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Co-cured carbon fibre/epoxy composite joints by advanced thermoplastic films with excellent structural integrity and thermal resistance

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A B S T R A C T

Carbon fibre/epoxy composite joints were assembled with Poly-etherether-ketone (PEEK) and Poly-ethylenimine (PEI) films using a co-curing process to prepare single-lap joint specimens. The joints were tested under quasi-static loading conditions at 22 °C and 130 °C and a fatigue loading condition. The experimental results demonstrated better or comparable structure integrity of the composite joints co-cured by PEEK and PEI films than the reference joints bonded by aerospace FM300 adhesives. In particular, the PEEK co-cured joints exhibited extraordinary mechanical performance at 130 °C and excellent fatigue resistance. For instance, the lap-shear strength at 130 °C and the fatigue life of the composite joints co-cured by 200 μm PEEK films was 2.1 times and 2.7 times higher than that of the aerospace adhesive joints, respectively. Overall, the results of this work proved that advanced thermoplastic films are promising alternatives to epoxy adhesives for the co-cure joining of thermoset composites with significantly enhanced structural integrity and thermal stability.

1. Introduction

The applications of carbon fibre reinforced plastics in aerospace industry have extensively expanded over the last decade, owing to their light weight, excellent structural performance and high design flexibility [1]. This brings in significant challenge in the development of suitable joining techniques. Adhesive bonding and mechanical fastening are currently the two dominating joining techniques for aircraft assembly. Among them, adhesive bonding offers many advantages over mechanical fastening, including the ability of making light-weight joints, bonding dissimilar materials, achieving relatively uniform stress-distribution along the bonding conjunctions and sealing the entire bonding area [2,3]. Accordingly, it is an ideal process for the joining of carbon fibre composites.

However, there are also some disadvantages of the adhesive bonding technique, and a foremost one is the requirement of a long curing process [4]. This shortcoming can be overcome by a concept of co-curing or co-bonding [5,6], i.e. the composite and the adhesive layer are concurrently cured during a single curing cycle. In this case, unlike the traditional secondary-bonding technique, no separate curing cycle is required for the adhesive layers of the composite joints. To date, many studies have employed the co-curing or co-bonding process for the joining of composite–composite [7,8], composite–metal [9,10] and composite sandwich [11,12] structures. For example, Hasan et al. [13] fabricated a full-scale wing demo using a co-curing process, and the post cure inspection showed minimal anomalies in the structures that satisfied the engineering requirements. It was also observed that the warpage of the laminates in the co-cured structures was less than that in their secondary-bonded counterparts. In another study, Kim et al. [14] manufactured composite hat-stiffened panels using three different processes, including co-curing, co-bonding and secondary bonding. The mechanical properties of the panels were evaluated using a pull-off test. It was observed that the average failure load of the co-cured hat-stiffened panels was 91.56 kN/m, that was 98% higher than that of the co-bonded ones and 217% higher than that of the secondary-bonded ones. Mohan et al. [15] studied the fracture behaviour of adhesively bonded composite joints that were manufactured by both of co-curing and secondary bonding processes. It was reported that both of the mode-I and mode-II fracture energies of the co-cured adhesive joints were slightly lower (approximately 10%) than that of the secondary bonded joints. Overall, in addition to the reduced assembly time and cost, the co-curing process can also be used to produce composite joints with relatively good structural integrity. It is worthy to mention that the absence of surface treatment to the composite adherends and no concern over weak bonds that can occur with secondary and co-bond processes are another significant benefits of the co-cure joining process [16].

Aerospace-grade structural adhesives are typically based on epoxies due to their prominent engineering properties, such as high modulus,
high strength, low creep and excellent chemical resistance [17]. Nevertheless, there are a number of general limitations of epoxy adhesives for engineering applications, such as the requirement of extensive toughening for the epoxy matrix [18,19], significant property degradation at high temperatures [20], a strict requirement of low temperatures for adhesive storage and transportation and a limited shelf life [21]. Additionally, for the co-curing or co-bonding joining of composite structures, a match between the curing cycles of the adhesives and the composites is required [22]. In specific, it is essential that the adhesives possessed the same curing temperature as the composites, and this considerably limited the adhesive selection. Moreover, the optimal curing pressure for aerospace film adhesives is typically much lower than that of the composite laminates, and hence a moderate curing pressure was normally used during a co-curing or co-bonding process in practical [22]. The mismatch between the practical curing pressure and the suggested optimal values for both of the adhesive and the composite can potentially cause overflow of the adhesive during the curing process and generate manufacturing defects within the cured composites. Herein, with an attempt to address the limitations that were mentioned above, advanced thermo-plastic films were proposed to replace epoxy adhesives for the co-curing joining of composite laminates for aerospace applications. Thermoplastic films based on Poly-etherether-ketone (PEEK) and Poly-ethyleneimine (PEI) polymers with different thicknesses were used for the co-curing joining of aerospace composite laminates. A benchmark aerospace adhesive was also used to prepare co-cured composite joints as a reference. The failure strengths of the composite single-lap joints under ambient and high temperatures were evaluated. The failure surfaces of the tested specimens were then analysed to understand the failure mechanisms of the composite joints under different loading conditions.

2. Experimental

2.1. Materials and sample preparation

The carbon fibre/epoxy prepreg was Hexply F6376C-HTS (12 K)-5%-35% (HEXCEL Composites, UK), that contained unidirectional high tenacity Tenax-E HTS45 standard modulus fibres (TOHO TENAX Europe GmbH) and the Hexply F6376 epoxy matrix system. The PEEK films were APTIVE 1000 series supplied by Victrex (UK) and the PEI films were supplied by LITE (Germany). In this paper, the thermoplastic film was referred to as the material followed by its thickness in a unit of μm, e.g. PEEK100 represents the PEEK film with a thickness of 100 μm. The benchmark adhesive was an aerospace-grade structural adhesive, FM300 from Solvay (UK). The areal density of the adhesive film was 146 g/m².

The following steps were used to fabricate single-lap joint specimens using a co-curing process, that is schematically shown in Fig. 1. Firstly, a hand layup process was used to prepare two carbon fibre/epoxy laminates with a stacking sequence of [0₁₆], and during which, 15 min of debulking at an under pressure of below 100 mbar was carried out in between every fourth layer. The two laminate layups were then assembled together, with a layer of PEEK or PEI film being placed at the overlap area, see Fig. 1 (a). It is worthy to mention that the semi-crystalline PEEK films possessed intrinsically low surface energies and poor miscibility with the epoxy matrix of the composites [23,24]. Accordingly, prior to the assembly of the single-lap layup in Fig. 1 (a), the two surfaces of the PEEK films were treated by a high-power UV-irradiation technique for 10s to improve their adhesion with the epoxy matrix of the composite laminates [24]. The surface treatment was carried out using a UV-irradiation chamber equipped with a LH6 MKII UV source (200 W/cm) and a Mercury D bulb in an atmospheric environment. The distance between the surface of the PEEK films and the bulb was about 200 mm.

Table 1 presents the intensities of the UV spectral ranges applied onto the PEEK surfaces, that were measured using a UV Power Puck from EIT Inc., USA. In contrast, the amorphous PEI polymers had good miscibility with the epoxy matrix, and hence, no special surface treatment was needed for them. After step (a) in Fig. 1, a piece of cured [0₁₆] composite and an additional layer of thermoplastic film was placed underneath the top layup as a support, and a piece of aluminium plate with a thickness of 2 mm was placed above the bottom layup of the joints, as shown in Fig. 1 (b). The supporting materials and the aluminium plate were added to ensure a uniform pressure distribution over the lap joints during the following curing process. To avoid the bonding with composite layups, the supporting items were wrapped with a layer of PTFE film with a thickness of 12.7 μm, and the aluminium plate was coated with release agent. The assembly in Fig. 1 (b) was then sealed in a vacuum bag and cured in an autoclave, see Fig. 1 (c). The curing schedule was at 4 bar gauge pressure and 180 °C curing temperature for 120 min dwell time, with a 200 mbar vacuum pressure in the vacuum bag through the entire curing process. After the curing, the joints were machined into individual specimens with desired dimensions, as shown in Figs. 1 (d) and (e). Composite joints bonded by the FM300 benchmark adhesive were also prepared using the same procedure for a comparison purpose.

2.2. Testing and characterisation

The single-lap joint specimens were tested under three different conditions, i.e. quasi-static loading conditions at 22 °C and 130 °C and a fatigue loading condition at an ambient temperature of about 22 °C. The quasi-static single-lap shear tests at 22 °C and 130 °C were carried out using a 250 kN Zwick-Roell (Z250 SW) testing machine, that was equipped with a temperature chamber. The specimens were fixed to the testing machine by two clamps with a misalignment, that ensured the force was applied in the middle plane of the overlap during the test. Three specimens were tested at a constant displacement rate of 3 mm/min for each set. The tension-tension fatigue test was performed using a 60 kN hydraulic fatigue machine at room temperature (about 22 °C). A load control mode was used, with the maximum load, stress ratio and frequency being 6 kN, 0.1 and 10 Hz, respectively. The maximum load was defined to be approximately 50% of the lap shear strength (LSS) of the benchmark adhesive joints, based on the results of the quasi-static single-lap shear tests. Four tests were repeated for each set of joints. It is noteworthy that the adhesive joints bonded by the benchmark adhesives exhibited cohesive failure in all the cases, and the failure surfaces of the adhesive bonded joints can be seen in the Supplementary data.

A laser microscope (VK-X1000 from KEYENCE Corporation) and a scanning electron microscope (JEOL JSM-7500F Field Emission Scanning Electron Microscope, SEM) were used for the analysis of the cross-section of the composite joints. The samples for cross-sectional microscopy were ground and polished, and then, the surfaces were etched by 1 ml of N-Methyl-2-pyrrolidone (NMP) to provide a better contrast [25]. Naked-eye observation and SEM analysis were used for fractographic analysis of the tested single-lap joint specimens, with the SEM samples being coated with a layer of 5 nm gold.

<table>
<thead>
<tr>
<th>Items</th>
<th>Wave length (nm)</th>
<th>Intensity (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVV</td>
<td>395–445</td>
<td>1996</td>
</tr>
<tr>
<td>UVA</td>
<td>320–390</td>
<td>1637</td>
</tr>
<tr>
<td>UVB</td>
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<tr>
<td>UVC</td>
<td>250–260</td>
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</tr>
</tbody>
</table>
3. Results and discussion

3.1. Interface morphology

Typical microscopy images of the cross-sections of the composite joints are shown in Fig. 2, with a focus on the interfaces between the composite adherends and the PEEK/PEI films. Fig. 2(a) shows the presence of a clear dark area at the interface between the epoxy composite and the PEI film. This dark area was the interdiffusion region that was formed by the mutual diffusion of the epoxy and the PEI into each other during the curing process [25]. In specific, during the co-curing process, the liquid epoxy resin diffused into the PEI polymer and partially swell or dissolve it, which in turn, led to the diffusion of the PEI polymer into the epoxy resin [26,27]. Once the gelation point of the epoxy was reached, the interdiffusion process stopped. After the curing, phase separation between the epoxy and the PEI resins took place and resulted in an interphase with gradient composition and morphology at the interface [26,27]. As confirmed by Fig. 2(b), numerous spherical features were formed by the phase separation process, and they were PEI particles at the epoxy side and epoxy particles at the PEI side. The presence of the interdiffusion region ensured a good bonding strength at the epoxy/PEI interface. However, it should be noted that interaction between the PEI and epoxy within the interdiffusion region was mainly physical contact, without any bonds being built.

Unlike the PEI co-cured joints, a clear boundary between the PEEK film and the epoxy composite was observed at their interface for the PEEK200 joints, without any sign of interdiffusion and phase separation, see Figs. 2(c) and (d). This was caused by an intrinsically poor miscibility between the PEEK film and the epoxy matrix. Additionally, the polar component of the surface free energy of PEEK was inherently low, while the epoxy matrix of the laminates possessed a much higher surface polar energy [8,24]. In this case, the polar–polar interaction at the PEEK/epoxy interface, that can generate strong hydrogen bonds and covalent bonds was very limited. Accordingly,
the adhesion between epoxy and PEEK is typically poor. In this study, the application of the high power UV-treatment to the PEEK films (as described in Section 2.1.1) broke the C–C–C–H species of the PEEK molecular chain, that was followed by the development of high polar C=O, O=O and O-C=O species [23,24]. In specific, our previous study had demonstrated that applying the same UV-treatment process to the PEEK surface significantly increased its oxygen content from 14.93% to 22.97%, and increased its surface polar energy from 3.64 mN/m to 6.14 mN/m [24]. Accordingly, the level of the polar–polar force between the epoxy matrix and the PEEK films had been significantly promoted. This subsequently formed more Coulomb interactions between permanent dipoles and between permanent and induced dipoles, and generated more hydrogen bonds and covalent bonds. Accordingly, a much stronger adhesion at the epoxy/PEEK interface was obtained, even without the formation of an interdiffusion region.

3.2. Single-lap shear tests under quasi-static loading condition

Fig. 3 (a) shows the lap shear strengths (LSS) of all the co-cured joints at 22 °C. It was observed that all the composite joints co-cured with the PEEK and PEI films exhibited higher LSSs than the adhesive joints. In particular, the LSS of the adhesively bonded joints was measured to be 18 MPa. For the PEEI co-cured joints, as the thickness of the film increased, the LSS increased from 19.4 MPa of the PEII60 joints to a maximum value of 24.2 MPa of the PEII75 joints, and then slightly decreased to 19.8 MPa of the PEII250 joints. The LSS of the PEII175 joints was 34.4% higher than that of the adhesive joints. The thickness of the PEEK films had no obvious effect on the LSS, i.e. a value of approximately 19 MPa was measured for all the PEEK co-cured joints, see Fig. 3 (a). For instance, the LSS of the PEK250 joints was 19.5 MPa, corresponding to an increase of 8.3% when compared to that of the adhesive joints. Fig. 3 (b) presents the LSSs of all the co-cured joint at 130 °C. The LSS of the adhesive joints dropped from 18 MPa to 15 MPa (by 17%) as the testing temperature increased from 22 °C to 130 °C. The LSS of the PEI co-cured joints were slightly higher than that of the PEEK co-cured joints. Moreover, the surfaces of the PEI co-cured joints were relatively rugged and associated with more visible fracture features than that of the PEEK co-cured joints. For the PEI co-cured joints, the failure concurrently initiated at the two interfaces, and then the two failure paths joined in the middle of the overlap during the testing process (trans-interfacial failure), as schematically shown in Fig. 4 (a). Differently, the failure of the PEEK co-cured joints took place at only one interface (single interface failure), leaving relatively smooth failure surfaces on both sides, see Fig. 4 (a). Noteworthily, a trans-interfacial failure was typically associated with the shearing failure of the PEI film through its thickness. This explained why the LSSs of the PEI co-cured joints were slightly higher than that of the PEEK co-cured joints, as shown in Fig. 3 (a). The photographs of the single-lap joint specimens that were tested at 130 °C are shown in Fig. 4 (b). Interestingly, the failure mode of the PEI co-cured joints changed from a trans-interfacial failure at 22 °C to a single interface failure at 130 °C. In contrast, a trans-interfacial failure was observed for all the PEEK co-cured joints at 130 °C, that was associated with extensive tearing, plastic deformation and breakage of the PEEK films, see Fig. 4 (b). This was caused by the significant softening of the PEEK polymer at a high temperature, with the ductility being improved and mechanical properties being reduced. During the loading process, extensive deformation and elongation took place to the softened PEEK resin, that relieved the stress concentration at the PEEK/composite interface and led to a trans-interfacial failure of the joints. Consequently, the trans-interfacial failure mode led to a complete shearing/tearing failure of the PEEK film. These phenomena resulted in the outstanding LSSs of the PEEK co-cured composite joints at 130 °C, as shown in Fig. 3 (b).

To understand the failure mechanisms of the composite joints, a microscopy analysis was carried out on their failure surfaces. Fig. 5 shows typical microscopy images of the failure surfaces of the PEI co-cured joints at 22 °C and 130 °C. It was observed that the failure of the PEI joints occurred at the interface between the polymer matrix and the carbon fibres in both of the cases, leaving the carbon fibres on one side of the surfaces and their corresponding fibre prints on the opposite side. Moreover, a large number of phase-separated PEI particles were observed on the surfaces of the debonded carbon fibres. During the failure process, these particles were pulled-out from the surrounding matrix, that left numerous holes within the fibre prints on the opposite side of failure surfaces, as shown in Fig. 5. This phenomenon indicated that a relatively good adhesion between the phase-separated PEI and the carbon fibres was obtained during the curing process. In this case, the PEI particles on the carbon fibres served as numerous mechanical lockers during the lap shear test, and ensured relatively good LSSs. The failure of PEI-toughened epoxy matrix was also observed at the intervals between the carbon fibres at both of 22 °C and 130 °C. By
taking a closer look at the SEM images, it was found that more intensive plastic deformation took place to the interval matrix at 130 °C owing to the thermal softening.

Typical microscopy images of the fracture surfaces of the PEEK co-cured joints at 22 °C and 130 °C are shown in Fig. 6. From Fig. 6(a), it was observed that both of the PEEK side and composite side of the failure surfaces were covered with a thin layer of PEEK resin, that underwent plastic deformation and breakage during single-lap shear tests at 22 °C. As the testing temperature increased to 130 °C, additional debonding of carbon fibres from the matrix occurred, that was evidenced by the presence of bare carbon fibres on some locations of the fracture surfaces, see Fig. 6(b). Moreover, by comparing Fig. 6(a) with Fig. 6(b), it was found that the plastic deformation and breakage of the PEEK resin and epoxy matrix were extensively more severe at 130 °C, owing to the softening of the PEEK polymer. These mechanisms contributed to the outstanding LSSs of the PEEK co-cured composite joints.

3.3. Single-lap shear tests under fatigue loading condition

Fig. 7 presents the number of cycles at failure for the fatigue tests of the adhesive joints and the composite joints co-cured with the PEI175 and PEEK200 films. It should be noted that only the PEI175 and PEEK200 co-cured joints were tested under a fatigue loading conditions in this study. This was because of the thickness of the PEI and PEEK films exhibited no significant effect on the lap-shear failure behaviour of the co-cured joints under quasi-static tests, as shown in Section 3.2.

It was observed that the single-lap joints co-cured with the PEI175 films exhibited similar fatigue life as the adhesive joints, i.e. the average number of cycles at failure was 58.5 k and 54.2 k for the adhesive joints.
Fig. 5. Typical microscopy images of the failure surfaces of the PEI co-cured joints at (a) 22 °C and (b) 130 °C.

Typical photographs and microscopy images of the fatigue failure surfaces of the single-lap specimens are shown in Fig. 8. The fatigue failure mode of the composite joints was single interface failure for the PEI co-cured joints and trans-interfacial failure for the PEEK co-cured joints, as shown by the photographs of the failure surfaces. Similar to the quasi-static tests, it was observed that one side of the failure surfaces of the PEI175 joints was featured with many debonded carbon fibres, whose surfaces were attached with numerous phase-separated PEI particles. Consequently, the corresponding fibre prints on the opposite side of the failure surfaces containing a large number of holes. These observations meant that the debonding of carbon fibres from the polymer matrix was still the main failure mechanism of the PEI175 joints under the fatigue loading condition. Additionally, many matrix hackle patterns presented within the interval regions of the carbon fibres, see Fig. 8 (a) due to the application of the fatigue shearing loads to the joints. The PEEK co-cured joints possessed obviously different failure surfaces between the fatigue test and the quasi-static test. As shown by Fig. 8 (b), a thick layer of fractured PEEK resins was observed on the carbon fibre side of the failure surfaces, that was teared off from the PEEK films during the fatigue loading process. Moreover, the insert SEM images of Fig. 8(b) clearly showed extensive plastic deformation, tearing and rolling of the PEEK resins on both side of the failure surfaces. These observations explained why the PEEK200 joints exhibited outstanding fatigue resistance to the applied shearing load.

3.4. Discussion

The LSSs and fatigue life of the composites joints co-cured with the PEEK and PEI films and the benchmark aerospace adhesive are summarised in Table 2. The values in the bracket indicate the increases of the LSSs when compared to that of the adhesive joints. It was clear that the composite joints co-cured with the PEI films possessed higher
LSSs than the adhesive joints at both of 22 °C and 130 °C. However, the fatigue resistance of the PEI co-cured joints was slightly poorer (7.4%) than that of the adhesive joints. Encouragingly, when compared to the benchmark adhesive joints, the LSSs of the PEEK co-cured joints were slightly higher at 22 °C and remarkably larger at 130 °C. Additionally, the fatigue life (number of cycles at failure under the fatigue loading) of the PEEK co-cured joints was 270% longer than that of the adhesive joints. Considering the benchmark adhesive (FM300) was a widely used structural adhesives for critical aerospace applications, it can be concluded that both of the PEEK and PEI films have demonstrated some promise for the co-cure joining of aerospace composite structures.

Especially, the PEEK co-cured composite joints exhibited outstanding LSSs at high temperature and excellent fatigue resistance, that can fulfil some specific application requirements. Moreover, the thermoplastic films possess many advantages over epoxy adhesives for co-cure joining of composite structures, that include infinite storage life, no special environment is required for transportation and storage, no limitations to the curing temperature and pressure of the composites, no overflow during a high-pressure curing process and excellent thermal stability. Accordingly, there is a huge potential of using advanced PEEK and PEI films to replace epoxy adhesives for the co-cure joining of composite components for aerospace applications.

### 4. Conclusions

In this study, we proposed to use advanced thermoplastic films, i.e. Poly-etherether-ketone (PEEK) and Poly-ethylenimine (PEI) for the
co-cure joining of aerospace composites, with an attempt to enhance the structural integrity. Composite joints bonded by an aerospace adhesive were also prepared as benchmark for a comparison purpose. The results of the single-lap shear tests demonstrated that all the PEEK and PEI co-cured joints possessed a higher lap shear strength (LSS) than the benchmark adhesive joints at both of 22 °C and 130 °C. Especially, an extraordinary mechanical properties being observed at 130 °C for the PEEK co-cured joints. Moreover, a comparable fatigue life as the adhesive joints was observed for the PEI co-cured joints, while the fatigue resistance of the PEEK co-cured joints was outstanding. The results of this experimental study shed lights on the development of co-cured composite joints with significantly enhanced structural performance and thermal stability by replacing traditional epoxy adhesives with advanced thermoplastic films.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.ijadhadh.2022.103247.

References


