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Research Article

Study on Properties of Heat-Resistant Hybrid Resin Containing Silicon and Composites

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In recent years, one kind of novel hybrid polymer containing silicon has already been reported in the field of high-temperature resistance polymer. Gradually, it has been a research hotspot in the field of high-performance matrix resins because of excellent heat resistance and dielectric properties. The composite was prepared by M-aminophenylacetylene terminated polymethyldiphenylethynyl silane (MDPES-2) as a matrix and nonalkali glass cloth as reinforced material using a hot press process. The cure reaction of MDPES-2 was characterized. Meanwhile, heat resistance, mechanical properties, and dielectric properties of MDPES-2 composites were systematically studied in this paper. The results showed that flexural strength at room temperature is 321 MPa and flexural strength retention at 240°C was 98.3%. Flexural strength retention after thermal treatment at 500°C for 7 min was 84%. In addition, ε and dielectric dissipation factor (tan δ) were 3.9 and 2.0×10^{-3} (10 GHz).

1. Introduction

With the rapid development of aerospace technology, it puts forward higher requirements on high-temperature-resistant composite materials. As a result, the research of high-temperature-resistant composite materials has become the priority development direction of advanced aerospace materials. The high-temperature-resistant performance of composite materials mainly depends on the matrix resin, so the research of high-temperature-resistant resin has an extremely vital significance.

The sol-gel method is one of the important ways to prepare organic-inorganic hybrid materials. Through the sol-gel method, scientists have prepared a variety of organic-inorganic hybrid materials containing silicon and graphene, which broadens the application of polymer materials. The range improves the mechanical properties, heat resistance, and residual carbon rate of polymer materials. Chiang et al. have prepared a phenolic/SiO_2 hybrid organic-inorganic nanocomposite, and the modified hybrid composite has good thermal properties. The temperature at which 5% weight loss occurs increased from 281°C to 350°C [1]. The bending strength is increased by 6-30%. The organic-inorganic phase formed by the multidimensional structure and molecular assembly prepared by the sol-gel method is of great interest to hybrid materials, but there are also products with low molecular weight, poor stability, and relatively low bond energy, which are low-level issues [1–5]. The performance of the silylyne hybrid resin prepared by the grit method is greatly improved compared with the organic-inorganic hybrid material prepared by the sol-gel method. The Td_5 of the cured resin under N_2 atmosphere (when the resin weight is 5%; the thermal decomposition temperature) is above 600°C, and the bending strength of the prepared glass fiber composite material can reach more than 200 MPa. The excellent dielectric properties, mechanical properties, and high-temperature ceramic properties have gradually attracted the attention of researchers [6–15]. Corriu et al. [16, 17] synthesized poly(methylene silicon-based ethinyl) series polymer by the organic lithium method. The result of

thermogravimetric analysis showed that the initial decomposition temperature of cured resin in argon gas was 450°C. And the mass loss rate at 1400°C was 13%~37% according to different substituents on the silicon atoms. Itoh et al. [18–22] synthesized poly[(benzene heartland of a silicon) and ethinyl-1,3- and benzene phosphite ethinyl] (MSP) [-Si(Ph)H-C≡C-C_6H_4-C≡C-] by dehydrogenation coupling reaction. The raw material contained diacetylene-benzene and phenylsilane. The relationship between the structure and heat resistance of the synthetic product was systematically researched. Td_5 of cured material in argon was as high as 860°C, and Td_5 in air was 567°C, which can be applied to high-temperature-resistant composites. Zhou et al. [23–35] synthesized a new kind of silicone resin methyl diphenyl acetylenyl silane (MDPES) and methyltriphenylacetylenyl silane (MTPES). The research results showed that MDPES and MTPES after crosslinking had excellent heat resistance and dielectric properties. By using DSC and FT-IR to track the polymerization crosslinking reaction, it is proved that the crosslinking reaction of MDPES included the hydrogenated silicon addition reaction between Si—H, C≡C bond, and the Diels-Alder reaction between the C≡C bond. MTPES is used as matrix resin of composites, which has the characteristics including high crosslinking density, rigid aromatic ring structure, excellent resistance to heat oxidation after introducing the silicon atoms into the molecular structure, and high carbon yield, and due to the low melt viscosity of the resin and absence of small molecules of gas in the curing process, it has good molding process properties.

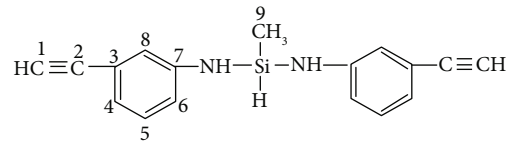
In this research, we selected m-aminophenylacetylene terminated polymethyldiphenylethynyl silane and named it MDPES-2. The curing properties of MDPES-2 and the heat resistance, mechanical properties, and dielectric properties of MDPES-2 matrix composites were studied. These characteristics provide a scientific basis for better understanding the relationship between resin structure and performance, optimizing curing process conditions, and further improving product quality. It is expected to become a promising new high-temperature-resistant resin matrix.

2. Experimental

2.1. Materials. MDPES-2 resin was prepared by the Key Laboratory of Special Functional Polymeric Materials and Related Technology of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology. The structural formula is shown in Table 1. FT-IR (KBr, cm^{-1}) 3380 (N-H), 2160 (Si-H), 1061 (Si-N), 1600~1450(benzene), ^{1}H NMR ($CDCl_3$,ppm)6.6-7.2 (m, *ortho* benzoyl, 4H), 5.05 (s, 1H,-SiH),3.8 (d, 2H,NH_2), 3.0(s, 1H,-C≡CH), 0.55(m, 3H,-CH_3). ^{13}C NMR: (TMS, ppm) 86.1(s,C1), 69.8(s,C2), 124.57(s,C2), 121.3(s,C4)30.87(s,C5)117.39(s,C6)147.36(s,C7)118.77(s,-C8)25.5(s,C9). Acetone was of analytical grade and purchased from Shanghai Feida Industry and Trade Co. Ltd.

2.2. Preparation of MDPES-2 Cured Resin and Casting Body. The size of the MDPES-2 resin casting body is 3 mm × 15 mm × 120 mm. The cured resin and casting body are cured according to the following curing system: 140°C/2 h → 160°C/2 h → 180°C/2 h → 200°C/2 h → 220°C/2 h → 250°C/4 h. The heating rate is 1°C/min. A black shiny resin cured product and resin casting body were obtained.

Table 1: The structural formula of MDPES-2 resin.

Resin	Structural formula
MDPES-2	

2.3. Preparation of MDPES-2 Composites. The MDPES-2 resin was evenly mixed in acetone and impregnated with the alkali-free glass cloth after heat treatment and dewaxed (resin content was 38%). After vacuum-drying at 60°C for 3 h, the prepreg (20 layers) was put into the press which was preheated to 140°C for pressing and forming. The pressure was 3 MPa, and the following curing system was used for pressing: 140°C/2 h → 160°C/2 h → 180°C/2 h → 200°C/2 h → 220°C/2 h → 250°C/4 h. The heating rate was 1°C/min.

2.4. Characterization. Fourier Transform Infrared Spectroscopy (FT-IR) analysis was carried out on the Nicolet Magna-IR 550 Fourier transform infrared spectrometer, and the KBr tablet pressing method was applied.

The curing process of MDPES-2 resin was determined by the NETZSCH DSC 200PC differential scanning calorimeter. The atmosphere was high-purity nitrogen, and the flow rate was 40 mL/min, with the reference material α-Al_2O_3. The heating rate was 10°C/min.

The PerkinElmer Pyris Diamond thermogravimetric analyzer was also used, with the heating rate 10°C/min. The temperature range was from room temperature to 1000°C, and the atmosphere was nitrogen.

The sample surface was observed by a S4800 Scanning Electron Microscope from JEOL Corporation of Japan. To observe the section morphology of bending damage, the fracture was coated with conductive adhesive and sprayed with gold in a vacuum after quenching by liquid nitrogen, and the phase structure was observed on the scanning electron microscope. The sample size was 10 mm × 10 mm.

The dielectric constant and dielectric loss tangent of MDPES-2 resin composites were measured by a H011 microwave complex dielectric constant tester from Shanghai Chunya company. The test condition was room temperature with a frequency of 10 GHz. The sample size was Φ 50 mm.

The energy storage modulus and vitrification transition temperature were measured by a Rheogel-4000 dynamic thermomechanical analyzer, which adopted a three-point bending mode. The test frequency was 1 Hz, and the temperature range was between room temperature and 400°C. The heating rate was 5°C/min.

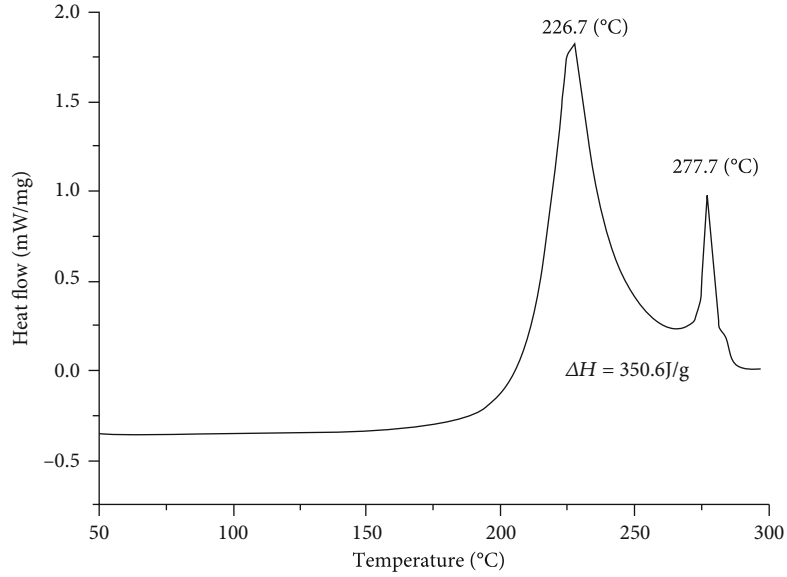


Figure 1: Dynamic DSC curve of MDPES-2 resin.

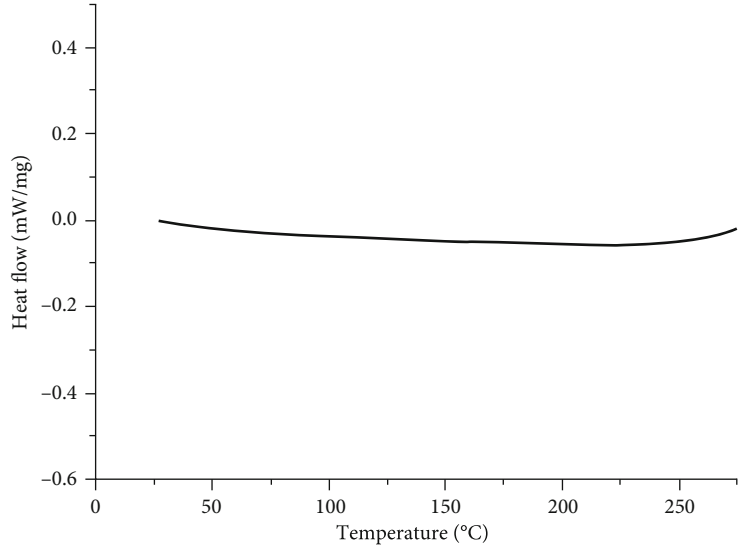


Figure 2: DSC curve of cured MDPES-2.

The flexural strength test, interlayer shear strength, and resin casting body bending strength test were conducted by the CMT4204 testing machine of New Sansi Material Testing Co., Ltd. The test standards are GB-T 1449-2005, GB-T 3357-82, and GB-T 2567-2008. The test conditions for the bending strength test include a span of 60 mm, a loading speed of 10 mm/min, and a sample size of 3 mm × 15 mm × 80 mm. The test conditions for the interlaminar shear strength test are a span of 15 mm, a loading speed of 2 mm/min, and a sample size of 3 mm × 6 mm × 25 mm. Both tests include room temperature and 240°C temperature conditions. The size of the resin casting body is 3 mm × 15 mm × 120 mm, the span is 48 mm, and the loading speed is 10 mm/min.

3. Results and Discussion

3.1. Dynamic Curing Reaction of MDPES-2 Resin. The dynamic DSC curve of MDPES-2 resin is shown in Figure 1. From the curve, it can be observed that the initial temperature (T_i), peak temperature (T_p), and final temperature (T_f) of MDPES-2 resin curing reaction were 195°C, 227°C and 278°C, 290°C, respectively, and the heat release was 351 J/g. Heat induces free radical polymerization, hydrosilylation of Si-H and C≡C, and Diels-Alder reaction between C≡C will happen in the process of heating up of MDPES-2 resin. As a result, two exothermic peaks occurred during the whole process of curing reaction, and highly crosslinked cured products were formed.

Table 2: Mechanical properties of MDPES-2 composite.

Mechanical property	Result
Flexural strength (MPa)	321
ILSS (MPa)	29

Table 3: Bending strength of MDPES resin casting.

Sample	Flexural strength (MPa)
MDPES	40.5
MDPES-2	80

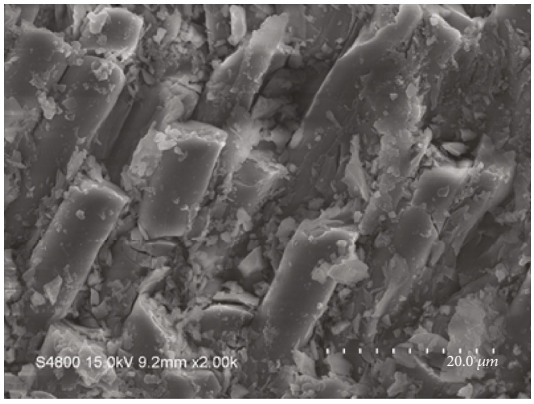


Figure 3: SEM of fractured surfaces of MDPES-2 composite (×2000).

After cooling of MDPES-2 resin cured products, DSC analysis was conducted again. At the heating rate of 10°C/min, they were heated from room temperature to 300°C, and no obvious exothermic peak was observed (Figure 2). This indicated that the silicon-hydrogen addition reaction of Si-H and C≡C as well as internal and external acetylenyl crosslinking reactions was basically completed. Meanwhile, there was no obvious glass transition temperature in Figure 2.

3.2. Mechanical Properties of MDPES-2 Composites and Resin Casting Body. The mechanical properties of MDPES-2 composites are listed in Table 2, and the bending strength of the cast body is listed in Table 3. The bending strength of the MDPES-2 composite is 321 MPa, and the interlayer shear strength (ILSS) is 29 MPa. Figure 3 is a scanning electron microscope (SEM) image of a cross-section of MDPES-2 composite material. In the sample, the fiber surface at the break of the composite material was covered by resin, and the resin tightly wrapped the fiber, indicating that the resin and the fiber have good adhesion, and there are some resin fragments at the fiber, indicating that the resin is brittle. The bending performance of the casting has increased from 40.5 MPa of MDPES to 80 MPa, indicating that this new structure greatly improves the mechanical properties of the resin.

Table 4: Retention ratio of mechanical strength at 240°C for MDPES-2 composite.

Property	Result
Flexural strength retention ratio (%)	98.4
ILSS retention ratio (%)	86

Table 5: Effect of thermal treatment at 500°C on mechanical property of MDPES-2 composites.

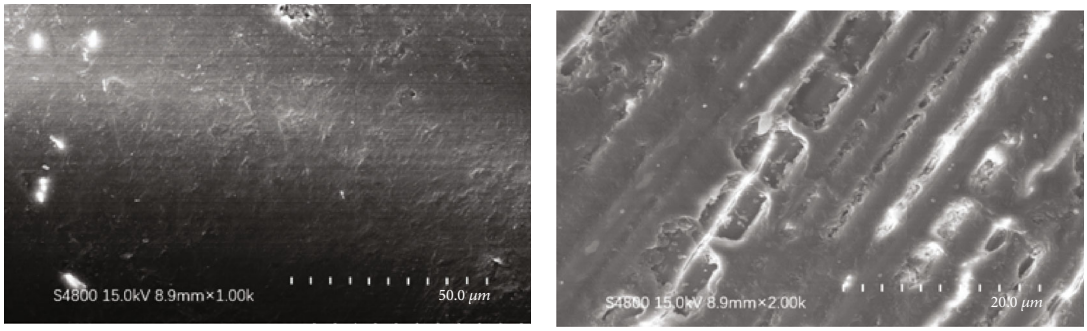
Heat treatment time (min)	Flexural strength (MPa)	Flexural strength retention ratio (%)	Quality retention ratio (%)
7	270	84	99.7
15	263	82	99.4
30	257	80	98.9

3.3. Dielectric Properties of MDPES-2 Composites. In this research, dielectric properties of MDPES-2 composites at 10 GHz were analyzed by a resonant tank. Results showed that the MDPES-2 composites had excellent dielectric properties: tan δ was 2.0×10^{-3} and ε was 3.9. Dielectric properties of the polymer depended on the dipole orientation and relaxation in the electric field, so the structure of polymer polarity and motion state of the dipole were the main factors affecting dielectric properties of polymer. The nonpolar character of the MDPES-2 resin molecular structure decided its excellent dielectric properties.

3.4. Heat Resistance of MDPES-2 Composites. As the reinforced materials, such as glass fiber and carbon fiber, had good heat resistance, the heat resistance of composites mainly depends on the heat resistance of the matrix. For the resin of advanced composites, one of the key factors was that the composites must be resistant to high temperature, in order to ensure that the composites had good performance at high temperature.

3.4.1. Retention Ratio of Mechanical Strength at 240°C. Table 4 shows the retention ratio of flexural strength and ILSS for MDPES-2 composites at 240°C. The molecular structure of MDPES-2 resin contained a large number of internal and external C≡C bonds, and Si-H bond was also introduced, which had a high crosslinking density. This molecular structure improved the high-temperature resistance of the material effectively. It can be seen from Table 3 that MDPES-2 composites had good mechanical properties at 240°C, with a flexural strength retention ratio of 98.4% and ILSS retention ratio of 86%.

3.4.2. Effect of Thermal Treatment at 500°C on Mechanical Property of MDPES-2 Composites. In order to further expand the application of MDPES-2 resin in the field of high-temperature resistance, the effects of different heat treatment times at 500°C on the mechanical and dielectric properties of MDPES-2 composites were researched. According to Table 5, the flexural strength of MDPES-2 composites after heat treatment at 500°C for 7 min, 15 min, and 30 min was 270 MPa,



(a) ×1000 (b) ×2000

Figure 4: SEM of surface of MDPES-2 composite after thermal treatment at 500°C for 30 min.

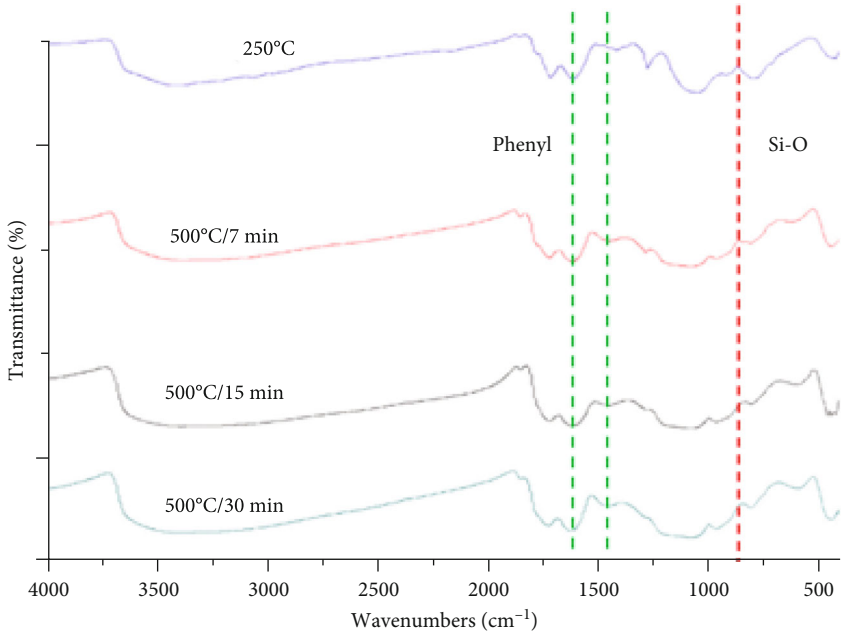


Figure 5: FT-IR spectrum of cured MDPES-2 before and after thermal treatment at 500°C.

263 MPa, and 257 MPa, respectively. Flexural strength retention ratios were 84%, 82%, and 80%, respectively. The quality retention ratios of composites were 99.7%, 99.4%, and 98.9%, respectively. With the extension of heat treatment time, flexural strength, flexural strength retention ratio, and mass retention ratio all decreased slightly but still maintained good performance.

After heat treatment in air at 500°C for 30 min, the sample surface of MDPES-2 composites was smooth and there was no bubble popping. Figure 4(a) shows the SEM image of the surface of MDPES-2 composites after heat treatment at 500°C for 30 min. The surface of the composites was kept flat and dense, which indicated that the MDPES-2 resin had great heat oxidation resistance, which was mainly attributed to the introduction of silicon atoms in the structure of MDPES-2 resin and the high crosslinking density of the system. When magnification times turned to 2000 (Figure 4(b)), it can be found that the fibers were closely connected with each other by the resin, and there were not many gaps between the fibers. The resin and the fiber still maintained a good interfacial bond, but the performance of resin peeling occurred in some areas. This was mainly due to part of the resin being oxidized ablation at high temperature.

Table 6: Effect of thermal treatment at 500°C on dielectric property of MDPES-2 composites.

Heat treatment time (min)	tan δ	ε
0	2.0×10^{-3}	3.9
7	3.1×10^{-3}	3.9
15	4.3×10^{-3}	4.1
30	6.2×10^{-3}	4.3

In order to characterize the structural changes of the cured MDPES-2 resin during the heat treatment at 500°C in

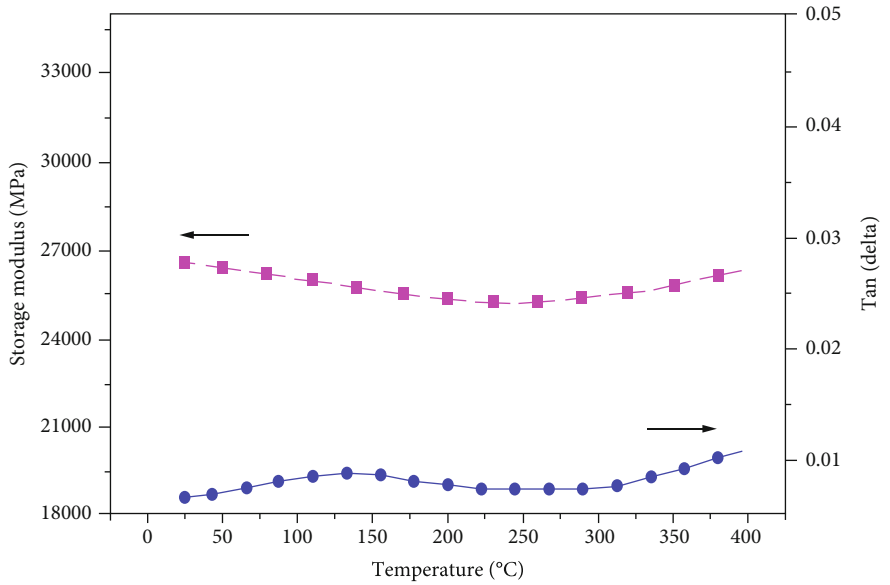


Figure 6: DMA curve of MDPES-2 composite.

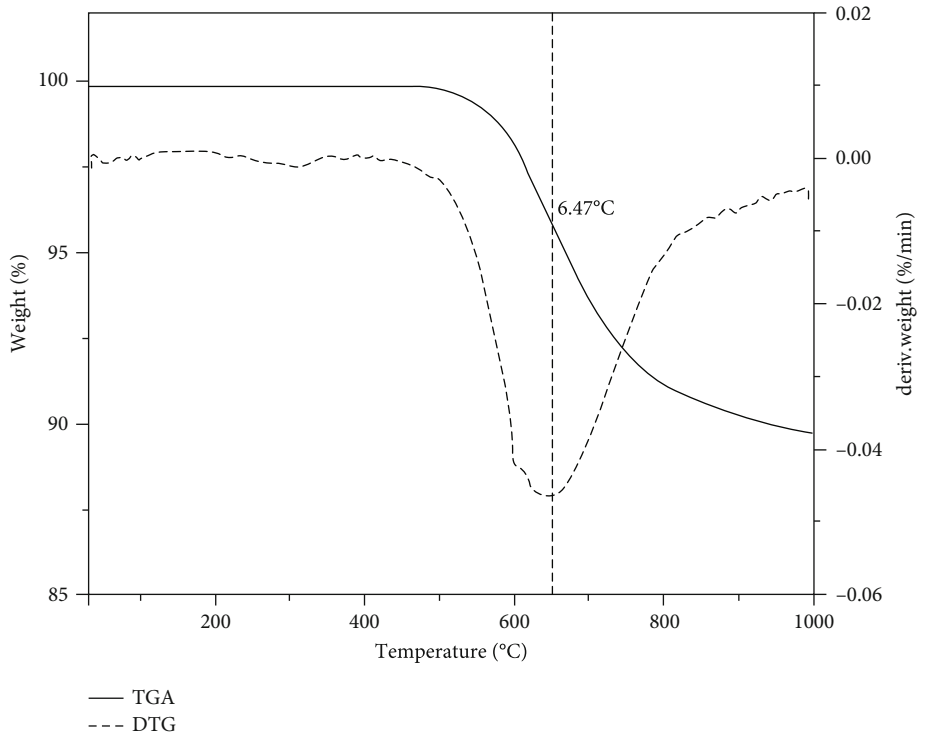


Figure 7: TGA curve of MDPES-2 resin in a flow of nitrogen.

air, the MDPES-2 resin at different stages of heat treatment was analyzed by infrared spectroscopy. Figure 5 shows the infrared spectra of MDPES-2 resin cured and treated at 500°C for 7 min, 15 min, and 30 min, respectively. It can be seen from Figure 5 that with the extension of heat treatment time, the characteristic absorption peak of benzene ring (1610-1440 cm^{-1}) still existed with no obvious change in strength, while the characteristic absorption peak of silica (798 cm^{-1}) gradually increased and widened, indicating the gradual formation of inorganic component silica.

3.4.3. Effect of Thermal Treatment at 500°C on Dielectric Property of MDPES-2 Composites. Table 6 shows the influence of heat treatment time at 500°C on the dielectric properties of MDPES-2 composites. According to Table 6, tan δ of MDPES-2 composites were 3.1×10^{-3}, 4.3×10^{-3}, and $6.2 \times$

10^{-3}, respectively, after heat treatment at 500°C for 7 min, 15 min, and 30 min, and ε were 3.9, 4.1, and 4.3, respectively. With the extension of heat treatment time, $\tan\delta$ and ε increased slightly. This was mainly due to the fact that after the heat treatment of MDPES-2 resin at 500°C in the air, some groups (such as the methyl group) were pyrolyzed to form a carbon structure, which made the dielectric performance of the material decreased slightly, but the overall dielectric performance remained in a good level.

3.4.4. Dynamic Mechanical Properties of MDPES-2 Composites. Figure 6 shows the DMA curve of MDPES-2 composites. As can be seen from Figure 6, the energy storage modulus of MDPES-2 composites decreased slightly from room temperature to 243°C and decreased from 26595 MPa to 25251 MPa. With the rise of temperature, the energy storage modulus increased. When the temperature was raised to 400°C, the energy storage modulus reached 26420 MPa, indicating that the postcuring of MDPES-2 resin occurred and the rigidity of the material was improved. At the same time, it can be clearly found from the curve of $\tan\delta \sim$ temperature in Figure 6 that the glass transition temperature of MDPES-2 composites was greater than 400°C.

3.4.5. Heat Resistance of MDPES-2 Resin. Figure 7 shows the TGA and DTG curves of the MDPES-2 resin casting matrix heated to 1000°C at a rate of 10°C/min in nitrogen. The MDPES-2 resin has excellent heat resistance, and Td_5 and mass retention at 1000°C are 644°C and 89.6%, respectively. It can be seen from Figure 7 that the cured material of MDPES-2 resin is stable in nitrogen at 550°C, and its thermal decomposition is mainly divided into three stages, in which the decomposition rate is faster at 550-650°C, and the decomposition rate reaches 647°C. The biggest loss rate is 6%. At 650-850°C, the decomposition rate slows down and the weight loss rate is 4%. At 850-1000°C, the decomposition rate slowed down significantly, and the weight loss rate was 1%. The structure of the MDPES-2 resin contains rigid structures such as benzene rings and internal and external acetylene groups, forming a conjugated structure that can improve the heat resistance of the material. MDPES-2 resin has structural symmetry, the length of saturated chain hydrocarbon and branched chain is short, and the content of internal and external acetylene groups and silicon-hydrogen bond is high, which effectively improves the crosslink density of the resin system. At the same time, the Si atoms in the MDPES-2 resin structure can form a thermally stable inorganic compound SiO_2, which plays a role of heat insulation and thermal oxidation resistance, effectively avoiding further thermal oxidation decomposition of the resin matrix. Therefore, MDPES-2 resin has high thermal stability after curing.

4. Conclusions

By changing the resin structure, the performance of MDPES-2 resin has been greatly improved compared with MDPES. The MDPES-2 resin composite has good overall performance, with a bending strength of 321 MPa and a bending strength retention rate of 98.4% at 240°C. The constant is 3.9, and the dielectric loss tangent is 2.0×10^{-3} (10 GHz). The strength after heat treatment at 500°C for 7 minutes is 84%. In addition, the bending strength of the MDPES-2 resin casting body reaches 80 MPa, which is 49% higher than MDPES. At the same time, it has excellent heat resistance. In a nitrogen atmosphere, the mass retention rates of Td_5 and 1000°C in a nitrogen atmosphere are 644°C and 89.6%.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors disclose that there is no conflict of interest regarding the publication of this manuscript.

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