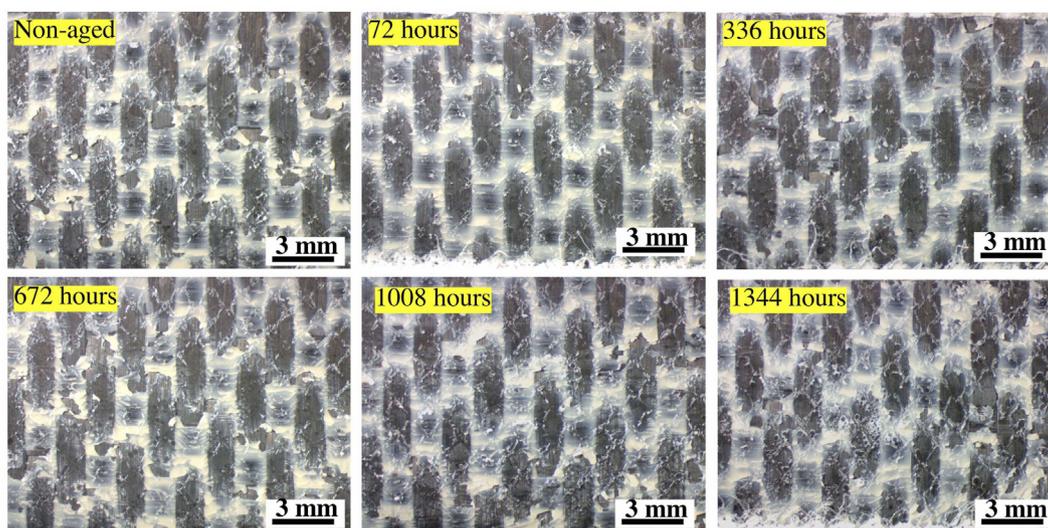
**Fig. 12.** Results of the investigations into the humidity resistance of the UV-treated adhesive joints. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

increased as the duration of UV-treatment increased, e.g. the LSS of the PEEKC/Al joints increased from 33.6 MPa for a 5 s treatment to 35.0 MPa for a 10 s treatment. Overall, the duration of the UV-treatment had no significant effect on the LSS for both the PEEKC/Al and

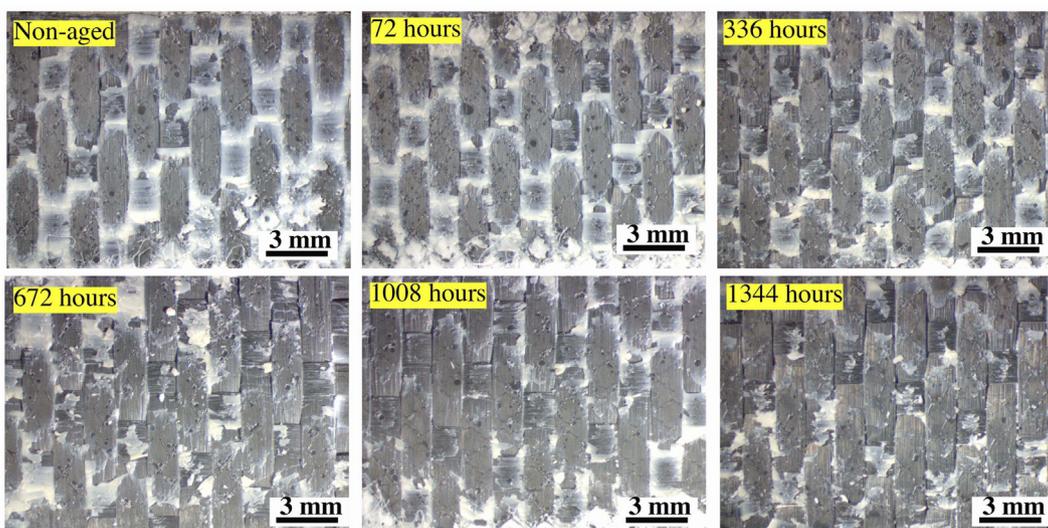
PPSC/Al joints. This means that a treatment of as short as 5 s was sufficient to achieve a strong bond between the adhesive and the PEEKC and PPSC substrates.

Fig. 6 (a) presents typical photographs of the failure surfaces of the PEEKC/Al joints. It is clear that almost the entire adhesive layer was well-attached to the Al side for the control PEEKC/Al joints, indicating a domination of an interfacial failure between the PEEKC substrate and the adhesive layer. The failure surfaces of all the UV-treated PEEKC substrates appeared much rougher than that of the control PEEKC substrate due to the presence of a layer of damaged polymer. Noteworthy, the entire surfaces of the Al substrates were covered with a layer of adhesive for all the PEEKC/Al joints. To investigate the failure mode of the PEEKC/Al joints, microscopy analysis of the failure surfaces of the PEEKC substrates was performed, as shown in Fig. 6 (b). A microscopy image of the surface of a non-bonded PEEKC substrate is also included as a reference. By comparing the failure surface of the control PEEKC substrate and the non-bonded PEEKC surface, it was found that the failure of the adhesive joints generated a large number of crack lines inside the PEEK matrix on the surface of the control PEEKC substrate. The layer of PEEK resin on the surfaces of the UV-treated PEEKC substrates was completely destroyed for all the UV-treated PEEKC substrates, with a number of spots on the surface showing bare carbon fibres. The insert figure indicated by the red arrow presents a typical SEM image of the region with bare fibres. It was observed that some carbon fibre delamination and breakage took place during the failure. The observations demonstrated that the UV-irradiation successfully increased the adhesion at the PEEKC/adhesive interface to a level that was sufficient to transform the failure mode from PEEKC/adhesive interfacial failure to substrate failure in the PEEKCs.

Typical photographs of the failure surfaces of the PPSC/Al joints are shown in Fig. 7 (a), and the corresponding microscopy images of the failure surfaces of the PPSC substrates are presented in Fig. 7 (b). For the control PPSC/Al joints, the failure happened at the PPSC/adhesive interface, leaving a clear PPSC surface without any visible damage (at this scale), as shown in Fig. 7 (a). Fig. 7 (b) shows that many crack lines exist inside the layer of PPS resin on the surface of the control PPSC substrate, which were also observed on the failure surface of the control PEEKC substrate in Fig. 6 (b). However, the extent of the crack lines on the control PPSC substrate was much less than that observed on the control PEEK substrate. This indicated a better adhesion between the adhesive and the non-treated PEEKC substrates, and explained why the LSS of the control PEEKC/Al joints was higher than that of the control PPSC/Al joints, as shown in Fig. 5. Similarly to the UV-treated PEEKC/Al joints, substrate damage inside the PPSC also took place for the UV-



(a) PEEKC failure surfaces



(b) PPSC failure surfaces

Fig. 13. Typical failure surfaces of the TPC substrates for the TPC/Al adhesive joints after humidity ageing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

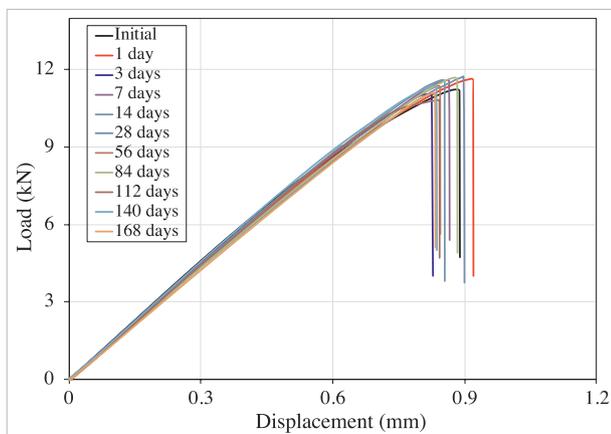
irradiated PPSC/Al joints, but in a more severe mode, i.e. bare carbon fibres were visible on a large portion of the PPSC surfaces (see Fig. 7(a) and (b)), where bundles of carbon fibres were observed to be delaminated and broken (see the insert image in Fig. 7 (b)). Noteworthy, the substrate damage took place at a LSS of around 35 MPa for the PEEKC substrates and around 39 MPa for the PPSC substrates, which were lower than the LSS for a cohesive failure of the adhesive (measured to be 40 MPa in Section 3.2). This explained why the LSSs of the TPC/Al adhesive joints were always lower than that of the Al/Al joints, as shown in Fig. 5.

#### 3.4. The TPC/EpoxyC adhesive joints

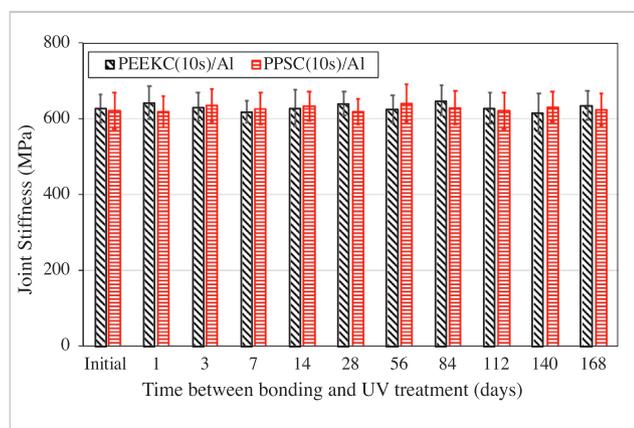
Representative load versus displacement curves from the lap shear tests of the TPC/EpoxyC adhesive joints are presented in Fig. 8. As observed with the TPC/Al joints, the application of the UV-treatment to the TPC substrates resulted in the following phenomena: the stiffness of the adhesive joints remained unchanged, i.e. a value within

543–576 MPa was obtained in every case; the maximum load significantly increased; and additional plastic deformation and damage took place before the final failure of the adhesive joints, evidenced by the non-linear section of the curves before the failure point. The LSSs of the adhesive joints between the TPC substrates and the EpoxyC substrates are shown in Fig. 9. The dashed line indicates the mean LSS of the EpoxyC/EpoxyC joints, as a reference. The LSSs were measured to be 14.8 MPa and 9.9 MPa for the control PEEKC/EpoxyC and PPSC/EpoxyC joints, respectively. The LSSs of all the UV-treated TPC/EpoxyC joints were found to be more or less the same as the LSS of the EpoxyC/EpoxyC joints, i.e. around 24 MPa. This value was far lower than the counterparts of the TPC/Al joints. This was due to the limitation of the adhesion strength between the EpoxyC and the adhesive, that was measured to be around 24 MPa in Section 3.2, i.e. the failure of all the TPC/EpoxyC joints initiated at the adhesive/EpoxyC interface once the tensile stress reached this limitation.

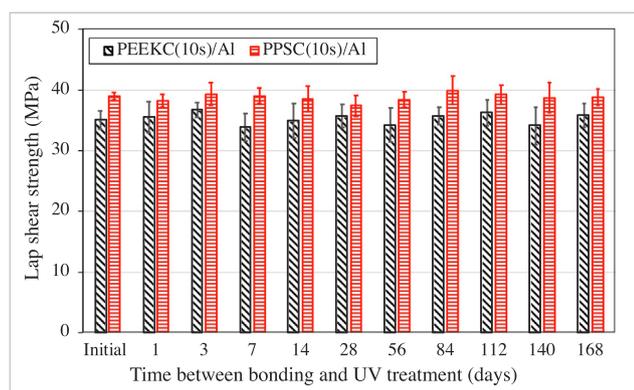
Typical photographs of the failure surfaces of the PEEKC/EpoxyC joints (on the left) and the PPSC/EpoxyC joints (on the right) are shown



**Fig. 14.** Representative load versus displacement curves of the TPC/Al adhesive joints cured at different times after the UV-treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



(a) Joint stiffness



(b) Lap shear strength

**Fig. 15.** Stability of the surface functionalisation of the UV-treated surfaces. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Fig. 10. Interfacial failure between the TPC substrates and the adhesive dominated the failure of the control PEEKC/EpoxyC and PPSC/Epoxy joints, leaving a clear surface on the TPC sides. The failure surfaces of the UV-treated PEEKC/EpoxyC and PPSC/EpoxyC joints appeared more or less the same as each other, i.e. both sides of the surfaces were attached with broken adhesive and supporting mesh with the majority of the epoxy adhesive left on the TPC sides. By making a

closer observation of the fracture surfaces, interfacial failure between the EpoxyC and the adhesive layer always took place at a portion of the bonding region for all the UV-treated TPC/EpoxyC joints. A comparison between a typical microscopy image of this interfacial failure region and an image for the adhesive-sparse side of the EpoxyC/EpoxyC joints (see Fig. 3) clearly shows the same failure mode, i.e. interfacial failure between the EpoxyC substrates and the adhesive layer, see the images in the middle in Fig. 10. The interfacial failure region was the location where the failure initiated, that always happened at a lap-shear strength of around 24 MPa (the adhesion strength of the adhesive/EpoxyC interface, see Section 3.2), and then failed the entire adhesive joints.

### 3.5. Humidity resistance and surface stability

The humidity resistance of the TPC/Al adhesive joints was studied by placing them in an environment of 80–90%RH at 56 °C, and representative load versus displacement curves from the lap shear tests of the ageing specimens are shown in Fig. 11. As expected, both the stiffness and the maximum load of the adhesive joints decreased upon an exposure to the high humidity and temperature. Moreover, a softening region (indicated by the black dashed boxes) exhibited at the beginning of the curves for the ageing specimens, and it became more prominent as the ageing time increased. This was very likely due to the relaxation of the moisture-induced residual stresses [35]. The joint stiffness and LSS of the ageing specimens are presented in Fig. 12. It should be noted that the stiffnesses of the joints were based on the linear sections of the load versus displacement curves, as indicated by the red dashed boxes in Fig. 11. It was found that the stiffness and LSS of the adhesive joints gradually decreased and then essentially plateaued (at an ageing time of around 504 hours) for both the PEEKC/Al joints and the PPSC/Al joints upon the humidity ageing. After an exposure of the TPC/Al adhesive joints to the ageing environment for 1344 h, the stiffness decreased from 627 MPa to 537 MPa (by 14%) for the PEEKC(10s)/Al joints, and from 621 MPa to 498 MPa (by 20%) for the PPSC(10s)/Al joints. At the same time, the LSS decreased from 35.0 MPa to 29.7 MPa for the PEEKC/Al joints, and 38.9 MPa to 33.8 MPa for the PPSC/Al joints. This corresponds to a decrease of 13.1% and 15.1% for the PEEKC/Al joints and PPSC/Al joints, respectively. It should be noted that the humidity ageing had no effects on the failure mode of the TPC/Al adhesive joints in all cases, and substrate damage inside the PEEKC or PPSC substrates was the main fracture mechanism, as observed in Section 3.3. Fig. 13 shows typical failure surfaces of the TPC side of the aged adhesive joints. There was no obvious visible difference between the failure surfaces of the non-aged PEEKC substrate and the PEEKC substrates aged for different times, i.e. the top layer PEEK resin was damaged during the failure process in all cases, as can be seen in Fig. 13 (a). Since substrate damage in the PEEKC substrate was still the main failure mechanism for the aged PEEKC/Al joints, the decrease in the LSSs of the PEEKC/Al joints owing to the humidity ageing was mainly attributed to the mechanical degradation of the PEEKC substrates. Differently to the PEEKC/Al joints, changes in the appearance of the PPSC failure surfaces due to the humidity ageing were observed for the PPSC/Al joints, i.e. the amount of PPS resin remaining on the failure surfaces of the PPSC substrates decreased. This indicates the degradation in the PPS/carbon fibre adhesion and/or in the mechanical properties of the PPS resin, that subsequently resulted in the mechanical degradation of the PPSC/Al joints.

Representative load versus displacement curves of the TPC/Al adhesive joints cured at different times after the UV-treatment are shown in Fig. 14, and the corresponding joint stiffness and LSSs are summarised in Fig. 15. It was found that the load versus displacement curves were essentially the same for all the adhesive joints, that resulted in more or less the same joint stiffness and LSS. Moreover, exactly the same failure mode (as observed in Section 3.3) took place for all the specimens in each case. This demonstrated that the surface functionalisation of the UV-irradiated PEEKCs and PPSCs remained unchanged

**Table 2**

Summary of the lap shear strengths of different adhesive joints. The values in the brackets indicate the percentage changes when compared to their corresponding references. UV-treatment was only applied to the thermoplastic composite substrates. The surfaces of all the aluminium substrates were treated by the co-blast technique. All the carbon fibre/epoxy substrates consisted of a layer of wet peel-ply as the bonding surface.

Joint type	Surface treatment	Failure mode	Conditioning	Strength	Stiffness
Al/Al EpoxyC/EpoxyC	Co-blast	Cohesive in adhesive	*	40.0 ± 1.4	632 ± 4
	Wet peel-ply	EpoxyC/adhesive interface	*	23.7 ± 1.1	560 ± 16
PEEK/Al	None	PEEK/adhesive interface	*	16.0 ± 2.4	624 ± 34
	5s-UV	PEEK damage	*	33.6 ± 3.1 (110%)	617 ± 30 (-)
	10s-UV	PEEK damage	*	35.0 ± 1.5 (119%)	627 ± 38 (-)
	20s-UV	PEEK damage	*	36.0 ± 0.7 (125%)	622 ± 22 (-)
PPSC/Al	None	PPSC/adhesive interface	*	11.1 ± 0.9	628 ± 26
	5s-UV	PPSC damage	*	37.5 ± 1.2 (238%)	616 ± 18 (-)
	10s-UV	PPSC damage	*	38.9 ± 0.6 (250%)	621 ± 48 (-)
	20s-UV	PPSC damage	*	38.6 ± 0.9 (248%)	632 ± 26 (-)
PEEK/EpoxyC	None	PEEK/adhesive interface	*	14.8 ± 0.9	547 ± 34
	5s-UV	EpoxyC/adhesive interface	*	22.9 ± 1.5 (55%)	576 ± 24 (-)
	10s-UV	EpoxyC/adhesive interface	*	24.6 ± 1.5 (66%)	560 ± 28 (-)
	20s-UV	EpoxyC/adhesive interface	*	23.4 ± 1.9 (58%)	554 ± 18 (-)
PPSC/EpoxyC	None	PPSC/adhesive interface	*	9.9 ± 0.7	559 ± 42
	5s-UV	EpoxyC/adhesive interface	*	24.7 ± 1.3 (150%)	543 ± 18 (-)
	10s-UV	EpoxyC/adhesive interface	*	25.1 ± 1.6 (153%)	562 ± 22 (-)
	20s-UV	EpoxyC/adhesive interface	*	24.1 ± 1.1 (143%)	567 ± 34 (-)
PEEK/Al	10s-UV	PEEK damage	1344 h	29.7 ± 1.9 (-15%)	537 ± 46 (-14%)
PPSC/Al	10s-UV	PPSC damage	ageing	33.8 ± 1.4 (-13%)	498 ± 34 (-20%)
PEEK/Al	10s-UV	PEEK damage	Bonded after	35.8 ± 1.9 (-)	624 ± 43 (-)
PPSC/Al	10s-UV	PPSC damage	168 days	38.8 ± 1.4 (-)	635 ± 39 (-)

over a duration of 6 months. It is worthy to mention again that the UV-treated TPCs were stored in air-allowed plastic bags at room temperature in a normal laboratory atmosphere, and hence no special storage environment is required to maintain the surface stability. This represents another significant advantage of the UV-treatment as a surface-preparation method of PEEK and PPS composites for adhesive joining.

### 3.6. Summary of the experimental results

To give a comprehensive understanding of the effectiveness of the UV-treatment for the surface activation of PEEK and PPS composites, Table 2 summarises the LSSs of all the adhesive joints studied in this work. The values in the brackets indicate the percentage changes when compared to their corresponding references. Overall, the application of a short-time UV-irradiation to the PEEK and PPS composites significantly improved their adhesion to the epoxy adhesive, and subsequently resulted in remarkable increases in the strengths of the adhesive joints in all cases. Moreover, the adhesive joints exhibited good resistance to humidity at high temperature, and the functionalisation of the UV-treated surfaces was very stable against time.

## 4. Conclusions

This work shows the significant promise of a high-power UV-irradiation technique for rapid surface-activation of carbon fibre reinforced PEEK composites (PEEK) and PPS composites (PPSC) for the adhesive bonding of dissimilar materials, i.e. aluminium alloy 2024-T3 and carbon fibre/epoxy composites (EpoxyC). A short time (between 5–20 s) UV-irradiation notably increased the amount of oxygen elements on the PEEK and PPSC surfaces, and decreased their water contact angles. As a consequence, the adhesions between an aerospace-grade epoxy adhesive and the PEEK and PPSC were significantly improved to a level that was sufficient to transform the failure from interfacial failure of the non-treated joints to substrate damage of the UV-treated joints. It was found that the duration of the UV-irradiation,

varied between 5–20 s, had no significant effect on the lap shear strength of the adhesive joints. Hence, a UV-irradiation lasting for as short as 5 s was sufficient to obtain a strong bond between the adhesive and the PEEK and PPSC substrates. Of equal significance, the results of a humidity ageing study demonstrated good performance of the UV-treated substrate/adhesive interface upon exposure of the adhesive joints to high humidity and temperature. Moreover, it was observed that the surface functionalisation (resulting from the UV-irradiation) remained stable for at least 6 months after the UV-treatment. This remarkable finding means that the PEEK and PPSC components may be surface activated and stored before being introduced to the production line for final assembly by adhesive joining.

### CRediT authorship contribution statement

**Dong Quan:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition. **Brian Deegan:** Methodology, Validation, Resources. **Lorcán Byrne:** Methodology, Resources, Writing - review & editing. **Gennaro Scarselli:** Validation, Resources. **Alojz Ivanković:** Conceptualization, Resources, Supervision, Funding acquisition. **Neal Murphy:** Conceptualization, Resources, Writing - review & editing, Supervision, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgements

The authors gratefully acknowledge the financial support of the Irish Composites Centre. Dong Quan received funding from the European Union's Horizon 2020 research and innovation programme

under the Marie Skłodowska-Curie grant agreement No. 842467. We would also like to thank Bombardier Aerospace (UK) for manufacturing and supplying the carbon fibre/epoxy composites.

## References

- [1] Thoppul SD, Finegan J, Gibson RF. Mechanics of mechanically fastened joints in polymer-matrix composite structures – a review. *Compos Sci Technol* 2009;69(3):301–29. <https://doi.org/10.1016/j.compscitech.2008.09.037>.
- [2] Pramanik A, Basak A, Dong Y, Sarker P, Uddin M, Littlefair G, et al. Joining of carbon fibre reinforced polymer (CFRP) composites and aluminium alloys - A review. *Compos Part A: Appl Sci Manuf* 2017;101:1–29. <https://doi.org/10.1016/j.compositesa.2017.06.007>.
- [3] Quan D, Murphy N, Ivankovic A. Fracture behaviour of a rubber nano-modified structural epoxy adhesive: Bond gap effects and fracture damage zone. *Int J Adhes Adhes* 2017;77:138–50. <https://doi.org/10.1016/j.ijadhadh.2017.05.001>.
- [4] Deng S, Djukic L, Paton R, Ye L. Thermoplastic/epoxy interactions and their potential applications in joining composite structures – a review. *Compos Part A: Appl Sci Manuf* 2015;68:121–32. <https://doi.org/10.1016/j.compositesa.2014.09.027>.
- [5] Li X, Liu F, Gong N, Yang C, Wang B. Surface topography induced high injection joining strength of polymer-metal composite and fracture mechanism. *Compos Struct* 2018;184:545–53. <https://doi.org/10.1016/j.compstruct.2017.10.020>.
- [6] Li X, Gong N, Yang C, Zeng S, Fu S, Zhang K. Aluminum/polypropylene composites produced through injection molding. *J Mater Process Technol* 2018;255:635–43. <https://doi.org/10.1016/j.jmatprotec.2018.01.008>.
- [7] Li X, Xu D, Gong N, Xu Z, Wang L, Dong W. Improving the strength of injection molded aluminum/polyphenylene sulfide lap joints dependence on surface micro-structure and composition. *Mater Des* 2019;179:107875. <https://doi.org/10.1016/j.matdes.2019.107875>.
- [8] Kinloch AJ. *Adhesion and adhesives: science and technology*. Chapman and Hall; 1987.
- [9] Goushegir S, dos Santos J, Amancio-Filho S. Friction spot joining of aluminum aa2024/carbon-fiber reinforced poly(phenylene sulfide) composite single lap joints: microstructure and mechanical performance. *Mater Des (1980–2015)* 2014; 54: 196–206. doi:10.1016/j.matdes.2013.08.034.
- [10] Arikani E, Holtmannsptter J, Zimmer F, Hofmann T, Gudladt H-J. The role of chemical surface modification for structural adhesive bonding on polymers – washability of chemical functionalization without reducing adhesion. *Int J Adhes Adhes* 2019;95:102409. <https://doi.org/10.1016/j.ijadhadh.2019.102409>.
- [11] Kinloch AJ, Kodokian GKA, Watts JF. Relationships between the surface free energies and surface chemical compositions of thermoplastic fibre composites and adhesive joint strengths. *J Mater Sci Lett* 1991;10(14):815–8. <https://doi.org/10.1007/BF00724747>.
- [12] Kinloch AJ, Taig CM. The adhesive bonding of thermoplastic composites. *J Adhes* 1987;21(3–4):291–302. <https://doi.org/10.1080/00218468708074976>.
- [13] Kodokian GKA, Kinloch AJ. Surface pretreatment and adhesion of thermoplastic fibre-composites. *J Mater Sci Lett* 1988;7(6):625–7. <https://doi.org/10.1007/BF01730315>.
- [14] Kodokian GKA, Kinloch AJ. The adhesive fracture energy of bonded thermoplastic fibre-composites. *J Adhes* 1989;29(1–4):193–218. <https://doi.org/10.1080/00218468908026487>.
- [15] Kinloch AJ, Kodokian GKA, Watts JF. The adhesion of thermoplastic fibre composites. *Philos Trans Roy Soc London Ser A: Phys Eng Sci* 1992;338(1649):83–112. <https://doi.org/10.1098/rsta.1992.0004>.
- [16] Popelka A, Krupa I, Novak I, Al-Maadeed MASA, Ouederni M. Improvement of aluminum/polyethylene adhesion through corona discharge. *J Phys D: Appl Phys* 2016;50(3):035204. <https://doi.org/10.1088/1361-6463/50/3/035204>.
- [17] Popelka A, Novk I, Al-Maadeed MAS, Ouederni M, Krupa I. Effect of corona treatment on adhesion enhancement of LLDPE. *Surf Coat Technol* 2018;335:118–25. <https://doi.org/10.1016/j.surfcoat.2017.12.018>.
- [18] Jin X, Wang W, Xiao C, Lin T, Bian L, Hauser P. Improvement of coating durability, interfacial adhesion and compressive strength of UHMWPE fiber/epoxy composites through plasma pre-treatment and polypyrrole coating. *Compos Sci Technol* 2016;128:169–75. <https://doi.org/10.1016/j.compscitech.2016.03.026>.
- [19] Borooj MB, Shoushtari AM, Haji A, Sabet EN. Optimization of plasma treatment variables for the improvement of carbon fibres/epoxy composite performance by response surface methodology. *Compos Sci Technol* 2016;128:215–21. <https://doi.org/10.1016/j.compscitech.2016.03.020>.
- [20] Silverstein M, Breuer O. Relationship between surface properties and adhesion for etched ultra-high-molecular-weight polyethylene fibers. *Compos Sci Technol* 1993;48(1):151–7. [https://doi.org/10.1016/0266-3538\(93\)90131-Y](https://doi.org/10.1016/0266-3538(93)90131-Y).
- [21] Tiwari S, Bijwe J, Panier S. Tribological studies on polyetherimide composites based on carbon fabric with optimized oxidation treatment. *Wear* 2011;271(9):2252–60. <https://doi.org/10.1016/j.wear.2010.11.052>.
- [22] Farris S, Pozzoli S, Biagioni P, Duo L, Mancinelli S, Piergiovanni L. The fundamentals of flame treatment for the surface activation of polyolefin polymers – a review. *Polymer* 2010;51(16):3591–605. <https://doi.org/10.1016/j.polymer.2010.05.036>.
- [23] Williams DF, Abel M-L, Grant E, Hrachova J, Watts JF. Flame treatment of polypropylene: a study by electron and ion spectroscopies. *Int J Adhes Adhes* 2015;63:26–33. <https://doi.org/10.1016/j.ijadhadh.2015.07.009>.
- [24] Sham ML, Li J, Ma PC, Kim J-K. Cleaning and functionalization of polymer surfaces and nanoscale carbon fillers by UV/Ozone treatment: a review. *J Compos Mater* 2009;43(14):1537–64. <https://doi.org/10.1177/0021998308337740>.
- [25] Mathieson I, Bradley R. Improved adhesion to polymers by UV/ozone surface oxidation. *Int J Adhes Adhes* 1996;16(1):29–31. [https://doi.org/10.1016/0143-7496\(96\)88482-X](https://doi.org/10.1016/0143-7496(96)88482-X).
- [26] Bok S, Lim G-H, Lim B. UV/ozone treatment for adhesion improvement of copper/epoxy interface. *J Ind Eng Chem* 2017;46:199–202. <https://doi.org/10.1016/j.jiec.2016.10.031>.
- [27] Seo J, Chang WS, Kim T-S. Adhesion improvement of graphene/copper interface using UV/ozone treatments. *Thin Solid Films* 2015;584:170–5. <https://doi.org/10.1016/j.tsf.2015.01.007>.
- [28] Moyano MA, Martin-Martinez JM. Surface treatment with UV-ozone to improve adhesion of vulcanized rubber formulated with an excess of processing oil. *Int J Adhes Adhes* 2014;55:106–13. <https://doi.org/10.1016/j.ijadhadh.2014.07.018>.
- [29] Liu J, He L, Wang L, Man Y, Huang L, Xu Z, et al. Significant enhancement of the adhesion between metal films and polymer substrates by UV/Ozone surface modification in nanoscale. *ACS Appl Mater Interfaces* 2016;8(44):30576–82. <https://doi.org/10.1021/acsami.6b09930>.
- [30] Le-The H, Tiggelaar RM, Berenschot E, van den Berg A, Tas N, Eijkel JCT. Postdeposition UV-ozone treatment: an enabling technique to enhance the direct adhesion of gold thin films to oxidized silicon. *ACS Nano* 2019;13(6):6782–9. <https://doi.org/10.1021/acs.nano.9b01403>.
- [31] Shi H, Sinke J, Benedictus R. Surface modification of PEEK by UV irradiation for direct co-curing with carbon fibre reinforced epoxy prepreps. *Int J Adhes Adhes* 2017;73:51–7. <https://doi.org/10.1016/j.ijadhadh.2016.07.017>.
- [32] Flanagan J, Schutze P, Dunne C, Twomey B, Stanton KT. Use of a blast coating process to promote adhesion between aluminium surfaces for the automotive industry. *J Adhes* 2018;1–22. <https://doi.org/10.1080/00218464.2018.1486713>.
- [33] O'Brien FEM. The control of humidity by saturated salt solutions. *J Sci Instrum* 1948;25(3):73–6. <https://doi.org/10.1088/0950-7671/25/3/305>.
- [34] Mohan J, Ivankovic A, Murphy N. Effect of prepreg storage humidity on the mixed-mode fracture toughness of a co-cured composite joint. *Compos Part A: Appl Sci Manuf* 2013;45:23–34. <https://doi.org/10.1016/j.compositesa.2012.09.010>.
- [35] Cheon M, Peppas NA. Models of moisture transport and moisture-induced stresses in epoxy composites. *J Compos Mater* 1993;27:1146–71. <https://doi.org/10.1177/002199839302701201>.