Dielectric response and percolation behavior of Ni–P(VDF–TrFE) nanocomposites

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Conductor–dielectric 0–3 nanocomposites using spherical nickel nanoparticles as filler and poly(vinylidene fluoride–trifluoroethylene) 70/30 mol.% as matrix are prepared using a newly developed process that combines a solution cast and a hot-pressing method with a unique configuration and creates a uniform microstructure in the composites. The uniform microstructure results in a high percolation threshold φ_c (> 55 vol.%). The dielectric properties of the nanocomposites at different frequencies over a temperature range from -70°C to 135°C are studied. The results indicate that the composites exhibit a lower electrical conductivity than the polymer matrix. It is found that the nanocomposites can exhibit an ultra-high dielectric constant, more than 1500 with a loss of about 1.0 at 1 kHz, when the Ni content (53 vol.%) is close to percolation threshold. For the nanocomposites with 50 vol.% Ni particles, a dielectric constant more than 600 with a loss less than 0.2 is achieved. It is concluded that the loss including high loss is dominated by polarization process rather than the electrical conductivity. It is also found that the appearance of Ni particles has a strong influence on the crystallization process in the polymer matrix so that the polymer is converted from a typical ferroelectric to a relaxor ferroelectric. It is also demonstrated that the widely used relationship between the dielectric constant and the composition of the composites may not be valid.

Keywords: Composite; dielectric; conductivity; percolation.

1. Introduction

Polymer-based dielectric composites, especially nanocomposites, have received tremendous attention for microelectronics applications, such as electronic packaging, embedded capacitors and energy storage.^{1–4} Many researchers and groups have been focusing on preparing composites with a high dielectric constant (ϵ_r), low dielectric loss ($\tan\delta$), and low processing temperatures.^{4–6} To fabricate the composites with excellent dielectric properties, there are three crucial issues. First, it is important to select a polymer matrix with excellent dielectric properties. Dielectric polymers, especially PVDF-based ferroelectric polymers with relatively high dielectric constant (> 10) and low loss, were widely used as the matrix.^{7–10} Second, how to prepare the composites with a uniform microstructure or how to distribute fillers in the matrix homogeneously?^{1,7,11} The properties of composites with a uniform microstructure are independent of the thickness and size of the sample,^{1,11} while the properties of composites with a nonuniform microstructure would change with the thickness and size of the sample used. Third, interfaces among the different phases in the composites also play an important role on dielectric properties.¹² The interfaces in the composites are dependent on the chemical natures of both filler and matrix.

Two types of dielectric composites have been widely studied in recent years: dielectric–polymer composites with dielectric fillers, and conductor–polymer composites with conducting fillers.¹ For dielectric–polymer composites, inorganic materials with a high dielectric constant, including ferroelectric ceramics,^{13–19} and some nonferroelectric ceramics, such as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$,^{7,20–23} were used as the filler. However, the main disadvantages of dielectric–polymer composite is that normally more than 50 vol.% of fillers is needed to achieve a high dielectric constant, which dramatically reduces the mechanical performance of the composites.¹

Recently, there is an increasing interest in the conductor–polymer composites because their dielectric constant can reach a high value only with very low volume fraction of conductive filler.^{24–31} The electrical property of a conductor–dielectric composite is determined by the percolation phenomenon.^{1,11} That is, when the volumetric content of conducting filler is higher than a certain value (i.e., percolation threshold φ_c), the composites are electrically conductive (i.e., the composites are conductors). If the filler content is lower than the φ_c , the composites are electrically insulative (i.e., the composites are insulators/dielectrics) and their effective dielectric constant (ϵ_r) increases with increasing filler

content (φ) as

$$\frac{\varepsilon_r}{\varepsilon_m} = \left(\frac{\varphi_c - \varphi}{\varphi_c} \right)^{-s}, \quad (1)$$

where ε_m is the dielectric constant of the polymer matrix, φ ($< \varphi_c$) is the volume fraction of conducting filler in the composite, and critical value (s) (> 0) is a constant. As the filler content approaches the φ_c , the dielectric constant increases with increasing filler content very rapidly so that a giant dielectric constant may be obtained in the composites when the φ is close to φ_c . It means φ_c is very critical for a conductor–dielectric composite. The φ_c is dependent on the geometry, shape, size and distribution of the conducting fillers.^{1,11} Therefore, conducting fillers with various shapes (spherical, core–shell, tube and bar/wire-like) and sizes ranging from micrometers to nanometers have been studied.^{1,11} Even numerous studies have been used to determine the percolation behavior.^{1,11} Among all the conductive fillers studied so far, the spherical metallic particles have many advantages over others, such as easy preparation, low cost, high stability and high repeatability on the particle geometry and properties. Therefore, it is of interest to study the metal–polymer composites.

The most critical issue is that the reported high dielectric constant observed in the conductor–dielectric composites is associated with a high loss when the volume fraction of conducting filler approaches φ_c . It is believed that the high loss is due to its electrical conductivity that originates from electrical channels formed by the conductive filler in the composites. Therefore, the composites with a uniform microstructure are highly desirable. Recently, a process that combines solution cast and hot-press was developed to prepare both dielectric–dielectric and conductor–dielectric composites with a uniform microstructure.^{15,21,27} It is experimentally found that the composites with a uniform microstructure exhibit a higher dielectric constant with a lower loss.^{15,21,27} For the composites with a uniform microstructure, its dielectric properties would be independent of the size and thickness of the samples used in the experiments. For the composites with a nonuniform microstructure, although the composites can exhibit a lower percolation threshold, its dielectric properties would be dependent on the size and thickness of the samples used in the experiments. Therefore, from an application point of view, the composites with a uniform microstructure are desirable.

For the composites with an ideal uniform microstructure, the conducting filler particles are well separated by the insulative polymer matrix ($\varphi < \varphi_c$). The composites with a uniform microstructure would also have a higher φ_c than the composites with nonuniform microstructure. Additionally, Eq. (1) indicates that the composites with a higher φ_c would have a higher tolerance on the composition.³¹ Therefore, it is of interest to study the dielectric response and percolation behavior of conductor–dielectric composites with a higher φ_c .

Here, nickel–poly(vinylidene fluoride–trifluoroethylene), Ni–P(VDF–TrFE), nanocomposite is studied. Ni was selected

since it is a very common metal and spherical Ni particles can be easily made into different sizes. P(VDF–TrFE) 70/30 mol.% was selected as polymer matrix since it is a typical ferroelectric polymer with a relatively high dielectric constant. The composites were prepared by using the newly developed process so that the composites have a uniform microstructure that results in a high φ_c (> 55 vol.%). The dielectric performance of Ni–P(VDF–TrFE) nanocomposites at different frequencies over a wide temperature range is studied. All the composites exhibit a similar temperature dependence as the polymer matrix. It is found that the ferroelectric-to-paraelectric phase transition behavior of the polymer matrix is strongly influenced by the appearance of Ni particles. When Eq. (1) is used to determine the percolation behavior, it is found that the fitted percolation threshold and critical value are dependent on the frequency and temperature used to measure the dielectric constant.

2. Experimental Details

2.1. Preparation of nanocomposites

The preparation of Ni–P(VDF–TrFE) nanocomposites was reported in our previous work.³¹ The P(VDF–TrFE) 70/30 mol.% copolymer was purchased from Solvay. The spherical Ni particles in size smaller than 100 nm were purchased from Sigma Aldrich. First, the copolymer was dissolved in *N,N*-dimethylformamide (DMF) for 12 h, then Ni nanoparticles were added into the solution with a further dispersion in an ultrasonic bath for 1 h. Second, the final mixed solution was cast on a quartz substrate (7.6 cm × 7.6 cm from Fisher Scientific) at 70°C for 8 h in an oven. Third, the as-cast film was peeled from the quartz substrate (immersing it into D.I. water if necessary). Finally, the films were folded and pressed at high temperature. Each as-cast film has two surfaces marked as top and bottom: the bottom is the surface contacted with the quartz substrate. The thickness of the as-cast films was about 50 μm. During the hot-press process, the stack of four layer as-cast films was configured in the following manner: the top of one as-cast film facing the top of the next as-cast film and the bottom of one as-cast film facing the bottom of the next as-cast film. As reported, by using this configuration, the composites would have a uniform microstructure with a higher dielectric constant and a lower loss.^{15,21} The hot-press was carried out at 150°C and the composite samples after the hot-press were annealed by placed between two glass plates at 140°C for 8 h. The thickness of the final composites was about 110–150 μm dependent on the composition, which ranges from 0 vol.% to 53 vol.% (i.e., 0, 10, 20, 30, 40, 50 and 53 vol.%) of Ni nanoparticles.

2.2. Characterization

The final samples were sputtered with gold on both surfaces as electrodes for the characterization of the dielectric

properties. An Agilent 4294A impedance analyzer was used to determine the dielectric property of the samples over a frequency range from 100 Hz to 1 MHz using $Cp \sim D$ function. For characterizing the temperature dependence of the dielectric response, the samples were tested over a temperature range from -70°C to 135°C with a heating rate of $3^{\circ}\text{C}/\text{min}$. During the test, four frequencies of 1, 10, 100 kHz and 1 MHz were used. The dielectric constant of the composites was calculated from the measured capacitance using the parallel plate mode.

3. Results and Discussion

Figure 1 shows the temperature dependence of the dielectric properties at four frequencies (i.e., 1, 10, 100 kHz and 1 MHz) for the nanocomposites with 0, 10, 20, 30, 40 and 50 vol.% of Ni, respectively. First of all, the nanocomposites exhibit a high dielectric constant with a low loss. For example, for the nanocomposites with 50 vol.% of Ni particles, the dielectric constant at 1 kHz can reach more than 600 with a loss less than 0.2 at temperature around 100°C . At room temperature, the dielectric constant at 1 kHz is more than 370 with a loss about 0.2.

From the results obtained in pure P(VDF-TrFE) (i.e., the matrix) shown in Fig. 1(a), one can find two characteristic temperatures: one is the glass transition temperature (T_g) associated with a peak in the dielectric loss over the

temperature range from -20°C to $+20^{\circ}\text{C}$; the other is the ferroelectric-to-paraelectric phase transition temperature associated with a peak in the dielectric constant around 113°C . For the glass transition process, the higher the frequency is, the higher the loss-peak temperature is and the higher the loss-peak value is. The phase transition process results in a peak in both the dielectric constant and loss with a well-defined temperature (T_{max}). At high temperatures ($> T_{\text{max}}$), the dielectric loss increases with increasing temperature due to the electrical conductivity except 1 MHz.

The dielectric constant of the composite with 10 vol.% of Ni shown in Fig. 1(b) exhibits the similar temperature dependence as that of the polymer matrix. However, the temperature dependence of the dielectric constant around T_{max} is much weaker than that observed in Fig. 1(a) (i.e., polymer matrix). For example, for the pure matrix, the dielectric constant at 1 kHz changes from 21 to 53 (i.e., more than 2.5 times) when the temperature is increased from 80°C to 108°C , while it changes from 39 (at 80°C) to 65 (at 108°C) (i.e., only about 1.7 times) for the composites with 10 vol.% of Ni. More interestingly, it is found that at high temperatures ($T > T_{\text{max}}$) the composite exhibits a lower loss than the matrix. For the composite with 20 vol.% of Ni, the temperature dependence of the dielectric constant and loss shown in Fig. 1(c) is similar to what observed in composites with 10 vol.% of Ni. The temperature dependence of the dielectric constant is weaker than that observed in composites with 10 vol.% of Ni particles. Again, the composites at high

Fig. 1. Temperature dependence of dielectric constant (solid) and loss (open) at different frequencies for the composites with different Ni contents: (a) 0% (i.e., pure polymer matrix), (b) 10 vol.%, (c) 20 vol.%, (d) 30 vol.%, (e) 40 vol.% and (f) 50 vol.%.

temperatures exhibit a lower loss than the polymer matrix. Additionally, it is observed that the frequency dependence of the dielectric constant of the composites with 20 vol.% of Ni is stronger than that with 10 vol.% of Ni. For the composites with 30, 40 and 50 vol.% of Ni, the temperature dependence of the dielectric constant and loss shown in Figs. 1(d)–1(f) is similar with that observed in composites with 10 vol.% and 20 vol.% of Ni and again the composites at high temperatures exhibit a lower loss than the polymer matrix. That is, at high temperatures all composites shown in Fig. 1 exhibits a lower loss, especially at low frequencies, than the pure polymer matrix. Comparing the dielectric constant of these composites at the same temperature, one can find that the frequency dependence of the dielectric constant increases with increasing Ni content and that the temperature dependence of the dielectric constant decreases with increasing Ni content. It is also observed that the frequency dependence of the dielectric constant-peak temperature increases with increasing Ni content. For example, the $T_{\max}$ obtained at different frequencies is almost the same for the polymer matrix, while the difference in the $T_{\max}$ obtained at 1 kHz and 1 MHz is about 2.8°C for composites with 50 vol.% of Ni.

In a brief summary, the dielectric constant of the composites shown in Fig. 1 indicates that, as the Ni content increases, the temperature dependence of the dielectric constant at temperatures lower than $T_{\max}$ weakens and the frequency dependence of the constant becomes stronger. For the composites studied here, except electrical conductivity no change is expected for the Ni particles over the temperature range shown in Fig. 1. Therefore, the change in the temperature and frequency dependence of the dielectric constant observed in the composites should originate from the change in polymer matrix. It is well known that P(VDF-TrFE) copolymer can be converted from a typical ferroelectric to a relaxor ferroelectric by reducing size of the crystals.^{32,33} Regarding dielectric constant, it is known that the dielectric constant of the relaxor ferroelectrics exhibits a weaker temperature dependence than the typical ferroelectrics at the temperatures lower than dielectric constant-peak temperature ($T_{\max}$) and that the dielectric constant of the relaxor ferroelectrics exhibit a much stronger frequency dependence than that of the typical ferroelectric.^{32,34} Additionally, it is known that the $T_{\max}$ of a typical ferroelectric is independent of the frequency, while that is dependent on the frequency for relaxor ferroelectrics.³⁵ Therefore, the results shown in Fig. 1 indicate that the crystallization process in the polymer matrix is strongly influenced by the appearance of Ni nanoparticles in the polymer, which results in smaller crystals in the polymer matrix. That is, the appearance of the Ni nanoparticles results in smaller-size crystals in the matrix.

To further study the influence of Ni content on the dielectric properties, the dielectric constant at 1 kHz versus temperature is plotted in Fig. 2(a) for all the composites, where the composites with 53 vol.% of Ni are included. Clearly, the dielectric constant increases with increasing Ni

content. For the nanocomposites with 53 vol.% of Ni particles, a dielectric constant at 1 kHz is more than 1500 with a loss of about 1.0 at around 100°C. At room temperature, the dielectric constant at 1 kHz is about 1000 with a loss of 1.0. That is, the nanocomposites exhibit an ultra-high dielectric constant when the Ni content is close to the percolation threshold.

The results shown in Fig. 2(a) also indicate that the temperature dependence of the dielectric constant at temperatures lower than $T_{\max}$ becomes weaker as the Ni content increases and that the change in the dielectric constant associated with T_g becomes smaller as the Ni content increases. Additionally, it is found that the $T_{\max}$ changes with the Ni content. The $T_{\max}$ obtained using the dielectric constant at 1 kHz for all the composites is presented in Fig. 2(b). Clearly, the $T_{\max}$ decreases with increasing Ni content. Initially, the $T_{\max}$ decreases with the Ni content slowly and, then, drastically when the Ni content is more than 40 vol.%.

The loss of the composites shown in Fig. 1 indicates that that all composites at high temperatures have a lower loss at 1 kHz than the polymer matrix. At low temperatures ($< T_g$), one can find that the loss decreases with increasing frequency and the frequency dependence of the loss increases with increasing Ni content as shown in Fig. 1. It should be mentioned that the measured loss may originate from two: one is from the polarization response and the other is due to the electrical conductivity. For the loss due to the electrical conductivity, the loss should increase with the temperature and decrease with increasing frequency.^{1,27} For the loss from polarization (i.e., the real dielectric loss), both temperature and frequency dependence can be very complicated. For the comparison, the temperature dependence of the loss for the composites with different Ni contents at 1 kHz and 1 MHz is presented in Figs. 2(c) and 2(d), respectively. Clearly, the loss at low temperatures increase with increasing Ni content as shown Figs. 2(c) and 2(d). Therefore, one may conclude that the measured loss in the composites is dominated by the electrical conductivity and that the electrical conductivity increases with increasing Ni content. However, at high temperatures ($> T_{\max}$), except for the composites with 53 vol.% of Ni nanoparticles, all the composites exhibit a lower loss at 1 kHz than the polymer matrix as shown in Fig. 2(c). That is, the loss of the composites is smaller than that of the polymer matrix. More interestingly, the loss at 1 MHz decreases with increasing temperature as shown in Fig. 2(d). The results shown in Figs. 2(c) and 2(d) at high temperatures clearly indicate that the measured loss in the composites reported here is dominated by the real dielectric loss rather than the electric conductivity. This also confirms that the Ni particles in the composites reported here are well separated or that the composites reported here have a uniform microstructure, which is highly desirable for the composites. Even for the composites with 53 vol.% of Ni that exhibit the ultra-high dielectric constant with a high loss, close to 1.0, its loss decreases with increasing temperature as shown in Fig. 2(d).

Fig. 2. (a) Temperature dependence of the dielectric constant at 1 kHz for all composites, (b) $T_{\max}$ obtained from the dielectric constant at 1 kHz versus the content of Ni, temperature dependence of dielectric loss at (c) 1 kHz and (d) 1 MHz for all composites, and temperature dependence of AC conductivity at (e) 1 kHz and (f) 1 MHz for all composites.

To further study the contribution of the electrical conductivity, the temperature dependence of the AC conductivity at 1 kHz and 1 MHz is shown in Figs. 2(e) and 2(f), respectively, for all the composites studied. At high temperature, the conductivity of some composites (10% and 20% Ni) is lower than that of the polymer matrix. For the composites with a high Ni content, although its conductivity is higher, the conductivity decreases with increasing temperature at high temperature. It is well known that the conductivity of a dielectric increases with increasing temperature. Therefore, the conductivity of the composites clearly indicates that the contribution of the conductivity to the properties of the composite is very limited. The composites should have a very low DC conductivity. Actually, the AC conductivity ($<10^{-4}$ S/m or 10^{-6} S/cm) at 1 kHz indicates that all composites can be considered as the insulators. The loss observed in all composites at high temperatures indicates that the observed loss is not dominated by the electrical conductivity. In other words, the observed loss is dominated by the polarization response. It is known that the relaxor P(VDF-TrFE) exhibits a higher loss than the ferroelectric P(VDF-TrFE).³² Additionally, it is well known that the mixture of conductor and dielectric induces new polarization mechanisms, such as Maxwell-Wagner effect.³⁶ Therefore, the observed loss including the high loss in composite with 53 vol.% of Ni may

originate from the dielectric loss of the matrix and the new polarization process induced by the mixture.

From the results shown in Figs. 2(c) and 2(d), the loss peak associated with the T_g weakens as the Ni content increases, which is consistent with the results shown in Fig. 2(a). That is, as the Ni content increases, the change in the dielectric properties associated with the T_g becomes small. It is well known that the glass transition temperature of the polymer decreases with the appearance of other nanoparticles.^{1,37,38} Therefore, the results shown in Figs. 2(a), 2(c) and 2(d) indicate that the glass transition process in the matrix becomes broader.

Figure 3(a) shows the dielectric constant ratio (ϵ_r/ϵ_m) of the nanocomposites to the polymer matrix at four frequencies (1, 10, 100 kHz and 1 MHz) at a temperature, -40°C , versus the volume fraction of Ni. First of all, the results clearly demonstrate that the composites reported here have a dielectric constant that is well higher than the dielectric constant of the matrix. For example, at 1 kHz, the ratio can reach more than 65. That is, the dielectric constant of the polymer can be improved by more than 65 times by adding Ni particles into the polymer matrix. The results shown in Fig. 3(a) clearly demonstrate that the composites have a percolation threshold of more than 53 vol.%. The high percolation threshold observed here is a direct result of the composites'

Fig. 3. (a) $\varepsilon_r/\varepsilon_m$ at different frequencies (1, 10, 100 kHz and 1 MHz) versus the Ni content (φ) of the composites at -40°C , (b) fitting curve (solid line) of $\varepsilon_r/\varepsilon_m$ at 1 kHz versus the Ni content (φ) using Eq. (1) and (c) fitting constants (φ_c and s) at -40°C versus the frequency.

uniform microstructure that is achieved by the unique process used to prepare the nanocomposites.

The nanocomposites reported here provide a unique opportunity to study the percolation behavior of the conductor–dielectric 0–3 composites using spherical fillers since the composites have a uniform microstructure. Therefore, Eq. (1) is used to fit the relationship between the dielectric constant and the Ni content of the composite. When the dielectric constant, shown in Fig. 3(a), at each frequency is fitted using Eq. (1), it is found that Eq. (1) can mathematically fit the results well as shown in Fig. 3(b) as an example (i.e., 1 kHz). The fitting results by using the dielectric constant at 1 kHz indicate that the fitting constant φ_c is 55.3 vol.% and the fitting constant s is 1.32. It is well known that the φ_c for a composite system is an intrinsic parameter.³⁹ That is, if Eq. (1) is valid, the fitting constant φ_c should be independent of the selection of the frequency at which the dielectric constant is used in the fitting process. However, when the dielectric constants at different frequencies are used, it is found that the fitting constants φ_c and s change as shown in Fig. 3(c). The data shown in Fig. 3(c) indicates that the composites have a percolation threshold of more than 55 vol.%. The variation of the fitting constants φ_c and s shown in Fig. 3(c) is much larger than the uncertainty of the fitting. This was also found in other composite systems.^{27,37}

In other words, one may not be able to determine the real percolation threshold of a composite system by simply using Eq. (1) with the dielectric constant at one frequency.

To further study the issue, the dielectric constant at different temperatures is fitted using Eq. (1). The results are shown in Fig. 4, where five temperatures (-40°C , 0°C , 40°C , 80°C and 130°C) were presented. From Fig. 1, one can find that 130°C is above the T_{max} , -40°C is below the T_g , 0°C is around T_g , 40°C and 80°C are above T_g but below T_{max} . In Fig. 4, both fitting constants are normalized using the values of the fitting constants at -40°C (i.e., $\varphi_c/\varphi_c, -40^\circ\text{C}$ and $s/s, -40^\circ\text{C}$ shown in Fig. 3(c), where $\varphi_c, -40^\circ\text{C}$ and $s, -40^\circ\text{C}$ are the fitting constant φ_c and s obtained at -40°C shown in Fig. 3(c). Clearly, the fitting constants change with the temperature selected. Combining the results shown in Figs. 3(c) and 4, one can find that the fitting constants φ_c and s using Eq. (1) are dependent on the selection of both frequency and temperature at which the dielectric constant is measured. This is certainly against the definition of these two parameters, especially φ_c .

There are two possible reasons for the change in the fitting constants φ_c and s with the selection of both the frequency and temperature for the dielectric constant. One is that Eq. (1) does not reflect the real relationship between the dielectric constant and the volume content of the composites. The other

Fig. 4. (a) $\varphi_c/\varphi_{c,-40^\circ\text{C}}$ and (b) $s/s_{-40^\circ\text{C}}$ at different frequencies (1, 10, 100 kHz and 1 MHz) versus temperatures for the nanocomposites.

is that the properties of the polymer matrix change with appearance of the Ni nanoparticles. In other words, the ε_m in Eq. (1) is actually dependent on the filler content. For the composite system studied here, as discussed above there is a clear change in the microstructure of the polymer matrix, which even results in a significant change in the T_{max} — a temperature reflecting the ferroelectric-to-paraelectric phase transition — as shown in Fig. 2(b). Therefore, one may use the influence of the Ni particles on the matrix to explain the dependence of the fitting constant on the temperature shown in Fig. 4. However, this argument would not be able to explain the frequency dependence of the fitting constants shown in Fig. 3(c). Therefore, the further study on the relationship between the dielectric constant and the composition of the conductor–dielectric composites is needed.

4. Conclusions

In this work, by using a newly developed process that combines a solution casting and a hot-pressing method with a special configuration, Ni–P(VDF–TrFE) nanocomposites with a uniform microstructure are created. Due to its uniform microstructure, the nanocomposites have a high φ_c (> 55%). The dielectric constant of the nanocomposites with 50 vol.% of Ni content can reach more than 600 with a loss less than 0.2, while the nanocomposites with 53 vol.% of Ni exhibit a dielectric constant more than 1500 with a loss about 1.0. The nanocomposites at high temperatures exhibit a lower loss than the pure polymer matrix. It is concluded that the loss observed in the composites is dominated by the polarization response rather than the electrical conductivity. It is found that the appearance of the Ni nanoparticles has a strong influence on the crystallization process of the polymer matrix, which results in a lower T_{max} and converts the polymer matrix from a typical ferroelectric to a relaxor ferroelectric. The percolation behavior in the composite system is investigated and it is found that two fitting constants obtained by fitting dielectric constant using Eq. (1) are dependent on the

selection of the frequency and temperature, which is against the definition of the percolation threshold and the physical significance of the s . It is indicated that the temperature dependence of the fitting constants may be explained using the influence of the Ni particles on the polymer matrix, but the frequency dependence of the fitting constant cannot be explained using the influence of the Ni particles on polymer matrix.

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