

# Biobased Epoxy Resin with Low Electrical Permissivity and Flame Retardancy: From Environmental Friendly High-Throughput Synthesis to Properties

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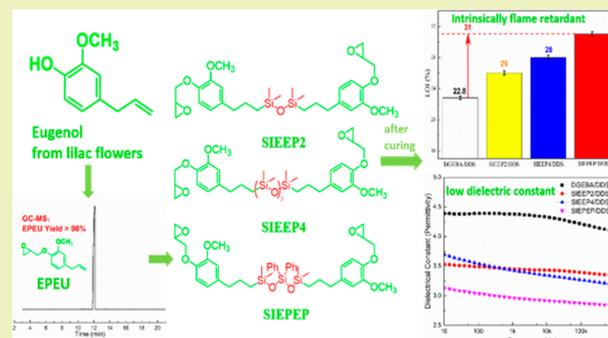
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## Supporting Information

**ABSTRACT:** Recent years have witnessed significant advances in biobased epoxy resins to replace their petroleum-based counterparts, especially diglycidyl ether of bisphenol A type epoxy resin (DGEBA). However, for meeting a great variety of the requirements, long-standing challenges include environmentally friendly preparation of epoxy resin with few toxic byproducts and improving their properties. Herein, we report a facile method to synthesize new silicone-bridged difunctional epoxy monomers in high yield. They are derived from naturally occurring eugenol by introducing the methylsiloxane and phenylsiloxane linkers of different chain lengths into their molecular backbones. These synthesized liquid epoxy monomers have definitive molecular structure with high purity. These silicone-bridged difunctional epoxy monomers exhibit much lower viscosity (<2.5 Pa s) than commercial DGEBA epoxy (10.7 Pa s) suitable for composites and prepreps. After curing, they exhibit a dielectric permittivity as low as 2.8 and good intrinsic flame retardancy with LOI value higher than 31, far outperforming DGEBA. All these advantages are stemmed from their siloxane-contained segments characterized by low polarity, very high dissociation energy, helical molecular structure, and high molecular volume. Overall, this work provides a very facile and scalable route access to a family of the multifunctional eugenol-based epoxy monomers with low dielectric constant and enhanced flame retardancy.

**KEYWORDS:** eugenol, epoxidation, low viscosity, dielectric properties, flame retardant



## INTRODUCTION

Epoxy resins are highly versatile and widely applied in many fields ranging from commercial paintings and adhesives to military carbon-fiber reinforced high-performance composites. Most of epoxy resins are made out of resource-limited petrochemicals, such as bisphenol A, bisphenol S, bisphenol F, and novolacs. Nowadays, the development of high-performance epoxy faces two obstacles: (1) its petroleum-based raw material's unsustainability during life cycle: from production and usage to waste, and (2) further improvement in special properties, such as dielectrical properties and flame retardancy.

With increasingly consumption of petroleum resources and energy, substituting traditional petroleum-based epoxy with renewable counterparts, especially biobased epoxy, becomes urgent. Many different plant resources have been derived

through fermentation and chemical transformation<sup>1</sup> to satisfy their usage as starting materials to prepare biobased epoxy monomers: vanillin,<sup>2</sup> soybean oil,<sup>3,4</sup> vanillyl alcohol,<sup>5</sup>  $\beta$ -cyclodextrin,<sup>6</sup> isosorbide,<sup>7</sup> syringaresinol,<sup>8</sup> quercetin,<sup>9</sup> phenolic acid,<sup>10,11</sup> itaconic acid,<sup>12–14</sup> gallic and vanillic acid,<sup>15,16</sup> multifunctional carboxylic acids,<sup>17,18</sup> lignin,<sup>19</sup> and so forth. The prepared epoxy exhibits improved mechanical modulus, strength, and so forth. To illustrate this, Sheng Wang and Songqi Ma et al.<sup>2</sup> recently prepared a bioepoxy based on vanillin, exhibiting a high glass transition temperature ( $T_g$ ) of 214 °C after curing. The contained diethyl phosphite group enhances its LOI value to higher than 30. Jian et al.<sup>4</sup> cured

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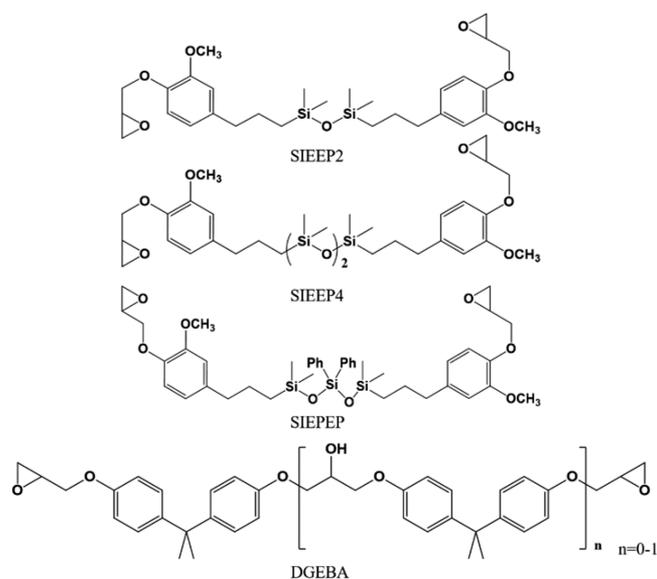
epoxidized soybean oil with castor oil-derived crystalline nylon oligomer, acquiring all plant oil-derived epoxy thermosets with dramatic enhancement in mechanical properties. With  $\beta$ -cyclodextrin and trehalose as raw materials, Reineke et al.<sup>6</sup> prepared suger-derived epoxy resin hardeners. After curing with trimethylolpropane triglycidyl ether, it exhibits a high Young's modulus of 1.8 GPa. The cured epoxy polymers are degradable in basic or acidic aqueous solution. Janiver et al.<sup>8</sup> prepared a renewable bisepoxide from syringaresinol using a chemo-enzymatic synthetic pathway with high yield and purity. After curing with amines, it exhibits a  $T_g$  ranging from 73 to 126 °C. Kristufek et al.<sup>9</sup> prepared epoxy from quercetin derivatives with high purity, exhibiting similar  $T_g$  and thermal stability as commercial DGEBA-type epoxy. Maiorana et al.<sup>10</sup> prepared diphenolic acid-derived epoxy resins with tunable properties and found that the esterification of its carboxylic groups reduces the viscosity of the epoxy monomers from 792 to 12 Pa s. The cured epoxy showed the  $\alpha$  transition temperature ranged from 86 to 158 °C depending on the length of the attached chain of *n*-alkyl via ester bond. Ma et al.<sup>12</sup> prepared a biobased epoxy monomer derived from itaconic acid with a low viscosity of 0.92 Pa s and a high epoxy value of 1.16. Aouf et al.<sup>15</sup> prepared a gallic acid-based multifunctional bioepoxy monomer with rather high epoxy functionality (3.8), and its isophorone diamine (IPDA) cured product showed a high  $T_g$  of up to 230 °C. Most of these syntheses started from preparation of bisphenol/multiphenol derivatives and further conducted the reaction with epichloride to prepare the epoxy. This research produced high purity epoxy with comparable properties as those of DGEBA-type epoxy, including high  $T_g$ , thermal stability, and mechanical properties.

With the rapid expansion in epoxy applications, although significant progress has been achieved for biobased epoxy resins, there remains a challenge for properties other than  $T_g$  and mechanical properties, such as flame retardancy and dielectrical properties, which are important prerequisites for many important applications. In the past, halogenated organic additives such as polybrominated biphenyls and polybrominated diphenyl ethers<sup>20</sup> were widely used to produce flame retardant epoxy materials. Unfortunately, these halogenated additives proved to be harmful to the endocrine system of human beings, and now EU has instituted regulations on restricting the use of such hazardous substances in electrical equipment (RoHS Directive 2002/95/EC).<sup>20,21</sup> In this case, developing biobased epoxy with low flammability while avoiding introducing halogen elements is very important to reduce potential fire and health hazards. Some researchers introduced organic phosphate moieties into the epoxy molecules to increase flame resistance, which however led to high moisture absorption and lower thermal stability.<sup>22–24</sup> Alternatively, a novel eugenol-based difunctional epoxy resin (TPEU-EP) was prepared with a full aromatic ester backbone, and 33DDS-cured TPEU-EP exhibited the self-extinguishing behavior in vertical burning test with 68 and 40% decreases in the heat release rate and total heat release, respectively.<sup>12</sup> However, TPEU-EP is a crystal solid with very high melting point (>150 °C) leading to poor processing ability for coatings, adhesives, and fiber-reinforced composites. Further, considering epoxy application, because they are widely used as insulating materials for electronic devices such as central processing units, exhibiting good dielectric properties, an especially low dielectric constant is necessary as well. Nevertheless, very few research activities on biobased epoxy resin address this issue.

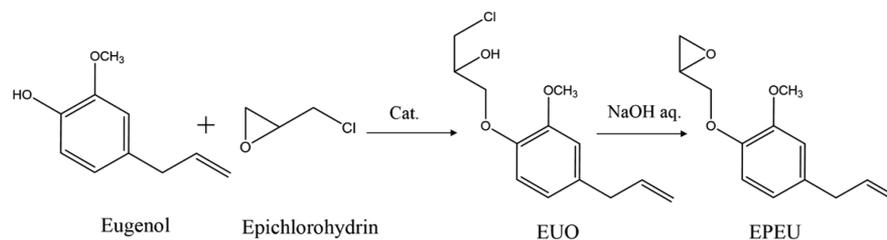
Here, we introduce silicone into biobased derivatives to prepare a silicone-containing bioepoxy. The silicone segments are proven being effective in improving epoxy's flame retardancy: Wang and Perng et al.<sup>25</sup> synthesized triglycidyl phenyl silane based on phenyl trimethoxysilane. It increased the LOI value of diglycidyl ether of bisphenol A epoxy from 22 to 26 with 25 wt % loading content and can further enhance the LOI to 29 with 50 wt % loading content. For epoxy, the most used siloxane components are polyhedral oligomeric silsesquioxanes (POSS), and it can also effectively improve epoxy matrix fire retardant properties. The glycidyl-terminated POSS reduced the peak heat release rate to over 30% lower than pure epoxy, being less than 800 kW/m<sup>2</sup> (POSS loading content: 3.7 wt %).<sup>26</sup> The silicone is also proved to be useful for reducing the dielectrical constant because the siloxane chain is hard polarize under a strong electronic field.<sup>27</sup>

Different from most of the previous bioepoxy synthetic routes,<sup>8,9,28</sup> which start from preparing bisphenol or multiphenol derivatives and then conducting epoxidation with epichloride or peroxides, our method first prepares epoxidized eugenol (EPEU), which is monofunctional. The eugenol is extracted from lilac flowers, so it is a biobased raw material. The initial steps of preparing epoxidized eugenol reduces the production of epoxidized oligomers (which are produced as byproducts during reactions between bisphenol and epichloride). Moreover, our method will be proven to be environmental friendly as it produces EPEU with extremely high yield with trace amounts of epichlorohydrin and eugenol remaining unreacted. The EPEU contains allyl groups, providing excellent molecular structure design flexibility. Here, we design a facile route to synthesize silicone-containing biobased epoxy monomers (SIEEP2, SIEEP4, and SIEPEP). From a molecular structure aspect (see Scheme 1), the SIEEP2 and SIEEP4 contain different lengths of dimethylsiloxane segments, whereas SIEPEP contains a diphenyl siloxane bridge. They are derived from bioresourced eugenol and functional silicone monomers with the advantage of easy access to raw materials, mild synthesis conditions, and extremely high yield. They are expected to exhibit better properties with respect to the

**Scheme 1. Molecular Structures of SIEEP2, SIEEP4, SIEPEP, and DGEBA**



## Scheme 2. Synthesis Route of EPEU



traditional DGEBA-type epoxy resin, especially on viscosity, flame retardancy, and dielectric behavior.

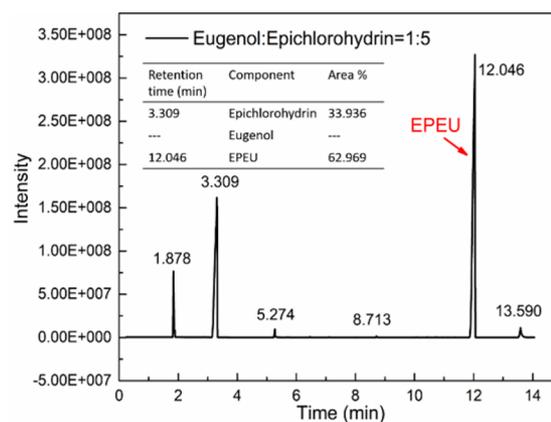
## RESULTS AND DISCUSSION

**Synthesis and Structural Characterization.** After an extensive literature survey, it is currently still quite difficult to synthesize a silicone-modified biobased epoxy resin with good yield and high purity simultaneously via a simple and scalable method. To meet this challenge, we developed a facile strategy to prepare silicone-containing biobased epoxies starting from hydrogen-containing siloxanes and naturally occurring eugenol as raw materials.

According to Scheme 2, the epoxidation of eugenol to prepare epoxidized eugenol (EPEU) was performed through glycidyletherification between a phenolic hydroxyl group and epichlorohydrin, which is similar to the well-established industrial procedure to manufacture diglycidyl ether of bisphenol A (DGEBA)-type epoxy resins. However, we made improvements to the synthetic method of EPEU.

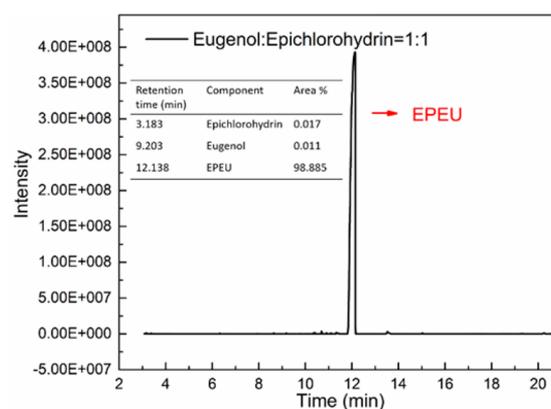
Modified according to previously reported methods,<sup>8,29,30</sup> we first conduct the reaction of eugenol with epichlorohydrin at a mol ratio of 1:5 (eugenol versus epichlorohydrin): To a 100 mL round-bottom flask equipped with a magnetic stirrer and a condenser were charged eugenol (16.42 g, 0.1 mol), epichlorohydrin (46.26 g, 0.5 mol) and benzyl triethylammonium chloride as phase transfer catalyst (2.27 g, 0.01 mol), which were stirred under nitrogen flow and reflux for 2 h to fully connect the epichlorohydrin to the phenyl hydroxyl group of eugenol. Then, the temperature was reduced to 65 °C, and 20 wt % sodium hydroxide aqueous solution (4.08 g, 0.102 mol) was dropped into the mixture in 1 h. The reaction was taken for another 3 h to end the reaction. The final mixture separates into two layers: the upper organic layer and the lower water phase layer. The components in the upper organic layer were analyzed by GC-MS spectra. According to the GC spectra in Figure 1, it can be observed that, due to the high mol ratio of epichlorohydrin versus eugenol, there is 33.936% of epichlorohydrin remaining in the products, whereas eugenol was undetectable. The target product, epoxidized eugenol (EPEU), was 62.969% by content in area percent. A minority of the eugenol was transferred to become 1-(4-allyl-2-methoxyphenoxy)-3-chloropropan-2-ol (EUO), appearing at the retention time of 13.590, but the content was low, being 3.497% (see Table S1 and Figure S1).

The byproduct of this reaction was low because the total area percentage of epichlorohydrin and EPEU was already as high as 96.905%. However, the remaining epichlorohydrin still requires considerable energy and cost to remove in industrial scale production. We try to further reduce the mole ratio of epichlorohydrin and eugenol to see whether it is possible to reduce epichlorohydrin content in the final reaction system while retaining a high yield of EPEU.

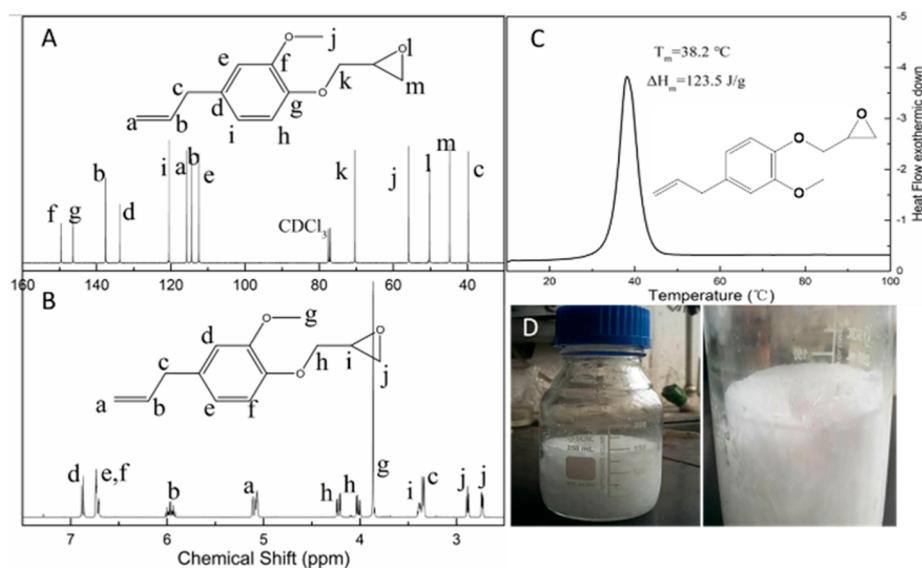


**Figure 1.** GC spectra of final mixtures in epoxidization reaction of eugenol (1:5 mol ratio of eugenol/epichlorohydrin).

Here, we optimized the reaction of eugenol with epichlorohydrin at a mol ratio of 1:1: To a 100 mL round-bottom flask equipped with a magnetic stirrer and a condenser were charged eugenol (16.42 g, 0.1 mol), epichlorohydrin (9.26 g, 0.1 mol), and benzyl triethylammonium chloride as phase transfer catalyst (0.23 g, 0.001 mol), which were stirred under nitrogen flow and refluxed for 2 h to fully connect the epichlorohydrin into the phenyl hydroxyl group of eugenol. Then, the temperature was reduced to 65 °C, and 20 wt % sodium hydroxide aqueous solution (4.08 g, 0.102 mol) was dropped into the mixture in 1 h. The reaction was taken for another 3 h to end the reaction. The upper organic layer of the reaction system was analyzed by the GC-MS spectra (Figure 2). The results showed that the EPEU content was as high as 98.885% by area content. It is amazing that the remaining epichlorohydrin was only 0.017%, and the unreacted eugenol

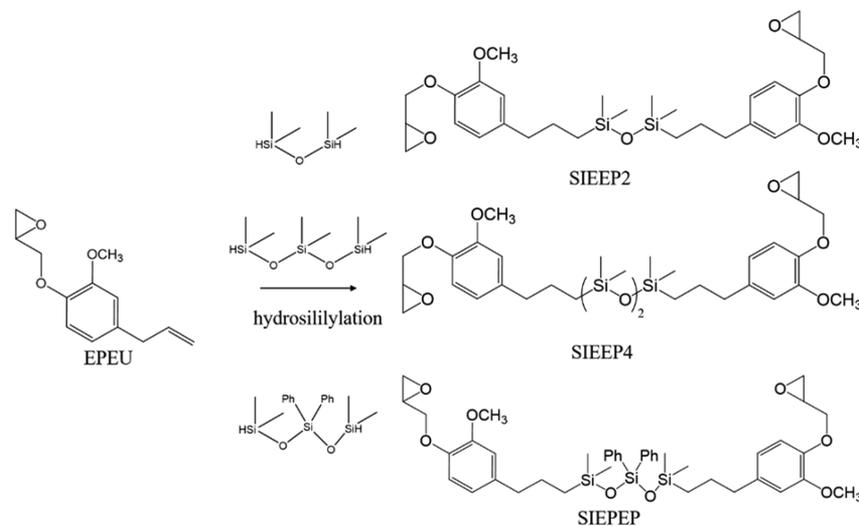


**Figure 2.** GC spectra of final mixtures in the epoxidization reaction of eugenol (1:1 mol ratio of eugenol/epichlorohydrin).



**Figure 3.** (A)  $^1\text{H}$  NMR and (B)  $^{13}\text{C}$  NMR of EPEU, (C) DSC scanning of EPEU, and (D) needle-like crystals of EPEU.

### Scheme 3. Synthesis Routes to Silicone-Containing Biobased Epoxy Monomers



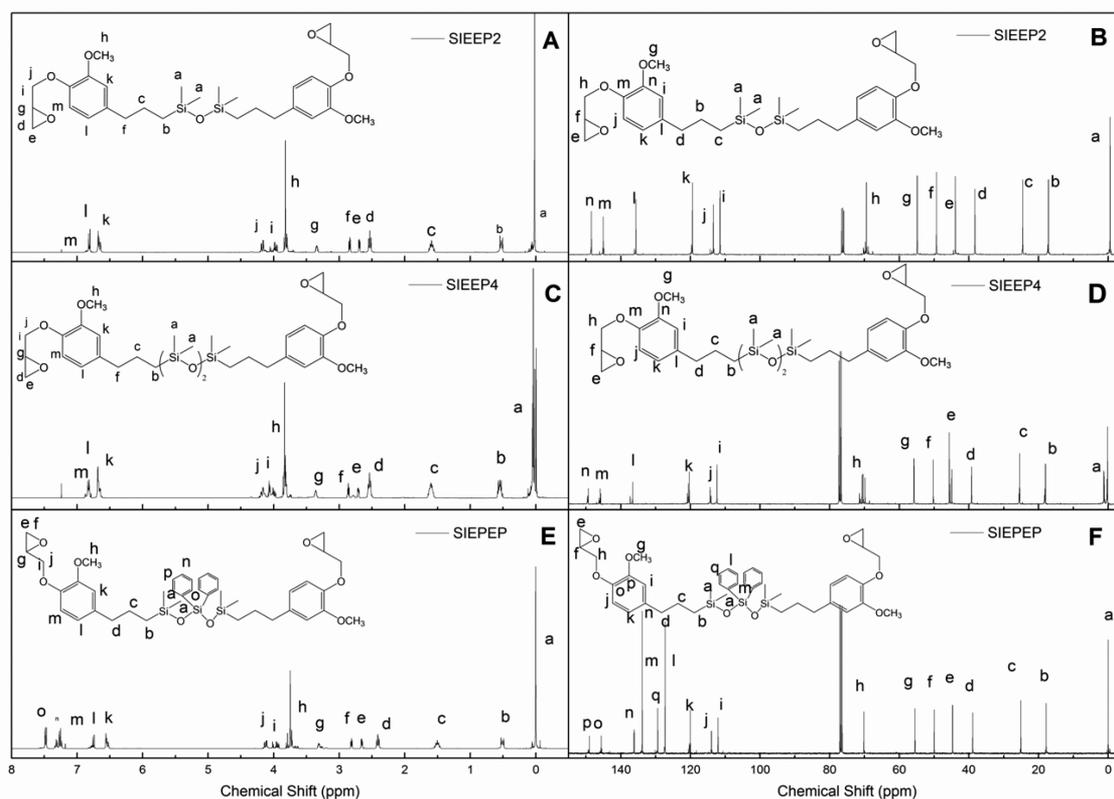
was 0.011% by area (see Table S2 and Figure S2). The optimized reaction was very highly efficient with trace amounts of unreacted epichlorohydrin and eugenol being detected. Thus, it is practicable, cost-effective, and environmentally friendly for industrial-scale production of EPEU.

The organic layer was further purified by crystallization from methanol at approximately  $-5\text{ }^\circ\text{C}$  for 12 h to produce high purity epoxidized eugenol (EPEU) as needle-like crystals (Figure 3D). As shown in Figure 3A and B, the obtained eugenol glycidylether displays  $^1\text{H}$  NMR signals for epoxy groups at 2.4–3.2 ppm. There is no impurity-related signal in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. The exothermic heat for the EPEU melting process is 123.5 J/g with the melting point of  $38.2\text{ }^\circ\text{C}$  (Figure 3c). It is obtained at high purity, which is a precondition for further reaction. It is a very promising method to realize the scalable synthesis of high-purity eugenol glycidylether EPEU.

Further, eugenol glycidylether inherits allyl group from eugenol whose terminal aliphatic  $\text{C}=\text{C}$  in principle can undergo high-selectivity and high-efficiency hydrosilylation reaction

(frequently very close to quantitative conversion) to introduce different silicone linkages into the molecular backbone of the resulting epoxy monomers (SIEEP2, SIEEP4, and SIEPEP; Scheme 3). More strikingly, we experimentally found that the involved hydrosilylation reaction can be carried out under mild conditions ( $60\text{ }^\circ\text{C}$ , compared with  $\sim 100\text{ }^\circ\text{C}$  or higher temperature in other literature) at a high speed (4 h totally) in a high yield of products (at least 97%).<sup>31</sup> The detailed process is described in the Experimental Section. Therefore, it is highly promising to synthesize these new biobased silicone-containing epoxy monomers on a large scale at a relatively low cost, affording high potential for applications from a synthetic point of view.

Structurally, the obtained SIEEP2, SIEEP4, and SIEPEP have two identical eugenol-derived epoxy-bearing moieties but different substituted siloxane chains to link them (Scheme 3). To illustrate, SIEEP2 has a Si-O-Si linker, and each Si atom is substituted by two methyl groups, whereas SIEEP4 has a longer Si-O-Si-O-Si linker with six methyl substituents in total. On the other hand, SIEPEP has a similar Si-O-Si-O-Si linker to that of SIEEP4, but with phenyl groupson the middle Si atom instead

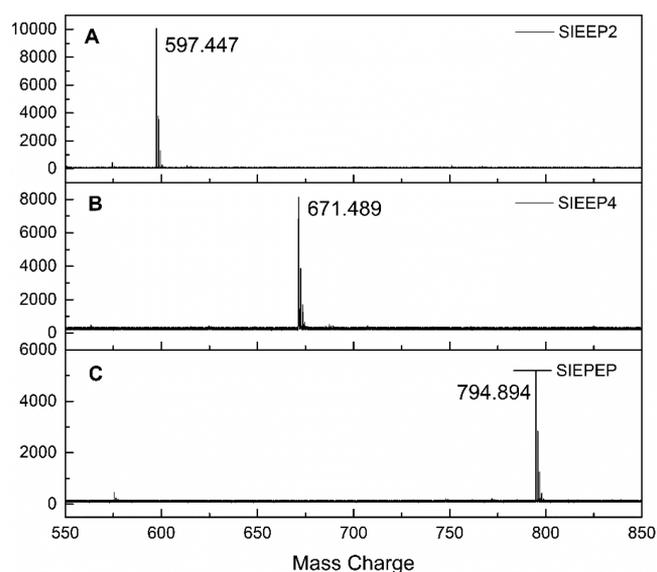


**Figure 4.** NMR spectra of epoxy resin: (A)  $^1\text{H}$  NMR of SIEEP2, (B)  $^{13}\text{C}$  NMR of SIEEP2, (C)  $^1\text{H}$  NMR of SIEEP4, (D)  $^{13}\text{C}$  NMR of SIEEP4, (E)  $^1\text{H}$  NMR of SIEPEP, and (F)  $^{13}\text{C}$  NMR of SIEPEP.

of methyl groups. The difference in the length of siloxane linker and nature of the substituents are expected to result in tunable properties, such as dielectric, thermal, and surface wetting properties as well as flammability, as will be discussed in the following subsection.

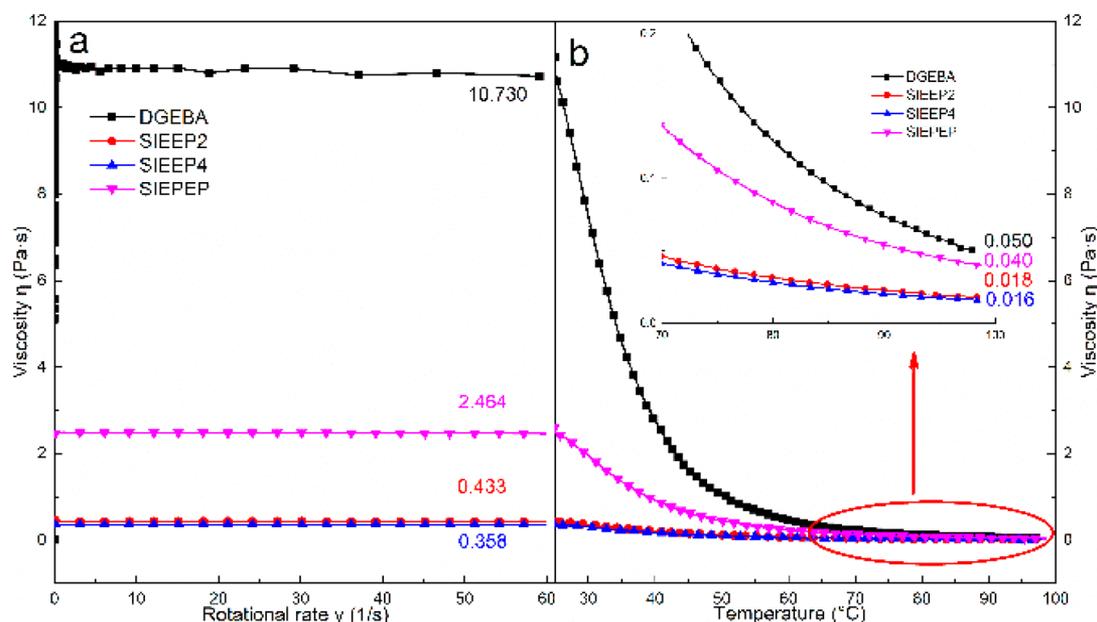
For verifying the molecular structure of the synthesized SIEEP2, SIEEP4, and SIEPEP, their  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR analyses have been conducted (Figure 4). After hydrosilylation reaction between the allyl group of eugenol glycidylether and active hydrogen atom of the three different silicone linkers, all of the obtained adducts (SIEEP2, SIEEP4, and SIEPEP) feature the same changes: the allyl-related signals completely vanish and new signals appear assigned to the siloxane linker (at 0.5, 1.9, and 2.9 ppm). The epoxy ring can be observed at a chemical shift of  $\sim 2.4$ – $3.2$  ppm in the  $^1\text{H}$  NMR spectra and 45 and 50 ppm in the  $^{13}\text{C}$  NMR spectra.<sup>31,32</sup> The hydrosilylation addition reactions are accomplished with side reactions being excluded. Further evidence from MALDI-TOF-MS spectra (Figure 5) confirms that SIEEP2, SIEEP4, and SIEPEP have the expected molecular weights of 574.447 (597.447–23, minus the weight of  $\text{Na}^+$ ), 648.489 (671.489–23), and 771.894 (794.894–23), which are in accordance with the values of their expected molecular structures.

Optimizing the preparation method is a key step to develop high-performance, low-cost biobased epoxies.<sup>33</sup> From a synthesis perspective, we have developed a highly cost-effective and environmentally friendly synthetic route to prepare flexibly designed silicone-containing biobased epoxies. They satisfy various requirements, including low cost of raw material, low production cost, few reaction steps, ease of purification, high productivity, and high yield.



**Figure 5.** MALDI-TOF-MS spectra: (A) SIEEP2, (B) SIEEP4, and (C) SIEPEP.

**Rheological Behavior of Epoxies.** The rheological behavior, especially the viscosity at room temperature and high temperature, is a key property for epoxy targeting on prepregs/composites. According to Figure 6a, all the epoxies exhibit stable viscosity with variation of rotational rate because they are Newtonian fluids. The commercial DGEBA (with epoxy equivalent value of 180 g/mol) exhibits a constant viscosity of  $\sim 10.730$  Pa s. The SIEPEP exhibits a viscosity of



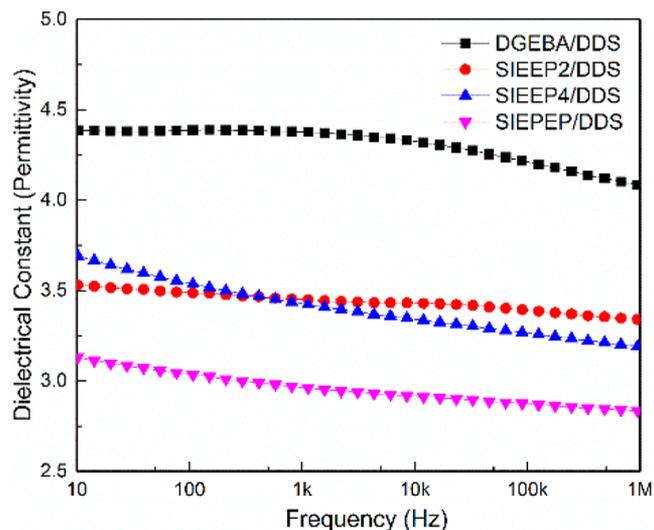
**Figure 6.** Rheological behavior of epoxies (without curing agent): (a) viscosity with the rotational rate varied from 0.01 to 60/s (temperature: 25 °C) and (b) viscosity at temperatures from 25 to 100 °C (rotational rate: 60/s).

2.464 Pa s, much lower than that of DGEBA. SIEEP2 and SIEEP4 exhibit further lower viscosities of 0.433 and 0.356 Pa s, respectively. Considering differences in their molecular structures, the siloxane chain reduces viscosity compared with bisphenol A main chain of DGEBA. Further, the SIEEP2 and SIEEP4 with methyl siloxane as main chain exhibit lower viscosities than that of SIEPEP, which contains diphenyl siloxane as the main chain.

Their viscosity reduces with temperature increasing (Figure 6b). At a temperature of 100 °C, the DGEBA exhibits a viscosity of 0.050 Pa s, whereas SIEPEP, SIEEP2, and SIEEP4 exhibit viscosities of 0.040, 0.018, and 0.016 Pa s, respectively. The silicone-containing biobased epoxy series, SIEEP2, SIEEP4, and SIEPEP exhibit much lower viscosities than those of DGEBA at both room temperature and high temperature, making them an ideal option as matrix of composites and prepreps.

**Dielectric Properties.** The dielectric properties are an important consideration for the use of epoxy resins as electrical insulating materials, which are strongly affected by their molecular structure. In particular, with increasing miniaturization of electronic devices, it is highly desirable to reduce the dielectric constant (permittivity) and loss factor of epoxy matrix. In general, after curing, general purpose bisphenol A epoxy resin (DGEBA) exhibits a dielectric constant of 4–6.<sup>34,35</sup> Here, we experimentally find that the commercial DGEBA cured by DDS (DGEBA/DDS) shows a dielectric permittivity of 4.4–4.15 from 10 to 1 MHz. In contrast, in Figure 7, our developed SIEEP2/DDS and SIEEP4/DDS systems exhibit considerably reduced dielectric permittivities of 3.7–3.3 and 3.55–3.5, respectively. Even better results (3.2–2.8) are observed in SIEPEP/DDS.

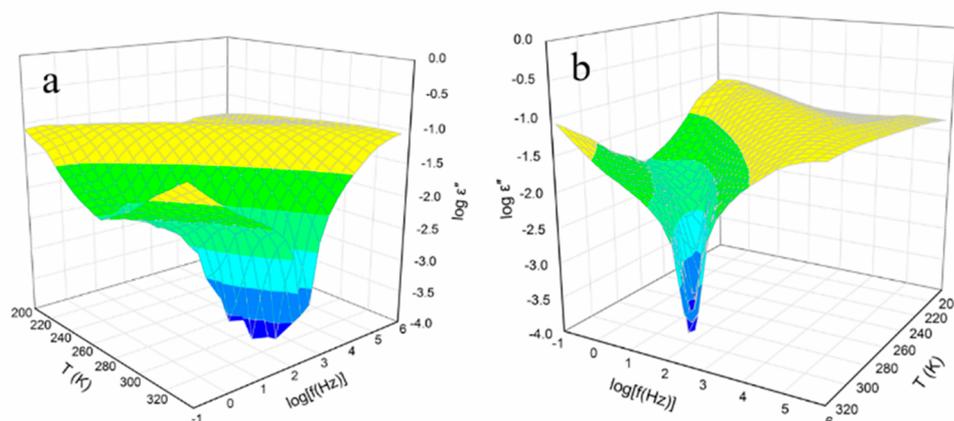
To further reveal the reason for low permittivity, we conducted a closer examination of dielectric loss ( $\log \epsilon''$ ) of the cured as a function of temperature and frequency (Figure 8). A strong dielectric response is observed, which can be related to the dipole movement, such as hydroxyl groups in the different chemical environments. There is one main relaxation



**Figure 7.** Relationships between dielectric permittivity and frequency at 20 °C.

process indicated by a peak in the dielectric loss. With increasing temperature, it shifts to higher frequencies as expected. This process is  $\beta$  relaxation and corresponds to the side group fluctuation.

For comparison, Figure 9 shows the dielectric loss  $\epsilon''$  spectra for SIEEP2/DDS, SIEEP4/DDS, and SIEPEP/DDS in a 3D representation. The  $\beta$  relaxation is observed similarly like DGEBA/DDS: With increasing frequency, its dielectric loss peak shifts to higher temperature. It is a relaxation process related to the molecular mobility of molecular dipoles, especially for hydroxyl groups at the side position. However, the intensity of the relaxation peak is much weaker compared with that of DGEBA/DDS, showing that the depolarization behavior of hydroxyl groups in SIEEP2/DDS. SIEEP4/DDS and SIEPEP/DDS are quenched in the cross-linked network. Comparing their molecular structures, the methyl siloxane segments can reduce the dielectric permittivity of the cured



**Figure 8.** Dielectric loss  $\epsilon''$  of DGEBA/DDS versus frequency and temperature in a 3D representation.

epoxy effectively, and the phenyl siloxane chain behaves even better. The Si–O bonds of the bulky siloxane chain tend to quench polarization behavior of hydroxyl groups and reduce the dielectric permittivity.<sup>36</sup> This explains the low dielectric permittivity of these silicone-containing biobased epoxies.

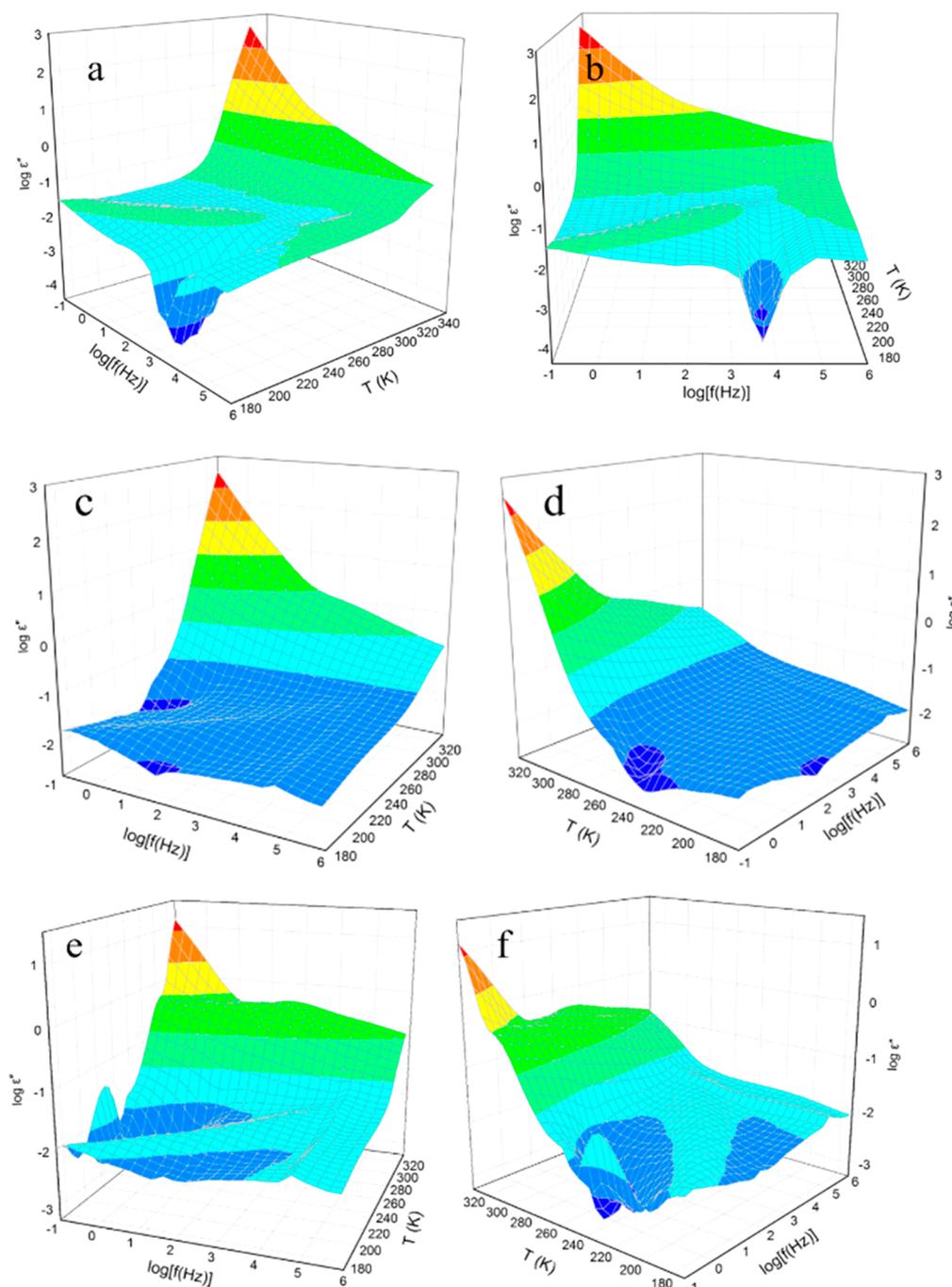
The low dielectric permittivity of the silicone-containing biobased epoxies is of importance for some applications, especially in microelectronic encapsulation perfectly compatible with continuing miniaturization of electronic devices to reduce static interference and increase running frequencies.<sup>27,37</sup> In this case, developing low dielectric constant insulating materials are urgently required.<sup>38</sup> Practically, the low dielectric constant polymers for microelectronic application includes polyimides, silicone-containing polyimides, fluorinated polyimides, polybenzoxazoles, and so forth, but conventional epoxy resins are excluded due to their high dielectric permittivity of over 3.5, which greatly restricts their applications.<sup>36,39</sup> Therefore, our proposed synthesis strategy is very effective for reducing dielectric permittivity of biobased epoxy resin outperforming DGEBA-derived systems, which will greatly broaden the potential of the biobased epoxy for high-tech electronic applications.

The unexpected low dielectric permittivity measured in the samples triggers interest in determining the chemical environment of the silicon atoms; with this perspective, X-ray photoelectron spectroscopy was performed. Figure 10 shows the XPS survey spectra recorded on the cured samples. We can observe the presence of a set of peaks that are generated by photoelectrons emitted from silicon, carbon, and oxygen atoms as well as from nitrogen and sulfur atoms. Inspecting the molecular structures of the materials used to synthesize the cured samples, we can associate the nitrogen and sulfur atoms to the 4,4'-DDS and the Si atoms to the synthesized monomers. Detailed analyses of the Si 2p core level spectra recorded on the samples indicate the presence of different Si bonding environments (see Table S3 and Figures S3–S5). In the Si 2p spectra of three samples, the main component at 101.5 eV (binding energy) can be associated with photoelectrons generated in Si atoms of the  $(\text{CH}_3)_2\text{Si}$ -segment. The low-intensity component at higher binding energy suggests the presence of debonding at the Si–C bond in the  $-(\text{CH}_3)_2\text{Si}-\text{CH}_2-$  segment. Following the debonding, we suggest the formation of  $(\text{CH}_3)_2\text{Si}-\text{NH}$ - and  $\text{CH}_3$ - groups. Inspecting Figure 9, the formation of  $(\text{CH}_3)_2\text{Si}-\text{NH}$ - and  $\text{CH}_3$ - groups has low impact on dielectric loss without increasing the polarity.

**Flame Retardant Properties.** The limiting oxygen index (LOI) is the minimum oxygen concentration (volume percentage) supporting candle-like combustion of samples, which is determined by gradually reducing the oxygen concentration in the oxygen and nitrogen mixture to a critical level. As shown in Figure 11, the LOI value of DGEBA/DDS is only 22.8, whereas the methyl siloxane-containing SIEEP2/DDS and SIEEP4/DDS exhibit LOI values of 26.0 and 28.0, respectively. This finding demonstrates that a longer length of the methyl siloxane chain of the epoxy monomer results in a higher LOI value. During the combustion, the Si–O-related moieties can migrate to the burning surface to form a protective barrier, which will retard the diffusion of oxidant and fuel. Additionally, the Si–O bond introduced can generate  $\text{SiO}_2$  without releasing combustible gases, therefore lowering the concentration of combustible fuels.<sup>40,41</sup> Moreover, for the SIEEP/DDS, where both methyl and phenyl groups are attached to the three siloxane atoms, a further increased LOI value of 31 is reached. This characteristic can be attributed to the easy carbonation of the phenyl rings and thus reduced generation of the combustible fuels.<sup>41</sup>

A further examination of the epoxy flame retardancy has been conducted by cone calorimeter test (CCT). CCT is an effective bench scale testing method to assess the flammability of the polymeric materials according to the protocols described in ISO 5660. In particular, CCT provides information on the peak heat release rate (PHRR), total heat release (THR), and total smoke production (TSP), all of which are key parameters in characterizing flame propagation and fire hazard of polymeric materials.<sup>26</sup>

Herein, the CCT results as summarized in Figure 12 and Table 1 show that DGEBA/DDS experiences an intensive burning process after the ignition with the PHRR as high as  $1451 \text{ kW/m}^2$ , whereas SIEEP2/DDS, SIEEP4/DDS, and SIEEP/DDS all display a significant decrease in the PHRR value. The siloxane-containing SIEEP2/DDS exhibits a much lower PHRR value than that of DGEBA/DDS ( $952$  vs  $1451 \text{ kW/m}^2$ ). The SIEEP/DDS and SIEEP4/DDS with longer siloxane chains exhibit further reduced PHRR values of  $781$  and  $662 \text{ kW/m}^2$  corresponding to 46 and 62% reduction of the DGEBA/DDS's PHRR value, respectively. Noticeably, SIEEP4/DDS and SIEEP/DDS with the longer siloxane chain exhibit PHRR values comparable to POSS/epoxy nanocomposites.<sup>26,42</sup> To illustrate, according to Franchini et al.,<sup>26</sup> the epoxy-based nanocomposites with 3.7 wt % of



**Figure 9.** Dielectric loss  $\epsilon''$  of (a,b) SIEEP2/DDS, (c,d) SIEEP4/DDS, and (e,f) SIEPEP/DDS versus frequency and temperature in a 3D representation.

glycidyoxypropyl-heptaisobutyl POSS (Gly-iBu POSS) and glycidyoxypropyl-heptaphenyl POSS (Gly-Ph POSS) glycidyl-phenyl POSS exhibited PHRR values of 782 and 622 kW/m<sup>2</sup>, respectively. SIEEP2/DDS expressed a 26% decrease in THR compared to that of DGEBA/DDS (80.4 vs 108.4 MJ/m<sup>2</sup>). Even lower CCT values are observed in SIEEP4/DDS and SIEPEP/DDS with longer siloxane chains (73.9 and 78.6 MJ/m<sup>2</sup>, respectively). The times to ignition (TTI) of SIEEP2/DDS, SIEEP4/DDS, and SIEPEP/DDS are reduced compared with that of DGEBA/DDS. Comparing their molecular structure, DGEBA contains the shortest methylene chain among them with the longest TTI value of 66 ± 2 s. Comparatively, SIEEP4 possesses the longest methylene and methyl siloxane chain,

exhibiting the shortest TTI value of 28 ± 1 s. Fortunately, longer TTI is detected for the phenyl siloxane-containing SIEPEP/DDS at 45 ± 2 s. The fire growth rate (FIGRA) is calculated by dividing the peak heat release rate (PHRR()) with time to peak heat release rate (T-PHRR). The DGEBA/DDS shows the highest FIGRA among them (11.16 ± 0.6 kW m<sup>-2</sup> s). The SIEPEP/DDS with phenyl siloxane chain exhibits a lower value than DGEBA/DDS, being 8.22 ± 0.5 kW/m<sup>2</sup> s, and SIEEP4 with a longer methyl siloxane chain exhibits the lowest FIGRA of 5.76 ± 0.5 kW m<sup>-2</sup> s. The long methyl siloxane chain contributes a lot in reducing the FIGRA value.

The markedly lowered PHRR and THR (Figure 13a) values indicate the decreased flammability of SIEEP2/DDS, SIEEP4/

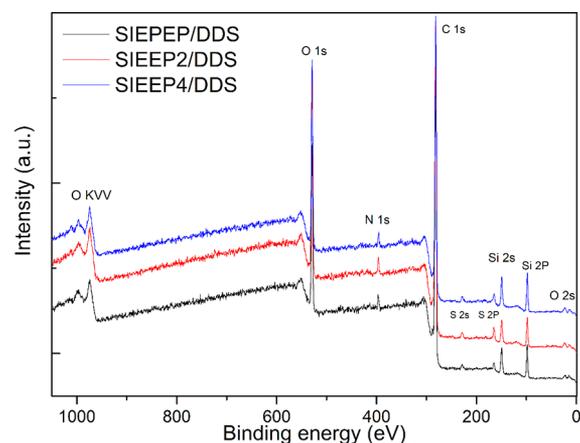


Figure 10. XPS spectra of cured epoxy/DDS.

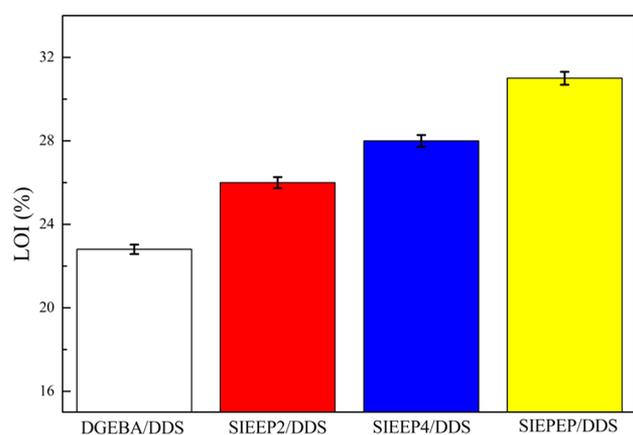


Figure 11. LOI values of epoxy/DDS-cured samples.

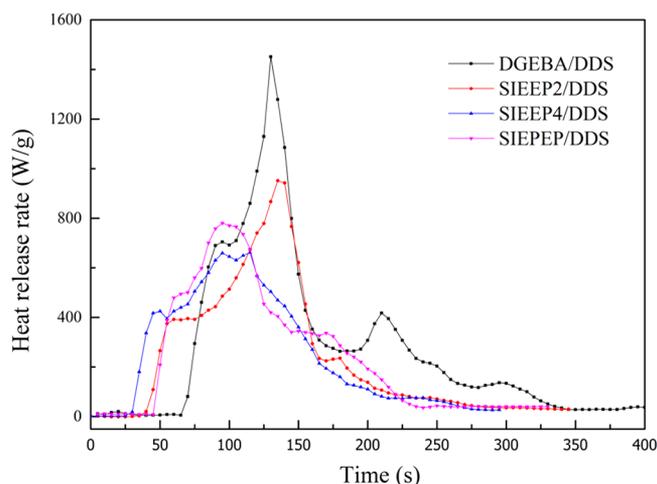


Figure 12. Heat release rate curves.

DDS, and SIEPEP/DDS with respect to DGEBA/DDS. This finding can be interpreted as follows: Incorporation of Si–O moieties into the epoxy network will reduce the release of the gaseous fuels during the pyrolysis of the epoxy network matrix. In addition, during the burning process, the Si–O-related moieties will migrate onto the burning surface, which functions as a barrier to slow the diffusion of oxidant and fuel and transportation of the heat into the polymer matrix underneath.

Moreover, a charring process will be promoted by introducing the Si–O moieties (see Table 1 residues).

On the other hand, DGEBA/DDS exhibits the highest TSP value of 36.4 m<sup>2</sup>, whereas SIEEP2/DDS, SIEEP4/DDS, and SIEPEP/DDS show decreased TSP values of 30.68, 29.68, and 32.52 m<sup>2</sup>, respectively (Figure 13b). More importantly, the methyl siloxane-containing SIEEP2/DDS and SIEEP4/DDS exhibit extremely low CO emission of only 0.04 and 0.05 kg/kg, less than one-third with respect to that of DGEBA/DDS (0.15 kg/kg). According to a study by Camino,<sup>43</sup> with such a high heating rate, the methyl siloxane and phenyl siloxane bonds contained in SIEEP2/DDS, SIEEP4/DDS, and SIEPEP/DDS mainly release cyclic siloxane oligomers and tetramer with partially rearranged oligomeric siloxane compounds. This process consume a large quantity of heat and thus reduce the production of CO.<sup>41</sup> All the silicone-contained biobased epoxy exhibits much higher residue yield than that of DGEBA/DDS, which is in accordance with their lower TSP values. The reduction of biobased silicone epoxy in TSP values and CO emission is of high interest because during a real fire disaster, smoke production and CO are the main reasons leading to casualties.<sup>44</sup>

## CONCLUSIONS

A series of silicone-contained biosourced epoxy resins have been synthesized by the optimized route. The preparation of EPEU can be achieved in extremely high yield with a trace amount of unreacted raw materials detected. The methyl siloxane and phenyl siloxane segments inserted within the bio-based epoxy network promote optimal properties in various aspects. After curing with DDS, they show excellent dielectric permittivity as low as 3.0, showing application potential in micro electrical device encapsulation. Moreover, they exhibit intrinsic flame retardancy with LOI values as high as 31 for the SIEPEP/DDS sample. All of these properties originate from their siloxane-containing structure. Our study shows a cost-effective, high yield route to enhance dielectric and flame-retardant properties of epoxy. These high-performance bioepoxies are expected to substitute petroleum-based DGEBA epoxies with applications in various areas ranging from fouling-release coatings to carbon fiber-reinforced composites.

## EXPERIMENTAL SECTION

**Materials.** Eugenol, epichlorohydrin, sodium sulfite anhydrous, sodium hydrogen carbonate, sodium sulfate anhydrous, 4,4'-diamino diphenyl sulfone (4,4'-DDS), and dichloromethane were purchased for Chinese domestic market and used as received. Chloroplatinic acid hexahydrate, isopropyl alcohol, 1,1,3,3-tetramethyl disiloxane, and 1,1,3,3,5,5-hexamethyl trisiloxane were purchased from ABCR GmbH in Germany. 1,1,5,5-Tetramethyl-3,3-diphenyl trisiloxane was kindly provided by Jiaxin United Chemical Co., Ltd. Epoxy C (Diglycidyl ether of bisphenol A type epoxy, DGEBA as short name with an epoxy equivalent value of 180 g/mol) was acquired from Faserverbundwerkstoffe Company, Germany. All chemicals were used as received.

**Synthesis.** To a 100 mL round-bottom flask equipped with a magnetic stirrer and a condenser were charged eugenol (16.42 g, 0.1 mol), epichlorohydrin (9.26 g, 0.1 mol), and benzyl triethylammonium chloride (0.23 g, 0.001 mol), which were then stirred under nitrogen flow and refluxed for 2 h. Then, the temperature was reduced to 65 °C, and 20 wt % sodium hydroxide aqueous solution (4.08 g, 0.102 mol) was dropped into the mixture in 1 h. The reaction was taken for another 3 h to end the reaction. The upper organic layer, which condensed with high purity EPEU, was further crystallized in methanol at a temperature of –5 °C to acquire EPEU in high yield (92%).

Table 1. Cone Calorimeter Test Results

samples item	DGEBA/DDS	SIEEP2/DDS	SIEEP4/DDS	SIEPEP/DDS
TTI (s)	66 ± 2	31 ± 1	28 ± 1	45 ± 2
PHRR (kW/m <sup>2</sup> )	1451 ± 32	952 ± 20	662 ± 17	781 ± 20
T-PHRR (s)	130 ± 2	135 ± 3	115 ± 2	95 ± 2
FIGRA (kW/m <sup>2</sup> -s)	11.16 ± 0.6	7.05 ± 0.5	5.76 ± 0.5	8.22 ± 0.5
THR (MJ/m <sup>2</sup> )	108.4 ± 1.1	80.4 ± 0.8	73.9 ± 0.8	78.6 ± 1.0
TSP (m <sup>2</sup> )	36.4 ± 0.5	30.7 ± 0.4	29.7 ± 0.4	32.5 ± 0.5
av CO emission (kg/kg)	0.15 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.13 ± 0.01
residues (%)	5.2 ± 0.2	14.2 ± 0.5	14.9 ± 0.4	0.7 ± 0.2

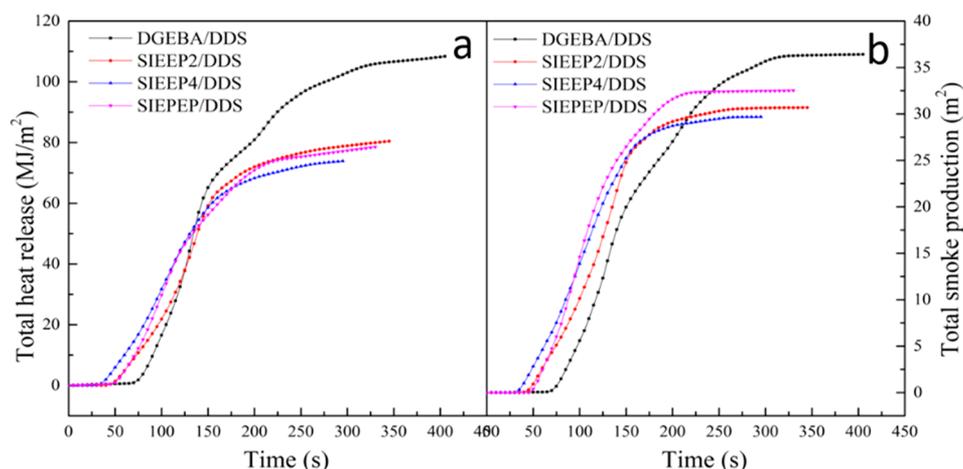


Figure 13. (a) Total heat release and (b) total smoke production curves.

To a three-necked 100 mL round-bottom flask equipped with a magnetic stirrer, dropping funnel, thermometer, and condenser were charged EPEU (20.6 g, 0.1 mol) and chloroplatinic acid in isopropyl alcohol ( $1.44 \times 10^{-2}$  g, Pt 0.8 wt %) and heated to 60 °C. Then, 1,1,3,3-tetramethyldisiloxane (6.72 g, 0.05 mol), 1,1,3,3,5,5-hexamethyl trisiloxane (10.42 g, 0.05 mol) or 1,1,5,5-tetramethyl-3,3-diphenyl trisiloxane (16.6 g, 0.05 mol) was added to the mixture dropwise in 3 h, and the reaction was carried out for another 1 h before end. The remaining catalyst was removed by flash chromatography. The reactions to prepare SIEEP2, SIEEP4, and SIEPEP had very good yields of 97, 97.5, and 97%, respectively, and their corresponding epoxy equivalent weight was determined by titration to be 290, 320, and 360 g/mol, respectively.

**Preparation of Cured Epoxy Samples.** The DGEBA, SIEEP2, SIEEP4, and SIEPEP are cured by 4,4'-diamino diphenyl sulfone (4,4'-DDS) to form a solid, cross-linked thermosetting polymer to test their XPS, dielectric relaxation spectra, and flame retardant behavior. A suitable amount of 4,4'-DDS was added to the epoxy (molar ratio of N-H group/epoxy group = 1:1), and the mixture was heated to 120 °C for 20 min to acquire a homogeneous viscous liquid. Then, it was poured into Teflon molds and placed into an oven to acquire the cured epoxy samples (curing cycle: 150 °C/2h, 180 °C/2h, 200 °C/2h).

**Characterization.** The GC-MS spectra were conducted on an Agilent 6890/5973 GCMS instrument (column: ZB-5MS column, 30 m  $\times$  0.25 mm  $\times$  0.5  $\mu$ m; carrier gas, hydrogen). The GC temperature was set as follows: inlet temperature, 270 °C; column temperature procedure, stable at 80 °C for 2 min, ramp to 250 °C at a rate of 20 °C/min, stable for 10 min to totally vaporize all the samples; detector temperature, 300 °C. The electronic energy of MS was set as 70 eV.

The molecular structures of intermediates and targeting compounds were characterized using <sup>1</sup>H NMR and <sup>13</sup>C NMR on a Bruker DRX 500 spectrometer (solvent, CDCl<sub>3</sub>; internal standard, tetramethylsilane).

The MALDI-TOF-MS analysis of the molecular weight was carried out on a Bruker MALDI-TOF-MS mass spectrometer equipped with a pulsed nitrogen laser (1 1/4 337 nm; pulse width 1/4 3 ns). The

MALDI-TOF-MS was operated at an accelerating potential of 20 kV in reflector mode, and gentisic acid (2,5-dihydroxybenzoic acid, DHB) was used as the matrix with acetone as the solvent. Sodium is used as the cationizing agent, and all the data shown were of positive ions.

Rheology behaviors of the epoxies were characterized with a HAKKE RS6000 Rheometer equipped with a Z38 rotor and Z43 measuring cup. For each sample, we first tested their viscosity at 25 °C with a rotational rate varying from 0.01 to 60 rad/s. Then, we tested their viscosities from 25 to 100 °C at a constant rotation rate of 60 rad/s.

The analysis of elemental chemical environment and evaluation of surface composition were conducted by X-ray photoelectron spectroscopy (XPS) using a VERSAPROBE PHI 5000 from Physical Electronics, equipped with a monochromatic Al K $\alpha$  X-ray source. The X-ray photoelectron spectra were collected at a takeoff angle of 45° with respect to the electron energy analyzer operated in the constant analyzer energy (CAE) mode. For the survey and the high-resolution detail spectra, the pass energies were 50 and 20 eV, respectively. For the compensation of built-up charge on the sample surface during the measurements, a dual beam charge neutralization composed of an electron gun (~1 eV) and an Ar ion gun ( $\leq 10$  eV) was used. To avoid degradation, the source was operated at 100W. Binding energies are all referred to the C 1s at 284.6 eV. Before introduction in the analysis chamber, the samples were freshly cut using clean blades to avoid surface contamination.

Dielectric behaviors of the cured epoxy products were characterized using dielectric relaxation spectroscopy (DRS). A high-resolution ALPHA analyzer (Novocontrol, Hundsagen, Germany) was used to measure the complex dielectric function  $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$  ( $\epsilon'$  = real part,  $\epsilon''$  = loss part, and  $i = \sqrt{-1}$ ) changing with frequency  $f$  (10–1–106 Hz) and temperature  $T$  (173–393 K). Samples were prepared in parallel plate geometry. Gold electrodes with a diameter of 20 mm were evaporated on both sides of the samples. Then, the samples were mounted between two gold-plated electrodes (20 mm) of the sample holder. All the measurements were done isothermally where the

temperature is controlled by a Quatro Novocontrol cryosystem with a stability of 0.1 K.

Flame retardant properties of the cured epoxies were evaluated in terms of limiting oxygen index (LOI) and cone calorimeter test (CCT) testing. LOI values of the cured epoxy were measured on an oxygen index meter (Fire Testing Technology Ltd.) with sample dimensions of  $130.0 \times 6.5 \times 2.9$  ( $\pm 0.1$ ) mm<sup>3</sup> according to the ASTM D2863-97. The CCT tests were conducted following the ISO 5660 procedures (without “frame and grid” application) on a cone calorimeter (Fire Testing Technology Ltd.). Specimens [ $100 \times 100 \times 2.9$  ( $\pm 0.1$ ) mm<sup>3</sup>] were irradiated with a heat flux of 50 kW/m<sup>2</sup>.<sup>45</sup>

## ■ ASSOCIATED CONTENT

### 5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b01212.

Table S1: Area content of components in GC spectra (mol ratio of eugenol/epichlorohydrin = 1:5, eugenol is undetected); Table S2: Area content of components in GC spectra (mol ratio of eugenol:epichlorohydrin = 1:1); Table S3: Relative concentration of elements in the cured samples as evaluated by XPS; Figure S1: MS spectra of components at different retention times in epoxidization reactions of eugenol (mol ratio of eugenol/epichlorohydrin = 1:5); Figure S2: MS spectra of components at different retention times in epoxidization reactions of eugenol (mol ratio of eugenol/epichlorohydrin = 1:1); Figure S3: Si 2p core level spectrum recorded on the SIEEP2 sample, and the resulting fitting showing the presence of two chemical environments for the Si atoms; Figure S4: Si 2p core level spectrum recorded on the SIEEP4 sample, and the resulting fitting showing the presence of three chemical environments for the Si atoms; Figure S5: Si 2p core level spectrum recorded on the SIEPEP sample, and the resulting fitting showing the presence of three chemical environments for the Si atoms (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Yao, K. J.; Tang, C. B. Controlled Polymerization of Next-Generation Renewable Monomers and Beyond. *Macromolecules* **2013**, *46*, 1689–1712.
- (2) Wang, S.; Ma, S. Q.; Xu, C. X.; Liu, Y.; Dai, J. Y.; Wang, Z. B.; Liu, X. Q.; Chen, J.; Shen, X. B.; Wei, J. J.; Zhu, J. Vanillin-Derived High-Performance Flame Retardant Epoxy Resins: Facile Synthesis and Properties. *Macromolecules* **2017**, *50*, 1892–1901.
- (3) Jian, X.-Y.; He, Y.; Li, Y.-D.; Wang, M.; Zeng, J.-B. Curing of epoxidized soybean oil with crystalline oligomeric poly(butylene succinate) towards high performance and sustainable epoxy resins. *Chem. Eng. J.* **2017**, *326*, 875–885.
- (4) Jian, X.-Y.; An, X.-P.; Li, Y.-D.; Chen, J.-H.; Wang, M.; Zeng, J.-B. All Plant Oil Derived Epoxy Thermosets with Excellent Comprehensive Properties. *Macromolecules* **2017**, *50*, 5729–5738.
- (5) Hernandez, E. D.; Bassett, A. W.; Sadler, J. M.; La Scala, J. J.; Stanzione, J. F. Synthesis and Characterization of Bio-based Epoxy Resins Derived from Vanillyl Alcohol. *ACS Sustainable Chem. Eng.* **2016**, *4*, 4328–4339.
- (6) Zhang, Q. X.; Molenda, M.; Reineke, T. M. Epoxy Resin Thermosets Derived from Trehalose and beta-Cyclodextrin. *Macromolecules* **2016**, *49*, 8397–8406.
- (7) Ma, S. Q.; Webster, D. C.; Jabeen, F. Hard and Flexible, Degradable Thermosets from Renewable Bioresources with the Assistance of Water and Ethanol. *Macromolecules* **2016**, *49*, 3780–3788.
- (8) Janvier, M.; Hollande, L.; Jaufurally, A. S.; Pernes, M.; Menard, R.; Grimaldi, M.; Beaugrand, J.; Balaguer, P.; Ducrot, P. H.; Allais, F. Syringaresinol: A Renewable and Safer Alternative to Bisphenol A for Epoxy-Amine Resins. *ChemSusChem* **2017**, *10*, 738–746.
- (9) Kristufek, S. L.; Yang, G. Z.; Link, L. A.; Rohde, B. J.; Robertson, M. L.; Wooley, K. L. Synthesis, Characterization, and Cross-Linking Strategy of a Quercetin-Based Epoxidized Monomer as a Naturally-Derived Replacement for BPA in Epoxy Resins. *ChemSusChem* **2016**, *9*, 2135–2142.
- (10) Maiorana, A.; Spinella, S.; Gross, R. A. Bio-based alternative to the diglycidyl ether of bisphenol A with controlled materials properties. *Biomacromolecules* **2015**, *16*, 1021–1031.
- (11) Yang, G. Z.; Rohde, B. J.; Tesefay, H.; Robertson, M. L. Biorenewable Epoxy Resins Derived from Plant-Based Phenolic Acids. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6524–6533.
- (12) Ma, S.; Liu, X.; Fan, L.; Jiang, Y.; Cao, L.; Tang, Z.; Zhu, J. Synthesis and properties of a bio-based epoxy resin with high epoxy value and low viscosity. *ChemSusChem* **2014**, *7*, 555–562.
- (13) Ma, S.; Liu, X.; Jiang, Y.; Tang, Z.; Zhang, C.; Zhu, J. Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers. *Green Chem.* **2013**, *15*, 245–254.
- (14) Li, P.; Ma, S. Q.; Dai, J. Y.; Liu, X. Q.; Jiang, Y. H.; Wang, S.; Wei, J. J.; Chen, J.; Zhu, J. Itaconic Acid as a Green Alternative to Acrylic Acid for Producing a Soybean Oil-Based Thermoset: Synthesis and Properties. *ACS Sustainable Chem. Eng.* **2017**, *5*, 1228–1236.
- (15) Aouf, C.; Nouailhas, H.; Fache, M.; Caillol, S.; Boutevin, B.; Fulcrand, H. Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. *Eur. Polym. J.* **2013**, *49*, 1185–1195.
- (16) Aouf, C.; Lecomte, J.; Villeneuve, P.; Dubreucq, E.; Fulcrand, H. Chemo-enzymatic functionalization of gallic and vanillic acids: synthesis of bio-based epoxy resins prepolymers. *Green Chem.* **2012**, *14*, 2328–2336.
- (17) Miao, J. T.; Yuan, L.; Guan, Q. B.; Liang, G. Z.; Gu, A. J. Biobased Heat Resistant Epoxy Resin with Extremely High Biomass Content from 2,5-Furandicarboxylic Acid and Eugenol. *ACS Sustainable Chem. Eng.* **2017**, *5*, 7003–7011.
- (18) Ma, S. Q.; Webster, D. C. Naturally Occurring Acids as Cross-Linkers To Yield VOC-Free, High-Performance, Fully Bio-Based, Degradable Thermosets. *Macromolecules* **2015**, *48*, 7127–7137.
- (19) Zhao, S.; Abu-Omar, M. M. Renewable Epoxy Networks Derived from Lignin-Based Monomers: Effect of Cross-Linking Density. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6082–6089.

- (20) Puttlitz, K. J.; Galyon, G. T. Impact of the ROHS directive on high-performance electronic systems. *J. Mater. Sci.: Mater. Electron.* **2006**, *18*, 347–365.
- (21) Cusack, P.; Perrett, T. The EU RoHS Directive and its implications for the plastics industry. *Plast. Addit. Compd.* **2006**, *8*, 46–49.
- (22) Tauber, K.; Marsico, F.; Wurm, F. R.; Schartel, B. Hyper-branched poly(phosphoester)s as flame retardants for technical and high performance polymers. *Polym. Chem.* **2014**, *5*, 7042–7053.
- (23) Liu, W. C.; Varley, R. J.; Simon, G. P. Phosphorus-containing diamine for flame retardancy of high functionality epoxy resins. Part II. The thermal and mechanical properties of mixed amine systems. *Polymer* **2006**, *47*, 2091–2098.
- (24) Hergenrother, P. M.; Thompson, C. M.; Smith, J. G.; Connell, J. W.; Hinkley, J. A.; Lyon, R. E.; Moulton, R. Flame retardant aircraft epoxy resins containing phosphorus. *Polymer* **2005**, *46*, 5012–5024.
- (25) Wang, W. J.; Perng, L. H.; Hsiue, G. H.; Chang, F. C. Characterization and properties of new silicone-containing epoxy resin. *Polymer* **2000**, *41*, 6113–6122.
- (26) Franchini, E.; Galy, J.; Gérard, J. F. Influence of POSS structure on the fire retardant properties of epoxy hybrid networks. *Polym. Degrad. Stab.* **2009**, *94*, 1728–1736.
- (27) Volksen, W.; Miller, R. D.; Dubois, G. Low dielectric constant materials. *Chem. Rev.* **2010**, *110*, 56–110.
- (28) Ma, S. Q.; Liu, X. Q.; Fan, L. B.; Jiang, Y. H.; Cao, L. J.; Tang, Z. B.; Zhu, J. Synthesis and Properties of a Bio-Based Epoxy Resin with High Epoxy Value and Low Viscosity. *ChemSusChem* **2014**, *7*, 555–562.
- (29) Fourcade, D.; Ritter, B. S.; Walter, P.; Schonfeld, R.; Mulhaupt, R. Renewable resource-based epoxy resins derived from multifunctional poly(4-hydroxybenzoates). *Green Chem.* **2013**, *15*, 910–918.
- (30) Fache, M.; Darroman, E.; Besse, V.; Auvergne, R.; Caillol, S.; Boutevin, B. Vanillin, a promising biobased building-block for monomer synthesis. *Green Chem.* **2014**, *16*, 1987–1998.
- (31) Li, C.; Fan, H.; Wang, D.-Y.; Hu, J.; Wan, J.; Li, B. Novel silicon-modified phenolic novolacs and their biofiber-reinforced composites: Preparation, characterization and performance. *Compos. Sci. Technol.* **2013**, *87*, 189–195.
- (32) Wan, J.; Gan, B.; Li, C.; Molina-Aldareguia, J. M.; Li, Z.; Wang, X.; Wang, D.-Y. A novel biobased epoxy resin with high mechanical stiffness and low flammability: synthesis, characterization and properties. *J. Mater. Chem. A* **2015**, *3*, 21907–21921.
- (33) Raquez, J. M.; Deleglise, M.; Lacrampe, M. F.; Krawczak, P. Thermosetting (bio)materials derived from renewable resources: A critical review. *Prog. Polym. Sci.* **2010**, *35*, 487–509.
- (34) Wan, J.; Zhao, J.; Gan, B.; Li, C.; Molina-Aldareguia, J.; Zhao, Y.; Pan, Y.-T.; Wang, D.-Y. Ultrastiff Biobased Epoxy Resin with High Tg and Low Permittivity: From Synthesis to Properties. *ACS Sustainable Chem. Eng.* **2016**, *4*, 2869–2880.
- (35) Bonnet, A.; Pascault, J. P.; Sautereau, H.; Rogozinski, J.; Kranbuehl, D. Epoxy-diamine thermoset/thermoplastic blends: Dielectric properties before, during, and after phase separation. *Macromolecules* **2000**, *33*, 3833–3843.
- (36) Volksen, W.; Miller, R. D.; Dubois, G. Low Dielectric Constant Materials. *Chem. Rev.* **2010**, *110*, 56–110.
- (37) Farrell, R.; Goshal, T.; Cvelbar, U.; Petkov, N.; Morris, M. A. Advances in ultra low dielectric constant ordered porous materials. *Electrochem. Soc. Interface* **2011**, *20*, 39–46.
- (38) Yuan, C.; Jin, K.; Li, K.; Diao, S.; Tong, J.; Fang, Q. Non-porous low-k dielectric films based on a new structural amorphous fluoropolymer. *Adv. Mater.* **2013**, *25*, 4875–4878.
- (39) Maier, G. Low dielectric constant polymers for microelectronics. *Prog. Polym. Sci.* **2001**, *26*, 3–65.
- (40) Zhou, W.; Yang, H. Flame retarding mechanism of polycarbonate containing methylphenyl-silicone. *Thermochim. Acta* **2007**, *452*, 43–48.
- (41) Hamdani, S.; Longuet, C.; Perrin, D.; Lopez-Cuesta, J. M.; Ganachaud, F. Flame retardancy of silicone-based materials. *Polym. Degrad. Stab.* **2009**, *94*, 465–495.
- (42) Qian, Y.; Wei, P.; Zhao, X. M.; Jiang, P. K.; Yu, H. Z. Flame retardancy and thermal stability of polyhedral oligomeric silsesquioxane nanocomposites. *Fire Mater.* **2013**, *37*, 1–16.
- (43) Camino, G.; Lomakin, S. M.; Lageard, M. Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. *Polymer* **2002**, *43*, 2011–2015.
- (44) Alarie, Y. Toxicity of fire smoke. *Crit. Rev. Toxicol.* **2002**, *32*, 259–289.
- (45) Kang, N. J.; Wang, D. Y. A green functional nanohybrid: preparation, characterization and properties of a beta-cyclodextrin based functional layered double hydroxide. *J. Mater. Chem. A* **2013**, *1*, 11376–11383.