

Recent Progress in Arylacetylene Resins

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Arylacetylene(AA) resins have been considered as a kind of extremely heat-resistant polymers and could be used as a thermally stable matrix of advanced composites and a precursor for carbon/carbon composites due to their easy processability, exceedingly high thermal stability and char yields. Scientists have paid great attention to this kind of polymers in the recent years. AA resins were first derived from the pre-polymerization of arylacetylene compounds like diethynylbenzene(DEB). Recently the co-polymerization of arylacetylene compounds with other active organic compounds such as chlorosilane and dichlorosiloxane has been an effective synthetic method.

The main characteristics of AA resins are: (1) easy processability(low viscosity), (2) curing by addition without any release of volatiles, (3) use of minimal pressure and temperatures for processing, (4) extremely high thermal stability due to highly crosslinked aromatic polymers after curing, (5) good mechanical and insulation properties, (6) low moisture absorption, (7) high residue yields on carbonization or ceramic formation(80~95%, high carbon/hydrogen ratio), *etc.*

At present, AA resins are mainly classified as polyarylacetylenes(PAAs) and silicon-containing arylacetylene resins. The following outlines the researches and development of AA resins.

1. Polyarylacetylenes

A typical arylacetylene resin, polyarylacetylene(PAA), was prepared by prepolymerization (cyclotrimerization) of DEB with a catalyst. In the early 1930s, Deluchat had prepared diethynylbenzenes by a laborious seven step synthesis starting from the corresponding xylene isomer. This route was obviously not satisfactory for relatively large scale preparation of diethynylbenzenes. A large quantity of *m*- and *p*-diethynylbenzenes was first synthesized from divinylbenzene in the late 1950s at the GE research laboratory. They found that DEB easily polymerized when heated. When ignited at room temperature in air an explosive reaction takes place; however, the experimental result showed that a total weight loss was only 5-6%. The early formulations of PAA underwent severe shrinkage and released large amounts of heat(highly exothermic reaction) during cure. Such processing difficulties limited DEB practical applications. In the 1970s, Hercules patented a process for the production of polyarylacetylene(PAA) by techniques that reduce the exotherm and shrinkage. PAA designated as HA 43 was available. Researches at the Aerospace Co. used HA 43 to produce a carbon-fabric reinforced ablative thermal protection system. In the early 1980s, the aerospace corporation's materials sciences laboratory overcame initial defects with PAA through the development of low-temperature pre-polymerization technique and polymer chain modifications. Up to now, there are a lot of researches focused on the investigations of PAA and its composites.

2. Silicon-containing arylacetylene resins

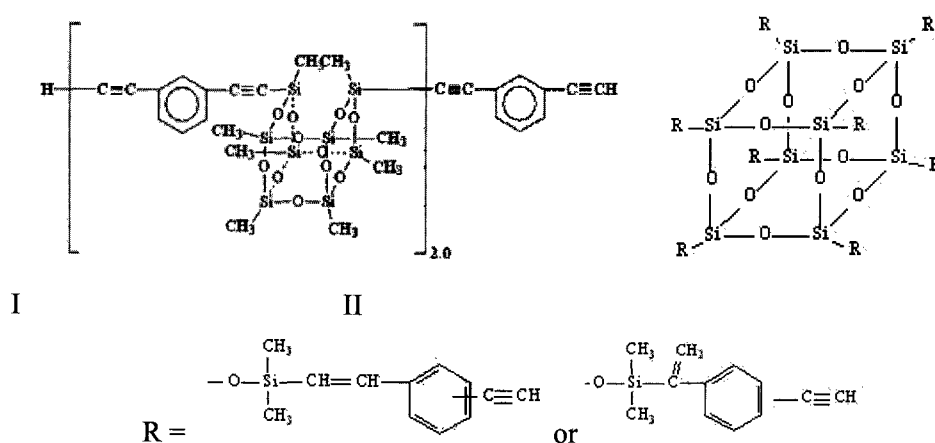
In the 1990s, silicon-containing arylacetylene resins with $[-SiR_2-C\equiv C-Ar-C\equiv C-]$ (R = H, alkyl or phenyl) units had been developed by Robert J. P. Corriu et al. on the basis of the work of L.K. Luneva, et al. in 1967. These resins show excellent thermal performance and high ceramic production capacity at a

sintering temperature after crosslinked. They could find wide potential applications as high performance matrices of advanced composites, heat-resistant materials, and ceramic precursors in high technology fields like aerospace and astronautics. One of typical silicon-containing arylacetylene resins, MSP resin, was explored in 1994 by M. Itoh, et al. and synthesized through the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of a magnesia base catalyst. The decomposition temperature at 5% weight loss and residue at 1000°C of the cured MSP resin are 860°C and 94%, respectively. Poly(silyleneethynylene phenyleneethynylene) terminated with phenylacetylene (designated as BLJ) with high thermal stability and good processability was exploited by P. Buvat, et al. through the condensation of dichloromethylsilane and a mixture of diethynylbenzene and phenylacetylene Grignard agents. In recent years, poly(dimethylsilylene ethynylenephenyleneethynylene)s capped with phenylacetylene have been developed by F. Huang, et al. and show excellent performance. The advantageous features of silicon-containing arylacetylene resins, *i.e.*, good processability, high ceramic yield after pyrolysis, excellent dielectric properties, high flame retardance and high radiation resistance, have attracted researchers in the field of new materials. However, the applications of the silicon-containing arylacetylene resins are limited by their brittleness, shrinkage during curing, and poor adhesion to reinforcements in composites.

To properly improve the properties of the silicon-containing arylacetylene resins, researchers have attempted various strategies, such as: (i) hybridization of organic/inorganic components, (ii) preparation of various resins with additional functionality, (iii) synthesis of novel resins, and (iv) blend with a high-performance resin. The advances in the development on these issues would be presented.

2.1 Organic/inorganic hybrid resins

A kind of hybrid resins were prepared from POSS unit and diethynylbenzene. These resins will cure at the temperature lower than 200°C. The structures of two resins are shown in Scheme I. A hybrid resin was synthesized from *m*-diethynylbenzene (DEB) and *diexo*-(CH₃)₈Si₈O₁₁F₂, which was made from octamethyl polyhedral oligomeric silsesquioxane and BF₃·OEt₂ in CHCl₃, through the Grignard method. Other hybrid resin was synthesized from octakis(dimethylsiloxy)octasilsesquioxanes (Q₈M₈^H) and DEB by a hydrosilylation reaction. The cured resins show high thermal stability (see Table 1).



Scheme I Schematic structures of the hybrid resins

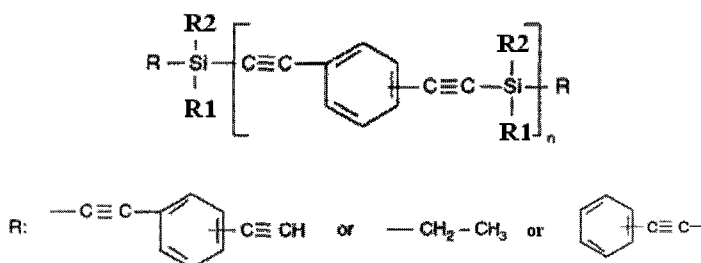
Table 1 TGA results for the cured hybrid resin under nitrogen*

Resin	Temperature at 5% weight loss/°C	Residual yield at 800°C/%
I	503	87.1
II	592	89.4

* heating rate of 10°C/min.

2.2 New silicon-containing arylacetylene resins with additional functionality

A series of arylacetylene resins containing methylsilylene, dimethylsilane, disiloxane, methylvinylsilane groups were synthesized by the condensation reaction between DEB organomagnesium reagents and dichloromethylsilane, dichlorodimethylsilane, dichlorodisiloxane, etc.



$R1 = Me; R2 = -H(P1), Me(P2), -CH=CH_2(P3)$

The curing behavior of these resins was traced by DSC and the results are listed in Table 2. The results show that the resins are processable and cured at temperature 200°C (ca). The cured resins show excellent thermal stability. When the cured resins were sintered at the temperature higher than 1300°C, β -SiC containing ceramic was obtained

Table 2 The characteristics of arylacetylene resins containing methylsilylene, dimethylsilane, methylvinylsilane groups

Resins	Appearance at RT	$T_i/^\circ\text{C}$	$T_p/^\circ\text{C}$	$\Delta H/(J/g)$	$T_{d5}/^\circ\text{C}$	$Y_r/\%$	$T_{d5}/^\circ\text{C}$	$Y_r/\%$	$\sigma_f^*(E_f)$ /MPa(GPa)
		DSC			N ₂		Air		
P1	Viscous liquid	199	214	624	688	92.8	544	33.1	183(40.8)
P2	Solid	210	233	259	648	91.4	531	29.5	243(43.5)
P3	Viscous liquid	208	228	262	646	91.6	540	31.5	168(34.7)

*Resin/T300 cloth composites ; Y_r : Residue yield at 800°C.

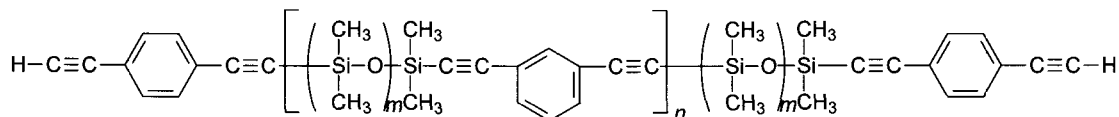
The resins could be used for the matrix of fiber reinforced composites. The mechanical properties of various composites with different reinforcements are listed in Table 3. The results indicate that the composites have good mechanical properties and excellent heat resistance.

Table 3 Flexural properties of composites

Specimen	Reinforcements	Flexural strength/MPa		Flexural modulus/MPa	
		RT	250°C	RT	250°C
GF-P2	glass fabric(2D)	248	268	23.9	20.6
CF-P2	T300 carbon fabric(2D)	275	315	59.8	70.4
UCF -P2	T700 unidirectional carbon fiber	1495	1202	118.1	105.6

2.3 Novel arylacetylene resins containing siloxane units

A series of novel resins were synthesized by the condensation reaction of 1,4-diethynylbenzene magnesium reagent with various α,ω -dichlorodimethylsiloxanes:



I : m = 1; II : m = 2; III : m = 3; IV : m = 4; V : m = 5

The resins are solids or viscous liquids and are soluble in common organic solvents such as benzene, toluene, chloroform, THF, acetone, butanone, *etc.* at room temperature. Differential scanning calorimetry (DSC) experiments show these resins can be thermally cured to produce highly crosslinked structures in temperature region 150~325°C. It is observed that the exothermal peaks shift to higher temperature region with increasing the siloxane chain length.

DMA studies reveal the glass transition temperatures of the cured resins decrease with the increase of the siloxane chain length.

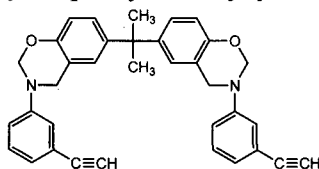
The cured resins are thermally stable in both N₂ and air. With increasing the length of siloxane units, the decomposition temperatures at 5% weight loss (T_{d5}) decrease both in N₂ and in air while the residue yields at 1000 °C increase in air. A possible explanation would be the formation of SiO₂ during the thermal decomposition of the cured resins in air.

Table 4 TGA data of the cured resins

Cured resin	T _{d5} /°C		Residue yield at 1000 °C /%	
	N ₂	Air	N ₂	Air
I _c	546	462	83.2	39.2
II _c	502	429	76.7	43.7
III _c	497	419	74.3	43.9
IV _c	495	417	72.9	48.3
V _c	489	407	68.8	49.3

2.4 The blends of an arylacetylene resin with an acetylene-functional benzoxazine

Polybenzoxazines are a recently developed class of thermosetting resins, which possess excellent mechanical properties, good adhesion to materials, good thermal and flame retardance properties and low coefficient of thermal expansion (CTE). An acetylene-functional benzoxazine (AFBoz) was used to blend with poly(dimethylsilylene ethynylenephenyleneethynylene) (P2) :



AFBoz

The viscosity response of P2-AFBoz resins to the temperature ramping at heating rate of 2 °C/min is shown in Figure 1. The blends exhibit good processable properties.

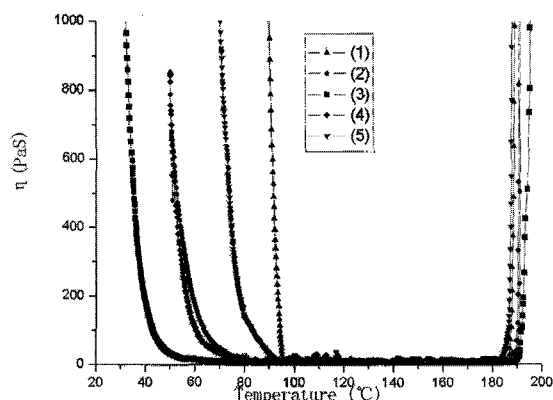


Figure 1 Viscosity vs. temperature curve for P2-AFBoz resins with various mass ratios [P2]/[AFBoz]: (1) 0.9:0.1(R1) ; (2) 0.8:0.2(R2) ; (3) 0.7:0.3(R3) ; (4) 0.5:0.5(R4) ; (5) 0.0:1.0(R5)

The DSC analysis results for P2-AFBoz resins show that the exothermic peak temperature for all the P2-AFBoz resins is about 230°C. The ring-opening polymerization of the benzoxazine ring and the polymerization and copolymerization of acetylene groups in blend resins occur at the same time and the crosslinking polymerizations will take place at *ca.* 200°C. The blending of P2 with AFBoz does not largely affect the polymerization activities of P2 and AFBoz themselves.

Table 5 shows the mechanical properties of cured P2 and P2-AFBoz resins. As shown in the table, the blend resins exhibit higher flexural properties than the pure P2 resin. This indicates that AFBoz could effectively improve the mechanical property of P2 resin.

Table 5 Mechanical properties of cured P2 and P2-AFBoz resins

Cured resin	Flexural strength/MPa
P2-c	22.6
R3-c	35.5
R4-c	36.9

The DMA measurements for different P2-AFBoz resins are tabulated in Table 6. The glass transition temperature T_g ($\tan\delta$ peak) for the cured P2-AFBoz resins decreases from 523°C to 342°C whereas the height of the $\tan\delta$ peak increases when the AFBoz loading increases from 20 wt% to 100 wt%. The addition of AFBoz will largely reduce T_g of the P2 resin and the decrease in T_g is related to the enhancement of chain segment mobility of cured resins.

Table 6 DMA analysis results of cured P2-AFBoz resins

Cured resin	Tanδ peak Temperature/°C	Tanδ peak height
R2-c	523	0.05
R3-c	521	0.08
R4-c	490	0.12
R5-c	342	0.28

Thermogravimetric analysis (TGA) in N_2 was performed to investigate the thermal stability of the cured P2-AFBoz resins. The temperatures at a weight loss of 5% (T_{d5}) of the cured resin are recorded along with the residue yield (Y_r) at 800 °C in Table 7. As shown in the table, T_{d5} of the cured P2 resin is much higher than that of the cured AFBoz resin (T_{d5} , 458°C). The decomposition temperatures and

residues of the cured blend resins reduce with the increase in the content of AFBoz in the blend resins; the extent of the reduction is enhanced with increased loading of AFBoz. The cured P2-AFBoz resin with a low content of AFBoz has excellent thermal stability. These results indicate that the addition of AFBoz to P2 resin to a certain content would not sacrifice the thermal stability of P2 resin too much.

Table 7 TGA analysis results of cured P2-AFBoz resins (in N₂)

Cured resin	T _{d5} /°C	Y _r /%
P2-c	631.1	90.9
1-c	611.2	89.7
3-c	575.7	88.5
4-c	508.3	82.7

Y_r(%) : residue percentage at 800°C

A P2-AFBoz blend resin was used as a matrix for composites. Table 8 presents the mechanical properties of carbon fiber (T700) reinforced composites. As shown in Table 8, the composites exhibit high flexural properties. The flexural strength of P2-AFBoz(R3) composite is higher than that of P2 composite both at RT and 300 °C, but the modulus is reduced a little. Therefore, P2-AFBoz resins could be a good matrix for advanced composites.

Table 8 Mechanical properties of unidirectional carbon fiber (T700) reinforced composites*

Composite	Measuring temperature /°C	Flexural strength/MPa	Flexural modulus/GPa
P2/T700	RT	1262	151.3
	300	1188	148.0
P2-AFBoz(R3)/T700	RT	1694.	146.7
	300	1268	140.2

*Resin content: 32 wt % (ca).

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