Polymer Degradation and Stability 96 (2011) 2276–2283

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Thermal stability of the copolymers of silicon-containing arylacetylene resin and acetylene-functional benzoxazine

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ARTICLE INFO

Article history:
Received 2 August 2010
Received in revised form
21 April 2011
Accepted 29 April 2011
Available online 7 May 2011

Keywords:
Silicon-containing arylacetylene resins
Acetylene-functional benzoxazine
Thermal property
Degradation
Ablation

ABSTRACT

Acetylene-functional benzoxazine resin (AFBEN) was used to modify silicon-containing aryacetylene resin (SCAAR). The thermal stability, degradation and ablation mechanisms were investigated. Based on the results of Py/GC/MS methods, we concluded that the cross-linking reactions of poly(dimethylsilyleneethynylene–phenyleneethynylene)(DMSEPE, a class of SCAAR) were due to (1) the Diels–Alder reaction between Ph–C≡C and C≡C, (2) the ring trimerization of C≡C and (3) radical polymerization of C≡C to form polyene structure. During the curing of AFBEN, polyene was the main product of the polymerization of ethynyl in AFBEN and the activation of the para positions of the aniline ring increased due to the introduction of ethynyl. XRD and XPS results showed that SiO_2 and SiC formed on the surface of the composites in the process of ablation.

1. 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 1000 °C of the cured MSP was 860 °C and 94% respectively [6–9]. Poly[silyleneethynylene phenyleneethynylene] terminated with phenylacetylene, (abbreviated as 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(dimethylsilyleneethynylene–phenyleneethynylene) terminated with phenylacetylene which could cure at the temperatures above 233 °C was synthesized and showed high heat-resistance and char yield [12]. The major advantages of silicon-containing arylacetylene resins included no volatility during curing, high decomposition temperature, high char yield after pyrolysis and high radiation resistance [13]. However, the application of SCARR was limited by its brittleness, shrinkage during curing and poor interface adhesion with reinforcements in composites.

Acetylene-functional benzoxazine resin (AFBEN) [14,15] was used to modify poly(dimethylsilyleneethynylenephenyleneethynylene) (DMSEPE). 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.

The mechanism of thermal degradation of benzoxazine showed that the Mannich Bridge was firstly decomposed to release predominantly the primary amine as volatile [16]. A formation of methylene bridge involving an early degradation process of Mannich bridge has even been observed [16]. Acetylene groups in AFBEN could copolymerize with the acetylene groups in DMSEPE resin to form highly crosslinking network structures during curing process to stabilize the Mannich Bridge from thermal degradation.

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

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doi:10.1016/j.polymdegradstab.2011.04.022

Table 1
Analysis of TGA results of DMSEPE/AFBEN blend resins.

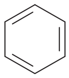
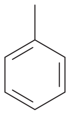
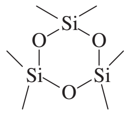
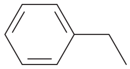
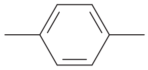
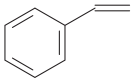
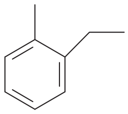
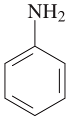
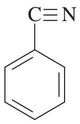
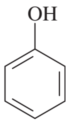
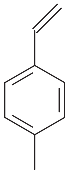
DMSEPE/AFBEN weight ratios	In N_2		In air	
	T_{d5} (°C)	Y_c	T_{d5} (°C)	Y_c
1.0:0.0	631.1	90.9	561.4	37.8
0.7:0.3	575.7	88.5	547.3	31.1
0.5:0.5	508.3	82.7	515.9	23.5

Y_c: weight residue at 800 °C.

resin when the contents of AFBEN increased. It appeared that, for the resins with 10 or 30 wt % AFBEN, there was only 1.2-2.4% decrease in char yield at 800 °C as compared with DMSEPE, suggesting that a cross-linking 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 contents of AFBEN had excellent thermal stability.

With our continuing efforts on developing DMSEPE/AFBEN resin, it is necessary to study the relationship between the

Table 2
Pyrolyzates of the cured DMSEPE/AFBEN resin identified by Py/GC/MS at 800 °C.

Retention (min)	Molecular weight	Structure	DMSEPE	DMSEPE/AFBEN-30	DMSEPE/AFBEN-50	AFBEN
3.10	78		39.54	28.05	17.74	0.99
4.99	92		28.06	26.22	37.32	1.63
5.96	222			0.88	0.3	
7.03	106		2.48	4.2	4.77	0.2
7.24	106		4.17	11.8	13.69	0.81
7.71	104		3.3	4.02	2.69	0.29
9.17	120		0.63	2.35	3.69	
9.53	93			0.44	1.86	3.66
9.68	103			0.89	1.64	
9.81	94					10.44
9.86	118		0.96	2.44	2.55	

(*continued on next page*)

Table 2 (*continued*)

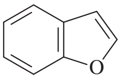
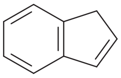
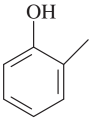
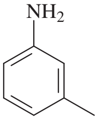
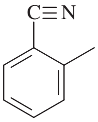
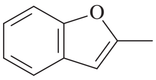
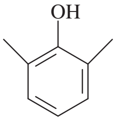
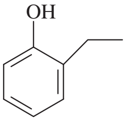
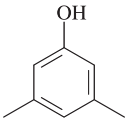
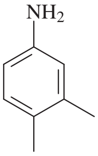
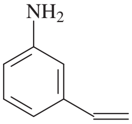
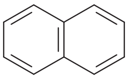
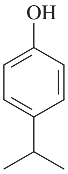
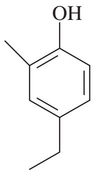
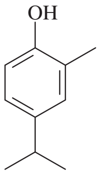
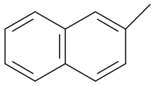
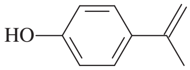
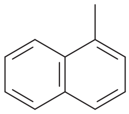
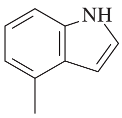
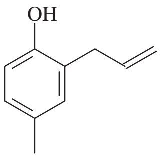
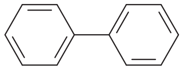
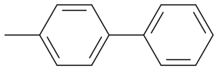
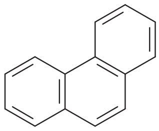
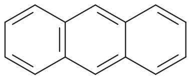
Retention (min)	Molecular weight	Structure	DMSEPE	DMSEPE/AFBEN-30	DMSEPE/AFBEN-50	AFBEN
9.92	118					2.67
10.85	116			0.82		
11.18	108					18.61
11.57	107				1.82	17.67
11.71	117				1.1	
11.85	132					1.48
12.08	122					6.09
12.63	122					0.82
12.82	122					2.09
13.17	121					6.12
13.91	119					2.44
13.45	128		7.99	7.62	4.26	
14.11	136					5.46

Table 2 (*continued*)

Retention (min)	Molecular weight	Structure	DMSEPE	DMSEPE/AFBEN-30	DMSEPE/AFBEN-50	AFBEN
14.22	136					2.24
15.14	150					6.98
15.24	142		1.91	3.4	2.42	
15.34	134					3.8
15.50	168		0.73	1.31	0.94	
16.18	131					1.29
16.35	148					4.22
16.48	154		2.3	2.44	1.11	
17.97	168		0.57	0.96	0.61	
21.91	178		1.28	1.13	0.58	
22.05	178				0.61	

structures and the degradation stability. In this paper, the thermal stability, degradation and ablation mechanisms were investigated.

2. Experimental

2.1. Raw 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 literature [12]. The reinforcement material was carbon fiber (T300–12 K).

2.2. Instrumentation

Electron ionization mass spectrometry (EI-MS) analysis was conducted on Micromass GCT. The pyrolysis/gas chromatography/

mass spectrometry (Py/GC/MS) analyses were conducted on a Frontier Lab Single-shot Pyrolyzer PY-2020i (PY Single-shot Pyrolyzer, quartz tube, temperature: 800 °C) and a Shimadzu GCMS-QP2010 chromatograph/mass spectrometer (Chromatographic column, 30 m × 0.25 mm × 0.25 m; carrier gas, helium gas; pressure, 34.0 kPa; total flow, 84.3 ml/min; column flow, 0.80 ml/min. The temperature of column was held at 40 °C for 1 min, and then increased with a heating rate of 10 °C/min, and finally maintained at 800 °C. The oxyacetylene flame test was performed according to China Standard GJB323A-96 standard 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 2800 °C. The dimension of an ablative sample dimension was Φ30 mm × 4 mm.

2.3. Preparation of DMSEPE/AFBEN resin

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.

2.4. Preparation of composites

With stirring, DMSEPE/AFBEN (40 g), short carbon fiber (60 g) and 100 mL THF were added into the flask for 2 h. The mixture was dried finally in vacuum, and the composite samples for the oxyacetylene flame tests were prepared from bulk molding compounds (BMC). 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 curing 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).

3. Results and discussion

3.1. Thermal stability of cured DMSEPE/AFBEN resins

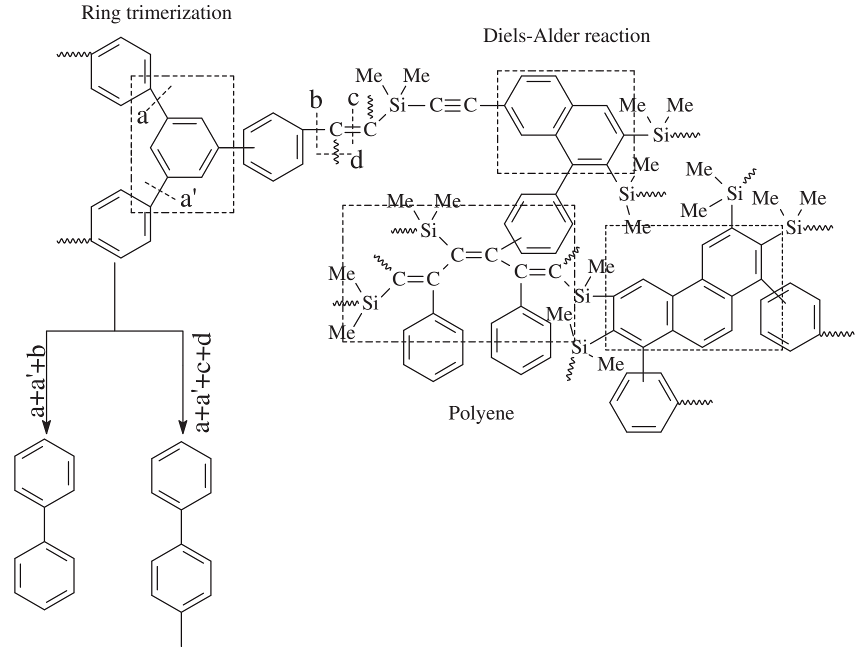
Thermogravimetric analysis (TGA) in air and N_2 was performed to provide an insight into the thermal stability of the cured DMSEPE/AFBEN resins. The temperatures at which a weight loss of 5% (T_{d5}) occurred were recorded along with the char yield at 800 °C in Table 1.

The TGA results in N_2 indicated that T_{d5} and the char yield Y_c of DMSEPE/AFBEN resins gave a decrease tendency relative to DMSEPE resin when the contents of AFBEN increased. It appeared that, for the resins with 10 or 30 wt% AFBEN, there was only 1.2–2.4% decrease in char yield at 800 °C as compared with DMSEPE, suggesting that a cross-linking 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 contents of AFBEN had excellent thermal stability.

3.2. Degradation mechanism of the cured DMSEPE/AFBEN resins

In order to trace thermal degradation of the DMSEPE/AFBEN resins, the Py/GC/MS combined technique, which is usually used to determine the thermal degradation mechanisms and the structures of a polymer, was utilized. The pyrolysis fragments are identified by MS analyses. The main compounds identified from the thermal pyrolysis of the cured DMSEPE/FBEN resins resin were tabulated in Table 2.

As shown in Table 2, the main pyrolysis products for the cured DMSEPE resin pyrolysized at 800 °C were styrene, naphthalene, biphenyl, phenanthrene, phenylnaphthalene, etc. This implied that the polymerization of ethynyle groups in PDMSEPE resin took place to form polyene, benzene rings or naphthalene rings as shown in Scheme 1. As degradation proceeded, styrene and methylstyrene could evaporate upon cleavage of C–C in the structure of polyene. The structures of naphthalene, phenanthrene, phenylnaphthalene

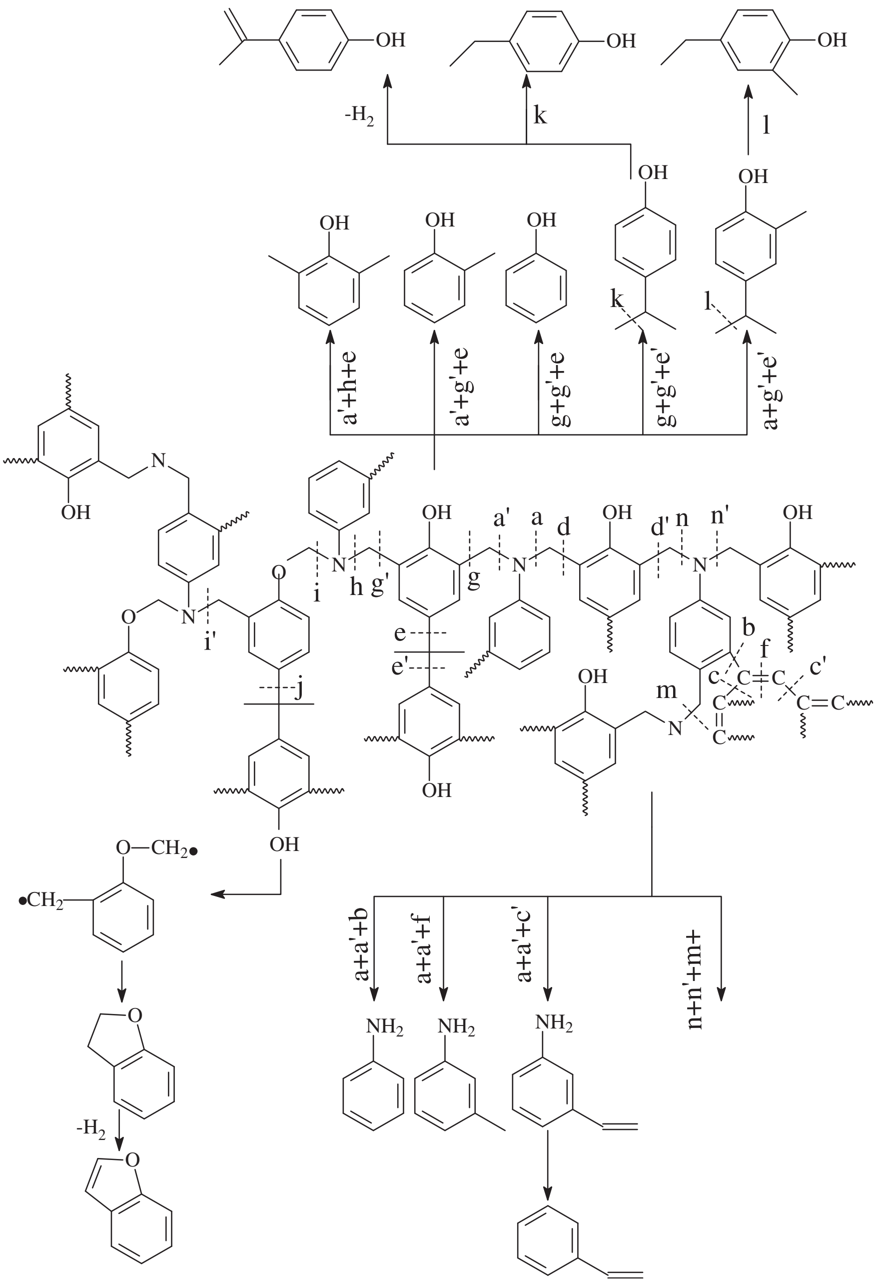


Scheme 1. Structure of the cured DMSEPE resins.

were products of Diels–Alder reaction between Ph–C≡C and C≡C. Based on the results of Py/GC/MS methods, we concluded that the cross-linking reactions of DMSEPE may be derived from (1) the Diels–Alder reaction between Ph–C≡C and C≡C and (2) the ring trimerization of C≡C and (3) radical polymerization of C≡C to form polyene structure.

For the Mannich based network, the pendant arylamine group was the most easily volatilized upon cleavage of the Mannich Bridge. As shown in Table 2, during the degradation process, aniline and its derivatives were observed and vinylaniline released upon cleavage of polyene structure as a products of polymerization of ethynyl in AFBEN. However, in the gases evolved, naphthalene, phenanthrene, phenylnaphthalene were not observed, implying that polyene was the main product of the polymerization of ethynyl in AFBEN. Due to the introduction of ethynyl into AFBEN, the activation of the para positions of the aniline ring increased, therefore the evolution of 3, 4-dimethylaniline was observed as shown in scheme. This indicated that para positions were possible polymerization sites during the ring-opening polymerization of benzoxazine. This phenomenon also was observed in alkyl-substituted aniline-based polybenzoxazines. As degradation continued, phenol and other substituted phenols could be observed due to cleavage of the isopropylene group of the Bisphenol A backbone as shown in Scheme 2.

As degradation proceeded of DMSEPE/AFBEN resins, cyclotrisiloxane was observed in the evolved gases. This may result from the reaction between the oxygen atoms dissociated from AFBEN and the silicon atoms in DMSEPE during the pyrolytic process.



Scheme 2. Structures and degradation mechanism of the cured DMSEPE/AFBEN resins.

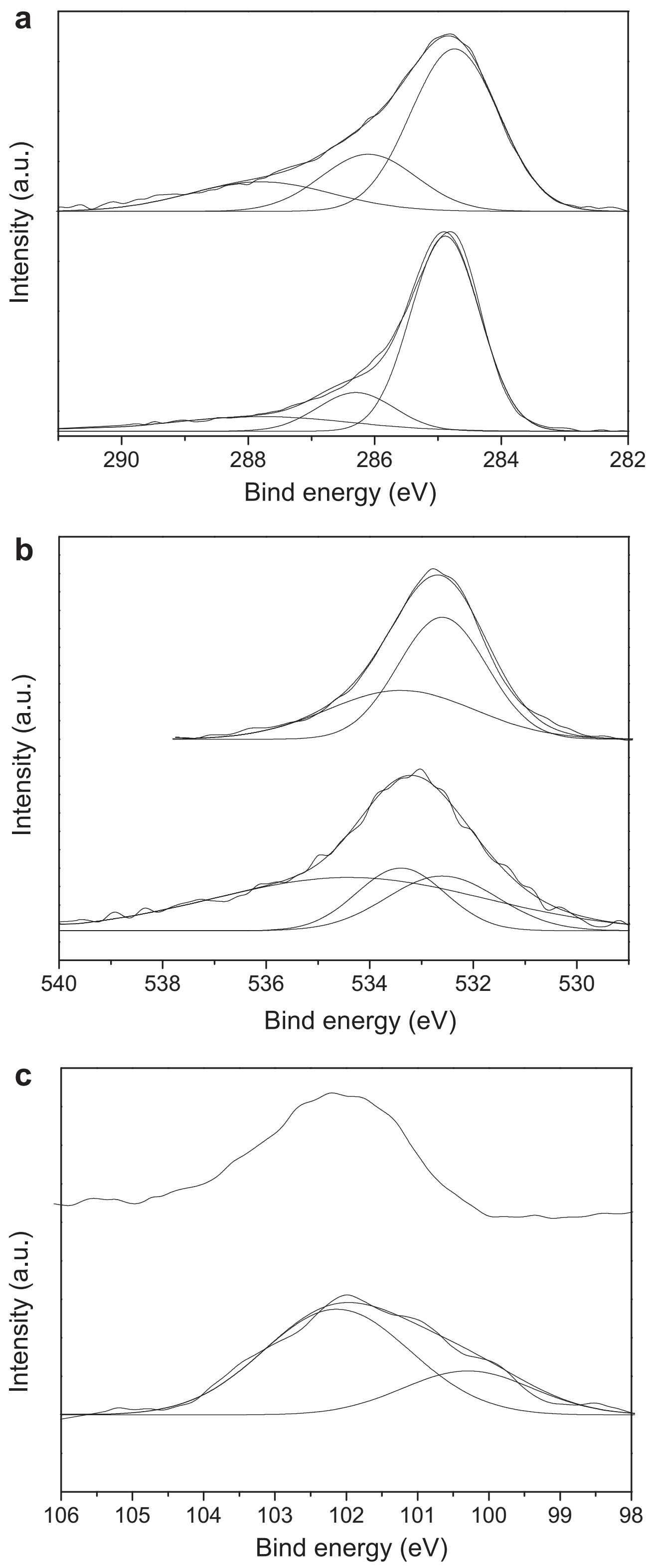
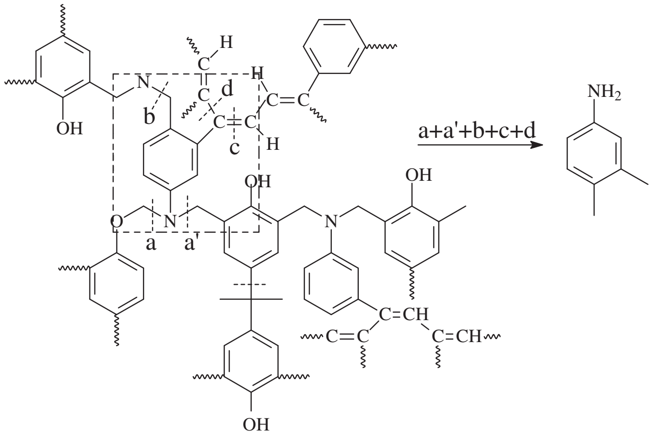


Fig. 1. The variations of the (a) C1s, (b) O1s, (c) Si2p XPS spectra of DMSEPE/AFBEN resins.



Scheme 3. Structure and degradation mechanism of arylamine methylene bridge network in the cured DMSEPE/AFBEN resins.

3.3. XPS

The oxyacetylene flame test was used to evaluate the thermal behaviors and ablation performance of the composites. As compared with carbon fibers reinforced DMSEPE composite, DMSEPE/AFBEN (weight ratio 0.7:0.3) composite had lower erosion rates.

The C1s, O1s, S2p and N1s XPS spectra of four samples, illustrating the variations of different elements after ablations were found in Fig. 1. After ablation, there were substantial differences in the C1s, O1s, Si2p and N1s spectra. This was most readily seen in Table 2, which contained the atomic percentages of the various elements, as determined from the spectral areas and relative sensitivity factors. As shown in Table 2, after ablated by oxyacetylene flame, the relative carbon contents on the surface of composites increased, while the contents of oxygen, nitrogen and silicon decreased simultaneously. Especially the nitrogen element, disappeared after ablation, maybe volatilize in the forms of aniline and its derivatives when the Mannich Bridge ruptured in the heat treatment process, as shown in Scheme 3.

Peak separations were carried out based on prior work, and three peaks in DMSEPE/AFBEN composites were given in Table 3. The surface groups have been determined to be C—C, C-OH and C=O groups for composites. After ablation, the contents of C—OH and C=O groups reduced, but that of the C—C increased, which was probably due to the destruction of the coupling agent on the surface of carbon

Table 3
The atomic percentages of the various elements on the sample surfaces.

		C%	O%	N%	Si%
SAR	Before ablation	73.8	19.4	0	6.7
	After ablation	88.2	8.3	0	3.5
SAR-30	Before ablation	71.3	20.9	2.3	4.5
	After ablation	90.6	8.1	0	1.3
SAR-50	Before ablation	71.1	21.9	2.7	4.3
	After ablation	87.5	11.2	0	1.3

Table 4
Component peaks and attributions of XPS spectra.

Peak No		Binding energy (eV)	Functionality
C1s	1	284.6	Graphitic carbon
	2	286.1	C—OH
	3	287.8	C=O
O1s	1	Approx. 531.4	C=O or C—O—C
	2	Approx. 533.3	C—OH
	3	Approx. 534.9	Si—O
Si2p	1	102.1	SiO_2
	2	100.3	SiC

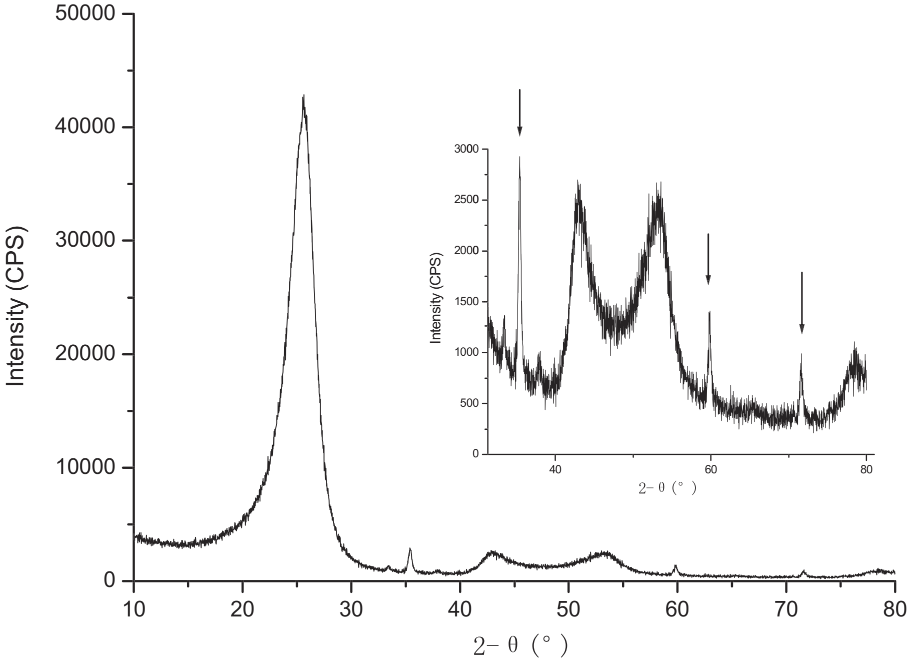


Fig. 2. XRD of DMSEPE/AFBEN composite after ablation.

fiber in the ablation process. As shown in Table 4, the XPS spectrum of O1s, SiO_2 and SiC have formed, which was confirmed by XPS spectrum of Si2p.

X-ray diffraction analysis (XRD) was used to study the cross section of the DMSEPE/AFBEN reinforced composites after ablation. Results of XRD showed that inorganic SiC ceramic would form after the composites ablated by oxyacetylene flame. As shown in Fig. 2, there were three peaks ($2\theta = 35.58^\circ$, 60.02° and 71.78°) attributed to SiC ceramic. Formation of SiC which possessed excellent thermal stability would increase the ablative resistance of the composite. SiO_2 and amorphous carbon were present as ablation products as shown in Fig. 2.

4. Conclusions

Acetylene-functional benzoxazine resins (AFBEN) was used to modify silicon-containing aryacetylene (SCAAR). The thermal stability, degradation and ablation mechanisms were investigated. Based on the results of Py/GC/MS methods, we concluded that the cross-linking reactions of DMSEPE were due to (1) the Diels–Alder reaction between Ph–C≡C and C≡C and (2) the ring trimerization of C≡C and (3) radical polymerization of C≡C to form polyene structure. During curing of AFBEN, polyene was the main product of the polymerization of ethynyl in AFBEN and the activation of the para positions of the aniline ring increased owing to the introduction of ethynyl into AFBEN. XRD and XPS results showed that SiO_2 and SiC formed on the surface of the composites in the process of ablation.

Acknowledgement

We gratefully acknowledged the financial support of the National High Technology Research and Development Program of China (Grant No. 2002AA305103) and Scientific Research Program Funded by Shaanxi Provincial Education Department (Program No.11JK0842).

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