Study on novel silicon-containing dipropargyl ethers

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Abstract. The silicon-containing dipropargyl ether (SDE) is a novel class of thermosetting resins with many fascinating advantages such as high thermal stability and ablative resistance. But it also suffers from some shortcomings such as low mechanical properties of cured resin. To improve the mechanical properties and some processing problems of it, three different structural SDE were synthesized by Grignard reaction. The solubility, cure shrinkage rate, cure reaction, thermal properties and mechanical properties were studied. The results indicate that the SDE resins are dissolved in most organic solvents. The cure shrinkage rate of SDE resins are no more than 1.5%. The initial temperature (T₁), peak temperature (Tₚ) and finish temperature (Tₖ) are more than 230°C, 280°C and 310°C. The temperature at 5% mass loss (Td₅) and residual yield at 800 °C (Yr 800°C) in nitrogen are over 410°C and 68%. Flexural strength of resins is over 12 MPa. The SDE resin is promising to be an excellent thermosetting resin.

1. Introduction
High temperature resistant resin has been widely used in aerospace, microelectronics, metallurgy, transportation and petroleum pyrolysis[1-3]. Thermosetting material, in particular, it has good thermal and mechanical property, and its size stability is better than the thermoplastic material[4]. Due to the excellent properties, it has been used in many fields and plays the role of replacing traditional material. With the development of The Times and industrial progress, the demand for high performance heat-resistant materials has become more and more, and the development of resin matrix materials with high quality and high strength and high heat resistance has become a hot topic in the research of materials[5].

Silicon-containing dipropargyl ether (SDE) is a new kind of organic-inorganic hybrid thermosetting resins, it containing alkynyl, benzene and silicon, which makes the SDE not only has good high temperature resistance performance, but also good high temperature ceramic and dielectric properties[6]. But it also has some weaknesses. Because of the high concentration of benzene ring, high cross linking density, as a result the resin has large rigidity, easy to occur the brittle fracture, so improve the mechanical properties of the matrix resin have become the key in the SDE resin[7-8].In 1994, Itoh et al[9]. inserted oxygen atoms into the main chain of aromatic resin and prepared a novel type of silicon-containing dipropargyl ether. Performance tests showed that, in the air, its Td₅ reached 470 °C, residual yield at 800°C was 43%. It has good heat-resistant performance; The mechanical properties had also been improved. In 1998, Okada et al[10].prepared the SDE resin which had diphenyl ring structures on the basis of predecessors. Study showed that the melting point of the resin was about 79 °C, The temperature at 5% mass loss and residual yield at 800°C in air were over 500°C and 50%, compared to previous single benzene ring structure, heat-resisting performance had been improved, In the same way, mechanical properties had also been improved.

In this paper, three kinds of novel SDE resins were synthesized by Grignard reaction and their
structures were characteristic by infrared analysis. After synthesis of novel SDE resins, some physical properties such as solubility, cure shrinkage rate, cure reaction, thermal property and mechanical property were tested.

2. Experimental

2.1 Materials

Tetrahydrofuran (AR), Toluene (AR), Hydrochloric (AR), Magnesium powder (AR), Sodium sulphate (AR) and Aceticacid were bought from Shanghai Tian Scientific Co., Ltd. Bromoethane (AR) and Dimethyldichlorosilance (AR) were obtained from Beijing HWRK Chem Co., Ltd. Dipropargyl bisphenol S, Dipropargyl bisphenol, Dipropargyl bisphenolfluorene were synthesized in our laboratory.

2.2 Synthesis Routes

Silicon-containing dipropargyl ether of bisphenol S (SPOBS) was carried out by using a typical way. The process was as follows. Magnesium powder (0.09 mol) and tetrahydrofuran (40 mL) were added to the 1000 mL flask and stir with a certain rate. Then, bromoethane (0.09 mol) and tetrahydrofuran (40 mL) were added, when Adding finished, changed temperature to 42 °C, and the temperature response 2 h. Then dipropargyl bisphenol S (0.04 mol) and tetrahydrofuran (580 mL) were added, changed temperature to 68 °C, 2 h at this temperature. Next dimethyldichlorosilance (0.03 mol) and tetrahydrofuran (40 mL) were added, after the temperature to 68 °C, reflux reaction for 2 h. and more, aceticacid (15 mL), toluene (100 mL), hydrochloric acid (10 mL) and water (100 mL) were dropped. Finally, the SPOBS was reached[11].

Silicon-containing dipropargyl ether of diphenol (SPODP) and silicon-containing dipropargyl ether of bisphenolfluorene (SPOBPF) were synthesized by using the same way.

2.3 Preparation of Cured Resins

First, the three resins were placed into the molds. Then, the molds were transferred to the vacuum oven. Finally, taking the curing process of 210 °C/2 h, 250 °C/2 h and 300 °C/4 h, and corresponding curing resins were obtained.

2.4 Measurements

The Fourier-transform infrared (FTIR) spectra of materials were recorded in a Thermo Fisher Nicolet 6700 spectrophotometer. Sample powder was pressed into a pellet with KBr. Solubility results were obtained by taking 0.1 g sample to the 3 mL corresponding solvent. The curing shrinkage rates were obtained by weighting the weight of uncured and cured resins. Differential scanning calorimeter (DSC) analysis were performed on TA DSC-Q2000 modulated system at a flow rates of nitrogen 15 cm³/min. Thermo gravimetric (TGA) curves were recorded in a Mettler Toledo TGA/DSC 1 instruments. The flexural test for the resin castings were carried out using a Tension Tester DXLL-5000 according to China State Standard GB/T 2570-1995.

3. Results and Discussion

3.1 FTIR Studies

The FTIR spectra of SPOBS are shown in Figure 1(a). The absence of terminal acetylene hydrogen at 3272 cm⁻¹; the peak at 3099 cm⁻¹ is attributed to the hydrocarbon bond in the benzene ring structure; the absorption band at 2962 cm⁻¹ is attributed to the C-H bond; the strong peak at 2910 and 2859 cm⁻¹ for the telescopic vibration peaks of methylene; C≡C stretching at 2187 cm⁻¹; the peak at 1592, 1494 and 1452 cm⁻¹ are attributed to the characteristic vibration peaks of the benzene ring skeleton; 1298 cm⁻¹ corresponds to the vibrational peak of the silicon carbon bond; 1150 and 1026 cm⁻¹ correspond to Ar-O-C vibration peaks. The groups in the SPOBS molecular structure can be found in the FTIR spectra of the Figure 1(a). The FTIR spectra of SPODP are shown in Figure 1(b). The absence of terminal acetylene hydrogen at 3277 cm⁻¹, the absorption band at 2963 cm⁻¹ is attributed to
the C-H bond; the strong peak at 2917 and 2865 cm\(^{-1}\) for the telescopic vibration peaks of methylene; C≡C stretching at 2187 cm\(^{-1}\); the peak at 1604, 1499 and 1453 cm\(^{-1}\) are attributed to the characteristic vibration peaks of the benzene ring skeleton; 1266 cm\(^{-1}\) corresponds to the vibration peak of the silicon carbon bond; 1179 and 1031 cm\(^{-1}\) correspond to Ar-O-C vibration peaks. The groups in the SPODP molecular structure can be found in the FTIR spectra of the Figure 1(b). The FTIR spectra of SPOBPF are shown in Figure 1(c). The absence of terminal acetylene hydrogen at 3286 cm\(^{-1}\); the peak at 3036 cm\(^{-1}\) is attributed to the hydrocarbon bond in the benzene ring structure; the absorption band at 2961 cm\(^{-1}\) is attributed to the C-H bond; the strong peak at 2911 and 2860 cm\(^{-1}\) for the telescopic vibration peaks of methylene; C≡C stretching at 2182 cm\(^{-1}\); the peak at 1604, 1504 and 1446 cm\(^{-1}\) are attributed to the characteristic vibration peaks of the benzene ring skeleton; 1295 cm\(^{-1}\) corresponds to the vibrational peak of the silicon carbon bond; 1178 and 1034 cm\(^{-1}\) correspond to Ar-O-C vibration peaks. The groups in the SPOBPF molecular structure can be found in the FTIR spectra of the Figure 1(c). The above infrared results show that the three kinds of synthesis are correct.

Figure 1. The FTIR spectra of (a)SPOBS, (b)SPOBP, (c)SPOBPF

3.2 Solubility Studies
The solubility of three kinds of silicon-containing dipropargyl ether resins are shown in Table 1. The novel resins can be dissolved in most common organic solvents. It can also be seen from the table that the three kinds of resins have good solubilities in the polar organic solvents such as dichloromethane, ethyl acetate and 1, 4-dioxane, etc. In a less polar solvent such as hexane, the solubility is small. The solubility of each resin is consistent.
Table 1. Solubility of silicon-containing dipropargyl ether resin

| Solvent       | SPOBS | SPODP | SPOBPF |
|---------------|-------|-------|--------|
| Hexane        | -     | -     | -      |
| Diethyl ether | +     | +     | +      |
| Dichloromethane| +     | +     | +      |
| Acetone       | +     | +     | +      |
| Trichloromethane| +   | +     | +      |
| Tetra chloromethane| + | +    | +      |
| Ethyl acetate | +     | +     | +      |
| 1,4-Dioxane   | +     | +     | +      |
| Dimethylformamide| + | +  | +      |
| Dimethylacetamide| + | +  | +      |

Note: “+”Soluble; “-”Insoluble.

3.3 Curing Shrinkage Rate Studies

The change of density and shrinkage rate of SPOBS, SPODP and SPOBPF resins before and after curing are shown in Table. It can be seen that the curing shrinkage rate of each resin is not very different, and the value is stable between 1.3 and 1.5%, and the value is relatively small. Before and after curing, the size of the sample size changes little, which can be very good to maintain the original appearance. However, the low shrinkage can cause the sample to die hard, and the solidified cooling spline can be broken easily.

Table 2. Curing shrinkage of silicon-containing dipropargyl ether resin

| Sample     | Uncured/g·cm⁻³ | Cured/g·cm⁻³ | Cure shrinkage rate/% |
|------------|---------------|--------------|----------------------|
| SPOBS      | 1.3327        | 1.3427       | 1.49                 |
| SPODP      | 1.3142        | 1.3315       | 1.30                 |
| SPOBPF     | 1.3210        | 1.3406       | 1.46                 |

3.4 DSC Studies

The DSC curves are recorded (Figure 2) to understand the melting and curing characteristics of SPOBS, SPODP and SPOBPF resins. The parameters obtained from DSC curves are tabulated in Table 3. DSC studies of resins showed that initial curing temperature (T_i) are high, the highest SPOBS resin starting temperatures as high as 250 °C, peak temperature (T_p) are 40 °C higher than the initial curing temperature, SPOBPF appeared two exothermic peak, curing of resin termination temperature (T_f) are above 310 °C. Therefore, it need high temperature for the resins to be cured completely. There is a difference in heat release, and SPODP has the highest heat release rate of 1148 J/g, and high heat release can easily lead to the occurrence of detonation, and it is necessary to pay attention to the control of the heating process.
Figure 2. DSC curves of silicon-containing dipropargyl ether resin

Table 3. DSC results of silicon-containing dipropargyl ether resin

| Sample  | $T_i/°C$ | $T_p/°C$ | $T_f/°C$ | $\Delta H/J·g^{-1}$ |
|---------|----------|----------|----------|---------------------|
| SPOBS   | 250      | 295      | 335      | 968                 |
| SPODP   | 248      | 283      | 311      | 1148                |
| SPOBPF  | 235      | 282      | 350      | 623                 |

3.5 TGA Studies

Thermo gravimetric analysis is one of the commonly used techniques for rapid evaluations of the thermal stability of different materials and also indicates the decomposition of polymers at various temperature. The TGA curves are for resins are shown in Figure 3 and parameters are tabulated in Table 4. The temperature of 5% mass loss ($T_{d5}$) of three resins are above 400 °C, especially the $T_{d5}$ of SPOBPF is reached more than 470 °C. The residual yield at 800°C in nitrogen are over 69%. The results indicate that the three kinds of resin have good thermal decomposition properties.

Figure 3. TGA curves of silicon-containing dipropargyl ether resin

Table 4. TGA results of silicon-containing dipropargyl ether resin

| Sample  | $T_{d5}/°C$ | $Y_C (800°C)/%$ |
|---------|-------------|-----------------|
| SPOBS   | 413         | 72              |
| SPODP   | 445         | 69              |
| SPOBPF  | 472         | 71              |

3.6 Mechanical Property Studies

The flexural properties for the three kinds of resin are summarized in Table 5. As can be seen from the table, the SPOBS has the highest flexural strength at ambient temperature and the strength is over 14 MPa. The other resins also have the good mechanical properties. They all have the almost flexural modulus. Mechanical properties of these resins show no significant difference. The possible reason for this phenomenon is that when cured, the cured structure has soft cross linking network and the resin displays mechanical properties typical of soft thermosets with high flexural strength[12].

Table 5. Mechanical properties of silicon-containing dipropargyl ether resin

| Sample  | Flexural strength/MPa | Flexural modulus/GPa |
|---------|------------------------|----------------------|
| SPOBS   | 14.05±1.92             | 2.46±0.08            |
| SPODP   | 12.30±0.67             | 2.18±0.13            |
### 4. Conclusion

Three kinds of SDE resins by Grignard reaction were prepared. The structures were represented by FTIR. These resins exhibit excellent solubility and had the low curing shrinkage rate. The cured resins displays good mechanical properties and high heat resistance. The temperature at 5\% mass loss (T_{d5}) and residual yield at 800°C (Y_{800°C}) in nitrogen are over 410°C and 68\%. Flexural strength of resins is over 12 MPa. The resin would be a good candidate of a high performance thermosetting resin.

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