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Study on properties of ultra-low dielectric loss mPPO/MTCLT composites prepared by injection molding

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A novel category of polyphenylene oxide/high-impact polystyrene (PPO/HIPS) alloy was used as the polymer matrix (abbreviated as mPPO) and loaded with different volume fractions (0, 10, 20, 30, 40, 50 vol.%) of $MgTiO_3$–$Ca_{0.7}La_{0.2}TiO_3$ (abbreviated as MTCLT) ceramics to prepare composites by injection molding. Its micromorphology, density, dielectric, thermal and mechanical properties were analyzed in detail. The experimental results show that the composites possess a compact microstructure because HIPS increases the fluidity of PPO. Due to the excellent dielectric properties of both mPPO and MTCLT, the composites have an extremely low dielectric loss. The realization of the high ceramic filler fraction greatly limits the thermal expansion of the polymer chain by introducing the interphase, so that the coefficient of thermal expansion of the composite material could be as low as 21.8 ppm/°C. At the same time, the presence of ceramic particles could reinforce the mechanical property of the composites. When the ceramic filler fraction is higher than 20 vol.%, the bending strength of the composite material is around 110 MPa. When the ceramic filler fraction is 40 vol.%, the composite possesses the best comprehensive performance. The dielectric constant is 6.81, the dielectric loss is 0.00104, the thermal expansion coefficient is as low as 25.3 ppm/°C, and the bending strength is 110.4 MPa. Due to its excellent properties, this material can be a good candidate in the field of microwave communication.

Keywords: Injection molding; composites; dielectric properties; polyphenylene oxide alloy.

1. Introduction

With the advent of the 5G, network communications have developed rapidly. Electronic devices are developing rapidly towards miniaturization and integration which requires electronic materials with tunable dielectric constants and extremely low dielectric losses.[1–3] Because a high dielectric constant (ε_r) could minimize the sizes of devices, a low-dielectric constant could fasten the transition speed and a low dielectric loss (tanδ) could increase the SNR value of devices. Although traditional dielectric ceramics have excellent dielectric properties, their brittleness greatly limits their application. Polymer matrix composites (PMCs) are composite materials composed of dielectric ceramics and polymers, which have both excellent dielectric properties of ceramics and high reliability of polymers.[4–6]

At this stage, low dielectric loss PMCs have received extensive attention from researchers. Thomas[7] investigated the dielectric properties of polytetrafluoroethylene (abbreviated as PTFE)/$Sm_2Si_2O_7$ composites, a low-dielectric constant of 3.92 and a low-dielectric loss of 0.0054 can be obtained when the volume fraction of ceramics was 40 vol.%. They[8] used nanoceramics to compound with PTFE, when the volume fraction of ceramics reached 25 vol.%, a low dielectric constant of 3.39 and a dielectric loss of 0.0315 can be obtained. According to Sasikala's report,[9] a PTFE-based composite possessed optimal dielectric properties (ε_r = 3.2, tanδ = 0.009) when loaded with 50 vol.% Mg_2SiO_4. Yuan[10] chose Si_3N_4 as the filler and PTFE as the matrix, when the filler volume fraction reached 62 vol.%, the composite possessed a dielectric constant of 4.03 and a low dielectric loss of 0.0014. Yao[11] reported that the PTFE-based composite was filled with 42.8 vol.% $(Na_{1/2}Nd_{1/2})TiO_3$ exhibited a dielectric constant of 9.45 and a dielectric loss of 0.0024. In our previous work,[12] PTFE was used to load $MgTiO_3$ ceramics with different particles sizes, a composite with a dielectric constant of 5.5 and an ultra-low dielectric loss of 0.00027 had been obtained.

The above researches show that PTFE is often used as the polymer matrix of composites, mainly because the structure of PTFE is highly symmetrical which gives PTFE an ultra-low-dielectric constant and dielectric loss.[13] Nevertheless, the highly symmetrical structure of PTFE without a branched-chain makes it possess a low viscous, low bending strength and difficult to prepare composites with a high ceramic filling ratio. At the same time, PTFE also has some disadvantages, such as high viscosity, high glass

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transition temperature, large coefficient of thermal expansion and so on. To further improve the electrical and thermal properties of composites, a polymer matrix with better properties is of great significance for the further development of dielectric composite materials.

Compared with PTFE, based on our own experiments, polyphenylene oxide (PPO) has a low-dielectric constant (2.6) and low-dielectric loss (0.0014) because its molecular chain also does not show large polarity. Thus, PPO is an engineering plastic with excellent dielectric performance. Moreover, because its main chain contains a large number of phenolic aromatic rings and two methyl groups close to the active points of two adjacent positions on the phenolic group, the molecular chain has high rigidity and high cohesion between molecules. In addition, the oxygen atom and the benzene ring are in the p-π conjugate state, so the flexibility provided by the oxygen atom is greatly reduced by the influence of the benzene ring. Therefore, PPO has high thermal stability and chemical corrosion resistance. Due to the high rigidity and strong interforce between the PPO molecular chains, PPO is difficult to deform under force, showing high mechanical strength, elastic modulus and outstanding creep resistance.[14–18] However, pure PPO has high viscosity at high temperatures and is difficult to compound with ceramics.[19] Therefore, HIPS with a low melting point and low viscosity is needed to form alloy for modification.

In this paper, we prepared three alloys and analyzed them. Then, we choose the PPO:HIPS = 2:1 alloy (abbreviated as mPPO) as the matrix and $MgTiO_3$-$Ca_{0.7}La_{0.2}TiO_3$ (abbreviated as MTCLT) ceramics with low- dielectric loss as the filler. The mPPO/MTCLT composites with different ceramic ratios were prepared by the extrusion method, and their electrical, thermal and mechanical properties were deeply studied.

2. Material and Methods

2.1. *Preparation of the PPO/HIPS alloy*

The polyphenylene oxide/high-impact polystyrene (PPO/HIPS) alloys were prepared by mechanical blending. The raw materials PPO and HIPS resin were weighted according to the volume ratio and then mixed by screw extruder pelletizer at 265°C. Afterward, we had analyzed them and chose the PPO:HIPS = 2:1 alloy as the polymer matrix.

2.2. *Preparation of mPPO/MTCLT composites*

The raw powders MgO (99.9%), CaO (99.9%), La_2O_3 (99.9%), and TiO_2 (99.9%) were mixed through a certain stoichiometric ratio. First, the raw powders were ball-milled with deionized water for 2 h to ensure full mixing, then the powders were dried at 110°C for 4 h and calcined at 1150°C for 4 h. After that, the calcined powders were ball-milled for 2 h and dried again. The dried calcined powders were granulated and sintered at 1350°C for 4 h to obtain MTCLT ceramic phase. Based on our previous experiments, the fine powders are easy to agglomerate and large powders are easy to settlement, the powders with a particle size around 10–20 μm
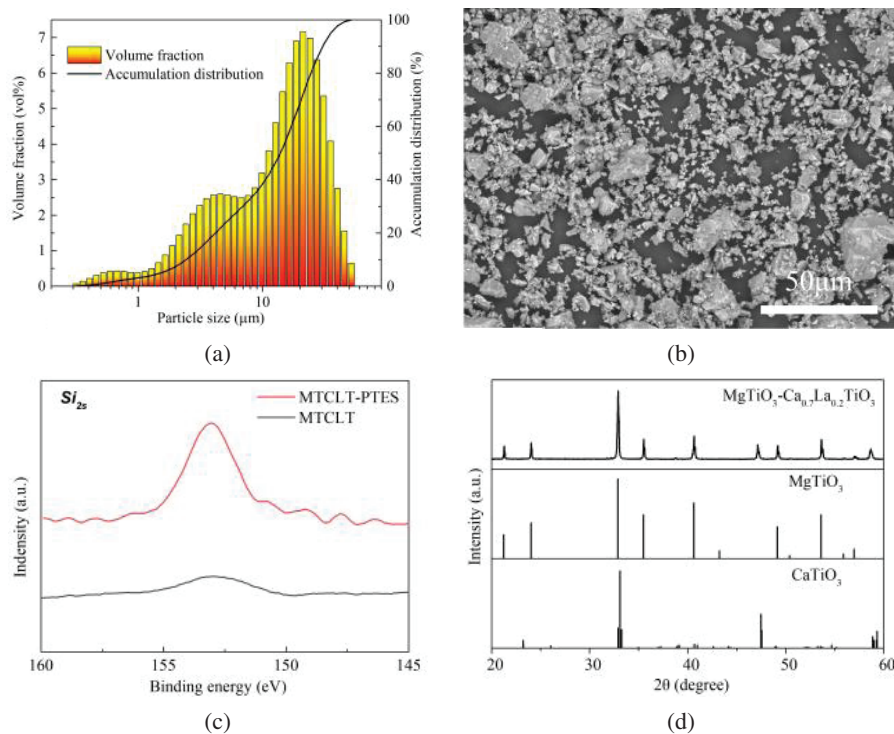

Fig. 1. Characterizations of the MTCLT ceramic powders: (a) Particle size distribution curve; (b) SEM image; (c) XPS spectra of MTCLT before and after surface-modified and (d) XRD patterns.

would be a good choice. Thus, the sintered ceramics were ball-milled again until the D_{50} reduce to 15 μm with a specific area of 975.6 m²/kg. The particle size distribution and micro-morphology are shown in Figs. 1(a) and 1(b), respectively. Since the ceramic powders are obtained by the impact and destruction of the ceramic block by zirconium ball, their geometric morphology is irregular polygon. Moreover, there are no obvious pores on the surface of ceramic powders, indicating that the ceramic block is compact, which is conducive to reduce the porosity of the composite. To improve the adhesion between the two phases, the surface of MTCLT ceramic powders was modified by phenyltriethoxysilane (abbreviated as PTES). The XPS spectra before and after modification are shown in Fig. 1(c). The results show that PTES was successfully bonded to the ceramic surface. Finally, the modified ceramic powders and mPPO are mixed by screw extruder pelletizer, following injecting, and demolding at 180°C to form mPPO/MTCLT composites.

2.3.　*Characterizations*

The particle size of the powders was measured by a laser particle size analyzer (Malvern 3000). The ceramic phase was determined by an X-ray diffractometer (D8 ADVANCE). The surface element analysis of ceramic powders was determined by X-ray photoelectron spectroscopy (ESCAlab250). The micro-morphology of the powders and composites was observed by scanning electron microscope (Magellan 400). The density of the material was calculated by the Archimedes method. The dielectric properties of the materials were tested by a split post-dielectric resonator (abbreviated as SPDR) with a vector network analysis (Agilent E8362B). The coefficient of thermal expansion (abbreviated as CTE) was measured by dilatometer (Netzsch DIL402C) with a heating rate of 5°C/min from 30°C to 150°C. The glass transition temperature was measured by differential scanning calorimeter (Netzsch DSC 404 C). The bending strength was measured by a universal materials tester (Instron 5566).

3.　Results and Discussion

The properties of the PPO/HIPS alloys are listed in Table 1. We can easily know that the ε_r of PPO is higher than that of HIPS. Since the tan δ of HIPS is much lower than that of PPO, the PPO/HIPS alloys exhibit a relatively lower tan δ than pure PPO. As for other properties, the CTE of PPO is lower than that of HIPS, while the T_g and the bending strength of the PPO are much higher. To sum up, the PPO/HIPS alloys show better superior thermal and mechanical properties while more PPO was loaded in the alloys. When PPO: HIPS = 2:1, the alloy exhibits a similar T_g and CTE to those of PPO, and it also has excellent dielectric and mechanical properties. Thus, we choose the alloy with PPO: HIPS = 2:1 as a matrix and loaded different volume fractions of the MTCLT ceramics.

Table 1.　Properties of the PPO/HIPS alloys.

Alloy	Density (g/cm³)	ε_r	tan δ (×10⁻³)	T_g (°C)	CTE (ppm/°C)	Bending strength (MPa)
HIPS	1.04	2.47	1.0	95	91.0	37.5
PPO: HIPS = 1:2	1.04	2.52	1.2	119	76.9	63.0
PPO: HIPS = 1:1	1.06	2.53	1.3	136	76.4	69.1
PPO: HIPS = 2:1	1.06	2.54	1.4	148	72.3	73.2
PPO	1.08	2.65	4.1	163	71.4	100.1

The XRD result of the MTCLT ceramic fillers is shown in Fig. 1(c). Compared with the $CaTiO_3$ (PDF #42-0423) and $MgTiO_3$ (PDF #06-0494), we can know that the $MgTiO_3$ phase in ceramics exactly matches the PDF standard card. But compared to the standard comparison card, the main peaks of the $CaTiO_3$ phase slightly shifted to a lower angle. This is because the ionic radius of La^{3+} (1.36 Å, CN = 12) is slightly larger than that of Ca^{2+} (1.34 Å, CN = 12). When La^{3+} occupies the position of Ca^{2+}, the crystal lattice expands, and the interplanar spacing increases.

To characterize the densification of the composites, we measured the experimental densities of MTCLT ceramics (ρ_c), mPPO (ρ_p) and the composites (ρ_{exp}). The theoretical density (ρ_{theo}) was calculated by the volume fraction of ceramics (V_f), ρ_c and ρ_p through the following formula[20]:

$$\rho_{theo} = (1 - V_f)\rho_p + V_f\rho_c. \quad (1)$$

The relative density of the composite (ρ_{rel}) was given by the following formula[20]:

$$\rho_{rel} = \rho_{exp}/\rho_{theo}. \quad (2)$$

The experimental and calculated results are shown in Fig. 2. The results show that the densities of composites increase with the increase in ceramic filler fraction. This is because the density of pure ceramics ($\rho_c \sim 3.96$ g/cm³) is much higher than that of pure mPPO ($\rho_p \sim 1.06$ g/cm³). The results show that the relative densities of the composites decrease slightly but are still higher than 99%. The increased porosity is mainly due to the increase of the two-phase interface in the whole system with the increase of ceramic content. Even after surface modification, there are still a few pores in the interface, so the porosity of the composite increases slightly. The experimental results show that the porosity of the composites remains below 1% even if the ceramic filling volume fraction reaches 60%. This is because the main chains of PS are flexible carbon–carbon single bonds whose rotation energy barrier is low. At the same time, the phenyl group on the side chain is a nonpolar group, which has a small interaction force in the molten state and small resistance to the internal rotation of the molecular chain, so it possesses excellent flexibility. Therefore, PS has good fluidity in the molten state.
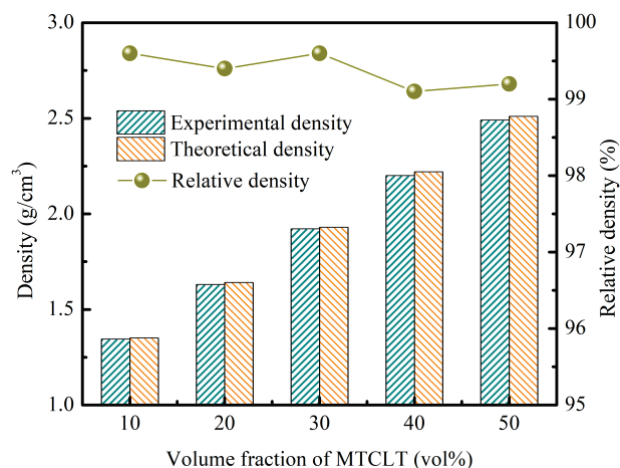
Fig. 2. Theoretical, experimental, and relative densities of the mPPO/MTCLT composites with the variations of volume fractions of MTCLT.

After compounding with PPO, the viscosity of the melt is successfully reduced and the density of the composite material is improved.

To prove the results of the densities test, we observed the micromorphology of the composites under different ceramic filling fractions (0–50 vol.%), and the results are shown in Fig. 3. The ceramic particles were evenly distributed in the mPPO matrix with no obvious agglomeration. This is mainly due to the particle size of powders that we adopted being at the micron level, which has lower surface energy compared to that of the nanopowders, so it is uneasy for the agglomeration to occur. At the same time, the modified mPPO possesses excellent fluidity and can fill the gaps produced by powder stacking, so there are no obvious pores in the composites.

The dielectric constant of the composite determines the size and transmission speed of the device, which is an important index. Therefore, we tested the dielectric constant of ceramics (ε_c), polymer (ε_p) and their composites, and the test results are shown in Fig. 4. To avoid too many experimental iterations, the prediction of the theoretical dielectric constant of composites ($\varepsilon_{\text{theo}}$) is particularly important. The following are several commonly used models. They are as follows:

Maxwell–Wagner model:[21]

$$\varepsilon_{\text{theo}} = \varepsilon_p \frac{2\varepsilon_p + \varepsilon_c + 2V_f(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - V_f(\varepsilon_c - \varepsilon_p)}. \tag{3}$$

Lichtenecker's rule:[22]

$$\ln \varepsilon_{\text{theo}} = (1 - V_f) \ln \varepsilon_p + V_f \ln \varepsilon_c. \tag{4}$$

Effective Medium Theory (EMT) model:[23]

$$\varepsilon_{\text{theo}} = \varepsilon_p \left[1 + \frac{V_f(\varepsilon_c - \varepsilon_p)}{\varepsilon_p + n(1 - V_f)(\varepsilon_c - \varepsilon_p)} \right]. \tag{5}$$

The comparison between the calculated results and the experimental values is shown in Fig. 4. Maxwell–Wagner equation is a classical formula derived from Green's function method. The formula is based on the perturbation effect on the matrix material after particle embedding. Therefore, the properties of filler and polymer matrix cannot be far different. In this system, the dielectric constant of ceramic materials is one order of magnitude different from that of the polymer matrix, resulting in the deviation between the calculated results and the experimental values.[24,25] Lichtenecker's rule is an application of Lichtenecker–Rother formula in a two-phase mixed system. It only considers the effects of the dielectric constant of polymer and ceramics and ceramic volume fraction on composites. In this system, the relative densities of the composites are more than 99%, and the interfacial pores
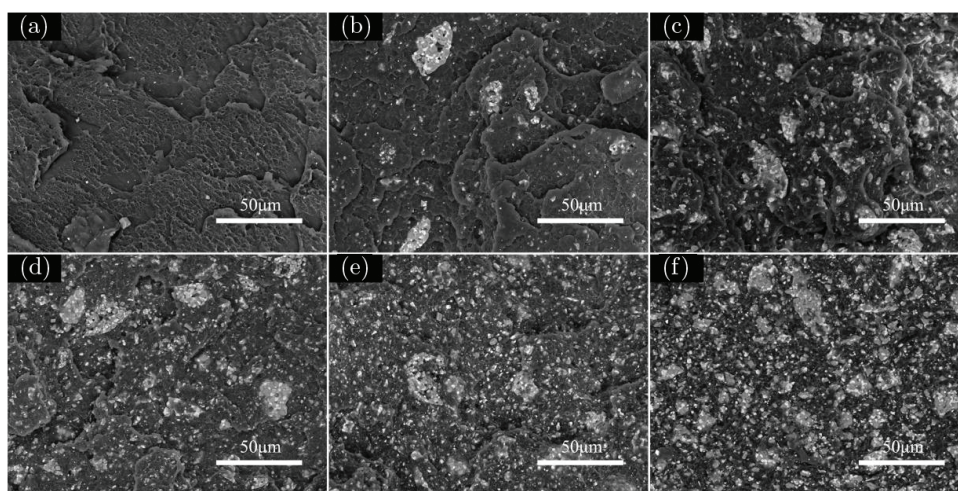

Fig. 3. The cross-sectional SEM images of the mPPO/MTCLT composites loading with (a) 0 vol.%, (b) 10 vol.%, (c) 20 vol.%, (d) 30 vol.%, (e) 40 vol.% and (f) 50 vol.% MTCLT.
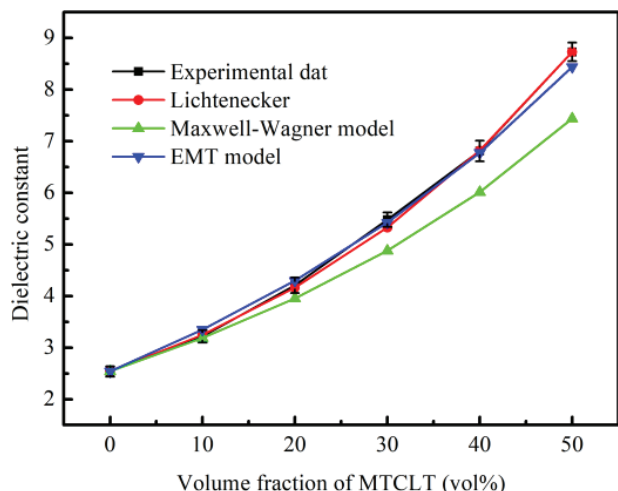
Fig. 4. Experimental and theoretical dielectric constant curves of the mPPO/MTCLT composites with the increasing volume fraction of MTCLT ceramic.

have little effect on the dielectric constant of the composites. Therefore, the formula matches the experimental results well. In contrast, the EMT model uses a morphology factor n, which not only matches the experimental values well but also makes the model have good universality. In this system, n is equal to 0.25, which is higher than the data obtained in the spherical particle system,[26] indicating that the particles are nonspherical, which matches the results observed by the micromorphology.

The dielectric loss of the material is a key parameter that affects the signal transmission quality of the devices. We tested the dielectric loss of composites with different MTCLT ceramic filler fractions (0–50 vol.%) at 10 GHz, and the experimental results are shown in Fig. 5. The results show that the dielectric loss of the composite decreases first and rises after the ceramic filling ratio reaches 50 vol.%.
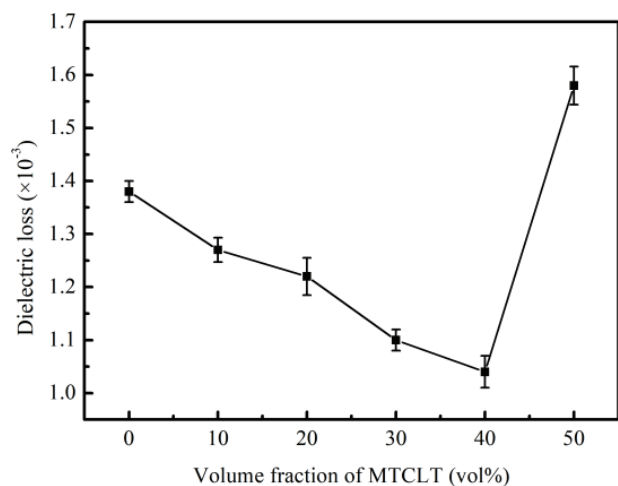
The dielectric losses of composite materials are divided into intrinsic dielectric losses and extrinsic dielectric losses.[27,28] The intrinsic losses include the intrinsic dielectric losses of mPPO and MTCLT ceramics, which are determined by the lattice structure of the material itself. The intrinsic dielectric loss of dielectric materials comes from the anharmonic interaction between dipole and external electric field in the process of polarization, and the structural symmetry is the decisive factor of this interaction force. Because the symmetry of dielectric ceramics is much higher than the resin, the dielectric loss of it ($\tan\delta\sim0.0005$) is much lower than that of the mPPO. So, with the increase of the ceramic filler fractions, the dielectric loss of composite materials decreases. However, the extrinsic loss is mainly determined by the two-phase interface, pores, and other factors. When the ceramic filler fraction reaches 50 vol.%, the two-phase interface is too much, which becomes the main factor affecting the dielectric loss of the composite material. Therefore, the dielectric loss of the composite material increases to 0.00158. The lowest dielectric loss of 0.00104 can be obtained when the ceramic filler fraction is 40 vol.%.

To meet the application in electronic devices, the CTE of the composite material needs to match the copper foil covered on the surface of the material to prevent the copper foil from falling off under thermal impact conditions. Therefore, we tested the CTE of MTCLT ceramics (α_c), mPPO (α_p) and the composites, and the experimental results are shown in Fig. 6. To predict the theoretical CTE of composite materials (α_{theo}), many prediction models were established.[29,30] The most commonly used one is the mixing rule:

$$\alpha_{theo} = V_f\alpha_c + (1-V_f)\alpha_p. \tag{6}$$

Fig. 5. Variations of dielectric loss of the mPPO/MTCLT composites with the increase of volume fraction of MTCLT.
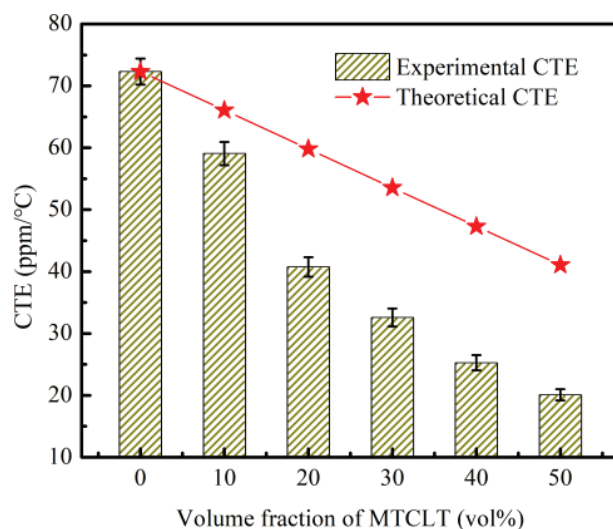

Fig. 6. The theoretical and experimental curves of CTE of the mPPO/MTCLT composites with the variations of volume fractions of MTCLT.

The calculation results are listed in Fig. 6. With the increase of the ceramic filler proportion, both the theoretical and experimental density of the composite materials decrease, mainly because the CTE of MTCLT (α_c~9.8 ppm/°C) is much lower than that of mPPO (α_p~72.3 ppm/°C). After MTCLT is heated, the energy increases, leading to the interatomic distance increase, and the volume expansion occurs macroscopically. In addition to the increase of interatomic distance, mPPO is accompanied by the transition of polymer chain from curled to the extended state, which leads to the CTE of mPPO being an order of magnitude larger than that of MTCLT ceramics. The experimental results also show that the experimental CTE of the composite material is below the theoretical value. This is because the theoretical model only considers the CTE of the two phases in the composite. The two-phase interphase can limit the movement of the polymer chain; the pore existing in the interphase with a very low-compression modulus could absorb the thermal expansion of the composite. Both factors will cause a decrease in CTE. When the ceramic filler fraction reaches 50 vol.%, the CTE is reduced to 21.8, matching the thermal expansion of copper foil.

To ensure the stable operation of the devices, the composite materials need to possess excellent reliability. We tested the bending strength of the composites, and the experimental results are shown in Table 1 and Fig. 7. Pure PPO, the main chain is a benzene ring that cannot rotate, has extremely strong rigidity, so the bending strength could be as high as 100.1 MPa. In contrast, the main chain of HIPS contains single bonds and can freely rotate, so the bending strength is only 37.5 MPa. After the two-phase compounding, although PS improves the fluidity of the composites in the molten state, it reduces the bending strength of the composites. With the addition of ceramics, there is a two-phase interface, which allows cracks to turn and 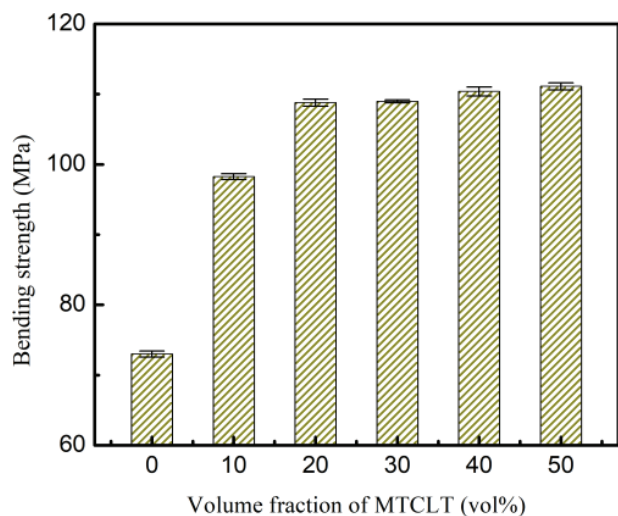move along the interface, which makes it toughening. Therefore, with the increase of ceramic filler fraction, the bending strength of composite materials increases significantly. When the ceramic filler fraction reaches 20 vol.%, the connection between the ceramics leads to the two-phase interface connecting, which instead promotes the expansion of the cracks. Thus, with the combination of the two factors, the bending strength of the composite is maintained around 110 MPa, when the filler fraction is 20–50 vol.%.

4. Conclusions

We prepared PPO/HIPS composite by injection molding. When PPO: HIPS = 2:1, the composite has a low-dielectric loss and good processability, which was compounded with MTCLT ceramics (V_f~0–50 vol.%) to prepare the composite material. Experimental results show that since mPPO has good fluidity, the relative density above 99% is guaranteed even when the ceramic volume fraction reaches 50 vol.%. When the ceramic filler fraction reaches 40 vol.%, the optimal dielectric performance can be obtained. The dielectric constant is 6.81, and the dielectric loss is as low as 0.00104. At the same time, the composite material also possesses a low CTE and excellent bending strength under the filler fraction. Thus, it can be an ideal material for application in the field of electronic communication.

Fig. 7. Bending strength of the mPPO/MTCLT composites with the increase of volume fraction of MTCLT.

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