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ORIGINAL PAPER

Study on the copolymers of silicon-containing arylacetylene resin and acetylene-functional benzoxazine

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Abstract An acetylene-functional benzoxazine (AFBEN) which was used to modify poly(dimethylsilyleneethynylenephenyleneethynylene) (DMSEPE) was synthesized by a solventless procedure. The modified resins (DMSEPE/AFBEN) were obtained by blending DMSEPE and AFBEN in different amount. The thermopolymerization of DMSEPE/AFBEN resins were investigated by DSC technique. The dynamic mechanical analysis showed that the storage modulus (*E*) of the cured DMSEPE/AFBEN resin containing less than 30 wt% AFBEN did not decrease at the temperature lower than 500 °C. When the AFBEN loading increased from 20 to 100 wt%, a decrease in glass transition temperature from 523 to 342 °C was observed. The thermal stability of the cured DMSEPE/AFBEN resins was determined by thermogravimetric analysis (TGA) in N_2 and air. The TGA results showed the cured DMSEPE/AFBEN resins had good thermal stability. The carbon fiber (T700) reinforced DMSEPE/AFBEN composites exhibited excellent mechanical properties (flexural strength: 1,694 MPa) at room temperature and high strength remaining of 76% at 300 °C.

Keywords Silicon-containing arylacetylene resins · Acetylene-functional benzoxazine · Thermal property · High performance resin · Advanced composite

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Introduction

The silicon-containing arylacetylene resin (SCAAR) composed of [$-SiR_2-C\equiv C-Ar-C\equiv C-$] ($R =$ alkyl or phenyl) units possess excellent thermal stability after curing. The SCAARs have already shown potential applications as ceramic precursors, heat-resistant materials and matrix of advanced polymer composites in aerospace and astronautics [1–5]. Poly(phenylsilylene)ethynylene-1,3-phenyleneethynylene (called as MSP) was prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of magnesia base catalysts. The decomposition temperature at 5% weight loss and residue at 1,000 °C of the cured MSP was 860 °C and 94%, respectively [6–9]. Poly[silyleneethynylenephenyleneethynylene] terminated with phenylacetylene (BLJ) with high thermal stability was prepared by the condensation of dichlorosilane and a mixture of diethynylbenzene and phenyl acetylene [10, 11]. In our previous study, poly(dimethylsilyleneethynylenephenyleneethynylene) (DMSEPE) terminated with phenylacetylene which could cure at the temperatures above 233 °C was synthesized and showed high heat-resistance and high char yield [12]. The major advantages of SCAARs included no volatility during curing, high decomposition temperature, high char yield after pyrolysis and high radiation resistance. However, SCARR application was limited by its brittleness, shrinkage during curing and poor interface adhesion with reinforcements in composites.

Polybenzoxazine was a recently developed class of thermosetting resins, which cured via a ring-opening polymerization to form a crosslinking network structure with the Mannich Bridge ($-CH_2-R-CH_2-$). During the curing process of polybenzoxazine resin, no byproducts were released and the volume shrinkage was very low. Polybenzoxazine also possessed many fascinating characteristics such as excellent mechanical properties, low water absorption, high glass transition temperature and high thermal stability, for which a possible explanation was the formation of extensive hydrogen-bonding networks [13]. To further improve the thermal properties, ethynyl [14], propargyl [15], and allyl group [16] have been introduced into the polybenzoxazine resins, which would form highly crosslinking network structures after cure. Thus thermal decomposition temperature and char yields of the polybenzoxazines would have significantly risen.

One apparent method to derive a new kind of resins both with high thermal stability and high mechanical property was to blend SCAAR and polybenzoxazine resin. Such blends could possibly benefit from the good physico-chemical characters of the two resins.

This study focused on investigating novel high-performance blend resins made of a SCAAR (DMSEPE) and an acetylene-functional benzoxazine (AFBEN). The thermal property of modified DMSEPE resins with the AFBEN was characterized by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The fiber reinforced composites were prepared and characterized.

Experimental

Materials

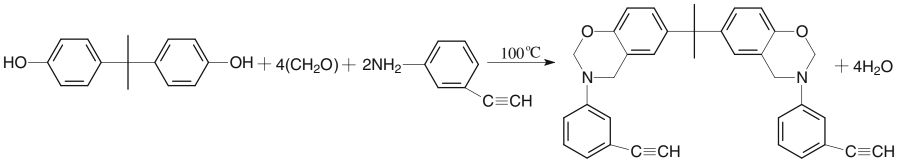
3-Aminophenylacetylene (Jiaozhou Fine Chemical Company) was freshly distilled prior to use. Chloroform, sodium hydroxide, bisphenol A, and paraformaldehyde (Shanghai No. 1 Reagent Factory) were used as purchased. DMSEPE was synthesized in our lab according to literatures [17, 18]. The reinforcement material was carbon fiber (T700–12K).

Instrumentation

Infrared spectra were recorded on Nicolet Magna 550 and the number of scans to acquire IR spectrum was 32. ^{1}H-NMR analyses were carried out on a Bruker AVANCE 500 (500 MHz) spectrometer. TGA was conducted on a METTLER TGA/SDTA 851 in nitrogen with a heating rate of 10 °C/min. DMA was carried out on a NETZSCH DMA 242 analyzer operating in the double-cantilever mode at the temperatures from 30 to 530 °C at the frequency of 1 Hz with a programmed heating rate of 3 °C/min. The sample dimension of DMA was $10 \times 5 \times 3$ mm^3. The flexural property of a composite was measured with a Shimadzu AG-50kNE universal tester and MTS Alliance RF/100 tester (USA) and the crosshead speed of the flexural test was 2 mm/min according to China Standard GB 3356. The sample dimension was $80 \times 12.5 \times 2$ mm^3. The oxyacetylene flame test was performed according to China Standard GJB323A-96 on the oxyacetylene ablation equipment. The pressure and flux of acetylene were 0.095 MPa and 1.116 m^3/h, and for oxygen 0.4 MPa and 1.512 m^3/h, respectively. The temperature of the oxyacetylene flame was measured using an optical pyrometer and reached as high as 2,800 °C. The dimension of an ablative sample dimension was Φ 30×4 mm^2.

Preparation of an acetylene-functional benzoxazine resin

An AFBEN resins was synthesized by a solventless procedure (Scheme 1) [14]. A total of 22.8 g bisphenol A (0.1 mol), 12.0 g paraformaldehyde (0.4 mol) and 23.4 g 3-aminophenylacetylene (0.2 mol) were added into a 100 ml flask equipped with a condenser, a thermometer, gas bypass and a stirrer. The reactants in the flask were kept at 100 °C for 20 min (Scheme 1). The crude reaction product was dissolved in chloroform and washed with 3 N NaOH solution three times and then rinsed with deionized water till pH of the washing water arrived at 7.0. The



Scheme 1 Synthesis of an acetylene-functional benzoxazine

chloroform solution was dried over sodium sulfate and then the solvent chloroform was removed. The resin was obtained in 86.2% yield, ^{1}H-NMR ($CDCl_3$, 500 MHz): δ4.58 (s, O–CH_2–N), 5.30 (s, Ar–CH_2–N), 3.03 (s, C$\equiv$C–H), 6.70–7.22 (m, Ar–H). FTIR (KBr): ν_{max} 1,225 cm^{-1} (C–O–C, asymmetric stretching), 1,331 cm^{-1} (CH_2 wagging), 2,102 cm^{-1} (C$\equiv$C, stretching vibration) and 3,271 cm^{-1} ($\equiv$C–H, stretching vibration).

Preparation of DMSEPE/AFBEN resins

Appropriate quantities of DMSEPE and AFBEN were charged into a three-necked flask with a mechanical stirrer, a condenser and a gas bypass. The mixture was heated to 130 °C, and maintained at this temperature with stirring till a homogenous liquid was obtained. A blend of DMSEPE and AFBEN resin (noted as DMSEPE/AFBEN) was obtained. The resins were cured in an oven under air at 150 °C for 1 h, 170 °C for 2 h, 210 °C for 2 h and 250 °C for 4 h.

Preparation of composites

A unidirectional prepreg was prepared from carbon fiber and a resin solution with a 40 wt% DMSEPE/AFBEN resin in THF by using a drum winding technique. Carbon fiber T700 was used as a reinforcement. The prepreg was dried on the mandrel to strip off the solvent. After removal from the drum, the resultant prepreg had good tack and drape. The prepreg was laid unidirectionally, plied stack, and further dried in a vacuum oven. The prepreg stack was pressed in a mold with a cure procedure: 2 h at 170 °C, 2 h at 210 °C and 4 h at 250 °C under the pressure of 3 MPa successively. The obtained composite had the resin content of 30 wt%.

The composite samples for the oxyacetylene flame tests were made from bulk molding compounds (BMC) of DMSEPE/AFBEN resin and short carbon fibers. The short carbon fibers (rayon-based carbon fiber) with the length of 20–30 mm were used. The BMC was pressed in a mold with a cure procedure: 2 h at 170 °C, 2 h at 210 °C and 4 h at 250 °C under the pressure of 3 MPa successively. The content of the resin in the composite sample was 40 wt% (ca).

Results and discussion

Rheological properties of a DMSEPE/AFBEN resin

The viscosity response of a DMSEPE/AFBEN resin (30 wt% AFBEN) to the temperature ramping at heating rate of 2 °C/min was shown in Fig. 1. The viscosity of the DMSEPE/AFBEN resin decreased dramatically with increasing the temperature from 30 to 60 °C. At the temperature above 90 °C, the viscosity of the resin was below 6.0 Pa s and maintained the low viscosity up to 180 °C. The resin viscosity increased rapidly at the temperature above 190 °C due to the curing reaction of the DMSEPE/AFBEN resin. The result showed the DMSEPE/AFBEN resin had a wide processing window.

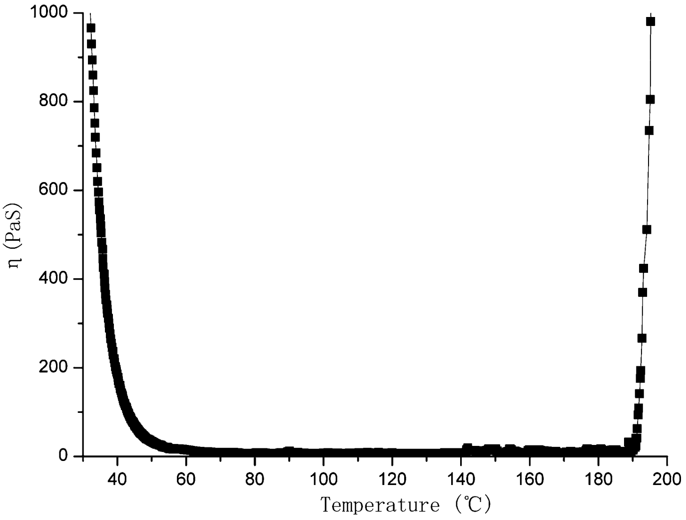


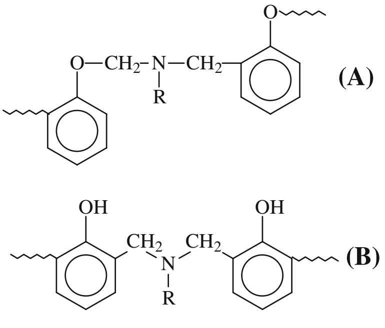
Fig. 1 Viscosity–temperature curve of DMSEPE/AFBEN resin (30 wt% AFBEN)

Curing behavior of DMSEPE/AFBEN resins

DMSEPE/AFBEN resins could be thermally cured by the ring-opening polymerization of AFBEN to form a phenoxy-based Mannich structure (structure A) and a phenol-based Mannich structure (structure B) as shown in Scheme 2 and copolymerization of acetylene groups in DMSEPE and AFBEN to form polyene, benzene rings or naphthalene rings [19]. DSC traced the cure behavior of DMSEPE/AFBEN resins, as given in Fig. 2 and the results for various resins were tabulated in Table 1.

The DSC curve for AFBEN showed an wide exothermic peak with onset at 201.1 °C and top at 219.9 °C and the amount of exotherm was 431.6 J/g. Exothermic peak of the ring-opening polymerization of benzoxazine ring overlapped with that of the polymerization of acetylene and no melting endothermic peak was observed, which indicated that AFBEN was noncrystalline. The DSC curve for DMSEPE showed an exothermic peak with onset at 208.8 °C and top at

Scheme 2 The structures of crosslinked polybenzoxazine



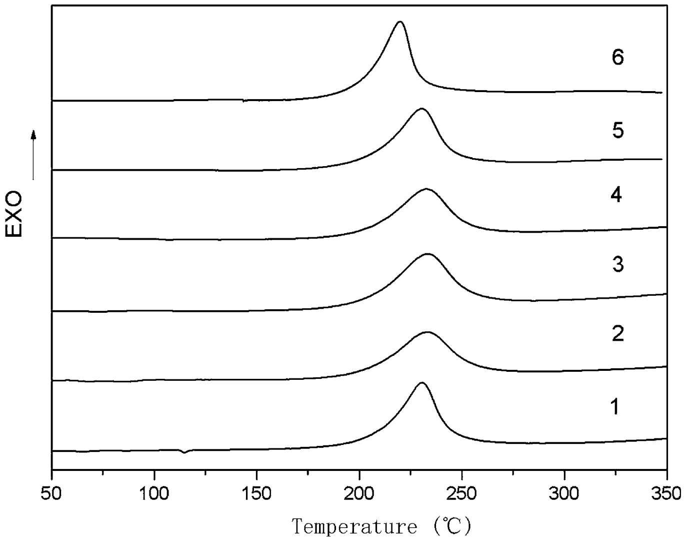


Fig. 2 DSC of DMSEPE/AFBEN resins with different weight content of AFBEN. Weight of AFBEN in resin (wt%): *1* 0.0; *2* 10.0; *3* 20.0; *4* 30.0; *5* 50.0; *6* 100.0

Table 1 DSC analysis results of AFBEN/DMSEPE resins

Weight of AFBEN in resin (%)	Onset exothermic temperature (°C)	Exotherm peak temperature (°C)	Δ*H* (J/g)
0.0	208.8	230.8	450.3
10.0	204.5	233.4	393.3
20.0	204.0	233.6	452.6
30.0	204.7	232.5	396.3
50.0	205.8	230.5	427.3
100.0	201.1	219.9	431.6

230.8 °C. A small melting endothermic peak appearing in the temperature range of 114–118 °C implied that DMSEPE resin was partially crystalline. It was noticeable that the exothermic peak occurred at lower temperature for AFBEN as compared with that for DMSEPE because of autocatalytic character of ring-opening polymerization of benzoxazine ring and higher reactivity of C≡C–H in AFBEN than that in DMSEPE [20].

It was observed that DMSEPE/AFBEN resins showed a unimodel reaction exotherm peak. This indicated that the exothermic peak of the ring-opening polymerization of benzoxazine ring overlapped with that of the polymerization and copolymerization of acetylene groups. No melting endothermic peaks were observed indicating that DMSEPE/AFBEN resins were noncrystalline due to the disturbance of order structure of DMSEPE molecules after blending with AFBEN. The exotherm peaks of DMSEPE/AFBEN resins were in the range from 230 to

233 °C, which were higher than that of AFBEN. This phenomenon resulted from lower reactivity of DMSEPE as compared with AFBEN.

Thermal properties

Glass transition temperature of cured DMSEPE/AFBEN resins

Glass transition temperature of cured DMSEPE/AFBEN resins was determined by DMA analysis. Generally, the temperature at the damping peak was identified as the glass transition temperature in a DMA curve. Damping peak ($t_g\delta$) could also provide insight into the network structures of the copolymers. Crosslink density and network homogeneity could be analyzed according to the height and width of the damping peak as the composition of copolymer was varied [21].

DMSEPE/AFBEN resins with the weight range of AFBEN from 20 to 100 wt% were cured to produce crosslinked polymer specimens with sufficient mechanical integrity for DMA. Samples containing less than 20 wt% AFBEN were excluded from the DMA because of their brittleness.

The DMA diagrams for different resins were shown in Fig. 3 and the results were tabulated in Table 2. The storage modulus (E) of cured DMSEPE/AFBEN resins containing less than 30 wt% AFBEN showed no obvious decrease before 500 °C. As for cured DMSEPE/AFBEN resins containing less than 30 wt% AFBEN, storage modulus increased in the temperature range from 300 to 425 °C. This phenomenon was resulted from further curing reaction of remaining ethynylene in backbond of polymer to form higher crosslinking network structure. In our recent research, ethnylene groups also observed after cured at 350 °C [22]. When the AFBEN

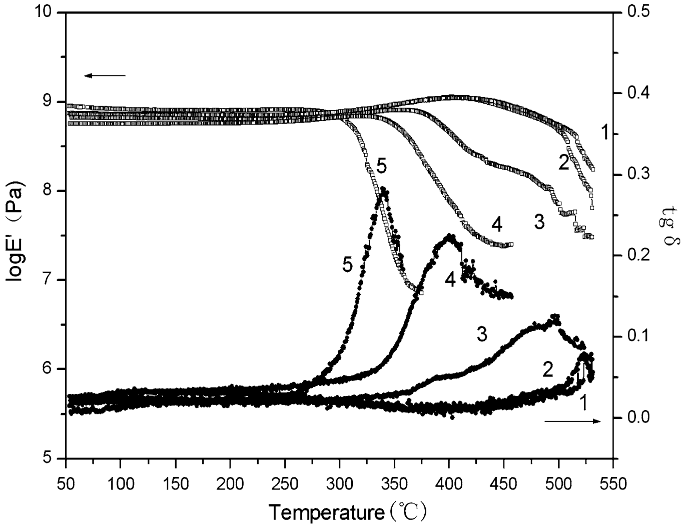


Fig. 3 The DMA curves of the cured DMSEPE/AFBEN resins with different weight content of AFBEN. Weight of AFBEN in resin (wt%): *1* 20.0; *2* 30.0; *3* 50.0; *4* 70.0; *5* 100.0

Table 2 DMA analysis results of DMSEPE/AFBEN resins

Weight of AFBEN in resin (%)	$t_g\delta$ peak temperature (°C)	Peak height
20.0	523	0.05
30.0	521	0.08
50.0	490	0.12
70.0	400	0.22
100.0	342	0.28

loading increases further, the range of temperature at which the storage modulus of crosslinked polymers decreased quickly shifted to lower temperature region.

As shown in Fig. 3, when the AFBEN loading increased from 20 to 100 wt%, a decrease in the temperature of $t_g\delta$ peak from 523 to 342 °C was observed. The height of the t_g peak for cured DMSEPE/AFBEN resins increased as the AFBEN content was increased. The height of $t_g\delta$ peak was associated with crosslinking density and decreasing height of $t_g\delta$ peak revealed a decrease in segmental mobility. This phenomenon illustrated that crosslinking density for the cured DMSEPE/AFBEN decreased with the increase in the content of AFBEN. For the polybenzoxazines, the density of crosslinking network was significantly lower as compared with other typical crosslinking polymers [23]. The intra and intermolecular hydrogen bonding in the network of the polybenzoxazines were strong to confine segmental mobility and contributed rigidity in the glassy state. Therefore polybenzoxazine exhibited high glass transition temperature. It should be pointed out that the decrease in crosslinking density for the cured DMSEPE/AFBEN resins could be explained from the low crosslinking density of AFBEN component.

As shown in Fig. 3, the width of the $t_g\delta$ peak of the cured DMSEPE/AFBEN resin broadened as the addition of AFBEN increased when the contents of AFBEN were less than 50%. However, when the AFBEN loading increased further, a decrease in width of the $t_g\delta$ peak was observed. This possibly resulted from the crosslinking structures and complexes of morphology of the cured resins due to the versatility of curing reaction. During the curing process of DMSEPE/AFBEN resin, ring opening polymerization of benzoxazine ring and polymerization of acetylene group took place and a copolymerization of acetylene group between DMSEPE and AFBEN would occur inevitably. There was difference of reactivity between benzoxazine ring and acetylene group, which would affect the morphology of crosslinked polymer.

Thermal stability of cured DMSEPE/AFBEN resins

Thermogravimetric analysis in air and N_2 was performed to provide an insight into the thermal stability of the cured DMSEPE/AFBEN resins. The TGA curves observed in air and N_2 were shown in Figs. 4 and 5, respectively. The temperatures at which a weight loss of 5% (T_{d5}) occurred were recorded along with the char yield at 800 °C in Table 3.

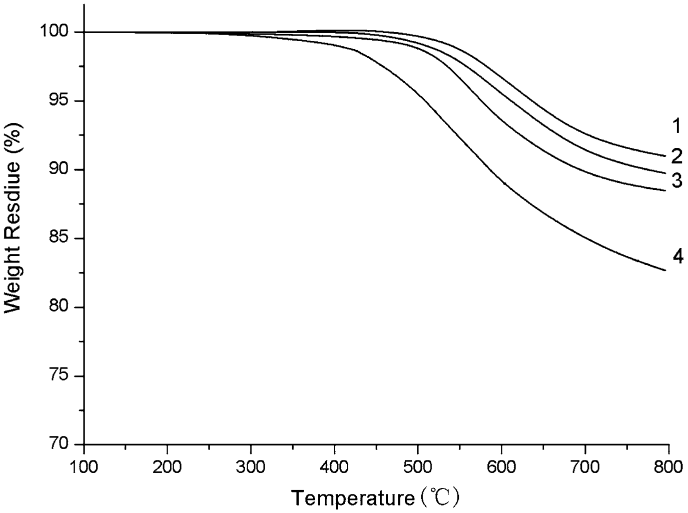


Fig. 4 The TGA curves of the cured DMSEPE/AFBEN resins with different weight content of AFBEN in N_2. Weight of AFBEN in resin (wt%): *1* 0.0; *2* 10.0; *3* 30.0; *4* 50.0

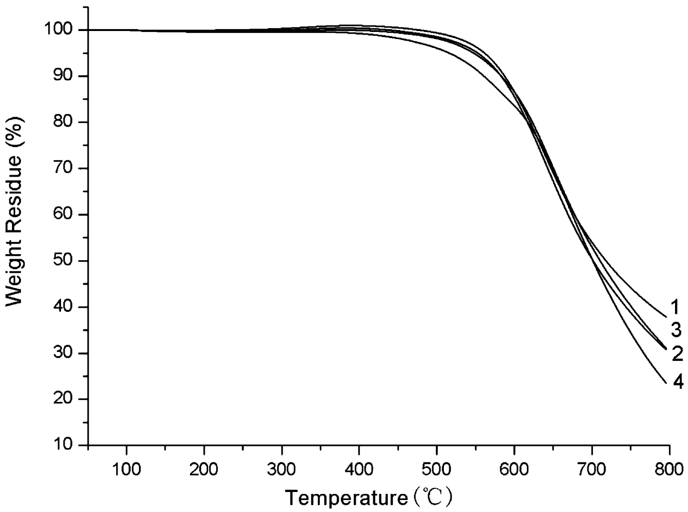


Fig. 5 The TGA curves of the cured DMSEPE/AFBEN resins with different weight content of AFBEN in air. Weight of AFBEN in resin (wt%): *1* 0.0; *2* 10.0; *3* 30.0; *4* 50.0

The mechanism of thermal degradation of benzoxazine showed that the Mannich Bridge was firstly decomposed to release predominantly the primary amine as volatile. A methylene bridge formation involving an early degradation process of Mannich Bridge has even been observed [24]. GC–MS analyses showed after the cleavage of the Mannich base, a terminal amine group was created, which would undergo further scission. As for cured AFBEN, the aromatic amine did not

Table 3 TGA analysis results of DMSEPE/AFBEN resins

Weight of AFBEN in resin (%)	In N_2		In air	
	T_{d5} (°C)	Y_c (%)	T_{d5} (°C)	Y_c (%)
0.0	631.1	90.9	561.4	37.8
10.0	611.2	89.7	552.7	30.8
30.0	575.7	88.5	547.3	31.1
50.0	508.3	82.7	515.9	23.5

Y_c weight residue at 800 °C

evaporate easily, even after the thermal cleavage of the Mannich base had occurred, because it was anchored by the crosslinking networks due to polymerization acetylene-functional group [25]. Acetylene group in AFBEN could copolymerize with the ethynyl and ethynylene groups in DMSEPE resin to form highly crosslinking network structures during curing process and this crosslinking network had excellent thermal stability in order to stabilize the Mannich Bridge. Thereby the T_{d5} of cured DMSEPE/AFBEN resins increased highly as compared with cured polybenzoxazine without acetylene group.

The TGA results in N_2 indicated that T_{d5} and the char yield Y_c of DMSEPE/AFBEN resin gave a decrease tendency relative to DMSEPE resin when the content of AFBEN increased. It appeared that, for the resins with 10 or 30 wt% AFBEN content, there was only 1.2–2.4% decrease in char yield at 800 °C as compared with DMSEPE, suggesting that a crosslinking reaction involving acetylene and benzoxazine occurred to form thermally stable structures, for example polyene, benzene rings and naphthalene rings. Thereby, the cured DMSEPE/AFBEN resin with low content of AFBEN had excellent thermal stability.

The TGA results in air showed that T_{d5} and the char yield Y_c of DMSEPE/AFBEN resins also gave a decrease tendency relative to DMSEPE when the content of AFBEN increased. The cured resin with 10 and 30 wt% AFBEN loading showed T_{d5} were 552.7 and 547.3 °C, and char yield 30.8 and 31.1% (800 °C). The results indicated the blend resin possessed the good thermoxidative stability.

Properties of a fiber reinforced composite

A DMSEPE/AFBEN blend resin was used as a matrix for carbon fiber reinforced composite. Table 4 presented the mechanical properties of carbon fiber (T700) reinforced DMSEPE/AFBEN (30 wt% AFBEN content) composite. As shown in Table 4, the composite exhibited high flexural properties. More remarkable was that the retention of the strength and the modulus of DMSEPE/AFBEN composite at 300 °C were 76 and 96%, respectively. The strength was higher than that of DMSEPE composite both at RT and 300 °C. Therefore, the DMSEPE/AFBEN resin would be expected to be used as the matrix of advanced composites.

The oxyacetylene flame test was used to evaluate the thermal behaviors and ablation performance of the composites. Table 5 listed the erosion rates for different composites. As compared with DMSEPE composite reinforced by carbon fibers,

Table 4 Mechanical properties of carbon fiber (T700) reinforced composite

	Flexural strengths (MPa)	Flexural modulus (GPa)
DMSEPE composite		
RT	1261.7	151.3
300 °C	1188.4	148.0
DMSEPE/AFBEN composite (30.0 wt% AFBEN)		
RT	1694.3	146.7
300 °C	1267.8	140.2

Table 5 Ablative properties of composites reinforced by short carbon fibers

Specimen	Erosion rate (mm/s)
DMSEPE composite	0.040
DMSEPE/AFBEN composite (30.0 wt% AFBEN)	0.033

carbon fiber reinforced DMSEPE/AFBEN (30 wt% AFBEN content) composite had lower erosion rates.

Conclusions

An acetylene-functional benzoxazine resin was used to modify silicon-containing arylacetylene (DMSEPE). A variety of DMSEPE/AFBEN resins with different weight content of AFBEN were prepared. The thermopolymerization of the DMSEPE/AFBEN resins were investigated by DSC. The thermal stability of the cured DMSEPE/AFBEN resins was determined by analysis of TGA in N_2 and air. The TGA results showed cured DMSEPE/AFBEN resins had good thermal stability. The results of DMA study showed that the storage modulus (*E*) of the cured DMSEPE/AFBEN containing less than 30 wt% AFBEN did not decrease obviously at lower than 500 °C and when the AFBEN loading increased from 20 to 100 wt%, the glass transition temperature decreased from 523 to 342 °C. The carbon fiber (T700) reinforced composites showed excellent flexural properties at room temperature and high property remaining at 300 °C. Therefore, the DMSEPE/AFBEN resin would be expected to be used as the matrix of advanced composites.

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