

Preparation and Properties of Modified Silicon-containing Arylacetylene Resin with Bispropargyl Ether

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A novel silicon-containing arylacetylene resin (MSAR) modified by dipropargyl ether of bisphenol A (DPBPA) and dipropargyl ether of perfluorobisphenol A (DPPFBPA) was prepared separately. The curing behaviors of modified resins, DPBPA/MSAR and DPPFBPA/MSAR, were characterized with differential scanning calorimeter (DSC). The kinetic parameters of modified resins were obtained by the Kissinger and Ozawa methods. The results of dynamic mechanical analysis (DMA) revealed that the glass transition temperature (T_g) of the cured DPBPA/MSAR reached 486 °C. According to the thermogravimetric analysis (TGA), the decomposition temperature (T_{d5}) of the cured resins and char yield (Y_c , 800 °C) decreased as the dipropargyl ether loadings increased, especially in air. With the same weight loading, thermal stability of DPBPA/MSAR was better than that of DPPFBPA/MSAR. The carbon fiber (T300) reinforced composites exhibited excellent flexural properties at room temperature with a high property retention at 300 °C.

Key Words : Silicon-containing arylacetylene resins, Dipropargyl ether, Thermal property, Composite

Introduction

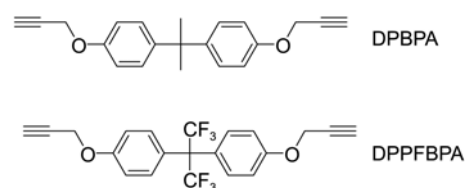
The silicon-containing arylacetylene resin composed of $[-SiR_2-C\equiv C-Ar-C\equiv C-]$ (R = alkyl or phenyl) units which possess excellent thermal stability after curing has already shown as promising ceramic precursors, heat-resistant materials and matrix of advanced polymer composites in aerospace and astronautics.¹⁻⁵ In recent years, some studies of silicon-containing polymers have been reported due to their potential applications. For example, poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (abbreviated as MSP) was prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of magnesia base catalysts and its residue at 1000 °C was 94% and the decomposition temperature at 5% weight loss was 860 °C under inert atmosphere.⁶⁻⁹ Poly[silyleneethynylene phenyleneethynylene] terminated with phenylacetylene, (abbreviated as BLJ) with high thermal stability was prepared by condensation of dichlorosilane and a mixture of diethynylbenzene-phenyl acetylene.^{10,11} In our previous study, poly(dimethylsilyleneethynylene-phenyleneethynylene) terminated with phenylacetylene was synthesized, which could cure at temperatures above 233 °C and showed high heat-resistant stability and char yield.¹²

The major advantages of silicon-containing arylacetylene include no volatility during curing, high decomposition temperature, high char yield after pyrolysis and high radiation resistance. But on the other hand, utilization of silicon-containing arylacetylene is limited by its brittleness, shrinkage during curing and poor interface adhesion with reinforcements in composites.

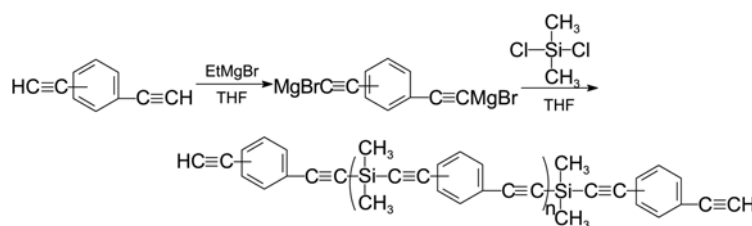
New kinds of thermosetting materials with terminal propargyl groups have been studied as high-performance polymers in recent years, owing to their excellent thermal stability, whether in air or nitrogen atmosphere, good processability, outstanding dielectric and mechanical properties.¹³⁻¹⁵

One apparent method to gain both thermal stability and mechanical property is to blend silicon-containing arylacetylene resin with bispropargyl ether. Such blends could probably benefit from the good physico-chemical attributes of the two resins.

Our purpose of this study is to investigate a novel high-performance silicon-containing arylacetylene resin modified by bispropargyl ether. Poly(dimethylsilylene-ethynylene-phenylene-ethynylene) (abbreviated as MSAR), dipropargyl ether of bisphenol A (DPBPA) and dipropargyl ether of perfluorobisphenol A (DPPFBPA) were synthesized in our laboratory as shown in Scheme 1. Kissinger and Ozawa methods have been applied to calculate the kinetic parameters for curing reaction of modified MSAR. The thermal property of modified MSAR was characterized by TGA and DMA. Using modified MSAR as the matrix, and carbon fiber as the reinforcement, the fiber reinforced composites were prepared. The thermal and mechanical properties of the



Scheme 1. Structures of DPBPA and DPPFBPA.



Scheme 2. Synthesis of MSAR.

composites were investigated.

Experimental

Materials. The dipropargyl ether of bisphenol A (DPBPA) and dipropargyl ether of perfluorobisphenol A (DPPFBPA) were prepared in our laboratory¹⁶ through condensation reaction from Bisphenol A (perfluorobisphenol A) and propargyl bromide as starting materials, benzyltriethylammonium chloride as phase transfer catalyst. Poly(dimethylsilylene-ethynylene-phenyleneethynylene) (MSAR) was synthesized in our laboratory by the condensation reaction of diethynylbenzene Grignard reagent with dichlorodimethylsilane, by the method previously described in literature.¹⁷ The synthesis route to MSAR is shown in Scheme 2.

Instrumentation. Differential scanning calorimeter (DSC) analyses were performed with a Universal V2.3 TA Instruments 2910 modulated system. The heating rate was 10 °C/min. Thermogravimetric analysis (TGA) was conducted on a METTLER TGA/SDTA 851 in nitrogen and air with a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was carried out on a NETZSCH DMA 242 analyzer operating in the double-cantilever from 50 to 530 °C at the frequency of 1 Hz with a programmed heating rate of 3 °C/min. The flexural property of the cured resin was measured according to ASTM790. The sample dimension was 80 × 15 × 4 mm, and the crosshead speed was 2 mm/min.

Preparation of Bispropargyl Ether/MSAR Resins. Appropriate quantities of MSAR and bispropargyl ether resin were charged into a three-necked bottom with a mechanical stirrer. The mixture was heated to 150 °C, and maintained with stirring until a homogenous liquid was obtained. The mixture was kept at this temperature for additional 120 min.

Table 1. Detail in Bispropargyl Ether/MSAR resin

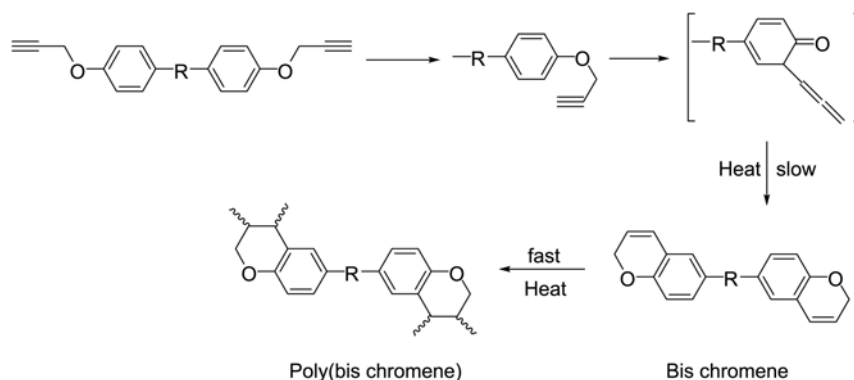
| | Modifier | MSAR/Bispropargyl Ether resin (Weight ratio) |
|-----------------|----------|--|
| DPBPA/MSAR-30 | DPBPA | 0.7:0.3 |
| DPBPA/MSAR-50 | DPBPA | 0.5:0.5 |
| DPPFBPA/MSAR-30 | DPPFBPA | 0.7:0.3 |
| DPPFBPA/MSAR-50 | DPPFBPA | 0.5:0.5 |

And finally, the DPBPA or DPPFBPA modified MSAR resins were obtained and denoted as DPBPA/MSAR and DPPFBPA/MSAR respectively as shown in Table 1.

Results and Discussions

The Curing Behavior of the Modified MSAR Resins.

The curing behaviors of DPBPA and DPPFBPA were traced by DSC. William. E. Douglas¹⁸ explained the uncatalysed thermal cure of DPBPA in detail and showed that propargyl groups rearranged to 2*H*-1-benzopyran structure (chromene) prior to polymerization, as seen in Scheme 3.¹⁸ Figure 1 showed the DSC profiles for DPBPA and DPPFBPA, and the results were tabulated in Table 2. DPBPA showed an exothermic peak with top at 278.8 °C and the amount of exotherm was 977.8 J/g, see Figure 1. The exothermic peak of DPPFBPA was 292.3 °C which was higher than that of DPBPA. The exotherm was attributed to the Claisen rearrangement and the polymerization. The Claisen rearrangement, being electrophilic in nature, is retarded by the presence of electron-withdrawing groups on the benzene ring.¹⁹ In the present case, perfluoroisopropylidene group is more electron-withdrawing than the isopropylidene group. The rearrangement reaction is a slow process which follows



Scheme 3. Mechanism of polymerization of bispropargyl ether.

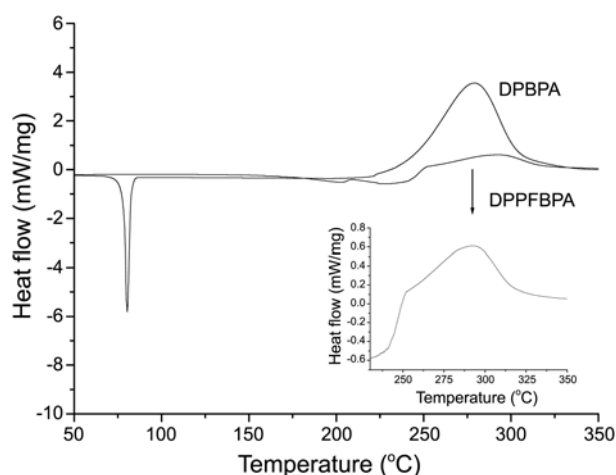


Figure 1. The DSC curve of DPBPA and DPPFBPA.

polymerization immediately, so reactivity of rearrangement determined the reactivity of curing reaction.

Figure 2 presented DSC trace of the bispropargyl ether/MSAR resin at a heating rate of 10 °C/min. It was observed that the bispropargyl ether/MSAR resin showed a unimodal reaction exotherm due to its thermopolymerization. Given the non-symmetrical shape of DSC curves, it has been assumed that they would represent two independent reactions. The overall exotherm of bispropargyl ether/MSAR resin was deconvoluted mathematically using Gaussian fitting as shown in Figure 3. A wide exothermic peak was split into Peak A and Peak B, and the peak positions and the amount of exotherm for both of the peaks were tabulated in Table 2. As shown in Table 2, the maximum temperatures of exotherm of Peak A were higher than that of MSAR suggesting Peak A be attributed to the copolymerization between bispropargyl ether and MSAR. And the maximum temperatures of exotherm of Peak B were in good agreement with that of bispropargyl ether. So Peak B was assigned to self-polymerization of the residual bispropargyl ether.

Kissinger²⁰ and Ozawa²¹ methods were used for the kinetic evaluation.

Kissinger methods:

$$\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R} \quad (6)$$

Flynn-Wall-Ozawa method:

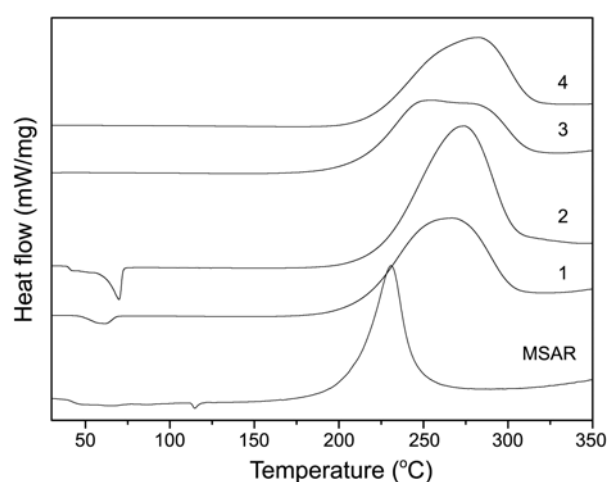


Figure 2. The DSC curve of bispropargyl ether/MSAR resin. (1) DPBPA/MSAR-30; (2) DPBPA/MSAR-50; (3) DPPFBPA/MSAR-30; (4) DPPFBPA/MSAR-50.

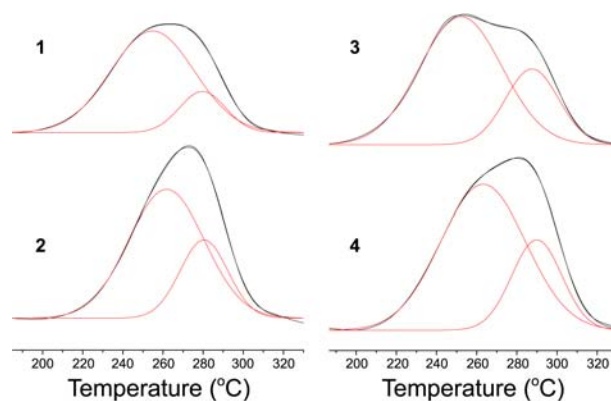


Figure 3. The DSC curves of bispropargyl ether/MSAR resin deconvoluted mathematically using Gaussian fitting. (1) DPBPA/MSAR-30; (2) DPBPA/MSAR-50; (3) DPPFBPA/MSAR-30; (4) DPPFBPA/MSAR-50.

$$\frac{d(\text{Log} \beta)}{d(1/T_p)} = -1.052 \frac{E_a}{R} \quad (7)$$

where T_p is the exothermic peak temperature. By the methods of Kissinger and Ozawa, the apparent activation energy was evaluated from the maximum reaction rate under the constant heating-rate condition. The results listed in Table 3

Table 2. Analysis of DSC result of bispropargyl ether/MSAR resin

| | Exotherm peak temperature (°C) | ΔH (J/g) | Peak A | | Peak B | |
|-----------------|--------------------------------|------------------|------------------|------------------|------------------|------------------|
| | | | Temperature (°C) | ΔH (J/g) | Temperature (°C) | ΔH (J/g) |
| MSAR | 230.8 | 450.3 | | | | |
| DPBPA/MSAR-30 | 263.8 | 623.8 | 254.7 | 506.8 | 279.6 | 116.9 |
| DPBPA/MSAR-50 | 272.2 | 838.6 | 261.8 | 605.4 | 280.2 | 233.2 |
| DPPFBPA/MSAR-30 | 254.7 | 549.4 | 252.3 | 397.9 | 288.7 | 151.5 |
| DPPFBPA/MSAR-50 | 279.1 | 570.7 | 262.8 | 417.8 | 290.0 | 152.2 |
| DPBPA | 278.8 | 977.8 | | | | |
| DPPFBPA | 292.3 | 321.3 | | | | |

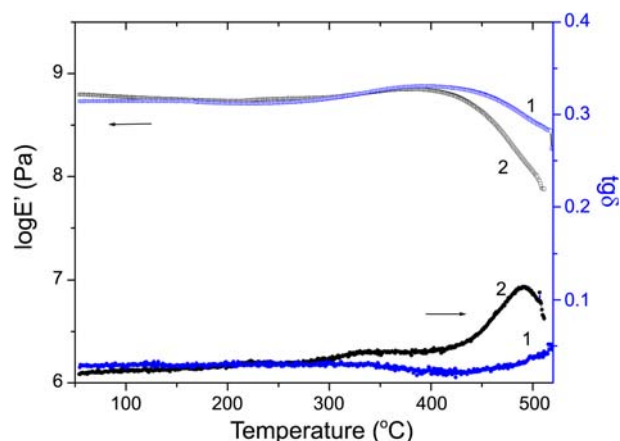
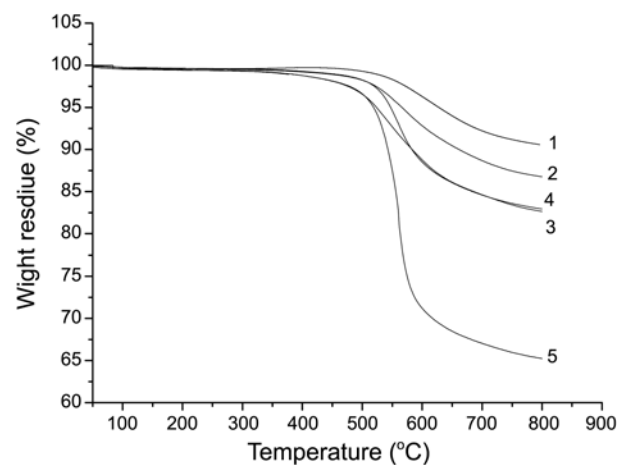
Table 3. The apparent kinetic parameters of cure reactions for Bispropargyl Ether/MSAR resin

| | Peak A (KJ/mol) | | Peak B (KJ/mol) | |
|-----------------|-----------------|------------|-----------------|------------|
| | Ozawa | Kinssenger | Ozawa | Kinssenger |
| DPBPA/MSAR-50 | 145.5 | 136.8 | 164.4 | 156.2 |
| DPPFBPA/MSAR-50 | 158.7 | 148.8 | 179.6 | 169.6 |

showed that the kinetic parameters of DPBPA/MSAR-50 and DPPFBPA/MSAR-50 obtained from methods of Kissinger agreed well with the results calculated by the Ozawa. This indicated that the values of apparent activation energy are believable. During the curing process of DPBPA/MSAR-50, the average activation energy of copolymerization between DPBPA and MSAR and polymerization of residual DPBPA were lower than those of DPPFBPA/MSAR-50. This phenomenon resulted from the high reactivity of DPBPA.

Properties of the Cured Bispropargyl Ether/MSAR Resin.

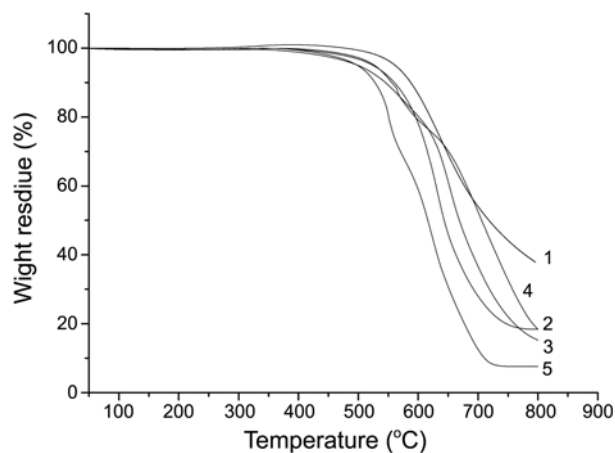
The curing procedure of the bispropargyl ether/MSAR resin was chosen as follows: 170 °C/2 h + 210 °C/2 h + 250 °C/4 h.

**Figure 4.** The DMA curve of the cured DPBPA/MSAR (1) DPBPA/MSAR-30; (2) DPBPA/MSAR-50.**Figure 5.** The TGA curves of the cured DPBPA/MSAR and DPPFBPA/MSAR with different weight ratios in N₂. (1) MSAR; (2) DPBPA/MSAR-30; (3) DPBPA/MSAR-50; (4) DPPFBPA/MSAR-30; (5) DPPFBPA/MSAR-50.

As shown in Figure 4, the storage modulus (*E*) of cured Bispropargyl Ether/MSAR resin was not decrease obviously before 400 °C. Glass transition temperature of the cured bispropargyl ether/MSAR resin was detected by DMA. Generally, in a DMA measurement, the damping was identified as the glass transition temperature because a large decrease in modulus occurred at this point. The *T_g* of the cured DPBPA/MSAR (with a weight ratio of DPBPA: MSAR = 0.3:0.7) was not observed before 530 °C, while the *T_g* of the cured DPBPA/MSAR (with 50 wt % DPBPA loading) decreased to 487 °C.

The TGA analysis (in N₂ and air) results of the cured bispropargyl ether/MSAR resins were shown in Figure 5, Figure 6 and Table 4. As the bispropargyl ether loadings increased, the values of decomposition temperature *T_{d5}* (5% mass loss) and char yield (*Y_c*, 800 °C) decreased. The main reason was probably owing to the poor thermal stability of isopropylidene and perfluoroisopropylidene in the backbone of DPBPA and DPPFBPA. With the same loading, thermal stability of DPBPA/MSAR was better than that of DPPFBPA/MSAR.

Properties of the Composite of Bispropargyl Ether/MSAR Resin. The DPBPA/MSAR-50 resin was used for the matrix of carbon fiber reinforced composite. As shown in Figure 7, The storage modulus (*E*) of the cured DPBPA/MSAR-50 composite did not show decrease visibly before 400 °C and its *T_g* was 486 °C.

**Figure 6.** The TGA curves of the cured DPBPA/MSAR and DPPFBPA/MSAR with different weight ratios in Air. (1) MSAR; (2) DPBPA/MSAR-30; (3) DPBPA/MSAR-50; (4) DPPFBPA/MSAR-30; (5) DPPFBPA/MSAR-50.**Table 4.** Analysis of TGA results of DPBPA/MSAR and DPPFBPA/MSAR

| | In N ₂ | | In air | |
|-----------------|----------------------------|-------------------------------|----------------------------|-------------------------------|
| | <i>T_{d5}</i> (°C) | <i>Y_c</i> , 800 °C | <i>T_{d5}</i> (°C) | <i>Y_c</i> , 800 °C |
| MSAR | 631 | 90.9 | 561 | 37.8 |
| DPBPA/MSAR-30 | 565 | 86.7 | 524 | 18.4 |
| DPBPA/MSAR-50 | 523 | 82.6 | 499 | 15.2 |
| DPPFBPA/MSAR-30 | 547 | 82.9 | 526 | 18.4 |
| DPPFBPA/MSAR-50 | 519 | 65.2 | 498 | 7.6 |

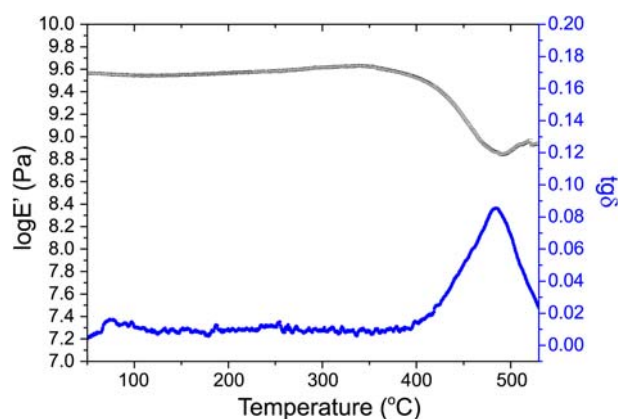


Figure 7. The DMA curves of DPBPA/MSAR-50 composite.

The carbon fiber (T300) reinforced DPBPA/MSAR-50 (50%:50% weight ratio) composite exhibited excellent flexural properties (flexural strength: 485 MPa; flexural modulus: 57.6 GPa) which were higher than that of MSAR composite (flexural strength: 275 MPa; flexural modulus: 59.4 GPa) at room temperature. More remarkable was that the retention rates of the strength and the modulus were 85% and 87%, respectively (flexural strength: 409 MPa; flexural modulus: 50.2 GPa) at 300 °C. Therefore, the resin would be expected to be used as the matrix of advanced composites.

Conclusions

New kinds of silicon-containing arylacetylene resin (MSAR) modified by dipropargyl ether were prepared and characterized by DSC, DMA and TGA analysis. The resin had low viscosity and a wide process window. The T_g of the cured DPBPA/MSAR reached 486 °C. The decomposition temperature (T_{d5}) of the cured resins and char yield (Y_c , 800 °C) decreased as the dipropargyl ether loadings increased, especially in air. The carbon fiber (T300) reinforced composites exhibited excellent flexural properties at room temperature with a high property retention at 300 °C. The results showed that the hybrid resins had good processability and thermal stability.

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