

Benzocyclobutene-functionalized hyperbranched polysiloxane for low-k materials with good thermostability

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ABSTRACT

Although hyperbranched polysiloxanes have been extensively studied, they have limited practical applications because of their low glass transition temperatures. In this study, we synthesized benzocyclobutene-functionalized hyperbranched polysiloxane (HB-BCB) via the Piers-Rubinsztajn reaction. The synthesized material was cured and crosslinking occurred at temperatures greater than 200 °C, forming a low-k thermoset resin with high thermostability. The structure of the resin was characterized using nuclear magnetic resonance (NMR) spectroscopy, viz. ¹H NMR and ¹³C NMR spectroscopy. ²⁹Si NMR spectroscopy was used to calculate the degree of branching. Differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetric analysis revealed that the cured resin possesses good high-temperature mechanical properties and exhibits a high thermal decomposition temperature ($T_{d5} = 512$ °C). In addition, the cured resin has a low dielectric constant ($k = 2.70$ at 1 MHz) and low dissipation factor (2.13×10^{-3} at 1 MHz). Thus, the prepared resin can function as a low-k material with excellent high-temperature performance. These findings indicate that the performance of crosslinked siloxane is significantly attributed to the introduction of BCB groups and the formation of the highly crosslinked structure.

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1. Introduction

Signal delay of interconnects is the main obstacle in the development of integrated microelectronic devices with high density. To overcome this limitation, it is necessary to develop high-performance materials with low dielectric constants, i.e., low-k materials [1]. An ideal low-k material needs to exhibit a low dielectric dissipation factor, good thermal stability, and low coefficient of thermal expansion. Various low-k organic materials have been developed, such as polyimides [2–5], organic siloxanes [6], polybenzoxazoles [7,8], epoxy resins [9,10], etc. Among them, benzocyclobutene (BCB) resins are considered to be high-performance materials with a wide-range of potential applications [3,11–15]. The ring-opening reaction of cyclobutene in BCB, followed by crosslinking and polymerization forms a highly crosslinked network structure [16]. The low polarity of this results in reduced dielectric constant and water absorption. In addition, the high extent of crosslinking enhances the thermal stability and increases the glass transition temperature of BCB-based resins [17]. Moreover, BCB can be thermally-cured at relatively low temperatures without the formation of byproducts.

Polysiloxanes are another important class of insulating materials that exhibit good thermal and chemical stabilities. However, their low glass transition temperature (T_g) limits their application as high-performance dielectric materials. To overcome this limitation, crosslinkable groups such as BCB can be introduced into the polysiloxane network to increase T_g by thermal curing of BCB. There have been reported many methods to incorporate BCB into siloxane polymers, such as Heck reaction [17,18], hydrosilation reaction [19], and hydrolysis and condensation reaction of BCB functionalized oxosilanes [12,20]. The Piers-Rubinsztajn (P-R) reaction has attracted considerable attention as an effective and facile approach for the synthesis of polysiloxanes [21–24]. Unlike other reactions which require precious metal catalysts, such as platinum in the hydrosilylation reaction and palladium in the Heck reaction, the P-R reaction is catalyzed by tris(pentafluorophenyl)borane [$B(C_6F_5)_3$], a weak Lewis acid [25]. In addition, this reaction is rapid even under mild conditions, and leads to the release of an alkane gas, which aids in the monitoring the reaction progress. The generation of Si-OH groups is also prevented in the P-R reaction; thus, the product formed has a low water absorption rate [6]. Recently, we have prepared a linear oligomer BCB functionalized

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polysiloxane by P-R reaction of BCB functionalized dimethoxysilane monomer (A2) with silphenylene/silbiphenylene hydrosilanes (B2) [26]. After cured, a linear oligomer showed low dielectric constants at 2.76 and 2.78 at 1 MHz. the synthesis of the monomers A2 and B2 were complicated and the dielectric constant can be further decreased.

Hyperbranched polymers usually exhibit different properties as compared to linear polymers because of their unique structure, in which numerous reactive functional groups are concentrated at the chain terminals [27]. Compared with a linear polymer, a hyperbranched polymer presumably possesses a larger free volume, owing to the formation of porous voids between two different chains in the structure. Thus, formation of a hyperbranched structure could be an effective approach to reduce the dielectric constant of polymers [7,28,29]. Based on this presumption, we have synthesized a BCB-functionalized hyperbranched polysiloxane (HB-BCB) by performing the P-R reaction with commercial diethoxymethylsilane (AB₂ type monomer) to construct a hyperbranched polysiloxane, and then substituting the remaining Si-OEt groups by the Si-H-functionalized BCB groups in a cascade reaction way. It's a facile and convenient method to prepare the BCB functionalized siloxane polymer. After curing, the material exhibited a low dielectric constant of 2.70 at 1 MHz, good high-temperature performance, and high thermostability.

2. Experimental sections

2.1. Materials and reagents

4-Br-BCB (97%) was purchased from Chem-target Technologies Co., Ltd, China. Dry toluene was obtained after refluxing and distilling toluene with sodium and benzophenone. Benzocyclobutene-4-yl-dimethylsilane (BCBSiH) was synthesized according to a previously reported procedure [19]. Diethoxymethylsilane (DEMS 98%) was purchased from Sun Chemical Technology Co., Ltd. (Shanghai). Neutral alumina was used as received. Tris(pentafluorophenyl)borane, B(C₆F₅)₃, was purchased from Tokyo Chemical Industry Co., Ltd.

2.2. Characterization method

Nuclear magnetic resonance (NMR) spectroscopy, viz. ¹H NMR, ¹³C NMR, and ²⁹Si NMR was conducted using a Bruker DRX-500 spectrometer with tetramethylsilane (TMS) as the reference and CDCl₃ as the solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VERTEX 70 FT-IR spectrophotometer.

Differential scanning calorimetry (DSC; TA Q200 calorimeter) and thermogravimetric analysis (TGA; TA Instruments Q500) were performed at a heating rate of 10 °Cmin⁻¹ under a N₂ atmosphere. Dynamic mechanical analysis (DMA; TA Instruments Q800) was conducted using the three-point bending mode at a heating rate of 3 °Cmin⁻¹ and a test frequency of 1 Hz. The dielectric properties were measured by the parallel-plate capacitor method using a Keysight E4980A precision LCR meter and Keysight 16451B as a test fixture at room temperature. The molecular weight was determined using gel permeation chromatography (GPC; Waters 1515 system) equipped with a refractive index (RI) detector using tetrahydrofuran (THF) as solvent at a flow rate of 1.0 mL min⁻¹. Calibration was accomplished with polystyrene standards.

2.3. Preparation of HB-BCB

In a 25 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, DEMS (1.34 g, 0.01 mol), and toluene (5 mL, 4.28 g) were added under nitrogen atmosphere using a three-way stopcock, and the reactor was placed in an ice-water bath. While stirring, B(C₆F₅)₃ (4 mg, 0.0078 mmol) in toluene was injected into the reaction mixture using a syringe. The ice-water bath was removed to increase the reaction rate. The generation of bubbles indicated the initiation of the P-R reaction. After the generation of bubbles stopped, BCBSiH (1.62 g, 0.01 mol) was slowly added to the reaction mixture using a syringe. The resulting solution was stirred for 1 h. The reaction was terminated by adding Al₂O₃ to deactivate the catalyst. The mixture was stirred for 10 min and filtered using a filter paper and an ultrafiltration membrane (0.45 μm). The solvent, toluene, was removed by rotary evaporation, and HB-BCB was obtained as a colorless viscous liquid. ¹H-NMR (CDCl₃, 500 MHz, ppm): 0.02–0.10 (3 H), 0.32–0.35 (6 H), 3.12 (4 H), 7.00–7.07 (1H), 7.24–7.25 (1H), 7.39–7.42 (1H). ¹³C-NMR (CDCl₃, ppm): –0.25–0.57, 3.26–3.58, 32.22–32.31–32.37, 124.17–124.24, 129.27, 133.82, 139.70–140.10–140.53, 147.76–147.89, 149.70–149.80. ²⁹Si-NMR (ppm): 0.18–1.57, 56.04–59.42, 63.94–66.78. GPC: M_w = 1555 g/mol, M_w/M_n = 1.25.

2.4. Curing of the resin

To prepare the bulk polymer, the glass mold with HB-BCB was degassed in a vacuum oven at 130 °C for 0.5 h, and then heated sequentially at 180 °C /1 h, 210 °C /1 h, 230 °C /1 h, 250 °C /1 h, 260 °C/1 h, and 290 °C /0.5 h under a nitrogen atmosphere. After cooling to 25 °C, the



Figure 1. Image of the cured HB-BCB.

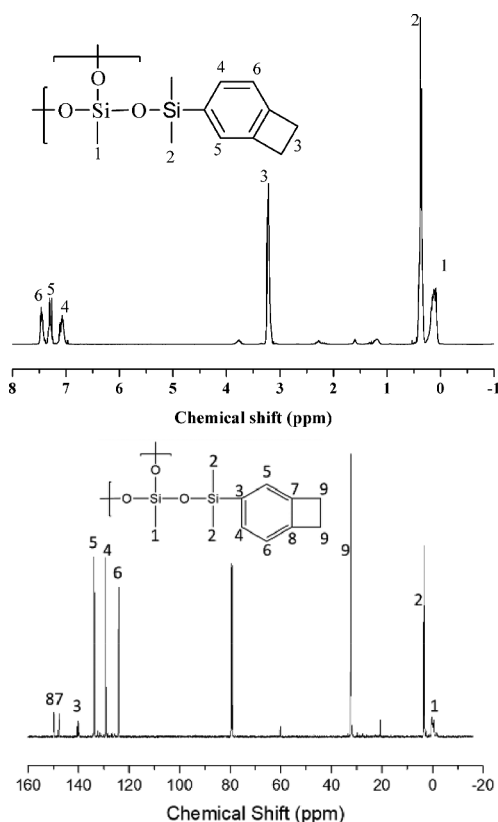
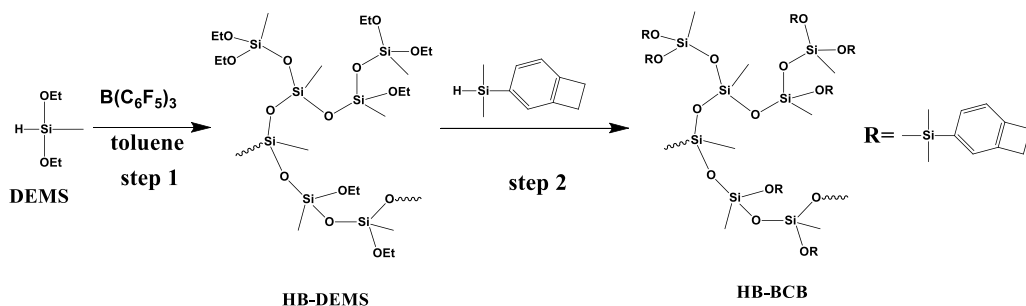


Figure 2. ^1H -NMR (above) and ^{13}C -NMR (below) spectra of HB-BCB.



Scheme 1. Synthesis of HB-BCB.

thermoset was removed from the glass mold and polished to an appropriate size for DMA and TGA analyses (Figure 1).

3. Results and discussion

3.1. Preparation and characterization of HB-BCB

Scheme 1 shows the synthetic approach used to prepare HB-BCB. DEMS was used as a precursor for the P-R reaction, and a hyperbranched polysiloxane (HB-DEMS) was produced (step 1). Then, BCBSiH was added to substitute the ethoxy groups (-O-Et) with the BCB functional groups, which enabled the crosslinking of the oligomer (step 2). As measured by GPC, HB-BCB showed a low average molecular weight of 1555 g/mol; thus, it is considered to be an oligomer.

The ^1H and ^{13}C NMR spectra are shown in Figure 2. The peaks corresponding to Si-H proton (4.5 ppm) and Si-OCH₂CH₃ protons (3.81 and 1.24 ppm) are almost disappeared in the ^1H -NMR spectrum of HB-BCB, indicating that the P-R reaction reached completion. In addition, the integration traces of peak 1 and peak 3 have a ratio of 3:1, which is in accordance with the stoichiometric ratio of DEMS and BCBSiH in the reaction. However, the formation of a hyperbranched structure cannot be verified solely on the basis of the ^1H and ^{13}C NMR spectra because the branched chains are formed by the Si-O linkages.

Thus, the ^{29}Si -NMR spectrum of the intermediate, HB-DEMS, is used to characterize the hyperbranched structure (Figure 3). The signals corresponding to the dendritic units (D), linear units (L), and terminal units (T) of the hyperbranched polymer can be clearly observed in the ^{29}Si -NMR spectrum of HB-DEMS. It has been reported that for silicon atoms connected to the same number of oxygen atoms, the introduction of -OEt groups increases the chemical shift value by approximately 7–10 ppm, indicating that larger chemical shift values correspond to Si atoms with more -OEt groups [30]. On the basis of this discussion, the peaks in the ^{29}Si -NMR

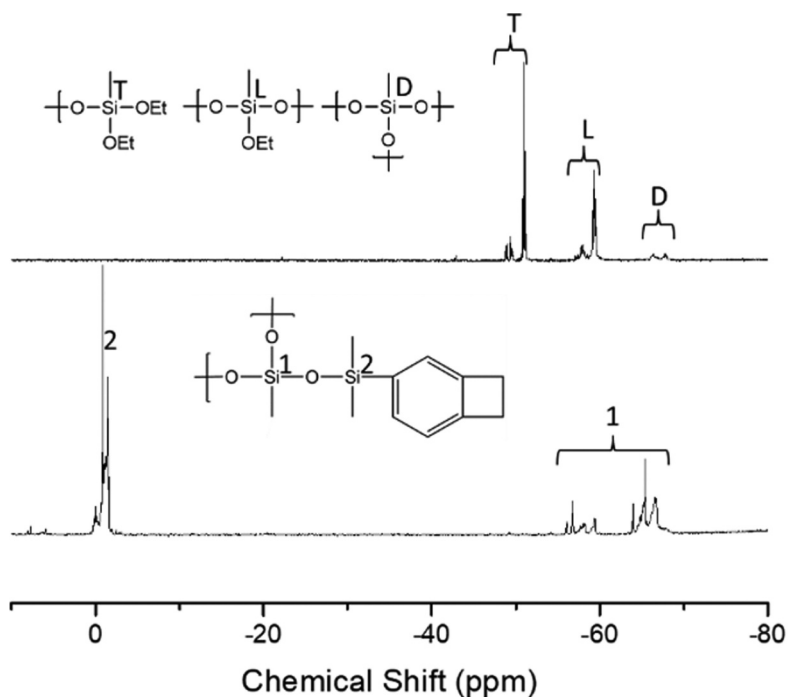


Figure 3. ^{29}Si -NMR spectra of HB-DEMS (above) and HB-BCB (below).

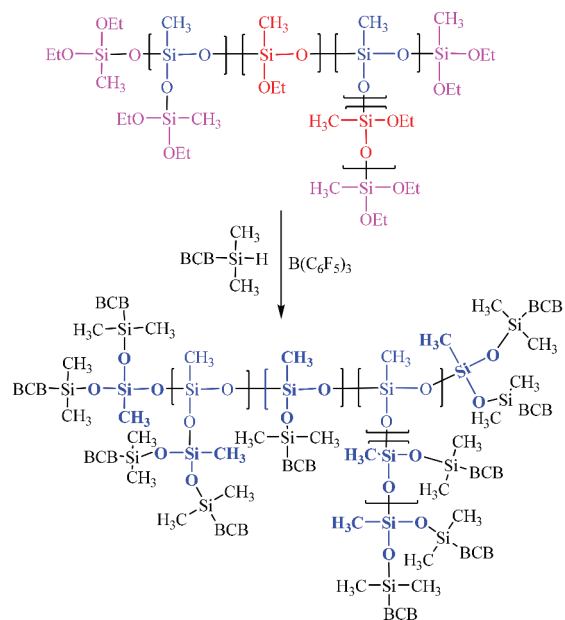
spectrum of HB-DEMS were easily assigned. The degree of branching (DB) was calculated by the following equation:

$$\text{DB} = (\text{D} + \text{T}) / (\text{D} + \text{L} + \text{T}) \quad (1)$$

where D, L, and T are the relative amounts of D, L, and T units, respectively. These units can be evaluated from the ratio of the integral intensities of the peaks in the ^{29}Si -NMR spectrum [31]. Using this equation (1), the DB of HB-DEMS was found to be approximately 0.45. In the ^{29}Si -NMR spectra of HB-BCB, there was no peak corresponding to the T unit. In addition, the intensity of the peak attributed to the L unit reduced significantly, possibly due to the substitution of the O-Et groups by the -O-SiMe₂BCB groups. These findings suggest that most of the core silicon atoms of the T and L units in HB-DEMS are converted to the D units in HB-BCB (Scheme 2). A new peak is observed at approximately -2 ppm, and it can be ascribed to -O-SiBCB group. Since the hyperbranched framework of HB-DEMS remains unchanged after the substitution reaction, it is reasonable to assume that the DB of HB-BCB is the same as that of HB-DEMS (0.45).

3.2. Curing behavior

The curing behavior of the synthesized HB-BCB is studied using DSC (Figure 4). The crosslinking process is exothermic and begins at a temperature of 200 °C. The



Scheme 2. T and L units change into D cores as HB-DEMS is converted to HB-BCB.

peak exotherm is observed at 251 °C and the crosslinking reaction reaches completion at 340 °C. These findings are in accordance with those reported for other BCB-based polymers. This curing behavior can be ascribed to the ring-opening of the four-membered ring in BCB, leading to the formation of *o*-quinodimethane intermediates, along with the crosslinking of the ring-opened BCB units. No significant glass transition

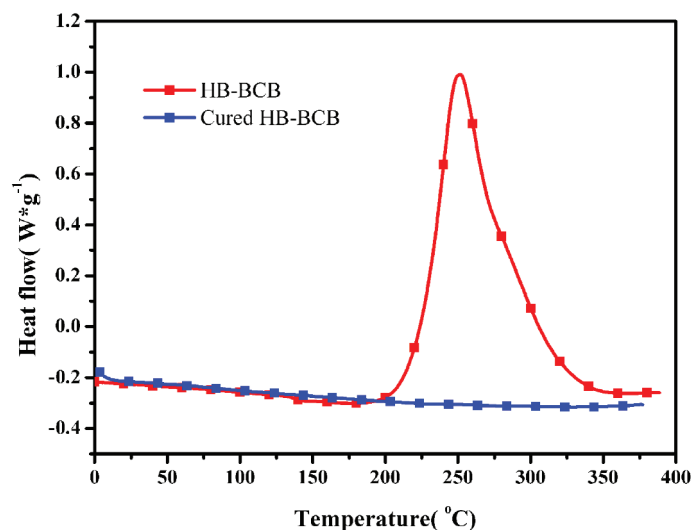


Figure 4. DSC curves of HB-BCB and cured HB-BCB.

was observed in the DSC curve of cured HB-BCB because it is highly crosslinked, and the movement of its segments is limited.

The formation of the highly crosslinked HB-BCB was also verified using FT-IR spectroscopy (Figure 5). The following discussion is based on the theoretical FT-IR data obtained by Ocola et al. [32]. A comparison of the FT-IR spectra reveals that the peaks at 1432 cm^{-1} and 2830 cm^{-1} , which are assigned to the CH_2 deformation and its overtone band, are not present in the spectrum of cured HB-BCB. In addition, the intensity of the peak at 2928 cm^{-1} , which is ascribed to the CH_2 symmetrical stretching vibration of BCB, significantly decreases after curing. The peak corresponding to the aromatic C-C stretching in BCB shifts from 1465 cm^{-1} to 1495 cm^{-1} after curing because the ring strain caused by the four-member ring is released after the ring-opening and crosslinking reactions. Moreover, in the FT-IR spectrum of the cured resin, there is no peak at

880 cm^{-1} , which may correspond to a combination band related to the four-member ring. These findings verify the ring-opening of cyclobutene in BCB, which leads to the formation of a highly crosslinked network structure.

3.3. Properties of the cured resin

After curing, the oligomer HB-BCB as viscous liquid converted into yellow transparent rigid plastic. Thermal stability of the cured resin is measured by TGA and the TGA curve is shown in Figure 6. It reveals a high thermal decomposition temperature at 5% weight loss ($T_{d5} = 512\text{ }^\circ\text{C}$) with a high char yield of 61% at $800\text{ }^\circ\text{C}$. The excellent thermal stability of the cured HB-BCB may be attributed to the siloxane framework and the highly crosslinked network structure constructed by the BCB group.

The DSC curve of the cured HB-BCB (Figure 4) show is smooth with no peak. Therefore, it is difficult to detect the glass transition temperature (T_g) for crosslinked resins using only DSC. Thus, DMA was used to measure the thermomechanical properties of the cured HB-BCB (Figure 7). The cured HB-BCB exhibits a high initial storage modulus of 2.4 GPa, attributing to the curing of HB-BCB and the formation of the highly crosslinked structure. The storage modulus decreases with increase in temperature: 0.78 GPa at $200\text{ }^\circ\text{C}$ and 0.58 GPa at $350\text{ }^\circ\text{C}$. The $\tan \delta$ curve of the cured HB-BCB exhibits a maximum at $178\text{ }^\circ\text{C}$ with a damping coefficient of 0.09, and the corresponding storage modulus is 0.94 GPa. The properties of cured HB-BCB differ from those of ordinary polymers that have a low storage modulus (<50 MPa) in the rubber state and a large damping

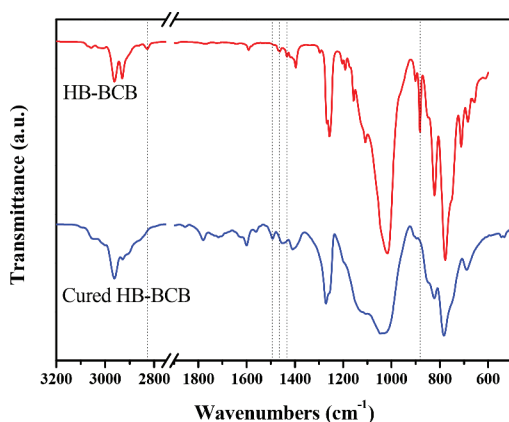


Figure 5. FT-IR spectra of HB-BCB and cured HB-BCB.

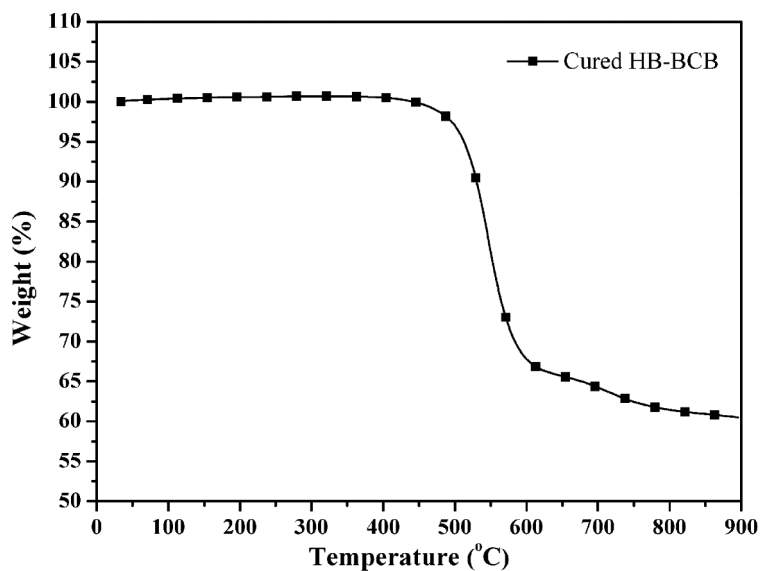


Figure 6. TGA curve of cured HB-BCB.

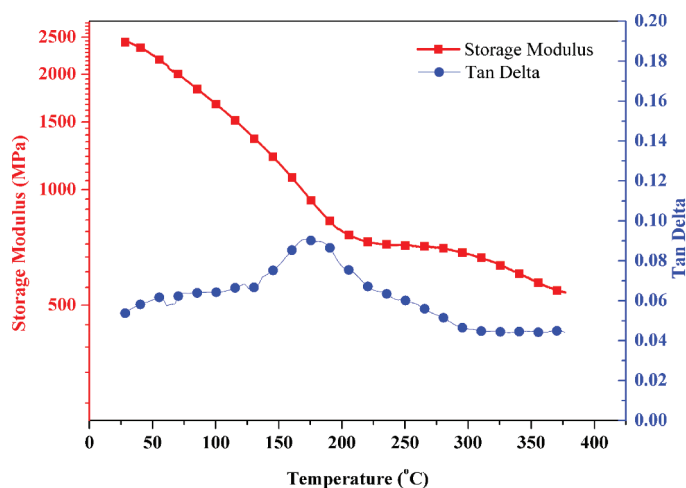


Figure 7. DMA curves of cured HB-BCB.

coefficient at the T_g [26]. Since the hyperbranched siloxane framework is surrounded by the rigid BCB cross-linked network, it is reasonable to assume that the tan δ peak may be regarded as a synergistic secondary relaxation of the siloxane structure confined by the highly crosslinked structure.

The cured HB-BCB exhibits a low relative dielectric constant of 2.70 and low dissipation factor of 2.75×10^{-3} at 1 MHz (Figure 8), which suggests that this material shows relatively good dielectric property, which may have potential applications in the field of microelectronics and packaging.

4. Conclusions

The HB-BCB resin, consisting of a hyperbranched polysiloxane framework functionalized with BCB, was successfully synthesized via the P-R reaction in a cascade reaction way. It's a facile and convenient method to prepare the BCB functionalized siloxane polymer. The obtained oligomer was cured and it was found that crosslinking occurred at temperatures greater than 200 °C. The hyperbranched structure was verified using NMR and FT-IR spectroscopy. The cured resin possessed a low dielectric constant ($k = 2.70$), low dissipation factor (2.13×10^{-3} at

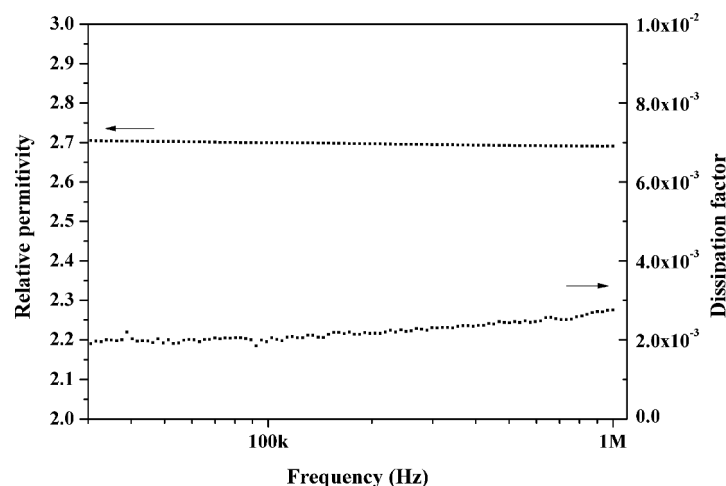


Figure 8. DMA curves of cured HB-BCB.

1 MHz), good high-temperature mechanical properties, and an extremely high thermal decomposition temperature ($T_{d5} = 512$ °C). The high performance of the cured resin can be ascribed to the introduction of BCB groups to form the highly crosslinked and low-polarity structure. In addition, the findings of this study demonstrate that the prepared resin may function as an ideal low-k material with excellent high-temperature performance. Thus, the HB-BCB resin can be potentially applied in the microelectronics industry.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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