

Novel Bismaleimide Resins Modified by Allyl Compound Containing Liquid Crystalline Structure

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ABSTRACT: A novel allyl compound containing liquid crystalline structure, i.e., 4,4'-bis(4-allyloxy benzoic acid) phenyl ester (BAOBE), was synthesized. The chemical structure of BAOBE was characterized by Fourier transform infrared (FTIR) spectroscopy and ^1H NMR spectra, and the liquid crystalline properties were confirmed by polarized optical microscopy (POM). Besides, a series of modified bismaleimide (BMI) resins were prepared based on *N,N'*-4,4'-bismaleimidodiphenylmethane (BDM), BAOBE, and *O,O'*-diallyl bisphenol A (DABPA). The results of thermogravimetric analysis (TGA) indicate that the modified resins have excellent thermal stability with the highest temperatures for 5% weight loss above 438°C. The results of dynamic mechanical analysis (DMA) suggest that the glass transition temperature (T_g) of the modified resins are above 280°C. Besides, the introduction of BAOBE leads to a significant improvement in the flexural and impact properties of the modified BMI resins. Compared with the resin with only DABPA as a modifier, the highest flexural and impact strength can reach 156.2 MPa and 15.6 kJ/m², increased by 19.2% and 90.2%, respectively. © 2016 Wiley Periodicals, Inc. *Adv Polym Technol* 2016, 00, 21667; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21667

KEY WORDS: Bismaleimide, Mechanical properties, Modification, Novel allyl compound, Thermal properties

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Introduction

Bismaleimide (BMI) resins are an important class of thermosetting polymers with excellent thermal stability, radiation resistance, good mechanical properties, and outstanding dimensional stability characteristics. It can be used as high-temperature resistance insulation materials and matrix resins for advanced composites. However, the application of BMI resins in aviation, aerospace, electronics, and other fields has been limited

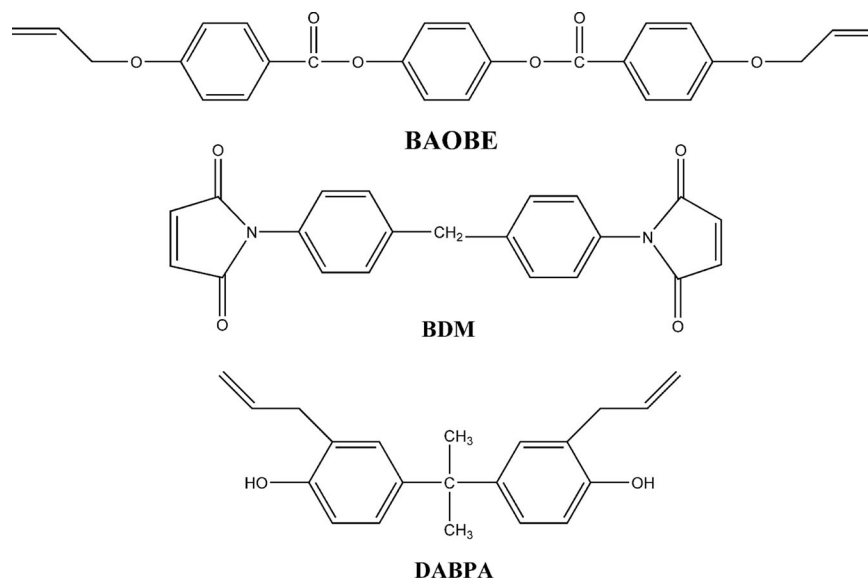


FIGURE 1. Chemical structures of materials used.

due to its poor toughness, which was caused by high cross-link density. Thus, many researchers have focused on the study to improve the toughness of BMI resins.¹⁻⁴

Numerous approaches have been developed to improve the toughness of BMI resins, such as the synthesis of novel BMI monomers with tailored molecular structure,⁵⁻⁹ copolymerization with allyl-terminated copolymers or aromatic diamines,¹⁰⁻¹⁴ blending modification with thermoplastic resins or liquid crystalline compounds, and so on.¹⁵⁻¹⁹ These methods can improve the toughness of BMI resins with a sacrificing of the thermal stability of resultant materials.²⁰ *O,O'*-diallyl bisphenol A (DABPA) modified BMI resin systems, whose prepolymers have lower softening point and higher solubility, have been developed successfully.^{21,22} However, these modified BMI resins are still lack toughness and cannot meet the required properties for advanced materials. Therefore, the BMI/DABPA resin systems need to be further improved.

In recent years, liquid crystalline polymers (LCPs) combining high cross-link density networks have been attracted wide attention as a new type of materials. During curing process, the incorporation of mesogens in thermoset networks and the use of new cross-linking reagents resulted in a network passing through a mesophase. The retained mesophase structure would increase the fracture toughness of the networks.^{23,24} Therefore, LCPs are expected to be applied as structural and self-reinforced materials. However, only a few liquid crystalline related to BMI were reported.

In this paper, we used the 4,4'-bis(4-allyloxy benzoic acid) phenyl ester (BAOBE) with the liquid crystalline property to modify DABPA/*N,N'*-4,4-bismaleimidodiphenylmethane (BDM) systems. With the unchanged molar ratio of allyl and maleimide double bond, we studied the effect of BAOBE and DABPA in different molar ratios on curing kinetics, dynamic mechanical properties, mechanical properties, and thermal stability of the modified resin systems.

Experimental

MATERIALS

P-hydroxy benzoic acid was purchased from Sinopharm Chemical Reagent (Beijing city, People's Republic of China). Bromopropene was purchased from Changzhou Xinhua Active Material Institute (Changzhou city, People's Republic of China). Quinol was purchased from Tianjin Damao Chemical Reagent (Tianjin city, People's Republic of China). BDM and DABPA were purchased from LaiYu Chemical (Laizhou city, People's Republic of China). The structures of BAOBE, DABPA, and BDM are shown in Fig. 1.

SYNTHESIS OF 4,4'-BIS(4-BASIC CARBOXYLIC ACID ALLYLOXY) PHENYL ESTER

Figure 2 shows the synthetic route of BAOBE. The BAOBE was synthesized according to the method reported earlier.²⁵ A mixture of 4-hydroxybenzoic acid (13.80 g, 0.1 mol), ethanol (100 mL), aqueous solution of NaOH (20 wt%, 30 mL), a bit of KI and allyl bromide (10 mL) was stirred at 75°C for 24 h. After that, the resulting solution and hydrochloric acid were poured into cool water to get white precipitate; then, the white precipitate was recrystallized several times with ethanol to obtain 4-allyloxybenzoic acid. Next, the mixture of 4-allyloxybenzoic acid (8.90 g, 0.05 mol), toluene (80 mL), and thionyl chloride (15 mL) was stirred at 60°C for 4 h under nitrogen. After evaporating the solvent, slight yellow oil was obtained and further reacted with the mixture of quinol (2.75 g, 0.025 mol), tetrahydrofuran (80 mL), and triethylamine (7 mL) at 60°C for 24 h. Finally, the resulting mixture was filtered while hot and the filtrate separated out white crystalline 4,4'-bis(4-basic carboxylic

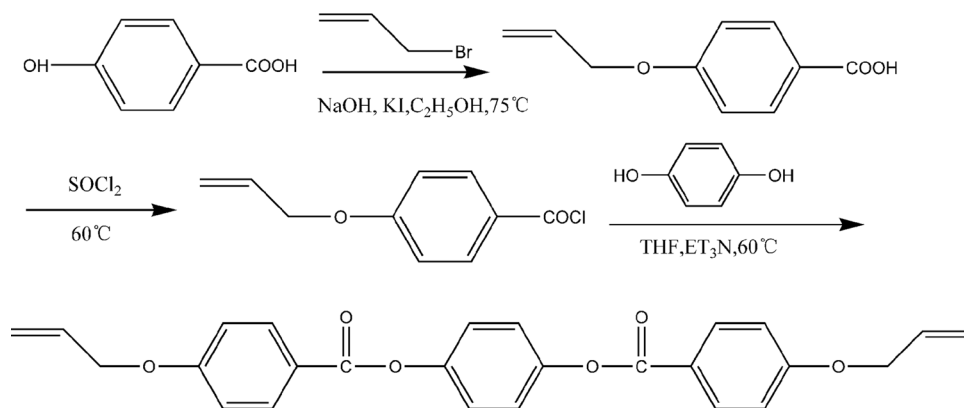


FIGURE 2. Synthetic route of BAOBE.

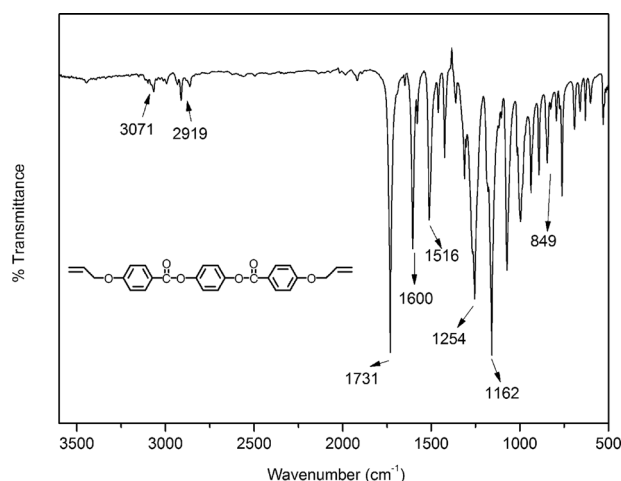
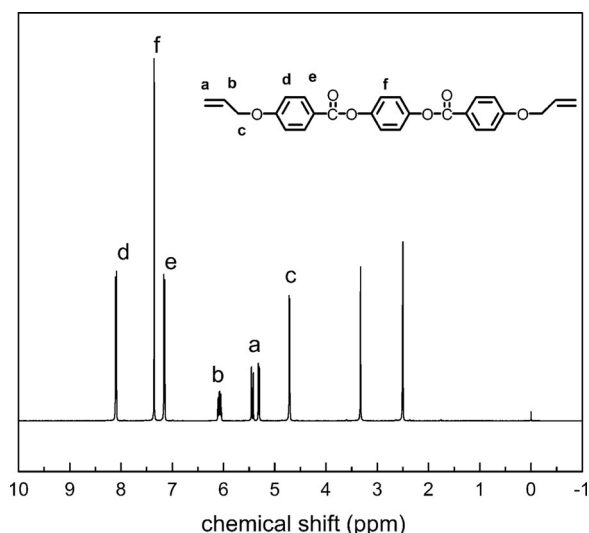


FIGURE 3. FTIR spectra of 4,4'-bis(4-allyloxy benzoic acid) phenyl ester.

FIGURE 4. ^1H NMR spectra of 4,4'-bis(4-allyloxy benzoic acid) phenyl ester.

acid allyloxy) phenyl ester after cooling. The total yield of three steps is 73.2%.

PREPARATION OF MODIFIED BMI RESINS

A mixture of purified BAOBE and DABPA was melted at 165°C , and then a certain amount of BDM was added in batches with stirring continuously at 145°C until the mixture became red-brown transparent liquid. The prepared transparent liquid was poured into a preheated mold and then placed in a vacuum oven to conduct degassing for 50 min. Finally, the prepolymers were cured by stepwise heating following: $180^\circ\text{C}/1\text{ h}$, $230^\circ\text{C}/2\text{ h}$, and $250^\circ\text{C}/6\text{ h}$. After the stepwise heating, the samples were cooled to room temperature slowly, then carved and polished to an appropriate size for testing. In modified resin systems, the total molar ratio of allyl and maleimide double bond was 0.87:1, and the molar ratio of BAOBE and DABPA was 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, and 6:4, marked as BAO0, BAO1, BAO2, BAO3, BAO4, BAO5, and BAO6, respectively.

CHARACTERIZATION

Infrared spectroscopy (FTIR) spectra were detected on a Nicolet-20DXB infrared spectrometer using KBr pellets in the region of $4000\text{--}400\text{ cm}^{-1}$. The signal-averaged over 32 scans.

Nuclear magnetic resonance (^1H NMR) were recorded on a Varian INOVA NMR spectrometer. Tetramethylsilane (TMS) was used as an internal standard in $(\text{CD}_3)_2\text{SO}$ for ^1H NMR measurements. The frequency of observation was 400 MHz.

Polarized optical microscopy (POM) graphs were recorded by Nikon OPTIPHOT₂-POL. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 204 instrument from room temperature to 380°C with the heating rate of 5 K/min, 10 K/min, 15 K/min, and 20 K/min under a flow of nitrogen (20 mL/min).

Dynamic mechanical analysis (DMA) was performed with a single-cantilever blending mode using TA Instruments Q800 DMA with amplitude of $20\text{ }\mu\text{m}$ from 50°C to 380°C . The driving frequency was 1.0 Hz, and the temperature ramp rate was 3 K/min. The dimensions of each specimen were $(35 \pm 0.02)\text{ mm} \times (6 \pm 0.02)\text{ mm} \times (2 \pm 0.02)\text{ mm}$.

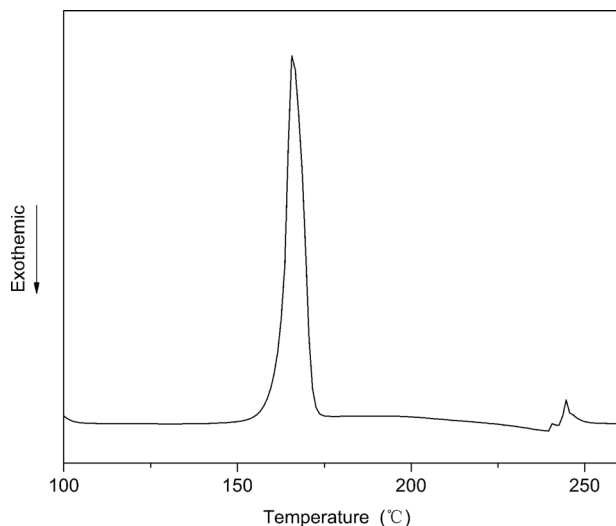


FIGURE 5. DSC curves of 4,4'-bis(4-allyloxy benzoic acid) phenyl ester.

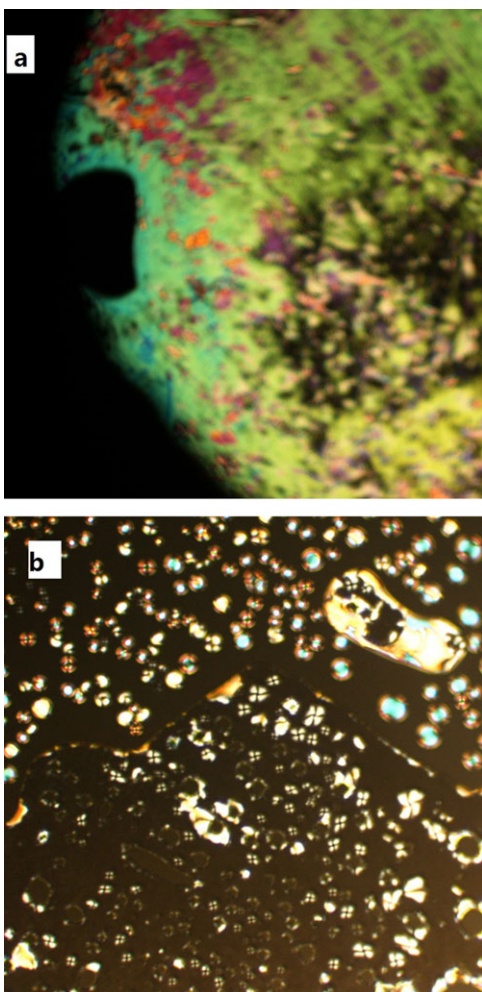


FIGURE 6. Polarizing microscope images of 4,4'-bis(4-allyloxy benzoic acid) phenyl ester.

Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer TGA-7 thermal analyzer from 25 to 800°C with the heating rate of 20 K/min under the purified nitrogen flow rate of 60 mL/min.

The flexural property was measured according to GB/1402-79 standard (rectangular specimen: 80 mm × 10 mm × 4 mm, span/depth = 16) of China with the three-point bending test mode. The samples were tested at a constant crosshead movement rate of 2 mm/min at room temperature. At least five samples for each system were tested, and the average value was taken as the tested value.

The fracture toughness of the cured BMI resins was evaluated from the impact strength according to ASTM D5942-96 standard. The tests were performed on the Charpy impact testing machines (XCJ-4).

The rupture morphologies of the resins were observed by a scanning electron microscopy (SEM; QUANTA 450, FEI) at an accelerating voltage of 20 kV.

Results and Discussion

SYNTHESIS AND CHARACTERIZATION OF 4,4'-BIS(4-ALLYLOXY BENZOIC ACID) PHENYL ESTER

Figures 3 and 4 show the FTIR spectroscopy and ^1H NMR of BAOBE. FTIR (KBr; cm^{-1}): 3071 ($=\text{C}-\text{H}$), 2919 ($\text{C}-\text{H}$), 1731 ($\text{C}=\text{O}$), 1600, 1516 ($-\text{Ar}$), 1254 ($\text{CH}_2-\text{O}-\text{Ar}$), 1162 ($\text{C}-\text{O}$), 849 ($p-\text{Ar}$). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$; δ , ppm): 8.10 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.36 (s, 1H, Ar-H), 7.15 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.08 (m, 1H, $-\text{CH}-$), 5.44 (d, 2H, $\text{CH}_2=\text{CH}$), 4.72 (d, 2H, $\text{CH}-\text{CH}_2-\text{O}-$).

LIQUID CRYSTALLINE BEHAVIOR OF 4,4'-BIS(4-ALLYLOXY BENZOIC ACID) PHENYL ESTER

The liquid crystalline behavior of 4,4'-bis(4-allyloxy benzoic acid) phenyl ester was examined using DSC and POM. Figure 5 shows the DSC curves of the BAOBE with a constant heating rate of 10 K/min in the temperature range between 100°C and 260°C. As shown in Fig. 5, a strong endothermic peak at 165.8°C was observed, which could be assigned to the melting of BAOBE; besides a blunt peak was observed at around 244.6°C, which indicated that the phase behavior of BAOBE changed from the liquid crystalline phase to the isotropic phase. The similar behavior was also found by Lu and co-workers.²⁶

Figure 6 shows the POM photographs of BAOBE at different temperatures. The BAOBE began to melt when the temperature reached 166°C, and it entered the liquid crystalline phase (Fig. 6a) when the temperature was up to 213°C. The texture color changed with the increasing temperature and disappeared at 245°C. With the decrease of temperature, the isotropic state changed to the liquid crystalline phase and the texture of BAOBE exhibited obvious birefringence (Fig. 6b, 200°C). The BAOBE began to crystallize when the temperature dropped further. Birefringence was only observed during the cooling process, and each phase transition temperature was consistent with the

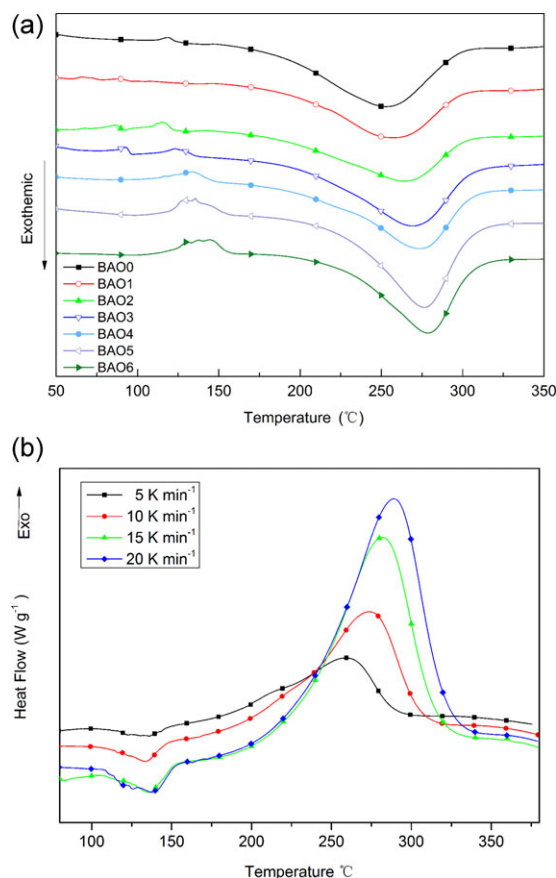


FIGURE 7. DSC curves of the (a) modified BMI resins (b) BAO4 resin at different heating rates.

results obtained by DSC, which confirmed that BAOBE was a typical monotropic nematic liquid crystalline.

THE DSC ANALYSIS OF THE MODIFIED BMI RESINS

The melting transition temperature (T_m) and the curing reaction temperature of the BMI are important parameters to the materials processing and preparation, which can be effectively characterized by DSC. The DSC curves of the modified BMI resins with BAOBE and DABPA in different molar ratios at a heating rate of 10 K/min are shown in Fig. 7a, and the values of curing characteristics are listed in Table I. The modified resin systems displays similar curing behavior with one main exothermic peak around 260–280°C and a shoulder peak at a lower temperature around 100–120°C, which indicates different cure regimes.

TABLE I. DSC Curing Characteristics of the Modified BMI Resins

Samples	BAO0	BAO1	BAO2	BAO3	BAO4	BAO5	BAO6
T_i^a (°C)	194.8	200.3	193.6	211.5	228.4	228.7	231.5
T_p^b (°C)	253.1	257.0	264.7	268.9	273.5	276.2	278.4
ΔH^c (J/g)	130.3	219.1	206.1	240.4	238.4	291.0	244.9

^aThe initial curing temperature.

^bThe exothermic transition temperature.

TABLE II. DSC Curing Characteristics of the BAO4 at Different Heating Rates

Sample	B (K/min)	T_i^a (°C)	T_p^b (°C)	T_f^c (°C)
BAO5	5	197.6	259.3	287.4
	10	228.4	273.5	305.0
	15	229.7	281.9	314.2
	20	241.2	289.0	321.3

^aThe initial curing temperature of BAO4.

^bThe exothermic transition temperature of BAO4.

^cThe final curing temperature of BAO4.

The shoulder peaks of 100–120°C are attributed to the Ene reaction between allyl and maleimide group, and the exothermic peaks located at 260–280°C is mainly due to the Diel–Alder reaction, thermal rearrangement, thermal cross-linking, and dehydration of the hydroxyl.^{27,28} Meanwhile, it is observed from the figure that the endothermic peaks appears at 140–150°C; this may be ascribed to the melting process of the Ene product. As we can see, the curing exothermic peak shifts gradually to higher temperature with the increasing content of BAOBE. This phenomenon can be explained from two perspectives. On the one hand, the allyl groups of BAOBE with the electron-withdrawing substitutes decrease the electron density in C=C double bonds, which indicates that BAOBE has less reactive than DABPA in the curing reaction process. On the other hand, the increasing concentration of BAOBE, which contains the long-chain and rigid rod liquid crystalline structure, results in the increasing viscosity of the systems, and the active groups have to overcome more resistance to move. As a result, the curing exothermic peaks shift to higher temperatures. In addition, as shown in the figure, the curing exothermic peak becomes sharper with the incorporation of a liquid crystalline modifier, demonstrating that the curing rate is increased due to the formation of the mesogenic phase at curing temperature.¹⁷

THE CURING KINETICS OF THE MODIFIED BMI RESINS

Curing reaction conditions will affect many properties of thermosetting resin material, such as modulus, strength, glass transition temperature, and so on. Besides, the curing reaction is constrained by the reaction rate; therefore, it is necessary to study the kinetic parameters especially the apparent activation energy and reaction order. In this section, we analyzed the DSC curves of BAO4 resin at different heating rates to calculate apparent activation energy and reaction order of the curing reaction. The DSC curves of BAO4 resin at different heating rates are shown in Fig. 7b, and the results are listed in Table II.

The curing exothermic peaks move to higher temperature with the increase of the heating rate. It is allowing for the curing reaction is not only affected by thermodynamics but also controlled by kinetics. Molecular chains in the curing system have enough time to move at a low heating rate, and active groups have a greater probability to occur collision, thus the curing reaction can occur at a lower temperature. Conversely, if the heating rate is too fast, the system will lack sufficient time to absorb external energy, thus the curing reaction occurs at a higher temperature.

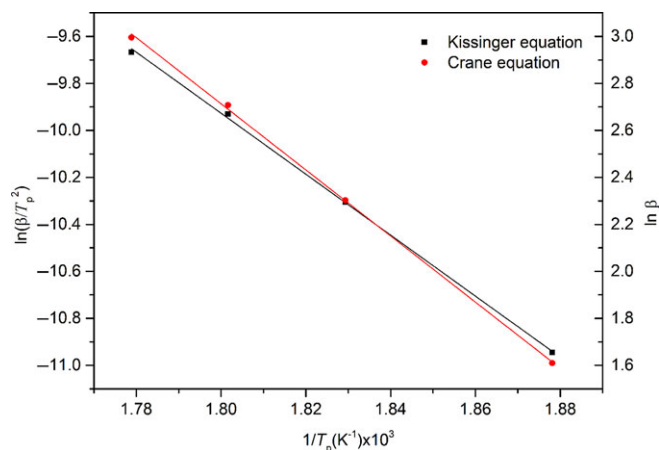


FIGURE 8. Plots of $\ln(\beta/T_p^2)$ and $\ln(\beta)$ versus $1000/T_p$ of BAO4.

The energy of activation (E_a) and order of reaction (n) for the curing reaction of BAO4 resin were calculated from DSC measurement by employing the Kissinger equation and Crane equation.^{29,30} Both methods use nonisothermal integral, we only need to determine the exothermic peak temperature at the different heating rates without determining the curing mechanism.

Kissinger equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} + \ln \frac{AR}{E_a}$$

Crane equation:

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{E_a}{nR}$$

where E_a is the activation energy, R is the gas constant, β is the heating rate, and T_p is the exothermic peak of the corresponding β . The kinetic plots are shown in Fig. 8. On the basis of the Kissinger and Crane equations, the E_a value was gained from the slope of the graph of $\ln(\beta/T_p^2)$ versus $1/T_p$ according to the Kissinger equation, and the order of reaction (n) value was obtained from the slope of the graph of $\ln \beta$ versus $1/T_p$ according to Crane equation. The curing reaction kinetic parameters are shown in Table III by calculation.

As shown in Table III, the E_a of the curing reaction is slightly higher than previously reported for around 80 kJ/mol²⁹, which can be attributed to the long-chain and rigid rod liquid crystalline structure of BAOBE. The rigid rod liquid crystalline structure can result in the increasing viscosity of the systems, and the active groups must need enough energies to overcome more resistance to move, as a result, the E_a becomes higher.

TABLE III
Kinetic Parameters of BAO4

Sample	E_a (kJ/mol)	A (min ⁻¹)	n
BAO4	107.873	8.81×10^9	0.9222

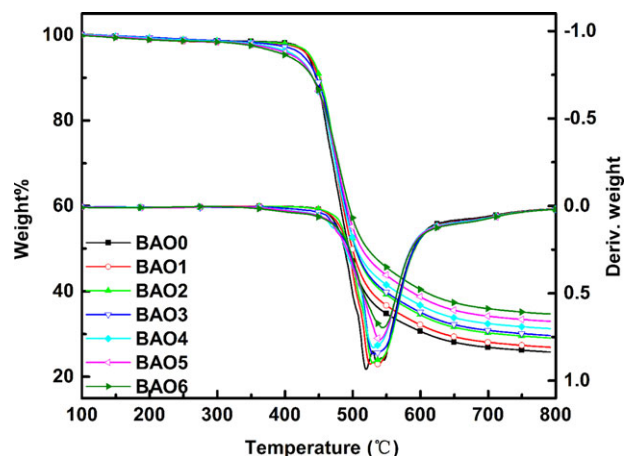


FIGURE 9. TGA and DTG curves of modified BMI resins.

THE THERMAL PROPERTIES OF THE MODIFIED BMI RESINS

Figure 9 shows the thermogravimetric curve (TG) and differential thermogravimetric curve (DTG) of modified resins at a heating rate of 20 K/min in nitrogen, and the thermal decomposition characteristic parameters are listed in Table IV. As can be seen, the modified BMI resins display similar behavior of weight loss, and thermal decomposition mechanism unchanged with the different proportions of BAOBE. On the one hand, the temperature of initial decomposition ($T_{5\%}$) tends to increase first and then decrease. The rigid rod liquid crystalline structure of BAOBE increases the rigidity of the cured resins, which leads to the increase of $T_{5\%}$. Besides, the symmetric structure of BAOBE also can improve thermal stability of modified BMI resins. However, when the proportion of BAOBE is excessive, the molecular chains become larger, and the lower cross-link density of cured resins results in the relative decrease of $T_{5\%}$. On the other hand, although the temperature of initial decomposition decreases, the modified BMI resins exhibit a slower rate of weight loss and higher residual weight with the increasing BAOBE. The similar phenomena was also been referred in a previous study,³¹ where they thought the slower rate of weight loss and residual weight might be attributed to the presence of more aromatic structure. As can be seen from Table IV, when the proportion of BAOBE is up to 20% in a modifier, the thermal stability with the

TABLE IV
Parameters for Thermal Decomposition of Cured Modified BMI Resins

Sample	$T_{5\%}$ ^a (°C)	$T_{10\%}$ ^b (°C)	T_{max} ^c (°C)	RW ^d (%)
BAO0	428	440	460	26.9
BAO1	435	449	474	28.1
BAO2	438	451	470	30.3
BAO3	427	447	480	30.9
BAO4	417	441	469	32.5
BAO5	414	441	477	34.2
BAO6	405	441	481	36.0

^aThe temperature for 5% weight loss.

^bThe temperature for 10% weight loss.

^cThe temperature corresponding to the maximum rate of weight loss.

^dThe residual weight percentage at 700°C.

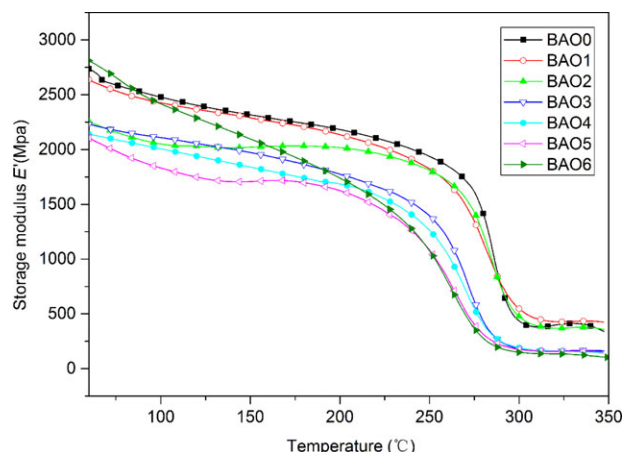


FIGURE 10. DMA spectra of modified BMI resins.

temperatures for 5% weight loss is above 438°C and the residual weight of the modified resins at 700°C is more than 30%, which displays excellent thermal stability compared with the modified resin that only used DABPA.

THE DMA ANALYSIS OF THE MODIFIED BMI RESINS

The thermal mechanical property of the modified BMI resins was analyzed by DMA spectrum as shown in Figures 10 and 11, and the results are listed in Table V. As we can see, in the glassy state (60°C), the storage modulus (E') tends to decrease at first and then increase with the addition of BAOBE. Under rubbery state (340°C), segment begins to move, the cross-link density becomes a major factor to impact the storage modulus E' .³² The storage modulus E' has a slight increase at first, demonstrating that the decreasing cross-link density is not obvious and the rigid units play a great role in maintaining the high modulus when a small proportion of BAOBE added. The motion of segment is strongly restricted by the rigidity of mesogenic units, which leads to the increase of the storage modulus E' . However, when the BAOBE is added further, the cross-link density is reduced obviously; therefore, the storage modulus E' decreases gradually.

Loss tangent $\tan \delta$ is caused by hysteresis phenomenon, the peak size reflects the size of internal friction when a polymer

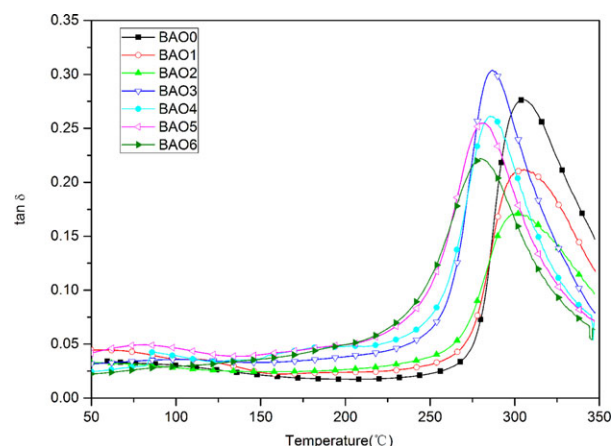


FIGURE 11. DMA spectra of modified BMI resins.

TABLE V
DMA Characteristics of the Modified BMI Resins

Sample	Storage Modulus, E' (MPa)		$\tan \delta$	
	60°C	340°C	T_g (°C)	Peak Value
BAO0	2736	389	311	0.270
BAO1	2636	434	305	0.220
BAO2	2255	376	302	0.172
BAO3	2231	166	287	0.304
BAO4	2139	158	285	0.262
BAO5	2104	152	281	0.255
BAO6	2811	117	280	0.222

occurs strain in alternating stress, and the peak temperature corresponds to the glass transition temperature (T_g). In addition, the morphology of a material can be indicated from the sharpness of peak. In the case of a compatible blend, the $\tan \delta$ temperature plot generally displays a single sharp peak, whereas for a partially compatible system, the plot always shows a broad peak or multiple peaks.^{33,34} As can be seen from Fig. 11, all of the cured BMI resins exhibit a single sharp $\tan \delta$ peak, indicating that these modified BMI resins may have a monophasic structure. On the other hand, the temperature at the maximum of $\tan \delta$ peak decreases gradually, which indicates that the T_g decreases with the increasing content of BAOBE. The result can be explained by the decrease in the cross-link density. Although the increased rigid rod liquid crystalline structure of network has a positive effect on the T_g , the decrease of the cross-link density plays a dominant role obviously. As a result, the incorporation of BAOBE has a negative effect on the values of T_g .

THE MECHANICAL PROPERTIES OF THE MODIFIED BMI RESINS

Figure 12 shows the relationship between the flexural property of cured modified BMI resins and the proportion of BAOBE. As we can see, the flexural modulus increases gradually whereas the flexural strength increases first and then decreases with the increase of BAOBE. The increased rigidity contributed

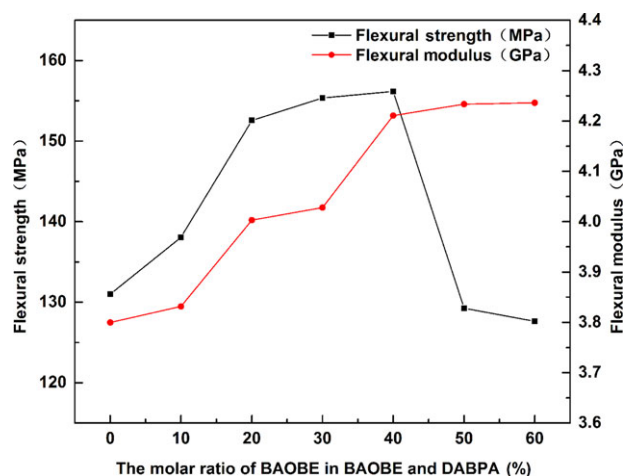


FIGURE 12. Flexural property of modified BMI resins with different BAOBE contents.

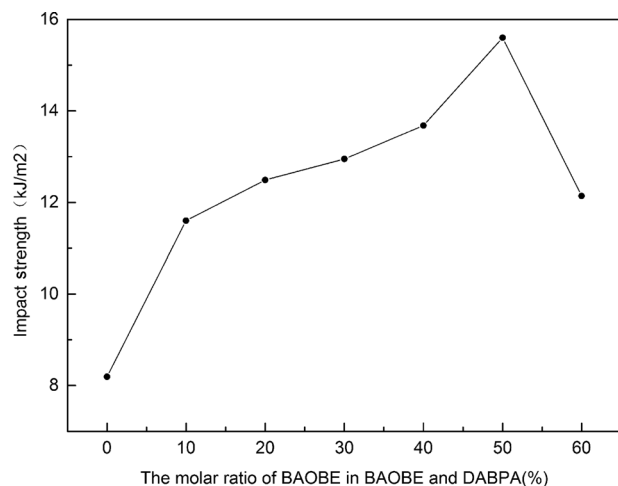


FIGURE 13. Impact strength of modified BMI resins with different BAOBE contents.

by the liquid crystalline-rod is responsible for the enhanced modulus and strength. However, when the molar ratio of BAOBE is above a certain value the viscosity of the modified resin increases prominently during curing process. Consequently, the defects of material such as air bubbles or holes would be formed easily. The reduced flexural strength is mainly due to the present of the defects. When the molar ratio of BAOBE and DABPA is 4:6, the flexural strength reached 156 MPa, and increased by 19.2% compared with the resin that only used DABPA as a modifier.

Figure 13 shows the relationship between impact strength of cured modified BMI resins and the proportion of BAOBE. As can be seen from the figure the impact strength increases at first and then decreases with the enhancing BAOBE content. The increased impact strength might be explained from two aspects. On the one hand, as mentioned above, adding BAOBE can decrease the cross-link density of the cured network, and the cross-link density has a great effect on the toughening.³⁵ On the other hand, the liquid crystalline phase would separate from the matrix in the form of microfibrs with a very high aspect ratio after curing, and the high rigidity as well as the molecular packing of liquid crystalline domains would act as crack stoppers, which prevent the propagations of cracks and increase the absorbed energy.^{36,37} However, when the proportion of BAOBE is too much, the increasing viscosity of the resins would result in the defects of material during the curing process, thus, the impact

TABLE VI
Mechanical Properties of Modified BMI Cured Resins

Sample	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (kJ/m ²)
BAO0	131.0	3.80	8.19
BAO1	138.0	3.83	11.60
BAO2	152.6	4.00	12.49
BAO3	155.4	4.03	12.95
BAO4	156.2	4.21	13.68
BAO5	129.3	4.23	15.60
BAO6	127.6	4.24	12.14

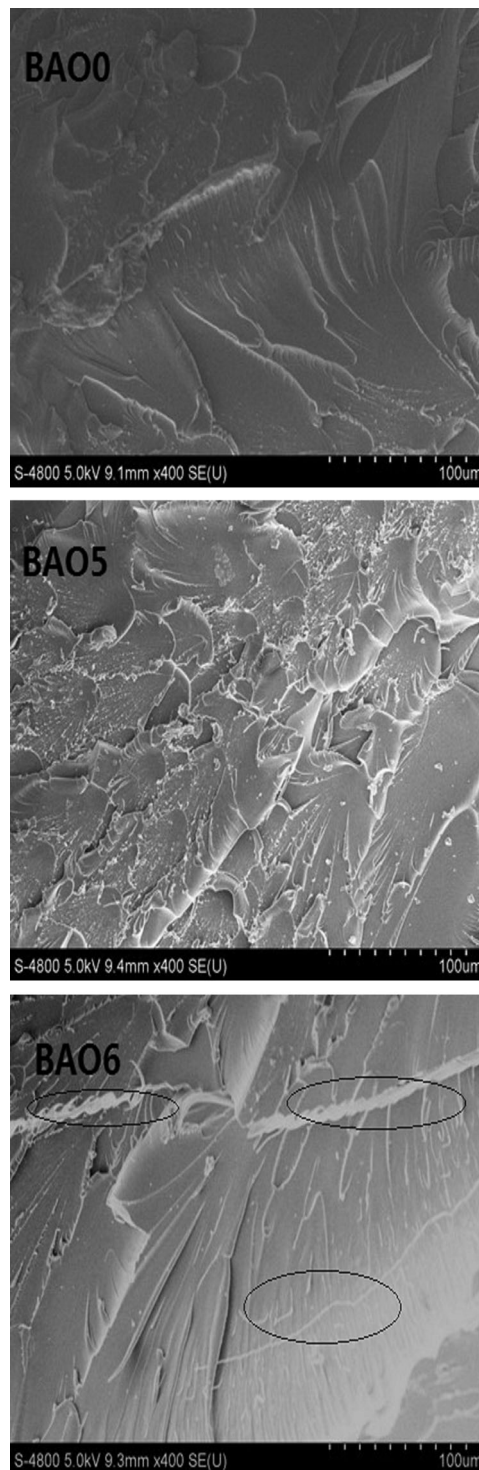


FIGURE 14. SEM images of modified BMI cured resins.

strength begins to decrease. When the molar ratio of BAOBE and DABPA is 5:5, the impact strength reached 15.6 kJ/m², increased by 90.5% compared with the resin that only used DABPA as a modifier. The parameters of mechanical properties are listed in Table VI.

Figure 14 shows the SEM image of fracture surfaces for the cured resins. As we can see, the fracture surface of the BAO0

system is smooth, and the cracks are developed forward to a single direction; hence, the fracture mode tends to be brittle fracture. However, the fracture surfaces of modified BAO5 resin becomes rough and exhibits more complicated crack propagations, which suggest that the fracture mode tends to be ductile fracture. And some crazes presented on the fracture surface of the BAO6 system are observed. This may be another evidence for the presence of the defect.

Conclusions

In our study, a novel allyl compound containing liquid crystalline structure was synthesized, and a series of modified BMI resins were prepared and investigated based on different molar ratio of BAOBE and DABPA. BMI resins modified with the BAOBE have a higher curing rate, and the modified BMI cured resins have excellent thermal stability with the highest temperatures for 5% weight loss above 438°C and glass transition temperature above 280°C. Besides, the introduction of BAOBE improves the flexural and impact property of the modified BMI resins significantly. Compared with the BMI resin that only used DABPA as a modifier, the highest flexural and impact strength can reach 156.2 MPa and 15.6 kJ/m², increased by 19.2% and 90.2%, respectively. In conclusion, the synthesized BAOBE may be a promising toughening agent for the modification of BMI/DABPA systems. And it can be speculated that similar allyl compound containing liquid crystalline structure will also have a positive effect on the toughening of BMI resins.

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