Simultaneous reinforcement and toughness improvement of epoxyphenolic network with a hyperbranched polysiloxane modifier

Liu hanchao,^a Zhang junqi,^a Gao xiaoxiao,^a and Guangsu Huang *^a

College of Polymer Science and Engineering, State Key Laboratory of Polymer Material Engineering, Sichuan University, Chengdu 610065, China Corresponding authors. Tel.: +86 28 854 634 33; fax: t86 28 854 054 02. E-mail addresses: guangsu-huang@hotmail.com (G. Huang)



Fig.S1 The FTIR spectrums of mixtures of reactants (i-ii)

After the first step of reaction, the absorption peak at 915 cm⁻¹, which is the characteristic stretching absorption peak of the epoxy group (C–O), disappears, indicating that all the epoxy groups on EMCH have been consumed. Then, in the spectrum of the product, the characteristic stretching absorption peak of hydroxy at 3400 cm⁻¹ to 3600 cm⁻¹ shows up, indicating the -Si-O-Me and -Si-O-Et have hydrolyzed into silanol groups (Si-OH).



Fig.S2 ²⁹Si NMR spectrum of HBPSi-1 (i), HBPSi-2 (ii) and HBPSi-3 (iii)

The ²⁹Si NMR spectrum of HBPSi is depicted in Fig.S2. Attribution of peaks in the ²⁹Si NMR spectrum of HBPSi is summarized in Table S1. Peaks numbered as Si(I) and Si(II)

D	Si(I)	Si(II)
Т	Si(VI)	Si(VII)
L	Si(III)	Si(IV) Si(V)

Table.S1 Attribution of peaks in the ²⁹Si NMR spectrum of HBPSi

are assigned to dendritic units (D). Peaks numbered as Si(III), Si(IV) and Si(V) are assigned to linear units (L). Peaks numbered as Si(VI) and Si(VII) are assigned to terminal unit (T). The degree of branching (DB) of HBPSi can be calculated as

follows:

$$DB_1=2D/(2D+L)$$
 eq₁

$$DB_2 = (D+T)/(D+T+L)$$
 eq2

Sample	DB_1	DB_2
HBPSi-1	0.92	0.85
HBPSi-2	0.94	0.89
HBPSi-3	0.97	0.90

Table.S2 The degree of branching of HBPSi.



Fig.S3 Exotherm DSC curves for samples with varying HBPSi-2 contents (a) and system of DGEBF and HBPSi-2.

DSC was used to characterize the formation of HBPSi-modified epoxy networks. Because the modified epoxies containing HBPSi-2 show the best overall performance, the DSC results are only demonstrated for the case of epoxy-HBPSi-2 system. As shown in Fig.S3 (a), the initial reaction temperature and peak temperature both decrease with increasing HBPSi-2 content. When the HBPSi-2 loading is higher than 5%, two obvious peaks appear in the exothermic curves. The reaction process of the epoxy and HBPSi-2 was studied by DSC analysis of the system of DGEBF and HBPSi-2. As shown in Fig. S3 (b), only one exothermic peak appears in the exothermic curve, indicating a one-stage curing process. Moreover, the initial reaction temperature and peak temperature of the HBPSi-2 and epoxy system are 80.3 °C and 141.5 °C, respectively, which are much lower than that of the DGEBF-phenolic system. Due to the higher reactivity between aliphatic amine and epoxy, it is much easier for epoxy to react with HBPSi-2 than with phenolic, leading to a lower cure onset temperature of the curing system with HBPSi-2 incorporated.



Fig.S4 Tensile curves of E-HBPSi-0 (a) and E-HBPSi-2 (b) at varying HBPSi loadings



Fig.S5 Higher magnified SEM images of fracture surfaces of 10% E-HBPSi-0 (a) and 10% E-HBPSi-2 (b).



Fig.S6 Variation of storage modulus (a) and tan δ (b) with temperature in neat DGEBF , 5% E-HBPSi-1,5% E-HBPSi-2 and 5% E-HBPSi-3.