

Chapter

Low-Temperature Resistant Toughened Epoxy Resin Composite for Liquid Oxygen Tanks

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Abstract

Integrated molding of composite liquid oxygen tanks has become a crucial technology for aerospace carriers to shorten manufacturing cycles, improve carrying efficiency, and reduce production costs. Operating in an environment of -183°C , carbon fiber-reinforced resin composites face challenges such as extreme low-temperature service conditions and incompatibility with liquid oxygen due to the coupling effects of mechanical, thermal, and chemical fields. This chapter focuses on developing a modified epoxy resin matrix that is both ultralow temperature resistant and liquid oxygen compatible, essential for manufacturing composite liquid oxygen tanks. By improving the durability and fire resistance of the epoxy resin, this research introduces a novel dual-system macromolecular network interpenetration and interchain chemical crosslinking mechanism, improving mechanical properties at both room and ultralow temperatures. Moreover, two newly developed phosphorus/nitrogen-based reactive flame retardants are synthesized and added to the resin, notably improving both flame retardancy and compatibility with liquid oxygen. The resulting modified epoxy resin systems demonstrate superior mechanical properties at both room and ultra-low temperatures, making them suitable for manufacturing carbon fiber-reinforced composite materials for liquid oxygen tanks. The findings highlight the potential of these materials to meet the stringent requirements of aerospace applications.

Keywords: epoxy resin, composites, reinforcement and toughness, cryogenic mechanicals, flame retardant, liquid oxygen compatibility

1. Introduction

With the rapid evolution of composite material technology and its increasing integration into aerospace applications, the pursuit of lightweight propellant tanks through the utilization of linerless all-composite materials has emerged as a significant focus for space launch vehicle development. Among the array of materials considered for the fabrication of next-generation lightweight cryogenic propellant tanks, carbon fiber-reinforced resin-based composites (CFRP) have attracted significant interest as an exceptionally promising structural material. This interest stems from their exceptional specific strength and modulus, low density, thermal conductivity

as well as outstanding corrosion resistance and fatigue properties [1]. However, the deployment of composite propellant tanks entails enduring severe operational conditions, including exposure to extreme temperatures, such as liquid hydrogen (-253°C) and liquid oxygen (-183°C) [2]. Moreover, there exists the critical challenge of mitigating the risk of material explosion attributed to oxygen incompatibility. Traditional bisphenol A-type epoxy resins exhibit deficiencies, such as inadequate mechanical properties and susceptibility to oxygen incompatibility at ultralow temperatures, rendering them unsuitable as resin matrixes for carbon fiber-reinforced resin-based composites. Hence, there is an urgent need to enhance the ultralow temperature mechanical properties and oxygen compatibility of epoxy resins.

This paper addresses several key challenges associated with epoxy resins, including high crosslinking density, brittleness, poor impact resistance, and molecular chain freezing at ultralow temperatures post-curing. To tackle these issues, a novel toughening and reinforcement modification approach is proposed. This approach involves the introduction of a dual-system macromolecular network interpenetration and interchain chemical crosslinking mechanism, aimed at enhancing the mechanical properties of epoxy resins both at room temperature and ultralow temperatures. Additionally, the paper presents the synthesis of two structurally distinct phosphorus/nitrogen reactive flame retardants through molecular structure design. The incorporation of these flame retardants improves the flame retardancy and liquid oxygen compatibility of the resins, resulting in a modified epoxy resin system suitable for use with liquid oxygen. The study further investigates the mechanical properties of the modified resins at both room and ultralow temperatures after the addition of flame retardants [3]. Furthermore, the paper explores the fabrication of carbon fiber-reinforced resin-based composites using both pure epoxy resin and modified epoxy resin as matrix materials. W-7011F plain weave fabric is employed as the reinforcing phase. The evolution of mechanical properties at room and ultralow temperatures is examined, and the influence of the resin matrix and ultralow temperature environment on the mechanical properties of the composite materials is analyzed through macroscopic and microscopic morphology analysis of composite fracture surfaces.

2. Preparation of experimental samples

2.1 Preparation of flame-retardant compounds

2.1.1 Preparation of BSEA

To prepare the desired compound, dissolve 5.00 g (18.65 mmol) of NEA in 30 mL of ethanol and transfer the solution into a 100 mL round-bottom flask. Subsequently, weigh 8.06 g (37.30 mmol) of DOPO and add it to the same flask. Stir the mixture and allow it to react at room temperature for 12 h. Following the reaction, gradually introduce the solution dropwise into deionized water to precipitate a yellow powder. Filter the suspension and transfer the resulting filter cake to a vacuum oven. Dry the material at 70°C to obtain a light yellow powder, BSEA, achieving a yield of 96.82%.

2.1.2 Preparation of PBAH

In a round-bottomed flask containing 50 mL of DMF, add 2.46 g (6 mmol) of BAPP, 1.47 g (12 mmol) of HB, and 2.59 g (12 mmol) of DOPO. Stir the reaction

mixture using magnetic stirring at room temperature for 12 h. Subsequently, slowly introduce the reacted solution dropwise into deionized water to precipitate a yellow powder. Following filtration, transfer the filter cake to a vacuum oven and dry at 70°C to yield a light yellow powder, denoted as PBAH, with a high yield of 96.42%.

2.2 Preparation of modified epoxy resin and epoxy resin composite materials

2.2.1 Preparation of BCI-modified epoxy resin

Bisphenol A epoxy resin and BCI were blended in an oil bath maintained at 80°C, following the predetermined ratio. Subsequently, the calculated amount of curing agent DDM was added, and mechanical stirring at 80°C was continued for approximately 30 minutes until complete dissolution of the DDM curing agent particles, resulting in a homogeneous and transparent brownish-red prepolymer. The obtained brownish-red transparent solution underwent vacuum defoaming treatment using a vacuum pump and defoaming bucket until all bubbles were eliminated. The defoamed prepolymer solution was then poured into a preheated stainless steel mold previously coated with a release agent. Subsequently, the mold was horizontally placed in a temperature-controlled oven and subjected to a gradient curing process at 100°C, 120°C, 140°C, 160°C, 180°C, and 200°C for 1 h. Upon completion of the curing process, the mold was cooled to room temperature within the oven to yield a series of EP/BCI composite materials. The resulting samples were polished using 200-mesh and 1000-mesh metallographic sandpaper, cleaned with ethanol, and dried, rendering them suitable for subsequent testing.

2.2.2 Preparation of BCI/BSEA-modified epoxy resin

Add self-made BSEA with calculated amount to bisphenol A-type epoxy resin and stir mechanically at 150°C for 5 h to ensure sufficient reaction between BSEA and epoxy resin. Then cool the mixture to 80°C and add BCI in proportion. After BCI and the above mixture are evenly mixed, add a certain stoichiometric ratio of DDM. Then continue stirring at 80°C for about 30 minutes until DDM is completely dissolved, resulting in a uniform and transparent brownish-red prepolymer. Perform vacuum defoaming treatment on the obtained brownish-red transparent solution using a vacuum pump and defoaming bucket. After the bubbles are completely removed, pour the prepolymer solution into a preheated stainless steel mold pre-sprayed with release agent. Finally, place the mold in an oven and cure according to the following process: 100°C/1 h + 120°C/1 h + 140°C/1 h + 160°C/1 h + 180°C/1 h + 200°C/1 h. After curing, cool to room temperature with the oven to obtain EP/BCI/BSEA composite material.

2.2.3 Preparation of BCI/PBAH-modified epoxy resin

Add self-made PBAH with calculated amount to bisphenol A epoxy resin and mechanically stir for 5 h at 150°C to ensure sufficient reaction between PBAH and epoxy resin. Then cool the mixture to 80°C and add BCI in proportion. After BCI and the above mixture are evenly mixed, add a certain stoichiometric ratio of DDM and continue stirring at 80°C until DDM is completely dissolved, obtaining a uniform and transparent brownish-red prepolymer. Perform vacuum defoaming treatment on the obtained brownish-red transparent solution using a vacuum pump

and defoaming bucket. After the bubbles are completely removed, pour the prepolymer solution into a stainless steel mold pre-sprayed with a release agent. Finally, the mold is placed in an oven and cured according to the following process: 100°C/1 h + 120°C/1 h + 140°C/1 h + 160°C/1 h + 180°C/1 h + 200°C/1 h. After curing, it is cooled to room temperature in the oven to obtain EP/BCI/PBAH composite material.

2.2.4 Preparation of carbon fiber-reinforced resin-based composite materials

Carbon fiber-reinforced resin matrix composites were prepared using the hand layup method and vacuum bag forming process using plain woven W-7011F carbon fiber cloth as the reinforcing phase. The preparation process of its laminated board is as follows: 1. Cut the W-7011F plain weave carbon fiber cloth into a square fabric of about 300 mm × 300 mm, cut the demolding cloth, isolation film, adhesive felt into a size of 400 mm × 400 mm, and cut the vacuum bag into a size of 500 mm × 500 mm for later use; 2. Lay plain woven carbon fiber fabric layer by layer on a glass plate sprayed with a release agent, and sequentially, lay release fabric, isolation film, and adhesive felt on top. Preheat to 80°C in an oven; 3. According to the preparation method of modified resin, prefabricate the matrix resin solution and defoaming it for later use; 4. Transfer the preheated glass plate and carbon fiber cloth from the oven to the preheated heating plate and use a brush to brush the prefabricated resin solution layer by layer in one direction onto the carbon fiber cloth. After brushing, lay release cloth, isolation film, and adhesive felt on the carbon fiber cloth in sequence; 5. Seal the vacuum bag membrane with high-temperature resistant sealant and arrange a vacuum nozzle and guide pipe at one corner of the vacuum bag for the discharge of resin liquid and bubbles; 6. Transfer the packaged vacuum bag along with the glass bottom plate to the programmed temperature-controlled oven and connect the guide tube to the vacuum pump through a vacuum resin collector with a vacuum gauge. Turn on the vacuum pump and check if the vacuum bag is leaking. If there is any leakage, adjust the airtightness inside the vacuum bag by adjusting the high-temperature sealing adhesive to ensure that the vacuum degree of the system inside the vacuum bag reaches the highest; 7. Heat up and cure according to the preset curing process: 100°C/1 h + 120°C/1 h + 140°C/1 h + 160°C/1 h + 180°C/1 h + 200°C/1 h. After curing, cool to room temperature with the oven, remove the vacuum bag, and obtain composite laminates; and 8. Cut the prepared carbon fiber resin-based composite laminates according to the size of the sample to be tested using a water jet. The cut sample should be polished and reinforced with reinforcement plates as needed for subsequent testing.

3. Results and discussion

3.1 Flame retardancy and liquid oxygen compatibility of BCI-modified epoxy resin

3.1.1 Mechanical properties of BCI-modified epoxy resin

Figure 1 illustrates the comprehensive mechanical properties of pure epoxy resin and BCI-modified resin at both room temperature and an ultralow temperature of 77 K [4]. This study evaluated several mechanical parameters, including tensile strength, elongation at break, bending strength, fracture toughness, and impact strength for both pure epoxy resin and EP/BCI composite materials. The radar plot

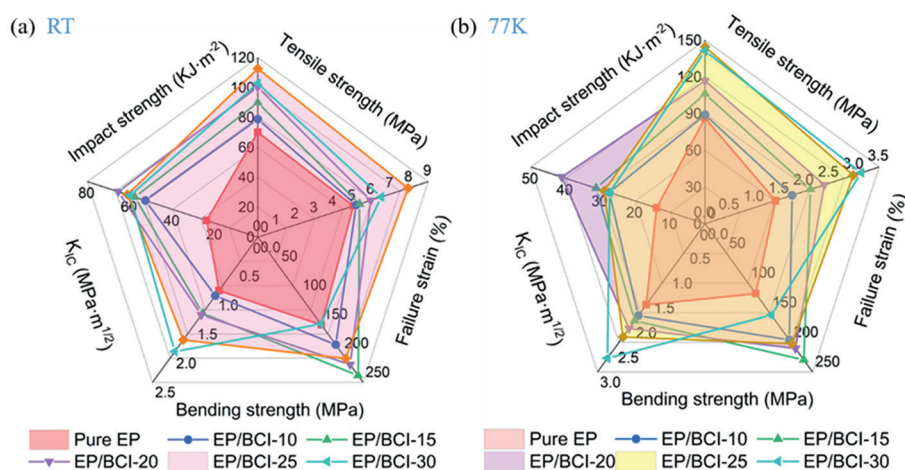


Figure 1.
 Comprehensive mechanical properties of EP/BCI composite material: (a) RT, (b) 77 K.

in the figure quantitatively depicts these comprehensive mechanical properties. As demonstrated in **Figure 1(a)**, the EP/BCI composite materials exhibit significantly enhanced mechanical properties at room temperature compared to pure epoxy resin, with the EP/BCI-25 variant showing the most superior performance. Similarly, **Figure 1(b)** reveals that at an ultralow temperature of 77 K, the mechanical properties of the EP/BCI composite materials are markedly improved relative to those of the pure resin. When tensile strength and elongation at break are prioritized, EP/BCI-25 offers the best overall mechanical performance. Conversely, when impact strength is the main concern, EP/BCI-20 is found to be optimal. The toughening mechanism of BCI in epoxy resin involves two primary processes: Initially, the introduction of BCI modifies the crosslinking network within the epoxy resin. Concurrently, a series of chemical reactions occur during the curing of EP/BCI composites. Specifically, BCI integration fosters the formation of a dual macromolecular network system that interpenetrates with the epoxy matrix. This alteration increases the internal free volume within the resin system and decreases the crosslinking density, as detailed in **Figure 2**.

This enhancement increases the mobility of molecular chain segments, preventing their complete immobilization at ultralow temperatures. Consequently, some internal stresses within the resin system can still be alleviated through the dynamic movements of these segments. Additionally, during the curing process, BCI-modified epoxy resin undergoes a chemical reaction that facilitates interchain chemical crosslinking between BCI and the epoxy matrix. The incorporation of BCI into the epoxy resin system significantly augments the resin's resistance to crack propagation, thereby substantially improving its overall mechanical properties. Ultimately, the integration of BCI serves to toughen the epoxy resin and elevate its comprehensive mechanical performance.

3.1.2 Flame retardancy of BCI-modified epoxy resin

The flame-retardant performance of EP/BCI composite materials was investigated. **Table 1** shows the flame-retardant rating and ultimate oxygen index of EP/BCI composite materials. From the table, it can be seen that the ultimate oxygen index of EP/BCI-25 reaches 29.6%, which is much higher than the ultimate oxygen index

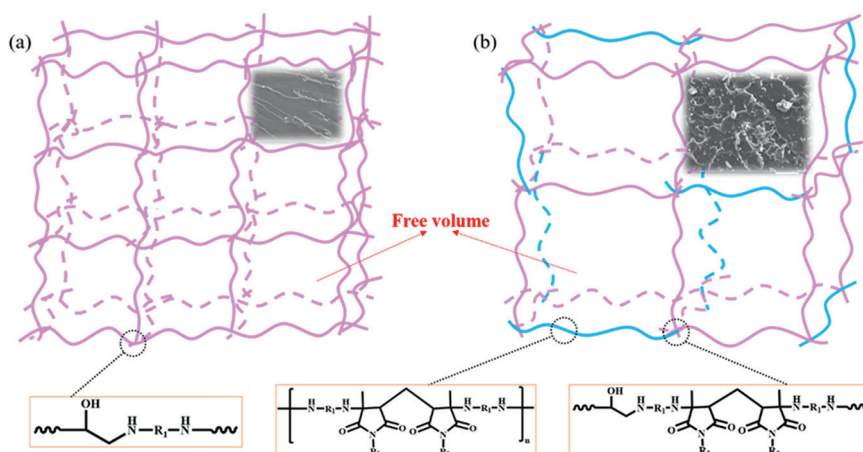


Figure 2.
Schematic diagram of crosslinking network of materials: (a) pure epoxy resin, (b) EP/BCI composite material.

Samples	LOI (%)	UL-94	HB	Dripping
Pure EP	27.8	NRa	HB-40	Yes
EP/BCI-10	28.3	NR	HB	No
EP/BCI-15	27.1	NR	HB	No
EP/BCI-20	27.9	NR	HB	No
EP/BCI-25	29.6	NR	HB	No
EP/BCI-30	29.0	NR	HB	No

Table 1.
Flame-retardant grade and ultimate oxygen index of EP/BCI composite materials.

of pure epoxy resin (27.8%). Both pure epoxy resin and EP/BCI composite materials have not passed the vertical combustion test. The horizontal combustion level of pure epoxy resin is HB-40, while the horizontal combustion level of EP/BCI composite materials is HB. Moreover, there are no melted droplets during the combustion level determination of EP/BCI composite materials, indicating that the flame-retardant performance of BCI-modified resin is improved compared to pure epoxy resin but still cannot pass the vertical combustion test. Therefore, the flame-retardant performance of EP/BCI composite materials still needs to be improved [5].

3.1.3 Liquid oxygen compatibility of BCI-modified epoxy resin

Through comprehensive analysis and research into the mechanical and flame-retardant properties of the EP/BCI-modified resin system under ambient and ultralow temperatures, it was discerned that the EP/BCI-25 variant exhibits superior mechanical and flame-retardant characteristics. Consequently, this section delves into the preliminary examination of liquid oxygen compatibility between pure epoxy resin and EP/BCI-25 *via* a 98 J liquid oxygen impact sensitivity assessment. **Table 2** presents the results of the liquid oxygen impact sensitivity test for both pure epoxy resin and EP/BCI-25. As depicted in the table, both pure epoxy resin and EP/BCI-25

Samples	Experiment phenomena (number of times)				Total number of tests	IRS (%)
	Burning	Explosion	Flash	Charring		
Pure EP	0	1	2	0	20	10.5
EP/BCI-25	0	1	2	0	20	10.5

Table 2.

Liquid oxygen shock sensitivity results of pure epoxy resin and EP/BCI-25.

experienced one explosion and two flashes out of 20 liquid oxygen impact tests. Upon computation, the liquid oxygen impact sensitivity coefficients for both sample groups were determined to be 10.5%, signifying the incompatibility of both pure epoxy resin and EP/BCI-25 components with liquid oxygen. Consequently, in order to develop a composite resin matrix resilient to ultralow temperatures and compatible with liquid oxygen, it becomes imperative to flame-retardant modify the EP/BCI-25 composite material to ensure its compatibility with liquid oxygen.

3.2 Flame retardancy and liquid oxygen compatibility of BCI/BSEA-modified epoxy resin

3.2.1 Flame retardancy of BCI/BSEA-modified epoxy resin

3.2.1.1 The influence of BSEA on the flame-retardant grade and ultimate oxygen index of epoxy resin

The influence of bisphenol S ethoxylate (BSEA) on the flame-retardant efficacy of epoxy resin was investigated using the limiting oxygen index (LOI) and UL-94 vertical combustion tests. The outcomes of these assessments are presented in **Table 3**. The LOI for pure epoxy resin and EP/BCI-25 were found to be 27.8% and 29.6%, respectively, and neither formulation passed the UL-94 rating test, indicating relatively poor flame-retardant properties. However, as the BSEA concentration increased, a noticeable improvement in LOI was observed. For example, EP/BCI/BSEA-2 (with 0.18 wt.% phosphorus) achieved an LOI of 30.7%, while EP/BCI/BSEA-3 (with 0.27 wt.% phosphorus) recorded an LOI of 31.8%, with both reaching a UL-94 classification of V-1. Furthermore, EP/BCI/BSEA-4 and EP/BCI/BSEA-5, containing 0.35 wt.% and 0.44 wt.% phosphorus respectively, attained LOIs of 32.1% and 32.8%, achieving the highest UL-94 rating of V-0. Notably, compared to pure

Samples	LOI (%)	UL-94	Dripping
Pure EP	27.8	NR	Yes
EP/BCI-25	29.6	NR	No
EP/BCI/BSEA-2	30.7	V-1	No
EP/BCI/BSEA-3	31.8	V-1	No
EP/BCI/BSEA-4	32.1	V-0	No
EP/BCI/BSEA-5	32.8	V-0	No

Table 3.

LOI and UL-94 test results of EP/BCI/BSEA composite materials.

epoxy resin, these BSEA-enhanced samples did not produce any melted droplets during combustion, demonstrating that the addition of BSEA significantly enhances the flame-retardant capabilities of epoxy resins.

3.2.1.2 Analysis of flame-retardant mechanism of BSEA-modified epoxy resin

The superior flame-retardant properties of BSEA-modified epoxy resin can be attributed to the synergistic effects of both gas-phase and condensed-phase mechanisms, as illustrated in **Figure 3**. Initially, during combustion, DOPO derivatives within BSEA release phosphorus-containing radicals such as $\text{PO}^\bullet$, $\text{PO}_2^\bullet$, and $\text{HPO}_2^\bullet$ in the gas phase. These radicals actively quench high-energy radicals, such as $\text{H}^\bullet$ and $\text{OH}^\bullet$, which are produced during the combustion of the resin. Furthermore, they can bind with the reactive sites of the resin matrix, effectively interrupting the radical chain reactions that propagate combustion. In addition to radical scavenging, BSEA also contributes to the generation of noncombustible gases such as N_2 , NO_2 , NH_3 , CO_2 , and PH_3 during thermal decomposition. These gases dilute the flammable gases emitted from the resin matrix, thereby impeding the exchange of oxygen and heat, which, in turn, diminishes the combustion intensity in the gas phase. Concurrently, in the condensed phase, phosphorus-rich residues promote the formation of a char layer, which acts as a physical barrier shielding the underlying resin from further combustion. This char layer expands and develops a porous structure due to the evolution of noncombustible gases, which disrupts the transfer of oxygen and heat, enhancing the material's flame retardancy. This dual-phase action renders the BSEA-modified epoxy resin highly effective at mitigating fire hazards.

3.2.2 Liquid oxygen compatibility of BCI/BSEA-modified epoxy resin

3.2.2.1 Sensitivity coefficient of liquid oxygen impact for BSEA-modified epoxy resin

The liquid oxygen compatibility of epoxy resin modified with BSEA was assessed using the 98 J liquid oxygen impact sensitivity test, with an analysis of the epoxy

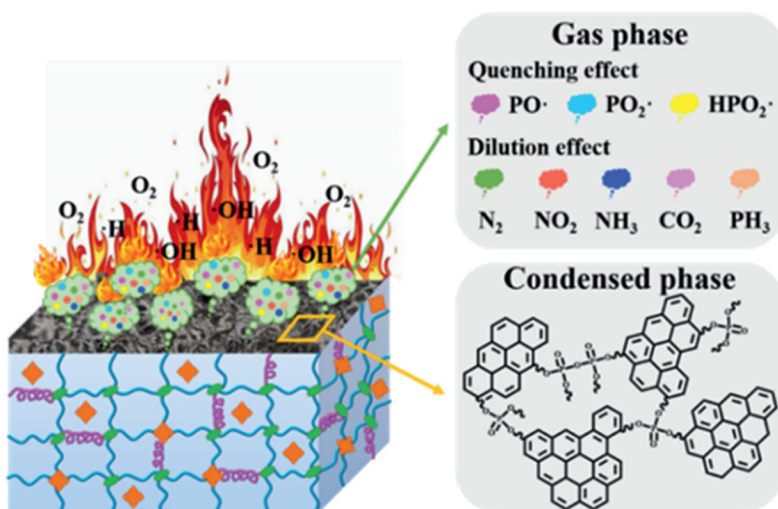


Figure 3.
Flame-retardant mechanism diagram of BSEA-modified epoxy resin.

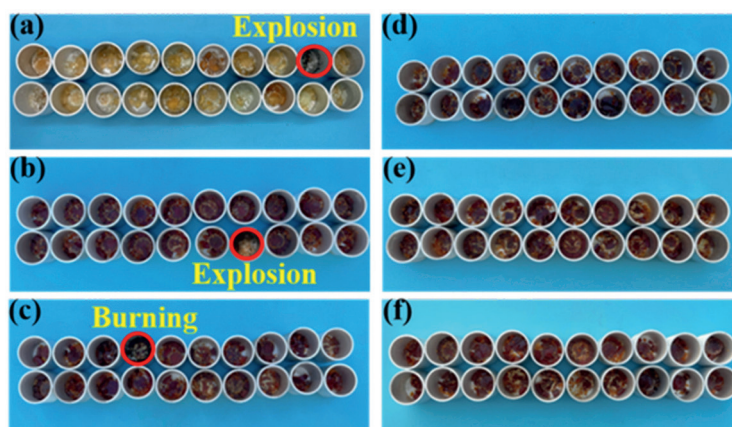


Figure 4.
Sample images after liquid oxygen impact test: (a) pure epoxy resin, (b) EP/BCI-25, (c) EP/BCI/BSEA-2, (d) EP/BCI/BSEA-3, (e) EP/BCI/BSEA-4, and (f) EP/BCI/BSEA-5.

resin's compatibility conducted *via* the impact reaction sensitivity coefficient. **Figure 4** presents digital images captured after the liquid oxygen impact testing, while **Table 4** provides details on the sensitivity reactions and liquid oxygen impact sensitivity coefficients of both pure epoxy resin and the modified resin throughout the liquid oxygen impact process. Observing **Table 4**, it becomes evident that both pure epoxy resin and EP/BCI-25 samples exhibited one explosion and two sparks during the liquid oxygen impact test. Upon calculation, the sensitivity coefficient for liquid oxygen impact was determined to be 10.5%. This suggests that both pure epoxy resin and EP/BCI-25 are incompatible with liquid oxygen, displaying a relatively high reaction strength with the oxidizer. During the liquid oxygen shock test, EP/BCI/BSEA-2 displayed one instance of combustion and one occurrence of coke formation, resulting in a sensitivity coefficient of 7.0%. Similarly, EP/BCI/BSEA-3 demonstrated two instances of coke formation during the liquid oxygen shock test, yielding a sensitivity coefficient of 4.0%. These results signify a gradual decrease in the sensitivity coefficient with the incorporation of BSEA. Furthermore, when the BSEA content reached 4 or 5 g, the modified resin exhibited no sensitivity reactions in 20 impact tests. Consequently, the liquid oxygen impact sensitivity coefficient was recorded as zero, indicating compatibility of the modified resin with liquid oxygen.

Samples	Experiment phenomena (number of times)				Total number of tests	IRS (%)
	Burning	Explosion	Flash	Charring		
Pure EP	0	1	2	0	20	10.5
EP/BCI-25	0	1	2	0	20	10.5
EP/BCI/BSEA-2	1	0	0	1	20	7.0
EP/BCI/BSEA-3	0	0	0	2	20	4.0
EP/BCI/BSEA-4	0	0	0	0	20	0
EP/BCI/BSEA-5	0	0	0	0	20	0

Table 4.
Liquid oxygen shock sensitivity results of EP/BCI/BSEA composite materials.

These findings align with the flame-retardant performance of BSEA-modified resin, underscoring the efficacy of enhancing flame retardancy as a means to improve the liquid oxygen compatibility of epoxy resin.

3.2.2.2 Analysis of liquid oxygen compatibility mechanism of BSEA-modified epoxy resin

The mechanism underlying the compatibility of BSEA-modified epoxy resin with liquid oxygen is depicted in **Figure 5**. During the liquid oxygen impact test, the mechanical energy primarily transforms into internal energy. Under high-energy mechanical impact, the R–OH bond in the resin breaks down, resulting in the formation of R[•] and OH[•] radicals. Subsequently, R[•] radicals react with liquid oxygen to generate ROO[•] radicals, which can further react with H[•] to form COOH[•] radicals. These COOH radicals release OH[•] radicals within the liquid oxygen environment, promoting the generation of C=O bonds. This formation of C=O bonds could be a crucial factor, influencing the epoxy resin's compatibility with liquid oxygen. Upon incorporating BSEA into the epoxy resin matrix, a significant amount of phosphorus-containing free radicals, such as PO[•] and HPO₂[•], are released during the liquid oxygen impact test.

These phosphorus-containing free radicals have the capability to capture high-energy free radicals, such as H[•] and OH[•], generated throughout the resin decomposition process. This capture interrupts the chain reaction of resin decomposition free radicals, akin to a flame-retardant mechanism. Consequently, this process ultimately renders the epoxy resin compatible with liquid oxygen.

Furthermore, the incorporation of BSEA enhances the comprehensive mechanical properties of the resin, bolstering its resistance to crack propagation. This enhancement results in greater dissipation of energy during liquid oxygen impact, thereby contributing to an improved extent of liquid oxygen compatibility for the resin.

3.3 Mechanical properties, flame retardancy, and liquid oxygen compatibility of BCI/PBAH-modified epoxy resin

3.3.1 Flame retardancy of CI/PBAH-modified epoxy resin

3.3.1.1 The influence of PBAH on the flame-retardant grade and ultimate oxygen index of epoxy resin

The influence of PBAH on the flame retardancy of epoxy resin was evaluated using the limiting oxygen index (LOI) and UL-94 vertical combustion tests, with the results detailed in **Table 5**. The LOI for the unmodified epoxy resin is recorded at 27.8%, which does not satisfy the criteria for the UL-94 rating, highlighting its relatively poor flame-retardant properties. However, with increasing PBAH concentrations, there is a noticeable enhancement in the LOI values. Specifically, the LOI for the EP/BCI/PBAH-3 formulation, containing 0.18 wt.% phosphorus, reaches 29.0%; for EP/BCI/PBAH-4 with 0.24 wt.% phosphorus, it increases to 30.1%; for EP/BCI/PBAH-5 with 0.30 wt.% phosphorus, it rises to 31.2%; and for EP/BCI/PBAH-6 with 0.35 wt.% phosphorus, it peaks at 31.7%. Remarkably, all four formulations achieved a V-0 classification in the UL-94 test, demonstrating the substantial flame-retardant efficacy of PBAH. Notably, compared to the baseline epoxy resin, the PBAH-enriched samples showed no signs of melting or dripping during combustion, underscoring the significant improvement in flame retardancy afforded by the incorporation of PBAH into the epoxy resin matrix.

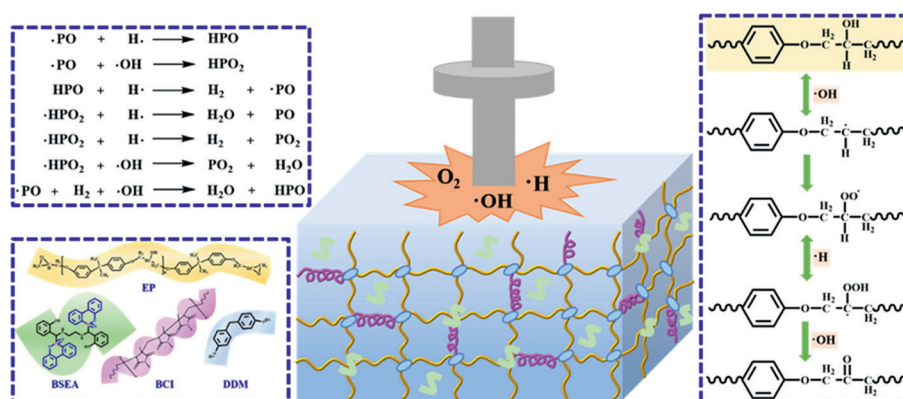


Figure 5.
Mechanism diagram of liquid oxygen compatibility of BSEA-modified epoxy resin.

Samples	LOI (%)	UL-94	Dripping
Pure EP	27.8	NR	Yes
EP/BCI/PBAH-3	29.0	V-0	No
EP/BCI/PBAH-4	30.1	V-0	No
EP/BCI/PBAH-5	31.2	V-0	No
EP/BCI/PBAH-6	31.7	V-0	No

Table 5.
LOI and UL-94 test results of EP/BCI/PBAH composite materials.

3.3.1.2 Analysis of flame-retardant mechanism of PBAH-modified epoxy resin

The superior flame-retardant performance of PBAH-modified epoxy resin can be attributed to the synergistic effects observed in both the gas-phase and condensed-phase mechanisms, as illustrated in **Figure 6**. In the gas phase, the incorporation of PBAH into the epoxy resin facilitates the release of phosphorus-containing radicals such as $\text{PO}^\bullet$, $\text{PO}_2^\bullet$, and $\text{HPO}_2^\bullet$ during combustion. These radicals effectively quench high-energy radicals such as $\text{H}^\bullet$ and $\text{OH}^\bullet$ produced during the resin combustion process. They also react with the active ends generated by the resin matrix, thereby disrupting the radical chain reaction that drives the combustion process. Moreover, PBAH generates noncombustible gases such as N_2 , NO_2 , NH_3 , CO_2 , and PH_3 during combustion. These gases serve as diluents, effectively isolating the combustion zone from ambient heat and oxygen, thereby reducing the intensity of combustion.

In the condensed phase, PBAH enhances the formation of a phosphorus-rich carbonaceous layer as the resin combusts. This layer swells due to the release of gases, forming a complex porous structure within the residual carbon. Such a layer acts as a physical barrier that impedes the transfer of heat and oxygen, thus further inhibiting the combustion of the underlying resin matrix. Additionally, the EP/BCI/PBAH formulations require a lower phosphorus content to achieve a V-0 rating, largely due to the phenyl ether structures in PBAH's molecular configuration. The incorporation of PBAH into the resin system increases the number of benzene rings, which elevates intra-chain rotational hindrance and enhances the thermal stability of the system.

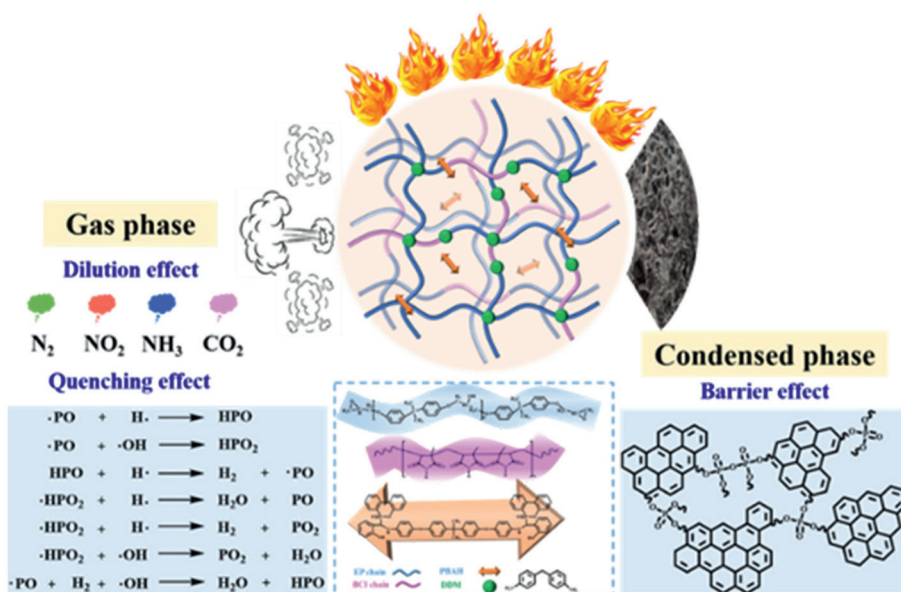


Figure 6.

Flame-retardant mechanism diagram of PBAH-modified epoxy resin.

Collectively, these results underscore that the combined gas-phase and condensed-phase actions of PBAH markedly elevate the flame retardancy of epoxy resin, surpassing that of BSEA in efficiency.

3.3.2 Liquid oxygen compatibility of CI/PBAH-modified epoxy resin

3.3.2.1 Sensitivity coefficient of liquid oxygen impact for PBAH-modified epoxy resin

The liquid oxygen compatibility of PBAH-modified epoxy resin was evaluated using the 98 J liquid oxygen impact sensitivity test, and the analysis was conducted based on the impact reaction sensitivity coefficient. **Table 6** presents the sensitivity reactions and shock sensitivity coefficients of pure epoxy resin and PBAH-modified resin during the liquid oxygen shock process. As evident from **Table 6**, pure epoxy resin exhibited one explosion and two sparks during the liquid oxygen impact test, indicating its incompatibility and heightened reactivity

Samples	Experiment phenomena (number of times)				Total number of tests	IRS (%)
	Burning	Explosion	Flash	Charring		
Pure EP	0	1	2	0	20	10.5
EP/BCI/PBAH-3	0	0	0	2	20	4.0
EP/BCI/PBAH-4	0	0	0	1	20	2.0
EP/BCI/PBAH-5	0	0	0	0	20	0
EP/BCI/PBAH-6	0	0	0	0	20	0

Table 6.

Liquid oxygen shock sensitivity results of EP/BCI/PBAH composite materials.

with liquid oxygen. In contrast, EP/BCI/PBAH-3 demonstrated two instances of coking during liquid oxygen shock, with a calculated sensitivity coefficient of 4.0%. Similarly, EP/BCI/PBAH-4 displayed a coking phenomenon once during the liquid oxygen shock process, with a sensitivity coefficient of 2.0%, showcasing a gradual decrease in sensitivity coefficient with the incorporation of PBAH. Notably, at PBAH contents of 5 or 6 g, the modified resin showed no sensitivity reaction in 20 impact tests, with a liquid oxygen impact sensitivity coefficient of zero, indicating compatibility with liquid oxygen. These findings align with the flame-retardant performance of PBAH-modified resin, underscoring the efficacy of enhancing flame retardancy as a means to improve the liquid oxygen compatibility of epoxy resin.

3.3.2.2 Analysis of liquid oxygen compatibility mechanism of PBAH-modified epoxy resin

The sensitivity reaction diagram illustrating the liquid oxygen compatibility of epoxy resin is depicted in **Figure 7**, while the mechanism elucidating the liquid oxygen compatibility of PBAH-modified epoxy resin is delineated in **Figure 7(b)**. During the course of exposure to liquid oxygen, the majority of mechanical energy undergoes conversion into internal energy, engendering localized hotspots on the resin matrix surface. The resin surrounding these hotspots undergoes free radical chain reactions. Upon high-energy mechanical impact, the R—OH bond within the resin decomposes, yielding R[•] and OH[•] radicals. These R[•] radicals can interact with liquid oxygen, producing ROO[•] radicals, while concurrently reacting with H[•] to generate [•]COOH radicals. The release of [•]COOH radicals within the liquid oxygen environment, along with the formation of C=O moieties, may constitute pivotal factors influencing the epoxy resin's compatibility with liquid oxygen.

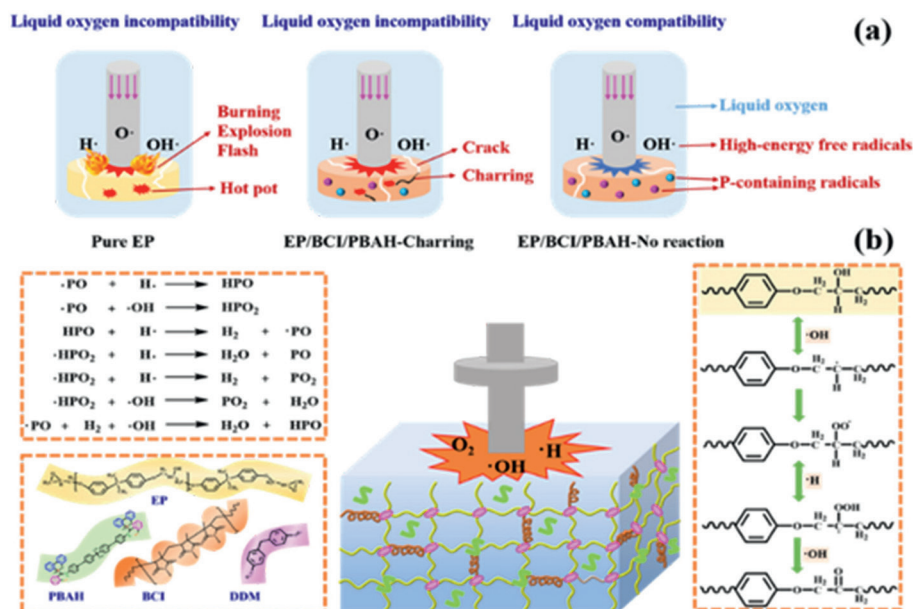


Figure 7.
 (a) Schematic diagram of sensitivity reaction for liquid oxygen compatibility, (b) mechanism diagram of liquid oxygen compatibility of PBAH-modified epoxy resin.

Upon integration of PBAH into the epoxy resin matrix, a profusion of phosphorus-containing free radicals, such as PO and HPO_2 , are liberated during the liquid oxygen impact evaluation. These phosphorus-containing radicals serve to sequester high-energy free radicals, such as H and $\text{OH}^\bullet$, generated during the resin decomposition process. This interception disrupts the free radical chain reaction involved in resin decomposition, akin to the flame-retardant mechanism observed in BSEA. Ultimately, this intervention renders the epoxy resin compatible with liquid oxygen.

Furthermore, post-PBAH modification, the resin's overall mechanical properties are augmented, thereby bolstering its resistance to crack propagation. Moreover, a heightened dissipation of energy during exposure to liquid oxygen impacts is achieved. Collectively, these enhancements contribute to an improved liquid oxygen compatibility of the resin to a discernible degree.

3.4 Mechanical properties of carbon fiber-reinforced epoxy resin-based composite materials

3.4.1 Optimization of epoxy resin matrix

In this study, we commenced by selecting an epoxy resin that showcased outstanding mechanical properties and compatibility with liquid oxygen from among those previously modified in the preceding chapters. This resin was chosen to serve as the matrix resin for fabricating carbon fiber resin-based composites. Among the candidates evaluated, both the pure epoxy resin and the EP/BCI-25 variant, which exhibited the most favorable comprehensive mechanical properties subsequent to BCI modification, were employed as control matrix resins.

Within the series of epoxy resin modifications involving BSEA, the EP/BCI/BSEA-4 and EP/BCI/BSEA-5 formulations demonstrated compatibility with liquid oxygen. Likewise, within the PBAH-modified series, the EP/BCI/PBAH-5 and EP/BCI/PBAH-6 formulations exhibited compatibility with liquid oxygen.

Consequently, we conducted a thorough assessment of the mechanical properties, including tensile strength, elongation at break, bending strength, fracture toughness, and impact strength, for both the EP/BCI/BSEA-4 and EP/BCI/BSEA-5 formulations, as well as for the EP/BCI/PBAH-5 and EP/BCI/PBAH-6 formulations. These evaluations were performed at both room temperature and ultralow temperatures. The outcomes of these assessments were visually depicted using radar plots, as depicted in **Figure 8**. Each radar plot delineates the area covered, serving as an indicator of the composite's comprehensive mechanical properties. These visual representations underscore the efficacy of the respective modifications in augmenting the overall performance of the materials under scrutiny.

Analysis of **Figure 8(a)** reveals that the radar area corresponding to EP/BCI/BSEA-4 at room temperature surpasses that of EP/BCI/BSEA-5, suggesting a superior comprehensive mechanical performance of EP/BCI/BSEA-4 under these conditions. Similarly, in **Figure 8(b)**, EP/BCI/BSEA-4 exhibits higher tensile strength, elongation at break, bending strength, fracture toughness, and impact strength at the ultralow temperature of 77 K compared to EP/BCI/BSEA-5. This is further corroborated by the substantially larger radar area associated with EP/BCI/BSEA-4, indicating its enhanced mechanical properties at ultralow temperatures in comparison to EP/BCI/BSEA-5. A thorough comparison demonstrates that EP/BCI/BSEA-4 outperforms EP/BCI/BSEA-5 in comprehensive mechanical properties, both at room temperature and

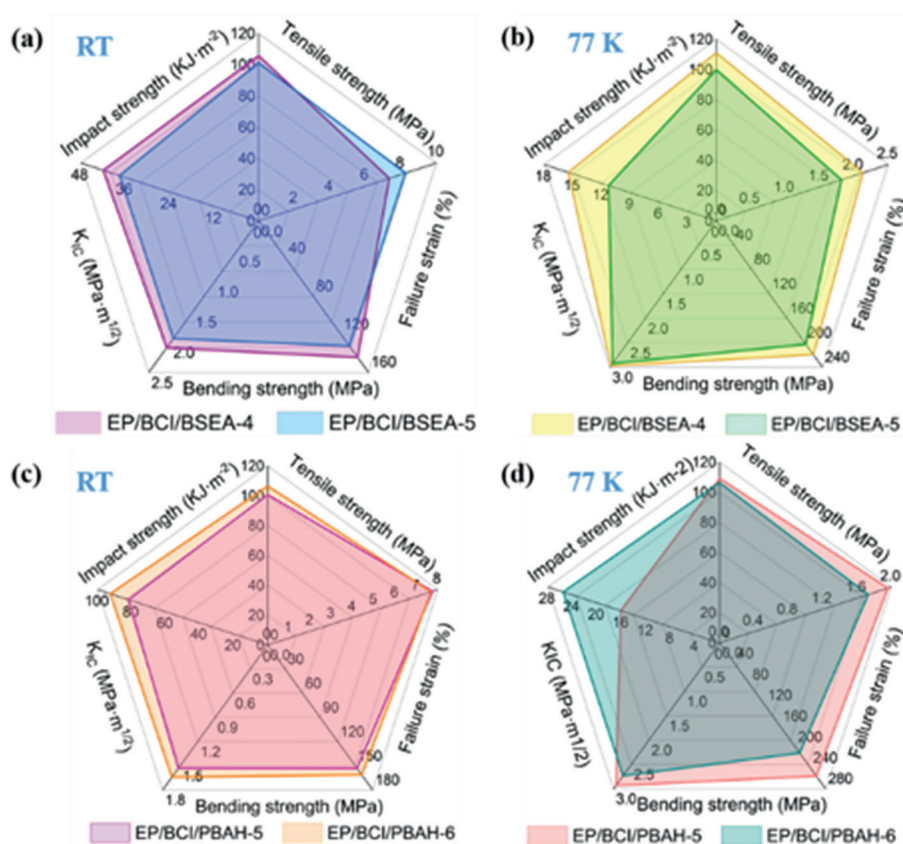


Figure 8. Comprehensive mechanical properties of EP/BCI/BSEA composite material: (a) RT, (b) 77 K; comprehensive mechanical properties of EP/BCI/PBAH composite materials: (c) RT, (d) 77 K.

ultralow temperatures. Consequently, EP/BCI/BSEA-4 was selected as the matrix resin for BSEA-modified epoxy resin in the fabrication of carbon fiber resin-based composites.

In **Figure 8(c)**, it is evident that the radar cross-sectional area corresponding to EP/BCI/PBAH-6 at room temperature surpasses that of EP/BCI/PBAH-5, indicating the superior overall mechanical properties of EP/BCI/PBAH-6 under these conditions. Examining **Figure 8(d)**, it becomes apparent that EP/BCI/PBAH-5 exhibits superior tensile strength, elongation at break, bending strength, and fracture toughness compared to EP/BCI/PBAH-6. However, EP/BCI/PBAH-5's impact strength is marginally inferior to that of EP/BCI/PBAH-6. Consequently, in ultralow temperature environments, if emphasizing impact strength, EP/BCI/PBAH-6 demonstrates better overall mechanical properties than EP/BCI/PBAH-5. Conversely, if stringent impact strength requirements are not in place, precedence should be given to tensile strength, elongation at break, bending strength, and fracture toughness, where EP/BCI/PBAH-5 outperforms EP/BCI/PBAH-6. Following thorough comparison and deliberation, the final selection was narrowed down to four representative matrix resins: pure epoxy resin, EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5. The thermal expansion coefficients of these four representative matrix resins were characterized, and carbon fiber-reinforced resin matrix composites were fabricated using the hand layup

method and vacuum bag forming process. Subsequently, the mechanical properties of the resulting carbon fiber-reinforced resin matrix composites were preliminarily explored and investigated.

3.4.2 Research on the mechanical properties of CFRP

3.4.2.1 Research on room temperature and ultralow temperature tensile properties of CFRP

Figure 9 illustrates the tensile properties of carbon fiber composites fabricated from pure epoxy resin and three modified resins—EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5—at room temperature. According to **Figure 9(a)**, the tensile strength of composites made from pure epoxy resin is recorded at 529.41 MPa. In contrast, composites fabricated with EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 exhibit significantly enhanced tensile strengths of 733.87 MPa, 659.64 MPa, and 702.61 MPa, respectively, representing increases of 38.6%, 24.6%, and 32.7% over the pure epoxy resin. As depicted in **Figure 9(b)**, the elastic modulus of the pure epoxy resin composite stands at 36.86 GPa, while those of composites incorporating EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 resins are measured at 47.06 GPa, 46.20 GPa, and 47.96 GPa, respectively, marking improvements of 27.7%, 25.3%, and 30.1%. These enhancements are primarily attributed to the superior tensile strength and elongation at the break of the modified resins compared to pure epoxy. Moreover, composites based on pure epoxy are susceptible to interfacial debonding between the resin and carbon fibers under tensile loads, which impairs the stress transfer capability of the resin matrix.

Concurrently, defects generated within the composite material led to the initial fracture of surrounding carbon fibers. As the tensile load intensifies, the load transitions across adjacent carbon fibers, culminating in an increasing number of fibers exhibiting fracture. This phenomenon prevents the fibers from exerting their strength simultaneously. However, in the modified EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 carbon fiber composites, the notable enhancements in tensile strength and elongation at break of the resin matrix, as compared to those of the pure epoxy resin composites, bolster the matrix's ability to transmit stress. This enhancement enables a greater number of fibers to concurrently contribute to load-bearing,

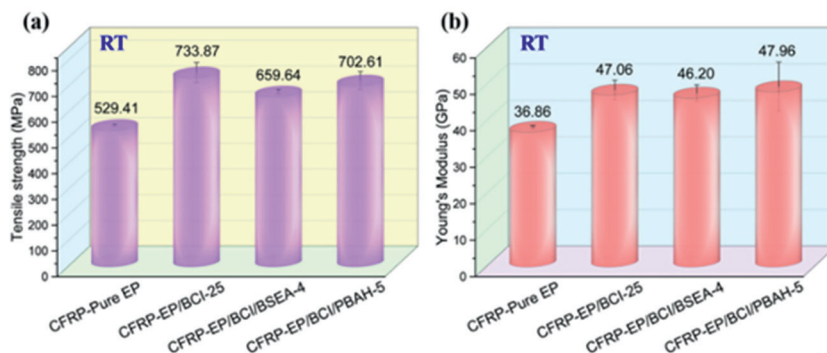


Figure 9. Tensile properties of carbon fiber resin-based composite materials at room temperature: (a) tensile strength, (b) elastic modulus.

thereby significantly improving both the tensile strength and elastic modulus of the carbon fiber resin matrix composites. Additionally, the residual thermal stress, generated by temperature fluctuations during the transition from high temperature to room temperature at the conclusion of the curing process, adversely impacts the mechanical properties of the carbon fiber resin-based composite materials. The modified EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 resins, featuring a reduced thermal expansion coefficient relative to pure epoxy resin, generate lower levels of residual thermal stress. This reduction in thermal stress contributes to an improvement in the mechanical properties of the modified carbon fiber composite materials.

Figure 10 presents a comparison of the tensile properties of carbon fiber composites fabricated using pure epoxy resin and three modified resins: EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 at ultralow temperatures. As illustrated in **Figure 10(a)**, the tensile strength of composites made with pure epoxy resin at ultralow temperatures registers at 493.13 MPa. In contrast, the tensile strengths of composites utilizing EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resins are 671.00 MPa, 637.11 MPa, and 666.63 MPa, respectively, representing increases of 36.1%, 29.2%, and 35.2% over the pure resin. **Figure 10(b)** shows that the elastic modulus of the pure epoxy resin carbon fiber composite is 36.19 GPa at ultralow temperatures, whereas the elastic moduli for composites modified with EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 are 46.65 GPa, 45.06 GPa, and 43.62 GPa, respectively. These values indicate improvements of 28.9%, 24.5%, and 20.5% over the pure epoxy resin composite. These enhancements in tensile properties at ultralow temperatures are consistent with the improvements observed at room temperature, suggesting that the modified matrix resins effectively bolster the mechanical properties of the carbon fiber composites under these conditions. Comparing **Figures 9** and **10** reveals a slight reduction in the tensile strength and elastic modulus of carbon fiber composite materials when transitioning from room temperature to ultralow temperatures. Specifically, the tensile strength of pure epoxy resin and its modified counterparts—EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5—at ultralow temperatures decreased by 6.9%, 8.6%, 3.4%, and 5.1%, respectively, compared to room temperature. Similarly, the elastic modulus experienced reductions of 1.8%, 0.9%, 2.5%, and 9.0%, respectively under the same conditions. This decline can be primarily attributed to the incongruent thermal expansion coefficients between the carbon fiber and resin matrix in ultralow temperature environments. As temperatures decline from room temperature

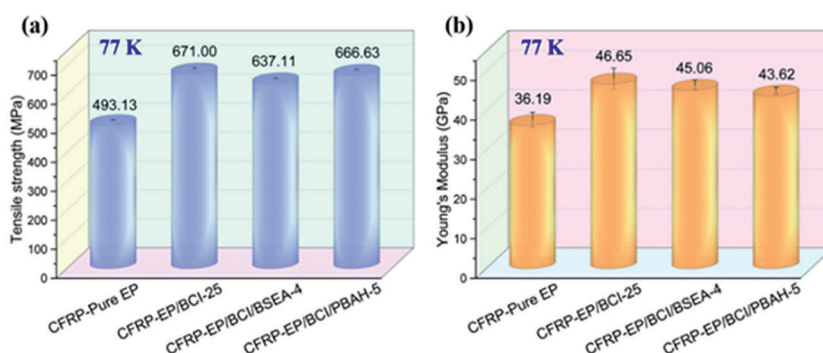


Figure 10. Tensile properties of carbon fiber resin-based composite materials at 77 K: (a) tensile strength, (b) elastic modulus.

to -196°C , the resin matrix undergoes considerable shrinkage, inducing significant thermal stresses within the carbon fiber composite material. Furthermore, the disparity in deformation between the carbon fiber and resin matrix may provoke interface debonding, consequently leading to the formation of microcracks. Hence, the presence of thermal stress and microcracks within the composite materials constitutes the primary factors contributing to the observed decrease in tensile strength of carbon fiber-reinforced resin matrix composites in ultralow temperature environments. Comparing **Figures 9** and **10** reveals a slight reduction in the tensile strength and elastic modulus of carbon fiber composite materials when transitioning from room temperature to ultralow temperatures. Specifically, the tensile strength of pure epoxy resin and its modified counterparts—EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5—at ultralow temperatures decreased by 6.9%, 8.6%, 3.4%, and 5.1%, respectively, compared to room temperature. Similarly, the elastic modulus experienced reductions of 1.8%, 0.9%, 2.5%, and 9.0%, respectively under the same conditions. This decline can be primarily attributed to the incongruent thermal expansion coefficients between the carbon fiber and resin matrix in ultralow temperature environments. As temperatures decline from room temperature to -196°C , the resin matrix undergoes considerable shrinkage, inducing significant thermal stresses within the carbon fiber composite material. Furthermore, the disparity in deformation between the carbon fiber and resin matrix may provoke interface debonding, consequently leading to the formation of microcracks. Hence, the presence of thermal stress and microcracks within the composite materials constitutes the primary factors contributing to the observed decrease in tensile strength of carbon fiber-reinforced resin matrix composites in ultralow temperature environments.

3.4.2.2 Research on the room temperature and ultralow temperature bending performance of CFRP

Figure 11 illustrates the bending performance of carbon fiber composite materials fabricated using both pure epoxy resin and modified variants—EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5—at ambient temperature. In **Figure 11(a)**, the bending strength of carbon fiber composites crafted with pure epoxy resin registers at 405.76 MPa, whereas those utilizing EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resins demonstrate bending strengths of 621.33 MPa, 647.72 MPa, 663.34 MPa,

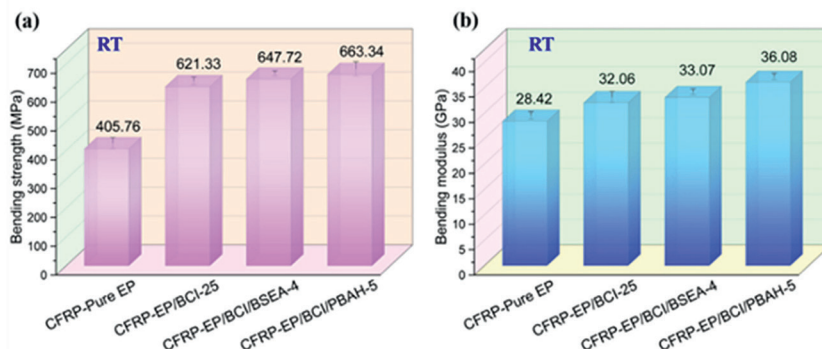


Figure 11. Bending performance of carbon fiber resin matrix composite at room temperature: (a) bending strength, (b) bending modulus.

and 663.34 MPa, respectively. This denotes an enhancement in bending strength by 53.1%, 59.6%, and 63.5%, respectively, in comparison to pure epoxy resin-based carbon fiber composites. The predominant failure modes observed in carbon fiber resin-based composites during bending include tensile failure, compression failure, shear failure, and delamination. During three-point bending tests, the upper layer of the material experiences compressive stress, leading primarily to compression-induced failures, such as fracture and buckling, while the lower layer undergoes tensile stress, resulting mainly in fiber fracture, pullout, and delamination. Shear failure predominantly occurs in the intermediate layer of the material. Notably, during three-point bending tests, the onset of failure in all four types of carbon fiber resin-based composite materials primarily manifests on the tensile side.

When the stress state on the outermost side of the tensile zone of the composite material reaches the maximum load that the material can withstand, the composite material begins to fracture and fail. At the same time, the load transfers to the adjacent fiber layer, leading to further failure and failure of the material.

The tensile performance results indicate that the tensile strength of the modified resin composites EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 at room temperature exceeds that of the pure epoxy resin composites. Additionally, the comprehensive mechanical properties of these modified resins enhance their stress transfer capabilities. Consequently, the bending strength of the modified composites EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 at room temperature is significantly improved compared to that of the pure epoxy resin composites.

As demonstrated in **Figure 11(b)**, the bending modulus of the pure epoxy resin carbon fiber composite material at room temperature is 28.42 GPa. In contrast, the bending moduli of the carbon fiber composite materials modified with EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 resins are 32.06 GPa, 33.07 GPa, and 36.08 GPa, respectively. Relative to the pure epoxy resin, these values represent increases of 12.8%, 16.7%, and 27.0%, respectively.

This enhancement in bending modulus is primarily attributed to two factors: First, the elastic modulus of the three modified resins within the carbon fiber composite materials is higher than that of the pure epoxy resin composite material on the tensile side. Second, on the compressive side, where the matrix resin predominantly bears the load, the elastic modulus of the modified resins also surpasses that of the pure epoxy resin. These two factors synergistically contribute to the higher bending modulus of the carbon fiber composite materials composed of EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resins at room temperature compared to the pure epoxy resin composite material.

Figure 12 presents the load-displacement curves for carbon fiber composite materials prepared with pure epoxy resin and modified resins—EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5—during bending tests. **Figure 12(a)** and **(b)** indicate that at both room temperature and ultralow temperatures, the four types of carbon fiber composites display similar load-displacement curves. Initially, the load and displacement exhibit a linear relationship until reaching the failure load, after which the load decreases and displays a sawtooth-like wave pattern. This pattern is primarily due to the failure of the outermost fibers on the tensile side after the material reaches its ultimate load, leading to a reduction in load-bearing capacity. Subsequently, the load is transferred to the adjacent fiber layer through the resin, which still retains some capacity to resist external loads, resulting in serrated fluctuations in the load. Comparing **Figure 12(a)** and **(b)** reveals that these serrated fluctuations are more pronounced at ultralow temperatures than at room temperature, suggesting that

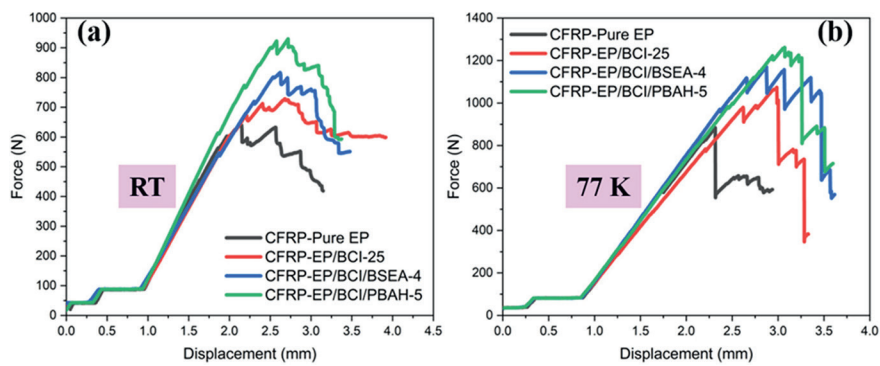


Figure 12. Bending load-deflection curve of carbon fiber resin-based composite material: (a) room temperature, (b) ultralow temperature.

carbon fiber composites possess greater resistance to external loads in ultralow temperature environments. This increased resistance is attributed to resin matrix shrinkage in ultralow temperature environments, enhancing the material's resistance to interlayer shear failure. Therefore, in ultralow temperature conditions, carbon fiber composites primarily exhibit interlayer shear-induced delamination failures, which manifest as pronounced sawtooth fluctuations on the load-displacement curves.

3.4.2.3 Research on room temperature and ultralow temperature interlaminar shear properties of CFRP

As illustrated in **Figure 13**, the interlayer shear properties of carbon fiber composite materials fabricated using both pure epoxy resin and modified resins—EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5—are delineated. In **Figure 13(a)**, it is evident that the interlayer shear strength of carbon fiber composites crafted with pure epoxy resin at room temperature registers at 29.92 MPa. In contrast, the interlayer shear strength of carbon fiber composites incorporating EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resins reaches 37.66 MPa, 49.57 MPa, and 45.77 MPa, respectively, marking increases of 25.9%, 65.7%, and 53.0% over pure epoxy resin composites. This enhancement primarily stems from the substantially improved

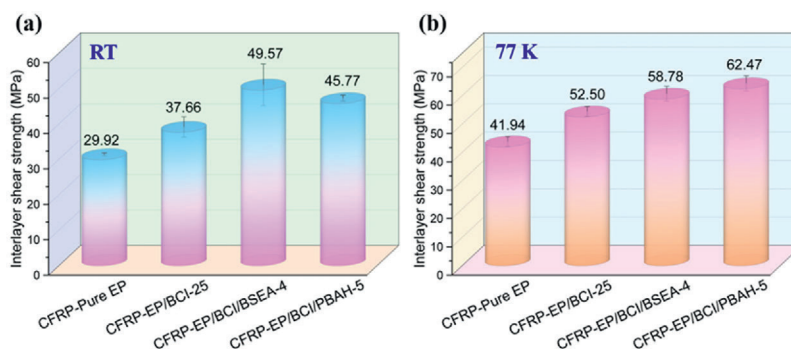


Figure 13. Interlayer shear strength of carbon fiber resin-based composite materials: (a) room temperature, (b) ultralow temperature.

fracture elongation and toughness exhibited by the modified EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 resins compared to pure epoxy resins. The fortified resin matrix facilitates more efficient load transfer, enhances crack propagation resistance, and bolsters delamination resistance in carbon fiber composites. Consequently, the interlayer shear strength of carbon fiber composites employing EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resins at room temperature surpasses that of pure epoxy resin composites. Notably, the incorporation of flame-retardants BSEA and PBAH in EP/BCI/BSEA-4 and EP/BCI/PBAH-5 carbon fiber composites has led to varying degrees of improvement in shear strength compared to EP/BCI-25. This observation underscores the efficacy of flame-retardants BSEA and PBAH in augmenting the interfacial bonding between the resin matrix and carbon fibers.

In **Figure 13(b)**, the interlayer shear strength of carbon fiber composites formulated with pure epoxy resin under ultralow temperature conditions is reported as 41.94 MPa. Conversely, carbon fiber composites incorporating EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resins exhibit interlayer shear strengths of 52.50 MPa, 58.78 MPa, and 62.47 MPa, respectively—reflecting increments of 25.2%, 40.2%, and 49.0% over pure epoxy resin composites. The interlayer shear failure mechanism observed in carbon fiber composite materials at ultralow temperatures mirrors that observed at room temperature. Under external loading, the resin matrix transfers stress loads to adjacent carbon fiber layers *via* shear stress across the interface layer, ultimately resulting in interlayer failure of the composite material. The fortified resin matrix facilitates enhanced load transmission, thereby effectively bolstering the interlayer shear strength of the composite material. A comparative analysis between **Figure 13(a)** and **(b)** reveals that the interlayer shear strength of the same carbon fiber composite material is notably elevated in ultralow temperature environments compared to room temperature environments. The interlayer shear strength of pure epoxy resin, EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 modified resin composite materials at ultralow temperature is increased by 40.2%, 39.4%, 18.6%, and 36.5%, respectively, compared to room temperature environment. This is mainly attributed to the increased toughness of the modified resin due to the shrinkage of the resin molecular crosslinking network in the ultralow temperature environment, which enables the resin matrix to transmit more loads when subjected to external loads. Moreover, the interface bonding energy between the resin and fibers is enhanced due to resin shrinkage at ultralow temperatures, resulting in strong resistance to interlayer shear failure of composite materials. The reddest result is that the interlayer shear strength of pure epoxy resin, EP/BCI-25, EP/BCI/BSEA-4, and EP/BCI/PBAH-5 resin matrixes in the ultralow temperature environment is better than that in the room temperature environment.

4. Conclusion

The integration of BCI into epoxy resin significantly enhances its mechanical properties at room and cryogenic temperatures, attributed to a novel dual-network interpenetrating and interchain chemical crosslinking mechanism. This modification results in substantial improvements in tensile strength, elongation, flexural properties, fracture toughness, and impact resistance. Reactive phosphorus/nitrogen flame retardants, BSEA and PBAH, developed from specific chemical compounds, further augment the resin's flame retardancy and liquid oxygen compatibility, achieving a UL-94 V-0 rating and higher oxygen index. Optimally formulated carbon fiber

composites exhibit superior mechanical performance over pure epoxy resin, particularly at cryogenic temperatures, due to improved interfacial bonding. This research addresses fundamental challenges in developing cryogenic and liquid oxygen compatible composite materials, offering vital theoretical and technical insights for advancing aerospace material technologies.

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