



Improving cryogenic mechanical properties of carbon fiber reinforced composites based on epoxy resin toughened by hydroxyl-terminated polyurethane

Cheng-Bing Qu^{a,b}, Tong Wu^a, Gui-Wen Huang^a, Na Li^a, Meng Li^{a,b}, Jun-Li Ma^{a,b}, Yu Liu^{a,**}, Hong-Mei Xiao^{a,*}

^a Key Laboratory of Technology on Space Energy Conversion, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, China

^b University of Chinese Academy of Sciences, Beijing, 100190, China

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ABSTRACT

In this study, the mechanical properties and crack densities of two kinds of hydroxyl-terminated polyurethane (HTPU1 and HTPU2) toughening epoxy/carbon fiber composites were investigated in detail by hot-press molding process. The results showed the toughening epoxy (EP) could effectively improve the mechanical strengths of composites at room temperature (RT) and cryogenic temperature (77 K) due to the improvement of interfacial adhesion between the matrix and fibers. EP/HTPU1 showed the best tensile properties of the EP matrix, but CF/EP/HTPU2 showed the highest longitudinal tensile strength, due to the existence of granular rubber precipitates after curing, which has the capability of cavitation leading to more balanced failure. Different tensile properties of matrix and composites showed the tensile properties of composites were strongly affected by the microstructure after curing and interfacial adhesion between matrix and fibers. Optical microscopy image analysis suggested that the presence of HTPU can prevent the formation of micro-cracks during thermal cycles at cryogenic condition of composite laminates.

1. Introduction

Due to high stiffness-to-weight ratio and high strength-to-weight ratio, carbon fibers reinforced polymer composites (CFRP) are regarded as the most promising material to fabricate cryogenic fuel tanks and gas cylinders etc. of the next generation rockets [1,2]. The most attractive advantage of CFRP composites is that they could significantly reduce the weight of rockets compared to the traditional metallic materials. Epoxy resin (EP) has been widely used as an appropriate matrix for CFRP to fabricate structure components owing to its excellent performance of mechanical properties, thermal properties and corrosion resistance, etc. [3–5]. In particular, as the structural material of cryogenic fuel tank, CFRP has to face a severe cryogenic environment, for example, the temperature of liquid oxygen is 90 K and that of liquid hydrogen is 20 K. However, the high brittleness and the poor resistance to crack propagation of EP matrix at cryogenic temperature greatly limit the application of CFRP in cryogenic fields [6,7]. An effective approach to increase the toughness of CFRP composites to against crack

propagation in the matrix is adding a secondary component, such as flexible polymer, thermoplastic resin or micro-sized or nano-sized fillers, etc [5,8–10]. Nevertheless, the viscosity of EP will be greatly increased by the additional thermoplastic resin, micro-sized or nano-sized fillers, then the process of resin processing will be significantly limited [11–13].

Pingkarawat et al. [14] employed the poly (ethylene-co-methacrylic acid) (EMAA) as a healing agent dispersing in DGEBA/diethyl toluene diamine to create the mendable systems, showing that EMAA significantly improved the fracture toughness of CFRP composites. Kinloch et al. [15] reported introducing rubbery micrometer-sized particles and nano-SiO₂ particles into the epoxy polymer, to give a multiphase “hybrid-toughened” polymeric material. The “hybrid-toughened” polymeric material can increase toughness without significant loss of other important properties such as modulus and thermal resistance. Groleau et al. [16] investigated the influence of the interlayered nylon particles to the mode II fracture toughness of CFRP composites. They found the mode II fracture toughness increased linearly with interply thickness in the ductile epoxy system. Furthermore, the plastic deformation ahead of

* Corresponding author.

** Corresponding author.

E-mail addresses: yliu@mail.ipc.ac.cn (Y. Liu), hmxiao@mail.ipc.ac.cn (H.-M. Xiao).

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the crack tip was limited by the particles in the brittle systems. Hence, blending flexible polymer such as polyurethane (PU) or hydroxyl-terminated polyurethane (HTPU) is a relatively convenient and cost-effective approach without compromising much processing ease and meanwhile modifying EP mechanical properties [17,18] and even improving fiber-epoxy interfacial adhesion [19,20]. There are many reports about blending PU or HTPU into EP for improving the toughness of EP [17,21–25], the mechanical properties of epoxy-based composites also could be enhanced by PU toughened EP [17,19,21,26]. Chern et al. [21] reported the preparation of interpenetrating polymer networks (IPNs) from polyurethane (PU) cross-linked epoxy, the mechanical strength of the polymer was enhanced by the IPN structure. Reghunadhan et al. [25] blended the recycled PU into epoxy matrix to modify diglycidyl ether of bisphenol-A, the result showed the strength and modulus of epoxy resin could be improved simultaneously with an increase of fracture toughness.

Li et al. [19] used polyurethane/epoxy (PU/EP) membranes as interleaf to synthesis PU/EP membranes-toughened CFRP composites. The result indicated that membranes-toughened composites exhibited higher interlaminar toughness (G_{Ic}) than pristine composites. Behnisch et al. [26] employed epoxy and polyurethane matrix systems respectively to fabricate CFRP composites, illustrating that the interlaminar shear strength of carbon fibers reinforced PU composites was higher than carbon fibers reinforced EP composites. As mentioned above, many studies have been conducted on toughening EP or CFRP composites by PU or HTPU at RT. It can thus be expected that PU or HTPU may be a good reinforcements for EP or CFRP composites at cryogenic temperature.

In our previous work [17], the mechanical properties at RT and 77 K of EP modified with two different molecular weights' HTPU (namely EP/HTPU1 and EP/HTPU2) have been studied. The results demonstrated that the cryogenic mechanical performance of EP has been highly influenced by homogeneous phase and rubber-like particles structure formed by EP/HTPU1 and EP/HTPU2 with the optimal amount 5 phr and 10 phr (weight ratios to diglycidyl ether of bisphenol-A), respectively. However, whether the knowledge about the RT and cryogenic mechanical behaviors of matrix can be transferred to the case for CFRP toughened by HTPU is not clear. There is a lack of studies to point out the effects of the HTPU especially HTPU with different phase structures after curing to the cryogenic mechanical properties of CFRP composites. Therefore, it is of great fundamental and practical importance to study the cryogenic mechanical behaviors of CFRP composites toughened by HTPU that are aimed to be employed in cryogenic engineering.

In the present work, two HTPU with different molecular weights (namely HTPU1 and HTPU2 respectively) were selected to toughen CFRP composites with two contents of 5 phr (weight ratios to diglycidyl ether of bisphenol-A) HTPU1 and 10 phr HTPU2, respectively. The composites of pristine CFRP, CFRP toughened by HTPU1 (namely CF/EP/HTPU1) and CFRP toughened by HTPU2 (namely CF/EP/HTPU2) composites were prepared via hot press molding process. Aiming to explore the potential applications of CF/EP/HTPU1 and CF/EP/HTPU2 composites in cryogenic engineering field, the tensile properties and flexural properties at RT and 77 K were systematically investigated and compared with those of pristine CFRP in detail, respectively. Moreover, the influence of thermal cycles at cryogenic condition on the micro-crack morphology and crack density of composites were investigated. 77 K was selected for cryogenic mechanical testing since liquid nitrogen (77 K) is easier to obtain.

2. Materials and experimental details

2.1. Materials

The epoxy resin (DGEBA) and the curing agent (DETDA) were respectively obtained from BLUESTAR Nantong Star Synthetic Materials

Co. Ltd. (Nantong, China) and Albemarle Corporation Charlotte (USA). The HTPU1 and HTPU2 were supplied by Institute of Polymer Science & Engineering, Tsinghua University (Beijing, China). Fig. S1 shows the characteristic spectra of the HTPU1 and HTPU2 analyzed by Fourier Transform ion cyclotron resonance mass spectrometry with an electro-spray ionization operating in the positive ion modes (FTMS-pESI), which indicates that HTPU1 and HTPU2 are different in molecular weight [17]. Unidirectional carbon fiber fabric (T800S, 12 K, diameter about 7 μm) was purchased from Toray Industries, Japan. The physical properties of T800S were shown in Table S1 (see the Supporting Information). The viscosity at 25 °C of HTPU1, HTPU2 and DGEBA provided by the manufacturer is 50 mPa s, 500 mPa s and 980 mPa s, respectively. All components were commercial products, and were used as received.

2.2. Preparation of the HTPU-toughened epoxy matrix and CFRP composites

Initially, 5 phr of HTPU1 or 10 phr of HTPU2 (the weight ratios to DGEBA) was dispersed into DGEBA under magnetic stirring for 30 min to form a mixture namely EP/HTPU1 and EP/HTPU2, respectively. After that, the curing agent DETDA in the ratio of 1:4 to DGEBA by weight was added to the mixture under stirring for another 30 min to obtain a homogenous HTPU-modified epoxy mixture. Finally, the HTPU-modified epoxy mixture was degassed by a vacuum rotary pump at 50 °C for 30 min to remove the air bubbles which dissolved in mixture. Meanwhile, the pure epoxy matrix (EP) was also prepared under the same condition.

The pristine CFRP, CFRP toughened by HTPU1 (namely CF/EP/HTPU1) and CFRP toughened by HTPU2 (namely CF/EP/HTPU2) composites were fabricated by hot-press process. A brief description was presented in Fig. 1 for the fabrication of CFRP composites. Firstly, the HTPU-modified epoxy matrix or pristine EP was coated to the CFs by hand paste process. The CFRP composites then were fabricated in unidirectional [0°] and [90°₂/0°₃90°₂] stacking sequences configuration by the hot-press process, respectively. The detailed curing process of the CFRP composites was shown in Fig. 2, the composites were first cured at 80 °C for 90 min, afterwards, continually cured at 140 °C for another 90 min. Finally, the CFRP composites were post cured at 140 °C for 90 min under a pressure of 5 MPa.

2.3. Characterization

The average contact angle of pristine EP, EP/HTPU1 and EP/HTPU2 on a single CF was measured by a droplet profiling method, respectively. The two ends of one single CF were suspended and fixed to two pieces of slide glass by glue to ensure straightening of CF. Subsequently, one drop of EP or EP modified by two kinds HTPU was carefully squeezed out from a syringe, the drop was spread out slowly on the surface of CF until it became round under its own surface tension and finally shaped into one partial spherical droplet. In the end the contact angle was measured and calculated. Five droplet tests were severally performed for each epoxy matrix and an average of five readings was taken.

The density of CFRP composites was measured using solid-liquid densimeter ET - 320D (Etnal, China) and calculated according to ASTM D 792. The volume fraction of CF was calculated as given equation (1):

$$V_f = \frac{D_c - D_m}{D_f - D_m} \quad (1)$$

where V_f is the volume fraction of CF in CFRP composites, D_c , D_m and D_f represents the density of CFRP composites, epoxy matrix and CF, respectively. In this work, the volume fractions of CF in pristine CFRP composite, CF/EP/HTPU1 composite and CF/EP/HTPU2 composite are $56.5 \pm 1.8\%$, $56.2 \pm 1.7\%$ and $56.7 \pm 1.7\%$, respectively.

The tensile and flexural tests of CFRP composites were performed at

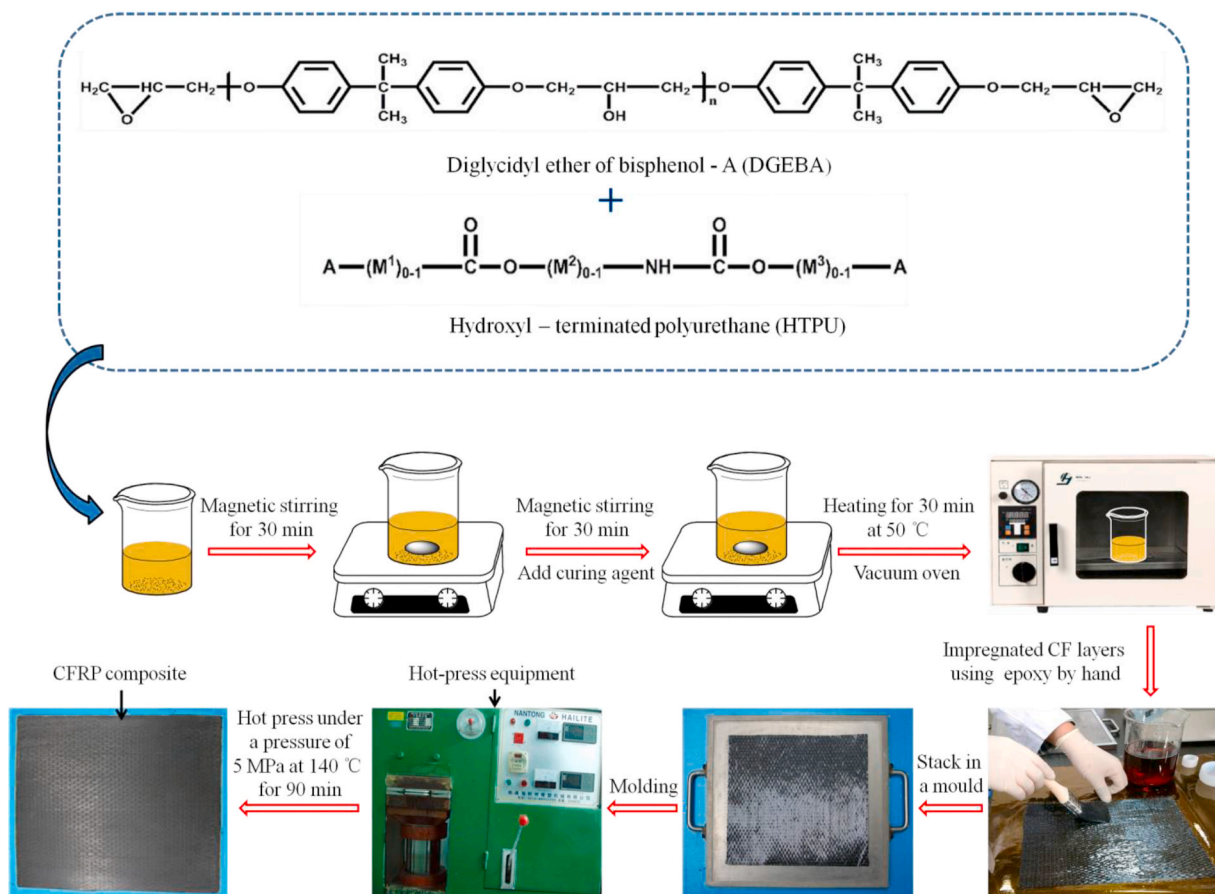


Fig. 1. The schematic diagram of the fabrication process of CFRP composites.

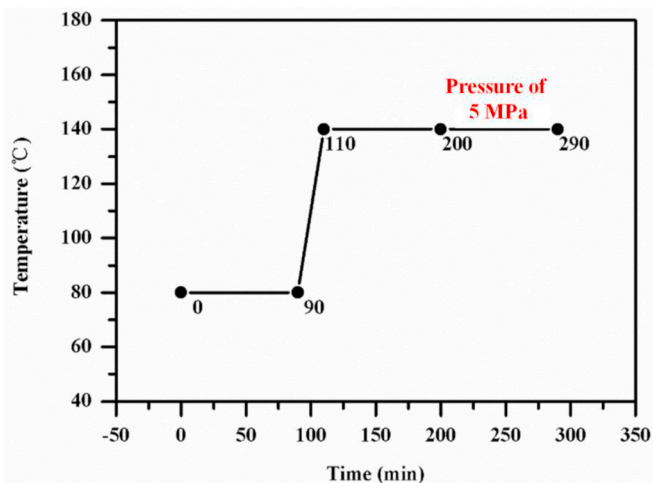


Fig. 2. Curing process of composite laminate molding process.

RT and 77 K according to ASTM D 3039 and ASTM D 7264, on an INSTRON 5882 machine. The crosshead speed was 2 mm/min for all tests. Five specimens were severally tested both at RT and 77 K for each CFRP composite. And all the reported values for the mechanical tests were the average values of five specimens. The 77 K temperature condition was achieved by dipping the samples fixed on the clamps in a liquid nitrogen filled cryostat designed in our laboratory [17].

In order to investigate the effect of thermal cycling on the density of micro-cracks in the composite laminates, different thermal cycles (1, 25, 50, 75, 100, 125, 150, 175 and 200) were performed for the pristine

CFRP and CF/EP/HTPU composites, respectively. As shown in Fig. 3, one thermal cycle consisted of firstly immersing samples in liquid nitrogen (77 K) for 10 min and then exposing to 300 K for 37 min. Before thermal cycling, the samples (100 mm × 25 mm × 2 mm) from each composites were prepared for optical microscopy through grinding, polishing and cleaning of the sample edges. The sides were polished using successively finer grit paper ranging from P220 to P1500, and then polished on cloth via polishing paste. The micro-cracks were examined using an optical microscope (OLYMPUS STM6, Japan) after conducting relevant thermal cycles of each composite.

Scanning electron microscope (SEM) images for the tensile testing failure surfaces of pristine CFRP composites, CF/EP/HTPU1 composite and CF/EP/HTPU2 composites at RT and 77 K, as well as EP, EP/HTPU1 and EP/HTPU2 at RT, were obtained with a Hitachi S-4800 Microscope (Japan). The samples for the SEM observation were prepared by directly spraying a thin gold layer on the samples surfaces.

3. Results and discussion

3.1. Morphological analysis of epoxy matrix

In order to better understand the effect of HTPU1 and HTPU2 on the EP due to their different molecular weights, SEM analysis was conducted to examine the morphology of the epoxy matrix after curing. Fig. 4 displayed the SEM images of the fracture surfaces of pristine EP, EP/HTPU1 and EP/HTPU2 after tensile test at RT. As shown in Fig. 4a and b, the fracture surface morphology of EP/HTPU1 was similar to that of pristine EP, which showed a homogeneous phase structure. By contrast, EP/HTPU2 (Fig. 4c) exhibited phase separation morphology features and the elastomeric rubber-like particles of HTPU2 were precipitated from matrix during the curing process of EP, which uniformly dispersed

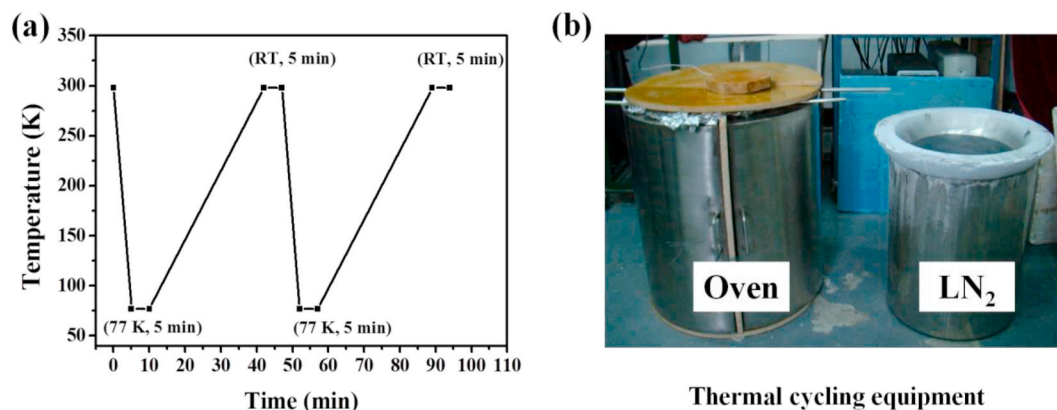


Fig. 3. Thermal cycling program (a) and thermal cycling equipment (b).

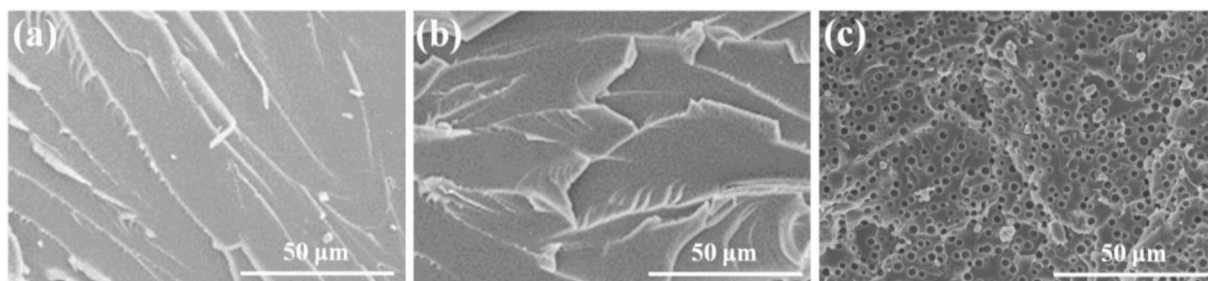


Fig. 4. SEM images of the tensile fracture morphologies under RT tests with the addition of the HTPU: (a) pristine EP, (b) EP/HTPU1 and (c) EP/HTPU2.

in the epoxy matrix. The phenomenon that EP/HTPU2 displayed obvious phase separation morphology features which was distinguished from EP/HTPU1 has been proved by Flory-Huggins solution theory in our previous work [17]. The different molecular weight of HTPU1 and HTPU2 is the main cause.

As shown in Fig. 4c, it is worth noted that the rubber-like particles and cavities where particles fell off appeared simultaneously on the fracture surface of EP/HTPU2. De-bonding of rubber-like particles of HTPU2 and matrix plastic deformation was visible in the tensile fracture surface, which was an obvious evidence for toughness improvement. Similar structures of EP/HTPU1 and EP/HTPU2 have been also demonstrated in the previous work [17,27]. It was believed that the energy dissipation involved in these deformation mechanisms has provided the toughness increase observed [27]. The observation was consistent with the increase of elongation at break of EP/HTPU2 at RT in Table S2.

3.2. Contact angle between CFs and the modified epoxy

It is generally accepted that a strong bonding between reinforcing CFs and matrix is beneficial to stress transfer from matrix to CFs. Better

stress transfer is expected to improve the mechanical properties of the CFRP composites. And wetting of the surface of CFs with EP is one of the important aspects for obtaining good interfacial bonding between CFs and EP [28,29].

The contact angle between CFs and the modified epoxy can be employed to characterize the wettability of matrix on the surface of CFs. Typical micrographs of pristine EP, EP/HTPU1 and EP/HTPU2 droplets formed on the surface of single CF were shown in Fig. 5. The average contact angles of CF-EP, CF-EP/HTPU1 and CF-EP/HTPU2 was measured to be $34.3 \pm 2.1^\circ$, $31.6 \pm 1.8^\circ$ and $33.9 \pm 1.9^\circ$ by the micro-Wilhelmy method, respectively. The results showed that the average contact angle was slightly decreased with the additional of HTPU. The contact angles of CF-EP/HTPU1 and CF-EP/HTPU2 were 7.9% and 1.2% lower than those of CF-EP, respectively. The viscosity of HTPU1, HTPU2 and pristine EP was 50 mPa s, 500 mPa s and 980 mPa s, respectively. So the reason for the change of contact angle may be attributed to two aspects: one was that the viscosity of EP decreased and the fluidity of matrix increased after adding low viscosity HTPU; the other reason may be that some chemical structure of EP/HTPU was similar to the sizing agent on CFs' surfaces, which exerting a positive effect on improvement of wettability based on the principle of "like dissolves like" [28,30,31].

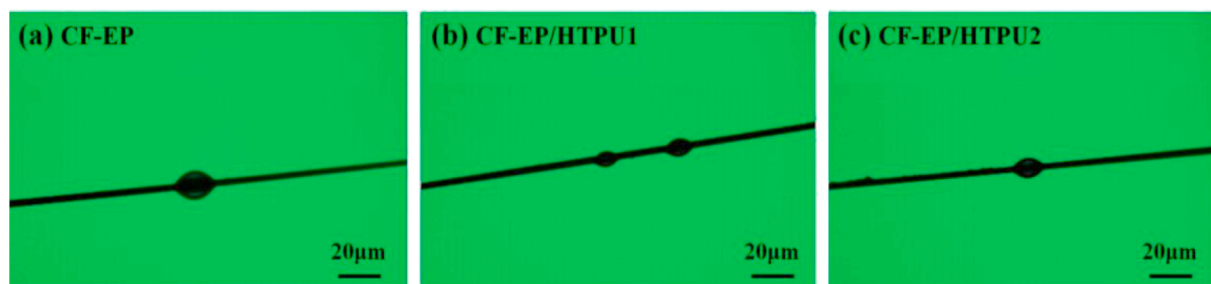


Fig. 5. Optical images of contact angles with micro-droplets on CF for (a) pristine EP, (b) EP/HTPU1 and (c) EP/HTPU2.

Although the above result indicated that the introduction of HTPU with lower viscosity can slightly improve the wettability of the epoxy matrix on the surfaces of CFs. However, the contribution of smaller contact angle in this case to the improvement of the interface between the fibers and matrix was limited. In other words, the change of contact angle between CFs and epoxy was only one index in the CF/epoxy interface improvement.

3.3. Tensile properties of the CFRP composites

3.3.1. Transverse tensile properties

The typical transverse (90°) tensile stress-strain curves of CFRP and CF/EP/HTPU composites at RT and 77 K were shown in Fig. 6a and c, respectively. The linear type of stress strain curve in Fig. 6a and c exhibited linear elastic behavior of composites until the failure of the interfacial de-bonding between CFs and matrix, which was confirmed by the linear fracture surface of the specimen in the digital photos in Fig. 6e and f. The transverse tensile strength and fracture strain at RT and 77 K of pristine CFRP, CF/EP/HTPU1 and CF/EP/HTPU2 composites were given in Fig. 6b and d, respectively. Compared to the pristine CFRP at RT

and 77 K, improvement rates in the transverse tensile strengths were respectively measured as 35.1% and 37.7% for CF/EP/HTPU1, and 13.8% and 28.3% for CF/EP/HTPU2. The results showed either HTPU1 or HTPU2 modified EP can enhance the transverse tensile strength of CFRP composites effectively. The phenomenon could be attributed to the better interfacial adhesion between CFs and EP, owing to the dissolution between sizing agent and EP/HTPU which improved the wettability of EP and prompts CFs well-combined with it [28,30,31].

Meanwhile, as shown in Fig. 6a and c, the slopes of stress-strain curves of CF/EP/HTPU which implied modulus of the composite were slightly higher than that of the pristine composites at RT and were equivalent to the pristine composites at 77 K. The slight improvement in modulus at RT of CF/EP/HTPU was considered to be the result of HTPU in its resin composition leading to the improvement modulus of matrix [17,32]. At 77 K, the reason about the same modulus of various composite could be mainly attributed to the almost equivalent enhanced modulus of matrix due to thermal shrinkage of EP at cryogenic temperature and the influence of HTPU maybe was insignificant [17].

In our previous work [17], as shown in Table S2 (see the Supporting Information), it was found that the addition of HTPU can slightly

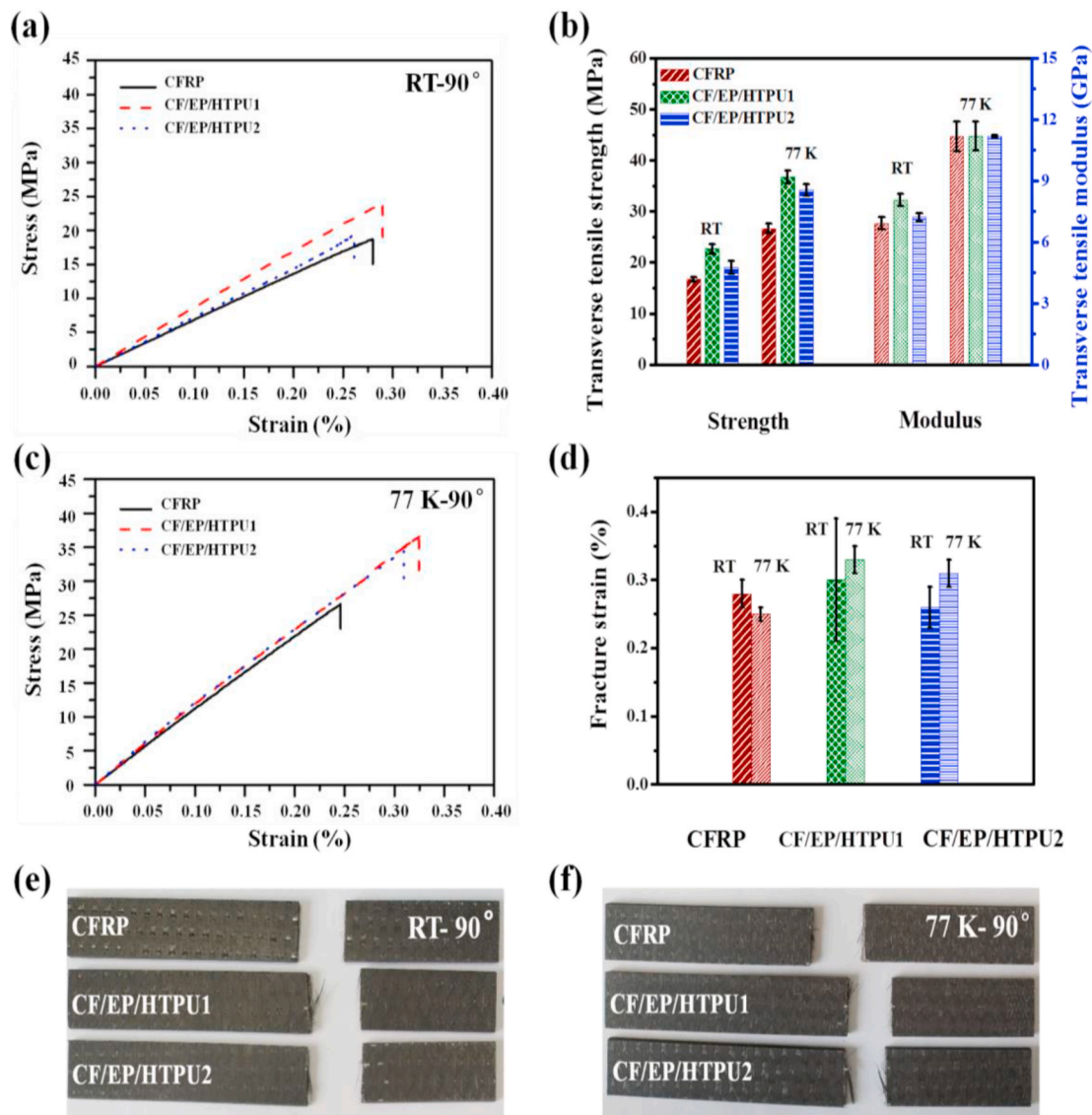


Fig. 6. Typical stress-strain curves and tensile properties: transverse tensile stress-strain curves of various CFRP composites at (a) RT and (c) 77 K, (b) corresponding comparison of tensile strength and modulus, (d) comparison of fracture strain, digital photos of the transverse tensile test specimens of CFRP and CF/EP/HTPU composites after tensile failure: (e) RT and (f) 77 K.

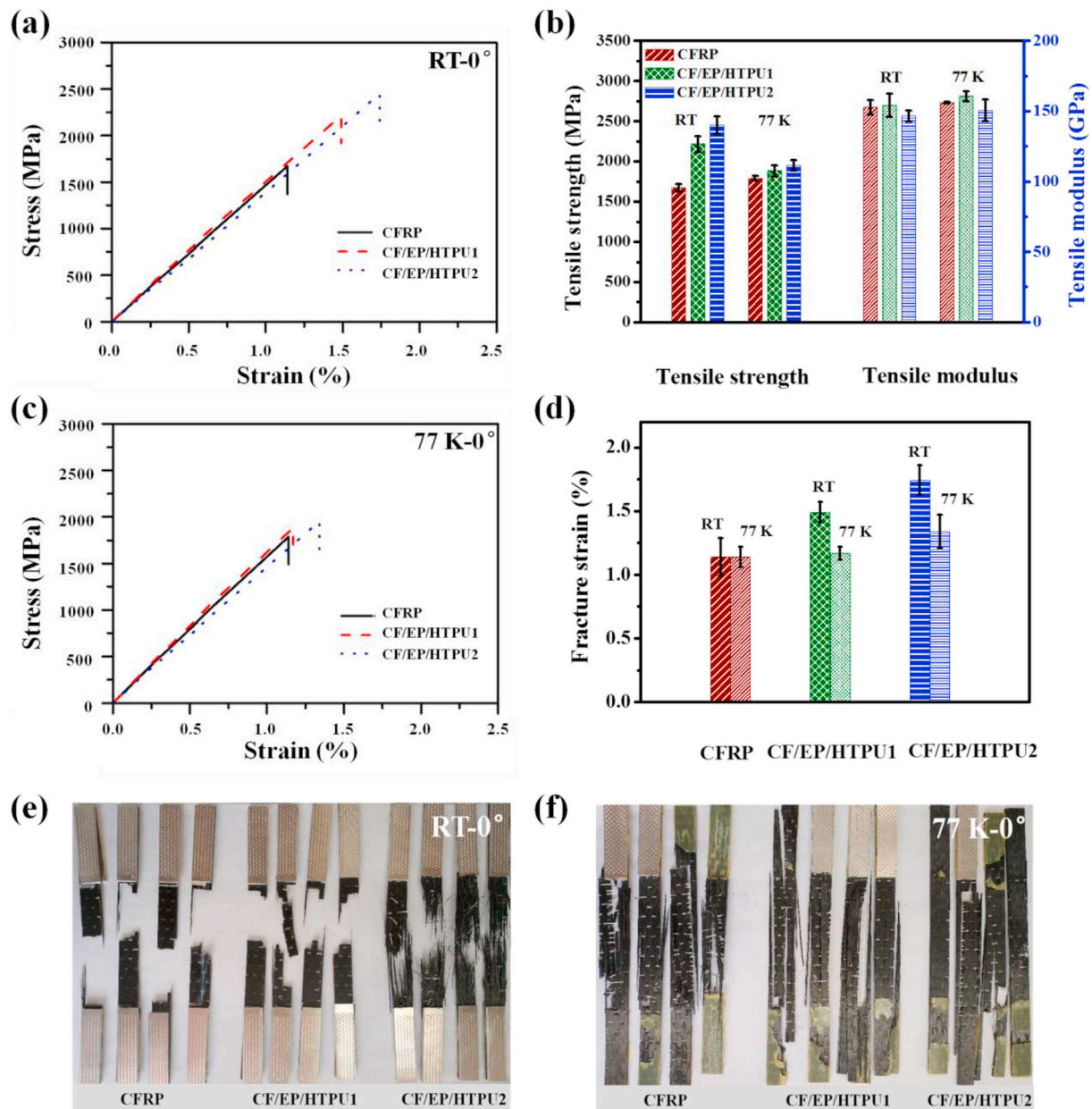


Fig. 7. Typical stress-strain curves and tensile properties: longitudinal tensile stress-strain curves of various CFRP composites at (a) RT and (c) 77 K, (b) corresponding comparison of tensile strength and modulus, (d) comparison of fracture strain, digital photos of the longitudinal tensile test specimens of CFRP and CF/EP/HTPU composites after tensile failure: (e) RT and (f) 77 K.

increase the EP/HTPU1 modulus while the EP/HTPU2 modulus slightly decrease at RT, but the change of the modulus at 77 K can be ignored. It is well known that the transverse tensile modulus of a composite generally follows established rule-of-mixture [32], which could be estimated by equation (2):

$$\frac{1}{E_2} = \frac{v_f}{E_{f2}} + \frac{(1-v_f)}{E_m} \quad (2)$$

where E_2 is transverse modulus of CFRP composites, V_f is the volume fraction of CFs in CFRP composites, E_{f2} and E_m represents the tensile modulus of the fiber toward the transverse direction and epoxy matrix, respectively. According to the manufacturer's data sheet [32], the relation between the modulus of along the fiber direction (E_{f1}) and E_{f2} can be estimated by $E_{f1} \approx 15 E_{f2}$. The transverse tensile moduli calculated by equation (2) and obtained from practical experiment were tabulated in Table S3, respectively (see the Supporting Information). For

the transverse tensile modulus, the calculation results showed great consistency with the experimental results at 77 K with maximum error of 5.15%. However, there was a big different between the calculation results and the experimental results at RT, the reason can be attributed to two aspects. On one hand, because E_2 was treated as a constant in theoretical calculation, the E_2 valuation of CF maybe was inaccurate at RT. However, it might be closer to the actual value at 77 K under the influence of cryogenic environment. On the other hand, the fibers were not strictly arranged at 90° due to sample preparation. Therefore, the influence of E_2 and imperfect fiber alignment on the experimental results at RT was more obvious than that of 77 K.

In addition, Fig. 6b revealed that the transverse strengths and moduli of all composites at 77 K were much higher than RT. It is well known that interfacial bonding properties can be represented by the transverse strength of unidirectional laminate, as the ambient temperature decreased from RT to 77 K, the thermal shrinkage of epoxy resin will

increase the clamping force to the CFs and grip the CFs tightly, leading to a relatively strong CF/EP interfacial bonding [28,32–34]. Obviously, this caused the transverse tensile strength of CFRP composites at 77 K to be higher than that at RT. Meanwhile, at 77 K, the arrangement of the polymer molecules became much denser and the chain of the molecules became much harder, leading to a higher transverse modulus compared to RT [13,17,35]. It is worth noting that, as shown in Fig. 6d, the fracture strain of CF/EP/HTPU at 77 K was slightly enhanced by the additional of HTPU1 and HTPU2, which implied that the epoxy resin has been toughened by HTPU at cryogenic temperature. The abovementioned results were agreeable to the previous studies [28,32,35], showing the transverse tensile properties of CFRP composites were enhanced at both RT and 77 K.

3.3.2. Longitudinal tensile properties

In order to further inspect the enhancing effects of HTPU1 and HTPU2 modified EP on the CFRP composites, the longitudinal (0°) tensile properties of CF/EP/HTPU1, CF/EP/HTPU2 and the pristine composites were investigated at RT and 77 K, respectively. The tensile strength, modulus, fracture strain and failure modes were all depicted in Fig. 7a–f. As shown in Fig. 7a and c, the longitudinal tensile stress-strain curves of various CFRP composites at both RT and 77 K exhibited linear elastic behavior until breakage.

The results of tensile tests can be seen in Fig. 7b and d, the CF/EP/HTPU composites experienced increases in both the tensile strength and fracture strain at both RT and 77 K in comparison with that of the pristine CFRP composites. For the CF/EP/HTPU1 composite, the tensile strength increased by 32.5% and 5.2% respectively at RT and 77 K compared to those of the pristine composites, the fracture strain increased by 30.7% and 2.63%. Similarly, the tensile strength and fracture strain of CF/EP/HTPU2 composite with the significant increase occurred respectively at RT and 77 K relative to pristine CFRP composites, where tensile strength increased by 46.5% and 9.1%, fracture strain increased by 52.6% and 17.5%.

The above results showed, at both RT and 77 K, modified the EP by HTPU can improve the tensile strength and fracture strain of composites effectively. The improvement was attributed to the toughened epoxy matrices, which can form a stronger interfacial bonding with CF due to the emergence of HTPU. The enhanced interfacial adhesion allowed a better shear load transfer from the EP/HTPU to the CFs, which thereby increased the composite tensile properties [32,36,37]. Similar results have been reported for unidirectional CF reinforced epoxy matrix composites [32,37,38].

As shown in Table S3 (see the Supporting Information), the tensile modulus of CF/EP/HTPU1 has a slight increase compared to pristine CFRP composites at both temperature conditions, while that of CF/EP/HTPU2 has a tiny decrease compared to pristine CFRP composites. As reported in our previous work [17], the modulus of EP/HTPU1 was a little higher than the pristine epoxy, while that of EP/HTPU2 was lower than it. According to the rule-of-matrix, the tensile modulus could be estimated by equation (3):

$$E_1 = E_f v_f + E_m (1 - v_f) \quad (3)$$

where E_1 is tensile modulus of CFRP composites, V_f is the volume fraction of CF in CFRP composites, E_f and E_m represents the tensile modulus of the fiber and epoxy matrix, respectively. The tensile moduli calculated by equation (3) and obtained from practical experiment were presented in Table S3 respectively (see the Supporting Information). As shown in Table S3, the experimental tensile modulus was clearly lower than the calculated value due to imperfect fiber alignment, non-uniform fiber distribution, local non-homogeneities and void content, etc [37].

In addition, as shown in Fig. 7b and d, the cryogenic tensile strength and fracture strain of CF/EP/HTPU1 and CF/EP/HTPU2 composites showed obvious decrease compared to that at RT respectively, while that of the pristine composite exhibited an increase in comparison with that

at RT. This is due to the mismatch of coefficient of thermal expansion (CTE) between CFs and EP/HTPU when the environment temperature dropped from RT to 77 K, which led to the sharp increase of thermal stress at CF/epoxy resin interface. The increased thermal stress may weaken the load transfer effect of CF/epoxy interface, resulting in the decreased tensile strength of CF/EP/HTPU at 77 K [36]. Furthermore, the tensile moduli of all composites at 77 K were slightly higher than those at RT due to the increase of matrix modulus at 77 K. The difference of tensile strength and fracture strain at RT and 77 K indicated that the toughening effect of HTPU on the CF/EP/HTPU composite was reduced in cryogenic temperature relative to ambient. Similar results have been.

Reported for unidirectional CF or plain woven CF reinforced epoxy matrix composites [1,32,35,37,39–41]. Actually, as shown in Fig. 7e and f, the changes in the tensile strength and fracture strain at 77 K were mainly attributed to the different failure modes [35,37]. As mentioned above, the different thermal shrinkage deformation of CFs and matrix could change the efficiency of stress transfer between fibers and matrix at cryogenic temperature, which would affect the failure modes of samples [32,36,39].

In this paper, the cryogenic fracture modes of CFRP composites (Fig. 7f) included splitting, partial fracture of CFs and edge delaminating compared to the explosive fracture mode at RT (Fig. 7e). As a result, the tensile strength of CFs could not be well exploited at cryogenic temperature. Hence, the tensile strength and fracture strain of CF/EP/HTPU composites will decrease significantly at 77 K [35]. Besides, an interesting phenomenon needed to be noted that the longitudinal tensile strength of CF/EP/HTPU2 was higher than that of CF/EP/HTPU1 at both RT and 77 K, which will be explained afterwards.

In summary, the transverse and longitudinal test results indicated that the epoxy resin toughened by HTPU with different molecular weights, affected the tensile strength of each composite more than the modulus at both RT and 77 K. In other words, it has little effect on the strength modulus of CF/EP/HTPU composites, and significant enhancement to the tensile strengths.

3.4. Flexural properties of the composites

The representative load-displacement curves obtained by the three-point flexural test and the flexural properties of the pristine CFRP and CF/EP/HTPU composites at RT and 77 K were exhibited in Fig. 8. As shown in Fig. 8a, the load-displacement of composites at RT displayed significant non-linear relationship after the loads approached their maximum values until destroyed completely, which implied ductile fracture behaviors. However, at 77 K, all the composites showed typical linear behaviors during the whole loading process until broken suddenly as shown in Fig. 8c.

The flexural strengths and modulus at RT and 77 K of all the composites were given in Fig. 8b and d and Table S4 (see the Supporting Information). The flexural strength of CF/EP/HTPU1 composite showed an increase by about 15% at RT in comparison with the pristine composite, while that of CF/EP/HTPU2 composite dropped by approximately 6%. The decrease phenomenon in flexural strength of CF/EP/HTPU2 can be explained by the existence of many small micropores identifying by SEM which will be explained afterwards in detail. However, as shown in Fig. 8d, the cryogenic flexural strengths of CF/EP/HTPU1 and CF/EP/HTPU2 composites were slightly higher than that of the pristine CFRP composites due to good interfacial adhesion between EP/HTPU and CFs.

Compared respectively to the pristine CFRP composite at RT and 77 K, the flexural moduli of CF/EP/HTPU1 and CF/EP/HTPU2 composites both have been slightly increase. But considering the standard deviation in the modulus of all composites, it could be concluded that there was little or no improvement in the flexural modulus of composites when toughened by HTPU. The reason was the shear stress had been transferred between matrix and CFs of all composites, but the deformation mainly dominated by CFs tension/compression, inducing the

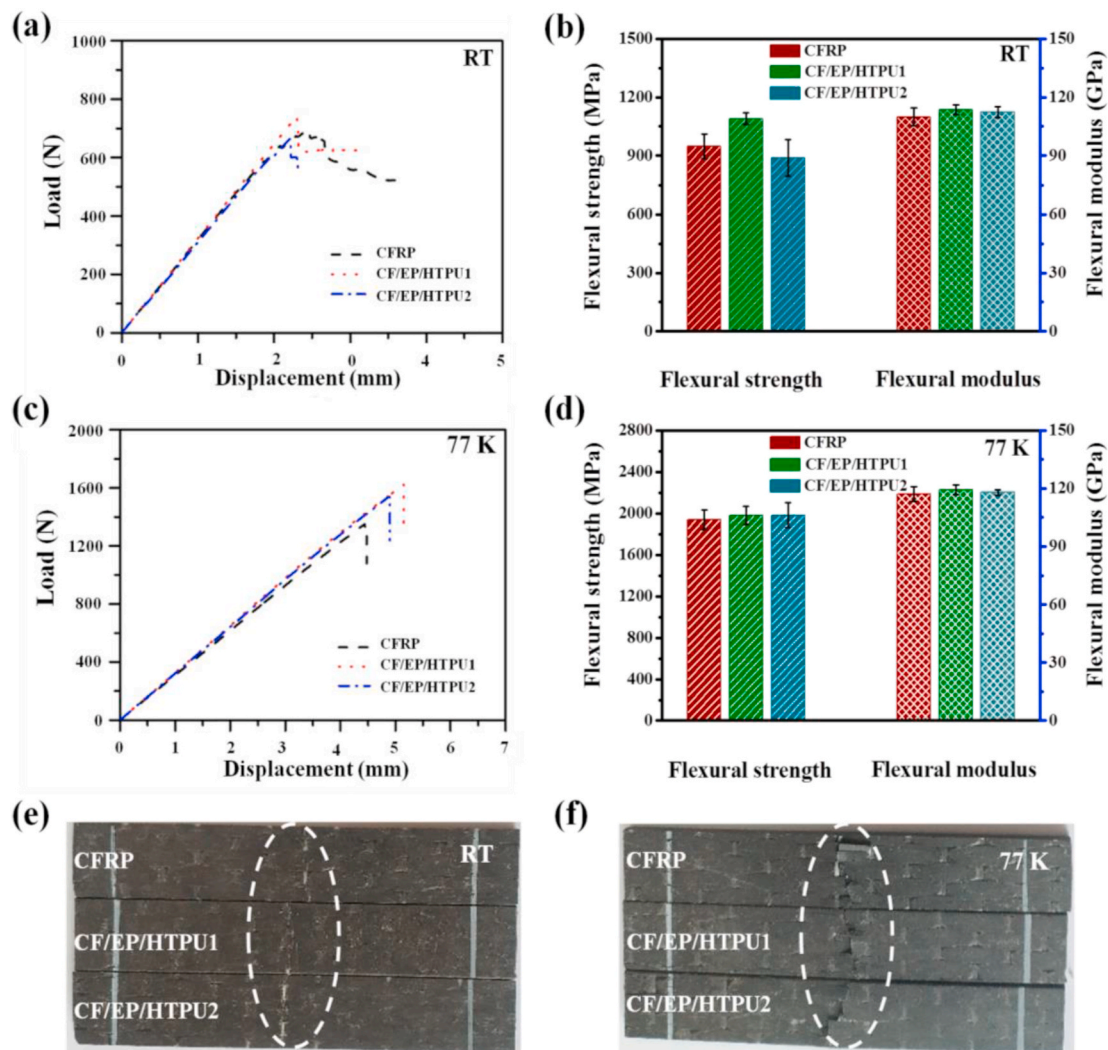


Fig. 8. Typical three-point bending load-displacement curves and flexural properties: load-displacement curves of various CFRP composites at (a) RT and (c) 77 K; corresponding comparison of flexural strength and modulus at (b) RT and (d) 77 K; digital photos of the bending test specimens of CFRP and CF/EP/HTPU composites after failure: (e) RT and (f) 77 K.

flexural modulus approached a constant [37,42].

In addition, the cryogenic flexural strength of all composites greatly enhanced by more than 50% compared to those at RT due to the enhancement in the matrix and the changes in failure modes [35,42,43]. This result was consistent with the experimental results reported in the previous works [35,42,43]. At RT, for the pristine CFRP and CF/EP/HTPU composites, as shown in Fig. 8e, compressive fracture within the upper half-region was observed as the main dominated failure modes. By contrast, at 77 K, as shown in Fig. 8f, both tensile and compressive fractures simultaneously happened within the upper and bottom half-regions due to the tighter interface of CF/epoxy, which caused by the thermal contraction of epoxy matrix. Delamination and fibers fracture were found as the main failure modes which implied that more energy was required to delaminate [35,42,43].

3.5. Influence of thermal cycling at cryogenic condition on the micro-cracking of the composites laminate

The morphology and density of micro-cracks in the CFRP composite laminates were studied after thermal cycling. The optical photomicrographs of the micro-crack morphologies of composite laminates developed as a result of cryogenic cycling were shown in Fig. 9a and b. It is obviously observed that the micro-cracks propagate from the outer edge

of the laminates and ended at the interface of 0° plies and 90° plies after thermal cycling. The reason for the micro-cracks occurred only in 90° plies was the interfacial de-bonding of CFs and matrix along the longitudinal direction of CF, generating by the mismatched CTE between CF and matrix as the temperature dropped lower. It has been widely reported that the axial and radial CTE of CFs was negative and positive respectively as the ambient temperature decreased [44]. When the environment temperature decreased from RT to 77 K, the sharply increased interface thermal stress caused by the large difference in the CTE between CFs and matrix, which may lead to the de-bonding at the fiber/matrix interface and then form a micro-crack. As shown in Fig. 9b, it is clearly seen that the micro-cracks propagated normal to the longitudinal direction of CFs. However, the propagation of micro-crack stopped at the interface between 90° plies and 0° plies due to the hinder of the fibers in 0° plies.

Fig. 9c exhibited the change of crack density as the number of thermal cycling. It is obviously found that the micro-cracks in CF/EP/HTPU1, CF/EP/HTPU2 and the pristine CFRP composites appeared after one thermal cycle (from 77 K to RT). The number of micro-cracks rapidly increased in the first 50 thermal cycles, after that the crack density of all composites tended to be stable with the increase of the cycle. After 200 cycles, the micro-crack densities of pristine CFRP, CF/EP/HTPU1 and CF/EP/HTPU2 were 3.39 cm^{-1} , 2.85 cm^{-1} and 3.15 cm^{-1} , respectively.

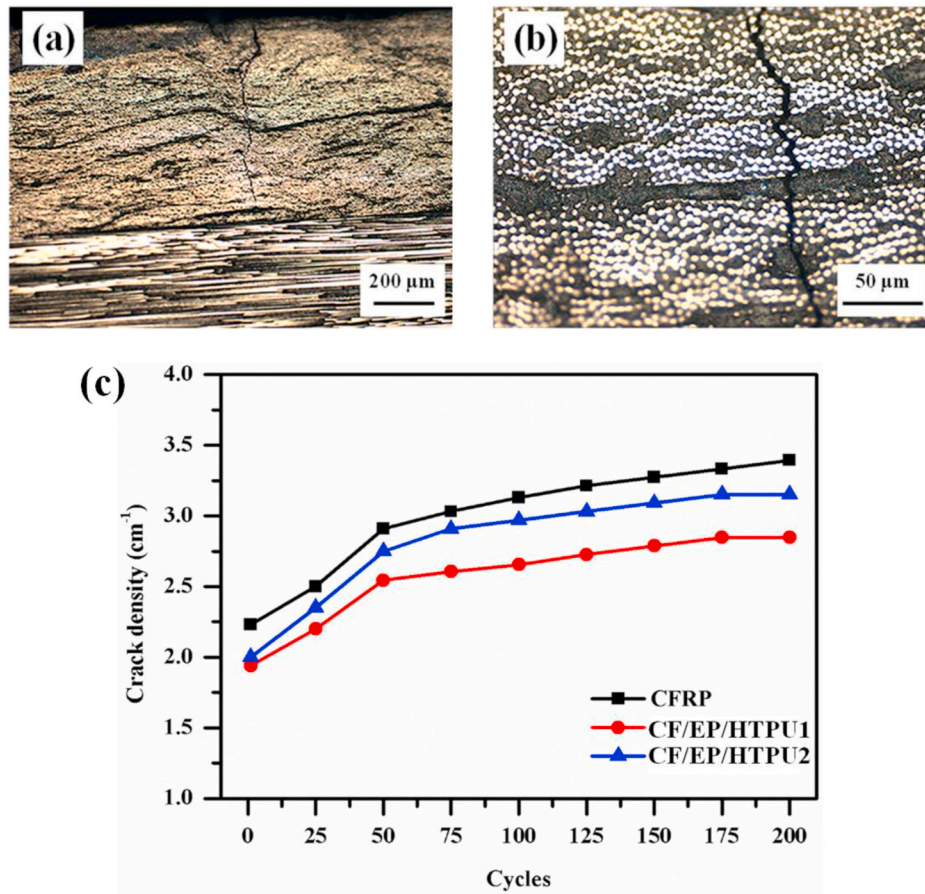


Fig. 9. Optical micrographs of CFRP composites after thermal cycling: (a) 100X and (b) 200X; (c) Micro-crack density in 90° plies of CFRP composite as a function of thermal cycles.

Compared with pristine CFRP, the micro-crack densities of CF/EP/HTPU1 and CF/EP/HTPU2 were reduced by 15.9% and 7.1% respectively. It should be noted that the crack densities of CF/EP/HTPU1 and CF/EP/HTPU2 were all significantly lower than that of the pristine CFRP composite in the whole thermal cycling process. The reduced micro-

crack densities of CF/EP/HTPU after thermal cycling between 77 K and RT proved that the toughening caused by HTPU1 and HTPU2 can effectively improve the micro-crack resistance of composites. It is noteworthy that the crack density of CF/EP/HTPU1 was greatly lower than that of CF/EP/HTPU2. The reason was attributed to the higher

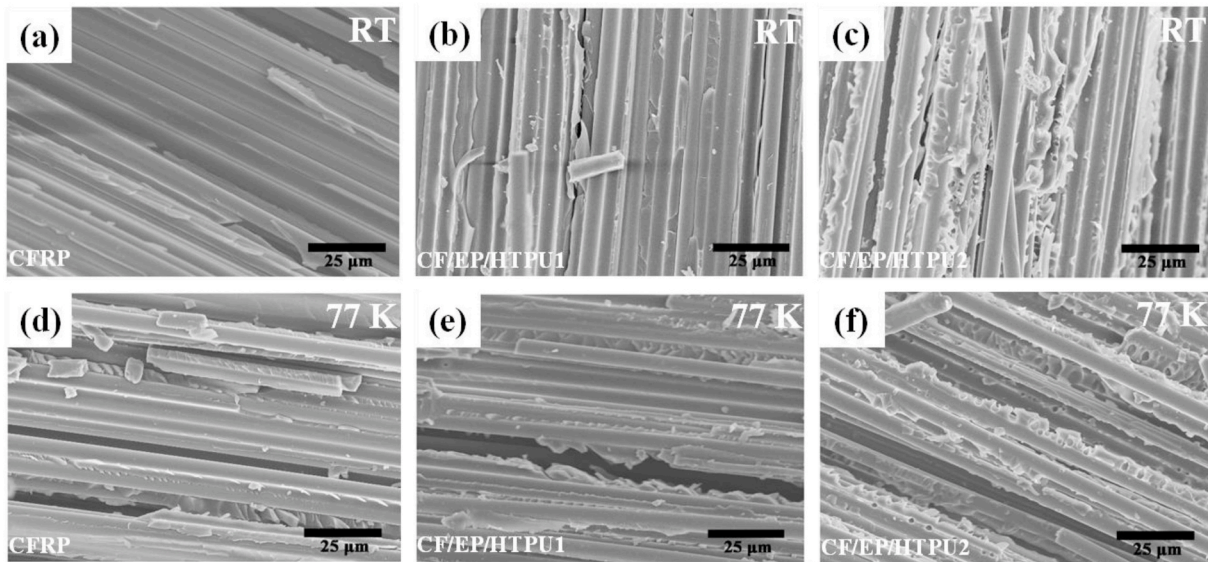


Fig. 10. SEM images of transverse tensile fracture surfaces: (a) pristine CFRP, (b) CF/EP/HTPU1 and (c) CF/EP/HTPU2 at RT; (d) pristine CFRP, (e) CF/EP/HTPU1 and (f) CF/EP/HTPU2 at 77 K.

toughness at 77 K of EP/HTPU1 compared to EP/HTPU2, which was shown in Table S2 (see the Supporting Information).

In fact, the leakage of cryogenic fuel through micro-cracks in the fuel tank will be a disaster for the cryogenic fuel tank made of CF/EP/HTPU material in the future. Therefore, when the temperature dropped from RT to low temperature, it was required to reduce the occurrence of micro-cracks in the composite materials used to manufacture the cryogenic fuel tank. In other words, the smaller the micro-crack density was, the less leakage paths of cryogenic fuel were, and the safer fuel tank was. Therefore, considering the low crack density of CF/EP/HTPU1 in the thermal cycling, HTPU1 was more resistant to low temperature fuel leakage than HTPU2.

3.6. Fracture mechanisms of the composites

To better understand the interface behavior and enhancement mechanical properties of HTPU1 and HTPU2 modified CFRP composites, as shown in Fig. 10, the transverse fracture surfaces of CF/EP/HTPU and the pristine CFRP composites after tensile tests at RT and 77 K were examined by SEM. Fig. 10a–c showed the fracture surfaces of three types of composites at RT, which displayed that the main failure mode was identified as the interfacial de-bonding between CFs and EP. In the pristine CFRP (Fig. 10a), the fracture surface was relatively smooth and less epoxy resin attaches on the CFs, indicating that de-bonding occurred easily at the interface between CF and matrix, which showed poor interfacial adhesion between them. In contrast, as shown in Fig. 10b and c, the fracture surfaces were pretty rough and more matrices attached on the surface of CFs in CF/EP/HTPU1 and CF/EP/HTPU2 due to the improvement wettability of EP which wrapped on the surfaces of CFs [45]. In addition, fibers breakage seemed to occur in the fracture surfaces of CF/EP/HTPU1 and CF/EP/HTPU2, which indicated the fibers were more likely to break than to separate from matrix due to the strong interfacial bond.

At 77 K, interfacial de-bonding, matrix fracture and fibers breakage were clearly found in Fig. 10d–f, which displayed that the cryogenic interfacial bonding strength of all composites was higher than that of RT. Comparing Fig. 10d and e, it can be found that the surface of fibers of CF/EP/HTPU1 was rougher and more matrices attached on it than that of pristine CFRP composites, as well as the CF/EP/HTPU2 in Fig. 10f, illustrating stronger interfacial adhesion between CFs and matrix via HTPU. Obviously, the above phenomenon was well correlated with the

increased transverse tensile strength of the composites in Fig. 6.

Furthermore, compared to the fracture surfaces of all composites at RT (Fig. 10a–c), more matrices obviously attached on the surfaces of CFs in the fracture surfaces (Fig. 10d–f) at 77 K. This change implied that the thermal shrinkage behavior of epoxy resin at cryogenic temperature led to stronger interfacial adhesion between matrix and CFs than RT [28, 32]. This phenomenon can be served as an evidence to certify the higher transverse strength at 77 K.

In order to further explain the effect of HTPU on the longitudinal tensile properties of CF/EP/HTPU, the tensile fracture surfaces morphologies at RT and 77 K obtained by using SEM were given in Fig. 11. As shown in Fig. 11a–c, it is obviously observed that there were clearly differences between the microstructures of the pristine CFRP and CF/EP/HTPU. For the pristine CFRP composite (Fig. 11a), CFs pulled-out, interfacial de-bonding and followed by fibers break-off were mainly observed. The pulled-out CF with a smooth surface implied that the interface de-bonding damage along the interface, which indicated the weak interfacial adhesion between CF and matrix. As a result, the matrix was no longer holding fibers together due to extensive interfacial failure.

In contrast, there was a clearly decrease in the amount of these damages for CF/EP/HTPU as shown in Fig. 11b and c. Furthermore, the surface of pulled-out fibers was tightly coated with EP/HTPU compared to that in pristine CFRP composites, and the interface between fiber and matrix was almost intact even after failure, meaning the failure mode changed from interface de-bonding to matrix failure. This evidenced stronger interfacial adhesion between fibers and matrix in CF/EP/HTPU than that of the pristine CFRP owe to the presence of HTPU1 and HTPU2 respectively in EP, leading to higher tensile properties [38].

The above changes indicated that the strength and toughness of interface regions between the fibers and matrix improved by introducing HTPU due to the “crack healing” effect and the potential chemical reaction between epoxy and CFs [37,38], which has been evidenced in the transverse tensile test at RT.

The cryogenic fracture surface of all composites were shown in Fig. 11d–f, which all exhibited similar terrace fracture surface with the simultaneous breakage of fibers and matrix excepting a small amount of fibers pulled out (see the voids in fracture surface) and interface de-bonding in Fig. 11d. This phenomenon revealed that in spite of the CF/EP interface in all composites enhanced by the thermal shrinkage of epoxy at 77 K, the interfacial adhesion between CFs and matrix in CF/EP/HTPU was still higher than that of pristine CFRP, which has been

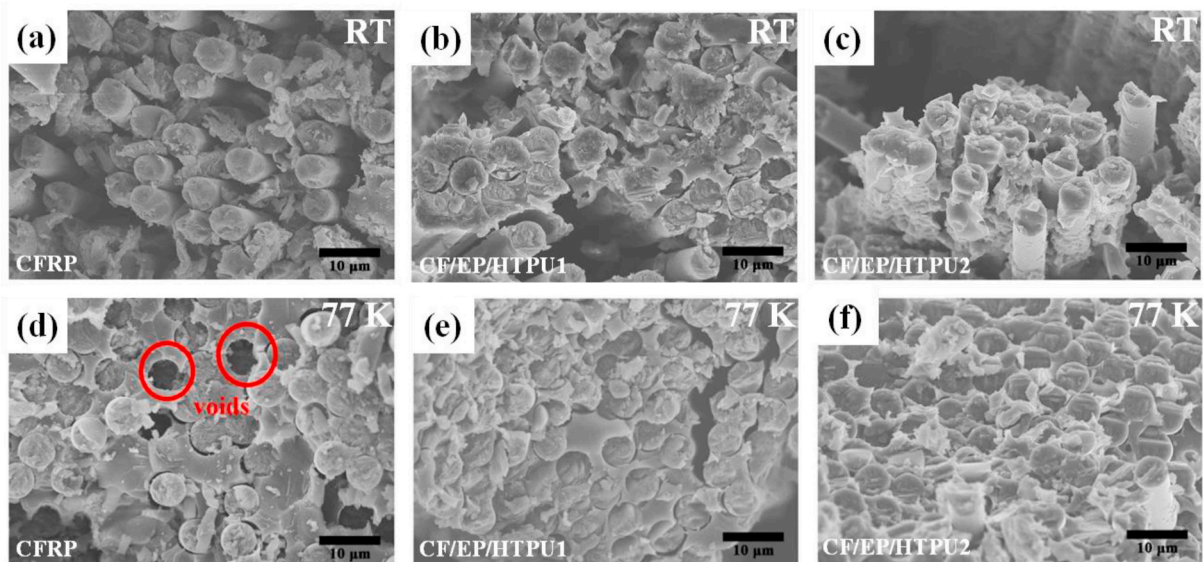


Fig. 11. SEM images of longitudinal tensile fracture surfaces: (a) pristine CFRP, (b) CF/EP/HTPU1 and (c) CF/EP/HTPU2 at RT; (d) pristine CFRP, (e) CF/EP/HTPU1 and (f) CF/EP/HTPU2 at 77 K.

evidenced in the transverse tensile test at 77 K. As a result, the tensile strengths of CF/EP/HTPU1 and CF/EP/HTPU2 were still great higher than that of the pristine composite at 77 K.

Remarkably, as shown in Fig. 11e and f, comparing to the neat fracture surfaces of CF/EP/HTPU at RT (Fig. 11b and c) terrace failure obviously presented in the cryogenic fracture surface. Although breakage of CFs and matrix simultaneously appeared in the fracture surfaces at RT and 77 K, less interface de-bonding occurred in the cryogenic tensile test, which would reduce the tensile strength by the increased “notch-sensitivity” [37]. And then the fracture modes of splitting and partial fibers fracture appeared in the composites at 77 K. Thus, it maybe had an unfavorable effect on the longitudinal tensile strength of the composite owe to the excessive cryogenic interfacial bonding strength between fibers and matrix [37].

In addition, to explain the aforementioned phenomenon that the longitudinal tensile strengths of CF/EP/HTPU2 were higher than those of CF/EP/HTPU1 especially at RT, high magnification SEM micrograph for the longitudinal tensile fracture surface of CF/EP/HTPU2 and the fracture surface of EP/HTPU2 were given in Fig. 12.

As shown in Fig. 12a and b, it can be obviously seen that the elastomeric rubber-like particles of HTPU2 were precipitated from matrix during the curing process of epoxy resin which widely distributed between the CFs bundles (Fig. 12c and d). However, as shown in Fig. 4b, the similar structure was not found in the SEM imagine of EP/HTPU1. In fact, it is difficult to directly verify the obvious ductile deformation of void and matrix in CF/EP/HTPU2 composites without the initial observation of phase separation [27]. As shown in Fig. 12c and d, due to the vibration caused by the huge release of energy and the deformation

of the matrix, only voids were left in the matrix, and the rubber-like particles fell off. The phenomenon of only voids in the matrix after tensile fracture was similar to that reported in the literature [12,46]. However, the cavitation in the matrix can be used as an indirect evidence of matrix deformation of CF/EP/HTPU2 composites during tensile process.

Garg et al. reported the elastomeric rubber-like particles have shown a higher ability in toughening epoxy due to their capability of cavitations leading to large matrix shear yielding [47]. Meanwhile, it is also proved that the rubber-like particles were toughened by plastic deformation and particle bridging caused by stress concentration [16]. Hence, the rubber-like particles in CF/EP/HTPU2 may lead to stress high concentration at its sporadic locations when subjected to external load which will cause the interfacial cracks growing parallel to the fibers [16, 37,47]. Subsequently, the interfacial cracks relieved the stress from the critically stress regions to promote the uniform distribution of stress in composite [37]. Compared with the neat fracture surfaces of CFRP and CF/EP/HTPU1 (Fig. 7e), the failure mode of CF/EP/HTPU2 completely changed to “explosive” failure mode at RT, which was due to the more uniform stress distribution caused by rubber like particles and cavitation in the composite. As a result, the tensile strength of the CF/EP/HTPU2 composite was remarkably improved because of the “explosive” failure mode at RT.

Moreover, as shown in Fig. 12c and d, it is noteworthy that some rubber-like particles located on the surface of CFs in CF/EP/HTPU2, in other words, some parts of CF did not have contact with epoxy resin. This may be the reason that the transverse strengths at both RT and 77 K of CF/EP/HTPU2 were lower than those of CF/EP/HTPU1 due to the decreased interfacial adhesion by partly contact of fibers and matrix. Besides, the above mentioned that the flexural strength of CF/EP/HTPU2 was lower than the pristine composite at RT. The main reason was the rubber-like particles’ capability of cavitations led to large matrix shear yielding between interlaminations in composites, as shown in Fig. 12, which decreased the transfer efficiency of shear stress from matrix to fibers and acted as starting points for sample failure causes [26,42,47].

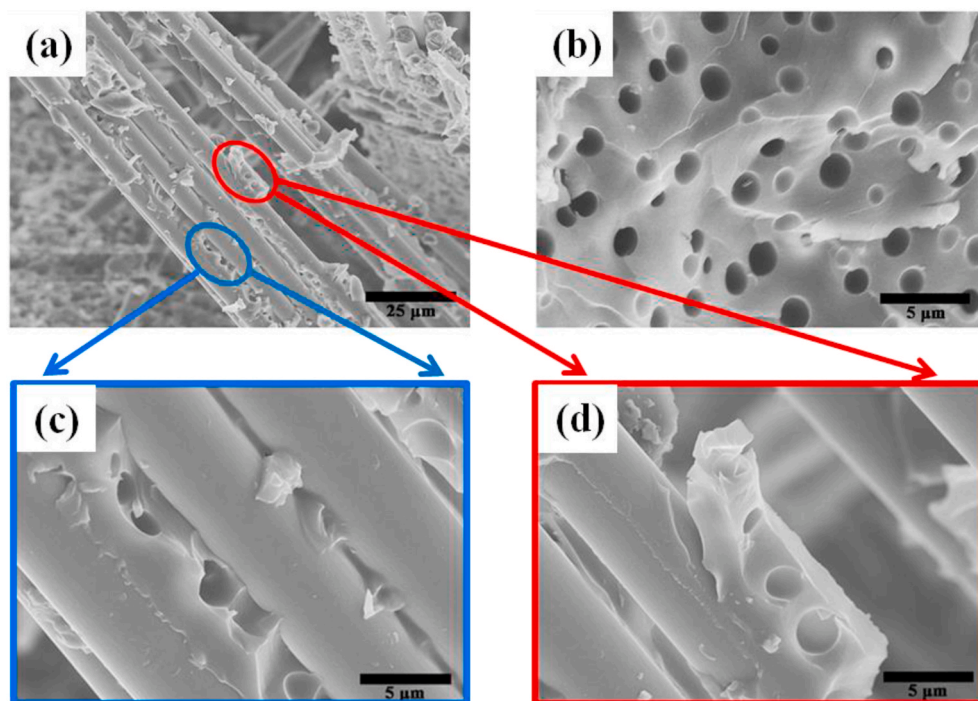


Fig. 12. The fracture surface of CF/EP/HTPU2 after longitudinal tensile test at RT: (a) CF/EP/HTPU2, (b) EP/HTPU2, (c) magnified image of blue circle at (a) and (d) magnified image of red circle at (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Interestingly, in our preliminary work [17], the result showed that the tensile mechanical properties of EP/HTPU1 were higher than EP/HTPU2, which was shown in Table S2 (see the Supporting Information). However, not all the tensile properties of CF/EP/HTPU1 were better than those of CF/EP/HTPU2. In other words, at RT and 77 K, even if the matrix showed excellent tensile mechanical properties in bulk form, it maybe behaved differently in CFRP composites [5,48]. The microstructure of resin matrix and interfacial adhesion between matrix and CF has great influence on the macro mechanical properties of CFRP composites.

4. Conclusions

In this work, the epoxy resin was toughened by HTPU1 and HTPU2, respectively, to improve the mechanical properties and crack prevention capability of CFRP composites at RT and 77 K. Owing to the lower viscosity of HTPU, the contact angle between EP/HTPU and the CFs surfaces obviously decreased, namely the wettability of epoxy resin on the surfaces of CFs improved. The transverse and longitudinal tensile properties of CF/EP/HTPU composites at both RT and 77 K are higher than those of the pristine composite, in which the improvement of interfacial adhesion between matrix and CF modified with HTPU is the main reason. In particular, CF/EP/HTPU2 shows the highest tensile strength in all the composites at RT and 77 K, because the rubber-like particles' capability of cavitations leading to a different failure mode of CF/EP/HTPU2. However, the three-point bending strength of CF/EP/HTPU2 composite at RT dropped by approximately 6% in comparison with the pristine composite. This result shows the microstructure of resin matrix has a great influence on the macro mechanical properties of fiber-reinforced polymer composites. The lower crack density of the CF/EP/HTPU composites suggests that the existence of HTPU can prevent the micro-crack of composite laminates at 77 K.

Credit Author Statement

Cheng-Bing Qu: Investigation, Methodology, Writing – original draft, Tong Wu: Investigation, Methodology, Writing – original draft, Cheng-Bing Qu: contributed equally to this work, Tong Wu: contributed equally to this work, Gui-Wen Huang: Methodology, Validation, Na Li: Resources, Meng Li: Investigation, Jun-Li Ma: Investigation, Yu Liu: Conceptualization, Writing – review & editing, Hong-Mei Xiao: Conceptualization, Supervision, Writing – review & editing.

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.

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Appendix A. Supplementary data

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