ABSTRACT: Effective heat dissipation has become a major concern with the rapid development of microelectronic devices. In general, thermally conductive fillers are incorporated into the polymeric matrix to increase the thermal conductivity of polymer composites. Herein, poly(catechol-polyamine) (PCPA) is employed to modify boron nitride (BN) platelets, referred to as BN-PCPA, and improves the interfacial compatibility between a thermally conductive filler and elastomer matrix, resulting in carboxylated acrylonitrile-butadiene rubber (XNBR) composites filled with BN-PCPA platelets with enhanced thermal conductivity. The influence of PCPA thickness on the mechanical properties, thermal conductivity, and dielectric properties of BN-PCPA/XNBR composites is systematically studied. Briefly, the interfacial compatibility between the BN-PCPA filler and XNBR matrix increases with increasing PCPA thickness, leading to enhanced thermal conductivity. The maximum thermal conductivity of 0.399 W/(m·K) has been rendered by the BN-PCPA-12h/XNBR composite, which is about 2.5 times of pure XNBR. This work provides an easy route to develop polymer composites with a relatively high thermal conductivity and high dielectric constant for potential application in practical electronic packaging.

1. INTRODUCTION

With the rapid development of miniaturized electronic devices, effective heat dissipation becomes a major concern. Various polymeric materials are widely used in electronic devices and communication equipment due to the easiness of processing, lightweight, high resistivity, and excellent corrosion resistance. However, most of the polymers render inferior thermal conductivity, hindering large-scale utilization in various applications. In general, thermally conductive fillers are incorporated into the polymeric matrix, such as metal oxides, metal nitrides, and carbonaceous materials, to enhance the thermal conductivity of polymer-based materials. The ceramic thermally conductive fillers, such as Al2O3, SiC, and ZnO, can improve the thermal conductivity of polymer composites and keep their insulation. However, the carbon materials, such as CNTs and graphene, can not only improve thermal conductivity but also enhance the electrical conductivity of polymer composites, which is not applicable to thermally conductive materials used in insulated occasions.

Boron nitride (BN) is a promising thermally conductive filler due to its lubrication, electrical insulation, chemical corrosion resistance, and good thermal conductivity. Moreover, BN/polymer composites exhibit a low coefficient of thermal expansion. However, the homogenous dispersion of BN platelets in the polymeric matrix is a difficult issue due to its high surface energy, resulting in inferior interfacial adhesion and high thermal resistance. Therefore, the filler surface is needed to be modified to ensure excellent dispersion and enhance the thermal conductivity and mechanical properties of BN/polymer composites.

In previous studies, different approaches have been adopted to modify the surface of BN. For instance, Xie et al. treated BN with hydrogen peroxide (H2O2) and heated in an autoclave under continuous stirring. The H2O2-modified BN (m-BN) was added into the polyvinyl alcohol matrix to prepare a thermally conductive composite, resulting in a thermal conductivity of 3.92 W/(m·K) at a m-BN content of 10 wt %. The enhanced thermal conductivity was ascribed to the improved compatibility between the inorganic filler and organic material. Qin et al. modified BN by a silane coupling agent to prepare thermally conductive polymethyl methacrylate (PMMA) composites via bulk polymerization. The maximum thermal conductivity was found to be 0.53 W/(m·K).
K) by the PMMA composites with the addition of 16 wt % modified BN, which is 2.8 times higher than the pure PMMA. Zhang et al. modified BN with dopamine and a decorated BN surface with silver nanoparticles, denoted as AgNPs/h-BN, resulting in AgNPs/h-BN/polyethylene naphthalate composites with a high thermal conductivity of 0.921 W/(m·K).

Recently, poly(dopamine) (PDA) is being investigated as a surface modification agent for inorganic fillers due to its excellent adhesion. The researchers found that the catechol groups and the cross-linked network in PDA are two key factors for the excellent adhesion of PDA. However, the high price of dopamine restricts its wide industrial applications. Luckily, the catechol and polyamine were found to polymerize in weak alkaline buffer solution and form a poly(catechol/polyamine) (PCPA) network on the surface of substrates, which exhibited an adhesive property similar to that of PDA.

Herein, the reaction products of catechol and polyamine were employed to form a PCPA layer on the surface of BN, denoted as BN-PCPA. Then, the as-prepared BN-PCPA was added into the carboxylated acrylonitrile-butadiene rubber (XNBR) matrix to prepare thermally conductive composites. Due to the enhanced interfacial compatibility between the BN-PCPA filler and XNBR matrix, the interfacial thermal resistance in composites was decreased. Moreover, different thicknesses of the PCPA layer were developed on the BN surface by controlling the reaction time of PCPA. The influence of the PCPA thickness on mechanical properties, thermal conductivity, and dielectric properties of XNBR composites has been systematically studied.

2. RESULTS AND DISCUSSION

The schematic illustration of PCPA layer formation on the BN surface is shown in Figure 1a, and the corresponding reaction mechanism is presented in Figure 1b. The catechol was oxidized into quinoid structures in an alkaline buffer solution, and then, the quinoid structures formed a cross-linked PCPA network via the Michael addition or Schiff base reaction with amine (TEPA). The catechol groups in polyphenols can adhere tightly to the surface of the substrates via covalent and noncovalent bonds with excellent adhesion properties.

During latex compounding, the strong interaction force may be formed between carboxyl groups of XNBR and imino groups and phenolic hydroxyl groups of BN-PCPA. Different thicknesses of the PCPA layer were developed by controlling the reaction time of PCPA. With the reaction time increased, the number of strong interfacial forces increased, leading to a stronger interfacial adhesion.

The surface elements of BN and BN-PCPA platelets were investigated via XPS, and the results are shown in Figure 2. One should note that the intensity of the C 1s peak significantly increases after PCPA modification, confirming
the presence of PCPA on the BN surface. In addition, compared with pristine BN platelets, the high-resolution C 1s spectra of BN-PCPA platelets exhibit an increased intensity of the C−N peak (285.5 eV) and a newly added C==O peak (288.1 eV), suggesting the successful incorporation of PCPA on the BN surface. Moreover, the intensity of the C−O peak gradually increases with the increase of modification time, which implies an increase of the PCPA content on the BN surface.

The surface morphology of pristine BN and BN-PCPA platelets were observed by HR-TEM. Figure 3a shows that the pristine BN exhibits a smooth surface, whereas a thin coating layer is observed on the surface of BN-PCPA platelets (Figure 3b−f). Also, the thickness of the PCPA layer increases with increasing modification time. It is easy to find that the thickness of PCPA on BN-PCPA-3h, BN-PCPA-6h, BN-PCPA-9h, and BN-PCPA-12h platelets are 1.1, 2.1, 3, and 4 nm, respectively. The content of the PCPA layer on the BN surface that increases with increasing modification time is also demonstrated by the TGA curves, and the results are shown in Figure 4. It can be seen that the mass residue of BN, BN-PCPA-3h, BN-PCPA-6h, BN-PCPA-9h, and BN-PCPA-12h platelets are 99.29, 98.23, 97.67, 97.17, and 96.93%, respectively, at 800 °C. The decreased mass residue of BN-PCPA with increasing modification time means that the weight content of the PCPA layer increases with increasing modification time.

The microstructure of BN/XNBR and BN-PCPA/XNBR composites were observed by SEM, as shown in Figure 5. Figure 5a shows that the BN/XNBR composite contains some defects due to the poor interfacial compatibility between pristine BN and the XNBR matrix. In general, an inorganic filler will aggregate and form aggregates in the polymer matrix due to their large specific surface area and surface energy. When the BN/XNBR composites were fractured at the liquid nitrogen temperature, the inorganic BN platelets were peeled off from the XNBR matrix, which resulted in defects at the cross section. However, the size of defects is significantly decreased in the BN-PCPA/XNBR composites. This phenomenon can be ascribed to the improved interfacial interaction between the XNBR rubber matrix and BN-PCPA filler, which resulted in less BN-PCPA platelets being peeled from the XNBR matrix. In addition, the size of BN-PCPA aggregates in BN-PCPA/XNBR composites is decreased with increasing modification time, which may be ascribed to the interfacial adhesion increases with increasing thickness of the PCPA layer.

The mechanical properties of pure XNBR and XNBR composites are displayed in Figure 6 and Table 1. Compared with the BN/XNBR composite with the same filler content, the tensile strength of BN-PCPA/XNBR composites are obviously improved, which is due to the enhanced interfacial adhesion between the thermally conductive filler and rubber matrix. However, the tensile strength of BN-PCPA/XNBR composites decreases with increasing modification time. There are two reasons to explain this phenomenon. First, the relatively soft PCPA layer coating on the BN platelets increases the whole content of the polymeric phase in the composites. Second, with the PCPA coated on the surface of BN, the reinforcing effect of BN-PCPA toward the XNBR matrix is much less than that of pristine BN platelets. In addition, the detailed mechanical properties, including tensile strength, elastic modulus, and elongation at break of pure XNBR and XNBR composites, are displayed in Table 1.

Figure 7 shows the frequency dependence of the dielectric constant ($\varepsilon_r$) and dielectric loss tangent (tanδ) of pure XNBR, BN/XNBR, and BN-PCPA/XNBR composites at room temperature. As shown in Figure 7a, the $\varepsilon_r$ is decreased with
increased frequency because the polarization of samples do not match the applied frequency. Moreover, the \( \varepsilon_r \) of BN/XNBR and BN-PCPA/XNBR composites is found to be lower than that of pure XNBR, which can be ascribed to the lower \( \varepsilon_r \) of BN than XNBR.\(^{18}\) The \( \varepsilon_r \) of BN-PCPA/XNBR composites gradually decreases with increasing PCPA modification time. For example, the \( \varepsilon_r \) of the XNBR composite filled with 30 vol% BN-PCPA-3h is 9.5 at 100 Hz, while the \( \varepsilon_r \) of the 30 vol% BN-PCPA-12h/XNBR composite decreases to 8.86 at 100 Hz, as shown in Table 1. One should note that the enhanced interfacial adhesion between the BN-PCPA filler and XNBR matrix limits the orientation polarization of polar groups in XNBR.\(^{37}\) In addition, the \( \varepsilon_r \) of the BN/XNBR composite is found to be smaller than that of BN-PCPA/XNBR composites, which can be ascribed to the inferior compatibility between pristine BN and the XNBR matrix and the presence of defects, decreasing the interface polarization of the composite. Figure 7b shows that the \( \tan \delta \) initially decreases with the increasing frequency followed by a gradual increase. One should note that the major polarization contribution in XNBR composites is rendered by interfacial polarization under low frequencies, whereas the dipolar relaxation becomes the dominant polarization force under high frequencies.\(^{38}\) However, the \( \tan \delta \) of BN-PCPA/XNBR composites remains lower than 0.55 at 10 Hz, which is highly advantageous for electronic devices.

The thermal conductivity of XNBR, BN/XNBR, and BN-PCPA/XNBR composites are presented in Figure 8 and Table 1. It can be seen that the thermal conductivity of BN-PCPA/XNBR composites are higher than the BN/XNBR composite and pure XNBR. As mentioned earlier, the PCPA modification facilitates the dispersion of BN in the XNBR matrix and, in turn, reduces the interfacial thermal resistance, forming an efficient heat conduction network (Figure 9). The decreased phonon scattering and acoustic impedance mismatch at the interface between the conductive filler and polymeric matrix is beneficial for forming the thermal transport in composites. The

Table 1. Mechanical, Dielectric, and Thermal Conductive Properties of Pure XNBR and XNBR Composites

| sample          | dielectric constant (100 Hz) | tensile strength (MPa) | elongation at break (%) | elastic modulus (MPa) | thermal conductivity (W/(m·K)) | \( k^*_{\text{eff}} \) | \( R^*_{\varepsilon} \) |
|-----------------|------------------------------|------------------------|-------------------------|------------------------|-------------------------------|-------------------------|-------------------------|
| pure XNBR       | 12.87                        | 2.59                   | 233.9                   | 2.06                   | 0.162                         | 1.0000                  |                         |
| BN/XNBR         | 8.36                         | 4.32                   | 125.8                   | 15.24                  | 0.355                         | 2.1885                  | 0.02777                 |
| BN-PCPA-3h/XNBR | 9.50                         | 8.20                   | 122.9                   | 14.65                  | 0.362                         | 2.2348                  | 0.02674                 |
| BN-PCPA-6h/XNBR | 9.24                         | 7.25                   | 131.8                   | 14.10                  | 0.364                         | 2.2397                  | 0.02663                 |
| BN-PCPA-9h/XNBR | 9.14                         | 6.65                   | 130.1                   | 13.20                  | 0.375                         | 2.3124                  | 0.02512                 |
| BN-PCPA-12h/XNBR| 8.86                         | 6.54                   | 164.3                   | 10.98                  | 0.399                         | 2.4584                  | 0.02239                 |

Figure 5. SEM images of (a) BN/XNBR, (b) BN-PCPA-3h/XNBR, (c) BN-PCPA-6h/XNBR, (d) BN-PCPA-9h/XNBR, and (e) BN-PCPA-12h/XNBR composites.

Figure 6. Stress–strain curves of pure XNBR and BN-PCPA/XNBR composites.
polar groups in PCPA on the surfaces of BN-PCPA could form strong adhesion with XNBR, thus decreasing the acoustic impedance mismatch and interfacial thermal resistance. Moreover, the thermal conductivity increases with increasing modification time. This phenomenon can be explained by the larger number of polar groups on BN-PCPA platelets, leading to larger interfacial adhesion and lower interfacial thermal resistance, thus resulting in larger thermal conductivity. The maximum thermal conductivity of 0.399 W/(m·K) has been rendered by the BN-PCPA-12 h/XNBR composite, which is 2.5 times of pure XNBR.

To understand the changing of interface thermal resistance between BN platelets and the XNBR matrix, the modified Hashin–Shtrikman model\textsuperscript{39} (eq 1) was used to fit the experimental conductivity coefficient ($k^*_{eff}$) of XNBR composites (Table 1).

$$k^*_{eff} = 1 + H \left\{ \exp \left[ \frac{K (\kappa_1 - 1) \phi_1}{J + \kappa_1 - 1} - 1 \right] \right\}$$

(1)

where $H$ is 0.204, $J$ is 2.8521, $\phi_1$ is the volume fraction of the filler, $\kappa_1$ is the thermal conductivity ratio of the filler to the polymeric matrix, and $K$ is the coefficient associated with the total thermal resistance of polymer composites that is related to following equation

$$K = 13.3347 \exp(-13.2701 R^*_c)$$

(2)

As shown in Table 1, the $R^*_c$ of BN-PCPA/XNBR composites are lower than that of the BN/XNBR composite and the $R^*_c$ of BN-PCPA/XNBR composites decrease with increasing PCPA modification time. The results suggest that the PCPA layer on the surface effectively reduced the interfacial thermal resistance between the BN platelets and XNBR matrix.

3. CONCLUSIONS

In summary, the PCPA was employed to modify the surface of BN and increased the thermal conductivity of BN-PCPA/XNBR composites. The PCPA modification improved the interfacial compatibility between the thermally conductive filler and rubber matrix, led to a good dispersion of BN-PCPA in the XNBR matrix. Moreover, the thermal conductivity of BN-PCPA/XNBR composites increased with increasing modification time due to the reduced interfacial thermal resistance and formation of a heat conduction network. The maximum thermal conductivity of 0.399 W/(m·K) has been rendered by BN-PCPA-12 h/XNBR composites, which was about 2.5 times of pure XNBR. This work provides an easy route to develop polymer composites with a relatively high thermal conductivity and high dielectric constant for potential application in practical electronic packaging.

4. METHODS

4.1. Materials. BN platelets (3 μm) were obtained from Beijing Huake Chemical Co., Ltd. (China). XNBR was purchased from Zeon Chemicals Yonezawa Co., Ltd.
Other reactants were obtained from the Beijing Chemical Plant (China).

4.2. BN-PCPA/XNBR Composite Preparation. BN-PCPA platelets were prepared by dispersing 4 g of BN into 100 mL of deionized (DI) water, and Tris–HCl was used to adjust the pH to 9.5. Then, 0.5 g of catechol and 1.5 g of tetraethylpentamine (TEPA) were added into the above reaction system and mechanically stirred for 3, 6, 9, or 12 h at 40 °C. Once the reaction was completed, the modified BN was filtered and dried in a vacuum oven.

Then, XNBR composites were fabricated by mixing 98 g of BN or BN-PCPA platelets and 222 g of XNBR emulsion with a solid content of 45 wt % by using the emulsion co-coagulation method with the content of BN or BN-PCPA filler (30 vol%). The largest amount of the filler was 30 vol% because the higher content of the filler made the entire system become viscous, which restricted the movement and orientation of BN-PCPA in the composites and decreased the flexibility of polymer composites, thus limiting their wide application as thermal management materials. Afterward, a certain content of a dicumyl peroxide curing agent was uniformly mixed into XNBR composites through a double-roll open mill. After 8 h, the as-prepared compound was vulcanized at 160 °C to obtain cured composites.

4.3. Material Characterization. Thermogravimetric analysis (TGA) was performed on TA SDT650 thermal analysis mass spectrometry under nitrogen. The surface composition of BN and BN-PCPA was conducted via an X-ray photoelectron spectroscopy (XPS, Thermo Electron Corporation) system by using ESCALAB 250. Scanning electron microscopy (SEM; FEI Quatro S field-emission microscope) and high-resolution transmission electron microscopy (HR-TEM; Hitachi H9000 microscope) were utilized to observed the microstructure of samples. An Instron 3366 tensile apparatus was used to measure the stress—strain curves at a speed of 50 mm/min. The elastic modulus values of samples were determined by the slopes of stress—strain curves at 10% strain. The dielectric behavior of composites was determined by using a broadband dielectric spectrometer (Novocontrol, Alpha-A, GmbH Germany). The thermal conductivity of the sample with a diameter of 20 mm and a thickness of 1 mm was characterized via a DRL-III flat thermal conduction instrument (Xiangtan, China). The following equation was as follows

\[
\lambda = \frac{-Q\Delta X}{A\Delta T}
\]

(3)

where \(\lambda\), \(Q\), \(X\), and \(A\) were the thermal conductivity W/(m-K), heat flux (W), thickness (m), and area (m²) of the samples, respectively. \(\Delta T\) was the temperature difference.

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**Notes**

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