Dielectric properties and thermal conductivity of core-shell structured Ni@NiO/poly(vinylidene fluoride) composites

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Abstract

To suppress the high loss of nickel (Ni)/poly(vinylidene fluoride) (PVDF) while remaining high dielectric constant (k) near the percolation threshold. In this study, core-shell structured Ni (Ni@NiO) particles were prepared by heat treatment of raw Ni powder under air atmosphere and incorporated into PVDF to prepare Ni@NiO/PVDF dielectric composites. The morphological, dielectric properties and thermal conductivity of the composites are characterized. The results indicate that compared with the raw Ni reinforced PVDF composites, the Ni@NiO particles endow PVDF with a high- k and rather low dissipation factor owing to the presence of NiO shell between Ni core and PVDF which serves as an interlayer between the Ni cores preventing them from contacting with each other. Additionally, the Ni@NiO/PVDF composites still possess a high thermal conductivity. Therefore, the as-prepared Ni@NiO/PVDF composites possess high- k but low loss, high thermal conductivity, making them promising for the industrial application as embedded capacitors.

Key Words: A. Polymer, elastomers, and plastics; A. Surfaces and interfaces; A. Metals; D. dielectric response; D. Heat conduction.

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1. Introduction

High dielectric constant (high-k) materials are able to store plenty of electric charges and balance the original electric field intensity, so that they exhibit great potential in micro-electronic, electrical and bioengineering fields [1-3]. Nowadays, high-k materials have been increasingly required because of the rapid development of high performance electronic components and electrical equipments, such as energy storage devices, embedded capacitors, electric accessories and actuators, etc [4]. Compared with the traditional inorganic high-k materials such as BaTiO₃, PZT, etc, polymeric composites have many advantages, such as good flexibility, easy processability, lightweight and low cost so that it is able to meet demands for miniaturization of microelectronics that has become a mainstream trend in microelectronic industry in recent years [5]. So, flexible polymeric composites with high-k and low dielectric losses have attracted intense research attention due to their potential applications in artificial muscles and skins, charge-storage devices, embedded capacitors and other flexible electronics [6-8].

So far, two classic routes have been widely used to prepare high-k polymer composites. One is the organic/inorganic hybrid strategy [4]. Namely one can enhance the dielectric constant of a polymer by introducing high-k inorganic particles, such as high-k ceramic particles (i.e., BaTiO₃, PZT, CaCu₃Ti₄O₁₂, etc) [4, 9, 10]. However, the enhancement of dielectric constant usually needs high loading of high-k particles, which may make the high-k composites lose the flexibility of the polymer matrix. Furthermore, the dielectric enhancement is usually low. Another approach is to prepare percolative composites by introducing electrically conductive particles into an electrically insulating polymer [11]. The fabrication of flexible dielectrics by incorporation of electric conductive fillers, i.e., metal particles (Au, Ag, Cu, Al) [2, 9, 11-15] or carbon fillers into a polymer [1, 5, 16-19]), has proven to be a promising strategy in producing films with advantageous dielectric properties. All percolative polymer composites loaded with conductive fillers can achieve very high dielectric constant near the

percolation threshold (f_c), but the materials are inevitably accompanied by a huge increase of dielectric loss tangent ($\tan\delta$), imposing considerable challenge and risk in precisely controlling the f_c composition to obtain reproducible products for practical applications [20]. So reducing the dielectric loss is the target of many investigations on preparing high-k electric conductor/polymer composites because suffering from an abrupt variant in dielectric loss is a fatal disadvantage for its practical use [6]. Many methods have been tried, mainly including the surface modification of conductors, the hybridization of conductors, and others, to avoid the interconnection between electric conductors, however, reducing the $\tan\delta$ into capacitor-tolerated values ($\tan\delta \leq 1$) while remaining high-k is still found to be difficult [1, 13, 15-20].

Currently, one of the trends in this area is to involve core-shell particles as fillers [20]. Core-shell particles have many advantages, such as good stability of the core particles from the protection of the shell and various properties came from the constituting material [17-19, 20]. By employing suitable shell material, the fillers could be more compatible with polymer matrix. Under delicate designing, composites with high-k and low loss could be achieved by controlling and optimizing the microstructure and electrical properties of the particles [20]. This type of core-shell structure is usually obtained by complicated chemical synthesis route with a high production cost such as CNTs@SiO₂ [18], CNTs@TiO₂ [19], Ag@C [13], or naturally self-passivation with a low fabrication cost [2], such as Al@Al₂O₃ [2, 9], Zn@ZnO [21].

Nickel (Ni) is an important ferromagnetic material, which shows diverse application as catalysts, magnet sensors, and conduction materials [22]. Other appealing properties of Ni particles are that they are cheap and readily available. Ni particle can endow polymers with a larger dielectric constant as well as a high loss near f_c due to the resultant leakage current within the composites [23-25]. For instance, Panda et al. reported that for Ni/PVDF composites, a high effective dielectric constant of

2500 ($\tan\delta=10$) at 100 Hz was observed near the $f_c \approx 0.27$ [22].

How to effectively suppress the loss while remaining a high-k of the Ni/polymer is the goal of our work. So, in the current study, the novel core-shell structured Ni@NiO particles were obtained by a facile heat treatment of raw Ni powder under air atmosphere, and the prepared Ni@NiO were used as the filler to prepare poly(vinylidene fluoride) (PVDF) composites with high-k but low dissipation factor. Up to now, the dielectric properties of PVDF reinforced by core-shell structured Ni@NiO particles in a wide frequency range have rarely been investigated. The present research is expected to provide a deeper insight into the effects of the NiO shell on dielectric properties and thermal conductivity of the Ni/PVDF composites in a wide frequency range.

2. Experimental

2.1 Materials

PVDF FR903 was purchased from 3F New Materials Co. (Shanghai, China). The raw nickel (*r*-Ni) powder (average particle size of 1-2 μm) were supplied by Wuxi Shunda Metallic Materials Co, and the flaky nickel (*f*-Ni) (average length $\sim 12 \mu\text{m}$ and thickness $\sim 1.0 \mu\text{m}$) particles were supplied by Shenyang Hangda Materials Co. The core-shell structured Ni@NiO (*c*-Ni) particles were prepared in our lab. The Dimethylformamide (DMF) was supplied by Tianjin Chemical Reagent Co., China.

2.2 Preparations

The core-shell structured *c*-Ni particles were prepared by the heat treatment of the *r*-Ni powder directly under air atmosphere at 550 °C for 2h to form NiO shell on the surface of Ni cores. A desirable amount of PVDF and filler powders for each sample was carefully weighed by using scale. First, PVDF powders were dissolved in the desired amount of DMF by stirring in 60 °C water bath for 30 min, at the same time, the preliminarily weighed filler powders (*c*-Ni or *r*-Ni, or *f*-Ni) were dispersed in DMF under sonication for 30 min. Then, the suspension was added into the PVDF

solution, and the obtained mixture was stirred for 8 h and then at 120°C to evaporate the majority of DMF. The resulting composite was heated at 120°C in a vacuum oven to remove the residual solvent. Finally, it was compression-molded at 200°C for 15 min under a pressure of about 15 MPa.

2.3 Characterizations

The structures of the *r*-Ni and the *c*-Ni particles were identified with a Shimadzu X-ray diffractometer-6000 (XRD) equipped with a graphite monochromatic instrument and a Cu anticathode (40 kV, 30mA, scanning rate 2°/min). The morphologies of the fractured interface of the composite specimens were observed using a JEOL JSM-7000F scanning electron microscope (SEM). The fractured surfaces were prepared in liquid N₂ and were sputtered with gold in vacuum prior to observation. An H-800 transmission electron microscope (TEM) purchased from Hitachi Co (Japan) was used to observe the nanoscale shell of the core-shell structured Ni.

The dielectric measurements of the samples were recorded using a Novocontrol Technologies Alpha-N high-resolution Dielectric Analyzer (Germany). The specimens for dielectric measurements were molded in the form of circular discs (diameter = 20 mm and thickness = ~1 mm). The thermal conductivity performances of the samples were tested using a Hot Disk thermal analyzer (TPS 2500, Sweden) at room temperature.

3. Results and discussion

3.1 X-ray diffraction

The core-shell structured *c*-Ni particles can be fabricated by forming a layer of NiO shell on the surface of Ni core when *r*-Ni particles were directly calcinated under air at high temperature. Fig.1 depicts the X-ray diffraction patterns of the *r*-Ni and *c*-Ni powder calcinated under 500°C for 3h and 550°C for 2h, respectively. It is found that the peaks at $2\theta \approx 37.33^\circ$, 43.3° , 62.81° , 75.3° and 79.5° corresponding to the different diffraction planes of NiO crystals, respectively, were seen to appear on

the surface of *r*-Ni powder. So, the *c*-Ni particles have been successfully prepared.

3.2 SEM micrographs

Appearances of the *r*-Ni and the *c*-Ni particles calcinated at 550°C for 2h are displayed in Fig. 2(a-b). We observe that the size of diameter of the *r*-Ni particles is about 1~2μm in comparison with 2~3μm for the *c*-Ni particles. Moreover, the surface of *c*-Ni particles with irregular shape became rough owing to the volume expansion during oxidation process. The TEM image of *c*-Ni particle is shown in the inset in Fig. 2(b), from which it can be seen that there is a layer of NiO shell with a thickness about 10-12 nm on the surface of core Ni. The TEM images of *r*-Ni and the *c*-Ni particles calcinated at 550°C for 2h are displayed in Fig. 3. We clearly observed that there is a layer of NiO on the surface of core Ni, serving as an interlayer between core Ni particles. Whereas, for *r*-Ni, the nanoscale shell is absent on the surface of core Zn as compared with the *c*-Ni. It is well known that the nanoscale shell layer has an important role in deciding the electrical properties of the composite particles and their polymeric composites. The morphologies of the fractured surfaces of the *r*-Ni/PVDF and *c*-Ni/PVDF are shown in Fig. 2(c-d). Fig. 2(e-f) presents the micrographs of *f*-Ni and *f*-Ni/PVDF composites.

3.3 Dielectric properties

Dielectric constant of a material represents the ability to store charges when the material is subjected to an electric field and reflects the dielectric properties of the material. Fig. 4 depicts the frequency dependence of the dielectric constant for *r*-Ni, *c*-Ni, and *f*-Ni/PVDF composites with various filler concentrations. A common feature that can be seen in three composites is that the addition of the conductive filler increases the dielectric constant of the composites. The increment of dielectric constant can be explained by the Maxwell-Wanger-Sillars (MWS) effect, which is associated with the entrapment of free charges between the insulator/conductor interfaces for heterogeneous

system, and can be characterized by the frequency dependence of the dielectric constant in the low frequency range [1]. In detail, the evolution process of the dielectric constant can be divided into three stages. When $f < f_c$, a small amount of conductive filler is incorporated into the polymer matrix and is isolated from each other. The capacitance of each microcapacitor is very low and the number of microcapacitors is inadequate, thus resulting in a slight increase in dielectric constant. And the dielectric constant decreases very slowly with the increase of frequency. From Fig. 4(a-b) when the loading of r -Ni is lower than 6.89 vol. %, the dielectric constant increases steadily, and is almost independent of frequency, indicating that there is insufficient accumulation of interfacial charges in the composites. Interfacial polarization enhanced gradually is considered to account for the improvement of dielectric constant. Once the $f \rightarrow f_c$, where the fillers are close to each other, and there are many r -Ni particles separated by very thin PVDF layers. A large number of charges are blocked at the interfaces between the r -Ni and the PVDF matrix because of the MWS interfacial polarization, leading to the formation of a large number of microcapacitors [2, 15], therefore, the dielectric constant undergoes a sharp increase in the low frequencies and is apparently dependent on frequency [3, 12]. Beyond the f_c , the dielectric constant keeps on rising because of the continuous formation of microcapacitors, and exhibits a strong frequency dependence in the low-frequency range, followed by a weak frequency dependence in the high-frequency range, suggesting that interfacial polarization is dominant for the capacitance of these microcapacitors, and can not follow with the external electric field [26]. Moreover, the dielectric loss also dramatically increases due to the formation of conductive network and the resultant leakage current within the composites. In this case, the composites turn into conducting materials rather dielectrics. For example, the dielectric constant rises from 135 (6.25 vol. %) to 1980 (7.89 vol. %) at 100 Hz. As the filler concentration increases to 31.8 vol. %, the dielectric constant decreases due to the resultant voids and defects at the interfaces within the

composites. From Fig. 4(d-e), we can observe that the *f*-Ni/PVDF composites also exhibit almost similar results as the *r*-Ni/PVDF system.

For polymers filled with conductive fillers, the percolation theory states that the variations of dielectric constant with frequency follow a power law as the *f* of the conductive fillers increases to the vicinity of the f_c and the fillers connect with each other to form a continuous path. Thus, the dielectric constant ε of the composites can be enhanced as described by the power law:

$$\varepsilon = \varepsilon_m (f_c - f)^{-s} \quad \text{for } f \leq f_c \quad (1)$$

where ε_m is the dielectric constant of the matrix and *s* is an exponent of about 1.

As shown in Fig.4 (b), the best fit of the dielectric constant with log-log plots of the power law for *r*-Ni/PVDF gives $f_c \approx 0.062$, and $s \approx 0.68$ according to Equation (1). As displayed in Fig 4(e), the best fit of the dielectric constant with log-log plots of the power law for *f*-Ni/PVDF gives $f_c \approx 0.123$, and $s \approx 0.59$. The lower f_c value can be ascribed to the high electric conductivity and small particle size of the *r*-Ni particles compared with the *f*-Ni particles.

Note that from Fig. 4(c), the dielectric constant of *c*-Ni/PVDF is inferior to that of *r*-Ni/PVDF and *f*-Ni/PVDF. For instance, the dielectric constant of PVDF with 16.7 vol. % of *c*-Ni at 100 Hz is 156, in comparison with 120600 and 265, respectively, for the *r*-Ni/PVDF and *f*-Ni/PVDF. Comparably, dielectric constant for *r*-Ni/PVDF or *f*-Ni/PVDF caused by interfacial polarization is rather prominent. However, it is noteworthy that the NiO shell effectively constrains and suppresses the contribution of *r*-Ni to the interfacial polarizations of Ni@NiO particles and Ni@NiO/PVDF composites, thus, resulting in a rapid decrease in dielectric constant. Typically, the dielectric constant of Ni@NiO/PVDF exhibits weak dependence on frequency in the range of frequency $10^3 \sim 10^5$ Hz, while it rapidly declines as the frequency exceeds 10^5 Hz.

Fig. 5 presents the dependence of dissipation factors on frequency at room temperature of

r-Ni/PVDF, *f*-Ni/PVDF, and *c*-Ni/PVDF composites. The dissipation factors of all samples decrease in the frequency range from 10^2 to 10^4 Hz, and then increase substantially over 10^4 Hz. The low-frequency dielectric response is a typical interface polarization behavior, resulting from macroscopical heterogeneous interface of the different diphasic structures. On the contrary, the high-frequency dielectric response is a Debye relaxation behavior derived from the C-F dipole orientation polarization of PVDF matrix [5]. For the *r*-Ni/PVDF composites, the dissipation factor increases with increasing the volume fractions of the *r*-Ni. There was no appreciable change in the loss behavior up to 6.25 vol. % of *r*-Ni loading. Afterward, the loss factor increases significantly at low frequencies with increasing the filler concentration up to 31.8 vol. %, primarily owing to direct current (DC) or quasi DC conduction caused by the percolation effect. At a high *r*-Ni loading, there were well-established particle clusters or partial connectivity of the filler (as seen in Fig. 2(c)), resulting in a rapid increased dielectric loss [19, 22-24]. Similarly, a significant variation in the dissipation factor for the *f*-Ni/PVDF was observed also at f_c because of high conductivity of *f*-Ni, as seen in Fig. 5(b).

The dielectric properties of polymer filled by conductors is closely correlated to the electrical properties of fillers, which have a significant influence on the migration and accumulation of charge carrier at the interfaces between the fillers and the matrix and therefore affect the interfacial polarizations [18, 20]. Therefore, in comparison with the *r*-Ni/PVDF and *f*-Ni/PVDF composites, the significantly decrease in the dissipation factors for *c*-Ni/PVDF composites was observed in Fig.5(c), and the maximum of dielectric loss of the composites still keeps a rather low level. The reasons can be mainly attributed to the insulating NiO shell on the surface of Ni cores, which serves as the interlayer against direct contact between adjacent Ni particles and suppresses the mobility of free charge carriers effectively [2, 18, 20]. Accordingly, it is reasonable to assert that the NiO coating layer plays a pivotal role in suppressing $\tan\delta$ of the composites by affecting relaxation. Fig.5(c-d) suggests that: 1) the *c*-Ni

loading does not have an appreciable influence on the dissipation factors in the measured frequency range; 2) the $\tan\delta$ in the range of frequency lower than 10^4 Hz has been significantly reduced to a very level owing to the electrically insulating NiO shell's effective suppression of the mobility of free charge carriers at the phase boundary area. In this study, remarkable reduction of $\tan\delta$ was achieved by introducing NiO interlayer between Ni cores to prevent them from connecting with each other directly. From the perspective of practical use, slightly sacrificing the dielectric constant for acquiring low $\tan\delta$ is acceptable.

The polarization of the composites with such a special core-shell-structured components is dominated mainly by the interfacial polarizations associated with the entrapment of free charge generated in the cores at the interfaces between the cores and the shell and the interfacial polarization at the interfaces between the shells and the matrix in the measured frequency range [13]. The electrically insulating shell plays an important role in determining these peculiar behaviors. Considering that $f \rightarrow f_c$, the dielectric constant increases with f because of the percolation. Given that $f \geq f_c$, the Ni cores are very close to each other but still isolated by a thin insulating layer, identical to a case where a large number of capacitors are connected with each other. The particle–particle junction is a capacitor, and above f_c , these junctions form an interparticle barrier layer of capacitor network connecting the top and bottom electrodes. The low $\tan\delta$ can be ascribed to the insulating NiO shells, thus preventing the formation of leakage current across the composites at $f \geq f_c$ [15].

Electrical transport in polymer-based composites occur either through direct contact between the conductive fillers or tunneling of electrons between the sufficiently close conductive particles [16]. Fig. 6(a-b) depicts the frequency dependence of alternating current conductivity (AC) for the r -Ni/PVDF and f -Ni/PVDF composites. Generally, variation of electric conductivity against filler concentration expressed in f is Sigmoidal curve, as shown in Fig. 6(d). This curve has three parts, initial region

where $f < f_c$, r -Ni or f -Ni particles are not in contact with each other, thus the hopping mechanism is dominant in the electronic transport [26]. The increase in conductivity with concentration can be attributed to the decreasing distance between conductors. Besides, the strong frequency dependence of conductivity indicates that the composites display an insulating nature. The second part where only a few continuous conducting networks are just formed when $f \rightarrow f_c$, there is an abrupt increase in conductivity. In this region small change in f causes remarkable increase in conductivity. This means the system changes from insulating to conducting. It is interesting to note that the conductivity values are almost independent of frequency in the low frequency range because of the formation of a conductive network and begin to increase at high frequency. Beyond f_c the change in conductivity becomes marginal [27], and the transition region shifts to high frequency. In this case, the composites show a conducting nature and the electrons can transport like in a typical inherently conducting material [26].

However, the results from Fig.6(c) suggest that the AC conductivity slightly increases with the filler loading and exhibits nearly linear ascending with frequency, indicating the insulating nature of the c -Ni/PVDF composites owing to the NiO insulating shell as an interlayer between the Ni cores. The interlayer can effectively prevent the core Ni particles from contacting with each other and from forming electric current across the composites. So, no obvious percolation is found in the c -Ni/PVDF composites. In this case, the NiO coating layer prevents the direct contact of the r -Ni particles, making them difficult to form a conductive network in the r -Ni/PVDF composites. Thus, electrons can only transport through adjacent r -Ni by inter-Ni tunneling [2, 13, 16]. Therefore, the conductivity is considerably reduced to very lower level compared with the r -Ni/PVDF or f -Ni/PVDF composites.

3.4 Thermal conductivity

Thermal conductivities of the pristine PVDF and the composites with r -Ni, f -Ni and c -Ni/particles

at various levels of filler loading are plotted in Fig.7. One can see that the pristine PVDF has a relative low thermal conductivity of 0.23 W/m K. When the filler is introduced, the thermal conductivity is significantly enhanced owing to the high thermal conductivity of Ni (~90 W/m K). Fig.7 suggests that: (1) at a low filler loading, the heat-conductive Ni particles encapsulated by a PVDF matrix can not touch each another, and have a weak interaction with each other, thereby resulting in a low thermal conductivity owing to the high interfacial thermal contact resistance between the Ni and the polymer matrix; (2) at a high filler loading, Ni particles begin to converge and form particle clusters or more compact packing structure within the matrix [2]. The thermal conductivities of the composite with 23.1 vol. % of *r*-Ni, *f*-Ni and *c*-Ni reach approximately 1.08 W/m K, 1.13 W/m K, and 0.9 W/m K, respectively, nearly five times than that of native PVDF. The *f*-Ni is much more effective in enhancing thermal conductivity of the composites at high filler loading because the *f*-Ni particles with a large aspect ratio easily formed bridges between themselves [2, 6], thereby resulting in a high thermal conductivity. The thermal conductivity of the *c*-Ni/PVDF is always slightly lower than that of the *r*-Ni/PVDF due to lower thermal conductivity of the NiO shell, thereby resulting in a slightly low thermal conductivity. The thermal conductivity of a composite is affected not only by the thermal conductivity of the components but also by other factors such as the morphology, dispersion, porosity, filler shape and size, and interaction between the two phases [2]. The precise prediction of the thermal conductivity of the composites from the thermal conductivity of the components and the loading of the filler is crucial for the design of composites. The following equations are used to calculate the thermal conductivity of the composites with filler particles at various levels of loading.

Maxwell-Eucken model

$$k_c = k_m \frac{2k_m + k_f + 2V_f(k_f - k_m)}{2k_m + k_f - V_f(k_f - k_m)} \quad (2)$$

Nielsen model

$$k_c = \frac{1 + ABV_f}{1 - B\psi V_f} \quad [B = (\frac{k_f}{k_m} - 1) / (\frac{k_f}{k_m} + A), \psi = 1 + \frac{V_f^2 (1 - V_m)}{V_m^2}] \quad (3)$$

where k_c , k_m and k_f are the thermal conductivity of composites, polymer and filler, respectively; V_f is the volume fraction of filler. The measured thermal conductivities are well matched with the theoretical predictions for low filler content only, and deviations occur at high filler content attributable to the imperfect dispersion of fillers and also to the air enclosed by the composites, which are not considered in the theoretical predictions. Maxwell's equation tends to underestimate thermal conductivity because it does not consider the mutual interaction between the particles. The Nielsen–Lewis model gives a good prediction for the thermal conductivity of the *r*-Ni/PVDF composites with a high filler loading. At a high filler concentration, the thermal conductivity of *f*-Ni/PVDF is evidently higher than those predicted from the Maxwell and Nielsen-Lewis models.

4. Conclusion

The dielectric constant and dissipation factor increase with an increase in the filler content for the three composites at all frequencies under investigation, especially remarkable for the *r*-Ni/PVDF, and *f*-Ni/PVDF composites. Compared with *r*-Ni or *f*-Ni reinforced PVDF, the *c*-Ni particles remarkably suppress the dissipation factor of the composites at a wider frequency range under the same filler loading. The reason can be attributed to the formation of a layer of NiO shell on the surface of *r*-Ni particle which serves as an interlayer between the Ni cores, thus preventing them from contacting with each other, and reducing the dissipation factor into capacitor-tolerated values ($\tan\delta \leq 1$). The thermal conductivities of the PVDF composites increase with an increase in the Ni content for the three composites. The thermal conductivity of the *c*-Ni/PVDF is slightly lower than that of the *r*-Ni/PVDF or *f*-Ni/PVDF due to low thermal conductivity of the NiO shell, thereby inhibiting phonon transfer and resulting in a slightly low thermal conductivity. The *c*-Ni/PVDF with favorite dielectric

performance and higher thermal conductivity, can be applied in embedded passive components and other related electronic and electrical industry.

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Fig. 1 X-ray diffraction patterns of raw *r*-Ni, *c*-Ni particles, the insets standing for the core-shell structure modes of Ni.

Fig.2 Microstructures of (a) *r*-Ni particles, (b) *c*-Ni particles, the inset standing the TEM of core-shell structured Ni, (c) 16.7 vol. % *r*-Ni/PVDF, (d) 16.7 vol. % *c*-Ni/PVDF, (e) *f*-Ni, and (f) 23.1 vol. % *f*-Ni/PVDF.

Fig.3 TEM of raw Ni particle (left), and core-shell structured Ni (right)

Fig.4 Dielectric permittivity dependence on frequency and loading for the PVDF composites with (a) r -Ni, (c) c -Ni, and (d) f -Ni, and Fig. 1(b, e) dielectric permittivity as a function of f_{Ni} loading at 100Hz, for the r -Ni/PVDF and f -Ni/PVDF systems, respectively, the inset shows a log-log plot of dielectric constant as a function of $f_c - f$.

Fig.5 Dissipation factor dependence on frequency and filler loading for the PVDF with (a) r -Ni, (b) f -Ni, (c) c -Ni, and (d) various composites at 100Hz.

Fig.6 AC electric conductivity dependence on frequency and filler loading for the PVDF with (a) raw r -Ni, (b) f -Ni, (c) c -Zn, and (d) scheme for electric conductivity against filler concentration.

Fig.7 The experimental thermal conductivity values and theory values calculated from Maxwell and Nielsen model of the composites