

Toward understanding the cross-linking from molecular chains to aggregates by engineering terminals of supramolecular hyperbranched polysiloxane

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Abstract

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1. Introduction

Aggregation and dispersion have long been regarded as mutually exclusive concepts, but this dichotomy is in fact a fundamental feature of the natural world. From the gravitational coalescence of dispersed celestial bodies in the universe, to the islands in the ocean, and even to the intricate network-formation of polymer cross-linking, this trend seems like ubiquitous across all scales of the natural world. This universal significance underscores the importance of understanding the mechanisms that govern aggregation and dispersion phenomena in diverse fields of science.^[1- 5]

Conventionally, the cross-linking of polymer is known as a network-formation process from linear monomer to three-dimensional structures, namely the crosslinked network.^[6- 8] But if substitute the linear monomer with a spatial topological macromolecule, such as dendrimer,^[9] star polymer,^[10] hyperbranched polymer.^[11] These topological macromonomers will occupy all or part of the cross-linking site to form a topologically-extended network with respect to their three-dimensional one, we coined it topological crosslinking networks (TCNs) that link through all or part of topological units. In such system, it could be recognized that the macromonomers should undergo both aggregation and dispersion behaviors during polymer crosslinking, which relies on their interface nature (for example, functional groups, surface energy, system temperature).^[12- 14] Therefore, the aggregate state and nano-interface control over the cross-linked structure, and attributes the final properties of the resulting polymer.^[15- 19]

Aggregate science contributes a fresh enlightenment to incline the view of the polymer crosslinking into a more refined and precise direction.^[15- 19] People customarily consider the crosslinking of chemical bonds at the molecular level, however, in case of a multi-components system,^[23] although many efforts have been made toward concepting supramolecular interpenetration or other related ideas among hydrogels and elastomers,^[24- 28] The crosslinking modes should be included but not limited in covalent-bonds and weakly supramolecular interactions. Especially, in case of a thermoset polymer system, over-agglomeration of additives has always been regarded as an undesired matter that dampens material properties,^[29, 30] but the aggregates at nano- or micro- scales could be the positive one reasoned from their nano-phase separation and forming a strong interface between double-phase polymer.^[31]

As a representative crosslinked example, epoxy resins (EPs) feature excellent thermal and mechanical properties due to their highly-crosslinked network-forming architecture,^[32- 34] which are widely involved in human society for aerospace, navigation, wind power. To meet the ever-growing demands for advanced application, the integrals on realizing high-performance and multi-function purposes still require an incisive understanding from structure-to-property relations toward in-principle building and tailoring polymers. The state-of-the-art work focuses their insights overlapping supramolecular chemistry,^[35- 38] dynamic covalent and/or no-covalent chemistry^[39- 42] to engineer the polymer network and to regulate the chemical crosslinks and physical entanglement, which inspires us insightful viewpoints to further understand the cross-linking, and the real formation of polymer.^[43]

In this study, three kinds of hyperbranched polysiloxane (HBPSi-R) were designed and synthesized, respectively, each featuring with different terminals but similar molecular backbone (Si-O-C), and they were copolymerized with epoxy resin/anhydride system to construct supramolecular HBPSi-R/epoxy interpenetrating polymer networks. The thermal performance, curing behaviors and mechanical properties of resulting materials were studied in a fresh viewpoint of aggregation and dispersion to co-polymer crosslinking. To contrast the terminal effects, the aggregation states and nano-interface were revealed, as the double-crosslinking

modes and their aggregate mechanism were proposed in combining their mechanical properties and different terminal groups. Highlighting the importance for understanding the polymer crosslinking from the concept of aggregate science, this work provides theoretical guidance toward in-principle tailoring material properties from a more refined molecular structure in polymeric science.

2. Results and discussions

2.1. Reagent materials and Methods

The reagent materials and method information are supplied in **S1**.

2.2. Synthesis and structural investigation of HBPSi-R

The synthesis of hyperbranched polysiloxane (HBPSi-R) bearing Si-O-C molecular backbone is straightforward using A_2+B_3 ester-exchange polycondensation, where R represent their terminal groups of amino (HBPSi-NH₂), epoxy (HBPSi-EP) and vinyl group (HBPSi-V). Synthetic details are described in **S1**. Briefly, a simple diol (1,3-propanediol, PDO) was employed as A_2 monomer to react with (3-aminopropyl) triethoxysilane, (3-glycidyloxypropyl) triethoxysilane and triethoxyvinylsilane, respectively, yielding liquid products (**Figure 1**). The concentration of hydroxyl group (-OH) was quantified by titration experiments, with details given in **S2.3**, yielding approximate -OH concentration of $1.69 \times 10^{-2} \text{ mol g}^{-1}$, $1.33 \times 10^{-2} \text{ mol g}^{-1}$ and $1.45 \times 10^{-2} \text{ mol g}^{-1}$ for HBPSi-NH₂, HBPSi-EP and HBPSi-V, respectively. Since the -OH concentration of HBPSi-R is much lower than that of epoxy resin, thus the incorporation of HBPSi-R does not change the equivalence dosage of epoxy formulation.

The chemical structure of HBPSi-NH₂, HBPSi-EP and HBPSi-V are evidenced by fourier transform infrared (FT-IR), ¹H nuclear magnetic resonance (¹H-NMR), respectively. To prove the proceeded polycondensation, the distillates from reaction systems were collected for IR detection, showing the same IR profiles compared with that of standard ethanol (See **Figure S1a**), demonstrating the as-expected polycondensation. ¹H-NMR was performed to assign the chemical shifts of protons in spectra of HBPSi-R (**Figure 1b**) and their monomers (**Figure S2**). It's noted that the protons from H1 and H2 in PDO are separated into three different modes in each spectrum of HBPSi-R, which is attributed to various linked modes of protons in dendritic, linear and terminal sites upon hyperbranched structure.^[44] Besides, the protons from amino, epoxy and vinyl groups can be recognized as marking a-e involving in the synthetic polymers (**Figure 1b**), indicating their characteristic groups. The FT-IR information of HBPSi-R and their monomers are presented in **Figure 1c** and **S2.1**, respectively. In the spectrum of HBPSi-NH₂, two peaks around 3300 cm⁻¹ are attributed to the stretching vibration of primary amine group, which can also be founded in the spectrum of its monomers (**Figure S1b**). In the spectrum of HBPSi-EP, the peak at 880 cm⁻¹ corresponds to the C-O-C absorption in epoxy group. In the spectrum of HBPSi-V, the peak at 1600 cm⁻¹ is attributed to the stretching vibration of carbon-carbon double bond.^[45] These results prove the hyperbranched structure information with the presence of characteristic terminals.

2.3. Fabrication of HBPSi-R/EP co-polymer system

The HBPSi-R/EP co-polymer system was fabricated using a thermoset workflow (**S1.3**). The resin matrix consisted of an epoxy resin (DGEBA, E51) and an anhydride curing agent (methyl tetrahydrophthalic anhydride, MTHPA). The fabrication of xHBPSi-R/EP composites involved a thermocuring process by casting method, where 'x' represents the mass fraction of HBPSi-R in the whole resin matrix. In brief, different mass fractions (3%, 6%, 9%) of HBPSi-R were mixed with 70 g of DGEBA epoxy resin and stirred at 80 °C for 15 min until a clear yellowish solution was obtained. Subsequently, 56 g of MTHPA and two drops of tris(dimethylaminomethyl)phenol (DMP-30, curing accelerator) were added and stirred for another 15 min. The mixture was then poured into a preheated mold, and then follows thoroughly degassing in an 80 °C vacuum for 30 min. The curing process involved a heating procedure of 120 °C for 2 h, followed by 150 °C for 3 h and 180 °C for 2 hours. After curing, the samples were demolded and prepared for testing.

Figure 2 illustrates a schematic model describing the distinct reaction modes of HBPSi-R with epoxy substrates. These HBPSi-R structures possess unique terminals and abundant -OH groups upon their molecular backbone (**Figure 2a**). The -OH groups can react with both DGEBA epoxy resin and anhydride curing agent, resulting in clear and uniform resin solutions after brief pre-polymerization. The characteristic terminal groups of HBPSi-R control over their crosslinking behavior and aggregate state of HBPSi-R. Specifically, the amino group in HBPSi-NH₂ react with both epoxy group and anhydride group, while the epoxy group in HBPSi-EP participates in the curing reaction likewise another epoxy component, and the carbon-carbon double bond (vinyl) in HBPSi-V does not react with epoxy resin and anhydride-type curing agent, which plays a supportable role in interpenetrating thermoset network with hyperbranched structure.

2.4. Curing and thermal performance of HBPSi-R/EP

To investigate the influence of HBPSi-R with varying terminal groups on the curing performance of epoxy resin, the pre-polymer resin compounds were initially characterized using isothermal differential scanning calorimetry (DSC, See **Figure 2b**). Upon the incorporation of HBPSi-R, the DSC thermograms exhibited a single exothermic peak resembling that of the native EP, indicating excellent compatibility of the three types of HBPSi-R with the epoxy/anhydride matrix. It is noteworthy that the peak temperature slightly decreased from 165°C to 155°C, suggesting that the inclusion of HBPSi-R does not compromise the processability of the epoxy resin. To determine the real chemical bonding of HBPSi-R within epoxy resin, Fourier-transform infrared (FT-IR) spectra of the cured resin samples were performed (**Figure 2d**). Obviously, a wider stretching vibration of Si-O at 1080 cm⁻¹ is recognized in spectra of HBPSi-NH₂/EP, HBPSi-EP/EP and HBPSi-V/EP, meanwhile, the peak intensity of hydroxyl group is significantly lower than that of the native EP, indicating the consummation of residual hydroxyl groups and confirming the participation of HBPSi-R in the copolymerization and crosslinking with the epoxy network. X-ray diffraction (XRD, **Figure S3**) profiles revealed that the branching structures did not influence the molecular arrangement, thereby maintaining the amorphous crosslinked structure of the epoxy resin.

Thermogravimetric analysis (TGA) was conducted to assess the impact of HBPSi-R on the thermal properties of materials. Given in **Figure 2c**, overall, the addition of hyperbranched polysiloxanes primarily enhanced the residual char of the materials while exerting minimal influence on the initial decomposition and main decomposition behavior (as indicated by the derivative thermogravimetry, DTG, shown in **Figure S7**). This improvement can be attributed to the introduction of the inert silicon-containing component. Notably, compared to neat EP, HBPSi-EP/EP exhibited the most substantial increase in char residue, rising from 6.0% to 11.7%, whereas the amino and vinyl variants showed a char residue of 9.5%. This can be attributed to the superior uniform dispersion of HBPSi-EP within the resin matrix compared to the other variants. The detailed curing and thermal parameters are supplied in **Table S3**.

2.5. Aggregation mechanism and crosslinking modes of HBPSi-R/EP

Based on the aforementioned discussion, hyperbranched polysiloxanes with similar molecular backbone (Si-O-C) but varying terminals could serve as nice model to explore the terminal effects on polymer crosslinking. The aggregate behaviors and crosslinking modes are proposed and described in **Figure 3**. It is important to note that HBPSi-R not only possesses abundant -OH groups for reactivity but also characteristic terminals (-NH₂, -EP, vinyl groups) for adjusting its overall interface features with epoxy resin. The -OH groups can react simultaneously with the DGEBA monomer (ring-opening) and the anhydride monomer (forming ester bonds), thus covalently crosslinking with epoxy network. In addition, it will also supramolecularly crosslinks within the network through hydrogen bond interactions. Therefore, the three systems should exhibit a consistent double-crosslinking behavior involving both covalent and supramolecular modes regardless of their end groups.

To elucidate the characteristic terminal effects, the distribution states of HBPSi-R were visually observed using transmission electron microscopy (TEM) and scanning transmission electron microscopy tools (STEM, the magnification images in **Figure 3**). A staining method was adopted to enhance the imaging clarity since HBPSi-R is embedded in the cured resin (**S1.4**).^[5] It can be founded that the hyperbranched components

are uniformly dispersed with varying aggregation degrees at the nanoscale. This fact indicates that HBPSi-R forms a series of supramolecular hyperbranched polysiloxane aggregates during polymer crosslinking, driven by their low surface energy^[46] and intermolecular hydrogen bonds^[47].

Specifically, HBPSi-NH₂ shows typical sea-island characteristic, where the HBPSi-NH₂ acts as the dispersed phase and the resin matrix serves as the continuous phase, featuring the tightest aggregation behavior with size of ~ 90 nm than HBPSi-V and HBPSi-EP as seen in Figure 3, coined as aggregately crosslinking whose supramolecular behavior dominates during polymer crosslinking, where the strong intermolecular hydrogen bonds between -NH₂ and -OH terminals drive the assembly of HBPSi-NH₂, as clearly defined by the silicon-rich scanning surface in element mapping. In contrast, HBPSi-EP shows dominant uniform dispersion behavior in its TEM image, without apparent nano-phase separation. This is referred to as evenly crosslinking, wherein HBPSi-EP behaves likewise to another epoxy component to covalently bond in such system (covalent-dominance in crosslinking). Between the two structure, HBPSi-V demonstrates uniform dispersion with also stable nano-sized aggregates, whose particle sizes is more regular than that of HBPSi-NH₂. This behavior, termed bulky crosslinking, arises from the moderate interface in which the non-reactive vinyl groups of HBPSi-V play a supportive role to make sure a balance between covalent and non-covalent supramolecular forms. These finds provide deeper insights from the holism of aggregate science into the terminal-dependent crosslinking of HBPSi-R within epoxy network, consequently influencing the overall material properties.

2.6. Mechanical performance of HBPSi-R/EP

The mechanical strength of HBPSi-R/EP was tested to contrast the terminal effects among the three hyperbranched structures modifying epoxy resin (**Figure 4a-c**), following the test results in **Table S4**. The impact fracture microsurfaces are presented in **Figure 4d-g**. Generally, the impact failure of thermosets often owns to their high crosslinking density and rigid polymer chains that are difficult to dissipate the impact energy.^[48] As the natural EP displayed typical brittleness “river-like” fracture covering a large microscopic area (**Figure 4d**), with impact toughness of only 12.9 kJ/m². In contrast, the incorporation of the hyperbranched structures, benefiting the merit of hyperbranched architecture and flexible Si-O-C chains, all demonstrate excellent strengthening and toughening effects, with a gradual decrease as the content is further increased. As shown in Figure 4a-c, HBPSi-V performs superior reinforcement effects regarding toughness, strength and modulus with respect to the other two hyperbranched structures, with an increasingly tough feature from native EP to HBPSi-NH₂, HBPSi-EP and HBPSi-V in SEM photographs (Figure 4d-g). The optimal impact strength of 28.9 kJ/m² was achieved with 3% incorporation of HBPSi-V, nearly three times higher than that of the pristine EP. Based on the aforementioned analyses, these hyperbranched structures possess similar molecular backbones with approximate hydroxyl concentration, as their terminals give rise to such significant differences in mechanical properties, which might be closely related to their unique crosslinking and aggregate behavior.^[49, 50]

Among the three structures, HBPSi-V bears a moderate aggregation and dispersion behavior due to its non-reactive vinyl group, which could forms an appropriate nano-silicone aggregates to toughen the polymer network in case of elastomer mechanism being dominant.^[51, 52] Meanwhile, their abundant -OH terminals can interact covalently and/or non-covalently within the epoxy network, acting as a supramolecular “nano-rivets” that tightly entangle within the network for strengthening effort.^[53] However, it should be note that excessive aggregation of HBPSi-R does a negative effect on mechanical performance, where the bulk agglomeration of excessive hyperbranched polymer becomes a stress concentration area, leading to the deterioration in impact strength. It is worth mentioning that the deterioration in impact strength is less significant in HBPSi-V/EP compared to HBPSi-NH₂/EP at the same filler load. Furthermore, the impact toughness of HBPSi-NH₂/EP is even lower than that of the pristine EP, indicating that HBPSi-NH₂ has a lower tendency to form bulk agglomerations than HBPSi-V at high filler additions. Regarding strength and modulus (**Figure 4b, c**), the flexural strength increases by 36.4% from 106.1 MPa to 144.7 MPa with the incorporation of 3% HBPSi-EP. Both HBPSi-V and HBPSi-EP exhibit better strengthening effects compared to HBPSi-NH₂, and HBPSi-V performs better at high filler loads (9%). Therefore, it is evident that the nano-reinforced and supramolecular

”nano-rivets” mechanisms both depend on appropriate aggregate and uniform dispersion of supramolecular HBPSi-V.

The thermomechanical behaviors were evaluated using dynamic thermomechanical analysis (DMA), as shown in **Figure 5**. Overall, the temperature-dependent storage modulus (E') curves in **Figure 5d-f** exhibit a consistent trend in all the three systems with increasing addition of hyperbranched polysiloxane. The co-crosslinking of HBPSi-R significantly improves the E' value from the room temperature region to the glass transition of the materials (**Figure 5a**), indicating the excellent reinforcement effect of HBPSi-R. The overall decreasing in crosslink density ($d_{crosslink}$) is presented in **Figure 5b** according to the rubber elasticity theory (**S3.1**).^[54, 55] As a results, the decrease in $d_{crosslink}$ is lower for HBPSi-NH₂ compared to HBPSi-EP and HBPSi-V, which further confirms the tightly aggregated nature of HBPSi-NH₂ that is unfavorable for forming the free volume in crosslinking network. As a whole, these hyperbranched structures can reduce the crosslinking density of thermoset but do not deteriorate their mechanical strength, which is attributed to their highly branched chains and abundant reactive terminals.^[44, 56] The glass transition temperatures (T_g) of EP, 6HBPSi-NH₂/EP, 6HBPSi-EP/EP, 6HBPSi-V/EP are 131°C, 118 °C, 111 °C and 110 °C, respectively, indicating they are glassy polymer at room temperature.^[57] The decrease in T_g is foreseeable due to the amorphous structure, as well as the flexible molecular chains of HBPSi-R. Therefore, the co-crosslinking of HBPSi-R encourages a weakly-crosslinked but high-strength thermoset network, and its terminal nature comprehensively affects the aggregation, dispersion, even to crosslinking and the final material properties.

Conclusion

In summary, we successfully synthesized three hyperbranched structures with a common Si-O-C molecular backbone but differing terminal groups. These structures were co-crosslinked with thermoset epoxy to explore their terminal effects on affecting the overall material performance. The special molecular characteristics of HBPSi-R involves abundant -OH groups for their reactivity, as well as distinctive terminals (-NH₂, -EP, vinyl groups) that impart characteristic interface features. All three variants of HBPSi-R exhibit well compatibility within the epoxy matrix, showcasing diverse nano-interface and aggregation behavior. Benefiting their spatial molecular configuration and flexible Si-O-C branches, HBPSi-R manifests exceptional strengthening and toughening effects regardless of their terminal groups. Among them, HBPSi-NH₂ predominantly exhibits the aggregation behavior from supramolecular interaction, while HBPSi-EP show predominantly exhibits dispersion behavior from covalent effect. HBPSi-V achieves a balance of the both, surpassing the other two structures in terms of optimal impact toughness (28.9 kJ mol⁻¹) and better mechanical performance under high dosage, where the non-reactive vinyl group acts as a supportable role during polymer crosslinking. These findings not only emphasize the pronounced reinforcement effects of HBPSi-R but also provide a fresh perspective from aggregate science in the context of polymer crosslinking.

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Conflict of Interests

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Supporting Information

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Figure 1

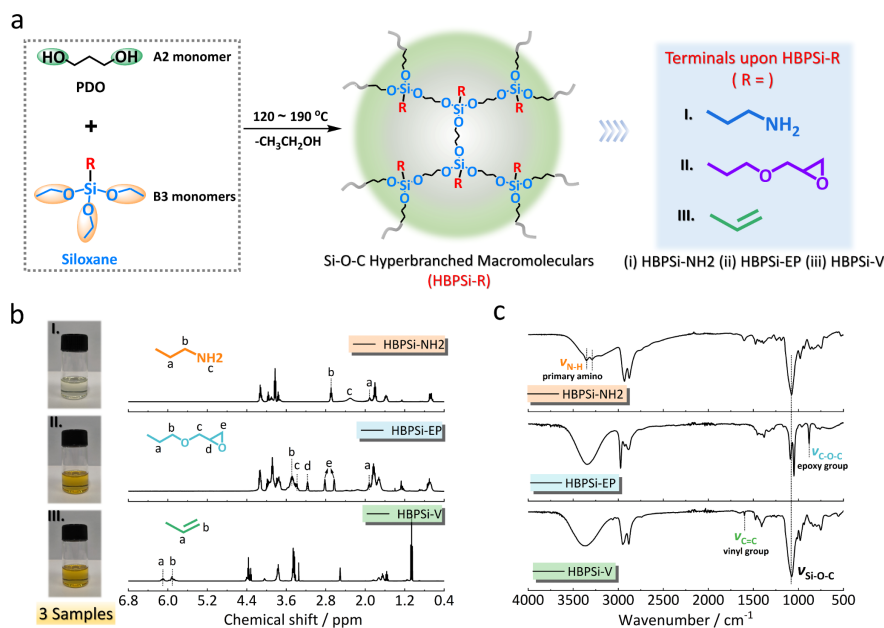


Figure 1. a) The synthesis route of HBPSi-R featuring with varying terminals, b) ^1H -NMR spectra and c) FT-IR information of the synthetic polymers

Figure 2

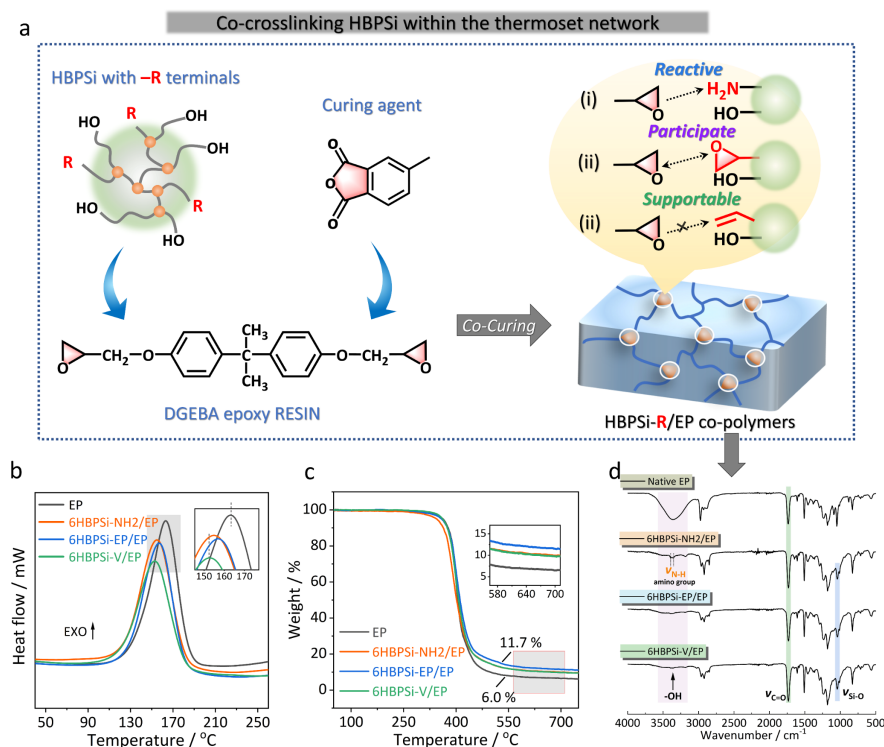


Figure 2. a) The schematic illustration for HBPSi-R/EP co-polymer systems with their unique reactive modes, b) DSC thermograms for pre-polymer mixtures at heating rate of $15^\circ\text{C}\cdot\text{min}^{-1}$, c) weight loss curves

under nitrogen atmosphere, d) FT-IR spectra of the cured samples, samples are 6HBPSi-NH₂/EP, 6HBPSi-EP/EP, and 6HBPSi-V/EP, respectively.

Figure 3

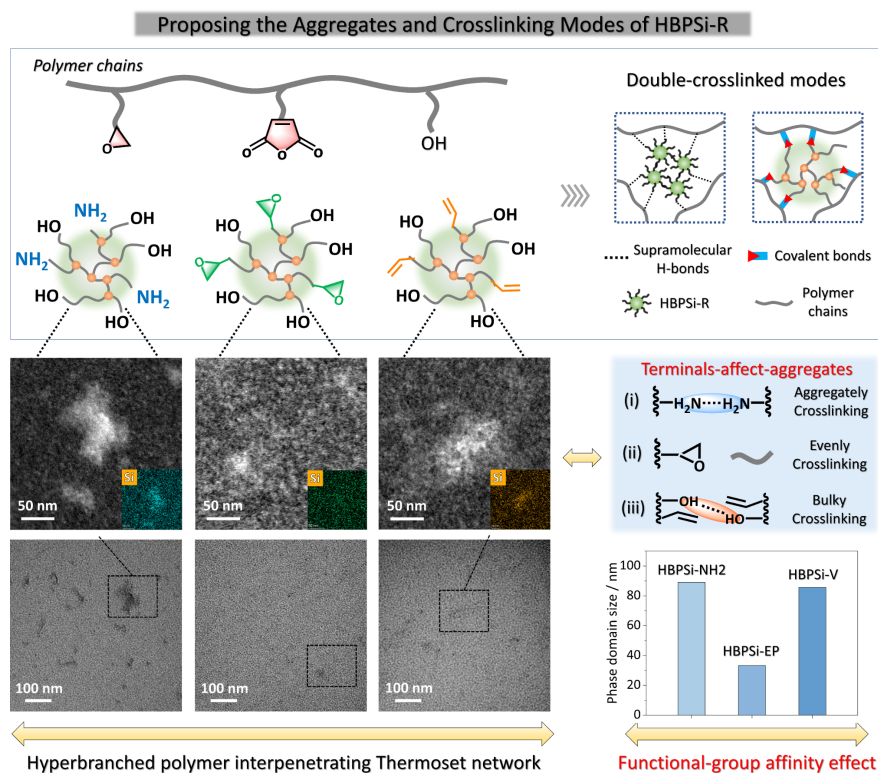


Figure 3. The schematic model and TEM morphologies describing the terminals effect and nano-crosslinking modes of HBPSi-NH₂, HBPSi-EP and HBPSi-V within the thermoset matrix

Figure 4

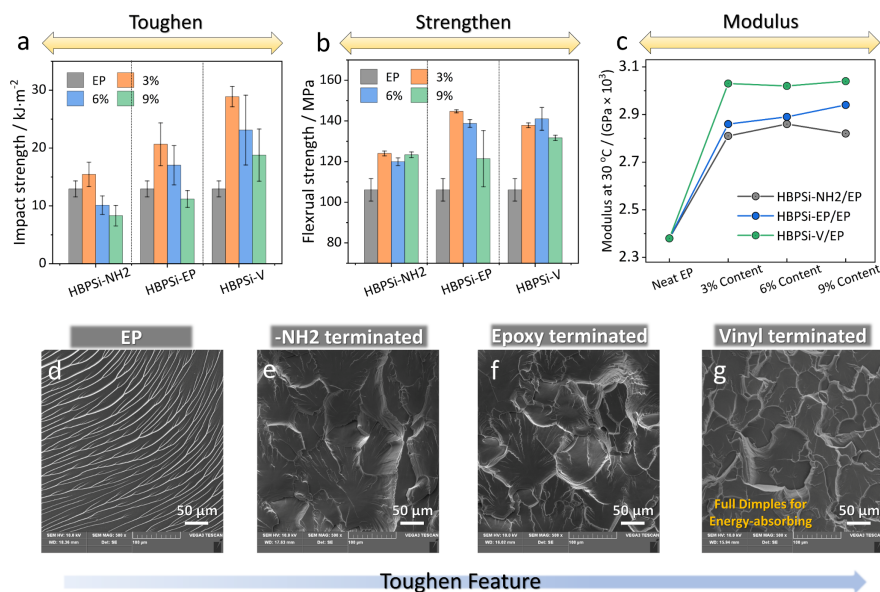


Figure 4. The mechanical performance test of a) impact strength, b) flexural strength, and c) modulus at 25 °C; d-e) SEM photographs indicates the impact tough fracture from native EP to HBPSi-NH₂/EP, HBPSi-EP/EP, HBPSi-V/EP

Figure 5

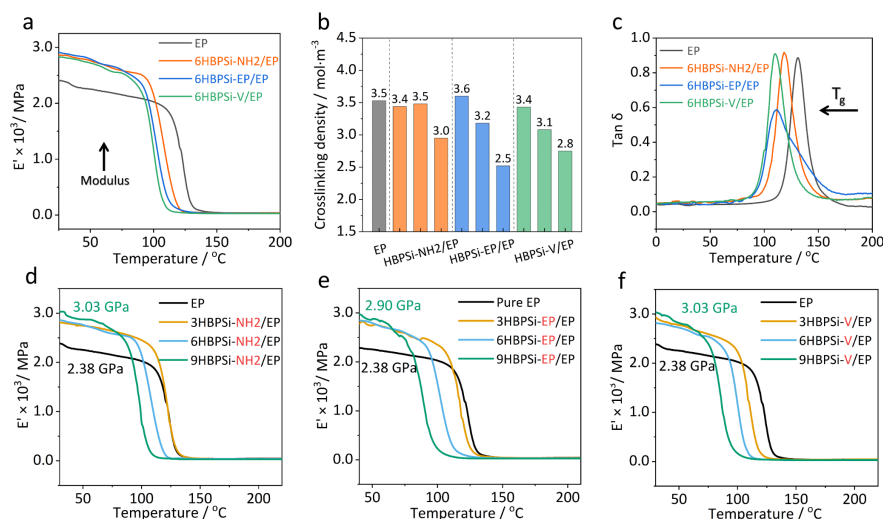


Figure 5. a) The temperature-dependent storage modulus of 6HBPSi-R/EP with distinct terminals, b) network crosslinking density, c) Tan δ curves; d-f) storage modulus curves with different content of HBPSi-R

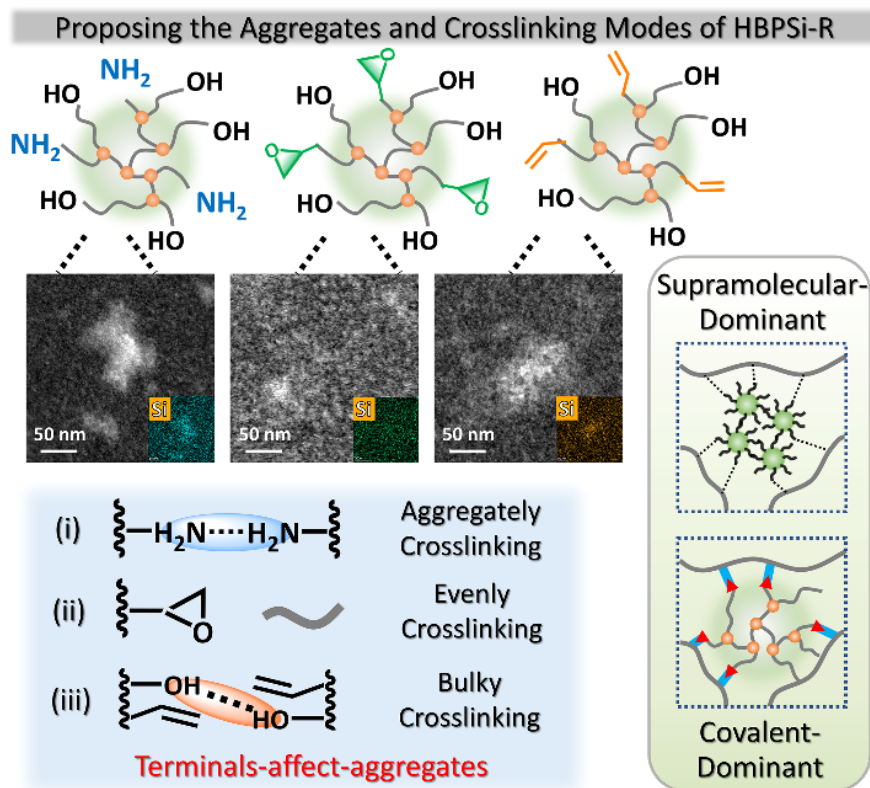
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This study presents a novel perspective towards the understanding of polymer crosslinking from individual molecular chains to the role of aggregates. The aggregate states and crosslinking modes are proposed by engineering amino, epoxy and vinyl terminals upon hyperbranched structures. Benefiting spatial molecular configuration and flexible Si-O-C branches, these hyperbranched structures demonstrate exceptional enhancements in both strength and toughness, and among other superior features, striking a delicate balance

between dispersion and aggregation, as well as forming robust nano-interfaces. This research emphasizes the significance of aggregate science in comprehending the intricacies of polymer crosslinking and offers valuable theoretical insights for tailoring material properties at a refined molecular level.

Yuanbo Zhang, Junshan Yuan, Jingzhi Hu, Zhixuan Tian, Weixu Feng, Hongxia Yan*

Toward understanding the cross-linking from molecular chains to aggregates by engineering terminals of supramolecular hyperbranched polysiloxane



Supporting Information

Toward understanding the cross-linking from molecular chains to aggregates by engineering terminals of supramolecular hyperbranched polysiloxane

Yuanbo Zhang, Junshan Yuan, Jingzhi Hu, Zhixuan Tian, Weixu Feng, Hongxia Yan*,

S1. Materials and Methods

S1.1. Materials

Siloxane monomers including a (3-aminopropyl)triethoxysilane (KH-550), a (3-Glycidyloxypropyl)triethoxysilane (A-1871) and a triethoxyvinylsilane (A-151) were purchased from Hubei Jiangnan New Materials Co.,Ltd, Both 1,3-Propanediol (PDO, AR) and Tris(dimethylaminomethyl)phenol (DMP-30) were obtained from Macklin Biochemical Co., Ltd. Methyl Tetrahydrophthalic Anhydride (MTHPA, mixture of isomers) were purchased from Qihua Chemical Co., Ltd. Epoxy resin, based on a bisphenol A diglycidyl ether (DGEBA, E51, epoxy value: 0.48 ~ 0.54) was purchased from Guangzhou Suixin Fine Chemical Co., Ltd. Solvents such as ethanol and acetone are provided by Guanghua Sci-Tech Co., Ltd. All chemicals were used as received without a further purification.

S1.2. Synthesis details of HBPSi-R

The synthesis of hyperbranched polysiloxanes (HBPSi-R) is straightforward using A_2+B_3 transesterification co-polymerization,^[1-5] where R represents their terminal groups of amino (HBPSi-NH₂), epoxy (HBPSi-EP), vinyl group (HBPSi-V). Siloxane monomers including KH-550, A-1871 and A-151 were used as the B₃ monomers with similar molecular structure but different functional groups, and a simple diol (PDO) was used as the B₂ reactant. The feed ratio follows in accordance from the Florey-Carothers law to avoid over-crosslinking. Briefly, 0.16 mol of siloxanes and 0.35 mol of PDO were put into a three-necked flask equipped with a mechanical stirrer, a N₂ inlet and a thermometer. The mixtures were heated from 120 °C to 180 °C at a heating rate of 5 °C h⁻¹, then maintain stirring until no more distillate generated. Theoretically, the distillates from all three reactions should be the same ethanol with low-boiling point, which could be consistently separated from the reaction system by a condenser to drive the polymerization proceeded. The distillates were collected for IR detection. Taking a rough purification by pressure-reduce drying to remove the small molecules from reaction, the liquid products can be final obtained (**Figure 1**).

S1.3. Fabrication of HBPSi-R/EP co-polymer systems

The fabrication of HBPSi-R/EP co-polymer systems employed a facile thermosetting workflow via casting methods. The resin matrix included a bisphenol-A diglycidyl ether epoxy resin (DGEBA, E51) and an anhydride-type curing agent (Methyl tetrahydrophthalic anhydride, MTHPA). A drop of tertiary amine (Tris(dimethylaminomethyl)phenol, DMP-30) was used as the curing accelerator. Firstly, 70 g of DGEBA with different mass fraction of HBPSi-R (3%, 6%, 9%) was pre-polymerized at 80 °C for 15 min. Since a uniform resin solution of xHBPSi-R/EP was obtained, where x is the mass fraction of HBPSi-R. 56 g of MTHPA and a drop of DMP-30 were added and stirred for another 15 min. The pre-polymer mixture was fully degassed in an 80 °C vacuum for 30 min and then poured into a pre-heated mold. The curing process underwent a heating procedure of 120 °C × 2h, 150 °C × 3h and 180 °C × 2h, and then demolding and tailoring for test.

S1.4. General characterizations

The fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Is50 spectrometer (U.S.A) equipped with an attenuated total reflectance (ATR) model. The nuclear magnetic resonance spectroscopy of ¹H, ¹³C and ³¹P (¹H-NMR, ¹³C-NMR, ³¹P-NMR) was performed using a Bruker Avance 400 MHz spectrometer. The concentration of hydroxyl groups was determined by a titration experiment in accordance with GB/T 7383-2007 (Chinese standard). XRD patterns of the cured thermoset samples was acquired on a Bruker XRD machine (D8 DISCOVER A25). The transmission electron microscope (TEM, FEI Talos F200X) equipped with an energy dispersive spectrometer (EDS, Thermo NS7) microanalyzer was used to observe the distribution and aggregate state of HBPSi-R within the resin, with the cured sample cut by LEICA UC7 freezing microtome at room temperature first, then staining by a phosphotungstic acid (1 wt.% aqueous solution, 2 h).

The mechanical properties were performed on an electro-mechanical tester (CMT 6303) in accordance with GB/T 2567-2008 (Chinese standard), with the sample dimension of 80 mm × 15 mm × 4 mm for flexural test and 80 mm × 10 mm × 4 mm for impact test. Dynamic thermomechanical analysis (DMA) was conducted using a three-point bending model on a NETZSCH DMA 242E machine at the frequency of 1 Hz. Differential scanning calorimetry was performed under nitrogen (N₂) atmosphere using a Mettler-Toledo DSC3 at a heating rate of 15 K·min⁻¹. Thermogravimetric analysis (TGA) was performed under N₂atmosphere using a STA 449F3 thermal analyzer with a heating rate of 15 °C·min⁻¹. The morphology of impact fracture surface was observed by a Scanning Electron Microscope equipped with a tungsten filament gun (TESCAN VEGA 3 LMH).

S2. Structural Investigations Supplements

S2.1. FT-IR information of HBPSi-NH₂, HBPSi-EP, HBPSi-V and their monomers

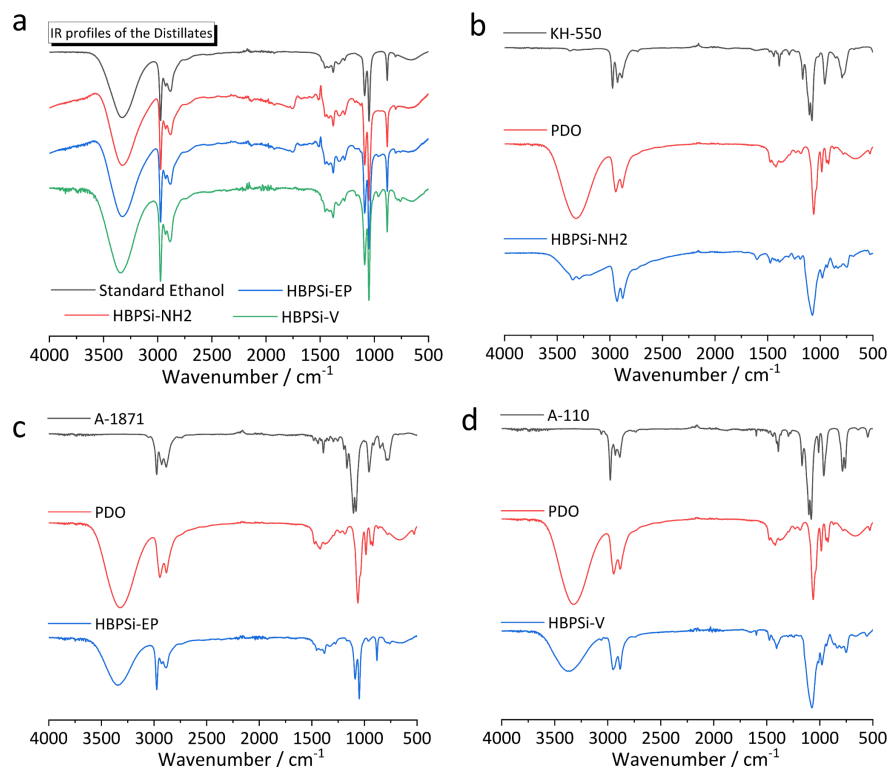


Figure S1 a) IR spectra of the reaction distillates from three systems show same IR profiles with that of the standard ethanol. IR spectra of b) HBPSi-NH₂, c) HBPSi-EP and d) HBPSi-V show significant -OH absorption compared with PDO (B2 monomer) and specific characteristic peaks compared with their B3 monomers, respectively.

S2.2. ¹H-NMR assignments of HBPSi-NH₂, HBPSi-EP, HBPSi-V and their monomers

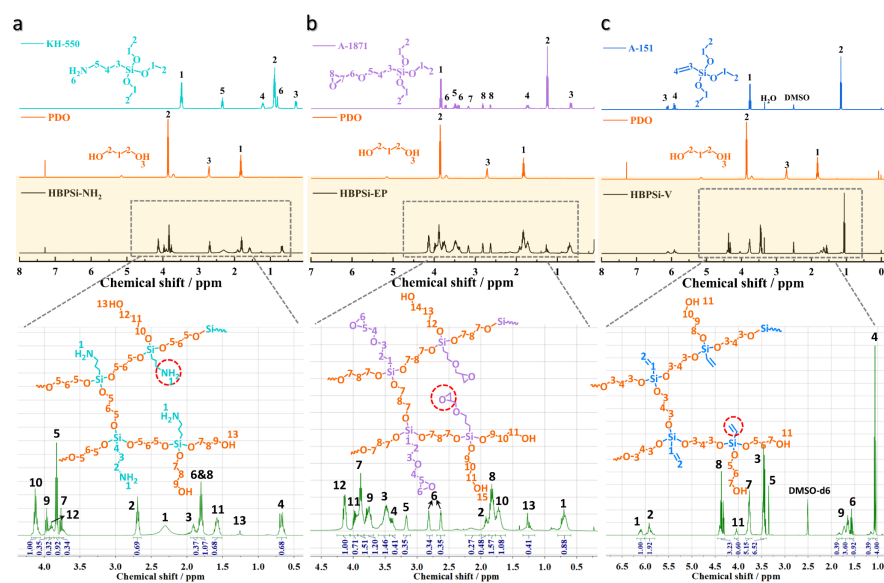


Figure S2 The ^1H -NMR assignments of a) HBPSi-NH₂, b) HBPSi-EP and c) HBPSi-V with their ^1H -NMR information compared with monomers, respectively.

As given in **Figure S2**, ^1H -NMR spectra of HBPSi-NH₂, HBPSi-EP and HBPSi-V were assigned on by one in accordance with their hyperbranched structures. Due to the different solubility in deuterated reagents, DMSO-d₆ was selected for HBPSi-V, and CDCl₃ were chosen for HBPSi-NH₂ and HBPSi-EP. It is noted that some small offsets as well as emerging new peaks can be recognized in comparison with their reaction monomers, indicating the proceed polymerization. Besides, it could be recognized that the H2 from PDO are separated into three link modes in the resulting hyperbranched polymers, corresponding to H5, H7, H9 in HBPSi-NH₂, H7, H9, H11 in HBPSi-EP, and H3, H5, H7 in HBPSi-V. These separated protons in NMR spectra after polymerization are attributed to the various linked modes of dendritic (D), linear (L) and terminal (L) units upon the hyperbranched backbone. Moreover, the protons from amino, epoxy and vinyl groups can be assigned in each HBPSi-R, indicating their characteristic functional groups within the synthetic polymers,

S2.3. Hydroxyl titration record of HBPSi-R

The concentration of hydroxyl group (-OH) was obtained according to a titrimetric method (GB/T 7383-2007, Chinese standard). Firstly, ~1.00 g of HBPSi-R was mixed with 25 ml phthalic anhydride pyridine solution (140.00 g to 1 L pyridine). The mixture was heating upon 115 °C for 60 min in a flask with condensing reflux. Then adding 4 ~ 5 drops of phenolphthalein indicator, the solution was titrated by 0.5 M sodium hydroxide solution (repeating 3 times) until the pink color maintaining more than 15 s. The control test was carried out for also 3 times without adding HBPSi-R. The $Q_{(OH)}$ can be calculated using *Eqn* (1).^[6]

$$Q_{(OH)} = \frac{c \times (V_0 - V_1)}{m_0} \quad (1)$$

Where c is the concentration of sodium hydroxide solution (0.50 mol·L⁻¹); V_0 and V_1 are consumed volume of sodium hydroxide solution, respectively; m_0 is the mass of HBPSi-R.

Table. S1 Titration experimental records for HBPSi-NH₂, HBPSi-EP, HBPSi-V

Run	Run	c (mol·L ⁻¹)	V_0 (ml)	V_1 (ml)	m_0 (g)	$Q_{(OH)}$ (mol g ⁻¹)
Control	Test 1	0.50	82.00	—	—	—
	Test 2	0.50	83.50	—	—	—
	Test 3	0.50	84.50	—	—	—
	Average	0.50	83.33	—	—	—
HBPSi-NH ₂	Test 1	0.50	83.33	50.00	1.025	1.62×10^{-2}
	Test 2	0.50	83.33	47.00	1.069	1.69×10^{-2}
	Test 3	0.50	83.33	46.00	1.052	1.77×10^{-2}
	Average	—	—	47.67	1.049	1.69×10^{-2}
HBPSi-EP	Test 1	0.50	83.33	54.50	1.008	1.43×10^{-2}
	Test 2	0.50	83.33	58.50	1.022	1.21×10^{-2}
	Test 3	0.50	83.33	56.00	1.015	1.35×10^{-2}
	Average	—	—	56.33	1.015	1.33×10^{-2}
HBPSi-V	Test 1	0.50	83.33	55.00	1.021	1.44×10^{-2}
	Test 2	0.50	83.33	54.50	1.017	1.42×10^{-2}
	Test 3	0.50	83.33	52.50	1.033	1.49×10^{-2}
	Average	—	—	54.00	1.024	1.45×10^{-2}

S3. Material Performance Supplements

S3.1. Calculation of network crosslinking density

Based on the rubber elasticity theory, the crosslinking density can be calculated using the equation (2), with the results listed in **Table S2** and **Figure 5b**.

$$d_{\text{crosslink}} = \frac{E'}{[2(1 + \gamma)RT]} \quad (2)$$

Where E' is the rubbery plateau storage modulus at $T_g + 40$ °C; γ represents the Poisson's ratio that is assumed to be 0.5 when the crosslinked network is incompressible for thermoset; R and T represent the gas constant and the Kelvin temperature, respectively. Note that the equation is applicable for lightly crosslinked materials and therefore is used only to qualitatively compare the crosslinking level in the casting resins.^[7, 8]

Table S2 Some parameters obtained from DMA results

Run	T_g / °C	E' at $T_g + 40$ °C / MPa	E' at $T_g + 40$ °C / MPa	$d_{\text{crosslink}}$ / mol m ⁻³
EP	131	39.1	3.53	3.53
3HBPSi-NH ₂ /EP	131	38.1	3.44	3.44
6HBPSi-NH ₂ /EP	118	37.4	3.48	3.48
9HBPSi-NH ₂ /EP	109	31.1	2.95	2.95
3HBPSi-EP/EP	127	39.5	3.60	3.60
6HBPSi-EP/EP	111	33.6	3.18	3.18
9HBPSi-EP/EP	97	25.8	2.52	2.52
3HBPSi-V/EP	121	37.1	3.43	3.43
6HBPSi-V/EP	110	27.9	3.08	3.08
9HBPSi-V/EP	94	32.5	2.75	2.75

S3.2. Thermal and thermomechanical test

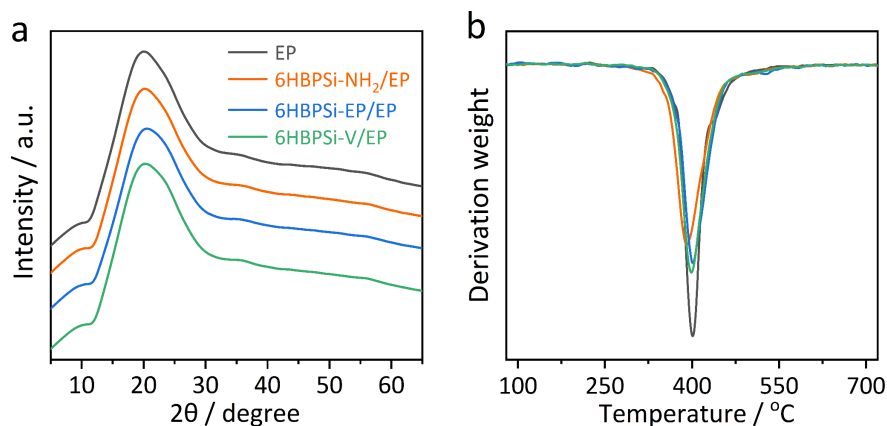


Figure S3 a) XRD profiles and b) derivation weight curves (DTG) of EP and its blend with HBPSi-NH₂, HBPSi-EP and HBPSi-V

Table S 3 Curing and thermal parameters of EP and its blends with HBPSi-R

Samples	DSC	DSC	DSC	TGA	TGA	TGA
	T_i (°C)	T_{Ex} (°C)	T_f (°C)	$T_{5\%}$ (°C)	T_{max} (°C)	Char yield (%)

Samples	DSC	DSC	DSC	TGA	TGA	TGA
EP	101	163	199	362	401	6.0
6HBPSi-NH ₂ /EP	99	157	194	344	392	10.1
6HBPSi-EP/EP	99	155	194	358	401	11.7
6HBPSi-V/EP	98	152	191	361	398	10.0

^a T_i : The initial peak temperature; T_{EX} : The peak temperature; T_f : The end of peak temperature.

^c $T_{5\%}$: The temperature at 5% weight loss; T_{max} : The temperature at maximum decomposition.

S3.2. Mechanical performance test

Table S4 Mechanical test results of EP and its blends with HBPSi-R

Run	Impact strength / kJ·mol ⁻¹	Flexrual strength / MPa
EP	12.94 ± 1.37	106.09 ± 5.53
3% HBPSi-NH ₂ /EP	15.45 ± 2.12	124.02 ± 1.18
6% HBPSi-NH ₂ /EP	10.13 ± 1.60	119.95 ± 1.89
9% HBPSi-NH ₂ /EP	8.32 ± 1.78	123.37 ± 1.36
3% HBPSi-EP/EP	20.65 ± 3.69	144.73 ± 0.72
6% HBPSi-EP/EP	17.03 ± 3.39	138.75 ± 1.93
9% HBPSi-EP/EP	11.20 ± 1.46	121.45 ± 13.81
3% HBPSi-V/EP	28.88 ± 1.75	137.85 ± 1.16
6% HBPSi-V/EP	23.10 ± 6.03	141.01 ± 5.61
9% HBPSi-V/EP	18.77 ± 4.51	131.69 ± 1.28

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