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Surface modification of PEEK by UV irradiation for direct co-curing with carbon fibre reinforced epoxy prepregs

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Abstract

Adding a layer of thermoplastic resin on the surface of thermoset composites enables welding as a possible joining method for thermoset composites. Adhesion at the thermoset/thermoplastic interface was achieved by direct co-curing of an UV irradiation treated PEEK film with aerospace grade carbon/epoxy prepregs. The effectiveness of UV irradiation for surface modification of PEEK was characterized using Fourier-Transformed InfraRed (FTIR) spectroscopy and contact angle measurement. The adhesion quality at the thermoset/thermoplastic interface was evaluated using a double cantilever beam test and Atomic Force Microscopy (AFM). UV treatment was found to effectively modify the chemical structure of PEEK surface and improve the wettability, which enables the development of a thermoset/thermoplastic interface by direct co-curing.

Keywords

Composites, thermoplastic, surface treatment, hybrid joints

1. Introduction

Compared to thermoset composites, thermoplastic composites show abilities to reduce both cycle time and costs for airframes, for example ribs, brackets and clips can be manufactured by press forming [1,2]; and fixed leading edges, rudders and elevators can be assembled by welding [3,4]. Thanks to these advantages, more and more thermoplastic composites are being used in newly designed aircraft [2–4]. Considering the relatively high cost of thermoplastic (TP) polymers, hybrid application of thermoplastic and thermoset composites can be a more

economical solution, where joining of composites becomes essential. Mechanical fastening and adhesive bonding are currently two of the mostly used joining methods, while there are disadvantages for both methods: mechanical fastening induces a significant weight increase and stress concentrations in the structure; adhesive bonding requires extensive surface treatment. Moreover, bonding is difficult to be applied on high grade TPs, such as polyether ether ketone (PEEK) and polyphenylene sulfide (PPS), due to their superior chemical resistance. Welding, however, has been found to be a fast and cost effective method for joining of thermoplastic composites, but it is inherently not suitable for thermoset composites. The cross-linked molecule structure of a thermoset resin, makes molecular diffusion not possible. Therefore, giving the co-curing of TP-film to thermoset composites will make welding a possible joining method for thermoset composites, which can improve the flexibility of the structural design and decrease the joining costs.

Adding a layer of TP resin on the top of thermoset composites is a way to add weldability to thermoset composites, where the key issue is to create a strong adhesion at the TS/TP interface. The adhesion can be achieved by two ways: indirect bonding and direct bonding [5]. For indirect bonding, a hybrid layer, usually a layer of fabric half impregnated by thermoplastic, is used at the interface between the TP and thermoset composites to create mechanical interlocking [6,7]. However, the hybrid layer has to be manufactured with an additional process, which is difficult to control. For direct bonding, an interface is created by inter-diffusion of epoxy molecules into the thermoplastic layer to form a semi-interpenetrating polymer network (SIPN) [8–10]. Such interface has been successfully created between epoxy, for both uncured resin [8,11] and prepregs [9,10], and TP films, mostly amorphous TPs such as polyethersulfone (PES), polyetherimide (PEI) and polysulfone (PSU). However, a SIPN is found to be difficult to develop between epoxy and semicrystalline TP films, except when the T_m of the TP film is lower than the glass transition temperature (T_g) of epoxy [12]. Since the aerospace grade thermoplastic polymers, i.e. PEEK and PPS, are usually semi-crystalline polymers with high melting temperatures (higher than the T_g of epoxy), direct bonding with epoxy is difficult.

In this study, UV irradiation was investigated to modify the surface properties of PEEK to enable direct bonding of PEEK with carbon fiber (CF)/epoxy prepregs, where the TS/TP interface was developed by co-curing. The effectiveness of UV irradiation on the surface modification of PEEK was evaluated using Fourier-transformed Infrared spectroscopy (FTIR) and contact angle measurement. The adhesion quality at the TS/TP interface was characterized using mechanical tests and atomic force microscopy (AFM), and the fracture surfaces were inspected using scanning electron microscopy (SEM).

2. Experimental

2.1 Materials and manufacturing process

Aerospace grade CF/epoxy prepregs, HexPly® 8552 from Hexcel and CyCom® 977-2 from Cytec, were used in this study. PEEK neat resin film in an amorphous state, APTIV® 2000 provided by Victrex, was used. The nominal thickness of the PEEK film is 100 µm, and due to the manufacturing process the film has two distinct sides: one smooth side and one rough side.

The PEEK films were irradiated using low pressure mercury short-wavelength ultraviolet (UV-C) lamps operating at the spectral wavelengths of 184.9 nm and 253.7 nm. The PEEK films were cleaned with Ethanol and dried in open air prior to the treatment. During the treatment, the films were placed in an enclosed volume (170 mm * 550 mm * 60 mm), with a distance of 5.1 mm from three 30 Watt tube UVC-lamps (Φ 16 mm), installed 50 mm apart. Both sides of the films were treated, in subsequent order. The UV treatments were conducted in laboratory air with a relative humidity of around 50%. The lamps were pre-heated for 5 min before the start of the treatment. The surface modification of PEEK is expected to start by removing organic contaminations from the surface followed by the oxidation of the surface [13]. The mechanism of UV/ozone cleaning and activation process is mainly based on two wavelengths: 184.9 nm and 253.7 nm. The spectral lines at 184.9 nm generate ozone (O₃) and atomic oxygen O (3P) by photolysis of oxygen gas in an endothermic reaction, while the spectral lines at 253.7 nm are easily absorbed by single C-C bonds of hydrocarbons as well as ozone, during which reaction O (1D) is generated [13]. The UV activation process is actually a continuous oxidation process as initiated by the reactive oxygen (and carbon) radicals [13].

To evaluate the effectiveness of UV treatment for surface modification of PEEK film, the surface chemistry of the PEEK film was inspected by Attenuated Total Reflectivity (ATR) FTIR spectroscopy (PerkinElmer Spectrum 100 ® Spectrometer). The surface wettability of the PEEK film was evaluated by contact angle measurement using Attension Theta ® contact angle meter. Distilled Water was used as the test liquid, and a constant volume of 5 µl was used for each droplet.

The TS/TP interface was created during the curing of laminates in the autoclave. The laminates were cured following the recommended curing cycle from the material supplier: cure temperature of 177 °C and autoclave pressure of 7 bar for Cycom® 977-2 samples; cure temperature of 180 °C and autoclave pressure of 7 bar for HexPly® 8552 samples. Before reaching the cure temperature, the samples were held at 140 °C for 1 hour to promote the development of the TS/TP interface by molecule diffusion [9].

2.2 Mechanical testing methods

Panels of 200 mm × 150 mm were made for the double cantilever beam (DCB) test, with the stacking sequence of $[0^\circ]_8/\text{PEEK}/[0^\circ]_8$, where $[0^\circ]$ represent one layer of Unidirectional (UD) prepreg and PEEK represent one layer of PEEK film. One layer of Teflon[®] film was put between the PEEK film (with the smooth side of the PEEK film facing the Teflon film) and the prepreg to create the pre-crack (see Figure 1). For each test series, five specimens with dimensions of 180 mm × 25 mm and a pre-crack length of 50 mm were cut from the panels and tested. The tests were performed according to the ASTM D5528-01 standard [14], and a cross-head displacement rate of 2.5 mm/min was used. A Zwick 20 kN testing machine was used to perform the tests, and a 1 kN load cell was used. The corrected beam theory was applied for data reduction of Mode I interlaminar fracture toughness (G_{IC}). The fracture surfaces of the samples were observed visually and by a SEM.

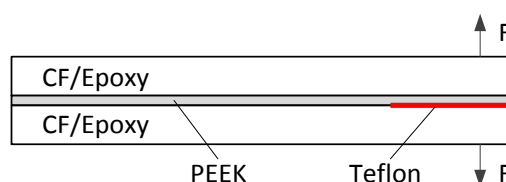


Figure 1. Schematic drawing of the sample for double cantilever beam test.

AFM was used to characterize the adhesion quality at the TS/TP interface. Some pieces were cut off from the same panel as that for the DCB samples and the cross-sections were analysed. The samples were embedded in a fast curing epoxy (Tecnovit[®] 4071), grinded, and polished for AFM observation. NT-MDT NTEGRA[®] Prima scanning probe microscopy, working in tapping mode and scanning by the probe, was used for the measurements.

3. Results and discussion

3.1 Characterization of surface modification

The chemical structure of the PEEK film surface was characterized using FTIR spectroscopy before and after the UV treatment. The PEEK films were treated for different irradiation times of 5 min, 15 min, 30 min and 60 min (UV radiant exposure of 9 J/cm², 27J/cm², 54 J/cm², and 108 J/cm²), as noted as PEEK_UV5, PEEK_UV15, PEEK_UV30 and PEEK_UV60, respectively. Both sides of the films were UV treated and measured by FTIR spectroscopy. Due to the fact that one side of the film was relatively rougher, the spectrum on the rough side of the film was found unstable, therefore only the results measured on the smooth side of the film were used. The IR spectrum was found to be unchanged when the UV treated samples were re-measured 4 days after the

treatment, which indicates that the effect of treatment is relatively stable. Even so, all the FTIR measurements were performed within 1 h after the UV treatment.

The IR spectrum measurements are shown in Figure 2. An overview of all the observed spectrum changes is listed in Table 1. The most evident changes in the spectrum is the appearance of new absorption values in the ranges from 1675 cm^{-1} to 1800 cm^{-1} and from 2700 cm^{-1} to 3600 cm^{-1} , and the levels of the values are found to increase steadily with the treatment time. The new values in the range from 1675 cm^{-1} to 1800 cm^{-1} could be due to the production of the ester band of O-C=O (with an absorbance wavelength of about $1730\sim 1740\text{ cm}^{-1}$ [15–17]), which indicates the photo-transformation of benzophenone unites [15,18]. The new values observed from 2700 cm^{-1} to 3600 cm^{-1} is in the range of polymeric hydrogen-bonded OH stretching [15,18], possibly in phenolics or alcohols. The FTIR results suggest the occurrence of chain scissoring under UV irradiation, i.e. change of aromatic ether bond to OH and O-C=O bonds [15].

Table 1. Changes of IR spectrum peaks of PEEK after UV irradiation.

Wavelength (cm^{-1})	Type of bond	Change of intensity after UV irradiation
927	Aromatic hydrogen [19,20]	Moderately decreasing
1100~1100	Ester [21]	Increasing
1156	Aromatic hydrogen [19,20]	Moderately decreasing
1185	Aromatic hydrogen [19]	Moderately decreasing
1216	Ether [15,19]	Decreasing
1487	Phenyl [19,22]	Decreasing
1650	Carbonyl [16,17,19]	Moderately decreasing

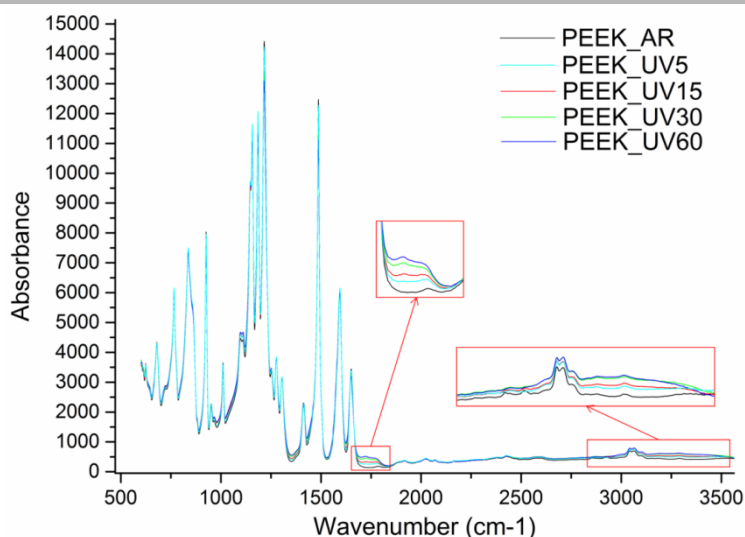


Figure 2. The Fourier-transformed Infrared spectroscopy (FTIR) spectrum of untreated PEEK (PEEK_AR) and UV treated PEEK for different times of 5 min, 15 min, 30 min and 60 min (PEEK_UV5, PEEK_UV15, PEEK_UV30 and PEEK_UV60).

The wettability of the surface of PEEK was evaluated by contact angle measurement, where the angle between the water drop and the sample surface at the drop edge was measured. Different samples, namely PEEK_AR (AR = As Received), PEEK_UV5, PEEK_UV15, PEEK_UV30 and PEEK_UV60, were measured. Since the contact angles measured on the rough side of the PEEK films were unstable, all the measurements were performed on the smooth sides of the films. For the UV treated samples, all the measurements were performed within 1 h after the treatment. As shown in Figure 3, an average contact angle of higher than 90° was measured on the surface of PEEK_AR (untreated PEEK), while UV irradiation of 5 min was found to successfully reduce the contact angle to a value less than 40° . The contact angle was found to continuously decrease with increasing of the UV irradiation time, and the lowest contact angle was measured for the PEEK_UV60 samples. The decrease of contact angle indicates the improvement of wettability on the surface of PEEK film by UV treatment.

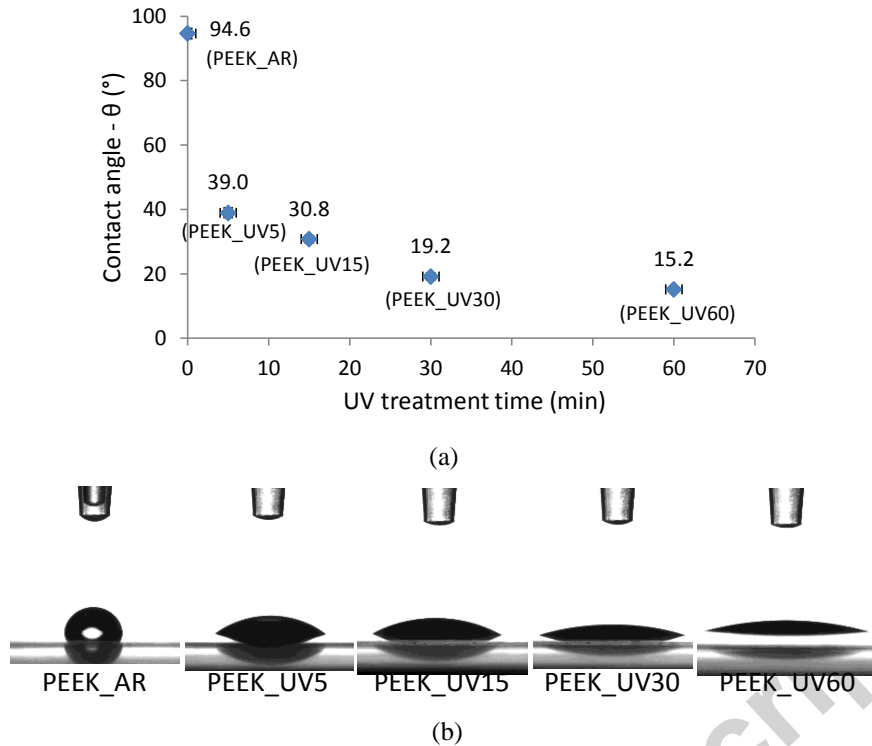


Figure 3. (a) The measured contact angles and (b) the shapes of water drops on PEEK films with different UV treatments: PEEK_AR (no UV treatment), PEEK_UV5 (5min), PEEK_UV15 (15min), PEEK_UV30 (30min) and PEEK_UV60 (60min).

3.2 Analysis of adhesion quality by mechanical testing

DCB tests were performed on the samples made of Hexply 8552 CF/epoxy prepregs and with different interfaces: with no PEEK film at the interface (benchmark); with an untreated PEEK film at the interface (PEEK_AR); with an UV treated PEEK film at the interface (PEEK_UV15, PEEK_UV30 and PEEK_UV60). Since the PEEK_AR samples failed prior to the test, no curve was recorded. As shown in Figure 4 (a), a smooth force-displacement curve was obtained in the benchmark samples, with a stable crack propagation. However, unstable crack propagations were observed for the samples with an UV treated PEEK film at the interface, distinguished by a saw-tooth like force-displacement curve (see Figure 4 (b)), and brittle failure was observed in the PEEK layers (see in Figure 6, SEM image of type 3 failure). The unstable crack propagation is known as stick/slip fracture, where “crack onsets” and “crack arrests” occurred alternately during the crack propagation. Dissimilar materials, PEEK and carbon/epoxy composite, were present at the interface of crack path, and this is believed to induce the unstable crack propagations [23] and the consequential brittle failures in the PEEK layer [24,25]. Due to the unstable crack propagation, two data sets: G_{IC_onset} (before crack jump) and G_{IC_arrest} (after

crack jump) should be calculated separately [22,24]. As shown in Figure 4 (b), the values of G_{IC_onset} are higher than the values of G_{IC_arrest} .

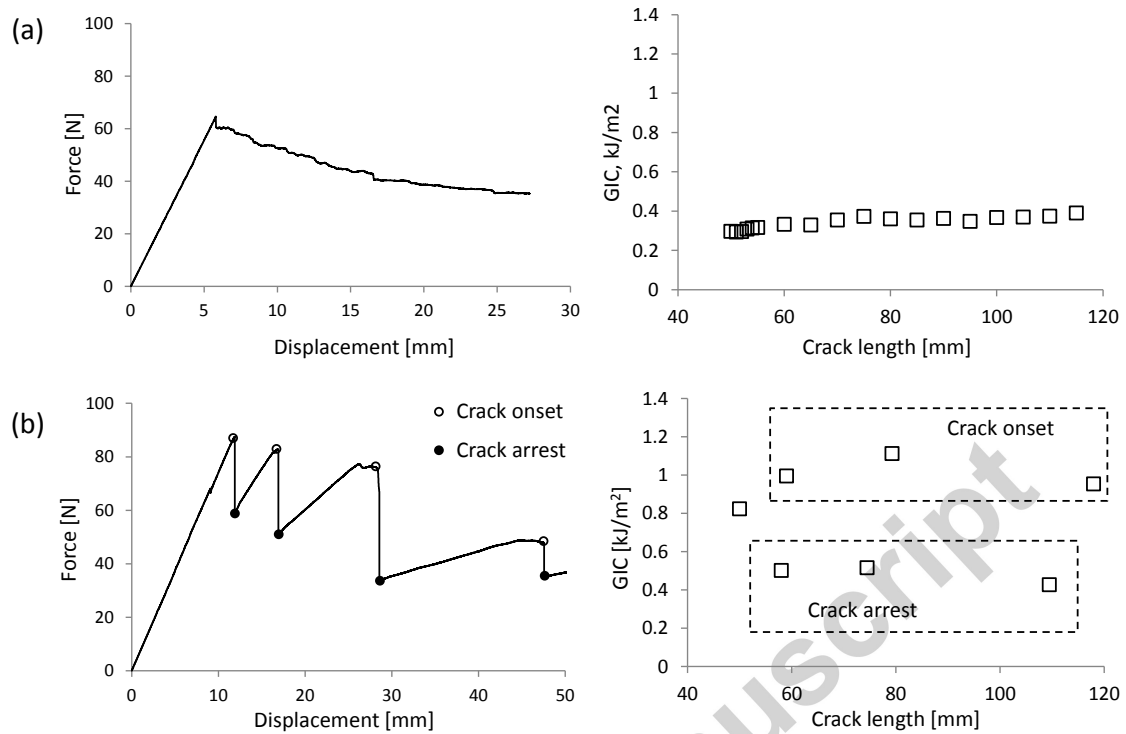


Figure 4. The force-displacement curves (on the left hand) and R-curves (on the right hand) of double cantilever beam tests of (a) Hexply 8552 CF/epoxy benchmark and (b) Hexply 8552 CF/epoxy with a layer of UV treated (15 min) PEEK film at the interface.

For comparison, the average G_{IC} ($0.5 * G_{IC_onset} + 0.5 * G_{IC_arrest}$) were calculated, as shown in Figure 5. The UV treated samples resulted in higher average G_{IC} than the benchmark samples. More specific, the higher G_{IC} was obtained by the PEEK_UV15 and PEEK_UV30 samples than the PEEK_UV5 and PEEK_UV60 samples. Four types of failure are observed on the fracture surfaces of the samples (see Figure 6), namely interfacial failure with smooth surfaces (type 1), interfacial failure with rough surfaces (type 2), PEEK failure (type 3) and laminate failure (type 4). As PEEK resin was observed on both sides of the samples for type 2 and type 3 failures, both of them belong to cohesive failure. The fracture surfaces of the DCB samples are shown in Figure 7. Cohesive failure (type 2 or type 3 failure) was observed as the main failure mode for the samples with an UV treated PEEK film at the interface, indicating the achievement of a strong TS/TP interface. Type 1 failure was observed in the samples with an untreated PEEK film at the interface, which resulted in negligible G_{IC} values. Type 4 failure was obtained in the benchmark samples, while the G_{IC} was found to be lower than the samples

with an UV treated PEEK film at the interface, indicating a lower resistance for crack propagation at the fibre-matrix interface than in the t PEEK film. For the samples with an UV treated PEEK film, the cracks were observed to propagate in the PEEK instead of jumping the adherend. This could be due to the high energy barrier for crack jump, since fibre fracture has to happen to enable a crack jump. It should also be noticed that even though cohesive failure was observed at the samples with an UV treated PEEK film, the obtained G_{IC} values are still lower than the typical values of carbon/PEEK composite systems (1.3-2.9 kJ/m²) [26,27]. Due to the existence of dissimilar microstructures at the crack path, brittle failure and unstable crack propagations were obtained in our samples instead of the commonly observed tough failure for carbon/PEEK composites, which could result in a lower G_{IC} .

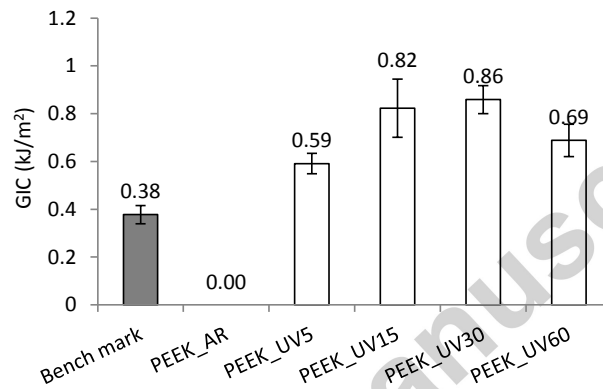


Figure 5. The average G_{IC} values for Hexply 8552 CF/epoxy benchmark, CF/epoxy with an untreated PEEK film and CF/epoxy with an UV treated (5 min, 15min, 30min and 60min) PEEK film at the interface.

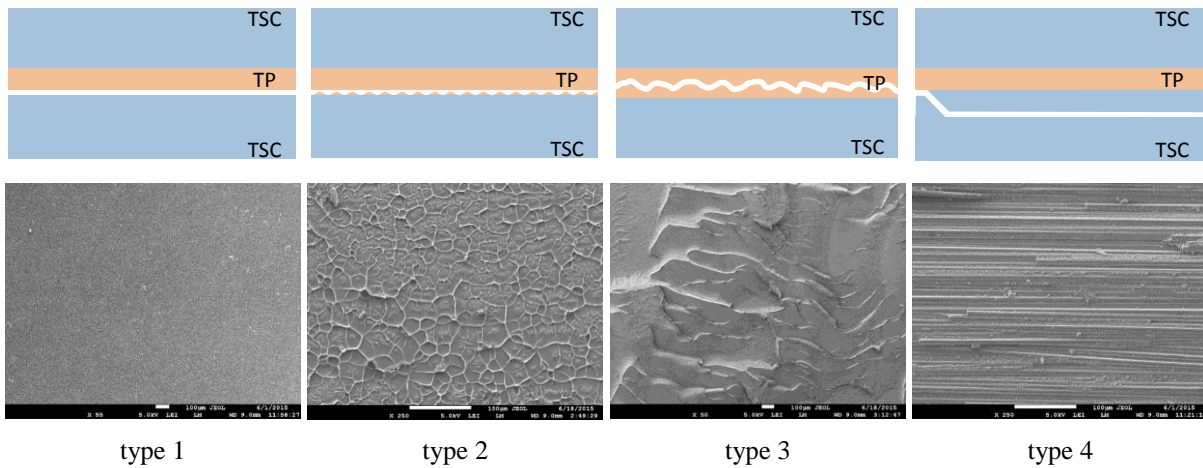


Figure 6. Schematic drawing (top) and SEM images (below) of the failure modes observed in this study. Type 1: interfacial failure with smooth surfaces; type 2: interfacial failure with rough surfaces; type 3: PEEK failure and type 4: laminate failure.

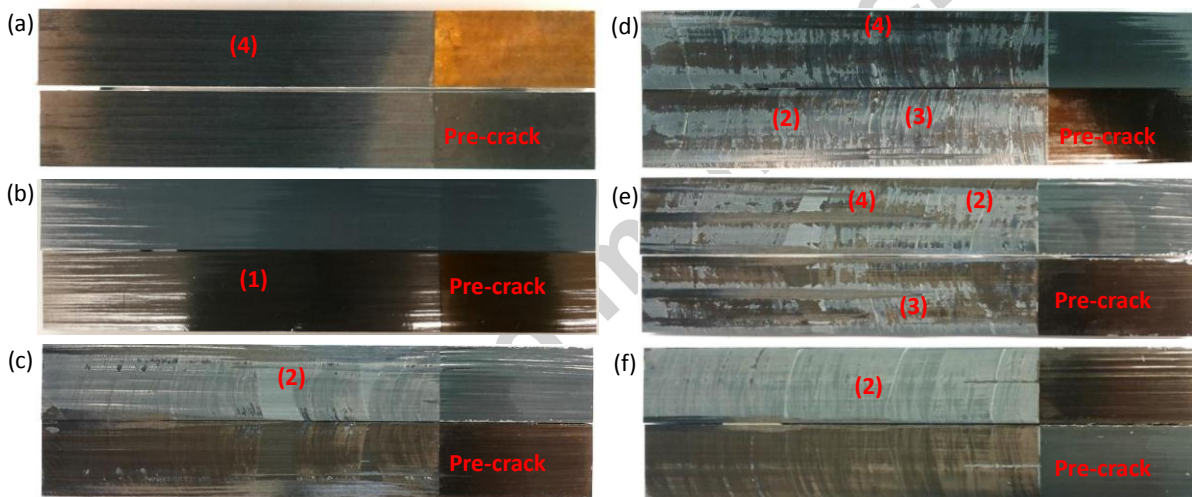


Figure 7. The fracture surfaces of Hexply 8552 CF/epoxy with different interfaces: (a) without PEEK film, (b) with PEEK_AR, (c) with PEEK_UV5, (d) with PEEK_UV15, (e) with PEEK_UV30, and (f) with PEEK_UV60. (1: interfacial failure with smooth surfaces; 2: interfacial failure with rough surfaces; 3: PEEK failure and 4: laminate failure)

A different type of prepreg, Cycom 977-2, was also tested to study the effectiveness of UV treatment for adhesion of PEEK film with other types of CF/epoxy prepreps. Specimens were tested with different configurations at the interface: no PEEK film at the interface (benchmark); with an untreated PEEK film at the interface (PEEK_AR); and with 15 min UV treated PEEK film at the interface (PEEK_UV15). Similar to the samples made of Hexply 8552: PEEK_AR samples failed at the interface prior to the test, and no force-

displacement curve could be recorded; Benchmark samples showed a smooth force-displacement curve and stable crack propagation at the interface (Figure 8 (a)); PEEK_UV15 specimens showed also saw-tooth like force-displacement curve and unstable crack propagation (Figure 8 (b)). As shown in Figure 9, the G_{IC} obtained from the samples made of Cycom 977-2 was comparable to the values of samples made of Hexply 8552. Moreover, as shown in Figure 10, the failure modes were found to be similar as the failure modes observed from the Hexply 8552 samples (Figure 7): type 2 or type 3 failure for PEEK_UV15 samples; type 1 failure for PEEK_AR; and type 4 failure for benchmark samples. Cohesive failure was found as the dominant failure mode of the UV treated samples, which indicates a strong TS/TP interface.

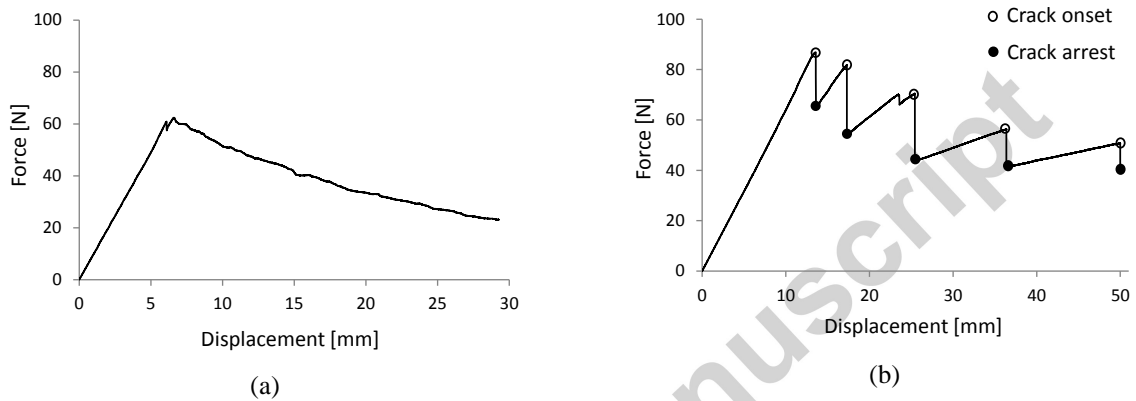


Figure 8. The force-displacement curve of double cantilever beam tests of (a) Cycom 977-2 CF/epoxy benchmark and (b) Cycom 977-2 CF/epoxy with a layer of 15 min UV treated PEEK film at the interface.

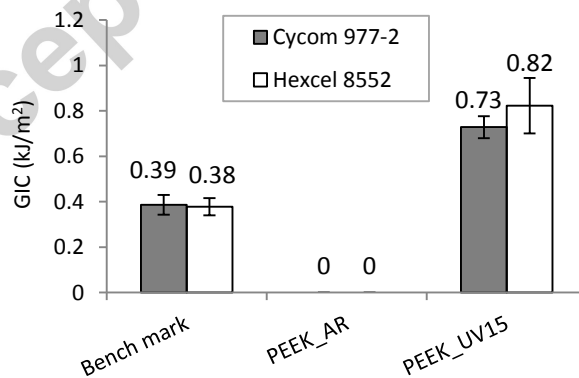


Figure 9. G_{IC} of CF/epoxy benchmark, CF/epoxy with an untreated PEEK film at the interface and CF/epoxy with a 15 min UV treated PEEK film at the interface.

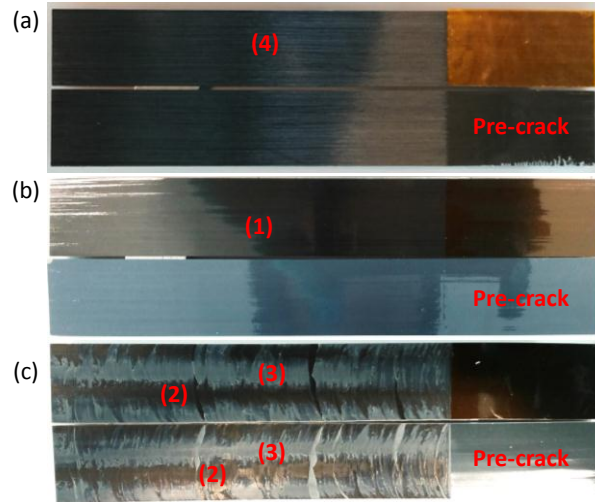


Figure 10. The fracture surfaces of Cycom 977-2 CF/epoxy with different interfaces: (a) without PEEK film, (b) with PEEK_AR, (c) with PEEK_UV5, (d) with PEEK_UV15, (e) with PEEK_UV30, and (f) with PEEK_UV60.

3.3 Analysis of adhesion quality by AFM

The TS/TP interface was also analysed by measuring the cross-section surface topology using AFM. The samples were made of Hexply 8552 CF/epoxy prepregs with different interfaces: a layer of PEEK_AR film or a layer of PEEK_UV15 film. The measured AFM images are shown in Figure 11. In theory, the spatial variation in the material properties is expected to result in different phase shifts [28,29], the phase difference from the piezo drive to the cantilever. However, the phase images obtained in our measurements contain too big scatters (see Figure 11 (b)), so useful information can hardly be derived from them. Therefore, height images (Figure 11 (a)) were mainly used for the analysis. The height images show directly the topology of the surfaces of the samples, but they can indirectly indicate the material properties due to the usage of tapping mode AFM. Since the whole surface areas of the samples were polished equally, the height variations observed in the samples should be caused by the diversity of e.g. material modulus and wear resistance. By taking this into account, the height image can also be useful to analyse the quality of interface. As shown in Figure 11 (a), a clear interface was observed in the sample with a PEEK_AR film at the interface, which may indicate poor adhesion between the epoxy and the PEEK. However, a less obvious interface was observed in the sample with a PEEK_UV15 film at the interface (see Figure 11 (b)), which could indicate better adhesion between the epoxy and the PEEK as a result of inter-diffusion of epoxy into PEEK during curing [8,9,11].

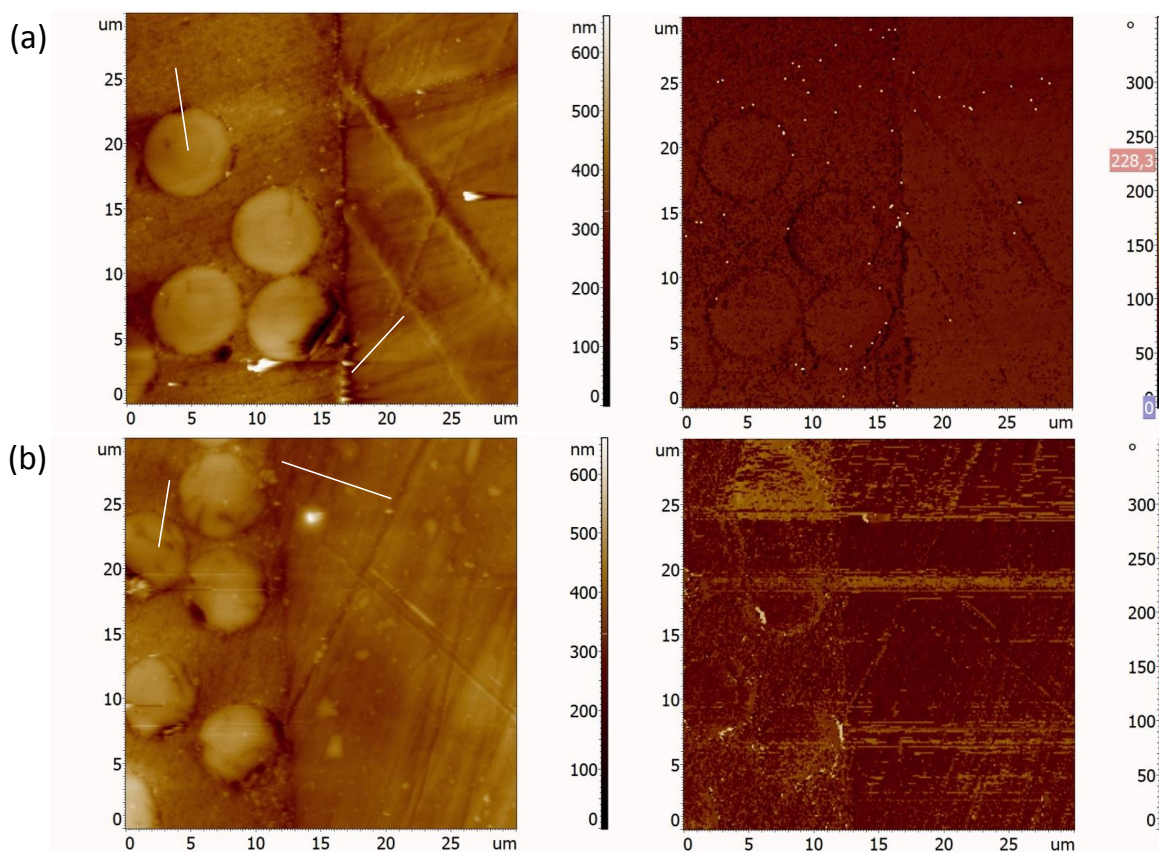


Figure 11. Atomic force microscopy (AFM) height images, on the left hand side, and phase images, on the right hand side, of (a) CF/epoxy with an untreated PEEK film at the interface, and (b) CF/epoxy with a layer of UV treated (for 15 min) PEEK film at the interface.

4. Conclusions

Adhesion between PEEK and aerospace grade carbon epoxy was achieved by co-curing. UV irradiation was used to treat the surface of PEEK film, and the UV irradiation induced surface modification of PEEK film that was characterized using FTIR and contact angle measurement. The adhesion quality at TS/TP interface was evaluated using DCB tests and AFM analysis.

The FTIR analysis showed that the chemical structure of PEEK surface is changed after UV irradiation. Higher absorption values were found in the ranges from 1675 cm^{-1} to 1800 cm^{-1} and from 2700 cm^{-1} to 3600 cm^{-1} , and the levels of the new values were found to rise steadily with the treatment time. Chain scissoring was regarded to be responsible for this change. The contact angle of the surface of PEEK was found to decrease with increasing treatment time, indicating a continuous improvement of wettability. The surface modification of PEEK by UV treatment was found quite stable, without noticeable aging effect.

Adhesion cannot be obtained at the TS/TP interface if an untreated PEEK film was used, while an UV treated PEEK film with a moderate irradiation time, from 15 to 30 min, resulted in strong adhesion at the TS/TP interface. Instead of interfacial failure which was observed in the samples with an untreated PEEK film at the interface, cohesive failure was found as the dominant failure type for the samples with a UV treated PEEK film at the interface.

The strongest adhesion at the TS/TP interface was obtained by UV irradiation of PEEK for a moderate time of 15 - 30 min. A shorter treatment time, i.e. 5 min, induced less surface modification on PEEK and consequently resulted in insufficient adhesion with the thermoset composite. A too long treatment time, i.e. 60 min, however, induced too much deterioration of the surface of PEEK and resulted in decline of adhesion quality.

UV irradiation and co-curing can be a way to produce good TP/TS interfaces as a precursor to the welding of hybrid composite structures. Further studies are required to assess the effect of elevated temperatures and moisture on the adhesion strength of the TS/TP interface, as well as the adhesion quality under different loading conditions. Welding experiments must also be performed to evaluate the performance and durability of TS/TP interface under real welding conditions.

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