Fabrication of β-cyclodextrin-crosslinked epoxy polybutadiene/hydroxylated boron nitride nanocomposites with improved mechanical and thermal-conducting properties

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**A B S T R A C T**

In this work, hexagonal boron nitride (hBN) was modified to introduce hydroxyl groups. The abundant hydroxyl groups in β-cyclodextrin (βCD) provide many reactive sites to form covalent links with epoxy groups in epoxy butadiene rubber (EBR). Therefore, we propose the utilization of biological βCD as a novel interfacial crosslinker, assisting in the dispersion of the hydroxylated hBN (mBN) via hydrogen bonding, to prepare EBR/βCD/mBN nanocomposites. Such interfacial interactions not only effectively promote the homogeneous dispersion of mBN in the matrix, but also enhance the mechanical property of nanocomposites. Meanwhile, a high thermal conductivity of 0.187 W/m K was obtained by introducing mBN (4 wt%), reaching 2.83 times of the value for the vulcanized butadiene rubber (BR, 0.066 W/m K). The promising mechanical and thermal conductivity properties of our new materials, and the environmentally friendly curing agent makes them attractive for thermal management application, the tread and sidewall compound of tire.

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1. Introduction

Rubber-based material is of great interest for various applications—from sealing ring in life to high-tech aviation tires [1]. Nowadays, the polybutadiene rubber (BR) has aroused increasing attention owing to promising mechanical properties and processing properties. A series of BR nanocomposites have been developed with dramatically improved properties. For instance, Prokúpek et al. [2] fabricated glass fiber/BR composites with enhanced tensile and flexural properties. Wang et al. [3] prepared modified graphene oxide/styrene-butadiene rubber composites with improved mechanical properties via physical entanglement. However, like most rubber-based materials, BR is a poor conductor of heat, and the large amount of heat it generates is accumulated during use, which cannot be transferred effectively and may result in a decrease in material properties with an accelerated aging.

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Recently, series of inorganic fillers have been employed to improve the thermal conductivity of rubber-based composites, such as metal oxides (ZnO, Al₂O₃) [4,5], carbonaceous nanofillers (CNTs, graphene) [6,7], metal nitrides (BN, AlN) [8,9] and clay [10]. However, most existing BR-based nanocomposites are fabricated by physically blending between polymer matrix and nanofillers with weak interface interactions, which restrict the reinforcing effects of fillers and result in unevenly dispersion of fillers in the rubber matrix.

Hexagonal boron nitride (hBN), a structural analogue of graphite, has recently attracted increasing attentions due to its high intrinsic thermal conductivity (as high as 2000 W/m K), low dielectric loss and anti-oxidation ability [11–14]. Based on the mentioned properties of hBN, it has been widely used in silicone rubber [15], natural rubber [6], polyurethane [16] and epoxy resin [17]. However, generally speaking, hBN particles cannot disperse uniformly in the matrix due to the high surface energy and amphiphobic nature, which resulting in high thermal resistance at the material interfaces. In addition, to the best of our knowledge, hBN has not yet been studied for BR as thermally conductive filler, which remains a challenge in the development of hBN/BR-based nanocomposites. The usual method to improve the dispersion of hBN is to modify the hBN surfaces by establishing a covalent or non-covalent relationship, such as silane [18,19], poly(dopamine) [20] and cationic polyacrylamide [21] functionalized hBN. The hydroxylation on the surface of hBN for further modification has been recently studied by various methods [22-24], which provide a potential facile way to fabricate hBN/rubber-based nanomaterial via chemical bonding for improving fillers dispersion and enhancing the interfacial interactions.

In this work, the epoxy group is introduced into the main chain of BR to obtain an epoxy butadiene rubber (EBR). Then, we propose the utilization of biological β-cyclodextrin (βCD), which not only serves as a novel nontoxic interfacial crosslinker to prepare EBR/βCD/mBN nanocomposites, but also assists in the good dispersion of mBN via hydrogen bonding (Scheme 1). In comparison with the method of covalent attachment, the non-covalent connection is more convenient and it will not change the origin intrinsic properties of hBN. The results show that the improvement of thermal conductivity in EBR/βCD/mBN (0.187 W/m K) is 283% higher than the vulcanized BR (0.066 W/m K). Therefore, this work utilizes the environmentally friendly curing agent for facile fabrication of novel BR-based nanocomposites with promising mechanical properties and thermal conductivity, which is attractive for thermal management application, the tread and sidewall compound of tire.

### 2. Experimental section

#### 2.1. Materials

Butadiene rubber [BR, cis-1,4 content of 97.0%, M₉ = 11.7 × 10⁴, M₉/M₈ = 2.2] was purchased from Dushanzi Petrochemical Company, Petro China. Hexagonal boron nitride (purity = 99.9%, 1–2 μm) was provided by Macklin Biochemical Co., Ltd. 3-Chloroperoxybenzoic acid (mCPBA, 85%, Adamas-beta), CH₂Cl₂ (≥99.5%, Beijing Chemical Works), CH₃OH (≥99.5%, Beijing Chemical Works), CDCl₃-d (99.8 atom% D, Cambridge Isotope) and β-cyclodextrin (98%, Aladdin) were used as received.

#### 2.2. Hydroxylation of hBN

300 mL mixed solution of concentrated sulphuric acid and nitric acid (1:3 by volume), mixing with 5 g hBN, was prepared. Subsequently, it was sonicated for 8 h at room temperature. The suspended solution was stirred magnetically for 72 h in an oil bath at 80 °C under a nitrogen atmosphere. After reaction, the suspension was centrifuged and washed with deionized water several times until the PH was adjusted to neutral. Then the product was filtered using a cellulose filter membrane and placed in a vacuum drying oven for 24 h at 60 °C. The modified hBN particles were stored in a desiccator. According to the literature, the modification of hBN, treated by the mixed acid method, can greatly benefit the formation of functional groups and defects on the surface of hBN. And this method is aiming to generate hydroxyl groups on the boron atoms at the edge of hBN via an oxidation process, which can be illustrated by the following Eqs. (1) and (2). Firstly, a high-concentration acidic solution produces plenty of oxidized radicals on the surface of hBN. Then, hydroxyl functional groups form on the hBN surface via a low-concentration acidic solution [25,26].

\[
\begin{align*}
3N-B + 2HNO_3 \rightarrow & \ 2N-B-NO_3 + B-N-H_2 \tag{1} \\
N-B-NO_3 + H_2O \rightarrow & \ N-B-OH + HNO_3 \tag{2}
\end{align*}
\]

#### 2.3. Preparation of βCD crosslinked EBR/mBN nanocomposites

The nanocomposites were prepared as follows. Typically, to a dichloromethane solution of BR (0.014 g/mL) was added a solution of the mCPBA in dichloromethane with gently stirring at room temperature for 30 min. Then, 20 phr (parts per hundred of rubber) of βCD was added to the solution with constantly stirring. After stirring for 15 min, 10 phr mBN dissolved in...
dichloromethane, which has been dispersed by ultrasonic for 30 min, was then added into the mixed homogeneous suspension with vigorously stirring for another 15 min. After mixing, the suspension was poured into cool methanol. The resulting sediment was washed twice with cool methanol and then dried in vacuum oven at 30 °C to achieve a constant weight. The dried precipitate was then conducted to compression at 160 °C under the pressure of 10 MPa for 18 min. The dimension of resulting molded samples was 60 mm × 60 mm × 2 mm. Other nanocomposites containing various contents of βCD (0, 10, 20 and 30 phr) and mBN (0, 5, 10 and 15 phr) were prepared by the same procedures. The synthesized nanocomposites are represented by rubber/x βCD/y mBN, wherein βCD and mBN are added with x and y phr based on the content of rubber matrix.

2.4. Characterization

The $^1$H-NMR spectra were conducted on an AVANCE 400MHZ spectrometer at room temperature with CDCl$_3$-d as a solvent. X-ray diffraction analysis was carried out using a X-ray diffractometer (Bruker-AXS) with monochromatic radiation at a wavelength of 0.154 nm. The 2θ angle ranged from 10° to 90°. Fourier transform infrared (FTIR) spectra were recorded from 600 to 4000 cm$^{-1}$, using a BRUGE Vertex-70 FTI spectrometer (KBr pellet technique). The mechanical properties of all samples were carried out by dynamic mechanical analysis (DMA MetravibDMA + 450) in tensile mode and tensile test (INSTRON-5869) under the tension condition with a frequency of 1 Hz. The samples were heated from −130 to 40 °C at a heating rate of 3 °C/min. Thermo-gravimetric analysis (TGA) was conducted on a SDTQ600 instrument from room temperature to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The tensile tests were performed using dogbone-shaped samples with a constant speed of 50 mm/min at room temperature. The morphology and elemental analysis of the prepared products were observed by transmission electron microscopy (TEM) on a Hitachi H-600 operated at 100 kV and scanning electron microscopy (SEM) with XL30ESEM/FEG scanning electron microscope operated at 25 kV. Measurement of the thermal conductivity (diameter 10 mm, thickness 3 mm) was carried out using the laser-flash diffusivity instrument (LFA427, NETZSCH).

3. Results and discussions

3.1. Hydroxylation of hBN

The successful hydroxylation of hBN was confirmed by IR spectroscopy. As shown in Fig. 1(a), the values of strong characteristic peaks at 804 and 1386 cm$^{-1}$ can be respectively attributed to the out-of-plane bending vibration of B–N–B bonds and the in-plane stretching vibration of B–N bonds. The
Double bonds’ partial epoxidation in BR was carried out by mCPBA. 1H-NMR spectroscopy was used to calculate the degree of epoxidation (%). Fig S1 in Supplementary material exhibited the 400 MHz 1H-NMR spectra of EBR with the assignments for all the most important resonances. In comparison with the BR signals, the spectrum of EBR appeared a new signal at 2.9 ppm, which was assigned to the oxirane ring. Based on the comparison of the multiplet centered at 2.9 and 5.31 ppm, an epoxidation degree of 25.2% was obtained and the reaction yield was near 95% [29]. Meanwhile, as shown in the Fig. 2, three characteristic absorptions peaks of oxirane ring appear in the FTIR curves of EBR compared with BR. And the values of characteristic peaks at 812, 880, 1127 cm⁻¹ can be attributed to the deformation of in-plane ring and C−O−C asymmetric stretching [30,31]. Therefore, it can be conducted that the epoxidation of BR has been achieved.

βCD is commonly produced by the enzymatic conversion of starch through cyclization reactions catalyzed by cyclodextrin glycosyltransferase and contains twenty-one hydroxyl groups per molecule [32,33]. The abundant hydroxyl groups in βCD provide many reactive sites, which can be served as a biological crosslinking agent to form covalent links with epoxy groups in EBR. Moreover, unreacted hydroxyl groups existing on the grafted βCD molecules make it possible to interact with mBN via hydrogen bonding. As depicted in Fig. 3, the hydroxyl groups in the βCD molecule were firstly employed to react with the epoxy groups in EBR. Then, in virtue of hydrogen bonding, the remaining hydroxyl groups could establish a connection with mBN. In this way, the βCD molecules can act as a bridge to connect EBR matrix with mBN.
In order to reveal the proposed covalent interaction between βCD and EBR, the changes of characteristic functional groups of EBR have been exhibited in the FTIR spectra. In comparison with the pristine EBR, the evident increasing peaks intensity at 3354 cm⁻¹ and 1029 cm⁻¹ representative for O-H and C-O-C, respectively, are shown in Fig. 2, which is attributed to the presence of reacted βCD. Moreover, the absorption peaks of epoxy group at 880 cm⁻¹ almost disappears, suggesting that the epoxy group is consumed completely during the reaction. Therefore, it can be confirmed that the EBR have ability to react with βCD molecules via cross-linking reaction.

Furthermore, vulcanization curves have been used to illustrate the covalent reaction. The torque-time curves of EBR cross-linked by S and various contents (0, 10, 20, 30, 40 phr) of βCD are exhibited in Fig. 4. And the formula of the vulcanization system is displayed in Table S1 in Supplementary material. As shown in Fig. 4, the torques of all the samples are increasing gradually as time goes on, indicating that the βCD is competent of being cross-linked with EBR without demanding other additives. It is also obviously obtained that the curing time is almost unchanged and the maximum torque becomes higher as the βCD content increases. Therefore, it can be concluded that the optimum curing time is about 18 min. And the increase of maximum torque can be ascribed to the successful cross-linking reaction.

3.3. Mechanical properties of EBR/βCD/mBN nanocomposites

The EBR/βCD/mBN nanocomposites with different contents of βCD and mBN were prepared, and DMA test was conducted to characterize their mechanical properties. The tensile storage modulus (E’) and tan δ of all composites are shown in Fig. 5(b). Concrete number of all samples is displayed in Table 2. The dynamic properties indicated that the elastic energy stored in the composites and the energy consumed in strain. And it is mainly depended on the state of nanofillers such as dispersibility, volume fraction, geometrical characteristics, and load transfer from the filler to the polymer matrix [17,34]. In the case of EBR nanocomposites with 10 phr mBN, the E’ of EBR increased markedly with increasing βCD content, due to the formation of covalent cross-linking network. The glass-transition temperature (Tg) of EBR/10mBN nanocomposites moved to a higher temperature as the rise of βCD content, suggesting that a covalent cross-linking structure has been constructed successfully. In addition, the tan δ peak of the EBR nanocomposites with 20 phr βCD shifted to the higher temperatures with the increasing loading of mBN, accompanied by significant increase of storage. For example, at 20 °C the E’ of the pure EBR and the EBR/20βCD composites containing various content of mBN at 0, 5, 10, 15 phr were 3.11, 5.01, 8.53, 9.62, and 12.05 MPa, respectively (Table S2 in Supplementary material). Moreover, the intensity of the tan δ decreased and glass-rubber transition zone broadened as the mBN content increased, which can be ascribed to the strong interactions between the hydroxyl on the βCD and the mBN via hydrogen bonding.

The stress–strain curves of EBR/βCD/mBN nanocomposites containing various βCD and mBN contents are exhibited in Fig. 5(c). Notably, because of the existence of covalent cross-linking structure and hydrogen bonding, it was obviously that mechanical properties of the EBR/βCD/mBN nanocomposites showed a remarkable enhancement in the case of fixing one (βCD, mBN) content and changing the other (mBN, βCD) content. For example, the tensile strength and Young’s modulus of EBR/30βCD/10mBN increased by 140% (from 2.60 to 3.64 Mpa) and 180% (3.53 to 6.35 MPa) compared to EBR/10mBN nanocomposite. The similar trend was also found at storage modulus mentioned above. In addition, the tensile strength and Young’s modulus became higher with the rise of mBN contents. However, the breakage elongation decreased as the βCD and mBN contents increased because the interfacial interaction between mBN and βCD-crosslinked EBR restricted the mobility of the rubber chains. These results manifested that the amount of hydroxyl groups on βCD have an important impact on mechanical properties of nanocomposites, which can bond with mBN via hydrogen bonding and simultaneously hinder the slipping of polymer chains during the stretching process. The results of tensile test are consistent with the dynamic mechanical test, indicating that there exists an interfacial interaction between the rubber matrix and mBN.

3.4. Morphology of nanocomposites

In general, the dispersion state of filler and the interfacial interactions can be studied from the morphology of the fractured surfaces. The cryogenically fractured surfaces of specimens were observed by SEM. The surface of pure EBR, as shown in Fig. 5(a), was very smooth and the river pattern emerges on the crack surface, indicating that it is a brittle fracture [25]. The EBR/mBN nanocomposites displayed a rough fracture surface. And the mBN were exposed in the rubber matrix randomly. Meanwhile, small mBN agglomerated and generated voids on the fracture surface, suggesting a weak interfacial interaction between fillers and rubber matrix. However, when introducing βCD as a crosslinker, the surface became smooth and the mBN particles were embedded and well dispersed in polymer matrix, suggesting that the mBN exhibited the desirable homogeneity and dispersion in rubber
matrix. The areas of agglomeration and voids cannot be discovered easily. This situation confirmed that a strong interface interaction between mBN and rubber matrix assisting in the good dispersion of mBN in the matrix. In addition, such homogeneous dispersion and good compatibility are beneficial for forming an efficient thermally conductive network.

3.5. Thermal stability

Thermogravimetric analysis (TGA) of the EBR/βCD/mBN nanocomposites was conducted and given in Fig. 6(a and b). Concrete numbers of T10% (temperature at 10% weight loss), T50% (temperature at 50% weight loss) and char yield are given in Table 1. As shown in Fig. 6(a), in the case of EBR/10mBN nanocomposite, the T10% and T50% were 392.3 °C and 451.1 °C respectively, which showed a great thermal stability. However, as the content of βCD increased, the thermal stability of the composite deteriorated. The stage of weight loss around 305–345 °C can be attributed to the degradation of βCD backbone in view of the previous report [35]. However, the βCD-cured EBR still shows good thermal stability above 300 °C. Fig. 6(b) depicts the thermal degradation behavior of the EBR/20βCD composites with different content of mBN. As the content of mBN increased gradually, the thermal stability and the char yield of nanocomposites increased. It is also observed that the value of T10% for the EBR/βCD composites with various contents of mBN (0, 5, 10, 15 phr) are 335.8, 336.4, 337.6 and 356.1 °C, respectively. And the EBR matrix in Fig. 6(a) displays the similar trend when introducing 10 phr mBN.

The nanocomposites filled with mBN possessed better thermal stability due to the formation of a BN char. It can serve as a barrier of mass transport and a separator between the rubber matrix and the surface when burning [36]. Moreover, as presented in Table 1, the char yields obtained by experiment are higher than the theoretical values calculated by the “mixture rule”. This situation indicated that there exists a synergistic effect in terms of retarding the thermal decomposition, which may be ascribed to the good dispersion state of mBN in the EBR/βCD matrix via hydrogen bonding, resulting in good interfacial adhesion, as well as offering a good barrier for heat and mass transfer [37].

3.6. Thermal conductivity

Furthermore, the thermal conductivity (TC) of the vulcanized BR (the formula of the vulcanization system is displayed in Table S1 in Supplementary material) and BR-based nanocomposites (containing 5, 10, 15 phr mBN) were studied by laser flash method, as depicted in Fig. 6(c). It is clearly shown that the thermal conductivities of all nanocomposites are related to the temperature (from 25 to 100 °C). It is also observed that the vulcanized BR possesses a very low thermal conductivity. Meanwhile, when only βCD is introduced, the thermal conductivity of the EBR/βCD composite is still very low as that

Fig. 5 – (a) SEM images of fracture surface of nanocomposites. (b) Representative DMA traces of EBR and EBR nanocomposites. (c) Stress-strain curves of EBR and EBR nanocomposites.
Fig. 6 – (a, b) TGA thermal degradation curves of βCD, EBR and EBR nanocomposites. (c) Thermal conductivity of the vulcanized BR and BR-based nanocomposites at different temperatures. (d) Thermal conductivity and the thermal conductivity enhancement of the vulcanized BR and BR-based nanocomposites at 25°C.

### Table 1 – Thermal properties of EBR/βCD/mBN nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>10% weight loss temperature (°C)</th>
<th>50% weight loss temperature (°C)</th>
<th>Char yield (% at 600 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mBN</td>
<td>/</td>
<td>/</td>
<td>99.21</td>
</tr>
<tr>
<td>EBR</td>
<td>385.4</td>
<td>447.5</td>
<td></td>
</tr>
<tr>
<td>EBR/10mBN</td>
<td>392.3</td>
<td>451.1</td>
<td></td>
</tr>
<tr>
<td>EBR/10βCD/10mBN</td>
<td>364.6</td>
<td>448.5</td>
<td></td>
</tr>
<tr>
<td>EBR/20βCD/10mBN</td>
<td>337.6</td>
<td>445.6</td>
<td></td>
</tr>
<tr>
<td>EBR/30βCD/10mBN</td>
<td>323.4</td>
<td>442.2</td>
<td></td>
</tr>
<tr>
<td>EBR/20βCD</td>
<td>335.8</td>
<td>442.8</td>
<td>1.86</td>
</tr>
<tr>
<td>EBR/20βCD/5mBN</td>
<td>336.4</td>
<td>444.6</td>
<td>5.75</td>
</tr>
<tr>
<td>EBR/20βCD/15mBN</td>
<td>356.1</td>
<td>450.6</td>
<td>12.68</td>
</tr>
</tbody>
</table>

of the vulcanized BR. However, after embedding mBN, the TC improved significantly at different temperatures. The TC of the vulcanized BR was 0.066 W/m K at 25 °C and increased as the temperature rised from 25 to 100 °C. However, the TC of the BR-based nanocomposites exhibited an opposite trend to that of the vulcanized BR. According to previous literature reports, the polymer transformed into the rubbery state above the glass-transition temperature (Tg). Over the Tg, the scattering process is mainly dependent on the structure scattering and vacant site scattering. With the increase of temperature, the variation of polymer properties are primarily controlled by the slippages of the rubber chain segments instead of the individual units, atomic groups, and small chain segments. In addition, a number of vacant sites or microvoids generated because of the initial slipping of dominant chain. The number and size of microvoids increased as the temperature rised, which led to an increase of thermal resistance in terms of vacant site scattering. Therefore, the thermal conductivity of the BR-based nanocomposites started to decrease with the rise of temperature [38].

Fig. 6(d) shows the TC enhancement of the vulcanized BR and the BR-based nanocomposites at 25 °C. The value of enhancement of TC increased as the content of mBN raised. For example, compared to the vulcanized BR, the TC of the nanocomposites is increased by 183% (from 0.066 W/m K to 0.187 W/m K) at 25 °C with introducing 5 phr (converted to a mass fraction of 4 wt%) mBN. These results show that the nanocomposites have a significant improvement in the TC, not only because of the high thermal conductivity of the
nanofiller itself, but also the interfacial interaction between the new cross-linking system and the nanofiller.

4. Conclusions

In summary, the EBR/βCD/mBN nanocomposites were prepared by solution blending and hot-pressing techniques. The biological βCD was used as an interfacial modifier to construct a covalently linked network assisting in the good dispersion of mBN via hydrogen bonding. The resultant nanocomposites exhibited a strong interfacial interaction between matrix and nanofillers. In addition, the nanocomposites possessed improved storage modulus, $T_g$ and thermal stability with the increasing loading of mBN. Meanwhile, the thermal conductivity of the BR-based nanocomposites (containing 4 wt% mBN) was 0.187 W/m K, which is 283% higher than the vulcanized BR (0.066 W/m K). This work may provide insight into the fabrication of novel hBN/BR-based nanocomposites with improving mechanical properties and thermal conductivity, which have potential for applications in thermal management, the tread and sidewall compound of tire.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.09.056.

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