Study on epoxy resin modified by hyperbranched polysiloxane containing active amino group and its properties

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Abstract

A novel phosphorous/silicon hybrid containing active amino was synthesized by bisphenol F epoxy resin modified by 0-(2,5-Dihydroxyphenyl)-10-hydro-9-oxa-10-phosphaphenanthrene-10-oxide (ODOPB) and hyperbranched polysiloxane (APTMS-HPSi). At first, APTMS-HPSi was synthesized by a simple reaction among aminoethylamino propyltrimethoxy silane (APTMS) and tripropylene glycol (TPG). ODOPB was used to modify bisphenol F epoxy resin. Then add different content of APTMS-HPSi to the phosphorus-containing modified epoxy resin (P-EP). Fourier Transform Infrared (FTIR) Spectroscopy was used to characterized the chemical structure of APTMS-HPSi. The effects of APTMS-HPSi content on key properties was systemically investigated. Results showed that the addition of APTMS-HPSi and ODOPB effectively improve the toughness and liquid oxygen compatibility. With the increase content of APTMS-HPSi, char yield and limited oxygen index (LOI) value of the cured resin increased, and the liquid oxygen sensitivity coefficient (IRS) decreased. The elongation at break was increased 45.32% by only 6wt% loading with APTMS-HPSi in epoxy resin, and at the same time the IRS of the modified resin was reduced from 7% to 0%. When the addition amount was 6wt%, the fracture elongation, impact strength and fracture toughness K\(_{IC}\) were increased by 52.1%, 81.8% and 54.3% respectively. Therefore, adding phosphorus and hyperbranched polysiloxane to the resin can improve the liquid oxygen compatibility and toughness of the epoxy resin at the same time.

1. Introduction

With the development of aerospace technology, lightweight and high-strength resin-based composite materials are replacing metal materials. As a representative of thermosetting resins, epoxy resin as a matrix of composite materials has been widely used in many fields, such as aviation, shipbuilding, and automobiles [1, 2]. Due to its excellent advantages such as good adhesion to fibers, chemical resistance, low shrinkage when cured, and outstanding mechanical and electrical resistance properties, epoxy resin is used as an excellent material in many fields such as electrical insulation, coatings, composite matrix materials [3]. However, the fracture toughness and resistance to crack propagation of the cured epoxy resins is poor, and its impact strength decreases at the same time [4]. These shortcomings limit the application of epoxy resin in some cutting-edge fields. In order to improve the toughness of the material, some approaches have been conducted, such as the introduction of flexible segments into the resin. In order to further improve the toughness and flame-retardant properties of epoxy resin, the simultaneous introduction of silicon-containing hyperbranched polymer and ODOPB composite matrix modification into epoxy resin provides a feasible idea.

Recently, it has been discovered that hyperbranched polymers are used as a new type of epoxy modifier to improve impact resistance [5, 6]. Because they have a certain degree of compatibility with uncured resins and lack of restrictive inter-chain entanglement, they will not reduce the processability of epoxy resins, and they have
In this study, under the action of a catalyst, silane monomers and polyols were copolymerized to obtain hyperbranched polysiloxanes. ODOPB was used to modify bisphenol F to obtain phosphorus-containing

Figure 1. Synthesis of amino-hyperbranched polysiloxane (APTMS-HPSi).

an adjustable viscosity ratio with uncured resins. In addition, numerous functional groups on the surface of hyperbranched polymers can enhance the interfacial adhesion between hyperbranched structures and resins, which is essential for improving toughness of the epoxy resin matrix. Ye et al [7] found that the addition of hyperbranched polyester not only significantly improves the flame retardancy of the resin, but also made it have better overall properties, including dielectric properties, thermal stability, toughness and stiffness. Li et al [8] found that the addition of hyperbranched polysiloxane to CE/BD resins can significantly change the chemistry of the cured product, thereby significantly affecting the resin properties including toughness, thermal and dielectric properties. Among many methods to improve its thermal stability and fire resistance [9], a commonly method is to introduce flame retardant elements into the resin. To-date, flame retardant modification of resins by adding flame retardants to resins is still an effective and common method to improve the flame retardancy of resins [10–12]. The addition of hyperbranched products can improve toughness, but a small amount of addition has limited improvement in liquid oxygen compatibility. The radical chain reaction theory believes that the root cause of polymer shock sensitivity is the formation of free radicals in the process of mechanical shock, which is similar to the combustion reaction. Therefore, the introduction of flame retardant elements can effectively improve the liquid oxygen compatibility of the material. In the field of high-efficient flame retardant materials, non-halogen epoxy resins were researched due to its environmentally friendly and high efficiency [13–15]. 9,10-dihydro9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives were the most commonly used flame retardant agents for epoxy resins due to its dramatic flame retardant effect [16–20]. Li et al [21] used DOPO and 3-glycidoxy-propyltrimethoxysilane (GLYMO) to modify the resin. The results showed that it was compatible with liquid oxygen according to the liquid oxygen impact test. Furthermore, due to the phosphorus/silicon synergistic mechanism, the hybrids exhibit significantly enhanced thermal stability compared to pure epoxy resins and DOPO-containing epoxy resins and silicon-containing epoxy resin hybrids.
modified resin. Characterized the thermal stability, liquid oxygen compatibility and fracture toughness of the modified resin when different proportions of APTMS-HPSi are added to epoxy resin with a phosphorus content of 0.5wt%. The influences of the APTMS-HPSi content on the mechanical and thermal properties were characterized with tensile test, charpy impact test, flexural analysis, thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials
DGEBF as an epoxy matrix was supplied by Royal Dutch Shell Co., Ltd (epoxy equivalent = 158–172 g per equiv.). Aminoethylamino propyltrimethoxy silane (APTMS, 95%), Tripropylene glycol (TGP, 98%), Barium hydroxide (99.99%), Tetrabutylammonium Bromide (95%), 10-(2,5-dihydroxyphenyl)−10-H-9-oxa-10-phosphaphenanthrene-10-oxide (ODOPB, 99%) were bought from Shanghai Aladdin Co., Ltd (China). Diethyl toluene diamine (DETDA) was purchased from Shanghai demao chemical Co., Ltd (China), and isophorone diamine (IPDA) was purchased from Shanghai Aladdin Co., Ltd (China).

2.2. The synthesis process of HBPSi
APTMS and TGP were added into a three-neck flask in proportion with mechanical stirring. The molar ratio of APTMS and TGP was set as 1:1.8 (–OH/–OCH3 was 1.2 ). Then Ba(OH)2 (0.5wt% of APTMS and TPG) was added into the flask in a nitrogen atmosphere. The mixture were stirred at 80 °C for 3 h until no water was generated. When the mixture was cooled to room temperature, the catalyst Ba(OH)2 were removed by filtration. After the mixture were dried at 60 °C in vacuum for 4 h to remove the remaining small molecules, a kind of Colorless transparent liquid was obtained and named as APTMS-HPSi. The synthesis mechanism of hyperbranched polymer (APTMS-HPSi) is shown in figure 1.

2.3. The synthesis process of P-EP
Add ODOPB (5.23wt% of Bisphenol F) and Bisphenol F into a three-necked flask with mechanical stirring. At this ratio, the mass of phosphorus element is 0.5wt% of Bisphenol F. Then tetrabutylammonium bromide (0.5wt% of ODOPB and Bisphenol F) was added into the flask and the mixture were stirred at 160 °C for 2.5 h until the mixture became transparent yellow liquid. Named this product as P-EP. The synthesis mechanism of Phosphorus-containing modified bisphenol F (P-EP) is shown in figure 2.

2.4. Preparation of APTMS-HPSi modified epoxy resin
Different amounts of APTMS-HPSi(2wt%, 4wt%, 6wt%, 8wt%, 12wt%,16wt%) were added to the P-EP and stirred for 20 min to obtain APTMS-HPSi modified P-EP. The mixture of DETDA and IPDA was the curing agent. Mix the curing agent in a ratio of DETDA:IPDA = 10:2 and stir for 15 min. Then add the mixed amine curing agent and different amounts of APTMS-HPSi to the mixture to the resin (Cepoxy/CNH = 1:1). After stirring for 15 min, the prepolymer was degassed at 70 °C for 15 min in a vacuum oven. The above degassed prepolymer was then carefully poured into the preheated mold at 80 °C inside the oven. The molds were then placed in an oven for programmed curing at 95 °C/1.5 h + 150 °C/4 h. Finally, the mold was naturally cooled to room temperature and demolded, the resin was named as P-EP/APTMS-HPSi.
2.5. Characterization

The Fourier transform infrared spectrometer (Nicolet 6700) used in this article is produced by Thermo Nicolet Company (USA). The test used KBr tableting method to prepare the detection samples and FTIR was tested in range of 400 \( \sim \) 4000 cm\(^{-1}\).

The NMR spectrometer used in this article was the Bruker AV400 NMR spectrometer, produced by Bruker (Switzerland), and DMSO-D6 was used as the solvent.

The unnotched impact strength was tested according to GB/T 2567–2008 using Charpy Impact Machine Tester (XCJ-L, China).

According to GB/T 2567–2008, the specimens for mechanical testing are prepared. The fixed ends of the two ends of the tensile specimen are rectangular, and the fixed ends and the test area are connected by an arc with a radius of 75 mm, which is similar to the dumbbell shape. The specifications used in this experiment are 200 mm \( \times \) 20 mm \( \times \) 4 mm. The flexural specimens were made into rectangular specimens with a size of 80 mm \( \times \) 15 mm \( \times \) 4 mm. The model of the electronic universal material testing machine used in this experiment is Instron 5967. The loading rate during tensile and bending tests is 2 mm min\(^{-1}\). Five samples are prepared for each system for testing.

Dynamic mechanical analysis (DMA) was performed using Perkin-Elmer DMA 8000. The tests were carried out from \(-90^\circ\)C to 250°C with a heating rate of 10°C min\(^{-1}\).

Thermogravimetric analysis (TGA) was carried out using NETZSCHSTA449F3 at a heating rate of 10°C min\(^{-1}\) in a nitrogen atmosphere. The tests were carried out from 30°C to 800°C. Ti represents the initial degradation temperature, which is the temperature at which the weight loss of the sample reaches 5wt%.

Scanning Electron Microscope (SEM, JSM-5610LV) was employed to observe the fractured surfaces of samples. To improve conductivity, all samples should be sprayed with gold before scanning the fracture surface of the samples. The accelerating voltage was 20 kV during the test.

The sample for the liquid oxygen impact sensitivity test is prepared according to the American Standard ASTM D2512–1995 (2008). The sample is a disc with a thickness of 1.3 mm and a diameter of 20 mm. According to the American Standard ASTM D2512–1995 (2008), in order to clearly characterize the liquid oxygen compatibility of the material, the above experimental results are digitally characterized and the liquid oxygen compatibility of the material is obtained.
Sensitivity coefficient is calculated through different weights of different phenomena. One set of samples we carry out 20 tests. When liquid oxygen incompatibility occurs, the weights of various phenomena are as follows: carbonization = 0.4; flash = 0.6; explosion = 0.9; combustion = 1.

The final liquid oxygen sensitivity coefficient is calculated by multiplying the number of occurrences of each incompatibility by the weight, and then dividing by the total number of tested samples. If there are unsafe phenomena of explosion, flashing, burning or carbonization in these 20 tests, the liquid oxygen sensitivity coefficient (IRS) of the sample is calculated according to the formula (1) according to the number of times of various phenomena in the test:

\[
IRS = \frac{\sum_{i} w_i n_i}{N}
\]

(1)

\(N\) represents the number of tests, \(w_i\) is the coefficient calculated when different phenomena occur, \(w_1, w_2, w_3,\) and \(w_4\) represent carbonization, flash, explosion, and combustion, and their values are 0.4, 0.6, 0.9, and 1, respectively. \(n\) represents the number of occurrences of this phenomenon. The smaller the IRS value of the material, the better the liquid oxygen compatibility of the material.

Figure 4. The FTIR spectra of APTMS, TPG, and APTMS-HPSi.

Figure 5. The FTIR spectra of the distillate.
3. Results and discussion

3.1. Curing mechanisms
In order to find the reasons for the different performances between P-EP resins and P-EP-APTMS-HPSi resin, the difference between the two crosslinking networks is first discussed. In P-EP resin, the epoxy group reacts with the active hydrogen in the mixed amine curing agent to form a network structure. When APTMS-HPSi was added to P-EP resin, APTMS-HPSi will react with the epoxy group in P-EP due to the presence of amino groups. APTMS-HPSi has many unoccupied spaces and flexible Si–O bonds, so the network of P-EP-APTMS-HPSi resins is expected to be flexible and tougher than that of P-EP resin. The reaction equation is shown in figure 3.

3.2. FTIR and $^1$H NMR
The FTIR spectra of APTMS, TPG, and APTMS-HPSi are shown in figure 4. APTMS (figure 4(a)) holds major peaks around 3363 cm$^{-1}$ and 3292 cm$^{-1}$, which are the vibration peaks of $–$NH$_2$, and the absorption peak at 1084 cm$^{-1}$ is the stretching vibration peak of the Si–O bond. The peak of the $–$OH group appears at 3416 cm$^{-1}$ in the FTIR spectrum of DPG (figure 4(b)). Figure 4(c) presents the spectrum of the hyperbranched polysiloxane APTMS-HPSi, in which the same amino vibration peaks of $–$NH$_2$ appear at 3363 cm$^{-1}$ and 3292 cm$^{-1}$, indicating that the $–$NH$_2$ did not participate in the reaction. The position of the absorption peak of silicon-oxygen bond in APTMS-HPSi is appeared at 1192 cm$^{-1}$ due to the change of the chemical environment. The

![Figure 6](image-url)

![Figure 7](image-url)
above can preliminarily prove that APTMS reacts with TPG, and the –NH₂ in the coupling agent does not participate in the reaction during the polymerization.

It can be seen from figure 5 that the –OH stretching vibration peak appears at 3384 cm⁻¹, the –OH bending vibration peak appears at 1414 cm⁻¹ and 656 cm⁻¹. The –CH stretching vibration peaks appear at 2946 cm⁻¹ and 2833 cm⁻¹, –CH bending vibration peaks appears at 1452 cm⁻¹, and C–O stretching vibration peaks appears at 1032 cm⁻¹. This spectrum is similar to the infrared spectrum of standard anhydrous methanol, and it is preliminarily inferred that the distillate is methanol.

The 1H NMR chart shown in figure 6 further supports the chemical structure of APTMS-HPSi. Figure 6 shows the ¹H NMR spectra of (a) APTMS-HPSi, (b) TPG, and (c) APTMS-HPSi. In figure 6(a), 1 represents (CH₃–O), and they appear at 3.17 ppm. In figure 6(b), 2, 3 respectively represent the chemical shift peaks of hydroxyl (OH–CH) and methyl (CH–CH₃), which respectively appear at 3.67 ppm and 1.03 ppm. In figure 6(c) 1, 2, and 3 represent the chemical shift peaks of (O–CH₃), hydroxyl (OH–CH) and methyl (CH–CH₃) respectively, at 3.17 ppm, 3.67 ppm and 1.03 ppm respectively.

Compared with the original material, the ¹H NMR spectrum of APTMS-HPSi is significantly weaker than the (O–CH₃) (3.17 ppm) peak in the coupling agent and the peak of the hydroxyl group (3.67 ppm) in the TPG is also significantly weaker. This is because the –CH₃ reacts with the –OH in the TPG, resulting in methanol discharge. The above ¹H NMR spectrum analysis can strongly prove the successful synthesis of APTMS-HPSi.
The $^{12}$C NMR chart shown in figure 7 further supports the chemical structure of APTMS-HPSi. Figure 7 shows the $^{12}$C NMR spectra of (a) APTMS, (b) TPG, and (c) APTMS-HPSi. In figure 7(a), 1 represents ($\text{O}–\text{CH}_3$), and the chemical shift is at 49.0 ppm. In figure 7(b), 2 and 3 respectively represent the methylene group ($\text{HO}–\text{CH}_2$) at 55.3 ppm and the methine group ($\text{HO}–\text{CH}_2$–$\text{CH}$) at 72.4–73.7 ppm. In addition, compared with the original material, the $^{12}$C NMR spectrum of APTMS-HPSi shows the absorption peaks of 1 ($\text{O}–\text{CH}_3$) at 49.0 ppm in APTMS and 2 ($\text{HO}–\text{CH}_2$) at 55.3 ppm and 3 ($\text{HO}–\text{CH}_2$–$\text{CH}$) in TPG disappear completely. It is proved that the methyl group in APTMS reacted with tripropylene glycol during the reaction.

Figure 8 shows FTIR spectrum of bisphenol F epoxy resin (EP), 10-(2,5-dihydroxyphenyl)-10-hydro-9-oxa-10-phosphaphenanthrene-10-oxide (ODOPB) and phosphorous modified resin (P-EP). In figures 8(a), (b), the absorption peak at 3505 cm$^{-1}$ is the stretching vibration peak of $–\text{OH}$ in the epoxy resin and the absorption peak at 3476 cm$^{-1}$ is the stretching vibration peak of $–\text{OH}$ in the P-EP. The stretching vibration peak of $–\text{OH}$ in the P-EP resin becomes stronger, which proves that the epoxy group reacts with the hydroxyl group in ODOPB to form a new hydroxyl group.

### 3.3. Impact strength

The impact strength of P-EP and P-EP/APTMS-HPSi resins are presented in figure 9. It can be seen that all each P-EP/APTMS-HPSi resins has higher impact strength than P-EP resin. When the content of APTMS-HPSi is 2wt%, the impact strength of the modified resin is 15.9 KJ m$^{-2}$, increased by 49.28%. There is an optimum stoichiometry between P-EP and APTMS-HPSi for obtaining the maximum impact strength. When the addition amount of APTMS-HPSi is 4 wt%, the impact strength reaches the maximum value of 38.4 KJ/m$^2$, increased by 142%.

APTMS-HPSi has a large number of flexible segments. When APTMS-HPSi is added to P-EP, the flexible segments in APTMS-HPSi are also incorporated into the resin matrix. The impact strength of the P-EP/APTMS-HPSi resin becomes better and the toughness improves. However, when the content of APTMS-HPSi reaches a certain value, the impact strength begins to decrease. This is because the excessive APTMS-HPSi contains many flexible segments, which reduces the cross-linking density of the modified resin and changes the mechanical properties of the APTMS-HPSi resin.
3.4. Tensile strength

In order to further discuss the toughening effect of HPSiE on P-EP resin, tensile strength and flexural strength test were also carried out. The results of tensile properties are shown in figure 10. Figure 10. shows that the modulus of elasticity of 0.5 wt% phosphorous epoxy resin is 2.78 GPa, the tensile strength is 81.0 MPa, and the elongation at break is 6.77%. The elongation at break of the pure epoxy resin without phosphorus modification is 7.40%, and the decrease in elongation at break after modification with P is because the introduced ODOPB contains rigid groups, which reduces the toughness. When the content of APTMS-HPSi is 6 wt%, the modulus of the modified resin is 3.36 GPa, increased by 20.9%; the tensile strength is 88.3 MPa, increased by 8.26%; the elongation at break is 10.3%, increased by 51.6%. Because APTMS-HPSi contains a large number of reactive terminal amino groups, it can react with epoxy resin. Through this chemical reaction, APTMS-HPSi can be chemically grafted to epoxy resin, resulting in improved toughness of P-EP/APTMS-HPSi resin. due to the resilient behavior and constant stress dissipating capability of a large number of flexible Si–O skeletons in APTMS-HPSi, the introduction of a small amount of APTMS-HPSi can improve the toughness of the resin [8, 22, 23]. But the addition of excess APTMS-HPSi reduces the crosslinking density of the epoxy resin and makes the resin performance worse.

3.5. Flexural and KIC properties analysis

The flexural strength can be used to evaluate the toughness of the material. The flexural strength of P-EP and P-EP/APTMS-HPSi resins are presented in table 1. The addition of a small amount of APTMS-HPSi can effectively improve the flexural strength of the epoxy resin. The flexural modulus of P-EP is 2.93 GPa, and the flexural modulus of P-EP-6 is 3.31 GPa, increased by 13.0%. With the addition of APTMS-HPSi, it shows a trend of increasing first and then decreasing. When the addition of APTMS-HPSi is 16 wt%, the flexural modulus is still 11.6% higher than that of P-EP.

The fracture toughness $K_{IC}$ of the P-EP resin is 2.08 MPa·m$^{1/2}$. When the APTMS-HPSi content is 4wt%, the fracture toughness $K_{IC}$ of the system is 3.39 MPa·m$^{1/2}$ and reaches the maximum value, increased by 54.3%.

Table 1. Flexural and $K_{IC}$ properties of modified epoxy resin cured product.

| Resin   | Flexural strength (MPa) | Flexural modulus (GPa) | $K_{IC}$ (MPa·m$^{1/2}$) |
|---------|-------------------------|------------------------|---------------------------|
| P-EP-0  | 94.3                    | 2.93                   | 2.08                      |
| P-EP-2  | 102                     | 3.07                   | 2.96                      |
| P-EP-4  | 105                     | 3.14                   | 3.39                      |
| P-EP-6  | 111                     | 3.31                   | 3.21                      |
| P-EP-8  | 109                     | 3.29                   | 2.51                      |
| P-EP-12 | 107                     | 3.22                   | 2.59                      |
| P-EP-16 | 110                     | 3.27                   | 2.12                      |
Excessive addition of APTMS-HPSi makes the mechanical properties worse. APTMS-HPSi contains a large number of flexible chain segments, and the free volume between chains is relatively large. When APTMS-HPSi is introduced into the epoxy resin, the free volume of the epoxy resin segment is also increased, thus improving the toughness of the resin.

### 3.6. Low temperature mechanical performance analysis

Table 2 shows the tensile properties of the modified resin after 50 h of immersion in a liquid oxygen environment. After being soaked at low temperature for 50 h, the tensile strength of P-EP is 75.8 MPa, the tensile modulus is 81.3 GPa, and the elongation at break is 8.08%. When the content of APTMS-HPSi is 6wt%, the tensile strength is 96.6 MPa, the tensile modulus is 3.70 GPa, and the elongation at break is 10.7%, which is 32.9% higher than that of P-EP resin. With the increase of the amount of APTMS-HPSi added, the elongation at break of the modified resin increases first and then decreases. It may be because in a low temperature environment, free electron activity is reduced, and the toughness of the material is reduced. However, the tensile strength of the resin modified with APTMS-HPSi is still greater than that of the resin without APTMS-HPSi.

| Resin | Tensile strength (MPa) | Tensile modulus (GPa) | Elongation at break (%) |
|-------|------------------------|-----------------------|------------------------|
| P-EP-0| 81.3                   | 3.04                  | 8.08                   |
| P-EP-2| 86.3                   | 3.12                  | 9.95                   |
| P-EP-4| 83.0                   | 3.22                  | 11.4                   |
| P-EP-6| 96.6                   | 3.70                  | 10.7                   |
| P-EP-8| 85.4                   | 3.35                  | 9.40                   |
| P-EP-12| 73.2                  | 3.34                  | 3.03                   |
| P-EP-16| 70.9                  | 3.26                  | 6.54                   |

### 3.7. Surface topography

The improved toughness for P-EP/APTMS-HPSi systems can be also confirmed by SEM micrographs of the fractured surfaces as shown in figure 11. The figure shows the 1000 × SEM images of pure epoxy resin, 2wt%, 4wt%, and 6wt% modified resin.

All SEM micrographs are homogeneous and monophase structure. It shows the good compatibility of epoxy resin and APTMS-HPSi. The fractured surface of the P-EP resin exhibits brittle feature, but with the incorporation of APTMS-HPSi into P-EP resin and the increase of APTMS-HPSi content, stream-like and fibrous patterns begin to appear followed by typical tough feature.

### 3.8. Thermal stability analysis

Figure 12 shows the thermogravimetric curves and differential curves of P-EP and P-EP/APTMS-HPSi resins. As shown in figure 12, there is only one thermal decomposition stage for P-EP/APTMS-HPSi resins, indicating that APTMS-HPSi has good compatibility with P-EP resin. With the addition of APTMS-HPSi increasing, the Ti
of the modified resin decreases. When the addition amount is 16wt%, T$_f$ decreases to 198 °C. The char carbon Y$_c$ of P-EP resin is 14.2%. When the addition amount of APTMS-HPSi is 6wt%, Y$_c$ is 15.4%; when the addition amount reaches 16wt%, Y$_c$ is 18.7%. The P-EP/APTMS-HPSi resin is heated to produce a polymetaphosphoric acid with a three-dimensional dense structure, which has stability and strong dehydration. At the same time, it will also promote the formation of the carbon layer. The formation of the carbon layer is accompanied by the generation of water, which can be cooled and placed for further combustion. In addition, the carbon layer acts as a thermal insulation on the surface of the resin, and can also inhibit the combustion of the material from emitting combustible gases.

Dynamic thermomechanical analysis (DMA) is used in this paper to determine the storage modulus (E$''$), loss modulus (E$''''$) and loss factor (tanδ) of the P-EP and P-EP/ APTMS-HPSi. Figure 13(a) shows the tanδ curves of the P-EP and P-EP/APTMS-HPSi resins. The temperature corresponding to the maximum value of Tanδ is the Tg of the resins. Table 3 shows the Tg of P-EP and P-EP / APTMS-HPSi. All Tanδ peaks are single and sharp peaks, indicating that –OH in APTMS-HPSi can be connected with epoxy resin to form a single-phase structure, which proves that P-EP/APTMS-HPSi has a single-phase structure and P-EP has good compatibility with APTMS-HPSi.

Figure 13(b) shows the secondary transition peaks of the P-EP/APTMS-HPSi at low temperature. The appearance of the β peak is generally caused by the rotation of the flexible group or chain segment. The appearance of β peak further proves that the addition of APTMS-HPSi increases the toughness of epoxy resin. The lower the temperature when the β peak appears, the better the low temperature resistance of the polymer.

![Figure 13. DMA curves of modified epoxy resin cured product.](image)

Table 3. Tg of modified epoxy resin cured product.

| Resin | Tg /°C | Tanδ | Peak temperature /°C |
|-------|--------|------|----------------------|
| P-EP-0 | 131 | 0.092 | −65.8 |
| P-EP-2 | 128 | 0.082 | −74.9 |
| P-EP-4 | 128 | 0.086 | −79.1 |
| P-EP-6 | 122 | 0.066 | −82.2 |
| P-EP-8 | 113 | 0.057 | −73.6 |
| P-EP-12 | 112 | 0.062 | −72.8 |
| P-EP-16 | 98.4 | 0.057 | −75.1 |

Table 4. The mechanical impact phenomena.

| Sample | Burning | Explosion | Flash | Charring | Test times | IRS (%) | LOI (%) |
|--------|---------|-----------|-------|----------|------------|---------|---------|
| P-EP-0 | 0       | 0         | 1     | 2        | 20         | 7       | 26.5    |
| P-EP-2 | 0       | 0         | 0     | 3        | 20         | 6       | 28.4    |
| P-EP-4 | 0       | 0         | 0     | 1        | 20         | 2       | 28.8    |
| P-EP-6 | 0       | 0         | 0     | 0        | 20         | 0       | 29.4    |
| P-EP-8 | 0       | 0         | 0     | 0        | 20         | 0       | 29.2    |
| P-EP-12 | 0     | 0         | 0     | 0        | 20         | 0       | 29.5    |
| P-EP-16 | 0     | 0         | 0     | 0        | 20         | 0       | 31.3    |
material. From figure 13(b), it can be seen that the shape of the modified epoxy resin is basically the same. From table 3, it can be seen that the temperature of the secondary transition peak is reduced from $-65.8 \, ^\circ C$ to $-75.1 \, ^\circ C$. It shows that with the addition of APTES-HPSi increasing, the low temperature performance of the resin becomes better.

3.9. Liquid oxygen compatibility and flame retardancy
The liquid oxygen compatibility test was carried out using a liquid oxygen impact tester according to ASTM D2512–95 (2008). Table 4 shows the number of times of various liquid oxygen sensitive phenomena of modified resin after modification of phosphorous-containing bisphenol F epoxy resin with different contents of APTMS-HPSi. It can be seen from the table that the phosphorus-containing resin that has not been modified by APTMS-HPSi has one flash and one carbonization, and there is obvious liquid oxygen incompatibility, and its liquid oxygen sensitivity coefficient is 7%. Compared with the unmodified resin containing phosphorus, its value decreased slightly but not significantly. When the addition amount of APTMS-HPSi reaches 4wt%, only one carbonization occurs, and the liquid oxygen sensitivity coefficient decreases to 2%. When the addition amount of APTMS-HPSi reaches 8wt%, there is no liquid oxygen sensitive phenomenon, indicating that the modified resin at this time is compatible with liquid oxygen.

According to the above-mentioned TGA and DMA tests, it can be known that the addition of APTMS-HPSi will increase the carbon residue rate of the epoxy resin, so the liquid oxygen compatibility of the material will also be improved. It can be seen from table 4 that as the content of APTMS-HPSi increases, the value of the liquid oxygen sensitivity coefficient decreases from 7% to 0%, which is consistent with the results of the thermal weight loss analysis, which proves that the increase in thermal stability can improve the liquid of the material.

The Limiting Oxygen Index (LOI) is an index that characterizes the combustion behavior of materials. It refers to the minimum volume fraction of the oxygen content in the mixture of $O_2$ and $N_2$ that can just make the material burn. According to table 4, the limit oxygen index value (LOI) of P-EP is 26.5%. When the amount of APTMS-HPSi is 6wt%, the LOI of P-EP/APTMS-HPSi resin is 29.4%. When the amount reaches 16 wt%, the LOI of P-EP/APTMS-HPSi resin is 31.3%, indicating that phosphorus modification improves flame retardancy.

When the LOI of the material is greater than 27, it indicates that the material is a flame retardant material. The LOI of pure epoxy resin is about 20%, which is a flammable material. And the LOI of P-EP is 26.5%, indicating that the addition of phosphorus can improve the flame retardancy of the epoxy resin. When the content of APTMS-HPSi in the epoxy resin is more than 2wt%, the LOI of the modified resin is greater than 27%. And the material belongs to the flame-retardant material has good flame retardancy. It shows that the introduction of APTMS-HPSi also improves the flame retardancy.

4. Conclusions
The addition of APTMS-HPSi into P-EP resin alternates the chemistry of the cross-linking network, and thus leading to significant influence on the properties including toughness, thermal as well as liquid oxygen compatibility. When the addition amount of APTMS-HPSi is 6wt%, the carbon residual rate $Y_c$ is 15.4%, and the LOI value is 29.4%. When the addition amount reaches 16wt%, the carbon residual rate $Y_c$ is 18.7%, and the limiting oxygen index value LOI is 31.3%. The IRS of P-EP resin is 7%, which is slightly lower than 8% of pure epoxy resin cured product. The introduction of phosphorous element slightly improves the liquid oxygen compatibility of epoxy resin. When the content is 6wt%, the IRS value becomes 0%, and the cured resin is completely compatible with liquid oxygen. As the content of APTMS-HPSi increases, the mechanical properties of the P-EP/APTMS-HPSi first increase and then decrease. Adding too much APTMS-HPSi leads to changes in the network structure and a sharp decrease in mechanical properties. Therefore, the introduction of ODOPB into the resin can effectively improve the liquid oxygen compatibility at a low addition amount of APTMS-HPSi.

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Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).
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