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Research Article

The Effect of Diallyl Bisphenol A Content as a Curing Agent on ILSS and Thermal Resistance of Bismaleimide/Carbon Fiber Composites

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ABSTRACT

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Diallylbisphenol A (DABA) was synthesized and used as a toughening curing agent for the fabrication of high-temperature bismaleimide (BMI)/carbon fiber composites. The aim of this study was to investigate the effect of DABA content on the curing behavior, thermal stability, mechanical performance, and ablation resistance of BMI/DABA resin systems in order to identify an optimized formulation for high-temperature composite applications. Differential scanning calorimetry (DSC) revealed that the BMI/DABA resin system exhibited a curing onset temperature of 170.1 °C, which is lower than the conventional curing temperature of BMI. Thermogravimetric analysis (TGA) was conducted on three BMI/DABA molar ratios (1/1, 1/0.86, and 1/0.77), together with a phenolic resin for comparison. Among the investigated formulations, the BMI/DABA (1/0.86) system exhibited 5% and 50% weight-loss temperatures ($T_{5\%}$ and $T_{50\%}$) of 391 °C and 598 °C, respectively. Oxyacetylene ablation testing showed that the BMI/DABA (1/0.86) composite exhibited a remarkably low weight loss of only 1.9%, indicating excellent ablation resistance. Interlaminar shear strength (ILSS) measurements further demonstrated that the BMI/DABA (1/0.86) composite achieved the highest ILSS values, reaching 61.34 MPa at room temperature and 58.66 MPa at 78 °C. These results demonstrate that the optimized BMI/DABA formulation provides an excellent balance of thermal stability, mechanical performance, and ablative resistance, making it a promising matrix resin for high-temperature aerospace and thermal protection applications.

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1. Introduction

High-performance resins are one of the most crucial compounds that are used in fields where thermal and mechanical properties are very important, like aerospace, and high-tech industries [1-6]. A common type of these resins consists of phenolic resins [7-9], epoxy resins [10-12], phthalonitriles [13, 14], cyanate esters [15-17], and bismaleimides [18-20], which have

applications in different fields [21, 22]. In addition to the development of high-performance resin systems, optimizing the processing and characterization of fiber-reinforced polymer composites is essential for achieving superior structural performance. For example, recent studies have demonstrated that processing parameters, such as those employed in abrasive water jet machining of glass fiber-reinforced polyester composites, can significantly influence

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the quality and performance of composite components [23].

Bismaleimide-based composites have attracted significant attention owing to their exceptional thermal stability, mechanical robustness, and resistance to harsh environments, making them highly suitable for advanced applications ranging from microelectronics to aerospace engineering [24, 25]. In recent years, considerable research efforts have been directed toward enhancing the physicochemical and functional properties of bismaleimide (BMI) resins, with the aim of broadening their practical utility in demanding industrial sectors. BMI resins, in particular, are well recognized for their outstanding high-temperature performance in aerospace structures. In addition to their thermal endurance, they also exhibit superior mechanical strength, remarkable corrosion resistance, and excellent abrasion resistance, positioning them as promising candidates for high-performance composites in extreme service conditions [26, 27].

Furthermore, BMI resins demonstrate fluidity comparable to that of conventional epoxy resins, while simultaneously overcoming one of the major shortcomings of epoxy systems: their relatively low thermal resistance. This combination of processability and superior heat tolerance makes BMI resins particularly attractive for high-performance applications where both ease of fabrication and long-term thermal stability are critical [28-31].

Conventional BMI resins are characterized by high cross-linking density, which imparts excellent thermal stability [32]. However, the increased degree of cross-linking in cured BMI systems often leads to pronounced brittleness, thereby limiting their practical applicability [33, 34]. In addition, unmodified BMI suffers from several inherent drawbacks, including a high melting point, poor solubility, and elevated molding temperatures, which further restrict its ease of processing [35]. Among these limitations, the intrinsic brittleness, manifested as reduced toughness, stands out as one of the most critical obstacles hindering the broader development and utilization of BMI-based materials [20, 36-38].

The curing of BMI resins proceeds predominantly through the homopolymerization of carbon-carbon double bonds, resulting in the formation of a densely cross-linked three-dimensional network without the release of small-molecule by-products [39]. This unique curing behavior not only minimizes molding shrinkage but also enhances the dimensional stability of the final product. Hence, their superior thermal stability, combined with

excellent mechanical strength and chemical resistance, renders them highly effective as matrix resins in the fabrication of advanced high-performance composites designed for demanding engineering applications [26, 40, 41].

In most practical applications, BMI resins are employed in combination with reactive comonomers such as vinyl and allyl compounds, allyl phenols, and aromatic amines, etc., in order to improve their processability and toughness. Akin [7] synthesized heat-resistant bismaleimide interpenetrating polymer network (IPN) coatings by incorporating Bisphenol A ethoxylate diacrylate, which was further modified with fluorinated and silicone side chains. The incorporation of these functional components led to substantial enhancements in the mechanical strength, thermal stability, and surface characteristics of the resulting coatings. Han et al. [42] developed a BMI resin system and successfully enhanced its toughness through the incorporation of poly(phthalazinone ether ketone), achieving a remarkable 50% increase in impact resistance at a loading of only 5 wt%. Based on this strategy, Yuan et al. [28] synthesized a bio-based allyl compound containing ether linkages, which was employed to toughen a BMI resin. This modification not only improved impact resistance by 37% but also contributed to enhanced thermal stability. More recently, Liu et al. [43] reported the introduction of a novel allyl compound containing both ether bonds and a 3-(triethoxysilyl)propyl functional group into a BMI resin matrix, leading to a 27% increase in impact resistance, along with notable improvements in thermal stability and glass transition temperature. These studies demonstrate the effectiveness of incorporating functionalized allyl compounds as viable approaches for simultaneously improving the toughness and thermal performance of BMI-based resins.

Among these approaches, copolymerization modification with allyl-based compounds, particularly Diallyl bisphenol A (DABA), has proven to be one of the most effective and well-established strategies for enhancing the toughness of BMI systems [44, 45]. The underlying mechanism of this copolymerization process can be described in two main steps. First, the carbon-carbon double bonds within the BMI structure undergo opening, enabling a diene addition reaction with allyl groups known as the Ene reaction to generate a reactive conjugated intermediate. In the subsequent step, this intermediate participates in a Diels-Alder reaction with additional BMI molecules, which promotes the development of a cross-linked polymeric network. The resulting cured resin possesses a ladder-like architecture, contributing

to improved toughness while maintaining the inherent thermal and mechanical advantages of BMI-based materials [46, 47].

Although DABA has previously been employed as a modifier for BMI resins, a systematic understanding of how the BMI/DABA molar ratio influences curing behavior, network formation, thermal stability, interlaminar shear strength, and oxyacetylene ablation resistance of carbon fiber composites remains limited. In particular, the relationship between resin formulation and the combined thermal and mechanical performance required for thermal protection applications has not been comprehensively established. Therefore, this work systematically investigates the effect of DABA content on the structure-property relationship of BMI/DABA systems and identifies an optimized formulation through combined thermal, mechanical, and ablative evaluations.

2. Experimental

2.1. Materials

Bisphenol A (BPA), allyl bromide, potassium carbonate (K_2CO_3), 4,4'-methylenedianiline (MDA), maleic anhydride, triethylamine (TEA), sodium acetate, acetic anhydride, acetone, N, N-dimethylformamide (DMF), sodium sulfate, chloroform, and sodium carbonate were purchased from Merck and used as received. A plain-weave carbon fiber fabric (Navid Co., Iran) was used as the reinforcement. The fabric had a density of 1.78 g/cm^3 , a tensile modulus of 230 GPa, a tensile strength of 3900 MPa, an areal weight of 200 g/m^2 , and a nominal thickness of 0.25 mm, according to the manufacturer's technical datasheet.

2.2. Synthesis of 4,4'-Bis(maleimido) diphenylmethane Resin (BMI)

BMI resin was synthesized based on a previously reported protocol [48]. Briefly, for the synthesis of BMI resin, 7.9 g (0.08 mol) of maleic anhydride was dissolved in 100 mL of dry acetone (dried over Na_2SO_4 for 2 h) and transferred into a 250 mL three-neck round-bottom flask. Separately, 7.28 g (0.04 mol) of MDA was dissolved in 50 mL of dry acetone and added dropwise over 30 minutes to the maleic anhydride solution, which was stirred under magnetic stirring. The temperature of the oil bath was gradually increased to 60°C , and the reaction mixture was refluxed under a nitrogen atmosphere for 1 hour. During this stage, a yellow precipitate of the amic acid intermediate formed, which was insoluble in acetone.

Subsequently, 10.38 mL (0.1 mol) of acetic anhydride, 0.3 g (0.004 mol) of sodium acetate,

and 5.1 mL (0.04 mol) of triethylamine were added to the reaction mixture. The resulting mixture was refluxed again under the same conditions for 2 hours. Upon completion of the reaction, the yellow solid was precipitated by the solvent/non-solvent method using ice-cold water. The solvent was decanted, and the obtained solid was washed several times with distilled water and then repeatedly with a 10 wt% aqueous sodium carbonate solution. The product was then dried in a drying oven at 90°C .

2.3. Synthesis of Diallyl Bisphenol A (DABA)

For the synthesis of DABA, 22.8 g (0.1 mol) BPA was dissolved in 250 mL of dry acetone and transferred into a 500 mL two-neck round-bottom flask. Then, 42 g (0.3 mol) of potassium carbonate was added to the solution. Subsequently, 20 mL (0.23 mol) of allyl bromide was added dropwise within 1 hour to the BPA/ K_2CO_3 solution under magnetic stirring. The temperature of the oil bath was gradually increased to 55°C , and the reaction mixture was refluxed under a nitrogen atmosphere for 20 hours.

After completion of the reaction, acetone was removed from the reaction mixture using a rotary evaporator, yielding the intermediate diallyl ether of BPA (DAEBA). The obtained intermediate was then placed in an oven at 180°C for 28 hours to undergo complete Claisen rearrangement, resulting in the formation of the DABA compound with a yield of 88%.

2.4. Preparation of BMI/DABA Blends

For preparation of the BMI/DABA blend, initially, DABA was heated to 130°C until fully melted. Solid BMI resin was then added gradually to the molten DABA. After approximately 15 minutes of stirring, a homogeneous brown mixture was obtained. For each mole of BMI resin, three different molar ratios of DABA curing agent, including 0.77, 0.86, and 1.00, were employed as shown in Table 1.

Table 1. Sample coding and composition percentages of BMI and DABA blends

Sample code	Wt% of BMI	Wt% of DABA
BMI/DABA 1/1	53.7	46.3
BMI/DABA 1/0.86	57.4	42.6
BMI/DABA 1/0.77	60.1	39.9

2.5. Preparation of BMI/DABA Composites and Curing Cycle

To prepare the carbon fiber composites, BMI and DABA were first mixed according to the desired formulation. The resin mixture was then

manually applied to plain-weave carbon fiber fabrics using a roller to ensure complete impregnation of the fiber bundles. Excess resin was removed by rolling until a uniform resin distribution and the target resin-to-fiber weight ratio (45:55) were achieved. The impregnated fabrics were subsequently used as prepregs (Fig. 1). The prepregs were placed in an oven at 150 °C for 50 min to partially cure the resin (B-stage), thereby preventing excessive resin flow during vacuum-assisted autoclave processing. After partial curing, the prepreg sheets were cut to the required dimensions and stacked into ten layers. The laminate was then vacuum-bagged and cured in an autoclave under a pressure of 4 bar using the following curing cycle: 150 °C for 1.5 h, 175 °C for 2 h, 200 °C for 4 h, and 250 °C for 9 h.



Fig. 1. Photograph of the prepreg preparation process

For comparison, a diglycidyl ether of bisphenol A cured with m-Phenylenediamine (DGEBA/m-PDA) composite was also prepared following a conventional epoxy curing schedule. The laminate was pre-cured at 80 °C for 2 h, followed by curing at 120 °C for 1 h, and finally post-cured at 150 °C for 3 h.

2.6. Preparation of BMI/DABA 40-layer Composite

To perform the oxyacetylene ablation test, it was necessary to prepare a composite piece with dimensions of 10 × 10 cm according to ASTM E285 standard test method [49]. To fabricate such a composite piece, the 40-layer composite was prepared. To this aim, 80 grams of the resin/curing agent mixture were used. Sized carbon fiber was employed as the reinforcement material (Fig. 2a).

The prepreg was initially pre-cured in an oven at 150 °C for 50 minutes. After this step, the prepreg layers were stacked, and the laminate was cured in an autoclave under a pressure of 4 bar, following this thermal cycle: 1.5 hours at 130 °C, 2 hours at 150 °C, 2 hours at 175 °C, and subsequently, a post-curing process was

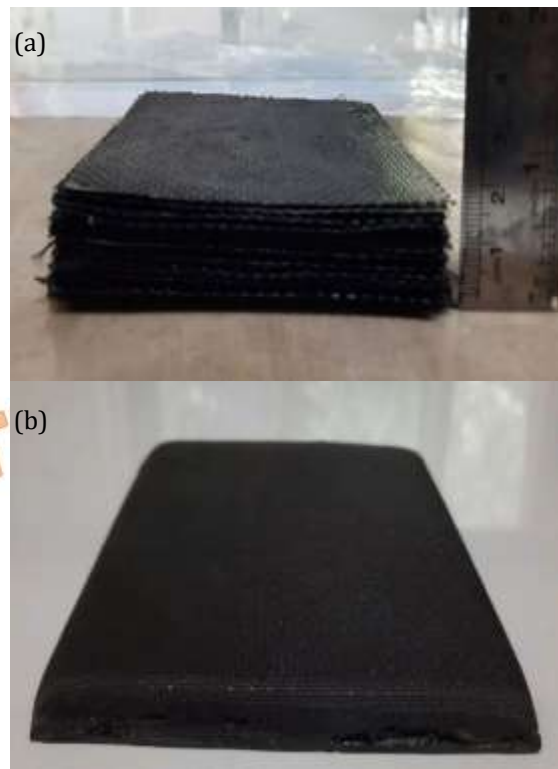


Fig. 2. (a) Stacking of the prepreg layers for fabrication of the 40-layer composite prior to autoclave curing, and (b) Fully cured 40-layer BMI/DABA/carbon fiber composite prepared for the oxyacetylene ablation test

performed in an oven at: 200 °C for 4 hours and 250 °C for 9 hours with a heating rate of 5 °C/min (Fig. 2b).

2.7. Characterization

2.7.1. FTIR Analysis

FTIR Analysis was used to identify the synthesized compounds and monitor the curing behavior of the synthesized resin with a Thermo Fisher Scientific (USA) spectrometer in the range of 4000-400 cm^{-1} . The degree of curing (DOC) was calculated by the area under the peak using Equation 1 [50].

$$DOC = \frac{(A_{690 \text{ cm}^{-1}})_0 - (A_{690 \text{ cm}^{-1}})_t}{(A_{690 \text{ cm}^{-1}})_0} \quad (1)$$

In Equation 1, $(A_{690 \text{ cm}^{-1}})_t$ and $(A_{690 \text{ cm}^{-1}})_0$ are the areas under the peak at 690 cm^{-1} , as the main characteristic peak of the maleimide group at time t and $t = 0$, respectively [51].

2.7.2. NMR Spectroscopy

The chemical structure of the synthesized resin was confirmed by ^1H -NMR and ^{13}C -NMR spectroscopy. Measurements were carried out using a Bruker AVANCE NEO, 400 MHz spectrometer (Germany). Deuterated dimethyl

sulfoxide (DMSO- d_6) solvent was used for the NMR experiment.

2.7.3. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to observe the effect of DABA on lowering the curing temperature of BMI and to study the curing behavior of the BMI/DABPA system. The measurements were performed using a NETZSCH 200 F3 instrument (Germany). The temperature range was from room temperature to 350 °C with a heating rate of 10 °C/min.

2.7.4. Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) was conducted to assess the weight loss behavior of the BMI/DABPA resin at various molar ratios. A Mettler-Toledo STARE SW12 instrument (Switzerland) was used from room temperature to 900 °C at a heating rate of 10 °C/min in an air atmosphere.

2.7.5. Oxyacetylene Ablation Test

Oxyacetylene ablation was used to evaluate the thermal insulation performance of the composite prepared from the homogeneous BMI/DABPA resin blend and carbon fiber using an oxyacetylene ablation test following the ASTM E285 [49] standard test method. The test was conducted using an oxygen pressure of 7 bar and an acetylene pressure of 2 bar, with a flame-to-sample distance of 25 mm.

2.7.6. Interlaminar Shear Strength Test (ILSS)

The ILSS specimens were machined to dimensions of 25 mm × 6 mm × 2 mm (length × width × thickness) and tested according to ASTM D2344 [52], using a three-point bending configuration at a crosshead displacement rate of 1 mm/min. For each formulation, five specimens were tested using a Santam STM-150 universal testing machine (Iran). The reported ILSS values

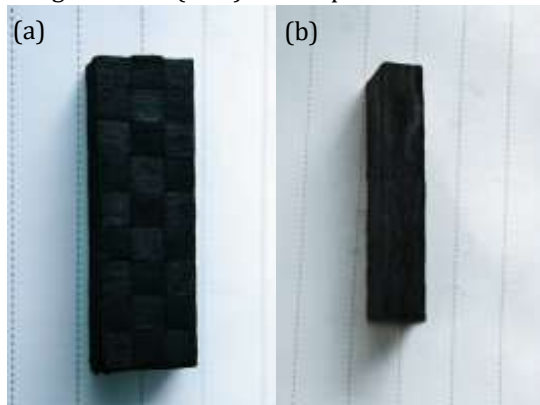


Fig. 3. photographs of the specimen before ILSS test: (a) front view, and (b) side view

represent the average of the five measurements. Representative photographs of the specimen before testing, including the front and side views, are presented in Fig. 3.

Representative photographs of the three-point short-beam loading configuration are shown in Fig. 4 [52].

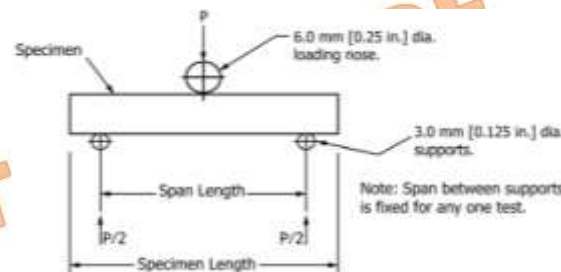


Fig. 4. Three-point short-beam loading configuration [52].

In addition to room-temperature measurements, ILSS tests were performed at an elevated temperature of 78 °C. Prior to testing, the specimens were conditioned in a laboratory air-circulating oven at 78 °C for 30 min to ensure complete thermal equilibration. The oven temperature was controlled using the built-in digital temperature controller throughout the conditioning period. After conditioning, the specimens were immediately transferred to the testing machine. The elevated-temperature tests were conducted under ambient laboratory conditions using the same three-point short-beam configuration, specimen dimensions, and crosshead speed as those used for the room-temperature measurements.

The FTIR, DSC, TGA, oxyacetylene ablation, and ILSS experiments were conducted at the Malek Ashtar University of Technology, Tehran, Iran, whereas the NMR spectroscopy measurements were performed at the Iran Polymer and Petrochemical Institute, Tehran, Iran.

3. Results and Discussion

3.1. Synthesis and Characterization of BMI Resin

The synthesis route of BMI resin is shown in Fig. 5a. As illustrated in the FTIR spectrum in Fig. 5b, the absorption bands observed at 1707 cm^{-1} and 1770 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of the imide C=O groups, respectively. The absorption bands at 1149 cm^{-1} and 1395 cm^{-1} correspond to the stretching vibrations of the C-N bonds, while the band located at 3038 cm^{-1} is attributed to the stretching vibration of vinyl C-H bonds. The absorption bands associated with the stretching vibrations of the aromatic ring C=C double bonds

appear at 1458, 1512, 1584, and 1603 cm^{-1} . Furthermore, the bands detected at 3099 cm^{-1} and 3038 cm^{-1} are assigned to the stretching vibrations of vinyl C-H and phenyl C-H bonds, respectively. The absorption band observed at 830 cm^{-1} is characteristic of out-of-plane bending vibrations of aromatic C-H bonds in para-substituted aromatic rings, while the absorption band located at 688 cm^{-1} corresponds to the C-H out-of-plane bending vibrations of the 1,2-cis-disubstituted imide group [53].

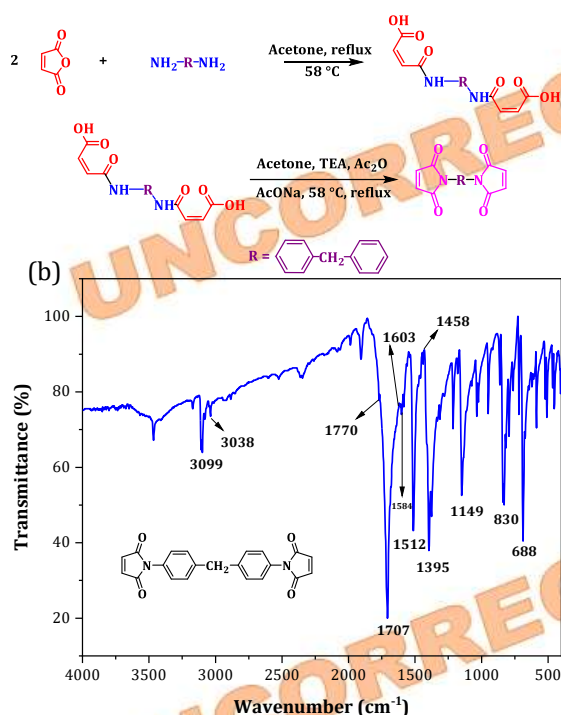


Fig. 5. (a) synthesis route of BMI resin, and (b) FTIR spectrum of the synthesized BMI resin

The $^1\text{H-NMR}$ spectrum of the synthesized bismaleimide resin is shown in Fig. 6. A singlet peak at 4.10 ppm corresponds to the CH_2 group located between two benzene rings, and a singlet peak at 7.16 ppm corresponds to the vinyl hydrogens of the imide ring. These two imide ring hydrogens, being equivalent, do not split each other and thus appear as a singlet at a single position. Two doublets in the chemical shift range of 7.2–7.4 ppm, with their characteristic splitting pattern, are attributed to the para-disubstituted benzene rings. Other characteristic peaks at 3.34 and 2.50 ppm are due to the DMSO solvent and residual water, respectively.

3.2. Synthesis and Characterization of DABA Curing Agent

The detailed mechanism and synthesis route of the DABA curing agent are shown in Fig. 7. In the initial step, BPA reacts with K_2CO_3 to generate the BPA^{-1} anion. The resulting anion subsequently undergoes nucleophilic

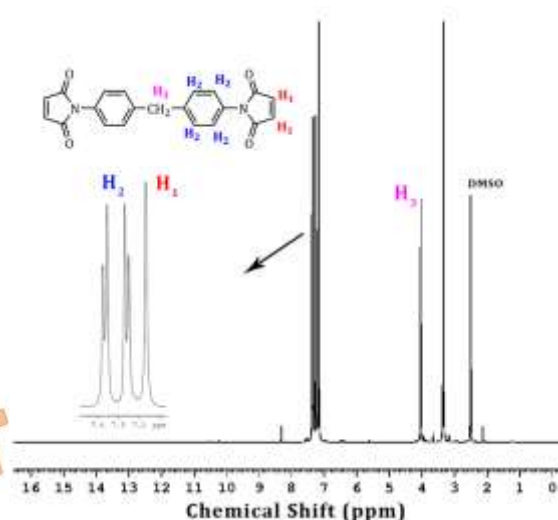


Fig. 6. The $^1\text{H-NMR}$ spectrum of the synthesized BMI resin

substitution with allyl bromide, in which bromide acts as an efficient leaving group, affording DAEBa. Thereafter, a Claisen rearrangement takes place, leading to the formation of DABA. To identify the functional groups and chemical bonds present in the structure of DABA, FTIR spectroscopy was employed. Figure 8 presents the FTIR spectra obtained from the curing agent, DABA, at two stages of the synthesis, including the intermediate compound formation (DAEBa) and the final DABA product.

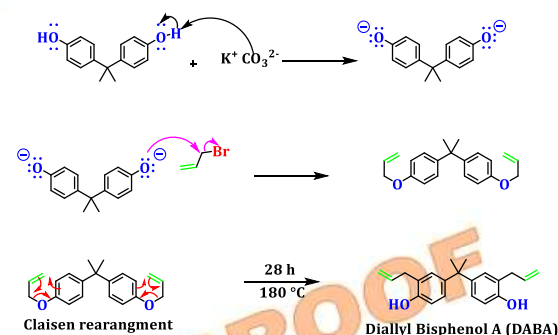


Fig. 7. Mechanism of the synthesis of DABA curing agent

The spectrum of BPA exhibits characteristic peaks at a wavenumber of 3336 cm^{-1} , corresponding to the phenolic hydroxyl (OH) group, and 1500 cm^{-1} for the aromatic $\text{C}=\text{C}$ stretching. As shown in Fig. 8, the absorption bands of the intermediate compound, DAEBa, appear at 1500 cm^{-1} for aromatic $\text{C}=\text{C}$ stretching and 1650 cm^{-1} for allylic $\text{C}=\text{C}$ bonds.

Additionally, the FTIR spectrum of DABA reveals absorption bands at 1504 cm^{-1} , while the peak at 3077 cm^{-1} is attributed to the aromatic C-H stretching. A broad absorption band in the 3414 cm^{-1} region corresponds to the hydroxyl group. This peak is shifted to a higher wavenumber compared to the OH of BPA. This is due to the steric hindrance around the DABA

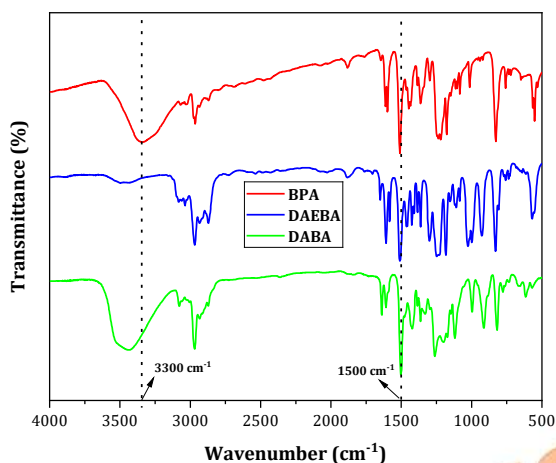


Fig. 8. FTIR spectra of BPA, DAEBA, and DABA compounds

hydroxyl group, which causes difficulty in the formation of intermolecular hydrogen bonds in comparison with BPA.

3.3. Curing Behavior and Curing Mechanism of BMI Resin with the DABA Curing Agent

The BMI resin undergoes a curing reaction in the presence of the DABA curing agent. As shown in Fig. 9a, the allylic groups of DABA participate in the curing reaction with the maleimide groups. The curing mechanism of bismaleimide with DABA proceeds in two stages. In the first stage, a reaction occurs between the maleimide and the diallyl groups, known as the Ene reaction. At this step, the double bond of the maleimide group acts as an enophile and reacts with the hydrogen of the allylic group of DABA (the ene), and a new σ bond is formed. In the subsequent stage, which initiates at a temperature of approximately 180 °C, the double bond of the maleimide reacts with the double bond formed as a product of the Ene reaction. As depicted in Fig. 9b, this interaction results in the formation of a ring structure through a Diels-Alder cycloaddition reaction. In this step, a concerted pericyclic reaction occurs, and another double bond of the maleimide moiety acts as a dienophile while the double bond of the ene reaction acts as a diene [54, 55].

The ^{13}C -NMR spectra of the samples before and after heating are shown in Fig. 10 and Fig. 11, respectively. The signals corresponding to each carbon atom have been assigned based on the molecular structure. A comparison of the ^{13}C -NMR spectra of these two compounds reveals a high degree of similarity, except for four new signals observed in the spectrum of Fig. 11, which result from the occurrence of the ene reaction.

Among these four new signals, as illustrated in Fig. 11, two are assigned to the carbonyl carbons C_{21} and C_{22} , while the other two are attributed to the saturated carbons C_1 and C_2 that are formed

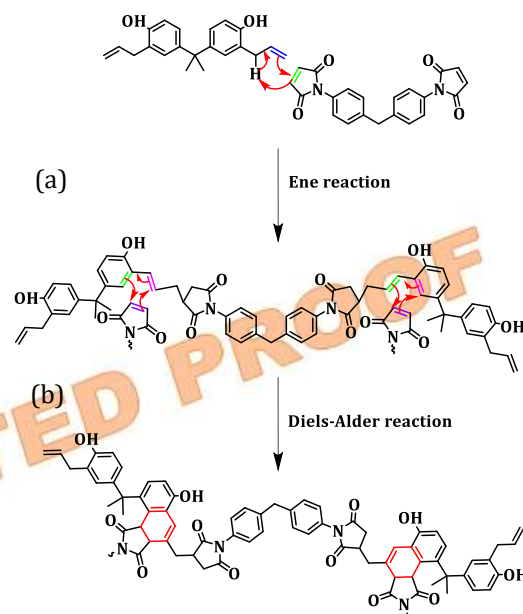


Fig. 9. (a) Ene reaction between BMI and DABA, (b) Diels-Alder reaction between BMI and DABA at 180 °C

as a consequence of the Ene reaction. Regarding the difference in chemical shift between carbonyl carbons, it can be explained that in the pre-heated sample, as shown in Fig. 10, the presence of a $\text{C}=\text{C}$ double bond adjacent to the carbonyl groups acts as an electron-rich center. This high electron density increases shielding of the carbonyl carbons, causing them to resonate at lower chemical shifts around 170.4 ppm. However, following the Ene reaction, the double bond moved to the other carbons and conjugated with the benzene ring, which can resonate with benzene and withdraw electrons from the carbonyl groups, resulting in the formation of two carbonyl carbons that resonate at higher chemical shifts at 176 and 179 ppm.

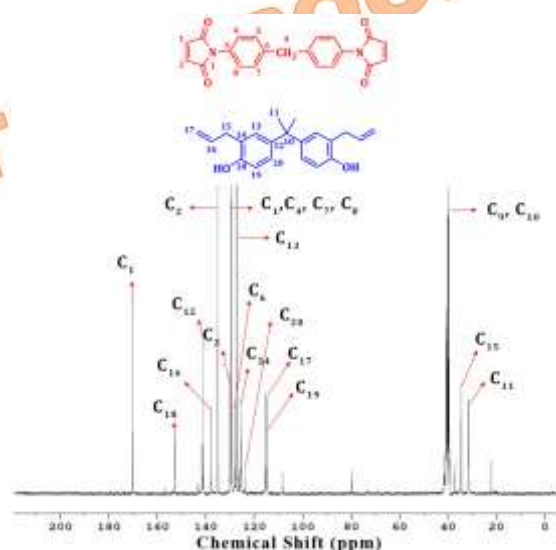


Fig. 10. ^{13}C -NMR spectrum of BMI/DABA before Ene reaction

The other two additional signals observed in Fig. 11 correspond to carbons C₁ and C₂, which are also generated after the Ene reaction. These carbons appear at lower chemical shifts due to the loss of the double bond. In the unheated sample, the presence of a conjugated carbonyl adjacent to the double bond leads to electron deficiency in these carbons due to resonance structures, causing them to resonate at higher chemical shifts.

The ¹³C-NMR spectra thus confirm the occurrence of the Ene reaction during the curing process of the BMI resin with DABA. In contrast, the second stage of curing, which involves the Diels–Alder reaction, cannot be tracked using ¹³C-NMR spectroscopy due to the cross-linking of the resin and its resulting insolubility in NMR solvents. Since solution-state NMR relies on complete dissolution and rapid molecular motion to obtain well-resolved spectra, the crosslinked resin cannot generate detectable solution-state ¹³C-NMR signals.

To observe the effect of DABA on lowering the curing temperature of BMI, the first sample (BMI/DABA 1/1) was subjected to a DSC test to compare the result with neat BMI. Based on the DSC thermogram shown in Fig. 12, for the neat BMI resin, the endothermic peaks observed at 161.7 °C correspond to the melting of this resin. The onset of the curing reaction occurs at 175.2 °C, the curing peak is observed at 230.7 °C, and the curing reaction is completed at 326.27 °C, which is common to the BMI resins.

For the BMI/DABA 1/1, the endothermic peak observed at 90.5 °C is attributed to the melting of the BMI/DABA mixture. According to this DSC curve, the onset of the curing reaction begins at 170.1 °C and is completed at 348.9 °C. For neat BMI, the endothermic melting transition occurs

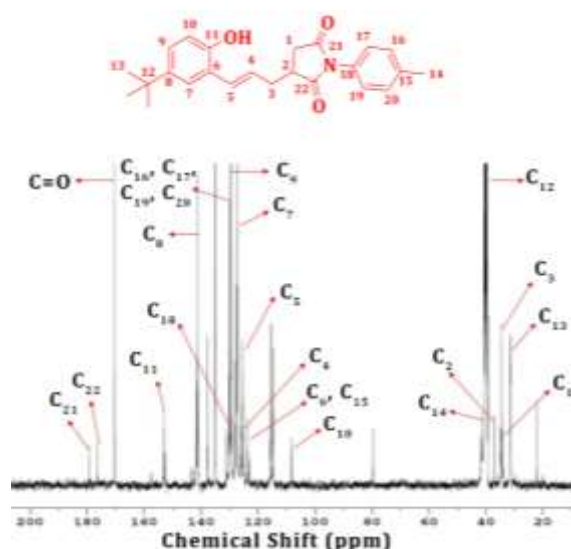


Fig. 11. ¹³C-NMR spectrum of BMI/DABA after ene reaction

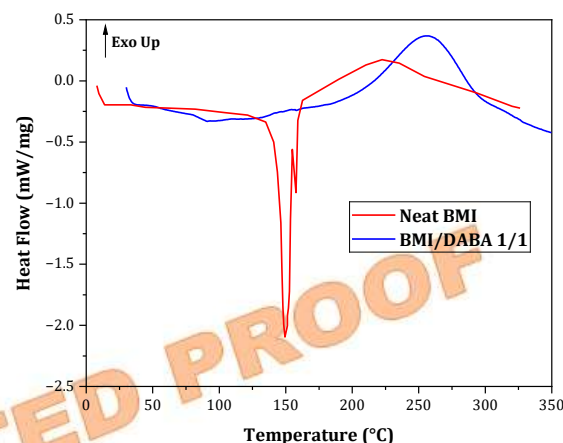


Fig. 12. DSC thermogram of neat BMI, and BMI/DABA 1/1 resin systems

at 161.7 °C, while in the BMI/DABA mixture, the melting temperature shifts dramatically downward to 90.5 °C. This decrease can be attributed to the disruption of BMI's ordered crystalline domains by the introduction of DABA. According to Fig. 5a and Fig. 9, neat BMI has relatively rigid aromatic structures capable of packing into ordered crystalline or semi-crystalline arrangements. DABA, by contrast, contains flexible allyl groups and a bulky bisphenol unit. When blended, the allyl groups interfere with the tight packing of BMI molecules, lowering the crystallinity of the system. The resulting material becomes more amorphous and disordered, which reduces the energy required for molecular mobility and phase transitions, thus decreasing the observed melting temperature. The onset of BMI curing for the neat resin is 175.2 °C, but in the BMI/DABA system, it decreases slightly to 170.1 °C. This shift arises from the reactive allyl groups of DABA, which act as co-monomers and introduce additional sites for thermal-initiated polymerization [56].

BMI typically cures through a homopolymerization of its maleimide double bonds, which requires a relatively high activation energy. When DABA is incorporated, its allyl double bonds can participate in ene reactions with the maleimide groups, thereby reducing the activation barrier for curing. In effect, DABA functions as a reactive diluent that facilitates the initial stages of polymerization at a lower temperature.

Table 2. DSC data of neat BMI and BMI/DABA 1/1 resin systems

Sample	T _i (°C)	T _p (°C)	T _f (°C)	ΔH (J/g)
Neat BMI	175.2	230.7	326.2	180.2
BMI/DABA 1/1	170.1	256.1	348.9	328.9

Additional data on the onset, peak, and end temperatures of the curing process for both pure BMI and the BMI/DABA mixture at a 1/1 molar ratio are summarized in Table 2.

Based on the obtained results for ILSS and TGA analyses (sections 3.4 and 3.6) for composites, since the optimum result was achieved for the BMI/DABA 1/0.86 sample, the curing procedure of this formulation was further monitored by FTIR spectroscopy. The FTIR spectra of this sample at different temperatures and reaction times are presented in Fig. 13.

To monitor the curing reaction for the BMI/DABA 1/0.86 mixture, the FTIR spectra were analyzed by monitoring changes in the absorption bands intensity at 690 cm^{-1} and 3100 cm^{-1} , which were used to investigate. These bands correspond to the out-of-plane bending and stretching vibrations of the C-H bonds in the double bonds of the maleimide group, respectively. In particular, the absorption band at 690 cm^{-1} , which represents the out-of-plane bending vibrations of C-H in the C=C bonds of the maleimide group before curing, was observed to decrease in intensity as the curing progressed. Upon completion of the curing process, this peak was eliminated, confirming the full consumption of the double bonds through the curing reaction.

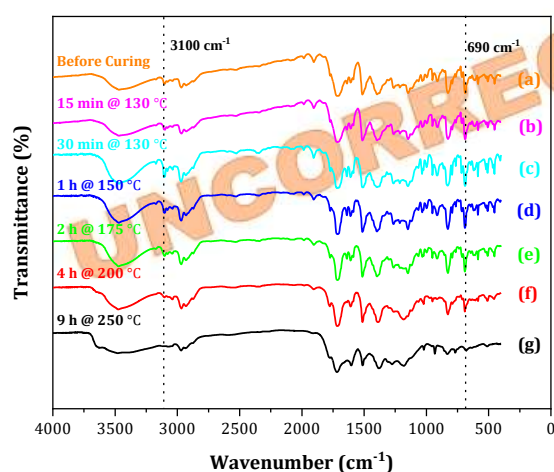


Fig. 13. FTIR spectra of BMI/DABA 1/0.86 resin system (a) before curing, (b) after 15 min @ $130\text{ }^{\circ}\text{C}$, (c) 30 min @ $130\text{ }^{\circ}\text{C}$, (d) 1 h @ $150\text{ }^{\circ}\text{C}$, (e) 2 h @ $175\text{ }^{\circ}\text{C}$, (f) 4 h @ $200\text{ }^{\circ}\text{C}$, and (g) 9 h @ $250\text{ }^{\circ}\text{C}$

For evaluating the DOC of BMI in the presence of DABA, equation 1 was used. For calculating the DOC, the area under the peak at 690 cm^{-1} , as the main characteristic peak of the maleimide group, was considered, as summarized in Table 3. Based on the data obtained at different temperatures and reaction times, the area under the 690 cm^{-1} peak corresponding to the maleimide group decreases with increasing temperature and reaction time, indicating the occurrence of a reaction between BMI and DABA.

Table 3. Calculating the DOC of the reaction

Time	Temperature ($^{\circ}\text{C}$)	Area under the 690 cm^{-1} peak	DOC
0	25	4552.69	0
15 min	130	2894.86	37
30 min	130	1466.14	67
1 h	150	929.78	79
2 h	175	864.93	81
4 h	200	633.47	86
9 h	250	217.45	95

3.4. Thermogravimetry of BMI Resin Cured by Different Amounts of DABA Curing Agent

To examine the thermal behavior of BMI/DABA blends with different molar ratios and to compare them with other high-temperature resins such as phenolic resins, TGA was carried out in air to evaluate weight loss as a function of temperature. As shown in Fig. 14, among the tested formulations, the BMI/DABA blend with a molar ratio of 1/0.86 shows the highest thermal stability, with 5% weight loss occurring only at $391\text{ }^{\circ}\text{C}$ and 50% weight loss delayed until $598\text{ }^{\circ}\text{C}$. This performance surpasses both neat BMI and the other BMI/DABA blends. The improved stability can be attributed to an optimal balance between crosslink density and network flexibility. At this ratio, the allyl groups from DABA react efficiently with the maleimide groups of BMI, creating a dense, interpenetrating copolymer network. The phenolic units of DABA also contribute rigidity and aromatic stability to the network, compensating for its aliphatic portions. Too much DABA introduces excess aliphatic content, which reduces overall thermal resistance, while too little DABA results in less effective copolymerization and weaker network stabilization.

The 1/0.86 ratio, therefore, represents a near-optimal composition for thermal endurance. The initial degradation step observed in the TGA curves is linked to the decomposition of DABA's aliphatic allyl groups and weaker linkages. Aliphatic chains typically undergo bond scission at lower temperatures due to their lower bond dissociation energy compared with aromatic or imide bonds. Thus, even in the crosslinked system, localized decomposition of allyl segments occurs first, marking the onset of weight loss. The later degradation stage corresponds to the breakdown of the BMI network. BMI contains aromatic rings and imide groups, both of which exhibit high thermal resistance due to resonance stabilization and strong C-N/C=O bonding in the imide structure. Decomposition of such structures requires significantly higher thermal energy, which causes higher-temperature weight losses. This step dominates the thermal behavior

once the more labile aliphatic segments from DABA have decomposed. When compared to phenolic resins, which are widely used as high-temperature adhesives and coatings, the BMI/DABA 1/0.86 blend demonstrates superior thermal stability.

Phenolic resins typically show significant degradation due to cleavage of methylene bridges and phenolic hydroxyl decomposition. In contrast, the BMI/DABA blend maintains structural integrity well beyond this temperature, with only gradual weight loss until nearly 600 °C. This indicates that the BMI/DABA copolymer not only matches but exceeds traditional phenolic systems in high-temperature endurance, making it particularly attractive for aerospace and electronic applications where both thermal resistance and mechanical performance are critical. The detailed data are presented in Table 4.

Table 4. TGA results for BMI/DABA blends with different molar ratios compared to the phenolic

Sample	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)
BMI/DABA 1/0.86	391	450	598
BMI/DABA 1/0.77	383	425	572
BMI/DABA 1/1	375	408	560
Phenolic	285	310	490

Table 5 summarizes the curing temperatures and thermal stability of the present BMI resin with representative BMI-based resin systems reported in the literature. The comparison provides a broader context for evaluating the thermal characteristics of the investigated resin system and highlights the range of properties reported for BMI-based thermosetting resins. As summarized in Table 5, the present BMI resin exhibits curing temperatures comparable to those of representative BMI-based resin systems reported in the literature. The initial, peak, and final curing temperatures (170.1, 256.1, and 348.9 °C, respectively) fall within the typical range reported for conventional BMI resins, indicating similar curing behavior. The thermal stability of the present resin (T_{5%} = 391 °C in air) is lower than that of some high-performance BMI systems, particularly those containing additional heteroatoms such as phosphorus and oxygen,

which are known to promote char formation and enhance thermal resistance. Phosphorus-containing BMI systems generally exhibit improved flame retardancy and higher thermal stability due to the formation of thermally stable phosphate or phosphonate structures during degradation. Furthermore, ether linkages can influence the crosslink density and degradation pathway of the network.

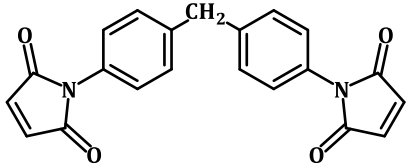
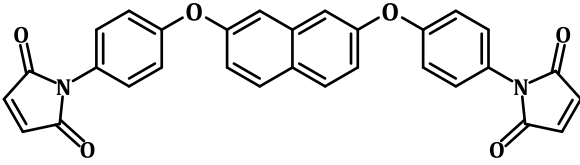
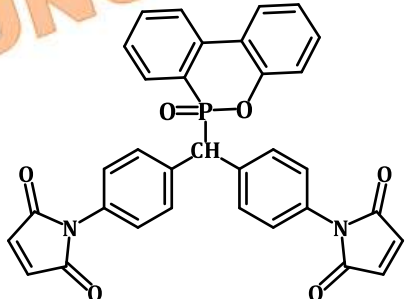
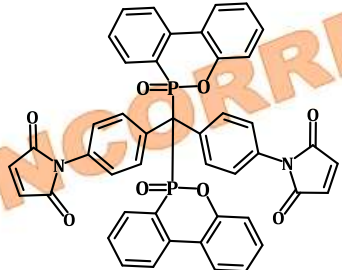
3.5. Oxyacetylene Ablation Test

The oxyacetylene ablation test provides an extreme evaluation of the thermal and thermo-oxidative stability of polymer matrix composites by subjecting them to very high heat flux and oxidative environments. BMI contains highly rigid aromatic backbones and thermally stable imide groups. The aromatic units confer strong π - π conjugation and high bond dissociation energies, while the imide rings provide exceptional thermal endurance due to resonance stabilization of the C=O and C-N bonds.

Under high-temperature oxidative conditions, these structural features resist bond cleavage and delay volatilization. Instead of undergoing rapid chain scission, BMI tends to form a stable carbonaceous char. This char layer acts as an insulating barrier, reducing oxygen diffusion and heat penetration into the bulk material, thereby protecting the underlying polymer and reinforcing fibers. The allyl groups participate in co-curing with the maleimide double bonds, leading to an interpenetrating, three-dimensional copolymer network.

This dense network structure enhances the thermal resistance by restricting segmental motion and delaying the onset of decomposition. The bisphenolic aromatic units in DABA contribute to thermal resistance. During thermal degradation, the aromatic fragments condense into stable polyaromatic structures, enhancing the integrity of the protective char layer under ablative conditions. The optimized 1/0.86 molar ratio ensures a balanced network. There is sufficient DABA to copolymerize efficiently with BMI and enhance thermal resistance, but not so much that excessive aliphatic segments compromise thermal resistance. This explains why this formulation showed the best results in ILSS, TGA, and now ablation performance.

Table 5. Comparison of the curing temperatures and thermal stability of the present BMI resin with published BMI-based resin systems

Structure	Ti (°C)	Tp (°C)	Tf (°C)	T5% (°C)	Ref.
	170.1	256.1	348.9	391, air	This work
	150	250	300	464.8, N2	[57]
	175	258.6	320	408.1, N2	[53]
	117.7	257.8	310.8	436.1, air	[58]
	117.7	257.8	311.6	427.5, air	[58]

However, phenolic degradation involves the breakdown of methylene bridges and the release of volatile byproducts such as CO, CO₂, and H₂O, which result in higher mass loss under severe thermal flux. In contrast, the BMI/DABA network produces a denser, more graphitized char structure with fewer volatiles, reducing overall mass loss during ablation.

The imide groups in BMI are significantly more resistant to thermal oxidation than the methylene linkages in phenolic systems, further enhancing stability. When combined with carbon fiber reinforcement, the BMI/DABA 1/0.86 resin not only adheres strongly to the fiber (as demonstrated by ILSS data) but also preserves fiber integrity during ablation. The synergy between the thermally stable matrix and carbon reinforcement thus accounts for the low mass loss of only 1.9%, a remarkable improvement over the phenolic composite. Table 6 shows the oxyacetylene ablation test results for this

composite. Figure 15 shows the image of a 40-layer fabricated composite before and after the oxyacetylene ablation test.

3.6. Interlaminar Shear Strength of BMI/DABA Composites

ILSS, a key parameter for assessing the mechanical performance of composites, was evaluated for the fabricated BMI/DABA composites with different molar ratios. The ILSS values, presented in Fig. 16 and summarized in Table 7, correspond to the maximum shear stress measured at 25 °C and at 78 °C, the latter representing a relevant high service temperature for advanced composites. Among the tested formulations, the BMI/DABA composite with a

Table 6. Oxyacetylene ablation test results for BMI/DABA 1/0.86 composite

Pre-test measurements		Post-test measurements		results		
Mass of the sample (g)	Back-side temperature (°C)	Mass of the sample (g)	Back-side temperature (°C)	Burn-back distance* (mm)	Percentage of mass loss (%)	Back surface temperature rise (°C)
141.9	27.5	139.2	60.9	1.69	1.9	33.4

*Burn-back distance: Distance from the original specimen edge to the ablated edge after flame exposure.

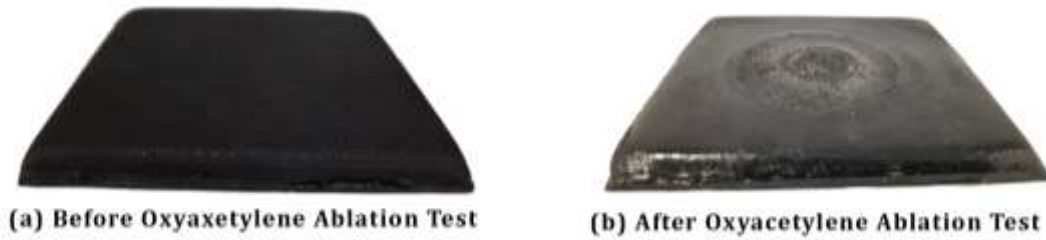


Fig. 15. Image of 40-layer composite in oxyacetylene ablation test

1/0.86 molar ratio exhibited the highest ILSS at both temperatures.

The superior ILSS of the BMI/DABA 1/0.86 composite can be attributed to the optimized curing characteristics and network architecture of the resin system. The TGA results indicate that this formulation achieves an appropriate balance between crosslink density and thermal stability, leading to a mechanically robust matrix capable of retaining its integrity under both room-temperature and elevated-temperature conditions. Such a network facilitates efficient stress transfer between the carbon fibers and the surrounding matrix, thereby enhancing the interlaminar shear performance of the composite.

According to Table 7, at 25 °C, the standard deviation ranges of the investigated formulations show partial overlap, particularly between the BMI/DABA 1/1 and BMI/DABA 1/0.86 composites, indicating that the observed differences should be interpreted with caution. In contrast, the separation between the BMI/DABA 1/0.86 and the DGEBA/m-PDA composites becomes much more pronounced at 78 °C, demonstrating the superior retention of interlaminar shear strength by the BMI/DABA system at elevated temperature. Although some overlap remains between the BMI/DABA formulations at 78 °C, the BMI/DABA 1/0.86 composite consistently exhibited the highest mean ILSS, confirming its favorable balance of thermal and mechanical performance.

In contrast, the equimolar BMI/DABA 1/1 formulation is expected to produce a highly crosslinked network that may exhibit increased brittleness due to restricted molecular mobility

and higher residual stresses. Conversely, the BMI/DABA 1/0.77 formulation contains a lower concentration of allyl groups, resulting in a reduced extent of copolymerization and a less homogeneous network structure, which is reflected in its comparatively lower thermal stability and ILSS.

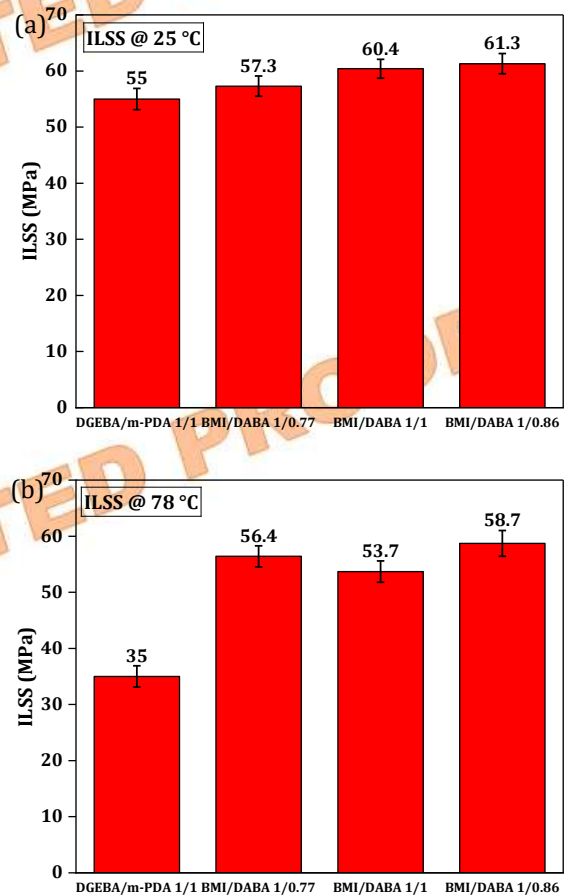


Fig. 16. ILSS values of composites prepared from the BMI/DABA, and DGEBA systems at (a) 25 °C, and (b) 78 °C

Table 7. ILSS results of BMI/DABA composites at 25 °C and 78 °C.

ILSS @ 25 °C							
Sample Name	No. 1	No. 2	No. 3	No. 4	No. 5	Ave	SD
BMI/DABA 1/1	57.9	59.3	60.4	61.4	62.9	60.4	1.7
BMI/DABA 1/0.86	58.6	60.3	61.3	62.5	63.7	61.3	1.8
BMI/DABA 1/0.77	54.6	56.3	57.3	58.4	59.9	57.3	1.8
DGEBA/m-PDA 1/1	52.2	53.9	55.0	56.2	57.7	55.0	1.9
ILSS @ 78 °C							
Sample Name	No. 1	No. 2	No. 3	No. 4	No. 5	Ave	SD
BMI/DABA 1/1	50.9	52.6	53.7	54.9	56.2	53.7	1.8
BMI/DABA 1/0.86	55.9	57.6	60.6	59.9	59.5	58.7	1.7
BMI/DABA 1/0.77	53.6	55.3	56.4	57.6	59.1	56.4	1.9
DGEBA/m-PDA 1/1	32.2	33.9	35.0	36.2	37.7	35.0	1.9

Therefore, the BMI/DABA 1/0.86 composition provides an optimum balance between network rigidity and toughness, resulting in improved thermal stability and interlaminar mechanical performance. Compared with the DGEBA/m-PDA composite, the BMI/DABA system exhibited superior ILSS retention at elevated temperature. Although the difference at room temperature was relatively small, the BMI/DABA composite maintained higher interlaminar shear strength at 78 °C, demonstrating the inherent thermal stability of the bismaleimide matrix. Unlike conventional epoxy resins, which undergo progressive softening as the service temperature approaches their glass transition temperature, the highly aromatic and thermally stable BMI/DABA network retains its load-bearing capability, thereby preserving efficient stress transfer across the fiber-matrix interface.

4. Conclusions

The systematic investigation of BMI/DABA blends has demonstrated that the incorporation of DABA into BMI resins significantly influences both curing behavior and thermal performance. DSC revealed that the presence of DABA reduces the melting and curing onset temperatures of BMI, owing to its disruptive effect on BMI crystallinity and the enhanced reactivity of its allyl groups, which facilitate earlier crosslinking. TGA analysis further confirmed that the BMI/DABA system with a 1/0.86 molar ratio achieves the highest thermal stability, exhibiting delayed weight-loss steps and superior char formation compared to other formulations and conventional high-temperature resins such as phenolics. ILSS measurements identified the same composition as the optimum formulation, reflecting its ability to form a dense, co-crosslinked network that enhances both thermal and mechanical performance. The outstanding thermal protection capability of this optimized system was validated by oxyacetylene ablation

testing, where the BMI/DABA (1/0.86) composite showed only 1.9% mass loss. This superior ablation resistance is attributed to the high aromatic content, thermally stable imide structures, and efficient char formation of the BMI/DABA matrix, which collectively protect the underlying carbon fiber and minimize erosion. Overall, the BMI/DABA 1/0.86 formulation offers a well-balanced combination of thermal stability, mechanical performance, and ablative resistance, surpassing traditional phenolic systems.

From a scientific perspective, this study provides new insights into the relationship between BMI/DABA composition, curing behavior, and the resulting thermal and mechanical properties, thereby contributing to the rational design of high-performance thermosetting resin systems. From a practical perspective, the optimized BMI/DABA composite shows strong potential as a matrix resin for high-performance carbon fiber composites in aerospace and thermal protection systems, where enhanced thermal stability, superior ablative resistance, and reliable structural integrity are required under extreme service conditions. Future work will focus on evaluating the long-term durability of the optimized BMI/DABA composite under extreme service conditions such as thermo-oxidative aging and moisture exposure, and investigating its compatibility with different reinforcement architectures for broader applications in advanced aerospace and thermal protection systems.

Finding Statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Conflicts of 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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