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# A novel epoxy-functionalized hyperbranched polysiloxane (HPSi) endowing methyl phenyl silicone resin (Si603) /epoxy systems enhanced compatibility and fire retardancy performance

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**Abstract** As compatibilizer of the epoxy resin (EP)/methyl phenyl silicone resin (Si603) blends, a novel hyperbranched polysiloxane (HPSi) with a great amount of epoxy groups was synthesized. The structure of HPSi had been analyzed by Fourier transform infrared spectra (FTIR) and nuclear magnetic resonance ($^1$H-NMR). Compatibility of EP/HPSi/Si603/DDM was characterized by Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), the results showed that HPSi significantly improved the compatibility of EP/Si603. The flame retardancy and thermal degradation behavior of EP/HPSi/Si603/DDM systems were investigated by limiting oxygen index (LOI), UL-94 vertical burning, themogravimetric analysis test (TG), FTIR and SEM. LOI value of the modified EP resin with 10% HPSi and 30% Si603 was 31(about 1.4 times of the corresponding value original EP resin), and passed V-1 of UL-94 rating. Specifically, its combustion residue at 800℃ was about 2.24 times of riginal EP resin. Moreover, structural analysis of the combustion residue by FTIR showed the formation of polyaromatic carbons. Additional, morphology of the residue char showed the compact, smooth, and tight structure of EP/HPSi/Si603/DDM systems. Mechanical properties such as tensile strength, flexural strength and flexural modulus of EP/DDM and EP/HPSi/Si603/DDM systems were evaluated and the result showed that these polymers also possess good mechanical properties. These outstanding integrated properties would make EP/HPSi/Si603/DDM systems attractive for practical applications.

**Keywords:** Hyperbranched polysiloxane; Compatibilizer; Methyl phenyl silicone resin; Flame retardancy; Thermal behavior.

## 1. Introduction

Epoxy resin (EP) is one of the most important commercial thermosetting materials owing to its high tensile strength and modulus, outstanding adhesive properties, good chemical resistance and superior dimensional stability [1-4]. It is widely used as adhesives, coatings, semiconductor encapsulation and matrices for advanced composites in electronic/electrical industries where a remarkable grade of flame-retardant is required. However, the flammability is a major drawback of epoxy resin and limits its applications, thus, to improve the flame retardancy of EP is an urgent problem and has attracted great attention [5,6]. To protect environment and human health, environmental friendly halogen-free fire retardant for epoxy resins has

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41 always been the focus [7], among which silicon-containing compounds is considered
42 as a promising choice due to its high flame-retardant efficiency [8,9].

43 As one of the silicon-containing compounds, methyl phenyl silicone resin (Si603)
44 with high thermal stability and carbon residue was selected to modify epoxies.
45 However, it is important to note that, the introduction of polysiloxane flame retardant
46 into the resin not only demonstrated poor compatibility with polymer matrix but also
47 lowered glass transition temperature ($T_g$) [10]. Therefore, how to overcome these
48 drawbacks without a decrease of the integrated properties of polysiloxane is worth
49 investigating.
50 Recently, Studies on the hyperbranched polymer used as compatibilizer have
51 received a growing prominence. Because of the hybrid inorganic-organic nature
52 [11,12], the hyperbranched polymer possessing epoxy group ,which can serve to
53 increase the compatibility with polymers, can improve the thermal stability and the
54 flame retardancy of the EP composites. In addition, the existence of highly reactive
55 groups provides the possibility for chemical modifications [13]. A typical example is
56 the fully end-capped hyperbranched polysiloxane with large branching degree and
57 amine-groups (AmeHBPSi), which was used to modify BMI resin to improve flame
58 retardancy, toughness, strength and thermal stability [14]. Juhua Ye [15] synthesized a
59 novel phosphorus-containing hyperbranched polysiloxane which was then used to
60 improve flame retardancy of cyanate ester resins.
61 The subject of this work is to improve the compatibility of methyl phenyl silicone
62 resin (Si603)/epoxy resin with hyperbranched polymer. Integrated performances
63 (including compatibilization, thermal degradation behavior, and the flame retardancy)
64 of HPSi/methyl phenyl silicone resin/epoxy resin systems were intensively
65 investigated.
66
67 **2. Experimental**
68
69 2.1. Materials
70
71 Diglycidyl ether of bisphenol A (DGEBA, EP, epoxy value = 0.44 mol/100 g) was
72 purchased from Wuxi Bluestar Chemical Co. Ltd. China. Methyl phenyl silicone resin
73 (Si603) was supplied by WACKER. Germany. γ-(2,3-Epoxypropoxy)
74 propytrimethoxysilane (KH560) and dimethoxydimethylsilane（DEMS）were bought
75 from Jinan Yijia Chemical Co.Ltd.China. Distilled water,
76 4,4-diaminodi-phenylmethane (DDM), ammonia, and anhydrous ethanol were
77 obtained from Chengdu Kelong Chemical Reagent Factory. All materials were used
78 without further purification.
79
80 2.2. Synthesis of polysiloxane (HPSi)
81
82 23.6g KH560, 18g DEMS and 150mL anhydrous ethanol were added to a 250 mL
83 three-necked round bottom flask equipped with a stirrer, a thermometer, and a
84 condenser. Then 0.4g ammonia, 7.56g distilled water were both added into the flask.

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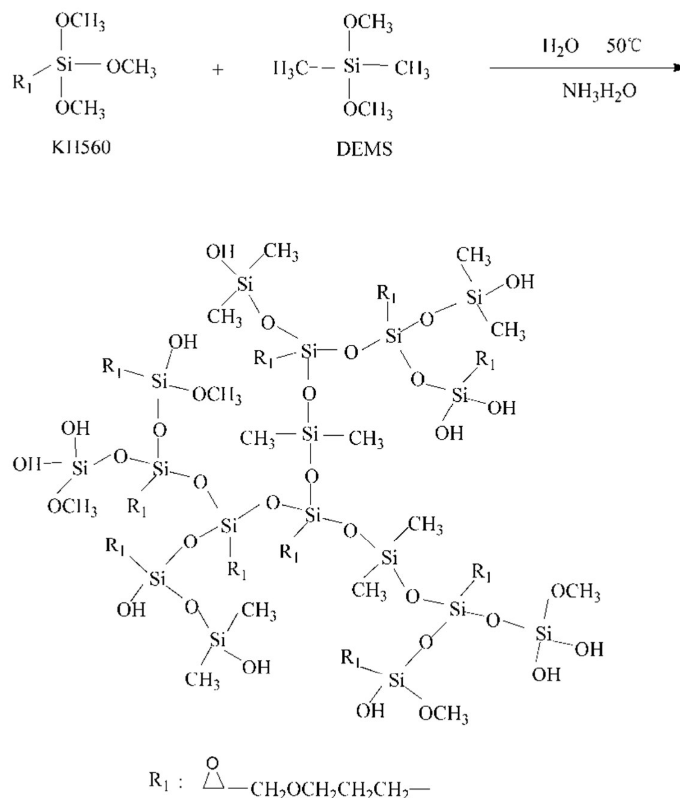
85 The temperature was raised to 50 °C and kept for 4.5 h. After that, 0.25g
86 1-chlorotrimethylsilane was added as capping agent. Finally, the product was dried to
87 eliminate methanol, ethanol, and water in a vacuum oven. Finally, a transparent and
88 viscous liquid, hyperbranched polysiloxane (coded as HPSi), was obtained. The
89 reaction mechanism of this system is shown in Scheme 1.




90

91 **Scheme 1** The synthesis of organic silicon resin (HPSi) by hydrolytic condensation.

92

93 2.3. Preparation of cured HPSi/EP/Si603/DDM blends

94

95 HPSi and epoxy with a ratio at 0.1:1(mass) was blended with vigorous stirring at
96 130 °C for 20 min to obtain a prepolymer. Then an appropriate amount of Si603 (10
97 wt%, 20 wt%, 30 wt%) was put into the above prepolymer. Third, stoichiometric
98 DDM was casted into the blends above to dissolve at 100 °C. Subsequently, the
99 blends were cast into a preheated aluminium mold for curing and postcuring
100 following the protocol of 80 °C/2 h+ 150 °C/3.5 h+165 °C/1.5 h. Then epoxy resin
101 specimens were obtained and subsequently machined to the desirable size for further
102 testing.

103

104 2.4. Measurements

105

106 Fourier transform infrared spectra

107

108 Fourier transform infrared spectra(FTIR) were recorded between 400 and 4000

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109 $cm^{-1}$ on a Nicolet Magna-IR 560 spectrometer (Nicolet Instrument Co, USA) with
110 KBr chip technique.
111
112 Nuclear magnetic resonance
113
114 $^1$H-NMR (400 Hz) spectra were recorded on a FT-80A NMR with $CDCl_3$ as the
115 solvent and internal standard.
116
117 Differential scanning calorimetry
118
119 DSC measurements were conducted on a Netzsch Q-200 ranging from room
120 temperature to 350℃ with a heating rate of 10℃ $min^{-1}$ under nitrogen atmosphere.
121
122 Scanning electron microscopy
123
124 The morphologies of the fractured surfaces of samples and the surface morphology
125 of the char obtained after the LOI tests were observed by Inspect-F SEM.
126
127 Thermogravimetric analysis
128
129 TG analyses were conducted on Netzsch TG209 at a linear heating rate of 10 K
130 $min^{-1}$ under pure nitrogen and air within the temperature range from 30 to 800 °C.
131
132 Limiting oxygen index
133
134 LOI data of all samples were obtained at room temperature on an oxygen index
135 instrument (XYC-75) produced by Chende Jinjian Analysis Instrument Factory,
136 according to GB/T2406-93 standard. The dimensions of all samples were 130 × 6.5 ×
137 3 $mm^3$.
138
139 Vertical burning tests
140
141 Vertical burning tests were performed according to UL-94 standard with samples of
142 dimensions 125 × 12.5 × 3.2 mm. In this test, samples were classed as V-0, V-1, V-2,
143 or unclassified according to their behaviour (dripping of burning material and burning
144 time).
145
146 Mechanical properties
147
148 Tensile and flexural tests were carried out on a Shimadzu AGS-J universal testing
149 machine, according to ASTM D638-08 and ASTM D-790. The rate of crosshead
150 motion was 20 ± 2 mm $min^{-1}$. The tensile and flexural tests of environmental chamber
151 were performed at 25 °C. Samples' dimensions were 80 × 10 × 4 $mm^3$. For each
152 mechanical test, the result was averaged by testing at least 10 samples. The result was

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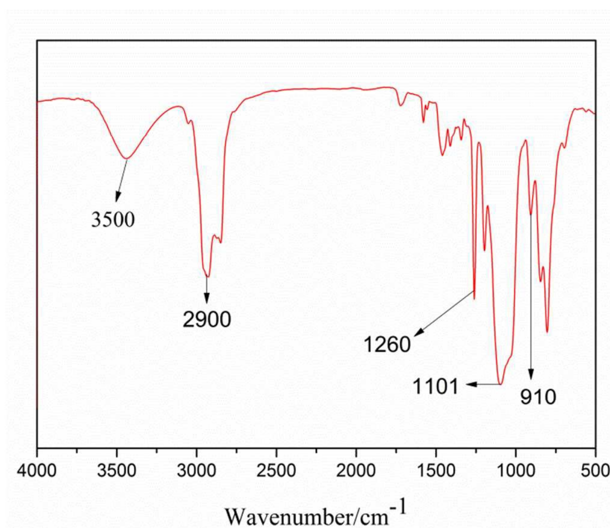
153 calculated based on the data after subtracting the data outside the margin of standard
154 deviation.
155
156 **3. Results and discussion**
157
158 3.1. Synthesis and characterization of HPSi
159
160 In order to confirm the molecular structure of HPSi, FTIR, $^{1}$H-NMR analyses were
161 carried out. Figure 1 is the FTIR spectrum of HPSi. The FTIR spectrum of HPSi
162 shows that the strong and wide peak at 1101 cm$^{-1}$ was attributed to bending vibration
163 of Si-O-Si groups, indicating that alkoxy groups were successfully changed into Si–
164 O–Si through the hydrolysis and condensation; however the broad peak centered at
165 3500 cm$^{-1}$ representing Si-OH groups can also be observed, demonstrating that Si–OH
166 groups in the raw material do not completely disappear during the condensation [16].
167 The emergence of the chemical shift at 2.79 ppm assigning to –OH groups in the
168 $^{1}$H-NMR of HPSi (Figure 2) also supports this statement. Moreover, a stretching
169 vibration of the oxirane ring group at 910 cm$^{-1}$ demonstrates that the polymerization
170 between KH560 and DEMS occurred. We can also see that a vibration peak (2840
171 cm$^{-1}$) assigns to methoxy, and the peaks in the range of 750 to 870 cm$^{-1}$ indicate the
172 existence of Si-$CH_3$. To further prove the structure of HPSi, Figure 2 shows the
173 $^{1}$H-NMR spectrum of HPSi (ppm): 2.6 (a),2.79 (b), 3.18 (c), 3.67 (d), 3.32 (e), 3.48
174 (f), 1.62 (g), 3.52(k), 0.67 (i), 7.12-7.66 (j) [17]. It suggests that the HPSi is
175 successfully synthesized.




176
177 **Figure 1** The FTIR of HPSi.

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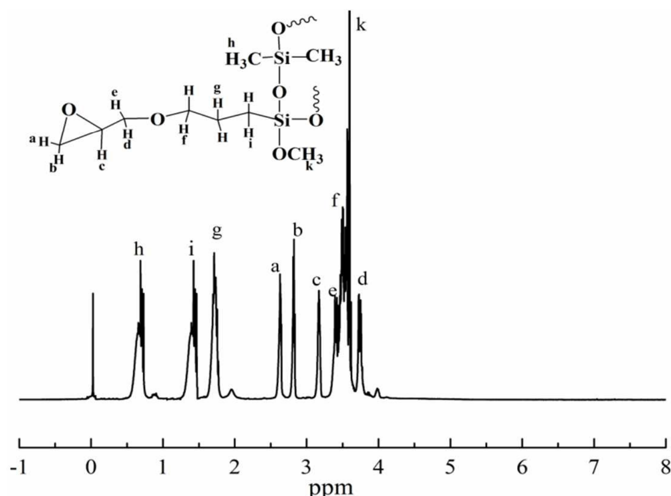


179 **Figure 2** The ^{1}H-NMR of HPSi.

180

181 3.2. Compatibility of cured HPSi/EP/Si603/DDM blends

182

183 Compatibility of EP/Si603/DDM improved by HPSi can be characterized by
184 measuring the glass transition temperature ($T_g$). Generally speaking, the homogeneous
185 morphology of the mixed epoxy systems exhibit only one $T_g$, while incompatible
186 mixtures exhibit two or more $T_g$. Differential scanning calorimetry (DSC) can
187 accurately detect the $T_g$ of the blends [18]. Figure 3 gives DSC curves of various
188 cured EP/Si603/DDM, EP/HPSi/DDM, EP/HPSi/Si603/DDM mixtures.
189 EP/Si603/DDM exhibits two separated $T_g$ at 74 and 154 ℃, which are close to the $T_g$
190 of Si603 and pure epoxy resin, respectively. Except EP/Si603, the rest of the curing
191 systems have a single $T_g$ between 119 and 127 ℃, which indicates that HPSi greatly
192 improved the compatibility of this system. This phenomenon mainly interpreted by
193 the fact that HPSi contains a large amount of epoxy groups and Si-O-Si bonds, which
194 have the similar structure with EP and Si603 resin, respectively. It can also be
195 observed that with the increase of Si603, $T_g$ of the whole system increases until
196 reaches the maximum value of 127 ℃, following which is an obviously decreases.
197 Owing to a relatively large space volume, Si603 resin usually has higher average free
198 volume that plays a negative role in increasing the concentration of the chain segment
199 of modified resins. At the same time, in the case of the EP/Si603/HPSi/DDM system,
200 there are strong interactions between Si603 and HPSi, which can conspicuously
201 increase the packing density of the polymer. The positive factor is dominant when the
202 content of Si603 is between 10 and 20 wt%, while when the content of Si603
203 increases from 20 to 30 wt% the negative factor will offset this positive effect. From
204 the data analysis of characterize scanning calorimetry (DSC), the addition of HPSi
205 successfully improves the compatibility of EP/Si603/DDM, which provides the
206 important prerequisite for Si603 as a flame retardancy of EP.

207 To further explore the influence of HPSi in the cured system, SEM morphologies
208 of the fractured surfaces of samples are shown in Figure 4. The sample of
209 EP/Si603/DDM resin is laminated with the translucent yellow bottom and the white

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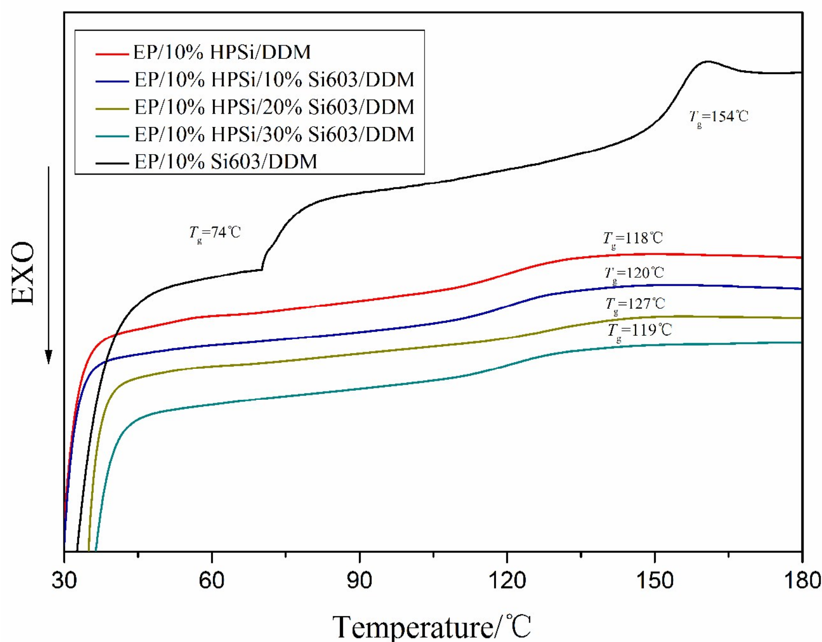
210 opaque upper. Figure 4a is the SEM photograph of EP/30%Si603/DDM cured sample。
211 Holes and balls are almost invisible because Si603 have migrated to the surface of the
212 matrix in the process of blending and curing. In addition, reuniting in the process of
213 blending was also responsible for the serious phase separation. Such phenomena
214 demonstrated the poor compatibility of EP/Si603, Si603 can't be well dispersed in the
215 EP matrix in the absence of compatibilzer. Morphology of the EP/10%HPSi/DDM
216 cured sample shows the compact, smooth, and tight surface in Figure 4b which
217 demonstrates the outstanding compatibility of EP/HPSi.

218 Cured EP/10%HPSi/30%Si603/DDM is transparent and uniform yellow. It can
219 be observed in Figure 4c that the fractured surface is flat. What's more, small balls
220 and circular holes appear on the fractured surface. These balls are evenly distributed
221 in the matrix, which could be attributed to that the Si603 is ideally dispersed in EP
222 matrix in the presence of HPSi. After placed in anhydrous ethanol for 20 hours , a
223 large number of circular holes appear on the fractured surface of
224 EP/10%HPSi/30%Si603/DDM (Figure 4d), which is caused by the dissolution of part
225 of the balls occupied by Si603 resin.
226




227
228 **Figure 3** The DSC curves of the blending systems.
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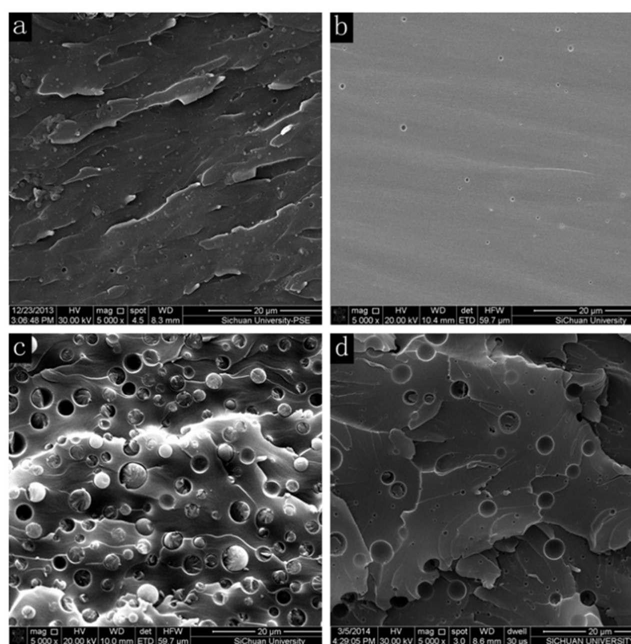

Figure 4 SEM of the section of the blending systems.

## 3.3. Flammability

LOI, the lowest volume concentration of oxygen sustaining burning of materials in the mixing gases of nitrogen and oxygen [19], is an important parameter for evaluating the ease of extinguishment of polymeric materials in the same atmosphere. The flame retardant properties of cured EP/DDM and EP/HPSi/Si603/DDM systems were evaluated by LOI values and UL-94. Data are listed in Table 1. It should be noted that the LOI value gradually increases from 26 to 31 (about 1.4 times of the LOI value of the EP resin) as the Si603content increases from 10 % to 30 %. At the same time, less smoke was produced after adding Si603 resin. What's more, the residue with Si603 resin could keep the original shape and form hollow shell after burning. The testing results show that vertical combustion performance of EP/10%HPSi/30%Si603/DDM system can achieve V-1 level and shows a good anti-drip property. However, the LOI value of pure EP is 21.5 and the UL-94 rating is NOT V-2 with unsatisfying anti-drip property. This indicates that the compatibilizing effect of HPSi have a good influence on flammability of EP/HPSi/Si603/DDM systems.

**Table 1** The values of LOI and UL-94 for finally cured systems

| Sample | LOI（%） | UL-94 |
|---|---|---|
| EP/DDM | 21.5 | NR |
| EP/10%HPSi/DDM | 23 | NR |
| EP/10% HPSi /10%Si603/DDM | 26 | V-2 |
| EP/10% HPSi /20%Si603/DDM | 28.5 | V-2 |
| EP/10% HPSi /30%Si603/DDM | 31 | V-1 |

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257 3.4. Thermal analysis

258

259 TG and DTG traces of cured EP/HPSi/Si603/DDM systems provided additional
260 information in regard to their thermal stability and thermal degradation behavior [20].
261 The thermal degradation behavior of the various samples in nitrogen atmosphere are
262 shown in Figure 5. The corresponding $T_{5\%}$, the $T_{max}$, and char yield ($Y_c$) at 800 °C are
263 summarized in Table 2. $T_{5\%}$ represents the temperature at which mass loss is 5 % for
264 the system (the initial decomposition temperature), $T_{1max}$ and $T_{2max}$ represents the
265 temperature of the first maximum mass loss rate for the system and the second
266 maximum mass loss rate for the system, respectively. $Y_c$ represents the char yields at
267 800 °C

268 It can be observed from Figure 5 that all cured resins except HPSi have one-stage
269 decomposition process, demonstrating that the original and modified EP resins have
270 similar degradation processes.

271 Figure 5 shows that the char residue at 800℃ is 39 % and $T_{5\%}$ and $T_{max}$ of cured
272 HPSi is 368℃ and 457℃, respectively. The degradation of HPSi in nitrogen
273 atmosphere has gone through two processes: unzipped degradation occurs before 400℃
274 and following silicone chain scission rearrangement [21]. When terminal hydroxyl
275 groups exist, a poorer heat resistance of the silicone resin is presented. As can be seen
276 from the FTIR spectrum of HPSi ( Figure 1), HPSi contains a small amount of
277 silicone hydroxy, which can initiate unzipped degradation through backbiting reaction,
278 which mainly produces low molecular weight annulations and thus thermal weight
279 loss happens. A small amount of unzipped degradation occurred during the
280 degradation processes probably because HPSi contains a large number of branches,
281 which greatly reduce the occurrence of unzipped degradation. At 457℃, cured HPSi
282 shows a $T_{max}$, which is mainly caused by the cleavage and rearrangement reaction of
283 Si-O-Si bonds.

284 TG shows that the addition of HPSi (10 wt% ) enhances the thermal stability of
285 EP/DDM system: $T_{5\%}$ and $T_{1max}$ of EP/HPSi/DDM are higher than that of EP/DDM.
286 This phenomenon originates from the decomposition of HPSi at inferior temperature
287 (368℃) that leads to the formation of the silicone-containing group, which will
288 participate in the cross-linked carbonization. Moreover, the Si–O group of HPSi is
289 able to absorb more thermal energy and its vibration could dissipate the thermal
290 decomposition energy [22]. However, with the increase of Si603 resin, $T_{5\%}$ and $T_{1max}$
291 of EP/HPSi/Si603/DDM systems are almost the same. While char residue at 800℃
292 remarkably increases from 16.01 % to 35.88 % with Si603 content increases from 0%
293 to 30 %. As being discussed above, silicone resins have the ability to convert the usual
294 organic decomposition to partially inorganic decomposition by forming the
295 carbon-silicon residue acting as thermal insulation [11,12,23,24] to prevent gas
296 evolution, and achieve ultimate improvement on flame retardation of this
297 silicone-containing epoxy system.

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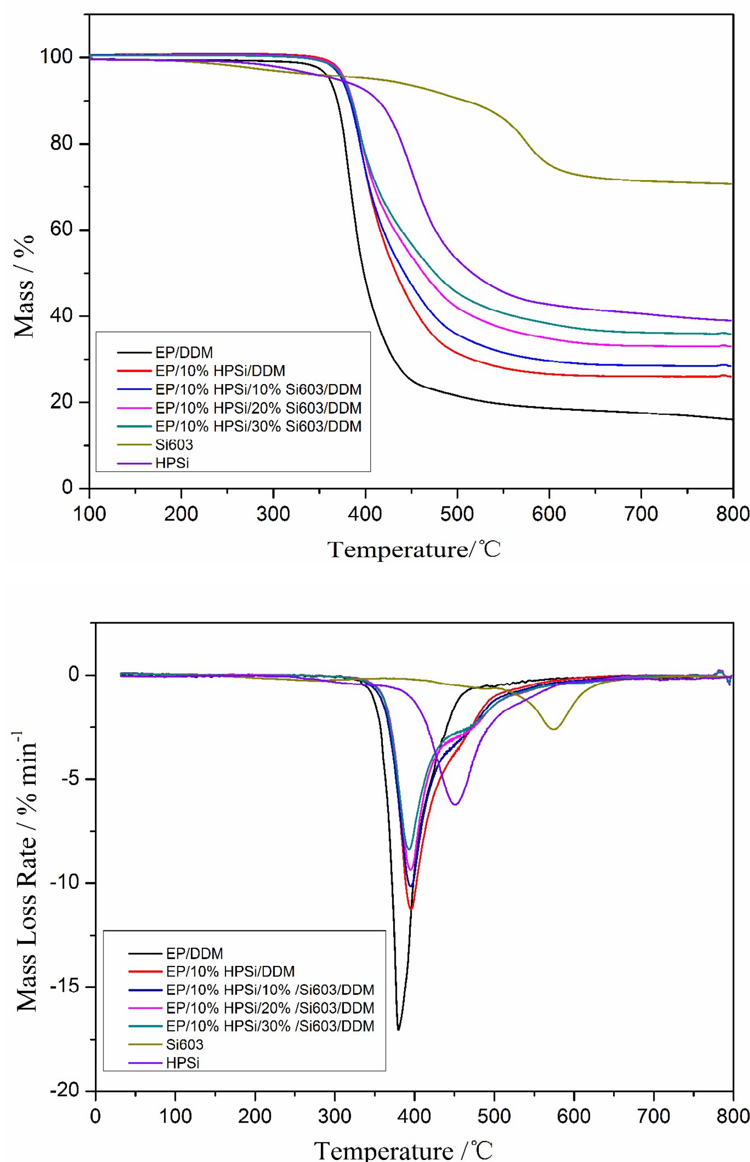


**Figure 5** The TG and DTG curves of the cured systems under $N_2$ atmosphere.

Figure 6 depicts the TG and DTG curves of cured EP/DDM, HPSi and EP/HPSi/Si603/DDM resins in air atmosphere and the corresponding $T_{5\%}$, the $T_{\max}$, and char yield ($Y_c$) at 800 °C are summarized in Table 3.

As can be seen that HPSi experiences three stages of degradation processes which occur at the temperature range of 300-510 ℃, 510-600 ℃ and 600-750 ℃ in air atmosphere, the largest thermal degradation peaks appear at 452 ℃, 540 ℃ and 653 ℃. When the temperature reaches 350 ℃, initial decomposition occurs and the char yield is 36.16% when the temperature reaches 800 ℃. Thus, due to the presence of oxygen, the decomposition mechanism of cured HPSi has changed. For HPSi in air atmosphere, thermo-oxidative degradation occurs, which includes thermal degradation of the main chain and the oxidation reaction of the organic groups. As can

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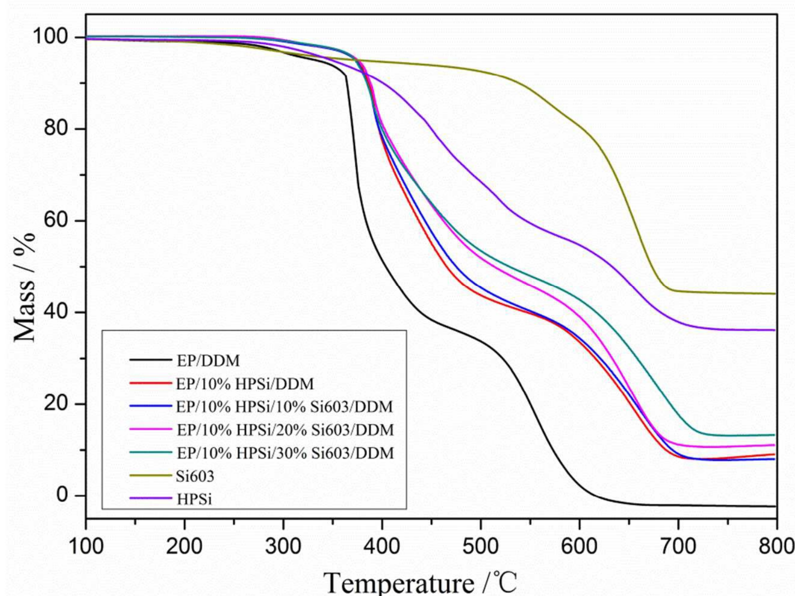
316 be seen from the figure that before the main chain degradation (600 ℃), the two
317 peaks appear, which due to the thermo-oxidative degradation of the side groups,
318 generating small molecules such as carbon monoxide, carbon dioxide, water and so
319 on.

320 For EP/DDM resin, bits of decompositions appear before 300 °C, which can be
321 attributed to the decomposition of unstable alkyl groups in the hybrids. The chain
322 scission of the isopropylidene linkage takes place, leading to the release of EP and its
323 derivates at the initial decomposition stage [25]. The thermal degradation of EP resin
324 can be divided into two independent steps: the first thermal decomposition occurs
325 between 362 and 470 °C, the second stage is from 470 to 700 °C with 0 % char
326 residue at 800 °C, which demonstrates that pure EP shows poor charring ability.

327 But the initial thermal decomposition of EP/HPSi/Si603/DDM systems, occurring
328 between 350 and 600 °C, are wider than that of EP/DDM resin, and the second stage
329 are from 600 to 700 °C. What's more, $T_{max}$ of EP/HPSi/Si603/DDM systems become
330 higher, especially the, with the content of Si603 resin increasing. The improvment can
331 be attributed to silicon in the condensed phase which leads to the formation of a
332 surface glassy char acting as a barrier to heat and mass transfer at high temperature.
333 As is shown in Table 3, as the content of Si603 increases, the char residue of the
334 overall system significantly enhances; when the amount of Si603 increases from 0 %
335 to 30 %, the char residue of EP/HPSi/Si603/DDM system combusted in air
336 atmosphere increases from 0 % to 13.21 %, indicating that HPSi enhances the thermal
337 stability and char formation ability of EP. This is reasonable as we can see from the
338 TG curve that Si603 resin possesses high thermal stability. When it is over 400 °C,
339 decomposition occurs in Si603 resin and the solid char yield in nitrogen and air at
340 800 °C is 70 % and 44 %, respectively. It demonstrates that charring ability and
341 thermal stability of Si603 resin is significantly higher than that of other resins.

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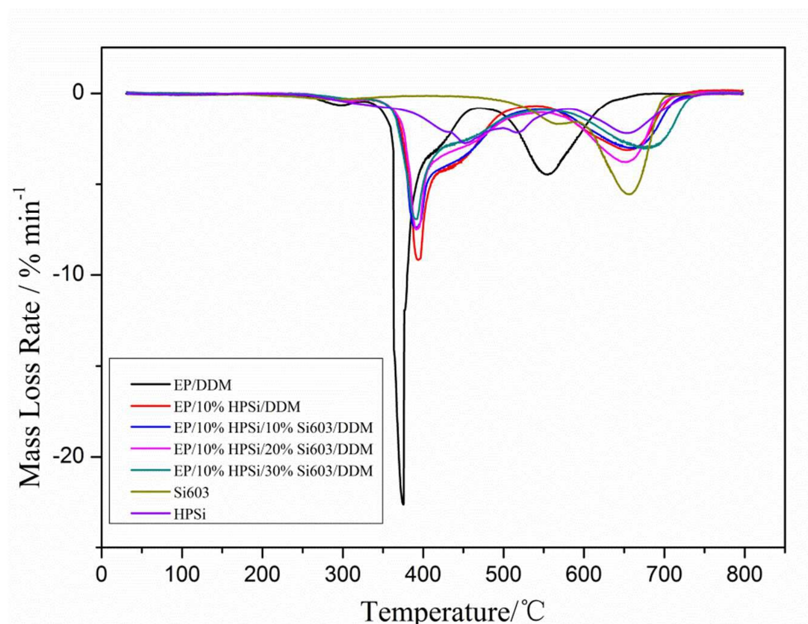


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344

345 **Figure 6** The TG and DTG curves of the cured systems under air atmosphere.

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347

348 **Table 2** The TG and DTG data of different systems under $N_2$ atmosphere.

| Sample | $T_{5\%}$ / ℃ | $R_{1peak}$ / (%℃$^{-1}$) | $T_{1max}$ / ℃ | $Y_c$ at 800℃ Cal. | $Y_c$ at 800℃ Exp. |
|---|---|---|---|---|---|
| EP/DDM | 350.8 | -17.07 | 379 | —— | 16.01 |
| Si603 | 410 | -5.22 | 574 | —— | 70 |
| HPSi | 368 | -6.22 | 460 | —— | 39 |
| EP/10%HPSi/DDM | 377.5 | -11.24 | 396 | 18.1 | 25.99 |
| EP/10%HPSi/10%Si603/DDM | 375 | -10.16 | 395 | 21.34 | 28.5 |
| EP/10% HPSi /20%Si603/DDM | 376 | -9.39 | 395 | 26.08 | 32.94 |
| EP/10% HPSi /30%Si603/DDM | 376.2 | -8.39 | 393 | 29.22 | 35.88 |

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358 **Table 3** The TG and DTG data of different systems under air atmosphere.

| Sample | $T_{5\%}$ / ℃ | $R_{1peak}$ / %℃$^{-1}$ | $T_{1max}$ / ℃ | $R_{2peak}$ / %℃$^{-1}$ | $T_{2max}$ / ℃ | $Y_c$ at 800℃ Cal. | $Y_c$ at 800℃ Exp. |
|---|---|---|---|---|---|---|---|
| EP/DDM | 334 | -22.59 | 375 | -4.47 | 555 | —— | 0 |
| Si603 | 380 | -5.43 | 566 | -4.06 | 656 | —— | 44 |
| HPSi | 350 | -2.76 | 452 | -2.20 | 653 | —— | 36.16 |
| EP/10%HPSi/DDM | 373.5 | -9.18 | 394 | -3.13 | 654 | 3.29 | 9.08 |
| EP/10%HPSi/10%Si603/DDM | 374 | -7.43 | 390 | -3.06 | 661 | 6.68 | 9.85 |
| EP/10% HPSi /20%Si603/DDM | 375 | -7.52 | 391 | -3.79 | 654 | 9.55 | 11.1 |
| EP/10%HPSi/30%Si603/DDM | 373 | -6.95 | 392 | -3.06 | 674 | 12 | 13.21 |

359

360 Figure 7 and Figure 8 show the experimental and theoretical TG curves of
361 EP/10%HPSi/30%Si603/DDM system in $N_2$ and air, respectively. The theoretical
362 curve was calculated based upon the mass percentage of the ingredient in the EP
363 system. The formula is as follows:

364 $M_{cal}=wt_{HPSi}\%*M_{HPSi\ exp} + wt_{EP}\%*M_{EPexp}+ wt_{Si603}\%*M_{Si603exp}$

365 $M_{cal}$ is the theoretical amount of carbon residue, $M_{exp}$ refers to the actual amount of
366 carbon residue, wt% refers to the corresponding proportion of ingredients.

367 As can be seen in $N_2$, when the temperature is below 350 ℃, the experimental and
368 theoretical curves are similar. However, the experimental mass of residual char
369 exceeds the theoretical one after 400 ℃. The experimental and theoretical TG curves
370 of EP/HPSi/Si603/DDM system in air are different after 350 ℃: the experimental
371 mass of residual char surpasses the theoretical one in the whole temperature range and
372 both decomposition stages occurs at higher temperatures. It could be deduced that the
373 addition of organic silicon obviously improves the mass of carbon residue and organic
374 silicon generates more stable substance at high temperatures, which effectively
375 improves the char-formation ability and thermal stability of the matrix.

376 Higher char yield of Si603 resin indicates that the carbonization mechanism
377 indeed plays an important role in flame retardation. It is well known that the general
378 flame retarding mechanism of organic silicone resin-based materials is thought to be
379 the formation of protective barrier during combustion. The improved flame retardancy
380 can be explained by a flame retarding mechanism: providing a barrier for heat and
381 mass transfer in the condensed phase at the same time preventing melted EP from
382 burning [26].

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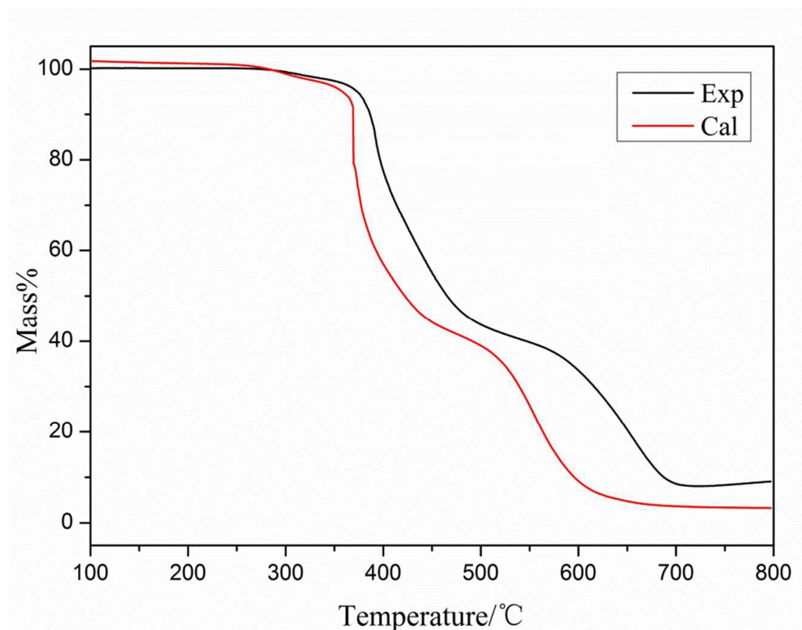
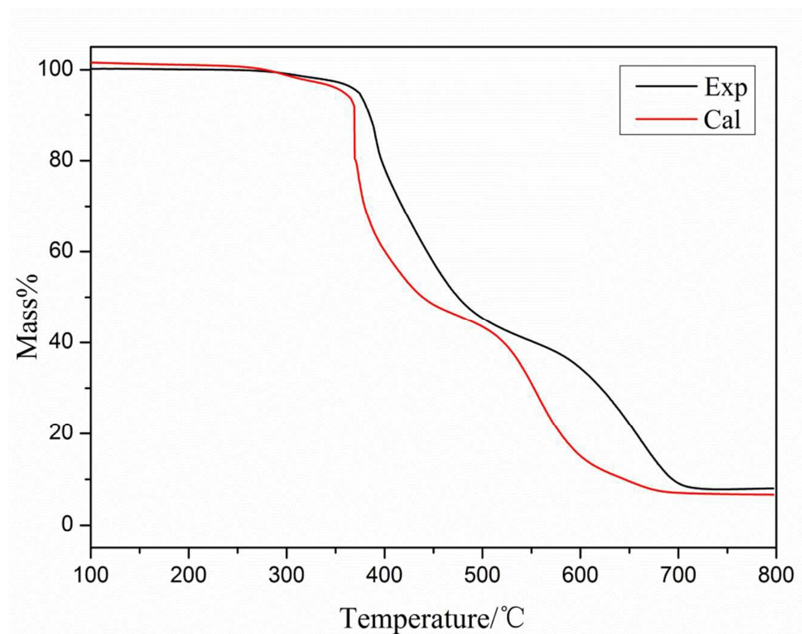



383

384 **Figure 7** Experimental and theoretical TG curves of EP/10% HPSi/30%Si603 under
385 $N_2$ atmosphere.
386




387

388 **Figure 8** Experimental and theoretical TG curves of EP/10% HPSi/30%Si603 under
389 air atmosphere.
390

391 3.5. Structural analysis of the combustion residue by FTIR
392

393 In order to understand the chemical alteration in the condensed phase of
394 EP/10%HPSi/30%Si603/DDM system, the combustion residue after

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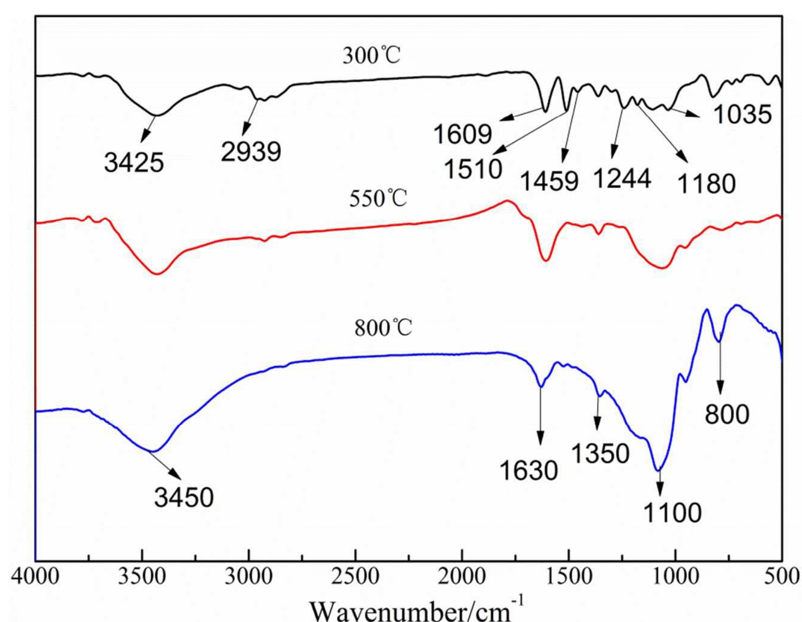
395 thermogravimetry under air atmosphere were investigated by FTIR. The FTIR spectra
396 at different degradation temperatures (300, 550 and 800 °C) are shown in Figure 9.
397 At 300 °C, the absorptions of –OH (3450 $cm^{-1}$), stretching vibration of $–CH_3$ and –
398 $CH_2$– (2939 $cm^{-1}$), C–C stretching vibration of aromatic ring (1609, 1510, 1459 $cm^{-1}$),
399 C–H vibration of $–C_6H_4–O–CH_2–$ (1244, 1035 $cm^{-1}$) and C–O stretching vibration
400 (1180 $cm^{-1}$) are the characteristic absorptions of pure epoxy resin [27]. At 550 °C, it is
401 found that the absorption peaks at 2939, 1609, 1459, 1244 and 1035 $cm^{-1}$ disappear
402 and the decrease in the relative intensities of the aromatic components related bonds
403 (1510 $cm^{-1}$) and ether bonds (1180 and1035 $cm^{-1}$) were detected, indicating that the
404 main decomposition happened in this stage. which is consistent with the TG results.
405 According to the shown information, the absorption of aliphatic components and the
406 C–C stretching vibration of aromatic ring at 1510 $cm^{-1}$ totally disappear at 800 °C.
407 However, bending vibration peak belonging to Si-O-Si groups centered at 1100 $cm^{-1}$
408 become stronger and wider and characteristic peaks belonging to polyaromatic
409 centered at 800 $cm^{-1}$ and 1630 $cm^{-1}$ become broader, indicating the formation of
410 polyaromatic carbons.
411




412
413 **Figure 9** The FTIR of char layer of EP/10% HPSi/30%Si603/DDM.
414
415 3.6. Morphology of the residue char
416
417 In order to explore how the structure of char determines the flame retardancy of EP,
418 we investigated the residues of char after LOI testing by SEM. Figure 10 presents
419 SEM micrographs of char residue of EP/10%HPSi/30%Si603/DDM and EP/DDM.
420 According to Figure 10a, for cured EP, there are many big holes due to insufficient
421 char formation or less condensed char during the burning process. This poor char
422 quality could not effectively protect the underlying EP from degradation during
423 combustion; therefore, EP can't pass UL 94-V0. However, the char surface of EP with

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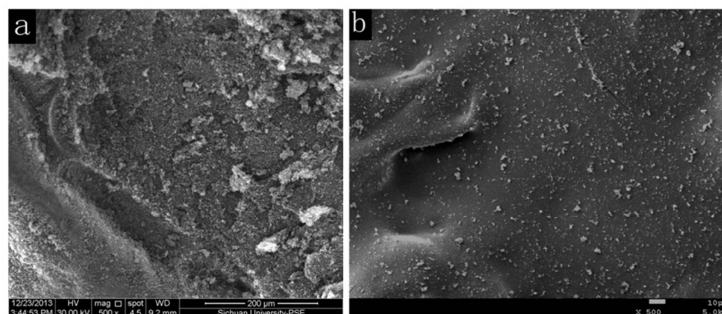
424 both HPSi and Si603, illustrated in Figure 10b, is compact, smooth, and tight. This
425 structure of the char for EP composites could prevent heat transfer between the flame
426 Si603 and the substrate and thus protect the underlying materials from further burning
427 and pyrolysis, which endows the material much higher LOI values. In addition, this
428 char structure could offer a good shield to prevent melted EP from burning, which
429 was proved in vertical flammability tests (Table 1).
430



431

432 **Figure 10** SEM of the char layer of EP/DDM and EP/10%HPSi/30%Si603/DDM
433 system.
434

435 3.7. Mechanical properties
436

437 Tensile strength is a measurement of the force required to pull sample to the point
438 where it breaks, and reflects the fracture resistance of materials. Flexural strength is
439 usually used for evaluating the mechanical properties of a material because the
440 flexural loading is very complicated and may contain multi-type loadings such as
441 tensile, shearing and/or compressing loadings [28]. Therefore, to evaluate the
442 integrated mechanical properties of a material, flexural strength is usually selected as
443 a typical parameter to evaluate the integrated mechanical properties. The flexural
444 modulus reflects the inherent energy of a material, and the ability to resist strain.
445 Moreover, it is also a property reflecting the stiffness of a material [29]. Therefore,
446 flexural modulus is usually selected as typical parameters to evaluate the stiffness of
447 the materials [29, 30].
448 The tensile strength, flexural strength and flexural modulus of
449 EP/HPSi/Si603/DDM composites are compared and the results are presented in Table
450 4. Overall, a continuous reduction in flexural strength, tensile strength and flexural
451 modulus showed up as the addition of Si603 increases. However, there is only an
452 almost negligible decline in the tensile strength, flexural strength and flexural
453 modulus of EP/10%HPi/10%Si603/DDM compared with that of the EP/DDM, which
454 is attributed to the better compatibility of EP/Si603/DDM improved by HPSi and the
455 improved homogeneity of the system to some extent offset the negative effect the
456 Si603 brings to the mechanical property. As the addition of Si603 increased, the
457 reduction in tensile strength, flexural strength and flexural modulus are obviously
458 observed. Owing to a large amount of unoccupied structure, a hyperbranched polymer
459 usually has higher average volume of free cavities that play a negative role in

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460 decreasing the concentration of the chain segment of modifed resins and the large
461 number of rigid pendant groups (benzene rings) from Si603 decreased the flexibility
462 of the compound provided by the siloxane linkages, hence the EP/HPSi/Si603/DDM
463 with a large content of Si603 (>20 wt%) possesses decreased toughness. These results
464 are in line with those in literature, in detail, a suitable content of
465 phosphorus-containing flame retardant will contribute a satisfactory flame retardancy
466 to a resin, but meanwhile, which usually brings a negative effect on the flexural
467 strength of the resin system [31,32].
468
469 **Table 4** Mechanical properties of EP/10%HPSi/Si603/DDM system with different
470 Si603 contents

| Specimen | Mechanical properties | | |
|---|---|---|---|
| | Tensile strength /MPa | flexural strength /MPa | flexural modulus /MPa |
| EP/DDM | 45.87 | 97.77 | 3579.6 |
| EP/10%HPi/10%Si603/DDM | 45.03 | 97.55 | 3553.5 |
| EP/10% HPSi/20%Si603/DDM | 40.76 | 89.57 | 3326.7 |
| EP/10% HPSi/30%Si603/DDM | 29.56 | 68.92 | 3182.6 |

471
472 **4. Conclusions**
473
474 A novel hyperbranched polysiloxane (HPSi) with epoxy groups was successfully
475 synthesized as compatibilizer by controlling hydrolysis and condensation between
476 c-(2,3-epoxypropoxy) propytrimethoxysilane (KH560) and dimethoxydimethylsilane
477 (DEMS). Experiments suggested that HPSi significantly improved compatibility of
478 EP/Si603/DDM systems.
479 What's more, a series of EP/10%HPSi/Si603/DDM hybrids containing 0 wt%, 10
480 wt%, 20 wt% and 30 wt% content of Si603 were prepared. The flame retardancy of
481 the products was examined by an LOI measurement and UL-94 vertical test. LOI
482 value of EP/10%HPSi/30%Si603/DDM was 31, which was about 1.4 times of the
483 corresponding value of neat EP, and a V-1 grade for the UL-94 can be achieved. TG
484 showed that the addition of HPSi (10 wt%) enhanced the thermal stability of
485 EP/DDM system.
486 The high silicon content and rich aromatic group structures of Si603 contributed an
487 excellent flame retardancy to epoxy resins. Specifically, the char residues of the
488 EP/10%HPSi/30%Si603/DDM system could reach 35.88 % in $N_2$ and 13.21 % in air
489 at 800 °C. Structural analysis of the combustion residue by FTIR indicated the
490 formation of polyaromatic carbons which slowed heat and mass transfer between the
491 gas and condensed phases. Based on this, the speculated degradation process of
492 silicon resin was obtained. These properties would make this epoxy attractive for
493 practical applications such as flame-retardant laminates.
494
495

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497

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