Research Article

Thermally stable polymer–ceramic composites for microwave antenna applications

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Abstract: Polymer–ceramic composites were prepared by twin screw melt extrusion with high-density polyethylene (HDPE) as the matrix and polystyrene-coated BaO–Nd_2O_3–TiO_2 (BNT) ceramics as the filling material. Interestingly, the incorporation of polystyrene (PS) by the coating route could significantly improve the thermal behaviors of the composites (HDPE–PS/BNT), besides the temperature stability of dielectric properties and thermal displacement. The microwave dielectric properties of the composites were investigated systematically. The results indicated that, as the volume fraction of BNT ceramic particles increased from 10 to 50 vol% in the composites, the dielectric constant increased from 3.54 (9.23 GHz) to 13.14 (7.20 GHz), which can be beneficial for the miniaturization of microwave devices; the dielectric loss tangent was relatively low (0.0003– 0.0012); more importantly, the ratio of PS to HDPE increased accordingly, making the composite containing 50 vol% BNT ceramics have a low value of temperature coefficient of resonant frequency ($\tau_f = -11.2$ ppm/℃) from −20 to 60 ℃. The GPS microstrip antennas were therefore designed and prepared from the HDPE–PS/BNT composites. They possessed good thermal stability ($\tau_f = 23.6$ ppm/℃) over a temperature range of −20 to 60 ℃, promising to meet the requirements of practical antenna applications.

Keywords: polymer–ceramic composites; microwave dielectric properties; thermal stability; GPS antenna

1 Introduction

For the practical use of antennas at high frequencies, dielectric materials are required to have a high dielectric constant (ε_r) for miniaturization, a low dielectric loss ($\tan\delta$) to facilitate the signal integrity, and a near-zero temperature coefficient of resonant frequency (τ_f) against temperature change [1,2]. Currently,

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commercial microwave ceramics usually have ε_r of 10–120, low $\tan\delta$, and near-zero τ_f. However, they are fragile and need high sintering temperature, making the processing difficult and raising the cost [3,4]. Therefore, they have been only used in a few fields, such as antennas for vehicle mounted GPS, resonators for base station, electronic filters, and so on. Polymers, such as polytetrafluoroethene (PTFE) and high-density polyethylene (HDPE), have low dielectric loss, high flexibility, and simplified process. Also, they have been predominantly used for microwave packaging and

substrates. Nevertheless, their low ε_r (< 3 at 10 GHz) limits the miniaturization for antennas. Polymer–ceramic composites of 0–3 connectivity have high ε_r, low $\tan\delta$, and high elasticity; more importantly, they can be processed easily [5–8]. They have been widely used as commercial microwave substrates and mini-antennas, such as some products from Rogers and Taconic [9]. However, the values of the temperature coefficient of dielectric constant (τ_{ε_r}) of polymer matrixes, such as PTFE and HDPE, are still very high. In fact, they are very sensitive to temperature change. So, directly compositing ceramics with such one type of composite matrixes (PTFE or HDPE) would make the materials have poor thermal stability [10,11]. The corresponding antennas cannot be used outdoor except extra temperature compensating circuits added, which greatly limits the applications of polymer–ceramic composites in the preparation of outdoor antennas.

Among the composite matrixes, both HDPE and polystyrene (PS) have excellent microwave dielectric properties, and more importantly, they exhibit opposite signs of τ_{ε_r}. Thus, thermally stable composites could be achieved by using HDPE and PS together. Herein, Bi substituted BNT in BaO–Nd$_2$O$_3$–TiO$_2$ system was chosen as the ceramic filler because it has a high dielectric constant of 88, a low dielectric loss of < 0.0005, and a τ_f of 0±5 ppm/℃ [12,13]; while HDPE was selected as the basic matrix. Then, a coating route with the incorporation of polystyrene (PS) was designed to improve the thermal behaviors of the composites. Specifically, the BNT particles were coated with PS through the liquid phase coating process, and the PS-coated BNT ceramics were used as the filling material. The polymer–ceramic composites were prepared from PS-coated BNT ceramics and HDPE through twin screw melt extrusion. The as-prepared composites showed high dielectric constant, low dielectric loss, high thermal stability, and good mechanical property. They are beneficial for the use in RFID (radio frequency identification) antennas (900 MHz, 2.4 GHz), satellite navigation antennas for GPS and Compass (1.575 GHz, 1.268 GHz), wireless broadband antennas (2.4 GHz, 5.8 GHz), and so on.

2　Experimental procedure

Polymer–ceramic composites were prepared by the PS-coated BNT ceramic particles, and followed by the twin screw melt extrusion with HDPE. Analytically pure BaCO$_3$, Nd$_2$O$_3$, TiO$_2$, and Bi$_2$O$_3$ (Chinese Medicine Group Chemical Reagent Co., Ltd.) were used as the raw materials to prepare BNT ceramics through conventional solid-state reaction route. Firstly, BaCO$_3$, Nd$_2$O$_3$, Bi$_2$O$_3$, and TiO$_2$ powder was weighed in stoichiometric proportion (BaNd$_{1.76}$Bi$_{0.24}$Ti$_5$O$_{14}$) and then milled for 6 h. The slurry was dried and calcined at 1100 ℃ for 3 h. The calcined powder was finely ground, and sintered at 1280 ℃ for 4 h. Then, the zirconia balls were used as grinding media and the ball to powder ratio was 15:1. The sintered powder was ground with a high energy ball mill for 30 min at 1500 rpm. After drying and sieving with a 120 mesh screen, the obtained BNT powder was then mixed with 2 wt% tetraethylbutane, and aged for 24 h to improve its compatibility with organic polymers. PS (DOW Chemical Co., USA) was dissolved in dimethylbenzene at 85 ℃. The prepared BNT powder was added to dimethylbenzene at 85 ℃, ultra-sonicated for 10 min, and mixed with the PS solution. The mixture of PS and BNT was stirred at 85 ℃ for 20 min and evaporated at 120 ℃ to dryness, and then ground and sieved through a 60 mesh screen to obtain PS-coated BNT powder. To ensure the composites to have good formability and higher content of PS (to compensate τ_f for the composites), the volume ratio of PS to BNT was fixed to 4:6.

The HDPE/PS-coated BNT (HDPE–PS/BNT) composites were prepared from HDPE (LG Chemistry Co., R. O. Korea) and PS-coated BNT powder (10–50 vol% BNT) by conical twin-screw extruder (HAAKE MINICTW, Germany) at 180 ℃ with 30 rpm. Wafers with a diameter of 70 mm and a thickness of 1 mm were prepared by compressing the composites at 200 MPa and 220 ℃ for 30 min. They were polished for further use. The volume fraction of the individual ingredients in the HDPE–PS/BNT composites is listed in Table 1.

Table 1　Volume fraction of the individual ingredients in the HDPE–PS/BNT composites

	BNT (vol%)	PS (vol%)	HDPE (vol%)	PS:HDPE
1	10	6.7	83.3	1:12
2	20	13.3	66.7	1:5
3	30	20.0	50.0	1:2.5
4	40	26.7	33.3	1:1.25
5	50	33.3	16.7	1:0.5

The phase compositions of the prepared HDPE–PS/BNT composites were characterized by X-ray diffraction (XRD) analysis with Cu Kα radiation (Rigaku D/Max-2500, Tokyo, Japan). The morphologies of the composites were observed with a scanning electron microscope (SEM; JEOL-JSM 6301F, Tokyo, Japan). Their enthalpies of phase transition were measured with a differential scanning calorimeter (DSC; DSC200F3, Netzsch, Germany). The microwave dielectric properties of the composites were measured by split cylinder resonator method. The dielectric properties of the composites at 1 GHz frequency were determined with an RF impedance/material analyzer (E4991A, Agilent, Santa Clara, CA, USA). The thermal expansion coefficients of the composites in the temperature range of 30–90 ℃ were measured with a thermomechanical analyzer (Dil402 PC, Netzsch, Germany). Density was measured by drainage method. The performances of the antennas prepared from the HDPE–PS/BNT composites were evaluated with a network analyzer (HP8720ES, Hewlett-Packard, Santa Rosa, CA, USA).

3 Results and discussion

Figure 1 shows the XRD patterns of the HDPE–PS/BNT composites with 0, 10, 30, 50 vol% BNT powder. It indicates that the sample with no BNT exhibits pure phase corresponding to HDPE. With BNT particles, the composites are mainly indexed to HDPE and $BaNd_2Ti_5O_{14}$ phases, and the $BaNd_2Ti_5O_{14}$ refraction peaks increase with the increasing BNT content.

The SEM images for backscattered electron of composites containing 10, 20, 30, and 50 vol% BNT

Fig. 1 XRD patterns of the HDPE–PS/BNT composites containing (a) 0, (b) 10, (c) 30, and (d) 50 vol% BNT.

particles are shown in Fig. 2. It can be seen clearly that BNT particles with size of 0.5–3 μm are uniformly distributed in the composites. HDPE and BNT are tightly combined with a clear interface, and any apparent pores cannot be observed, indicating a uniform microstructure of the composites. It indicates that the ultra-sonication processing and PS coating could effectively improve the dispersiveness of BNT particles into HDPE matrix. For example, as shown in the SEM images, the composite particles with size over 10 μm are barely observed even in the composite containing 50 vol% BNT.

DSC analysis of endothermic and exothermic processes can be used to qualify and quantify the relationship between temperature and structural transition. PS is amorphous, and no crystallization and melting peaks can be observed in its DSC curve (Fig. 3), while the crystalline polymer HDPE shows an endothermic peak at 132.5 ℃. The HDPE–PS/BNT composites containing 10, 30, and 50 vol% BNT also show endothermic peaks at such equivalent temperature, and the intensity of the endothermic peaks decreases with the increase of BNT content. This implies that the crystalline behavior of HDPE cannot be largely influenced by the ceramic particles or PS phase.

Table 2 lists the experimental and calculated enthalpies of fusion for the HDPE–PS/BNT composites containing different amounts of BNT. The calculated results can be obtained by multiplying the HDPE weight fraction in the HDPE–PS/BNT composites by 183.1 J/g that is the experimental enthalpy of pure HDPE. It shows that the experimental results are well consistent with the calculated ones. These results indicate that the composites maintain good crystalline of HDPE, and they primarily consist of two phases with HDPE as the matrix and PS mainly coated on the surfaces of BNT particles.

Figure 4 shows the experimental and calculated dielectric constants of HDPE–PS/BNT composites at about 10 GHz. Here, Lichtenecker equation (Eq. (1)) and the effective medium theory (EMT, $n = 1.6$, Eq. (2)) model are used to calculate the dielectric constants of HDPE–PS/BNT composites. The corresponding equations are given as follows:

$$\log \varepsilon_c = v_f \log \varepsilon_f + v_m \log \varepsilon_m \tag{1}$$

$$\varepsilon_c = \varepsilon_m \left[1 + \frac{v_f (\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n v_m (\varepsilon_f - \varepsilon_m)} \right] \tag{2}$$

where ε_c, ε_f, and ε_m are the dielectric constants of
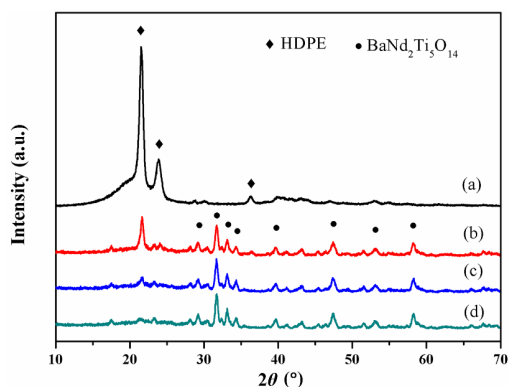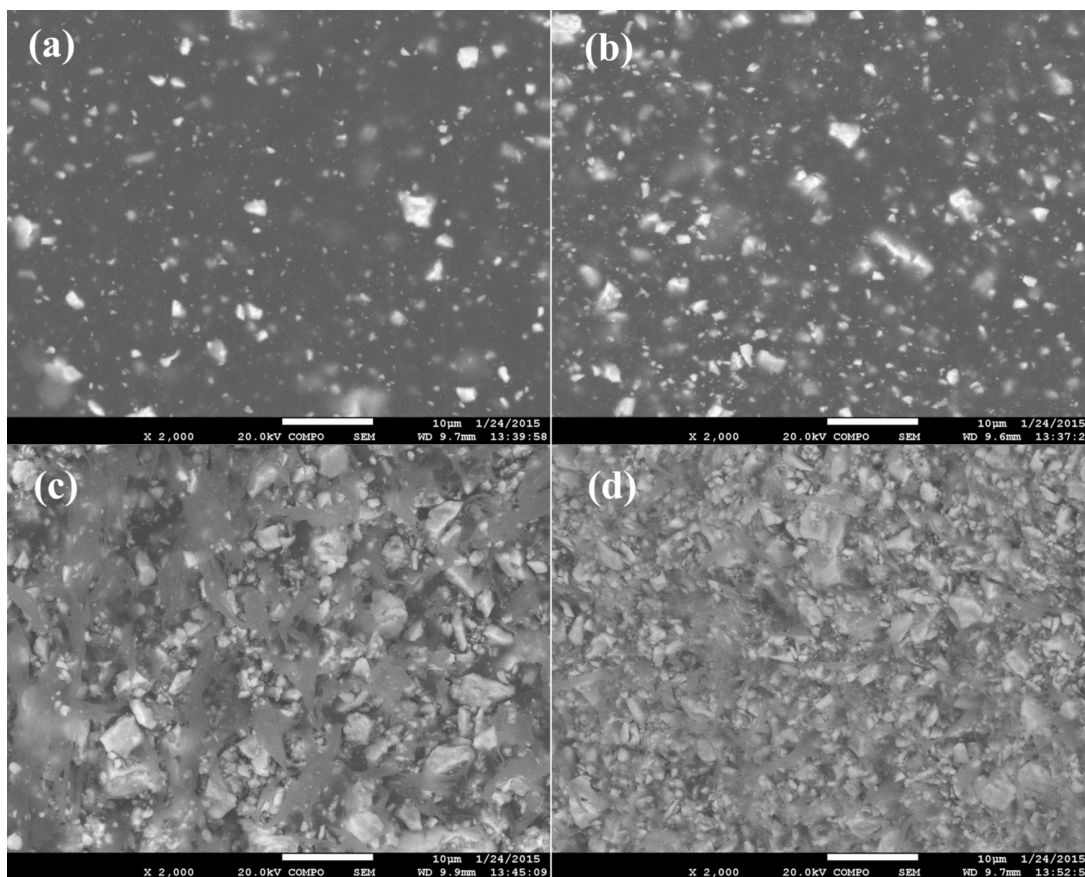
Fig. 2 SEM images of the HDPE–PS/BNT composites containing (a) 10, (b) 20, (c) 30, and (d) 50 vol% BNT.
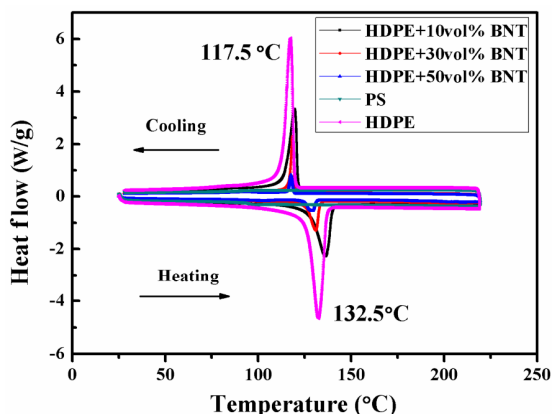
Fig. 3 DSC curves of HDPE, PS, and HDPE–PS/BNT composites containing 10, 30, and 50 vol% BNT.
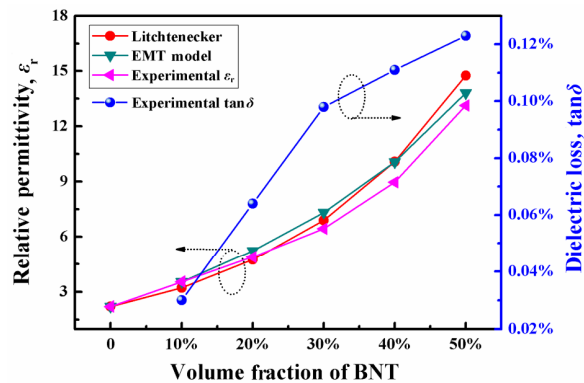

Fig. 4 Comparison of experimental dielectric constant with different theoretical model and variation of dielectric loss of HDPE–PS/BNT composites with different BNT volume fractions.

Table 2   Experimental and calculated enthalpies of fusion of HDPE, PS, and the HDPE–PS/BNT composites containing 10, 30, and 50 vol% BNT (Unit: J/g)

	HDPE	10 vol% BNT	30 vol% BNT	50 vol% BNT	PS
Experimental	183.1	100.6	32.1	9.7	0
Calculated	183.1	100.7	36.2	8.5	0

the composites, BNT, and HDPE, respectively; v_f and v_m are the volume fractions of BNT and HDPE, respectively; n is the correction factor to compensate for

the shape of the fillers used in polymer–ceramic composites [1]. It is clear that the calculated results of the composites with low BNT contents are consistent with their corresponding experimental results. For the composites with high BNT contents, the calculated values are higher than their experimental results. It can be explained that, in those simulation models, the round ceramic particles are ideally suspected to distribute

uniformly within the composites [14]. However, the aggregation is increased with the increase of BNT content, leading to the reduction of the interaction between polymer and BNT. So the inner structure of the composites is derived from the modeling structure. As the BNT fraction increases from 10 to 50 vol% (Fig. 4), the dielectric constants of the composites increase from 3.54 (9.23 GHz) to 13.14 (7.20 GHz), while the dielectric losses increase from 0.0003 to 0.0012. As discussed above, the PS coating of BNT can improve the interaction between the polymer and BNT, and reduce deficiencies such as pores, resulting in a low dielectric loss. Therefore, the dielectric loss of the composites containing high amounts of BNT is still very low.

The relation between frequency and dielectric constant is one of the main aspects for the composites used in high frequencies. Figure 5 shows the variation of dielectric constant of the composites containing different amounts of BNT in the frequency range of 10 MHz to 1 GHz. It can be clearly seen that the dielectric constants of all composites containing 10–50 vol% BNT almost remain sturdy within the ramping frequency, indicating that composites have stable frequency performance. These materials would have good applications in high frequencies.

Figure 6 shows the temperature dependence of dielectric constant of HDPE and PS at 1 GHz over a temperature range of −40 to 100 ℃. At the initial ramping temperature of −40 ℃, they possess similar dielectric constants. With the increase of temperature (−20 to 60 ℃), HDPE and PS exhibit different temperature dependences: the dielectric constant of HDPE decreases, while that of PS increases. The τ_{ε_r}
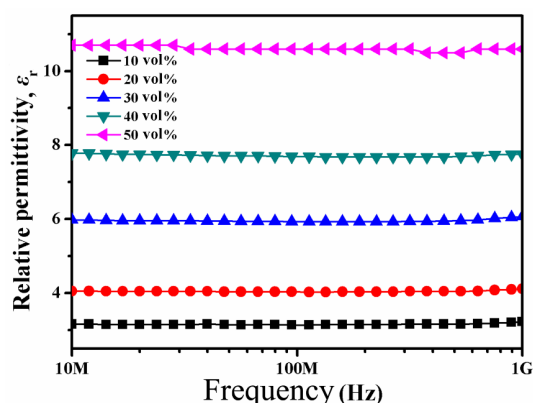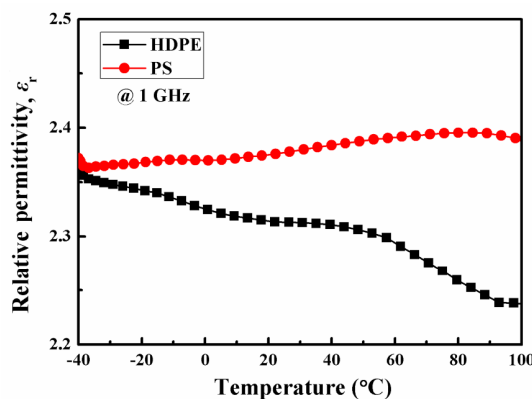

Fig. 6 Temperature-dependent dielectric constant of HDPE and PS at 1 GHz.

values of HDPE and PS are therefore determined to be −278 ppm/℃ and 124 ppm/℃, respectively. With the increasing temperature, the polymers (HDPE) expand due to their high expansion coefficients. In fact, the number of the polarized groups per volume would be decreased as the expansion of the polymers, which could possibly induce the decrease of dielectric constant consequently. Thus, the dielectric constant of HDPE decreases with increasing temperature. The dielectric constants of PTFE and PP show similar changes with the increase of temperature. Although only limited free charges could be produced in PS backbone stimulated by the increasing temperature, a large amount of charge carriers would be induced by the impurity ionization and chemical bond breaking of its phenyl rings, leading to a high electron density. In addition, the phenyl rings can reduce the resistance to electron mobility, providing a channel for electron mobility. Therefore, the increase of the electric dipole moment caused by the phenyl rings suppresses its decrease with respect to the thermal expansion. The dielectric constant of PS mainly shows an increase with the increasing temperature. Also, the dielectric constant of epoxy has a similar relationship with temperature [15].

The temperature dependence of dielectric constant of substrate materials can significantly affect the performance of antennas. Figure 7 shows the variation of dielectric constant at 1 GHz with temperature for the composites containing different amounts of BNT, over a temperature range of −40 to 160 ℃. As the BNT content increases from 10 to 50 vol%, the dielectric constant of the composites remains stable at temperatures lower than 80 ℃. For example, the dielectric constant of the HDPE–PS/BNT composite containing 50 vol% BNT
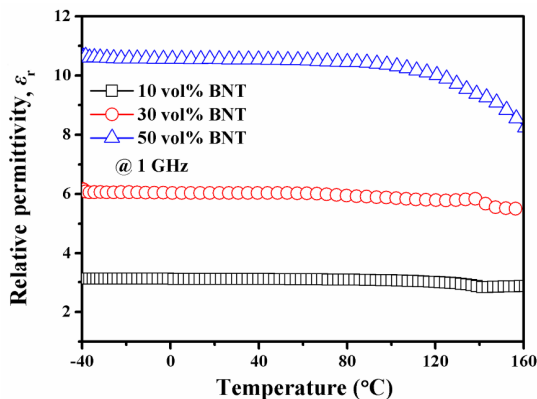

Fig. 5 Variation of dielectric constant of the composites containing different amounts of BNT in the frequency range of 10 MHz to 1 GHz.

Fig. 7 Variation of dielectric constant for the composites with 10, 30, and 50 vol% BNT at 1 GHz over a temperature range of −40 to 160 ℃.

slightly decreases from 10.575 to 10.510 as the temperature increases from −20 to 60 ℃, resulting in a τ_{ε_r} of −76.8 ppm/℃. These results indicate that the composites have better thermal stability than the conventional polymer–ceramic composites that usually have a very high temperature coefficient of dielectric constant. In addition, PS and HDPE, as the two independent phases, can complement each other in the temperature coefficient of dielectric constant.

Figure 8 shows the thermal displacement curves of PS and HDPE–PS/BNT composites over a temperature range of 30–90 ℃. It has been reported that the displacement of HDPE occurs at about 60 ℃; however, its melting point is as high as 130 ℃. This behavior can affect the thermal stability of HDPE/BNT composites. PS has a large phenyl ring backbone, which can avoid rotation and displacement at temperatures below its glass transition temperature. Therefore, PS has better mechanical property and strength. As shown in Fig. 8, the glass transition temperature of PS is at about 80 ℃.
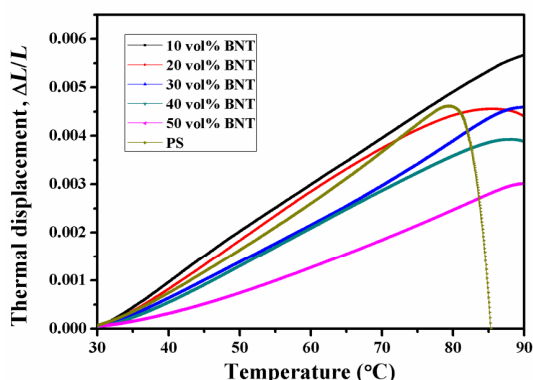

Fig. 8 Thermal displacement of the composites containing various amounts of BNT over a temperature range of 30–90 ℃.

Therefore, no displacement occurs to HDPE–PS/BNT composites at temperatures lower than 80 ℃. PS is located near the interfaces between ceramic particles and polymer. This configuration of interfaces can significantly affect the thermal properties of the composite materials. In addition, the thermal expansion coefficient of the composites decreases with the increase of BNT content, which is favorable to its thermal stability.

In general, for a substrate material used in antennas, the temperature coefficient of resonant frequency (τ_f) is the key factor for the thermal property of the devices. The τ_f value of a linear microwave dielectric material can be calculated with Eq. (3):

$$\tau_f = -\left(\alpha_L + \frac{\tau_{\varepsilon_r}}{2} \right) \tag{3}$$

where α_L is the linear thermal expansion coefficient of the material. For the composite containing 50 vol% BNT shown in Fig. 6, τ_{ε_r} is 76.8 ppm/℃ over a temperature range of −20 to 60 ℃. Its α_L value is about 49.6 ppm/℃ (Fig. 8). Therefore, using Eq. (3), the calculated τ_f is −11.2 ppm/℃, meeting the primary requirement of microwave antenna materials. The HDPE–PS/BNT composite containing 50 vol% BNT has a high dielectric constant and a small value of τ_f, which can facilitate the miniaturization and thermal stability of antennas.

GPS microstrip antenna has been widely used due to its simple and low-cost fabrication process [16,17]. In order to demonstrate the feasibility of the as-prepared composites for antenna substrates, the GPS microstrip antennas were designed from the composite containing 50 vol% BNT by Ansoft HFSS. The size of substrates used in antennas is 35 mm × 35 mm × 4 mm with two sides coated with Cu foil as the electrodes. Figure 9 shows the images of a prototype antenna, and the geometric dimensions of ground plane (a) and emitting surface (b) are also given. The S_{11} curves of the designed GPS antenna were measured at different temperatures, and the results are shown in Fig. 10. The resonant frequency of the antenna at 20 ℃ (room temperature) is 1.591 GHz. As can be seen, the resonant frequency slightly changes from 1.590 to 1.593 GHz as the temperature increases from −20 to 60 ℃, exhibiting excellent thermal stability. Its τ_f is +23.6 ppm/℃, meeting the requirement for antennas (0±30 ppm/℃). The composite has good potential in the outdoor
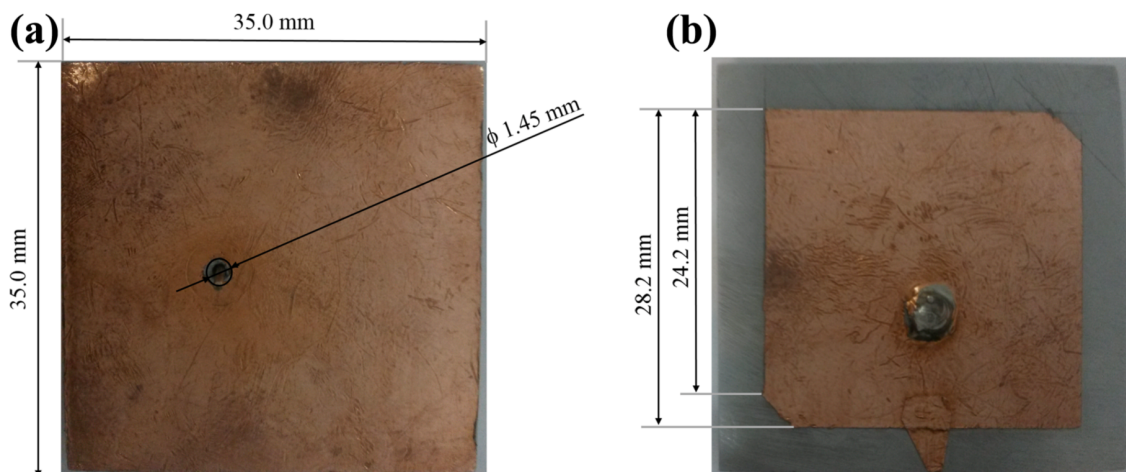
Fig. 9   (a) Ground plane and (b) emitting surface of the designed GPS antenna.
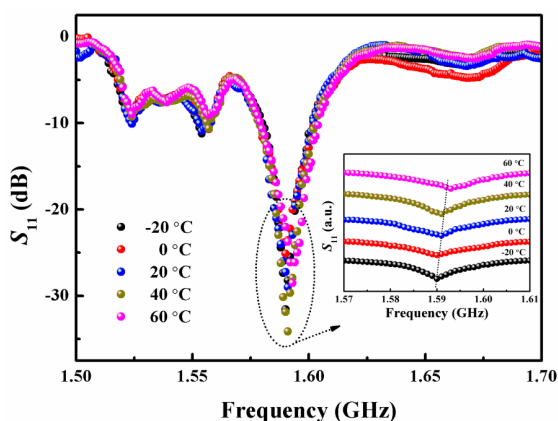

Fig. 10 S_{11} curves of GPS antenna at different temperatures. The inset shows the details of resonant frequency.

environments without extra temperature compensating circuits added at various temperatures.

4   Conclusions

The twin screw extrusion of PS-coated BNT ceramic powder and HDPE improved the interfaces between the polymer and ceramics, which resulted in composites with high dielectric constant, low dielectric loss, and good thermal stability. The dielectric constant and dielectric loss of the HDPE–PS/BNT composite containing 50 vol% BNT at 7 GHz were 13.14 and 0.0012, respectively. GPS antennas were prepared with the HDPE–PS/BNT composite containing 50 vol% BNT as the substrate. Its temperature coefficient of resonant frequency remained at +23.6 ppm/℃ over a temperature range of −20 to 60 ℃, meeting the requirements for outdoor antennas. The HDPE–PS/BNT composites are temperature-stable with high relative permittivity. Also, they are easy to fabricate for promising candidates in the design of antennas.

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