Novel Metal-Polymer Composite with High Percolation Threshold

by

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Abstract

0-3 metal-polymer composite based on nano-size Ni particles was studied.

A nanocomposite with nano-size Ni particles embedded into copolymer poly [vinylidene fluoride-co-trifluoroethylene] P(VDF-TrFE) 70/30 mol% has been prepared via a hot-pressed solution casting method. The uniform dispersion of Ni nanoparticle is improved by the processing method and the dielectric properties of composite films on volume fraction of Ni are fully investigated over a frequency range of 100Hz~1MHz. The percolation threshold of the composite is pretty large (53 vol%), attributed to increased adhesiveness between the filler and the polymer and better homogeneity of filler dispersion.

Meanwhile, the dielectric constant of Ni nanoparticle-P(VDF-TrFE) 70/30 composite film is about 300 at 1000 Hz with low dielectric loss of 0.2, showing the potential for applications in advance electronics.

For the Ni-P(VDF-TrFE) composite, temperature dependence of dielectric properties has been demonstrated within Ni-P(VDF-TrFE) 70/30 mol% composites due to the temperature dependence of polymer matrix.

In order to understand the dielectric behaviors of conductor-dielectric composites, the percolation equation was investigated further.

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CHAPTER 1

INTRODUCTION AND RESEARCH OBJECTIVES

1.1 Capacitance and Dielectric

In the electronic and electrical industry, capacitor represents one of the most fundamental devices. It serves the purpose of filtering unwanted signals, of allowing alternating current (AC) signals to pass while blocking direct current (DC). It can act as a battery or as a power source. In general the capacitor is a very versatile device, and as such, it has many properties based on the application where it is used.

The defining characteristic of a capacitor is its ability to store electric charge. This ability is called its capacitance C, and is defined by the following relationship:

$$C = \frac{Q}{V} \tag{1-1}$$

where Q is the stored charge and V is the potential difference connected across the electrodes. The SI unit of capacitance is the farad, which is 1 coulomb per volt. And the most common subunits of capacitance in use today are the millifarad (mF), microfarad (μF), nanofarad (nF), picofarad (pF) and femtofarad (fF).

The capacitance of a capacitor with flat, parallel electrodes separated by vacuum is directly proportional to the active electrode area A and inversely proportional to the separation d as described by the following equation:

$$C = \mathcal{E}_0 \frac{A}{d} \tag{1-2}$$

where $\mathcal{E}_0$ is a universal constant having the value of 8.85×10^{-12} F/m.

When two parallel electrodes are separated by a distance d with dielectric materials, the capacitance can be expressed as:

$$C = \mathcal{E}_0 \mathcal{E}_r \frac{A}{d} \tag{1-3}$$

where $\mathcal{E}_r$ is the relative permittivity, sometimes denoted by the symbol ‘k’. Figure 1.1 is the schematic representation of a parallel plate capacitor with a dielectric, (grey) which reduces the internal electric field and increases the capacitance.

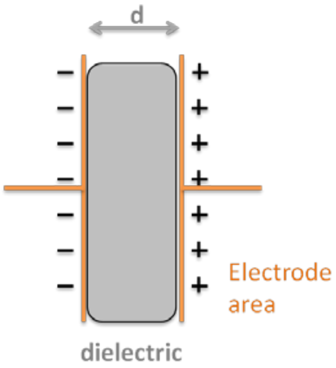

Figure 1.1. Schematic representation of a parallel plate capacitor with dielectric

From the equation (1-3) we can see how effective a capacitor to store energy depends on the material used for the dielectric. And each material has unique dielectric permittivity and dielectric strength, which is the maximum voltage that can be applied across the electrodes without breakdown. If breakdown occurs, current will flow between the electrodes. Table 1.1 gives a list of some dielectric materials with their dielectric constant and characteristic dielectric strength.

Table 1.1. Material used in current capacitors [1]

Material	Dielectric Constant	Dielectric Strength (MV/m)
Air	1.007	3
Paper	3.7	180
Mica	7	150
Glass	4.0-6.0	20
Rubber	2-3.5	12
Water	80	-

1.2 Fundamental Aspects of Dielectric

The term dielectric is typically used to describe materials that can be polarized by an applied electric field. There is a relationship between the induced dielectric polarization density $\vec{P}$ and electric field $\vec{E}$:

$$\vec{P} = \varepsilon_0 \chi \vec{E} \qquad (1\text{- }4)$$

where ε_0 is the electric permittivity of free space, and the dielectric susceptibility χ is a measure about how easily it polarizes in response to an electric field.

And there is a relationship between the dielectric susceptibility and ε' electric permittivity (or dielectric constant) of a material:

$$\chi = \varepsilon' - 1 \qquad (1\text{- }5)$$

If a time-varying electric field is applied to a dielectric material, the relative permittivity changes with frequency and becomes a complex number:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \qquad (1\text{- }6)$$

where ω is angular frequency and $\omega = 2\pi f$, j is the imaginary unit, ε' and ε'' are the real and imaginary parts of relative permittivity respectively. For the real dielectric, the measurement result of the imaginary part ε''_{eff} comes from the two parts: the imaginary part of the dielectric ε'' and contribution from the conductivity σ:

$$\varepsilon''_{eff} = \frac{\sigma}{\varepsilon_0\omega} + \varepsilon'' \qquad (1\text{- }7)$$

ε'' shows possible dissipative effects, which sometimes are characterized by means of the so-called dielectric loss (loss tangent):

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (1\text{- }8)$$

1.3 Classification of Dielectric Materials

There are many different ways to classify the dielectric materials according to different considerations.

I: The most basic classification is in terms of the state of dielectric materials, such as gases, liquids, and solids states.

II: Electronic Industries Association (EIA) gave a classification based on materials characteristics: Dielectric materials with a relatively low permittivity (15~500) and a dielectric loss ≤ 0.003 over a working temperature range from -55 °C to +85 °C; Dielectric materials based on ferroelectrics with high permittivity (500~20,000); Dielectric materials based on conductive phase with very high capacitances and very low breakdown field.[2]

III: In addition, dielectric materials also can be classified into two major categories: nonpolar materials and polar materials.[3]

A nonpolar material is defined as a material obtaining no permanent dipole moments so that their dielectric constants are relatively small, such as silicon, diamonds, paraffin, and carbon tetrachloride. In contrast, a polar material is defined as a material possessing a permanent dipole, such as ferroelectric crystal.

IV: In terms of dielectric constant, dielectric materials have been categorized into low permittivity (low-Ɛ material) and high-Ɛ material. In microelectronics systems dielectrics with a low dielectric constant are highly desirable, while for some other applications, such as capacitors, dielectrics with a high dielectric constant are preferred.

V: Materials can be categorized into inorganic or organic based on the chemical composition. The dielectric constant and strength of some inorganic and organic materials are given in Table 1.2.

Table 1.2. Dielectric constant and dielectric strength of some current dielectric materials [2]

Materials		Dielectric constant	Dielectric strength(MV/m)
Inorganic	Tantalum oxide	11	4
	Quartz, fused	3.85	20
	Reconstituted mica	7.8	64
	High-Voltage ceramics	500-6000	2
Organic	Epoxy	4	16
	Polyethylene	2.2-2.4	50
	Polypropylene	2.3	140
	Polyester	2.8-4.5	32
	Teflon	2.4	60
	Nylon	3.2	14

As shown in Table 1.2, inorganic materials such as ceramic usually exhibit relatively high dielectric constants, but low breakdown fields, whereas organic materials generally have higher dielectric strength but low dielectric constant. On the other hand, polymers have attributes such as low process temperature, flexibility, and the ability to withstand a high mechanical impact. In contrast, Ceramics and crystals are brittle and require a high process temperature.

Most applications need to combine the good properties to get the materials that are easy to fabricate and flexible, and possess high dielectric constants so that different kinds of composites have been widely studied.

1.4 General Concepts for Composites

In industry and material science, the composite is the material consisting of two or more constituents with significantly different physical or chemical properties in an attempt to obtain some unique properties. The matrix is the “glue” that holds the composite together and usually the softer phase compared to filler.[4]

1.4.1 Connectivity of Two phase composites

Properties of composite materials depend not only on the type of filler and that of the matrix, but also on how they are coupled. This coupling concept is called connectivity and was first classified by Newnham *et al.*[5]

For a two-phase system, connectivity is defined by combination of terms m–n. Here m represents the connectivity of the active phase (filler) while n represents the connectivity of the inactive one (matrix).There are 10 different patterns for binary composites on the basis of connectivity: 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3, where 0/1/2/3 represent the number of dimensions of self connection for each component in the composite. If a phase is self-connected in three directions, its connectivity is termed as 3. If self-connected in two directions, its connectivity is termed as 2, and so on.

A 0-3 composite is defined as a 0-dimension particle embedded inside a 3-dimensions matrix, such as a ceramic particles embedded in a polymer as shown in Figure 1.2.

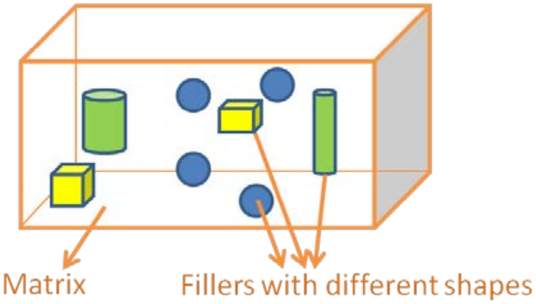

Figure 1.2. Schematic of 0-3 composite [6]

1.4.2 Mixing Rule for Permittivity in Two-Phase Composites

Properties of composites generally show different trends in electrical properties compared to pure constituent phases. The dielectric properties of a mixture consisting of different materials need to be predicted. For a 2-phase composite, we consider two well-known simple cases, the parallel model and the series model. The models can be considered as capacitors connected in a circuit in two ways as shown in Figure 1.3 (a) and Figure 1.3 (b).

The effective dielectric constant Ɛ' of the mixture can be simply written as:

$$\mathcal{E}'^{n} = \nu_1 \mathcal{E}_1{}'^{n} + \nu_2 \mathcal{E}_2{}'^{n} \qquad (1\text{- }9)$$

where ν_1 and ν_2 are the volume fractions of the dielectric-1 and dielectric-2 with dielectric constants $\mathcal{E}'_1$ and $\mathcal{E}'_2$, respectively, and n is either +1 for the parallel case or -1 for the series case.

In most cases, 2-phase composites are mixtures of their components, which can be described by mixing models as shown in Figure 1.3 (c), so the effective dielectric constant of the composite lies between the values determined by Equation (1-8) for *n*=-1 and *n*=1 as is illustrated in the shadow area in Figure 1.4.

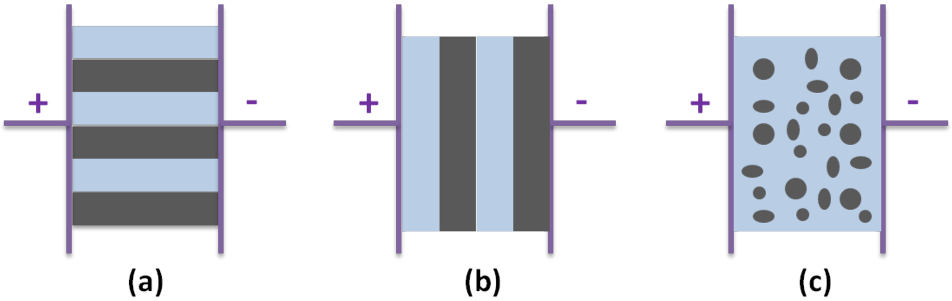

Figure 1.3. Ideal connection ways of two-phase composites: (a) parallel model, (b) series model, and (c) a mixing model; Vertical purple lines stand for electrodes. [7]

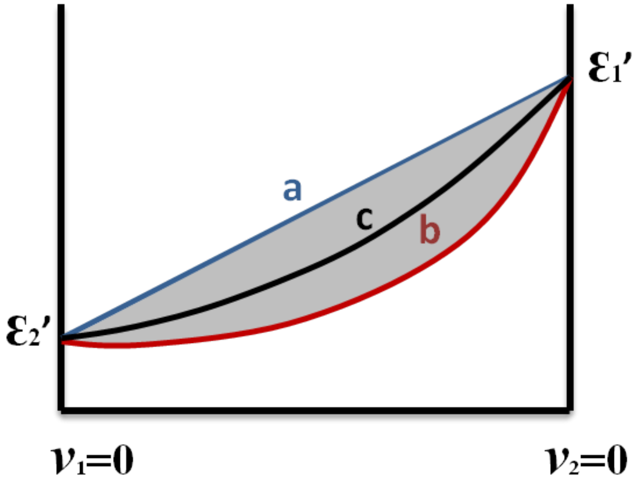

Figure 1.4. Schematic of dielectric constant of two phases 1 and 2 vs. their volume fraction in the mixture: a, parallel connection; b, series connection; c, real composite.[6]

1.5 Current Developments of Polymer-Matrix Dielectric Composite

1.5.1 High-Ɛ Composites Based on Polymer Matrix

A great deal of effort has been given to development of the polymer-based composites as dielectrics, especially 0-3 composites, in which the flexible polymer matrix is filled with isolated particles.

For the performance of 0-3 composite, polymer matrix plays a key role. Various polymers have been used based on their processibility, flexibility, melting temperature, glass transition temperature, dielectric response, and dielectric strength. Examples of these are epoxy, poly(methyl metha-crylate) (PMMA), polystyrene(PS), poly(vinyl chloride) (PVC), polyetherimide, polyurethances (PU), poly(vinylidene fluoride) (PVDF), and PVDF-based co/ter-polymers.

Among these polymers, PVDF and its co/ter-polymer have been widely used as polymer matrices since these polymers exhibit a relatively high dielectric constant (>10).

The properties of composites are dependent on not only the polymer matrix but the fillers in polymer. These fillers include dielectrics such as ceramics, and conductive materials such as metals, conducting polymers and carbon based materials. According to the type of fillers, the polymer-based 0-3 composites can be classified into two types: dielectric-dielectric composites where the fillers are dielectric materials and conductor-dielectric composites where the fillers are conducting materials.

1.5.1.1 Ferroelectric Polymers

The polymer matrix plays an important role in the dielectric properties. Unfortunately, most of polymers exhibit very low dielectric constants (mostly less than 5). Poly(vinylidene fluoride) (PVDF) and its copolymer poly [vinylidene fluoride-co-trifluoroethylene] P(VDF-TrFE) have been paid more attention recently due to their higher dielectric constant property (~10).Therefore, a great deal of research has focused on the development of dielectric composites using PVDF and P(VDF-TrFE) as Matrix.

1.5.1.2 Ferroelectric Property

A ferroelectric crystal is defined as a kind of material that exhibits a reversible spontaneous electric polarization. There is a critical temperature, called the Curie temperature, which marks the dramatic change from ferroelectric phase to paraelectric phase. At this temperature, the dielectric constant can reach its maximum value that is three to four orders of magnitude higher than that in the ferroelectric phase. And the dielectric constant of a ferroelectric material is strongly dependent on temperature.

1.5.2 Dielectric-Dielectric Composites

For dielectric-dielectric composites, various ferroelectric ceramics with high dielectric constant have been widely used as the fillers in the composites, such as $BaTiO_3$ (BT), $PbZrO_3$ (PZT), $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) and $Pb(Mg_{1/3} Nb_{2/3})O_3$ (PMN). During the last decade, nonferroelectric ceramics with high dielectric constant have been studied [8]. $CaCu_3Ti_4O_{12}$ (CCTO) ceramics were reported to exhibit a dielectric constant as high as 10^5 .The summary [2][6] for ceramic-polymer composites is shown in Table 1.3.

Table 1.3. Dielectric properties of some current ceramic-polymer composites at room temperature

Ceramic-polymer composite		**Concentration of filler (vol%)**	**@Frequency**	**ε'/loss**
Ceramic	**Polymer**			
BT	PMMA	60	1kHz	40/0.012
BT	Epoxy	40	1kHz	44/0.2
BT	PVDF	70	1kHz	152.3/<0.1
BT	PS	70	1kHz	100/<1
BT	Polyamide(PA)	70	1MHz	80/0.02
PMN	Epoxy	40	100kHz	24/0.05
PZT	PU	30	1kHz	24/<0.7
BST	P(VDF-TrFE)70/30	50	1kHz	80/<0.2
CCTO	P(VDF-TrFE)55/45	50	1kHz	194/<0.2
CCTO	Epoxy	40	100Hz	50/-
CCTO	PVDF	55	100Hz	95/<0.24
CCTO	PS	64	100Hz	80/-
CCTO	Polyimide	40	100Hz	49/<0.2

From the table above, we can conclude that the advantages of ceramic–polymer composites include relatively low dielectric loss. However, most of these composites have relatively low dielectric constant (<100) and high ceramic loadings (>50vol%). High ceramic loadings will degrade the flexibility so that limit the potential progress.

Therefore, many investigations focus on the conductive filler-polymer composite, which could possess a high dielectric constant at a low filler concentration and thus make it possible to preserve the flexibility of the polymer matrix.

1.5.3 Conductor-Dielectric Composites

Common conductive fillers are metallic or graphitic and can be classified in to three categories based on the shapes: particle, fiber and core-shell.

1.5.3.1 Theoretical Models for Conductor-Polymer Composites

The dielectric properties of this kind of composite cannot be explained by classical mixing rules but by percolation theories. The change of dielectric constant of a conductor-dielectric as a result of the conductive phase structure is shown in Figure 1.5.

At the lower concentration of filler, conductive particles are separated from each other and randomly distributed into the matrix (Figure 1.5 (a)), and the corresponding electric properties of the composites are dominated by the matrix. With increasing the filler concentration, local clusters of particles begin to form and dielectric constant increases. As the filler content approaches a certain value, the pattern of conductive particles creates the infinite conductive cluster and the network of channels connected by the conductive fillers as shown in Figure 1.5 (c). At the same time, the dielectric constant increases abruptly, reaching a very high value. This critical value of filler content is the so-called percolation threshold ν_c. Further growth of the filler content causes more conductive channels in the composites to form a conductive skeleton [Figure 1.5 (d)] and dielectric constant to start decreasing.

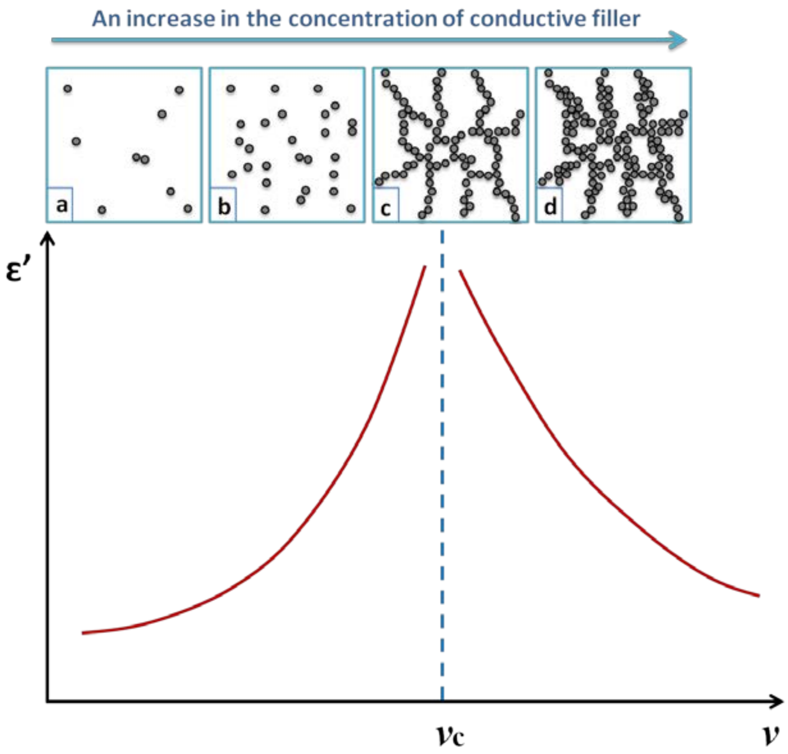

Figure 1.5. Schematic of changes in the dielectric constant of composites with concentration (*dashed blue line* is corresponding to percolation threshold ν_c), and composites' microstructure showing the geometric phase transition of fillers.

When the filler content is less than the percolation threshold, the composite is an insulator/dielectric. However, when the filler content is higher than the percolation threshold, the composite becomes a conductor. Therefore, around the percolation threshold, an insulator–conductor transition occurs.

Most researchers are focusing on concentration of the filler approaching the percolation threshold from low concentration side since the dielectric constant undergoes a sharp rise in order to get the giant dielectric constant. The dielectric constant of the composite near this transition often obeys the following equation [9]:

$$\varepsilon' \propto (\nu_c - \nu_{filler})^{-s} \text{ for } \nu_{filler} < \nu_c \qquad (1\text{- }10)$$

where ν_c is the percolation threshold, ν_{filler} is the volume fraction of conductive fillers, and s is the critical exponent. The equation (1-9) can be written as:

$$\varepsilon' = \varepsilon'_m \left(\frac{\nu_c - \nu_{filler}}{\nu_c}\right)^{-s} \qquad (1\text{- }11)$$

where ε'_m is the dielectric constant of polymer matrix.

1.5.3.2 Quantum Tunneling Mechanism

However, if the fillers disperse homogeneously, even when the content of fillers is above the percolation threshold, the cluster shown in Figure 1.5 (c) would not occur. Instead, the dielectric constant can be predicted by another equivalent theory: quantum tunneling mechanism [10], as shown in Figure 1.6. The distance between the fillers is decreasing with increasing the content of fillers. As the distance is small enough, the electrons can tunnel through the adjacent conductive particles and the dielectric constant continues increasing. At the same time, the composite exhibits an insulator-conductor transition.

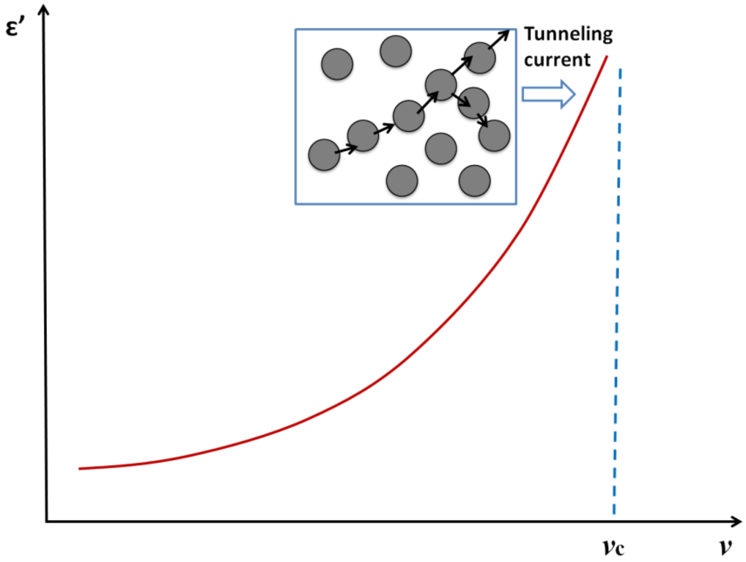

Figure 1.6. Quantum tunneling mechanism for changes in the dielectric constant of composites with increasing concentration of fillers

1.5.3.3 Metal Particles Embedded in Polymer

Among the various kinds of conductive or semiconductive fillers, the most typical example is metal. Many different metals with size ranging from micrometers to nanometers and shape (spherical, core-shell, tube, and bar/wirelike) have been used in development of high-dielectric-constant composites. A large dielectric constant enhancement has been observed in a number of composites using Ni, Ag, Cu, Fe, and Al as the concentration approaching to percolation threshold, shown in Table 1.4.

Table 1.4. Dielectric properties of some current metal-polymer composites at room temperature

Metal-polymer composite		**Concentration of filler**	**@Frequency**	**Ɛ'/loss**	**Ref.**
Metal	**Polymer**				
Ni	PVDF	@ v_c=17 vol%	100Hz	400/0.18	[11]
Ni	PVDF	@ v_c=20 vol%	1kHz	67/<0.2	[12]
Ni(20-30nm)	PVDF	@ v_c =28 vol%	1kHz	1273/~2	[13]
Ni(20 μm)	PVDF	@ v_c=57 vol%	1kHz	955/1.22	[14]
Zn	PVDF	@ v_c=32 vol%	1kHz	337/<0.2	[12]
W	PVDF	@ v_c=23 vol%	1kHz	194/<0.2	[12]
Al(3.0μm)	Epoxy	@ 80 wt%	10 kHz	109/0.02	[15]
Al(1.0 μm)	Epoxy	@ 70 vol%	1kHz	95.49/0.05	[16]
Ag(flake)	Epoxy	@11.43 vol%	10kHz	2000/0.24	[17]
Ag (40nm particle)	Epoxy	@ v_c=22 vol%	1kHz	300/0.05	[18]
Ag nanowires	PVDF	@ v_c=20 vol%	1kHz	378/0.15	[19]
Stainless steel fiber(SSF)	PVDF	@ 10 vol%	50Hz	427/~1000	[20]

The large enhancement observed in the dielectric constant of the composite can be explained by the percolation theory. As discussed above, when the metal filler content is in the neighborhood of the percolation threshold, the composites have a significant increase in dielectric and electrical properties, due to the fact that conductive paths are formed and the interparticle tunneling happens.

Data for dielectric properties of some current metal-polymer composites from Table 1.4 can be plotted, as shown in Figure 1.7. The dielectric properties can be described by dielectric constant Ɛ' and 1/tanδ, as shown in Figure 1.7 (a). For the practical application, high values of Ɛ' and 1/tanδ combined are always in demand. The dielectric properties also can be described using imaginary Ɛ", which can be converted by following equation: $\varepsilon'' = \varepsilon' tan\delta$ [see equation (1-7)], as shown in see Figure 1.7 (b).

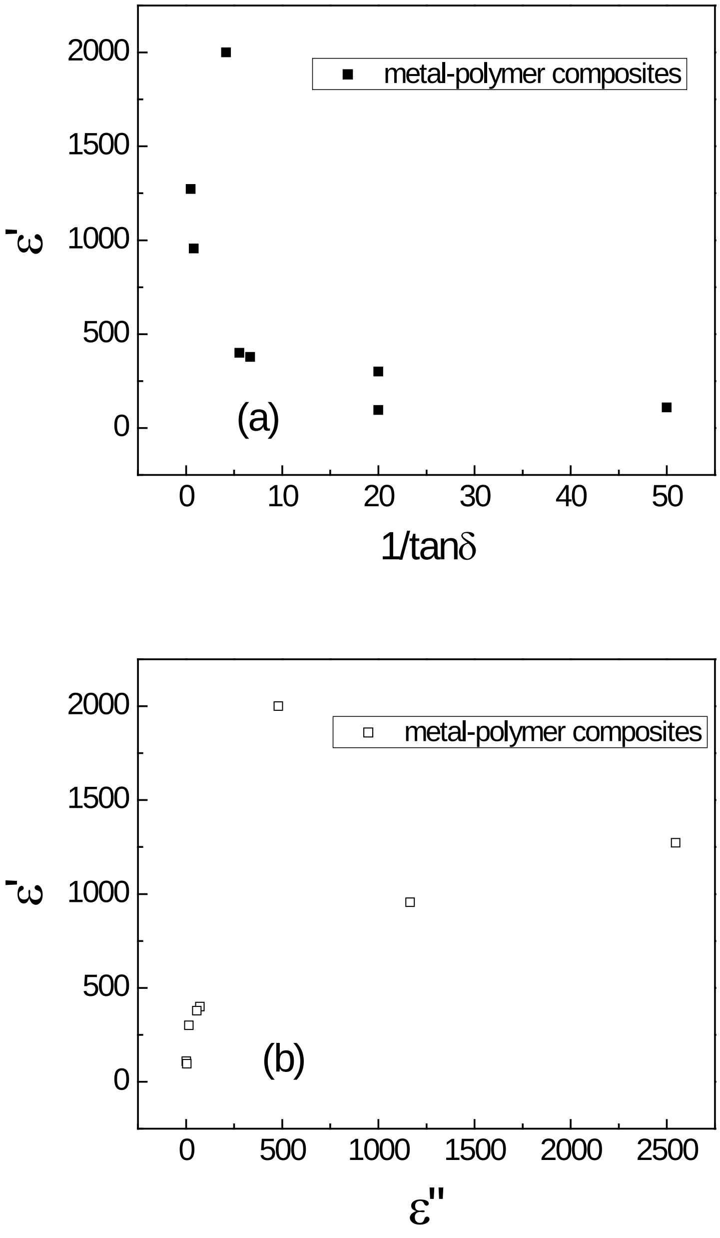

Figure 1.7. Summary of dielectric properties of some current metal-polymer composites at room temperature

1.6 Effects on Dielectric Properties of Conductor-Polymer Composites

From Table 1.4, we can find out that the dielectric properties of conductor-polymer composites are dependent on not only the concentration of fillers, but also the geometric factors (shape and size) of the fillers. For example, a dielectric constant of 2000 is reported for an epoxy filled with 10 μm silver flakes[17], while a dielectric constant of 300 is reported for an epoxy filled with silver particles with a diameter of 40 nm [18].

1.6.1 Influence of the Filler Size

The size, shape of the filler and its volume fraction in the composite actually play a significant role in the dielectric constant and the percolation threshold by affecting the interparticle distance and the interfacial area.

Panda *et al* [13] observed a threshold composition of 0.28 in cold compacted Ni (20-30nm)-PVDF. Further, they also prepared by following the same processing method but using 20μm Ni particles. In this case, the percolation threshold increased to ν_{Ni}=0.57 [14].

As the particle size reduces, the number density of the particles will increase leading to a corresponding decrease in interparticle distance, which in turn leads to an increase in the number of nearest neighbors for a particle with the result that the number of particles in the cluster increases in the matrix. As a consequence electrons find it easier to tunnel particles clusters [14]. The percolation threshold can be obtained for the composites with nano-sized fillers at a lower concentration than with micro-sized fillers.

In addition, Panda *et al* found large enhancement in dielectric constant occurs in the low frequency region with significant dispersion over the whole frequency range. These changes have been attributed to more leakage current resulting from decrease in interparticle distance and improved interparticle contacts due to increased surface area.

1.6.2 Influence of the Processing Conditions

Compared to Panda, Dang *et al.* [11] demonstrated ideal percolative behavior in hot-molded Ni (micro-size)-PVDF composites with a percolation threshold f_{Ni}=0.17. And their experiment showed that the composites with nano-sized metal particles have a lower dielectric constant with a low dielectric loss compared to those with micro-sized metal particles. The dielectric constant of 400 with a loss of 0.18 is obtained in a PVDF filled with micro-sized nickel particles [11], while a dielectric constant of 70 with a loss of 0.1 is obtained in PVDF filled with nano-sized nickel particles.[21]

The reason for this difference is due to the different processing conditions. A higher percolation threshold has been attributed to increased adhesiveness between the filler and the polymer, leading to better homogeneity of filler dispersion.

Accordingly, dielectric properties of metal-polymer composite are dependent on processing conditions and size.

1.6.3 Influence of the Dispersion of Conductive Fillers

In the classic 0-3 percolation model, the randomly distributed metal fillers form conducting networks (clusters) within the matrix. When the size of the largest cluster approaches the size of the matrix, discharge between electrodes (percolation) happens. Based on a random distribution, the cluster volume, $V_{cluster}$, is proportional to the product of the number of fillers that in the cluster, $N_{filler,}$ and the average filler volume, V_{filler}, as [18]

$$V_{cluster} \propto N_{filler} V_{filler} \tag{1- 12}$$

Derived from (1-11), at the threshold concentration:

$$\bar{V}_{cluster} \propto \bar{N}_{filler} V_{filler} \tag{1- 13}$$

where $\bar{V}_{cluster}$ and $\bar{N}_{filler}$ are the threshold cluster volume and threshold filler number, respectively. And the threshold filler number is proportional to the threshold filler concentration $\bar{C}_{filler}$:

$$\bar{C}_{cluster} \propto \bar{N}_{filler} \tag{1- 14}$$

For a specific system, the percolation probability, P, is always proportional to the filler concentration but inversely proportional to the threshold concentration:

$$\mathrm{P} \propto 1/\bar{C}_{cluster} \tag{1- 15}$$

Therefore,

$$\mathrm{P} \propto \frac{V_{filler}}{\bar{V}_{cluster}} = (\frac{D_{filler}}{\bar{D}_{cluster}})^3 \tag{1- 16}$$

where D_{filler} and $\overline{D}_{cluster}$ are the diameters of filler and the threshold culster, respectively. This means that the percolation probability is closely related to the size ratio of the filler to the composite thickness. For the bulk samples, the insulation matrix is considered to be infinitely large in three dimension compared with the size of the fillers. Therefore, the influence of the size on the percolation probality is negligible. However, in pratical application, dielectric materials need to be fabricated into thin layers(usually micrometer range). Therefore, the influence of the size on the percolation is signicifant.

Moreover, uniform dispersion of nanoparticles in nanocomposite materials is required because nanoparticle agglomerates will lead to undesirable electrical or materials properties. Therefore, dispersion of nanoparticles is an extremely important contributor for achieving improved dielectric properties and reproducibility.

1.7 Low Percolative and High Percolative

Dielectric materials with high dielectric constant are required for the reduction in the dimension of electric devices.

Discussed above, for polymer-ceramic composites, a high filler loading is used because a higher filler loading will generally lead to a higher dielectric constant. In attempt to improve the material processibility, many researches concentrate on investigating the conductive-dielectric composite with low percolation threshold to acquire the high dielectric constant with the low loading of fillers. Among them, Rao and Wong reported a high dielectric constant of 2000 in an Ag-flake-doped epoxy composite at a filler concentration of 11.43vol%, shown in Table 1.5 [17].

However, it is very risky to prepare percolative dielectrics with a threshold composition due to the abrupt variation of dielectric constant near the threshold. According to Rao et al., the dielectric constant increased from 200 to 2000 when the filler concentration only increased from 11.03 vol% to 11.43 vol%, and then decreased to nearly 0 at 11.52 vol%. In other words, a small deviation from the percolation threshold could result in significant drop of the dielectric constant, making it rather difficult to control the parameters of the preparation process, as shown in Figure 1.8. The issues mentioned above are considered as drawbacks for conducting fillers/polymer composite systems.

In addition, these low percolative composites require not only the precise control of filler loading but extreme uniform distribution of filler [15]. Practically, it is impossible to fulfill such demanding uniform distribution over a large area at all.

Table 1.5. Dielectric constant and loss factor (tanδ) of Epoxy-Silver composite measured at 10 kHz [17]

Silver Volume Ratio (%)	Dielectric Constant	Loss Factor
7.38	17	0.013
8.7	19	0.0134
9.61	35	0.014
11.03	200	0.015
11.13	500	0.017
11.23	1000	0.019
11.28	1500	0.15
11.43	2000	0.24
11.52	0.1	5.33
11.77	0.1	7.2
12.02	0.1	8.4
14.66	0.1	9.1
20.69	0.1	10

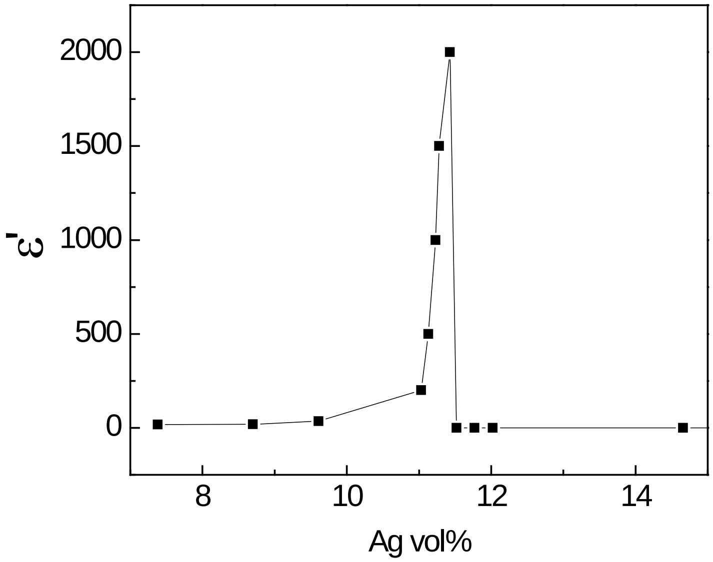

Figure 1.8. Dielectric constant of Epoxy-Silver composite measured at10 kHz vs. vol% of Ag [17]

In contrast, Al-epoxy composites in Table 1.4 show high percolation thresholds. With composites containing 80 wt% 3.0μm aluminum, a dielectric constant of 109 and a low dissipation factor of about 0.02 (@10 kHz) were achieved [15]. Chong Chen et al [16] obtained a dielectric constant of 99.45 with a loss tangent about 0.05 at room temperature in an Al/epoxy composite with the 1.0 μm aluminum content of 70vol%.

These metal composite with high percolation threshold could be attributed to a tunneling network composed of the self-passivated Al particles with outside thick Al_2O_3 shells. Compared to the composites with low percolation threshold, composites with high percolation threshold have a wider volume fraction range of the percolation threshold concentration, making the material reproducible for practical applications. This is definitely an advantage for manufacturability.

Based on equation (1-10), the variation of dielectric constant for percolative composites with different percolation thresholds (v_c=10%, v_c=30% and v_c=60%) can be simulated, as shown in Figure 1.9. Assume that s=1 and dielectric constant for a polymer matrix is 10. The dependences of dielectric constant on conductive filler content can be considered as two stages. In the first stage, the dielectric constant increases gradually with increasing filler contents in the composites. This stage can be considered "safe" for the preparation. In the second stage, the dielectric constant abruptly increases near the percolation threshold, as shown in the shadow in Figure 1.9 (b). Compared to the composite with low percolation threshold (10%), the composite with high percolation has a wider “safe” range of volume fraction, which makes the material reproducible for application, as shown in Figure 1.9 (a). And the dielectric constant of the composite with percolation of 60% in the “safe” stage can be achieved higher than the dielectric constant of the composites with percolation of 10%, as shown in Figure 1.9 (b).

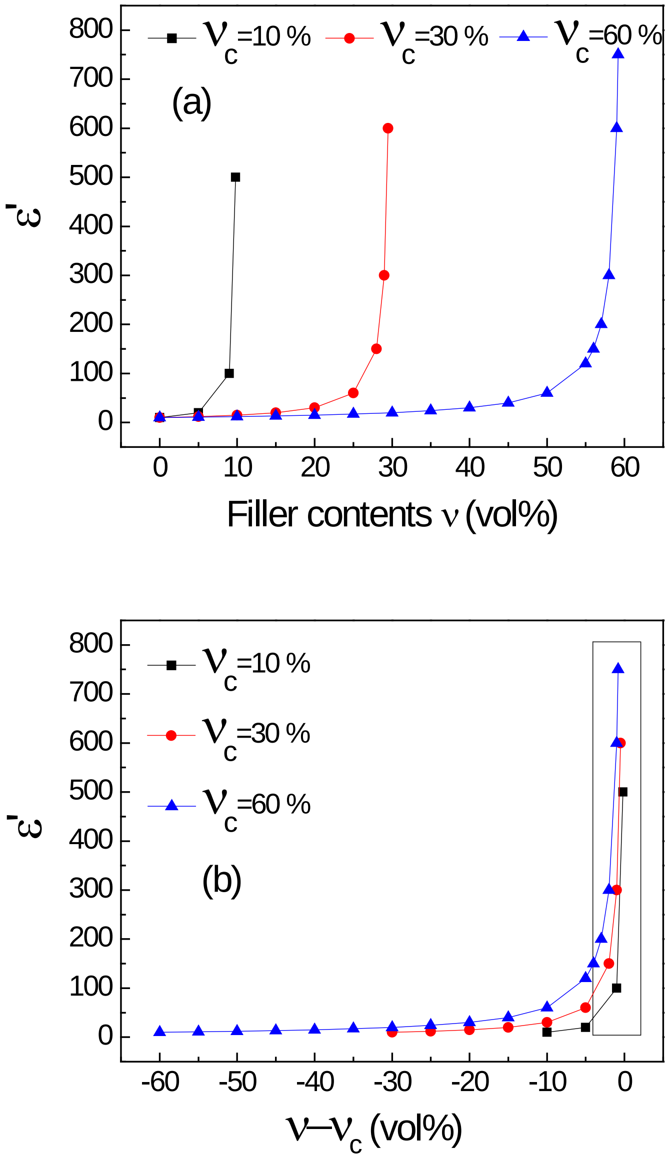

Figure 1.9. Dielectric constant data simulated according to Equation (1-10)

1.8 Dielectric Loss

Most research is focusing on enhancement of the dielectric constant in order to acquire the high-k percolative materials. These remarkable increases in dielectric constant, however, are always associated with significant increases in electrical conductivity and dielectric loss due to the 'insulator–conductor' transition occurring at the percolation threshold. According to Li [20], the loss tangent is less than 0.3 for the composite of filler content $v < v_c$, but the very high loss tangent (1000) near 100 Hz is observed at v_c. Such an increase of loss tangent is inevitable when the volume fraction v is close to the percolation threshold. In particular, the loss tangent of composite undergoes a sharp increase at low frequency, which is the consequence of the significantly raised conductivity and also considered as the evidence of the large leakage current on the composites.

However, these percolative composites with high dielectric loss are not desirable for further applications. Therefore, low dielectric-loss material or high-Ɛ and low dielectric-loss material would be investigated.

In order to apply percolative systems for manufacturing of materials with the high dielectric constant and low dielectric-loss, the fundamental understanding of the dielectric loss of the polymer-conductive filler composites needs to be obtained, and a viable method to obtain a percolative composite with reproducible high dielectric constant and low dielectric loss needs to be developed.

One possible method is to control the processing condition to avoid the conductive clusters and achieve composite with homogeneous dispersion due to the fact that the insulator generally has the lower loss. More research on this subject is needed.

1.9 Meaning and Objectives

1.9.1 Meaning of Studying Dielectric

Dielectric materials have many applications, such as capacitors and electronic package. For electronic package purpose, dielectric materials are used to enclose and protect an electronic device in order to reduce the overall noise between operating supplies such as power and ground.

The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy in materials. In addition, it is important to explain various phenomena in electronic, optics, and solid-state physics.

To achieve the giant dielectric constant, conductive-polymer composites have been investigated. However, it is risky to prepare percolative dielectrics with a threshold composition due to the abrupt variation in the vicinity of the threshold. Further the high dielectric constant observed in the conductor-dielectric composites is usually associated with the unwanted high dielectric loss. The issues are considered as drawbacks for conducting fillers/polymer composite systems. Therefore, it is meaningful to develop a novel low-cost conductor-dielectric composite.

1.9.2 Objective of This Research

In this work, Ni (nano size)-P(VDF-TrFE) 70/30 mol% composites based on percolation theory are studied. P(VDF-TrFE) is a candidate polymer matrix due to its high dielectric constant. Among the various kinds of conductive fillers, the metal particle is chosen by the fact that it is easy to prepare the uniform composites using particles. Ni as filler can be cheaply obtained, which will decrease the cost of final products. Unlike Al, Ni is not easily oxidized in air.

The goal for this work is to develop a percolative composite with high dielectric constant and low loss and to investigate the percolation theory in the metal-polymer composite.

In order to achieve the goal, the following objectives are designed:

1. Improve the processing condition to achieve more uniform distribution of metal powders inside the polymer system.
2. Improve dielectric properties and reproducibility.
3. Investigate the percolation theory in the metal-polymer composite, especially for the high percolative composite.

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CHAPTER 2

PROCESSING IMPROVEMENT AND CHARACTERIZATION METHODS

2.1 Introduction

Homogeneous dispersion of fillers into a polymer matrix is crucial to the properties of polymer-based composites, especially for the nanoparticle-polymer composite, because nanoparticle agglomerates will lead to undesirable electrical or materials properties. Therefore, uniform dispersion of nanoparticles in nanocomposite materials is required in order to achieve improved dielectric properties and reproducibility. This section will describe in detail, the experiment procedures that were improved in order to acquire more uniform hot-pressed solution casting composite film and certain specific experimental test.

2.2 Preparation of the Ni nanopowder-P(VDF-TrFE) composite films

Ni (nano size)-P(VDF-TrFE)70/30 mol% 0-3 composite was prepared by traditional casting method and hot pressing technique. In order to acquire the high concentration Ni-P(VDF-TrFE) composites, the traditional glass plate was replaced by the quartz substrate. In addition, hot pressing technique was improved through preheating the sample to attain a more uniform one. The overall process flowchart for Ni-P(VDF-TrFE) 0-3 composite fabrication is shown in Figure 2.1.

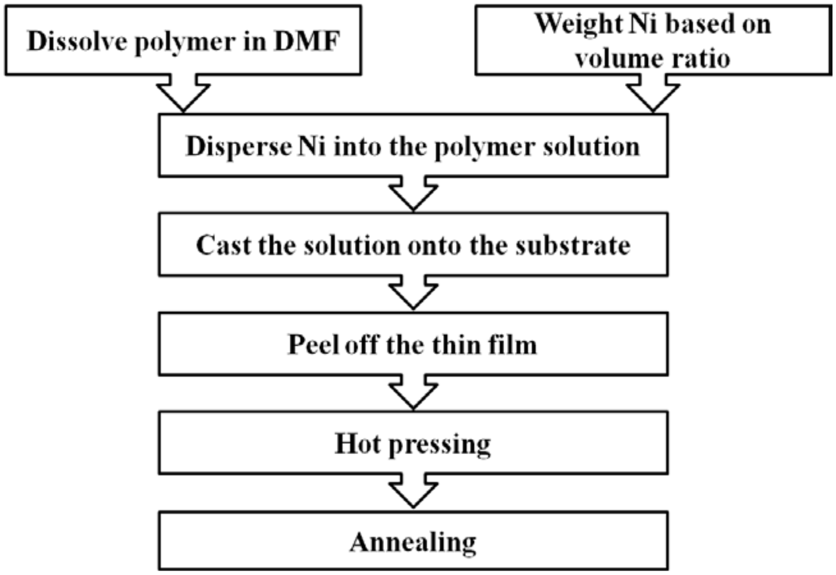

Figure 2.1. Process Flowchart for hot-press solution casting composite

2.2.1 Solution Casting Process

In order to deal with the uniform issue to make the repeatable experimental result, the first step is to try to make a more uniform as-cast film.

Compared with solid phase processes (mechanical approaches), a solution process, one of the liquid phase processes, is to mix the components with the aid of the solvent. This mixing process is to ensure better dispersion of fillers and stronger interfacial interaction.

Dimethyl formamide (DMF) has been chosen as a suitable solvent for P(VDF-TrFE) 70/30 mol% copolymer, which was dissolved in DMF under magnetic stirring for 12 hours. After the P(VDF-TrFE) was dissolved in DMF, filler Ni particles were added into the solution. The nano Ni powder with diameter less than 100 nm was purchased from Sigma Alorich. Figure 2.2 shows the identification of the purity of the nano Ni (D<100 nm) with XRD (Bruker D8). Three characteristic peaks for Ni (2θ=44.8°, 52.0°, 76.7°) were observed, and peaks for the oxides were not observed.

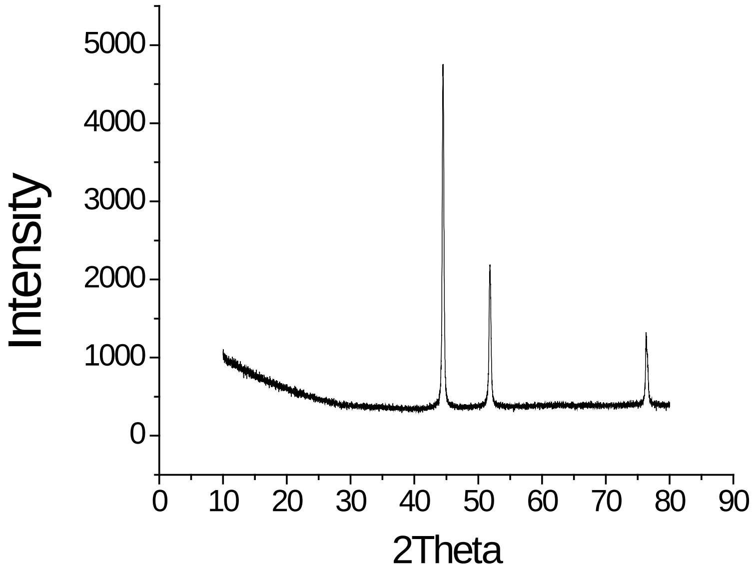

Figure 2.2. XRD pattern of Ni nanopowder

In an attempt to achieve uniform distribution of Ni powder inside the polymer solution, a mixing procedure was taken. First, the composites were hand-stirred for 15 minutes as a premixing step. And then the solution from the first step is further dispersed in an ultrasonic chamber for 1 hour.

The final Ni-P(VDF-TrFE) solution was cast on a glass plate at 70ºC for 8 hours. After 8h heating, the composite films were formed after drying the DMF solvent. The cast film was released from the glass plate by immersing it into D.I. water. The final product is a flexible film.

The Ni-P(VDF-TrFE) composites with different Ni volume concentrations (5, 10, 15, 20, 25 vol%) were initial attempt to make. A volumetric ratio table for Ni-P(VDF-TrFE) samples on a 10 cm × 15 cm solution casting glass plate is given in Table 2.1. The weight of polymer is fixed and the weight of Ni is changed based on the volume ratio. As shown in Table 2.1, a fixed amount of solvent (25 ml) was used, since this appropriate amount of solvent is not only enough to ensure uniform dispersion of Ni particles within the polymer solution but also effective to be evaporated.

Table 2.1. Volumetric ratios in Ni- P(VDF-TrFE) composites samples

Volume percentage of Ni (%)	70/30 P(VDF-TrFE) (g)	Ni (g)	DMF (ml)
0%	1	0	25
5%	1	0.2661	25
10%	1	0.5619	25
15%	1	0.8924	25
20%	1	1.2642	25
25%	1	1.6856	25

However, when the concentration is higher than 20 vol%, as-cast film cannot be peeled off from the glass substrate. Therefore, the big glass substrate was replaced by the quartz substrate with 7.6×7.6 cm (3×3 in, Fisher Scientific), in order to fix the peeling off problem of thin film with higher concentration. A similar solution casting method was followed by the preparation of another batch sample using the smaller quartz substrate.

Table 2.2.Volumetric ratios in Ni- P(VDF-TrFE) composites samples using the quartz substrate

Volume percentage of Ni (%)	70/30 P(VDF-TrFE) (g)	Ni (g)	DMF (ml)
0%	0.3	0	10
10%	0.3	0.1686	10
20%	0.3	0.3793	10
30%	0.3	0.6502	10
40%	0.3	1.0114	10
50%	0.3	1.5170	10

Replacing the quartz substrate not only fixed the peeling-off problem, but improved the dielectric properties that will be discussed in the next chapter. The difference between the glass substrate and quartz is chemical composition, which plays a role in the interaction with the solution cast onto the substrate.

2.2.2 Hot Pressing Process

In this work, it was found that the as-cast film will consist of two layers: a polymer rich layer and a Ni rich layer (shown in Figure 2.3) because of the poor wettability between metal and polymer matrix. This situation can be considered as a series capacitor circuit of high and low capacitance capacitors, resulting in a lower effective capacitance (discussed in chapter 1). Therefore, a hot pressing process is needed to improve the uniformity of Ni-polymer composite.

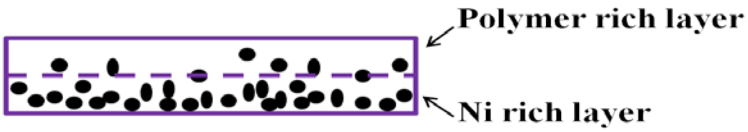

Figure 2.3.Schematic of cross section view

During a hot pressing process, stacked layers of as-cast film were pressed at high pressure and temperature. Small pieces of as-cast film were cut and folded in a selective manner. There are two different stacking patterns, as shown in Figure 2.4: (a) The top (polymer rich) layer of the film was placed facing the bottom (Ni rich) of the film; (b) The bottom layer of the film was placed facing the bottom the film. In this work, pattern b) was applied to make a 4-layered composite film, shown in Figure 2.4 (c).

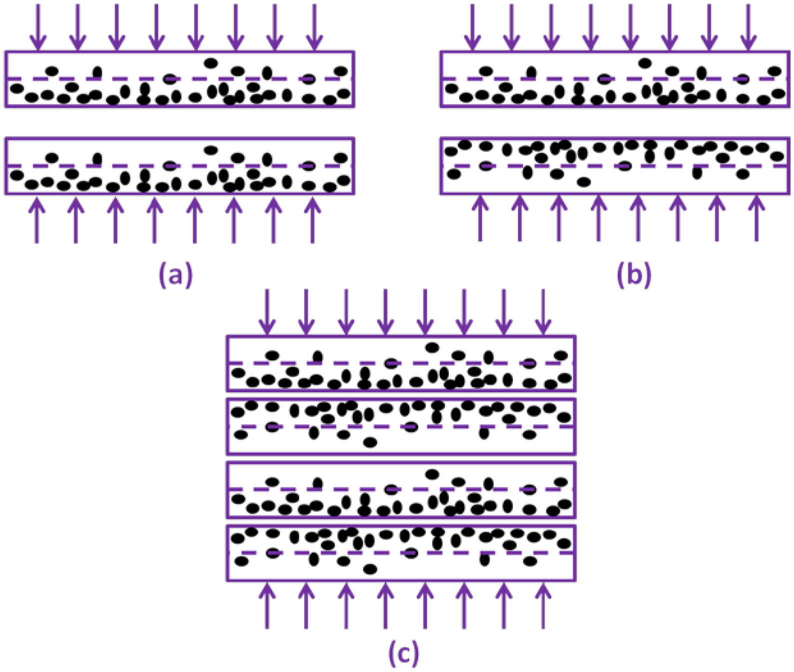

Figure 2.4. Diagram of stacking patterns

Then, this 4-layered composite film was placed in mound plates and after applying the force (10 tons) at 150 ^{o}C the 4-layer film would become 1 plate. The pressure and temperature set here was modified several times until that the plate was observed uniform. The images of the cross section view are shown in Figure 2.5, in which there are several apparent layers and the interface images are shown in Figure 2.6.

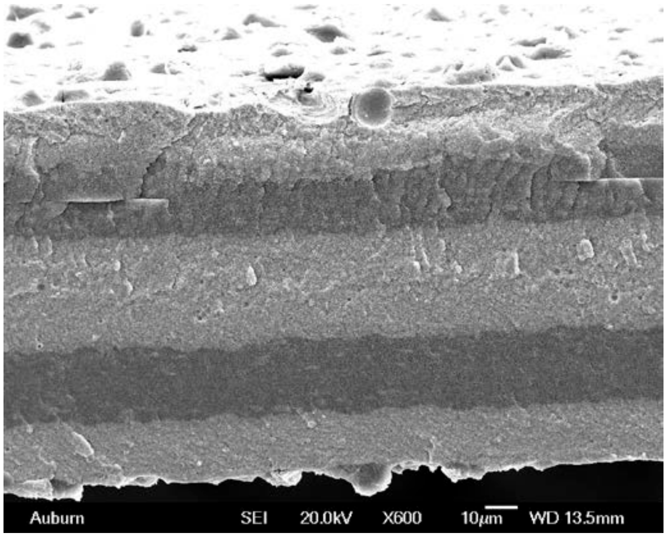

Figure 2.5. SEM image of 4-layer Ni-P (VDF-TrFE) 70/30 composite

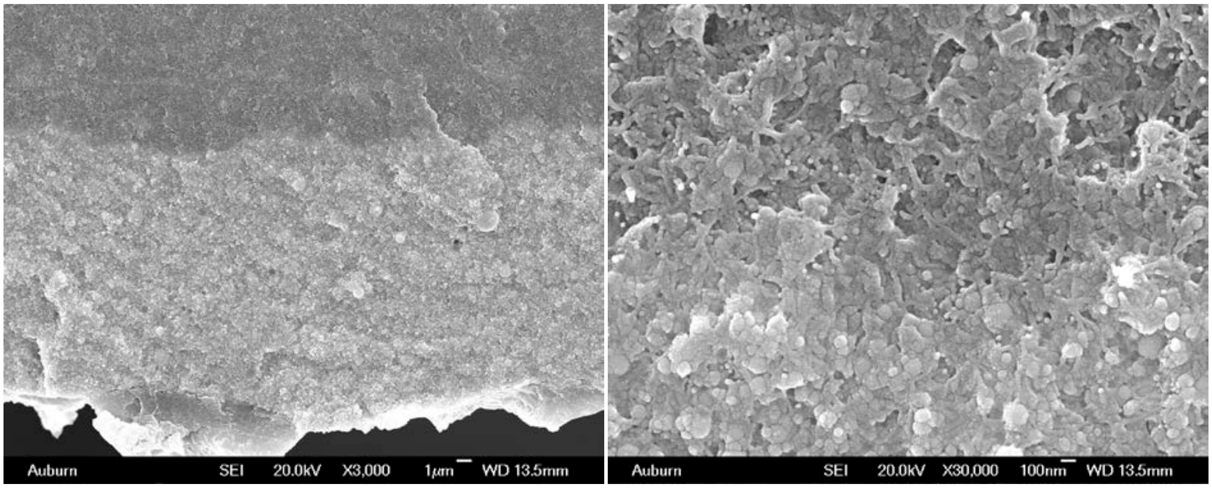

Figure 2.6. Interface image of 4-layer Ni-P (VDF-TrFE) 70/30 composite

In order to eliminate the interfaces of many layers, it is necessary to make sure the molten polymer run through the Ni rich regions. The preheating processing before applying the force is needed to improve the uniformity of the multi-layer composite. Therefore, stacking films were preheated in the mound 20 minutes at 150 ^{o}C and then pressed 10 seconds at tons.

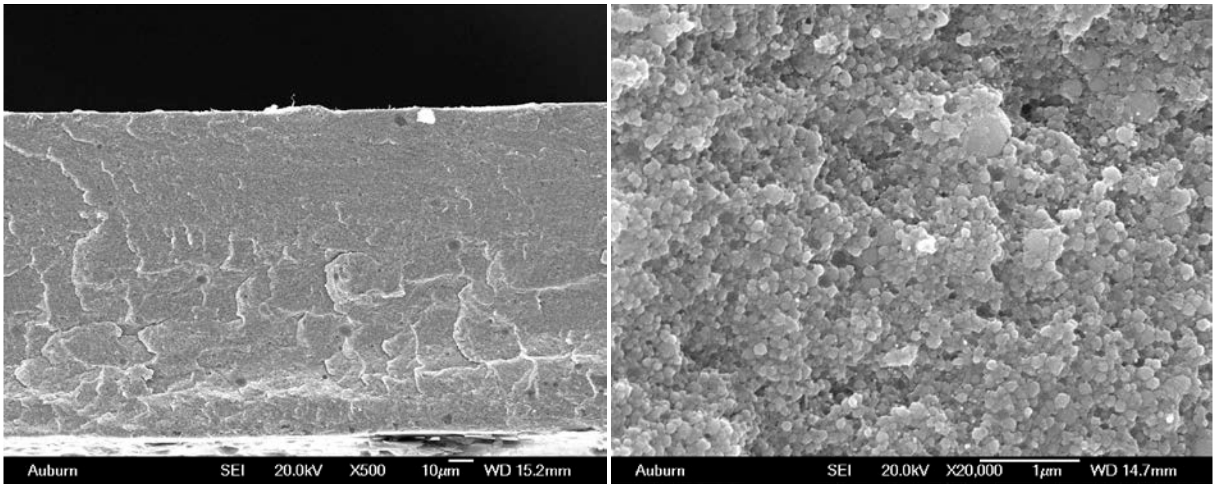

Figure 2.7. The images of 4-layer nano Ni-(VDF-TrFE) 70/30 with preheating 20 min before hot pressing

Figure 2.7 shows that the image of the cross section view with different magnifications. There is no apparent interfacial layer in the cross section view. In short, 20 min preheating before the hot pressing can improve the interfacial issue of the multiple-layer configuration.

2.2.3 Annealing Process

The removal of the residual DMF solvent and the improvement in crystallinity of P(VDF-TrFE) play an important role on the overall electrical properties of the Ni-P(VDF-TrFE) composites. Therefore, an additional process was carried out to improve the dielectric properties of composites. A hot-press solution casting films were put between two glass plates and annealing was carried out at 120 ^oC for 10 hours in an oven. In addition, people found that hot-press samples followed by thermal annealing yields a dense microstructure and higher dielectric constants [1][2].

2.3 Materials Characterization Methods

2.3.1 Microstructure Analysis Using SEM

The morphologies and the composition distribution of the Ni nanopowder-P(VDF-TrFE) composite films were examined by JEOL JSM 7000F FE-SEM (Scanning Electron Microscopy). For the SEM fractographs, to obtain the neat fracture surface and cross section of good quality, the sample needs to be frozen and broken in liquid nitrogen, avoiding brittle fracture, And there must be a conductive layer on the top of the surface observed by SEM, so samples were stuck on carbon tape and then a layer of gold was deposited using a Pelco SC-6 sputter coater.

2.3.2 Dielectric Analysis Using Impedance Analyzer

The dielectric properties of the composite are not only dependent on volume fraction of the fillers but frequency. Therefore, dependence of dielectric response on the volume fraction of Ni particles at specific frequency and room temperature would be identified.

Those samples were sputtered with gold on top and bottom surfaces as electrodes using a PelcoSC-6 sputter coater. A special mask was used for coating the electrodes with diameter 3.2 mm, as shown in Figure 2.8. In order to obtain an electrode surface covered well by gold, 30 seconds per coating and 4 times for each side is necessary. The optical microscope images of the electrodes are shown in Figure 2.9 and Figure 2.10.

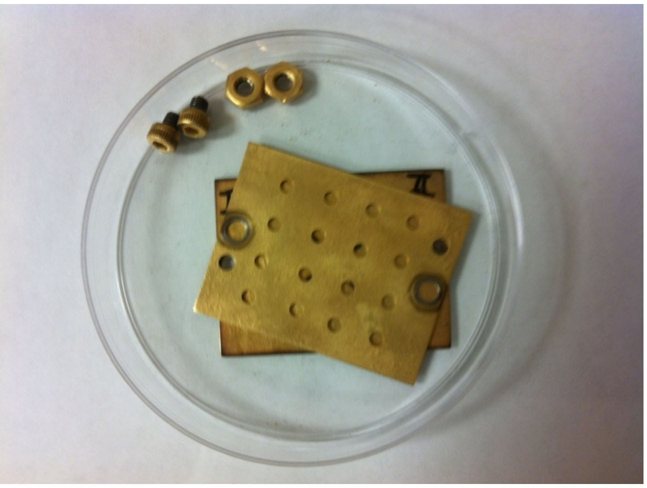

Figure 2.8. Image of mask with holes diameter of 3.2 millimeters.

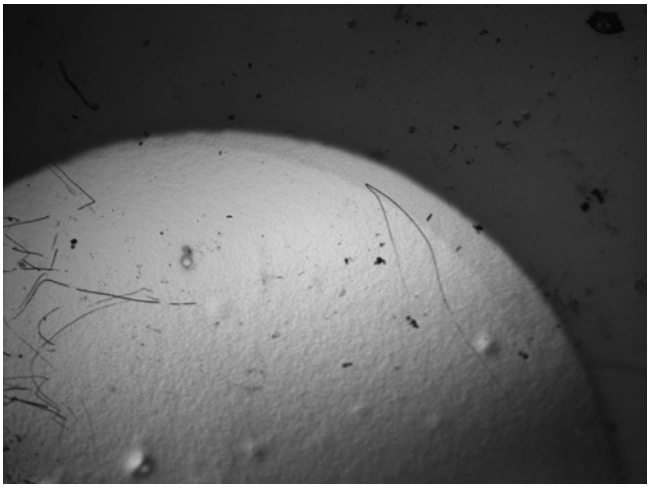

Figure 2.9 The electrode surface of pure P(VDF-TrFE) 70/30

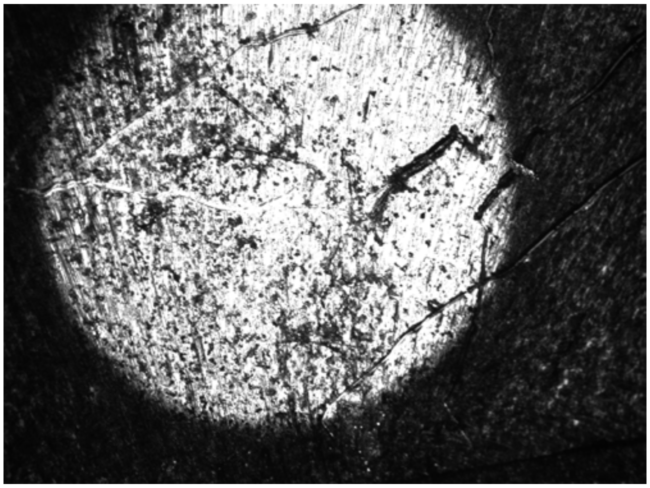

Figure 2.10.The electrode surface of a 4-layer sample 60% nano Ni- P(VDF-TrFE)

And then the dielectric properties were measured by an Agilent 4294A impedance analyzer in frequency ranges of 100 Hz–10MHz at room temperature.

From impedance analyzer, we can get the capacitance then to convert to the dielectric constant:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \tag{2-1}$$

C is capacitance, ε_0 is a universal constant having the value of 8.85×10^{-12} F/m. d is the thickness of the sample that can be measured, and *A* is area of electrodes of the capacitor that can be calculated based on the diameter of mask.

In addition, many research works [3] have proved a strong temperature dependence of dielectric permittivity in conducting fillers-polymer composites. In this work, a temperature range of 30 ºC to 150 ºC is used to characterize the temperature dependence of the dielectric response, which would be discussed in the next chapter.

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CHAPTER 3

STUDY OF DIELECTRIC BEHAVIOR AND STRUCTURE ON Ni -P(VDF-TrFE) COMPOSTES

3.1 Introduction

In this chapter, the hot-press solution casting Ni-P(VDF-TrFE) composites were studied mainly by impedance analysis and microstructure analysis.

Dielectric materials are often used in different environments, such as in measurement of frequency and of environmental temperature. It is found that these factors have a decisive effect on the dielectric properties of polymer matrix composites. The Agilent 4294A impedance analyzer was employed to characterize the dielectric property of the samples over a frequency range of 100 Hz to 1 MHz.

In order to characterize the temperature dependence of the dielectric response, samples were put into a test fixture that is connected to the impedance analyzer and then heated using a Fisher Isotemp 800 Series Programmable oven with temperature range of 30 ºC to 150 ºC. The setup is shown in Figure 3.1: inset is the test fixture for holding the samples.

Figure 3.1. Setup of temperature dependence measurement showing impedance analyzer, temperature over and test fixture for holding samples

Uniformity and reliability of Ni-P(VDF-TrFE) composite can be identified: The microstructure of the cross section of the sample was observed using scanning electron microscope (SEM JSM-7000F, JEOL); The influence of uniformity on the dielectric constant Ɛ' was studied by comparing Ɛ' of different samples with the same processing and concentration.

3.2 Impedance Analysis

3.2.1 Frequency Dependence of Dielectric Properties at Room Temperature

Dielectric behaviors of the composites as a function of volume fraction v_{Ni} and frequency have been studied at room temperature. In this work, three individual samples with the same concentration were measured and the average of them was used to indicate the results.

3.2.1.1 Dielectric Properties with the Big Glass Substrate

The initial solution casting composite films on the big glass substrate were studied. Figure 3.2 shows the dielectric constant and loss of the Ni- P(VDF-TrFE) composites with different Ni concentrations from 0% to 20%.

The films with Ni concentration higher than 20% are not prepared because the solution casting film with higher concentration using the glass substrate cannot be peeled off.

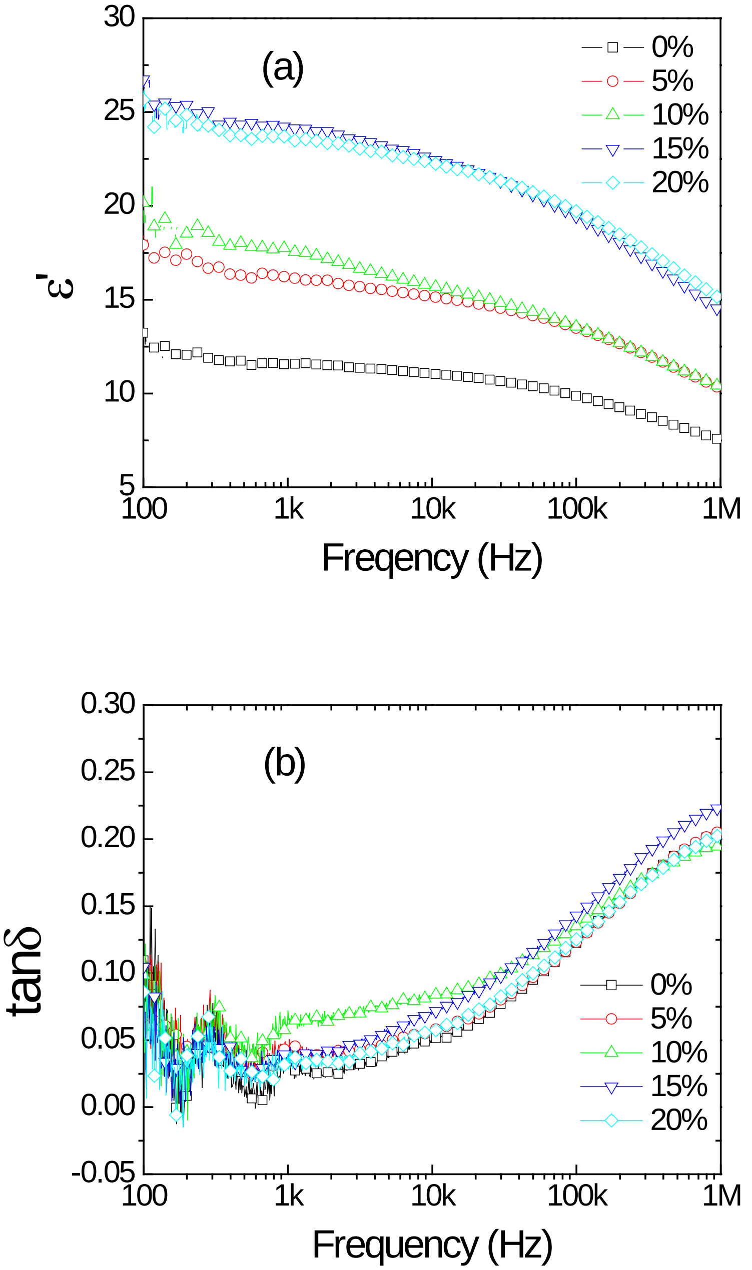
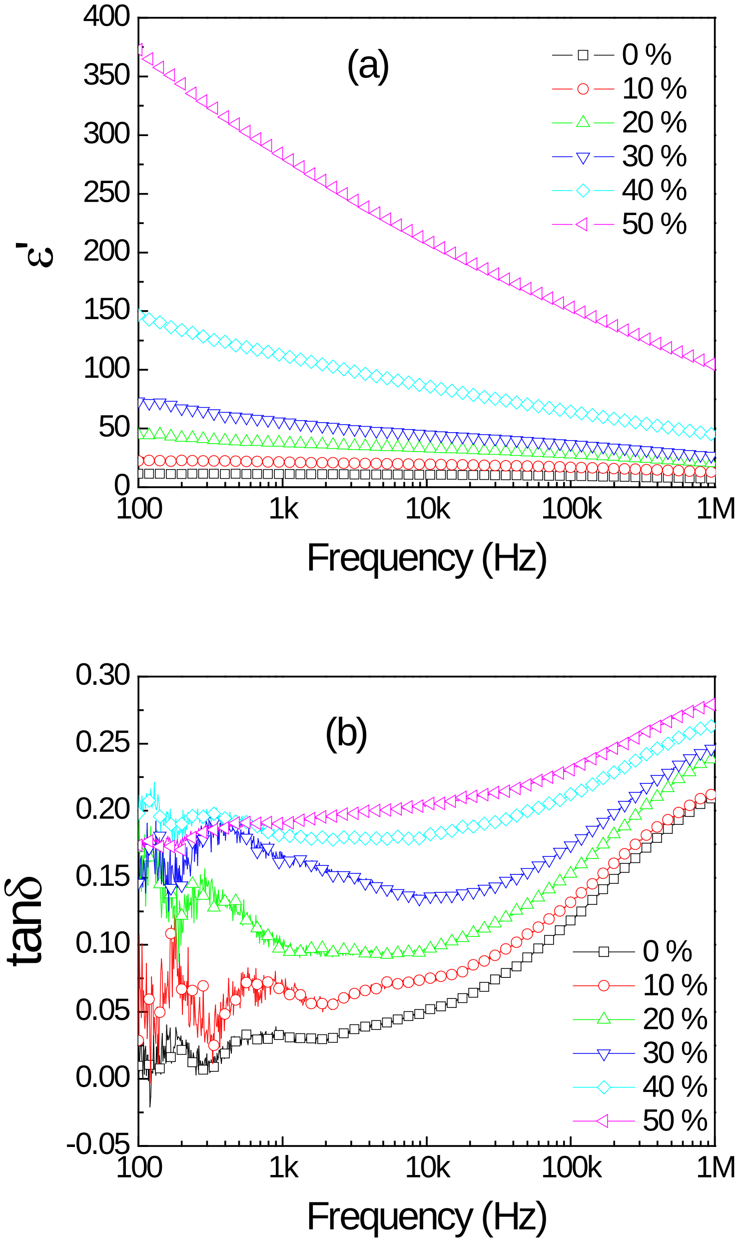


Figure 3.2.The dielectric responses (a) dielectric constant and (b) dielectric loss as a function of frequency for the composites using the big glass substrate

3.2.1.2 Dielectric Properties with the Quartz Substrate

The experiment was improved by replacing the glass substrate with quartz substrate and dielectric behaviors of Ni-P(VDF-TrFE) composites as a function of frequency are shown in Figure 3.3: (a) Ɛ' vs. frequency; (b) tanδ vs. frequency; (c) Ɛ" vs. frequency and (d) Complex permittivity plots Ɛ" vs. Ɛ', also named Cole-Cole plot. The concentration of Ni varied from 0 vol% to 50 vol%, the Cole-Cole plots were found to vary from an uncompleted semicircular shape to a somewhat flattened shape. For an ideal dielectric the Cole-Cole plot is a perfect single semicircle [1]. It is to note the higher concentration of the conductors in the composites, the further the Cole-Cole plot departs from the semicircular diagram.



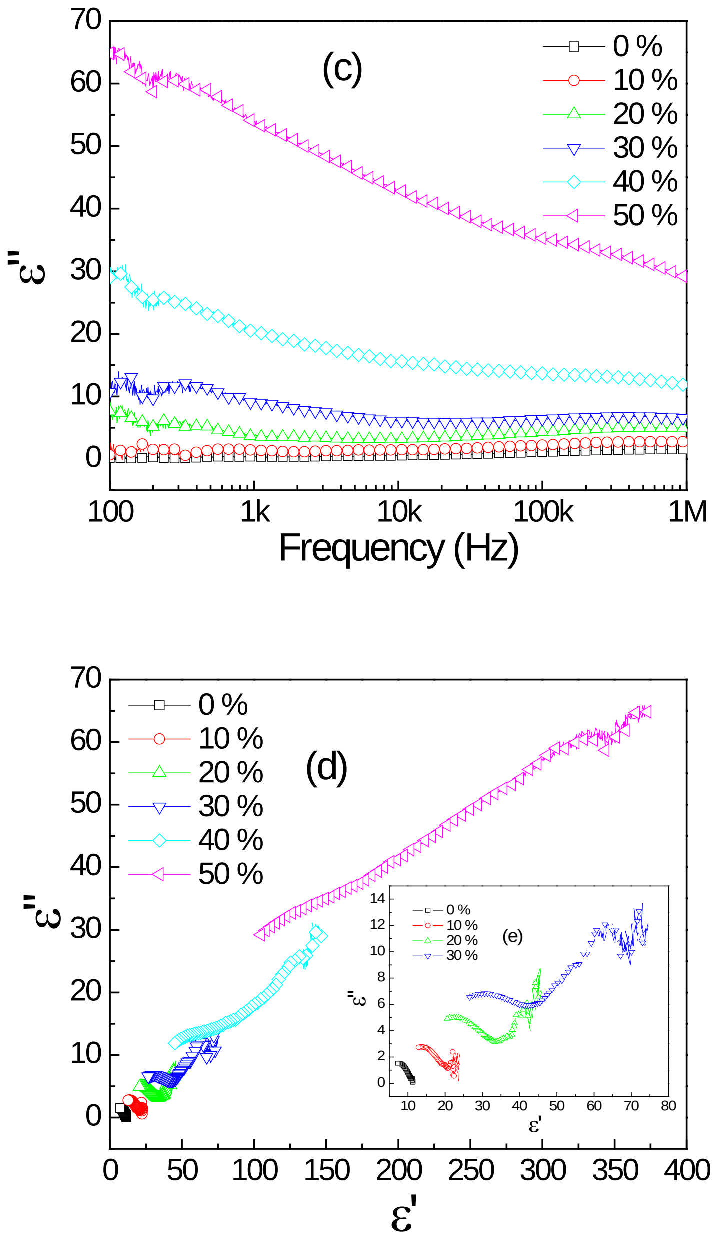
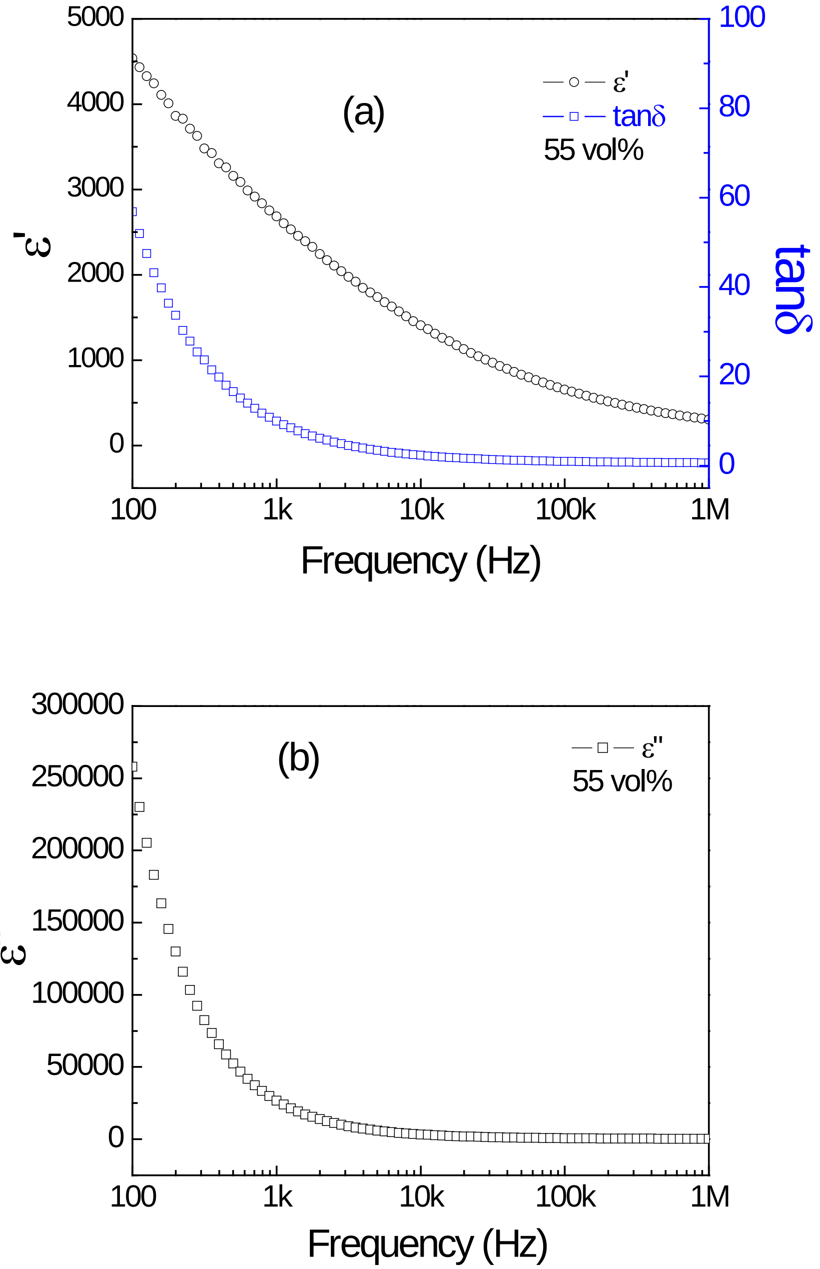


Figure 3.3. Dielectric responses (a) dielectric constant, (b) dielectric loss (c) Ɛ" as a function of frequency and (d) Cole-Cole pole for the composites using the small quartz substrate

In order to approach the percolation threshold as closely as possible, a series of Ni-P(VDF-TrFE) composites with higher volume fraction of Ni were prepared and studied. The first trial was adding 55vol% Ni into the polymer matrix. The dielectric measurement results of the three samples were not consistent and dielectric properties for one of them was selected to show in Figure 3.4. A very high loss of 55 near 100 Hz, as shown in Figure 3.4 (b), may be considered as the evidence of the large leakage current in the composite. At the same time, the dielectric constant is correspondingly high at 100Hz. However, the dielectric constant is not real due to the fact that the composite becomes a conductor. As discussed above, the percolation threshold is the critical point undergoing the insulator-conductor transition. Therefore, 55 vol% is already over the percolation threshold and the composite with 53 vol% is prepared for study.



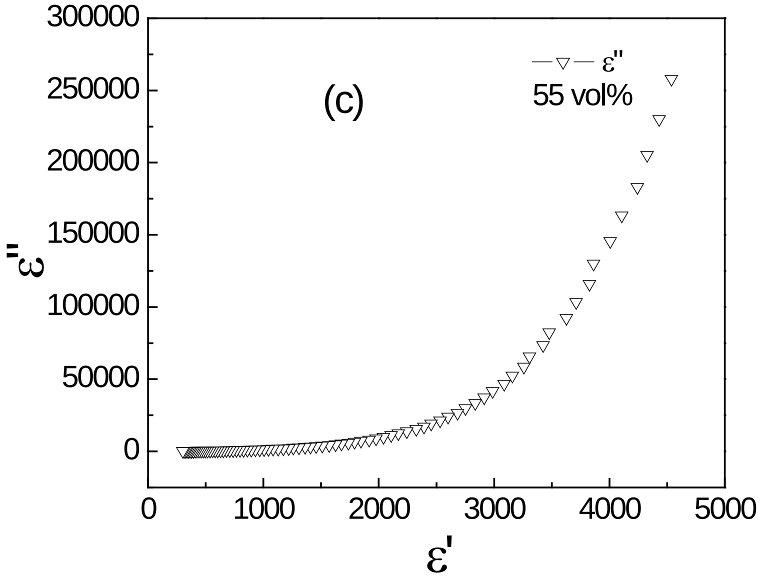
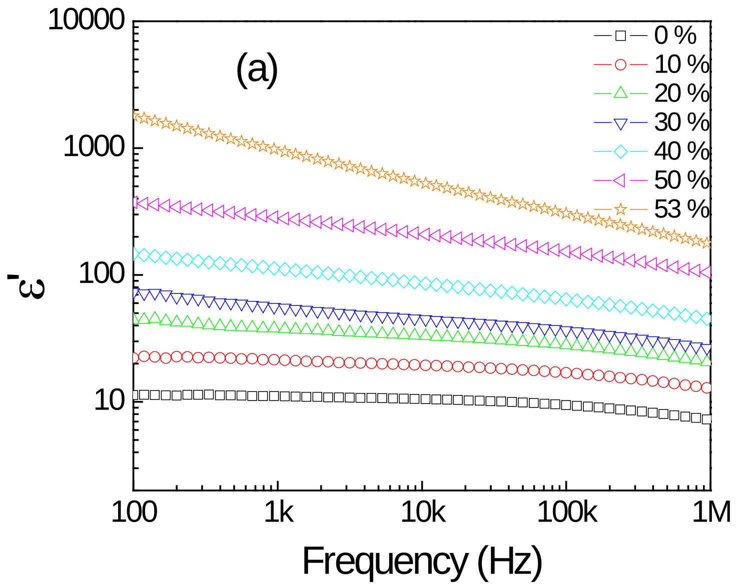
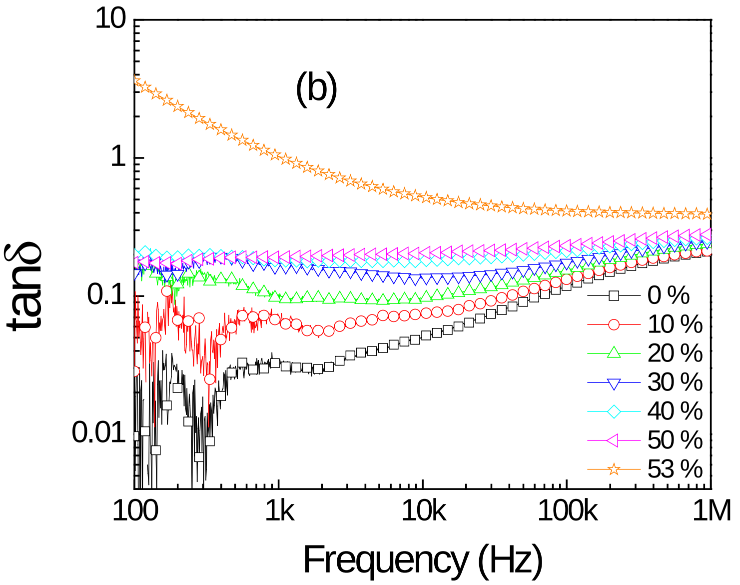


Figure 3.4. Dielectric response (a) dielectric constant and dielectric loss (b) Ɛ'' as a function of frequency and (c) cole-cole pole of Ni-P(VDF-TrFE) composite with 55 vol% Ni

Figure 3.5 shows the log-log representation of dielectric response of Ni-P(VDF-TrFE) composites with Ni concentration from 0 vol% to 53 vol%. The values in the Figure are dependent on both the measuring frequency and Ni volume fraction.

With increasing frequency from 10^2 Hz toward 10^6 Hz, the dielectric constant of samples displays a slight drop at the lower filler loading. And at higher concentration the dielectric constant reduces more rapidly with increasing frequency. In conclusion, increasing the filler content, the dependence of dielectric properties on frequency was becoming stronger. When Ni addition was below 40 vol%, it exhibited relatively weak frequency dependence.


(a)
10000
1000
100
10
ε'
100
1k
10k
100k
1M
Frequency (Hz)
0 %
10 %
20 %
30 %
40 %
50 %
53 %


(b)
10
1
0.1
0.01
tanδ
100
1k
10k
100k
1M
Frequency (Hz)
0 %
10 %
20 %
30 %
40 %
50 %
53 %

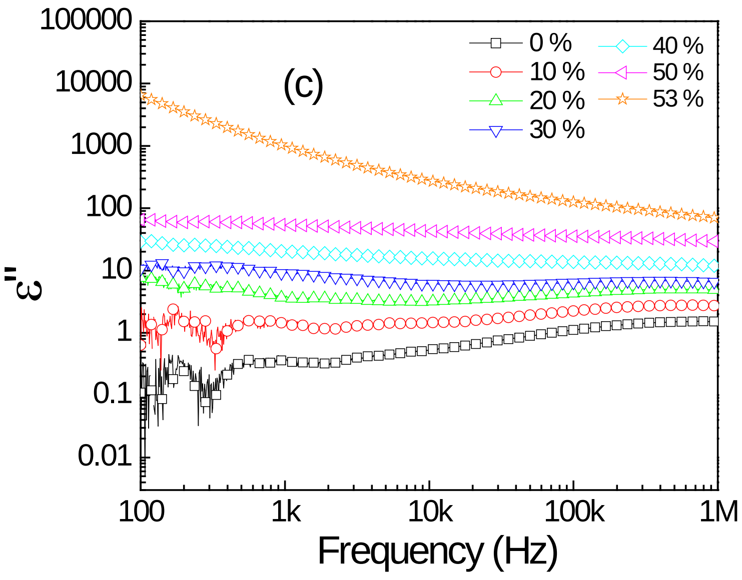
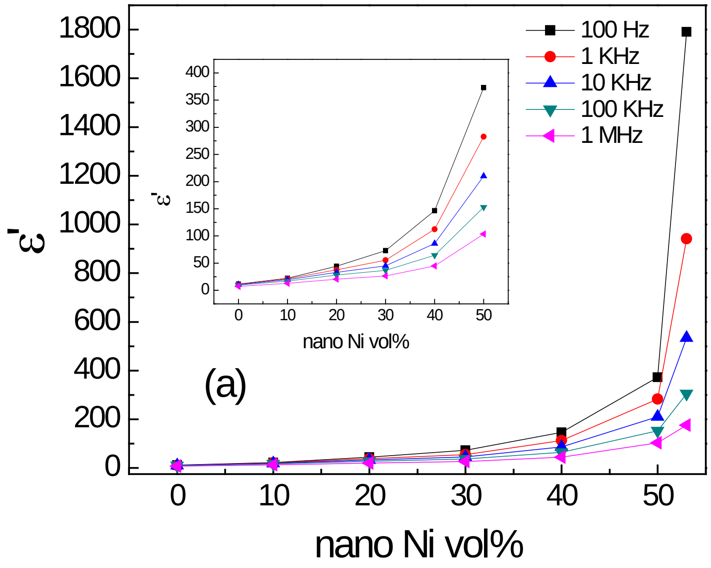


Figure 3.5. log-log representation of frequency dependence of dielectric response (a) dielectric constant (b) dielectric loss (c) Ɛ" of Ni-P(VDF-TrFE) composites

In order to get a better idea about the dependence of dielectric constant on Ni concentration, Figure 3.5 (a) and (b) can be repotted to show dielectric constant and loss with Ni volume fraction as variable, as shown in Figure 3.6.



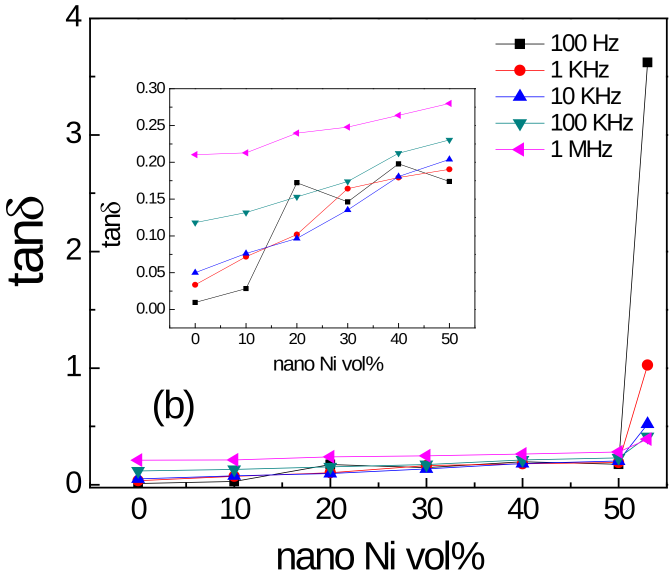


Figure 3.6. Volume fraction dependence of the dielectric properties (a) dielectric constant (b) dielectric loss for Ni-P(VDF-TrFE) composite at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively.

As shown in the Figure 3.6 (a), the dielectric constant rises gradually with increasing filler contents in the composites until the filler content reaches 50%. Subsequently, the dielectric constant increases abruptly. In particular, when the volume fraction increases from 50% to 53% at 100 Hz, the dielectric constant rises steeply from 373 to 1791 about 140 times higher than the dielectric constant of pure P(VDF-TrFE), while it is rising from 283 to 941 at 1 kHz. This sharp increase of dielectric constant can be explained by the percolation theory.

The sensitivity of the dielectric constant can be reflected by the rate of change of dielectric constant with respect to volume fraction, as shown in Figure 3.7. $\frac{d\varepsilon'}{dv_n}$ the derivative of dielectric constant with respect to volume fraction v_n can be achieved by OrginPro using discrete data by formula:

$$f'(x_i) = \frac{1}{2}\left(\frac{y_{i+1}-y_i}{x_{i+1}-x_i} + \frac{y_i-y_{i-1}}{x_i-x_{i-1}}\right) \qquad \text{(3-1)}$$

Calculate the derivative at point P_i by taking the average of the slopes between the point and its two closest neighbors. For this derivative function applied, the result of two end points 0% and 53% is problematic. And the change from point 50% to 53% is so significant as to bring some errors to the 50%. However, it can roughly show that the rate of change is increasing with increasing v_n. In particular, the extreme sensitivity of the dielectric constant near the conductive fillers content of 53% makes it difficult to control the parameters of the preparation process. The issues mentioned above are considered as drawbacks for conducting fillers-polymer composite systems. Therefore, the concentration of Ni is not supposed to be prepared near 53% in concern with the application and the “safe” range is before 50%. In addition, when the filler concentration is lower than 40%, the dielectric constant will stay constant even filler concentration changes a lot.

On the other hand, as shown in the Figure 3.6 (b), the dielectric loss for the composite film containing 50 vol% Ni is about 0.17 at 100 Hz and maintains a value under 0.28 irrespective of the frequency, which is attractive for practical use. However, the loss of the composite undergoes a sharp increase at low frequency at 53 vol%, at which the loss was 3.62. Such increase of the loss tangent is the inevitable consequence of the significantly raised conductivity in the composites and can be considered as one important feature of the percolative composite.

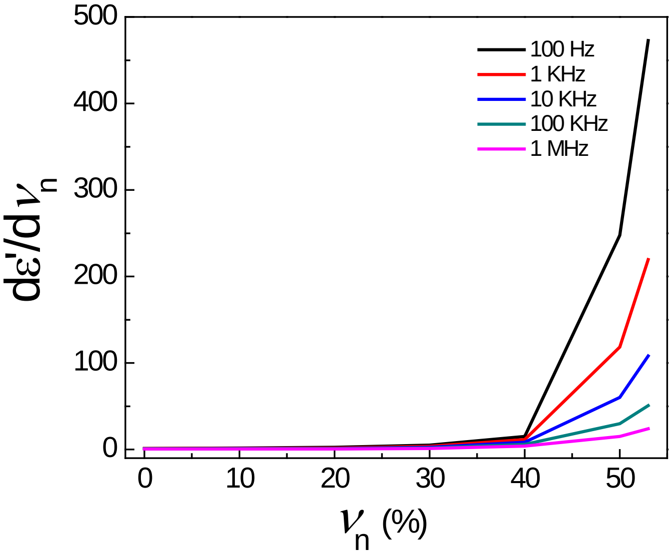


Figure 3.7. Rate of change of dielectric constant with respect to volume fraction at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively

3.2.2 Temperature Dependence of Dielectric Properties

It is known that the dielectric constant is a function of both the frequency and the temperature. In order to understand how temperature affects the dielectric behavior, temperature dependent measurements were carried out. The dielectric properties of composites with various concentrations were measured over a temperature range of 30 ºC to 150 ºC with the interval of 5 ºC. Figures 3.8 through Figure 3.13 show the shows temperature dependence of dielectric properties for Ni-P(VDF-TrFE) composites with different contents of Ni at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

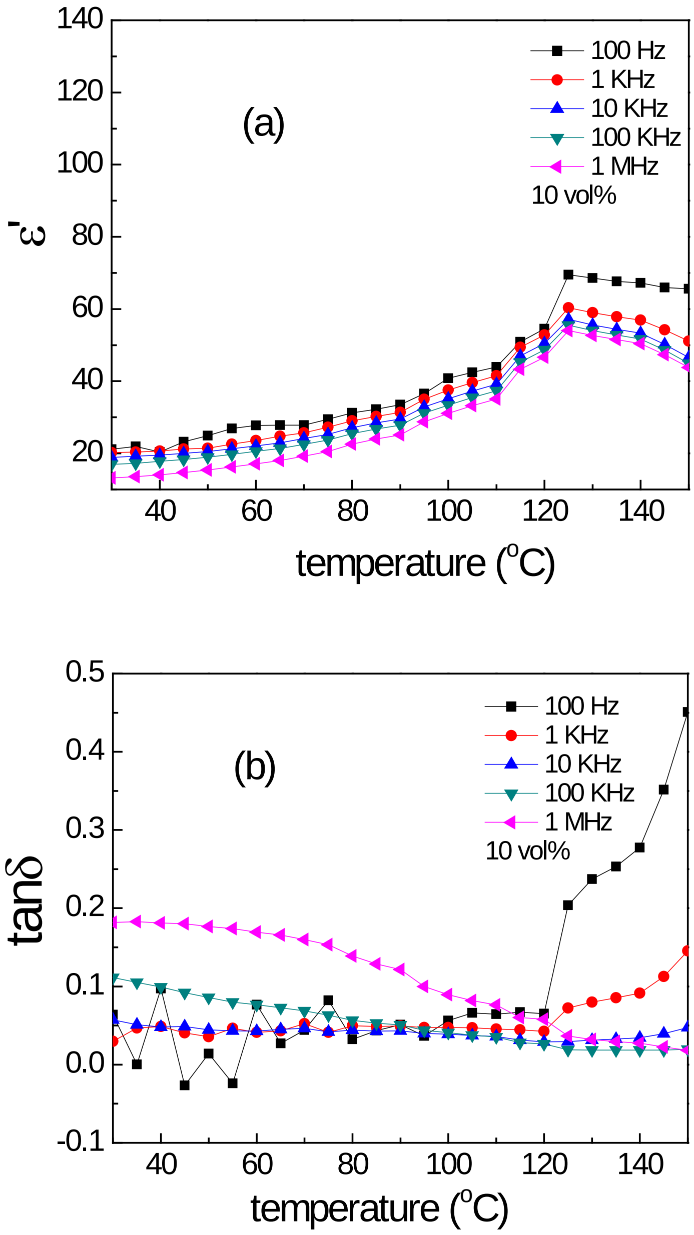


Figure 3.8.Temperature dependence of (a) dielectric constant and (b) dielectric loss of Ni/P(VDF-TrFE)70/30 with 10% Ni

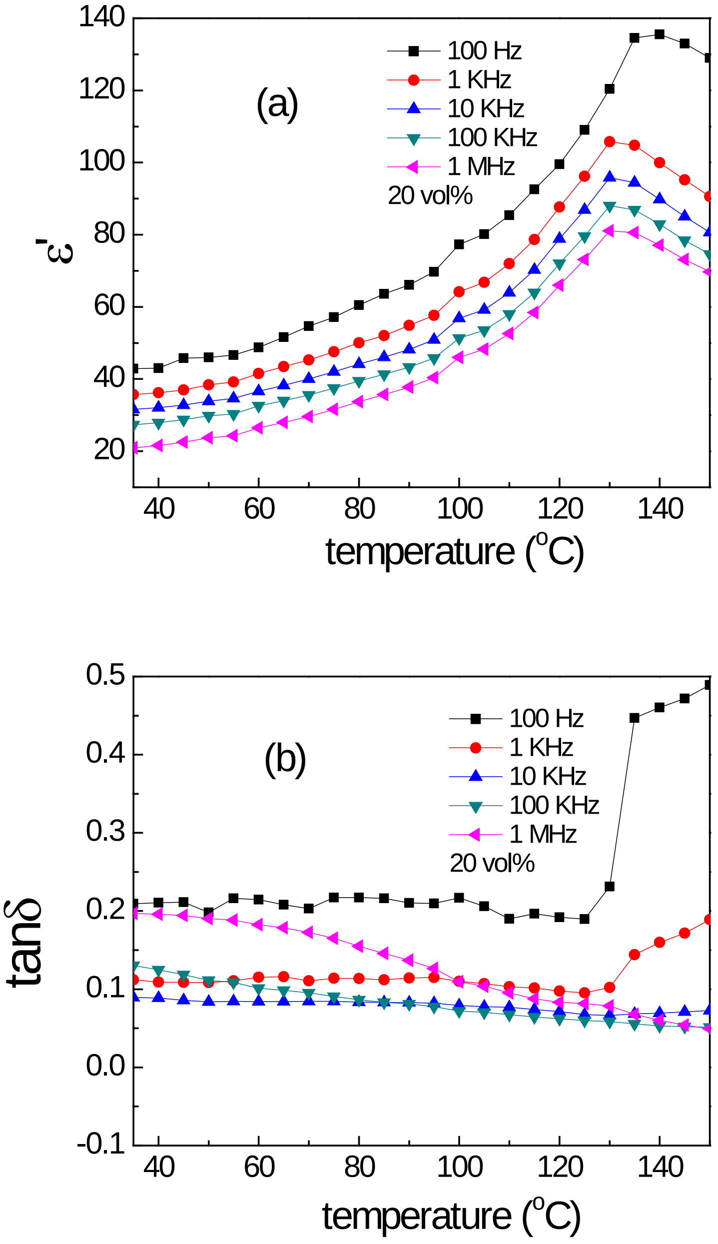


Figure 3.9. Temperature dependence of (a) dielectric constant and (b) dielectric loss of Ni/P(VDF-TrFE)70/30 with 20% Ni

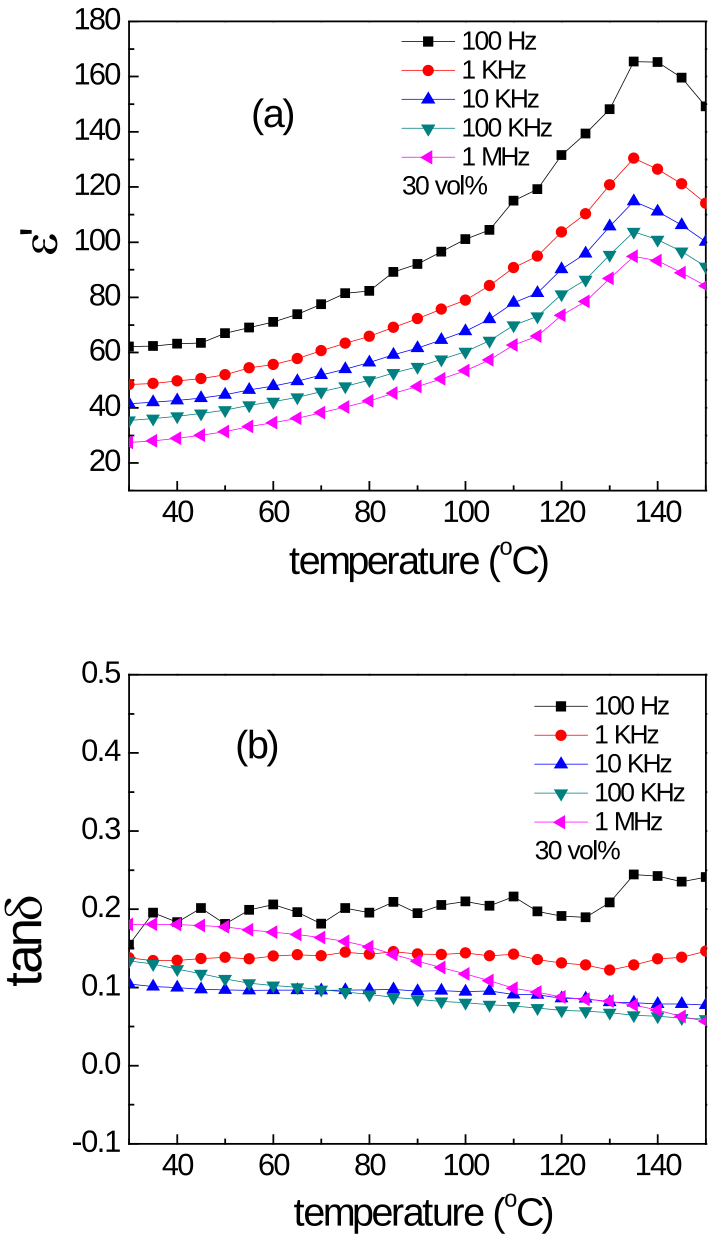


Figure 3.10. Temperature dependence of (a) dielectric constant and (b) dielectric loss of Ni/P(VDF-TrFE)70/30 with 30% Ni

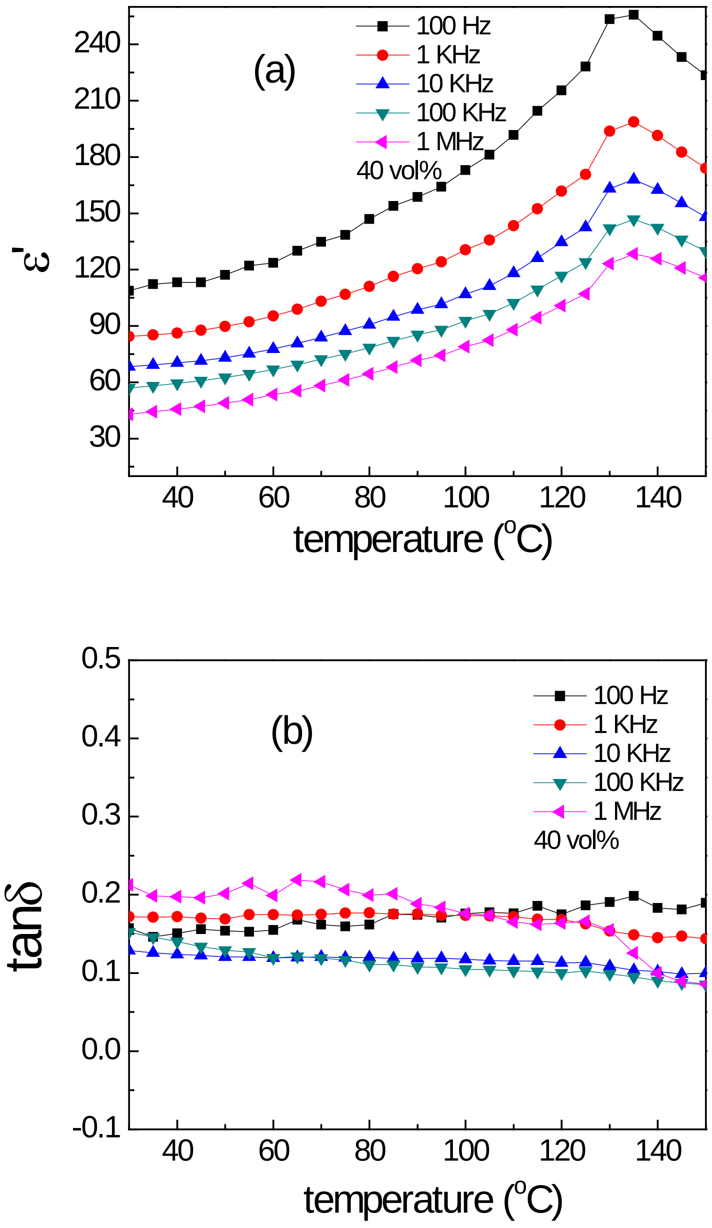


Figure 3.11. Temperature dependence of (a) dielectric constant and (b) dielectric loss of Ni/P(VDF-TrFE)70/30 with 40% Ni

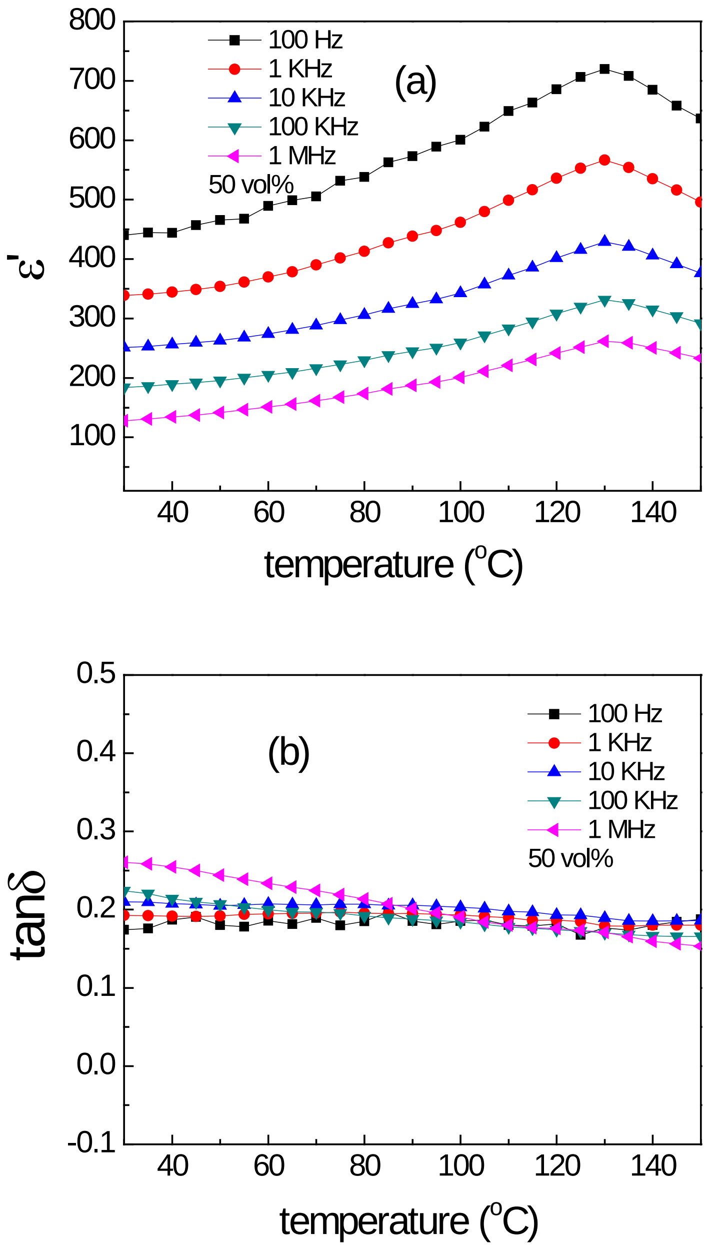


Figure 3.12. Temperature dependence of (a) dielectric constant and (b) dielectric loss of Ni/P(VDF-TrFE)70/30 with 50% Ni

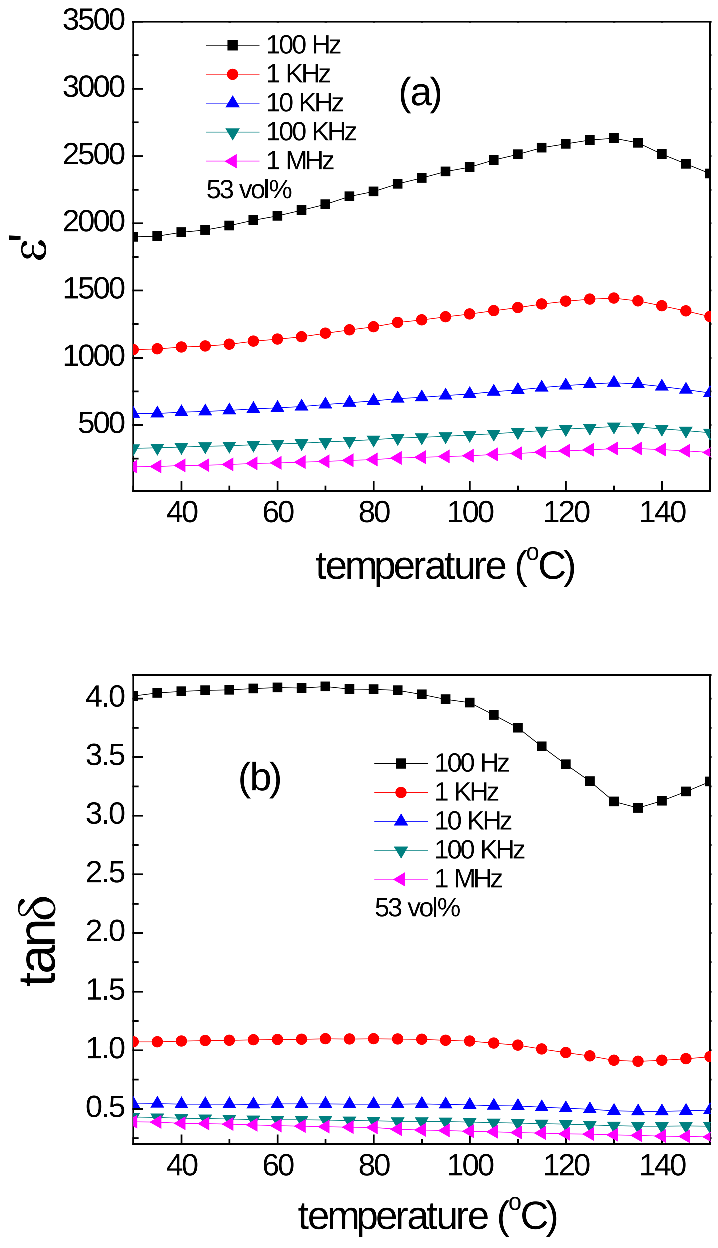


Figure 3.13. Temperature dependence of (a) dielectric constant and (b) dielectric loss of Ni/P(VDF-TrFE)70/30 with 53% Ni

Different frequencies tended to give the similar tendency that the curves reached their dielectric constant peaks and then leveled off, as shown in Figure 3.8-3.13. There is a contribution of temperature for an increment in the dielectric value of the composites, especially for composites with low volume fraction of Ni, shown in Table 3.1.

Table 3.1. Summary of dielectric constant at room temperature and peak temperature

Samples	Dielectric constant at 1 kHz	
	@ 30 ºC	peak @ temperature
Ni-P(VDF-TrFE) with 10 vol%	20.2	60.3 (@125 ºC)
Ni-P(VDF-TrFE) with 20 vol%	36.2	105.8 (@130 ºC)
Ni-P(VDF-TrFE) with 30 vol%	48.5	130.4 (@135 ºC)
Ni-P(VDF-TrFE) with 40 vol%	84.4	193.7 (@130 ºC)
Ni-P(VDF-TrFE) with 50 vol%	338.7	566.4 (@130 ºC)
Ni-P(VDF-TrFE) with 53 vol%	1060	1443 (@130 ºC)

These peaks are attributed to the contribution of the polymer matrix, since peaks occur near 130 ºC regardless of filler volume%. And this kind of peak temperature is known as the Curie temperature for phase transition from the ferroelectric phase into paraelectric phase.

Frequency dependence results show in the Figure 3.14-Figure 3.20, in which 40 ºC, 60 ºC, 80 ºC, 100 ºC are selected in concern with the application, of which the temperature range is generally chosen between 30 ºC to 100 ºC. Figure 3.14 shows the dielectric properties of pure P(VDF-TrFE) 70/30, which is the one layer as casting film with annealing 12 hours at 120 ºC.

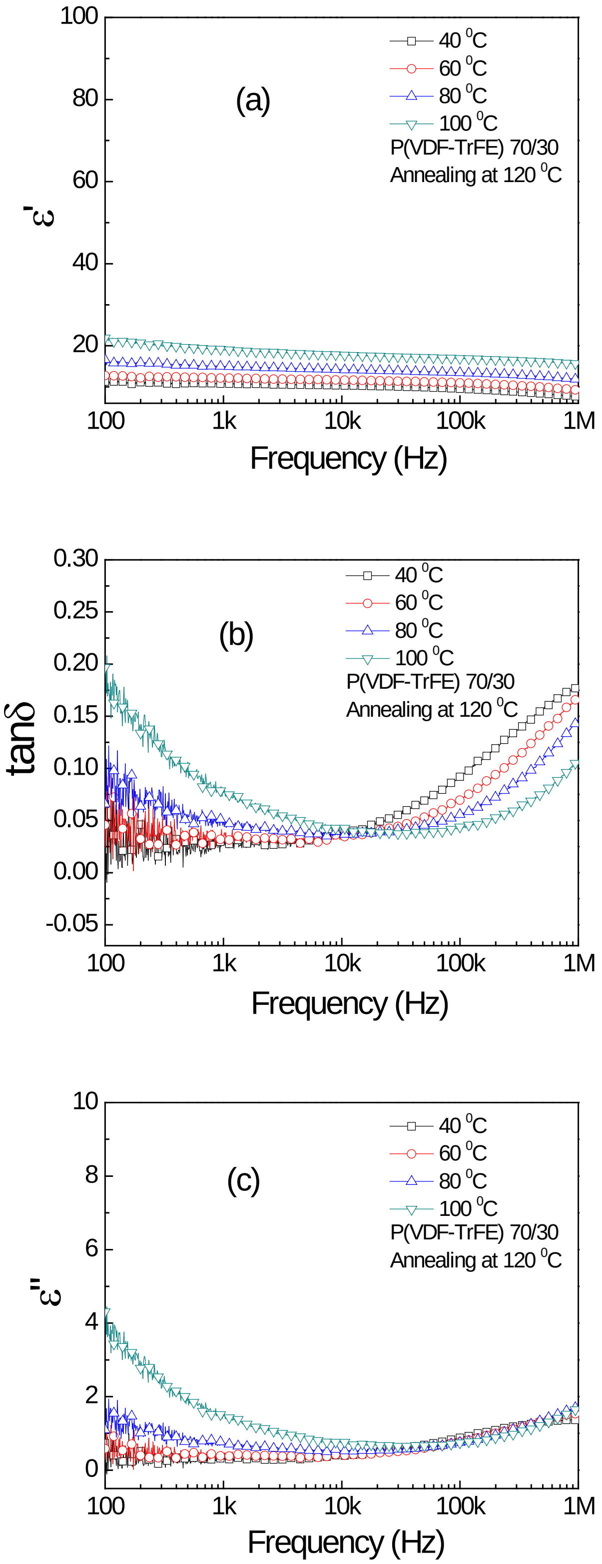


Figure 3.14. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ" of pure P(VDF-TrFE) 70/30 at different temperature

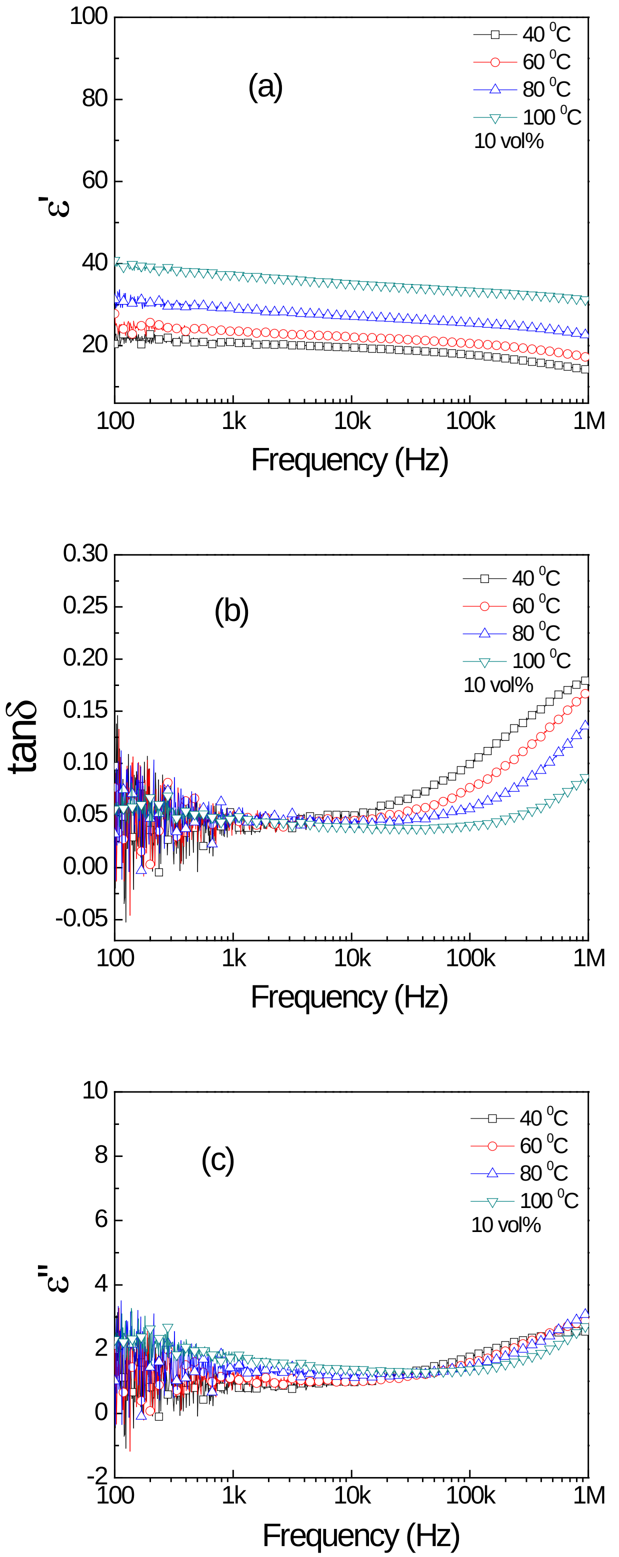


Figure 3.15. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ'' of Ni-P(VDF-TrFE) composites with 10 vol% Ni at different temperature

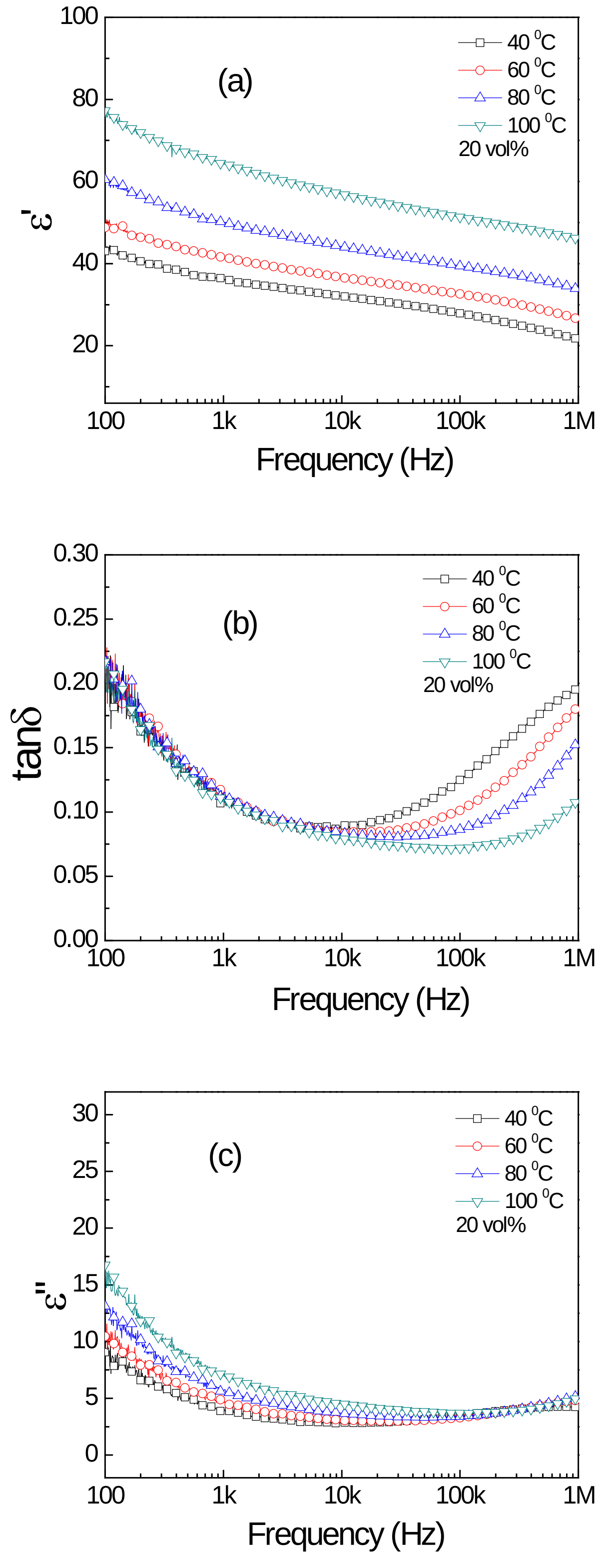


Figure 3.16. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ" of Ni-P(VDF-TrFE) composites with 20 vol% Ni at different temperature

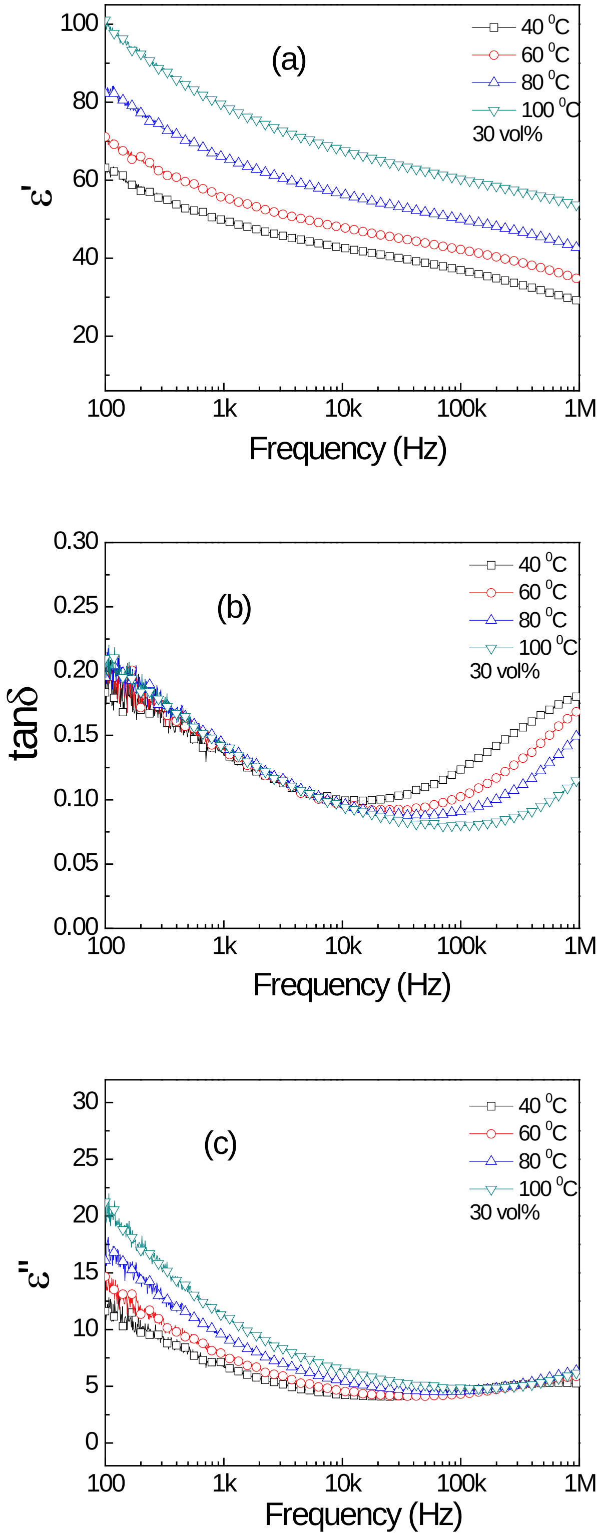


Figure 3.17. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ'' of Ni-P(VDF-TrFE) composites with 30 vol% Ni at different temperature

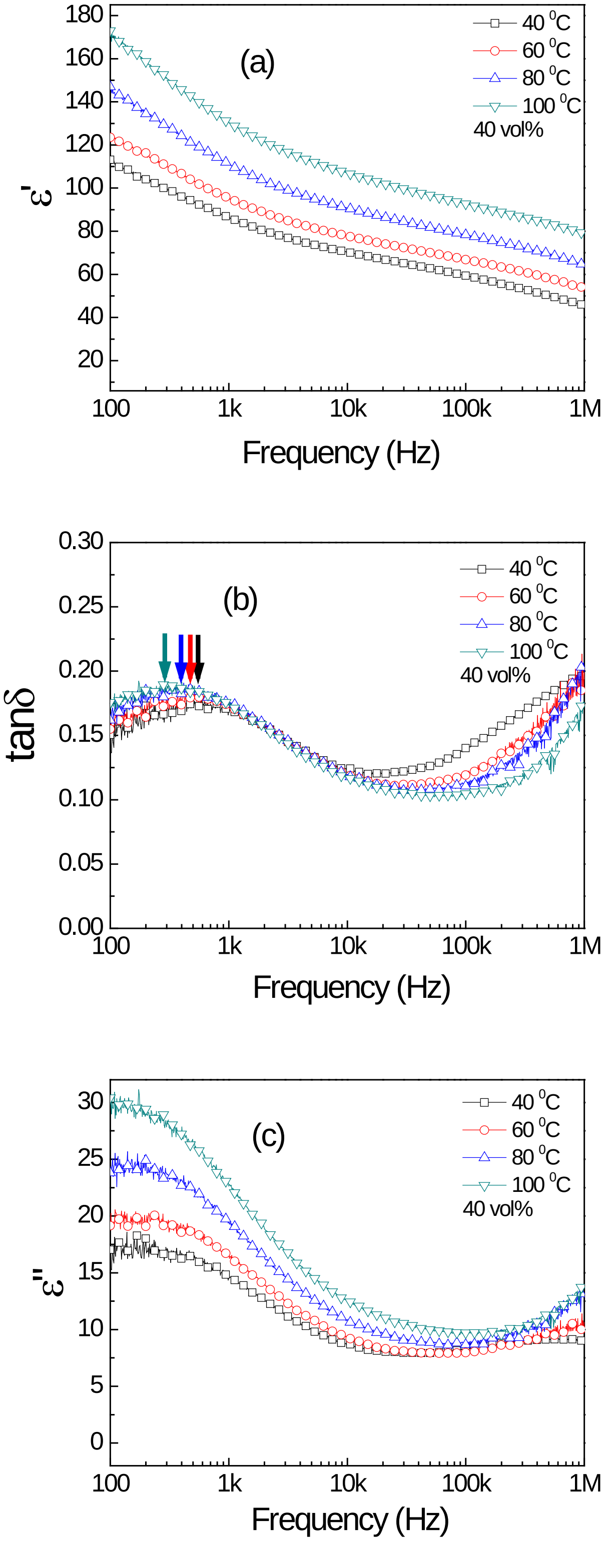


Figure 3.18. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ'' of Ni-P(VDF-TrFE) composites with 40 vol% Ni at different temperature

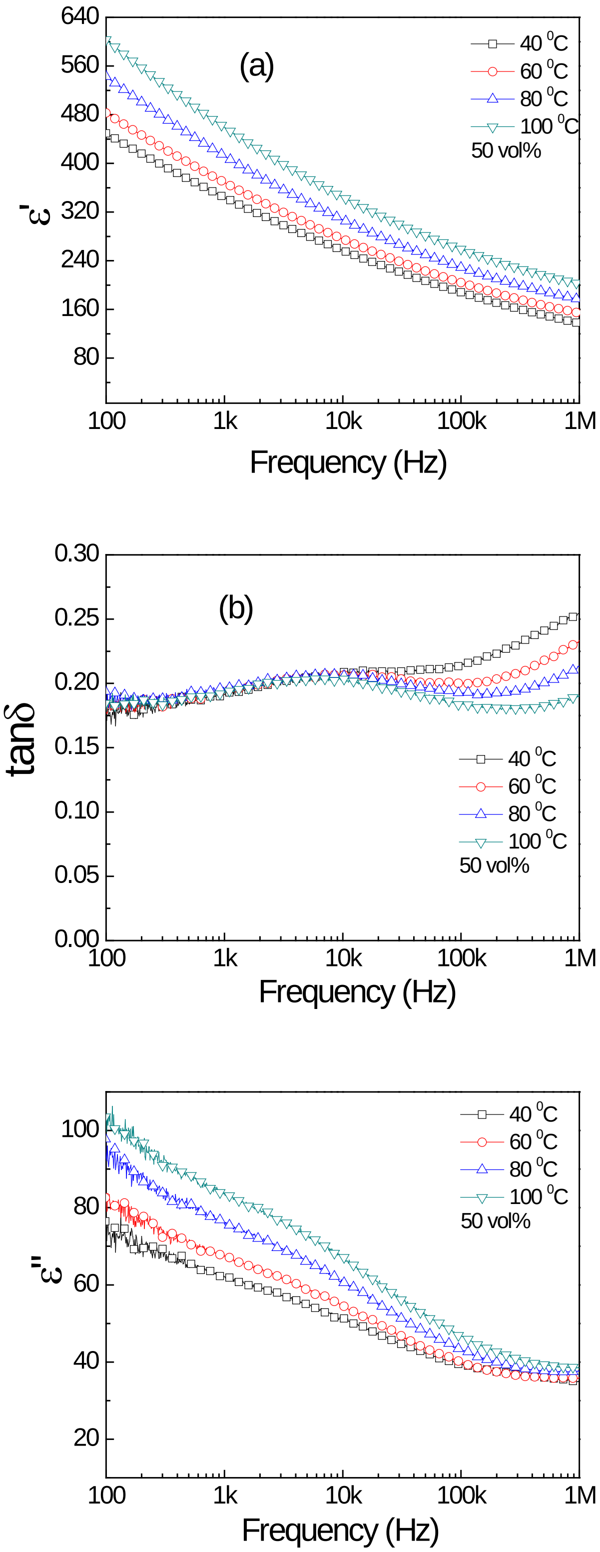


Figure 3.19. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ'' of Ni-P(VDF-TrFE) composites with 50 vol% Ni at different temperature

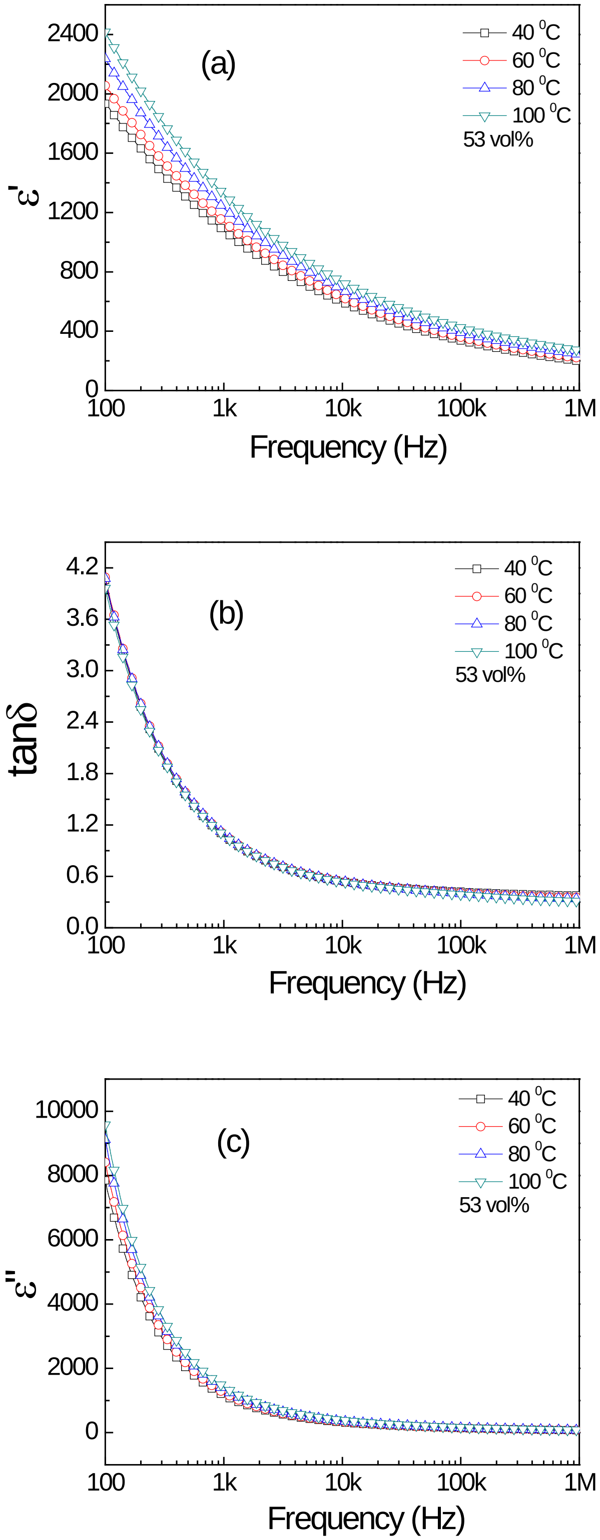


Figure 3.20. Frequency dependent of dielectric properties (a) dielectric constant (b) dielectric loss (c) Ɛ'' of Ni-P(VDF-TrFE) composites with 53 vol% Ni at different temperature

Figures 3.14-3.20 indicate that the temperature dependence of the dielectric properties of the composites becomes weaker with increasing content of Ni. When the content of Ni is 53 vol% the dielectric curves are almost overlapping. Therefore, the composite with 53 vol% shows more resistant to temperature induced structure change.

All the tanδ results in composites show a relaxation phenomenon at low frequency, as shown in Figure 3.15 (b)-Figure 3.20 (b). The relaxation peak is first obvious when the Ni concentration is 40 % and shifts to higher frequency with increasing the content of Ni. Correspondingly, the relaxation time τ decreases. This phenomenon can be concluded that the relaxation time becomes smaller with increase of the conductivity.

In addition, it is found that the observed relaxation peak shifts to lower frequency with increasing temperature in the Figure 3.18.This phenomenon can be explained by Maxwell-Wagner effect. The relaxation time τ for a dispersion of conducting spheres in an insulating dielectric can be described by:

$$\tau = \frac{\varepsilon_0 \varepsilon'_m (2+\nu)}{\sigma(1-\nu)} \qquad (3\text{- }2)$$

where ε_0 a universal constant, σ is the conductivity of the conducting sphere, ε'_m is the relative permittivity of the non-conducting medium, and ν is the volume fraction of the conducting particles.

For a certain composition, the conductivity of Ni is so high as to be considered constant. Therefore, τ is just related to ε'_m the dielectric constant of the polymer. Increasing temperature, ε'_m will increase, as shown in Figure 3.14, so relaxation time will increase and peak will shift to the low frequency.

On the other hand, with the increase of the content of Ni, the conductivity increases so much that the change of $\frac{(2+\nu)}{(1-\nu)}$ can be ignored. The relaxation time from the equation (3-1) will shorten with increasing concentration of Ni.

However, for the applications used in a particular temperature range, sometimes weak temperature dependency is demanded. Therefore, how to decrease the temperature dependent instability of dielectric constant is a very important challenge. Progresses should been made in this direction.

3.3 Uniformity and Reliability of 0-3 Composite

Uniformity of Ni-P(VDF-TrFE) composite can be identified by two parts. First, scanning electron microscope can be used to observe the microstructure. And the reliability on the dielectric measurement was studied by comparing different samples with the same processing and concentration.

3.3.1 Microstructure Analysis

As discussed in Chapter 1, uniform dispersion of nanoparticles in nanocomposite materials is required because nanoparticle agglomerates will lead to undesirable materials properties. Therefore, dispersion of nanoparticles is an extremely important contributor for achieving improved dielectric properties and reproducibility.

Figure 3.21 shows the microstructures of the hot-pressed solution casting Ni-P(VDF-TrFE) composites with 50 vol% Ni at different magnifications.

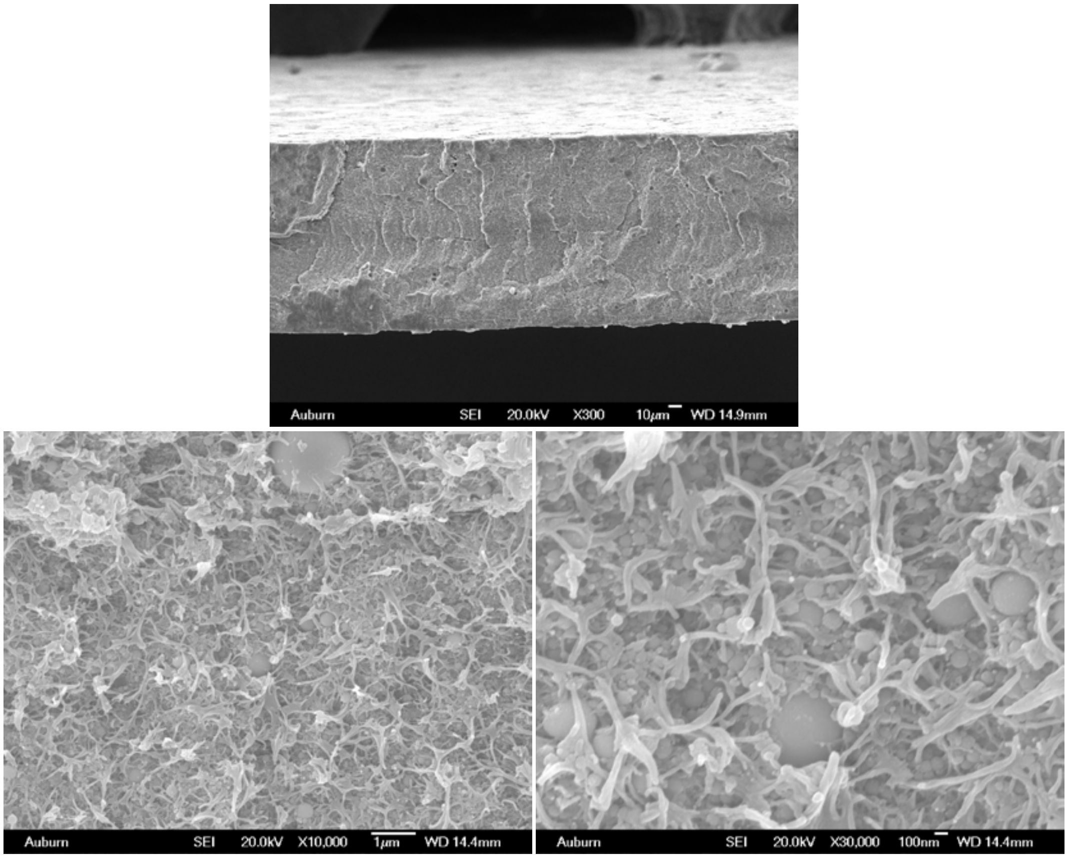


Figure 3.21. SEM image for the cross section of 4 layers 50vo% Ni (nanopowder)-P(VDF-TrFE) composite with hot pressing.

In the Figure, polymer is self-connected into a continuous network and Ni nano particles are randomly distributed in the polymer, thus forming a homogenous composite. This is clear evidence of the improvement of the hot pressing processing. Even for the Ni-P(VDF-TrFE) composite with high concentration, the dispersion of Ni can be very uniform.

3.3.2 Uniformity of Dielectric Properties

In this work, the repeatability on the dielectric constant was studied. For each sample with the same composition and processing conditions, three individual samples were prepared and corresponding measurements were carried out. Reliability result of dielectric constant (Error bars indicate standard deviation) at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively are shown in Figure 3.22. The corresponding experimental results are shown in Table 3.2.

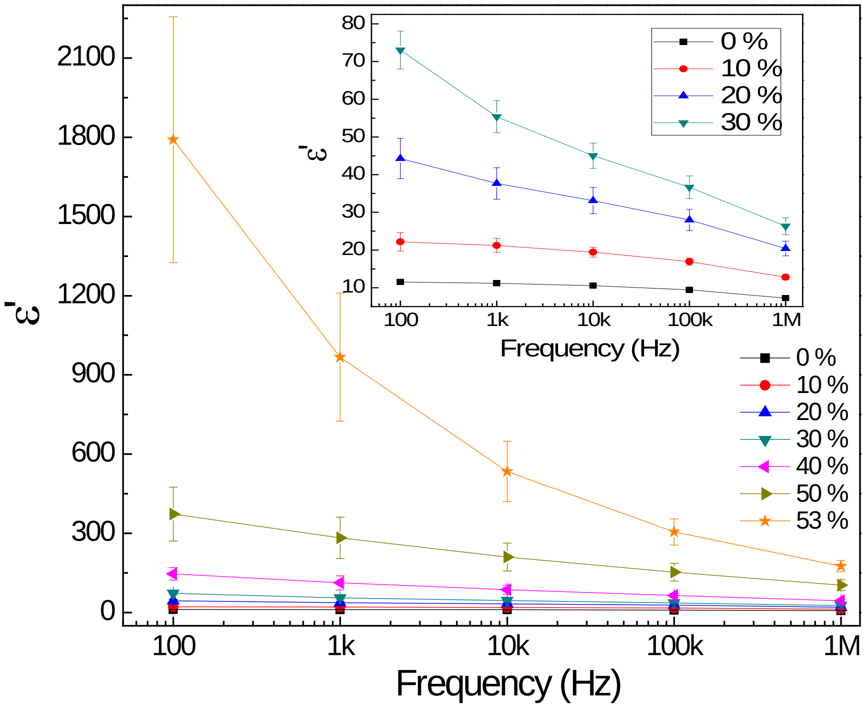


Figure 3.22. Reliability result for the dielectric constant of Ni-(VDF-TrFE) composite

Table 3.2. Summary of reliability measurement results

	sample	Dielectric property (ε'/tanδ)					
		0 vol%	10 vol%	20 vol%	30 vol%	40 vol%	50 vol%
1 kHz	#1	11.8 /0.03	19.0 / 0.05	39.4 / 0.11	54.0 / 0.17	150.2 / 0.15	200.7 / 0.18
	#2	11.1 /0.04	21.1 / 0.05	41.7 / 0.10	51.0 / 0.15	91.1 / 0.18	259.3 / 0.19
	#3	10.6 /0.03	23.6 / 0.11	31.9 / 0.09	61.1 / 0.17	96.0 / 0.21	387.9 / 0.20
	AVE	11.0 /0.03	21.2 /0.07	37.7 /0.10	55.4 /0.16	112.4 /0.18	282.6 /0.19
	SD±	0.5 /0.002	1.9 /0.027	4.2 /0.011	4.3 /0.007	26.8 0.023	78.2 /0.00
10 kHz	#1	11.2 / 0.05	17.8 / 0.07	34.0 / 0.11	42.8 / 0.15	110.6 / 0.23	155.2 / 0.18
	#2	10.5 /0.05	19.6 / 0.06	36.9 / 0.09	42.6 / 0.12	72.0 / 0.15	193.6 / 0.20
	#3	10.0 /0.05	21.0 / 0.10	28.5 / 0.09	49.8 / 0.13	75.8 / 0.16	281.7 / 0.23
	AVE	10.6 /0.05	19.4 /0.08	33.1 /0.10	45.0 /0.14	86.1 /0.18	210.2 /0.20
	SD±	0.5 /0.001	1.3 /0.015	3.5 /0.009	3.4 /0.012	17.3 /0.037	53.0 /0.020
100 kHz	#1	10.0 / 0.12	15.6 / 0.128	28.3 / 0.16	34.2 / 0.18	75.7 / 0.26	118.1 / 0.21
	#2	9.4 / 0.12	17.3 / 0.12	31.2 / 0.15	35.0 / 0.17	58.1/ 0.18	142.8 / 0.23
	#3	9.0 / 0.12	17.9 / 0.14	24.4 / 0.14	40.9 / 0.17	59.5 / 0.20	198.2 / 0.26
	AVE	9.5 /0.12	16.9 /0.13	28.0 /0.15	36.7 0.17	64.4 /0.21	153.0 /0.23
	SD±	0.4 /0.002	1.0 /0.009	2.8 /0.007	3.0 /0.007	8.0 /0.035	33.5 /0.021

Figure 3.22 shows that increasing the content of Ni, ±standard deviation increases. However, it is too hasty to conclude that the uniformity of the composites will become decreases with increasing the content of fillers and the composites with higher concentration have poor uniformity. The relative error should be compared.

Standard deviation divided by the average value represents the relative error for each composition at different frequency, as shown in Figure 3.23. Based on the experimental results, we can notice that the composites with the Ni concentration lower than 40% are very uniform and for the composites with volume fraction of 40%, 50% and 53%, the relative errors increase. Therefore, the uniformity becomes poor when the filler concentration is increasing.

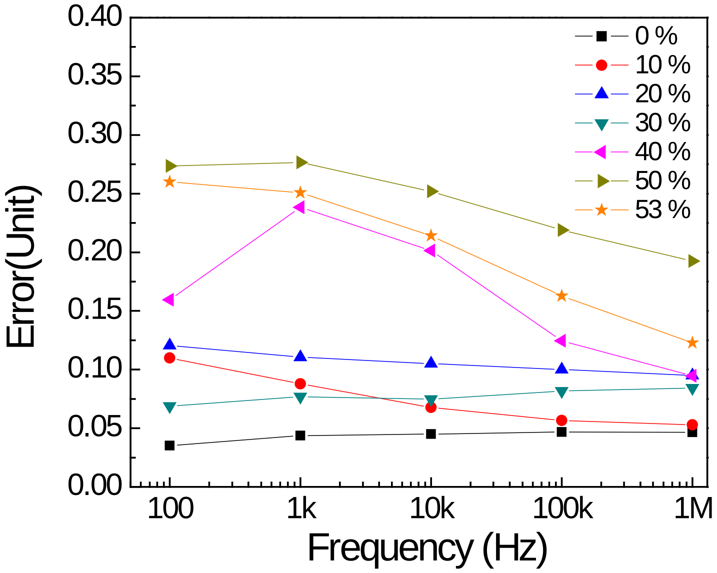


Figure 3.23. Relative error results for the dielectric constant of Ni-(VDF-TrFE) composite

Reference

[1] A. M. Bondar and I. Iordache, "Carbon/ceramic composites designed for electrical application," *Journal of Optoelectronics and Advanced Materials*, vol. 8, pp. 631-637, Apr 2006.

CHAPTER 4

INVESTIGATION OF PERCOLATIVE BEHAVIOR IN Ni -P(VDF-TrFE) COMPOSTES

4.1 Introduction

Compared with the previous reported Ni-PVDF with nano size (v_{Ni}=20 vol% [1], v_{Ni}=28 vol% [2]), the percolation threshold of this work is pretty high (53 vol%).

The possible reasons for the high percolation threshold would be studied in this chapter. It is likely to have a thin polymer layer for the surfaces of hot-press solution casting samples so that it is hard for the metallic volume fraction to reach the percolation, which is supposed to be reached for the composite sample with the same content of metallic-filler but without such insulating layers on the top and bottom surface.

In addition, in order to investigate the percolation theory in metal-polymer composite, the fitted dielectric data were summarized based on the percolation theory.

4.2 Identification of High Percolation Threshold

Possible reason for the high percolation threshold due to the processing condition is needed to identify. It is likely the thin polymer layer for the top and bottom surfaces of hot-press solution casting samples pushes the percolation threshold to be higher. SEM fractograph is shown in Figure 4.1 to indicate the top and bottom.

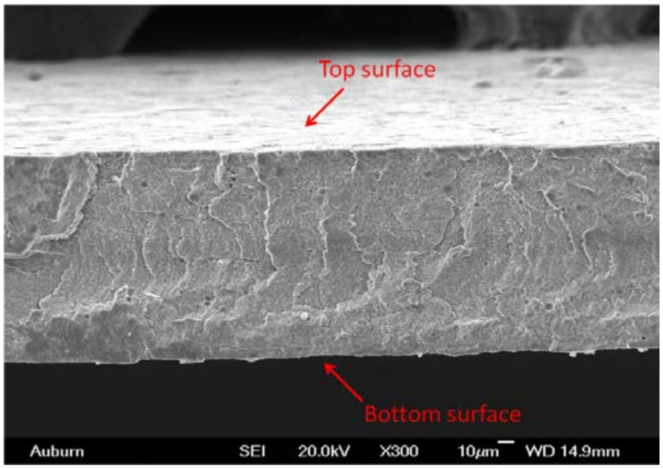
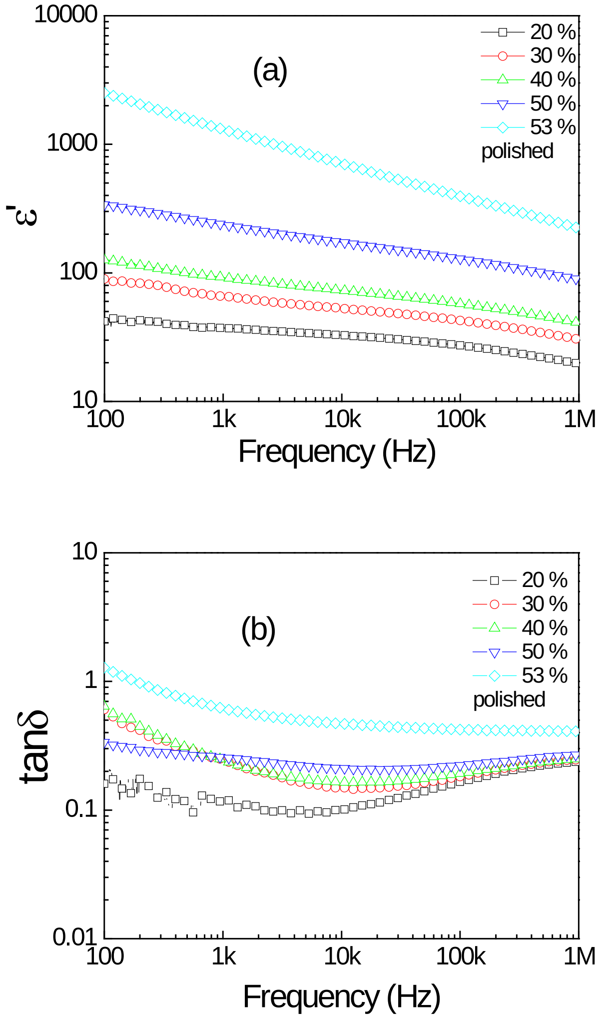


Figure 4.1. SEM fractograph of Ni-P(VDF-TrFE) composite

In order to investigate whether there were polymer layers and how these layer affect the dielectric properties and percolation threshold, the Ni-P(VDF-TrFE) composite samples with 20%, 30%, 40%, 50% and 53% were polished then measured respectively.

After applied hot pressing process, the samples were polished with sand paper by hands. The gauge of the sand paper is 4000. Then the samples were placed into cup with water that is put into the ultrasonator in order to clean the surfaces. At last, annealing was carried out at 120 ^{o}C for 10 hours in an oven. The results of the dielectric behaviors for the sanded samples are indicated in Figure 4.2. The corresponding dielectric results for the same batch of samples before polishing are shown in Figure 4.3.



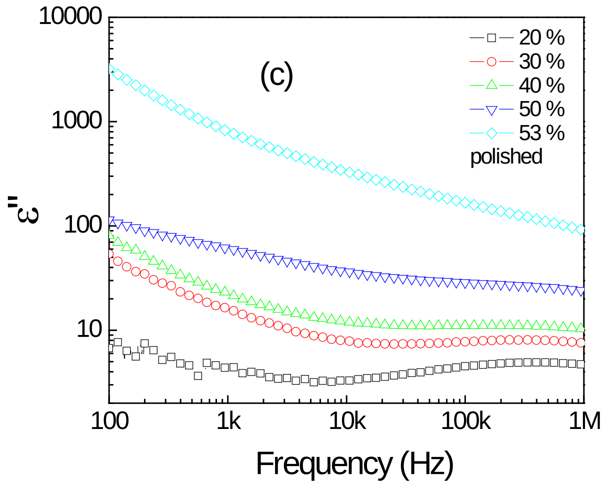
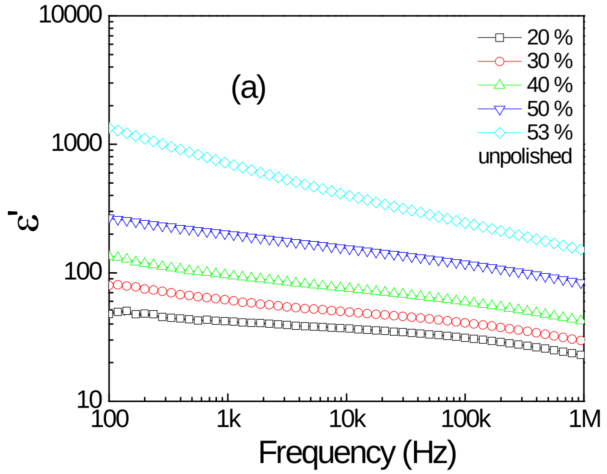


Figure 4.2. log-log representation of frequency dependence of dielectric response (a) dielectric constant (b) dielectric loss (c) Ɛ" for the polished samples



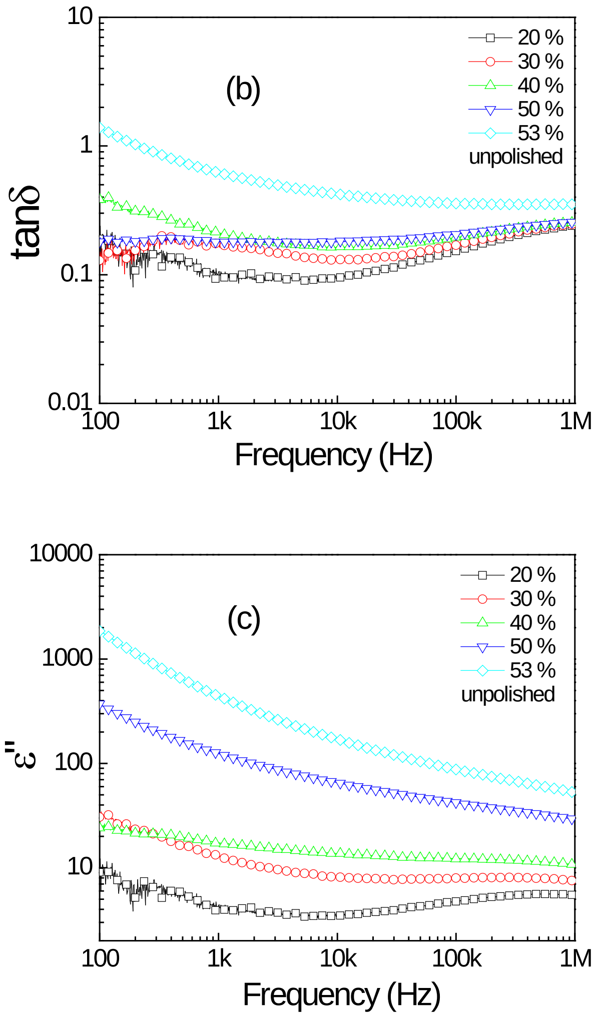


Figure 4.3. log-log representation of frequency dependence of dielectric response (a) dielectric constant (b) dielectric loss (c) Ɛ'' for the unpolished samples

Compared with the dielectric response of unpolished samples, the dielectric constant of the polished ones is increased, especially for the composite with 53 % Ni, which indicates that surfaces of the samples had an influence on the dielectric properties in particular to the high concentration composites.

The volume fraction dependence of the dielectric properties for the polished samples and unpolished samples are shown in Figure 4.4 and Figure 4.5 respectively. The trends of polished samples are so similar to the ones for the unpolished samples. The dielectric constant of polished samples was rising gradually with increasing filler contents in the composites and increases steeply when the volume fraction is to 53%. When the volume fraction increases from 50% to 53% at 100 Hz, the dielectric constant rises from 339 to 2512, while it rises from 237 to 1307 at 1 kHz.

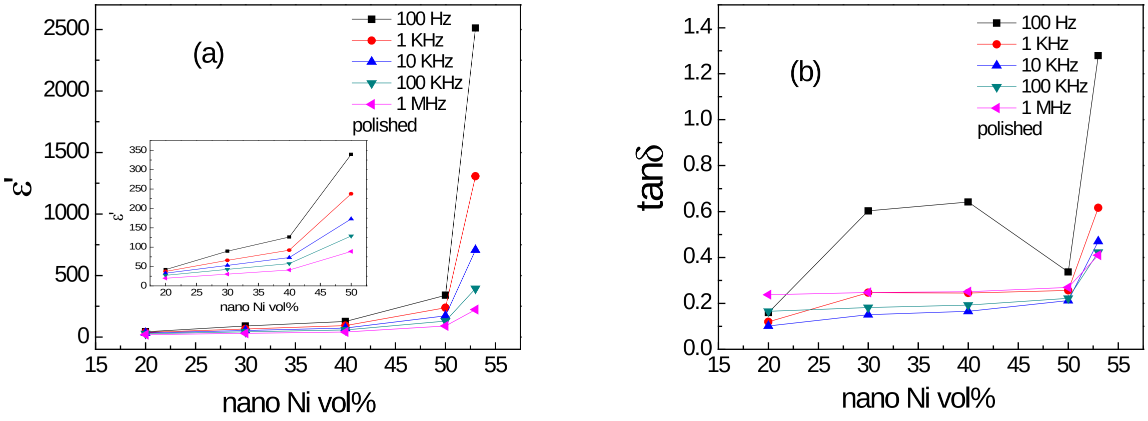


Figure 4.4. Volume fraction dependence of the dielectric properties (a) dielectric constant (b) dielectric loss for the polished samples at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively

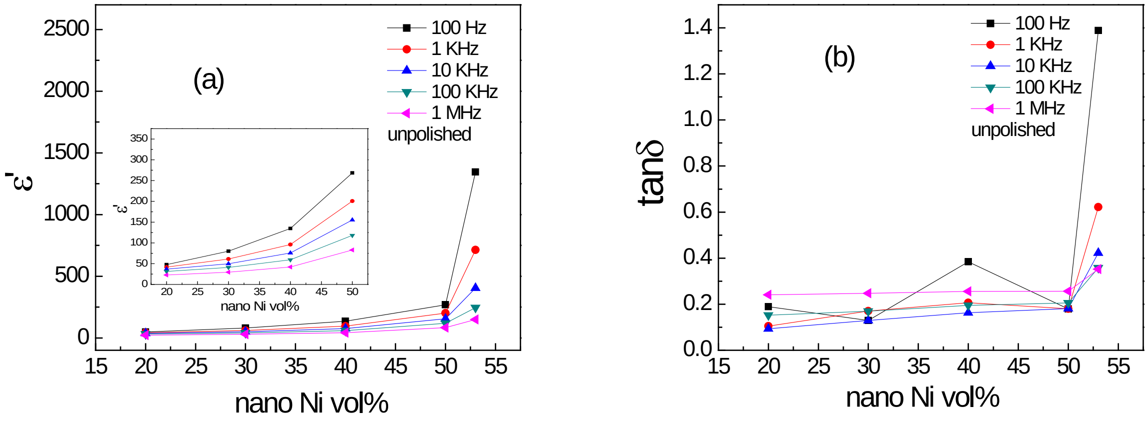


Figure 4.5. Volume fraction dependence of the dielectric properties (a) dielectric constant (b) dielectric loss for the unpolished samples at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively

In short, the layers on the surface of the hot-press solution casting samples have an effect on the dielectric properties but not on the percolation threshold. Although it seems to have little significance, the hand polishing was not always consistent, so that some samples were polished heavily and some polished very little.

As discussed above, we believe that such high percolation threshold in a metal-polymer composite depends strongly on uniform dispersion of fillers due to the process conditions. In particular, the nano particles are easy to aggregate to form the clusters, the fact of that is supposed to contribute to a very low percolation threshold. However, in the system in which the high percolation was achieved, the high percolation can be attributed to increased adhesiveness between the filler and the polymer and the better homogeneous dispersion of filler due to the processing conditions.

On the other hand, for the ideally random dispersion system, the onset of percolation occurs when the interparticle distance is small enough with adding metal particles that the quantum tunneling occurs.

In this work, a higher loading of the nano Ni at the percolation threshold gives the higher value of dielectric constant for Ni-P(VDF-TrFE) composite, but a moderate of loss less than 1.4.

4.3 Investigation of the Percolation Theory

4.3.1 Power Fit Using Percolation Equation

Most researchers are focusing on the concentration of the filler approaching the percolation threshold from low concentration side since the dielectric constant undergoes a sharp rise in order to get the giant dielectric constant. The dielectric constant of the composite near this transition point often follows the percolation theory, as discussed in the chapter 1, and generally percolation equation to fit the experimental data is:

$$\varepsilon' \propto \left(\nu_c - \nu_{filler}\right)^{-s} \text{ for } \nu_{filler} < \nu_c \qquad \text{(4- 1)}$$

The linear fit is to achieve ν_c and s from the log-log plots:

$$log\varepsilon' = -slog\left(\nu_c - \nu_{filler}\right)\text{+C} \qquad \text{(4-2)}$$

where C is a constant.

In this work, normalized percolation equation used to fit is:

$$\varepsilon' = \varepsilon'_{\text{m}}\left(\frac{\nu_c - \nu_{Ni}}{\nu_c}\right)^{-s} \quad \nu_{Ni} < \nu_c \qquad \text{(4- 3)}$$

The equation can be rewritten as:

$$\varepsilon'/\varepsilon'_{\text{m}} = \left(\frac{\nu_c - \nu_{Ni}}{\nu_c}\right)^{-s} \quad \nu_{Ni} < \nu_c \qquad \text{(4- 4)}$$

Equation (4-4) can be considered as a power function with $\varepsilon'/\varepsilon'_{\text{m}}$ as y, $\frac{\nu_c - \nu_{Ni}}{\nu_c}$ as x and s as the power. Therefore power fitting can be carried out. The values of $\varepsilon'/\varepsilon'_{\text{m}}$ and ν_{Ni} are well known. The value of ν_c

need to be tried from 0.53 and the corresponding value of s can be given from the power fitting. Then the best fit can be achieved by comparing the coefficient of determination R^2 from each trials. R^2 is a statistic to give information about the goodness of data fit of a model. The range is from 0 to 1: 0 denotes that model does not explain any variation and 1 denotes that it perfectly explains the observed variation.

The experiment data from 20 vol% to 53 % at 1 kHz, 10 kHz and 100 kHz have been selected to fit and the results are shown in Table 4.1-Table 4.3. The best fits are v_c=0.55, s=1.34 at 1 kHz, v_c=0.56, s=1.34 at 10 kHz, and v_c=0.57, s=1.31 at 100 kHz respectively according to R^2 value, as shown in Figure 4.6 (a)-4.8 (a).

The Variation of the dielectric constant of the Ni-P(VDF-TrFE) composite with Ni volume fraction was plotted in comparison with theoretical curve from percolation equation, as shown in Figure 4.6 (b)-4.8 (b). The bottom insets are the dielectric loss, which undergoes a large change near the percolation threshold. The value of the loss at 1 kHz is about 0.19 when v=0.5, but 1.02 when v_c=0.53, Simiarly, it is about 0.20 when v=0.5, but 0.52 when v_c=0.53 at 10 kHz. Such simple Ni-P(VDF-TrFE) composites exhibit a slightly lower dielectric loss.

Table 4.1. Power fit results at 1 kHz

v_c	Fitting results	
	s	R^2
0.53	1.14	0.8814
0.54	1.12	0.9798
0.55	1.34	0.9942
0.56	1.51	0.9928

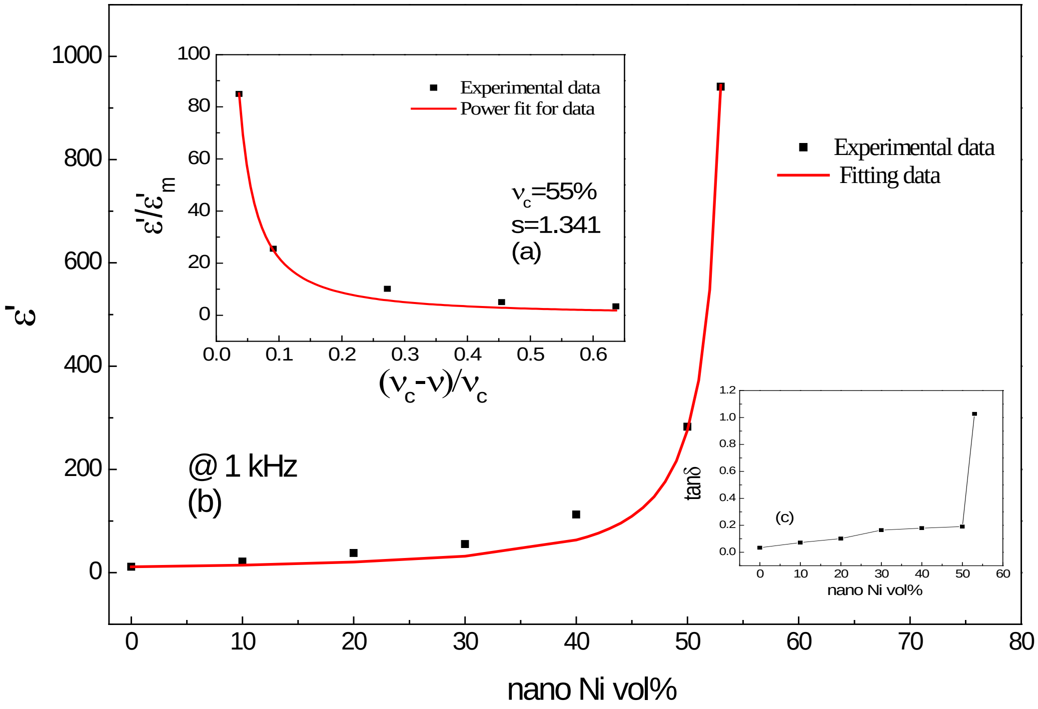


Figure 4.6. (a) The best fit of the dielectric data to equation (4-4); (b)Variation of the dielectric constant of the Ni-P(VDF-TrFE) composite with Ni volume fraction in comparison with best model fitting; and (c) Dielectric loss with vulme fraction at 1 kHz

Table 4.2. Power fit results at 10 kHz

v_c	Fitting results	
	s	R^2
0.53	1.05	0.884
0.54	0.99	0.9533
0.55	1.19	0.984
0.56	1.34	0.9924
0.57	1.48	0.9920

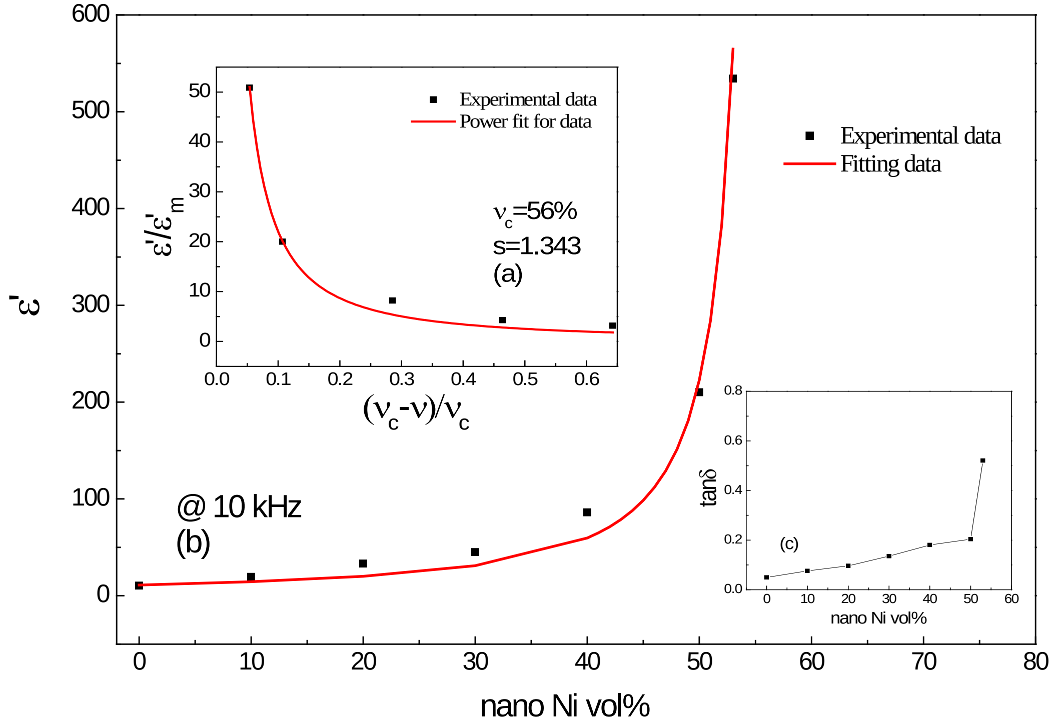


Figure 4.7. (a) The best fit of the dielectric data to equation (4-4); (b)Variation of the dielectric constant of the Ni-P(VDF-TrFE) composite with Ni volume fraction in comparison with best model fitting; and (c) Dielectric loss with vulme fraction at 10 kHz

Table 4.3. Power fit results at 100 kHz

v_c	Fitting results	
	s	R^2
0.53	0.98	0.8822
0.54	0.88	0.9015
0.55	1.06	0.9563
0.56	1.20	0.9788
0.57	1.31	0.9982
0.58	1.42	0.9910

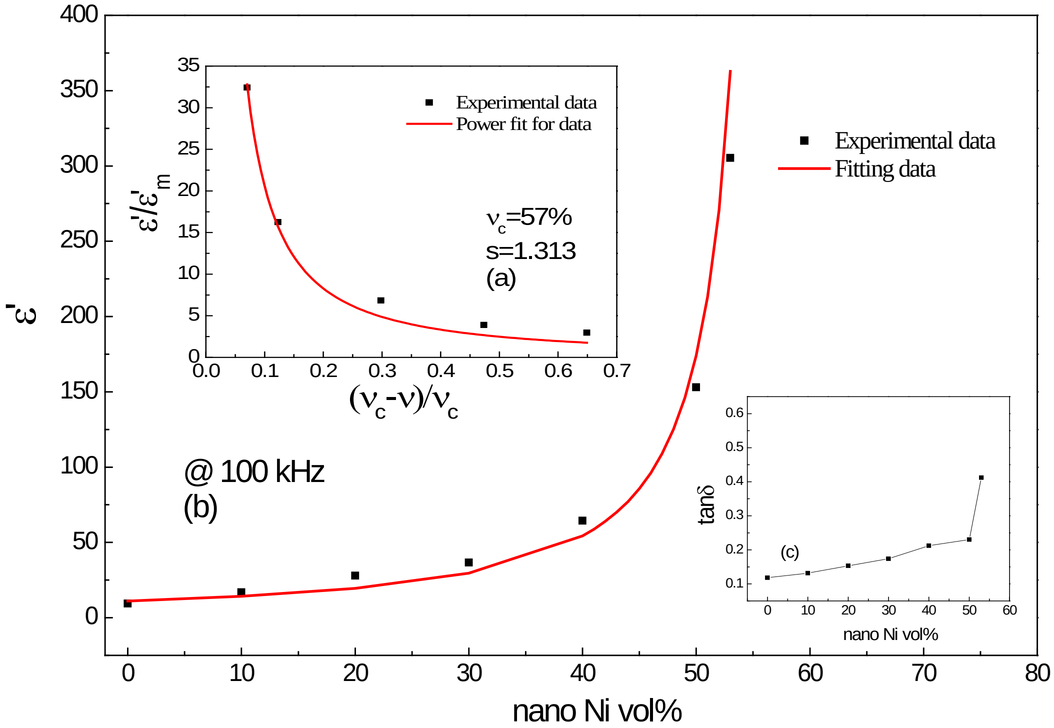


Figure 4.8. (a) The best fit of the dielectric data to equation (4-4); (b)Variation of the dielectric constant of the Ni-P(VDF-TrFE) composite with Ni volume fraction in comparison with best model fitting; and (c) Dielectric loss with vulme fraction at 100 kHz

As shown in Figure 4.6 (b)-4.8 (b), the experimental values of the dielectric constant are in good agreement with the percolation theory. However, they are only good for composites with the small range near the percolation threshold. This is believed to be related to the limitation of the model equation itself. In addition, it is noted that when the value of ν_c at different frequency is fixed, s from the fitting is different at the different frequency, as shown in the Table 4.4. More studies would be carried on about percolation equation.

Table 4.4. Power fit results at different frequency

@ Frequency	Fitting results	
	ν_c	s
1 kHz	0.55	1.34
10 kHz	0.55	1.19
100 kHz	0.55	1.06

4.3.2 Study of Parameters in the Percolation Equation

According to percolation equation $\frac{\varepsilon'}{\varepsilon'_m} = \left(\frac{\nu_c - \nu_{filler}}{\nu_c}\right)^{-s}$, the variation of $\varepsilon'/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composites represents $(\frac{\nu_c - \nu_{filler}}{\nu_c})^{-s}$ with frequency at room temperature, as shown in Figure 4.9. For each curve, ε' is the dielectirc constant of the composite with 10 vol%, 20 vol%, 30 vol%, 40 vol%, 50 vol%, 53 vol% Ni repectively.

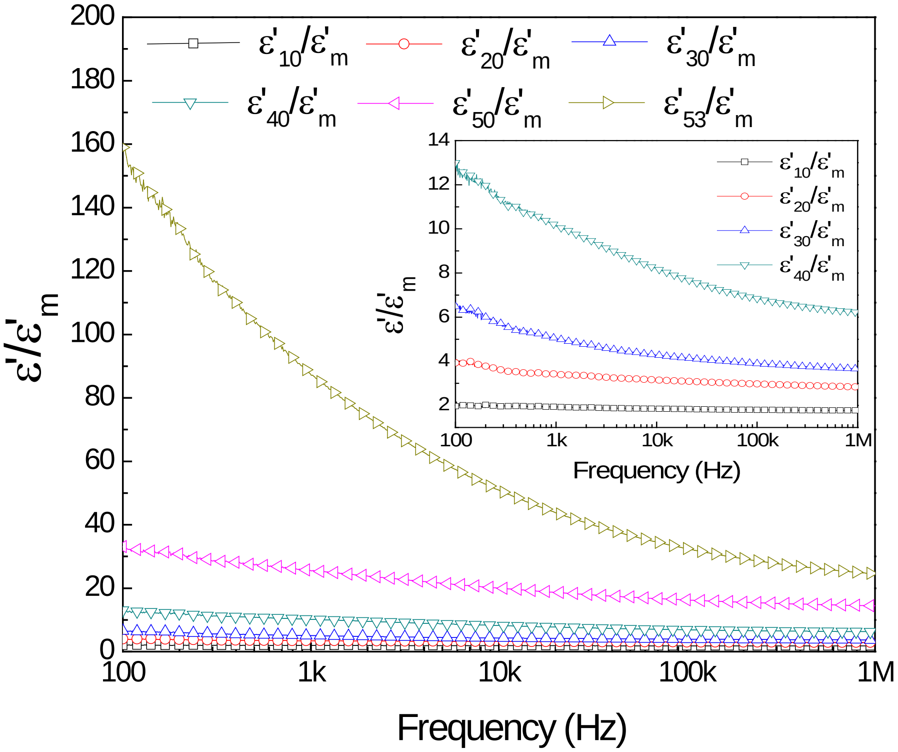


Figure 4.9. Variation of Ɛ'/Ɛ'$_m$ of the Ni-P(VDF-TrFE) composite with frequency at room temperature

According to Figure 4.9, the curves are not constant but frequency dependent. Therefore, $(\frac{\nu_c-\nu_{filler}}{\nu_c})^{-s}$ is related to the frequency dependence.

For each curve Ɛ'/Ɛ'$_m$ in the Figure 4.9, temperature influence would be studied in Figure 4.10-4.15: (a) Variation of Ɛ'/Ɛ'$_m$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of Ɛ'/Ɛ'$_m$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature. Temperature 30^{o}C-100 ^{o}C (below the transition temperature 120 ^{o}C) were selected. If $(\frac{\nu_c-\nu_{filler}}{\nu_c})^{-s}$ is temperature independent, curves in (a) should be straigte lines and in (b) will overlap.

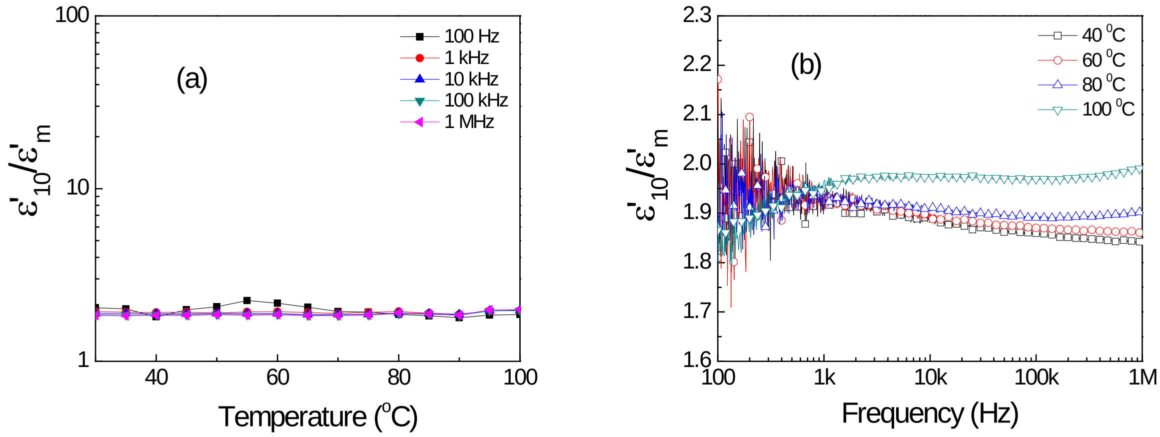


Figure 4.10. (a)Variation of $\varepsilon'_{10}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of $\varepsilon'_{10}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature

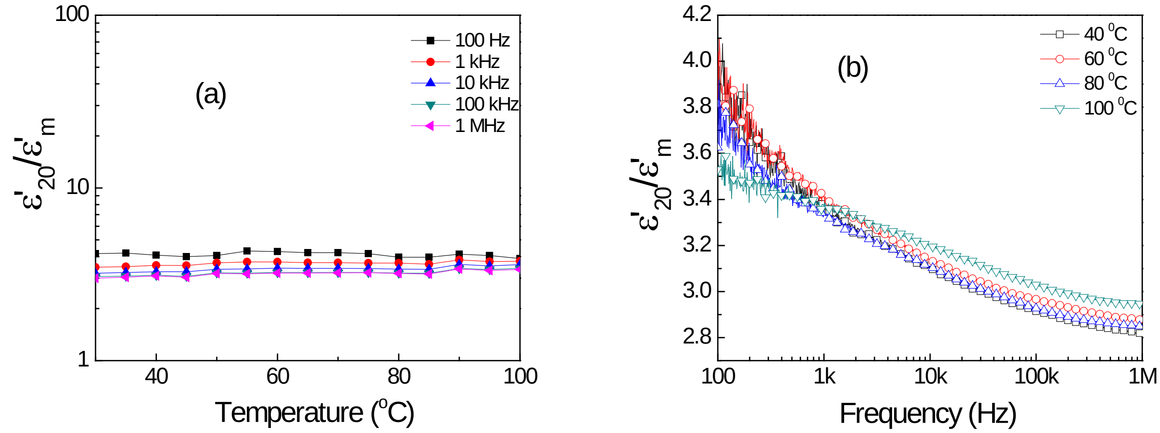


Figure 4.11. (a)Variation of $\varepsilon'_{20}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of $\varepsilon'_{20}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature

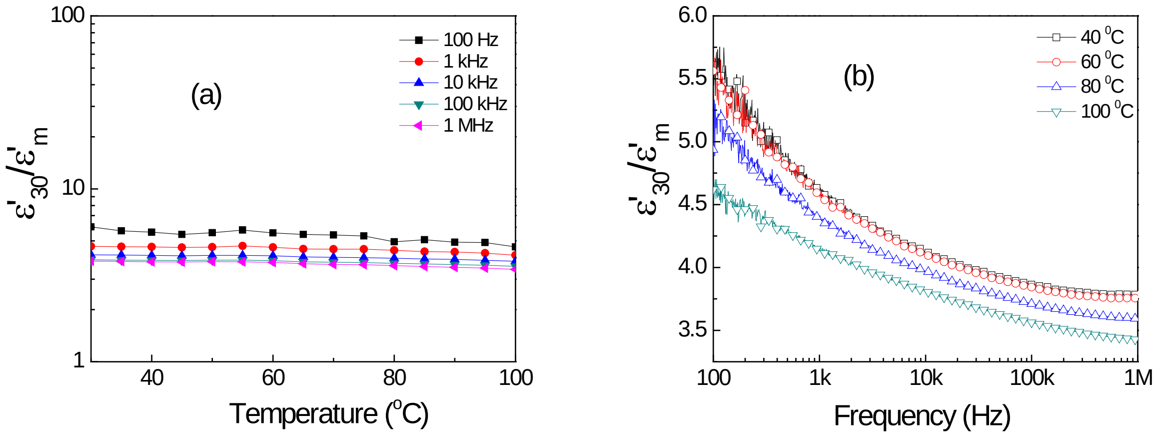


Figure 4.12. (a)Variation of $\varepsilon'_{30}/\varepsilon'_{m}$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of $\varepsilon'_{30}/\varepsilon'_{m}$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature

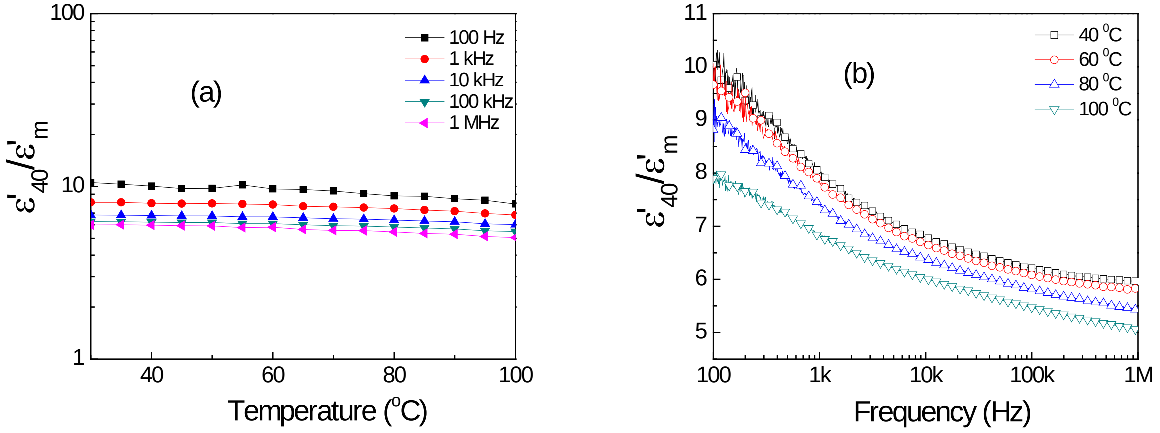


Figure 4.13. (a)Variation of $\varepsilon'_{40}/\varepsilon'_{m}$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of $\varepsilon'_{40}/\varepsilon'_{m}$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature

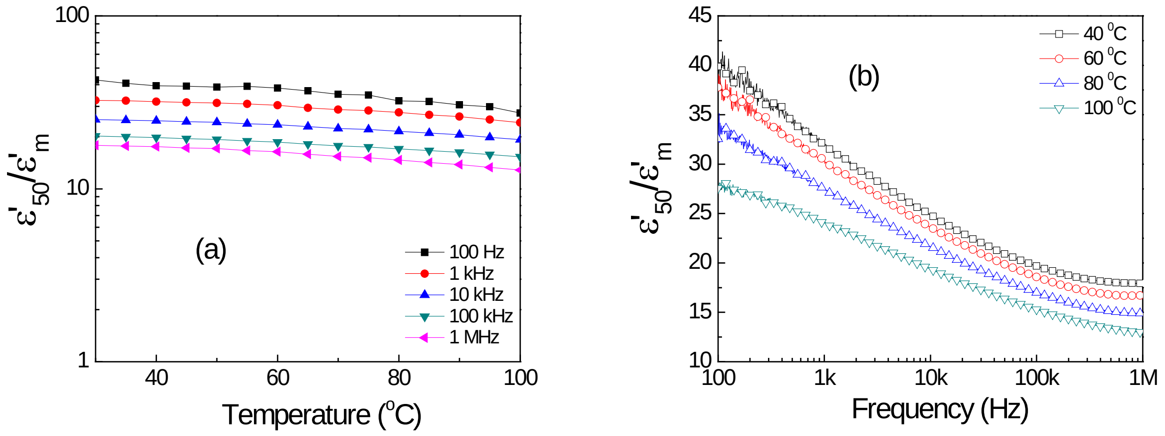


Figure 4.14. (a)Variation of $\varepsilon'_{50}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of $\varepsilon'_{50}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature

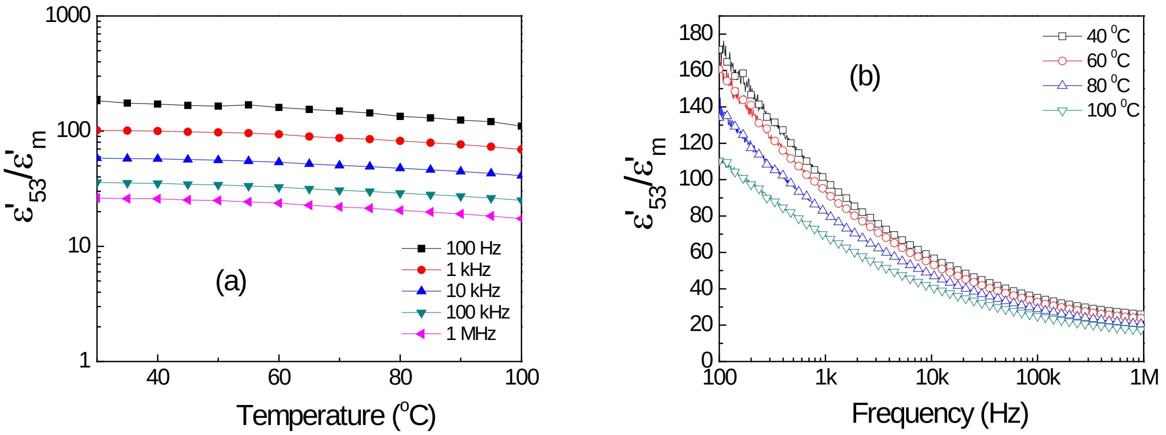


Figure 4.15. (a)Variation of $\varepsilon'_{53}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with temperature at 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz respectively; (b)Variation of $\varepsilon'_{53}/\varepsilon'_m$ of the Ni-P(VDF-TrFE) composite with frequency at different temperature

From the Figure 4.10-4.15, $(\frac{\nu_c-\nu_{filler}}{\nu_c})^{-s}$ is temperature dependent, although curves in Figure 4.10 (a)-4.2 (a) show a weak temperature dependence.

Power fitting is carried out at different temperature, as shown in Figure 4.16-4.17. And more results are indicated in Table 4.5, which shows that ν_c almost stay constant and s is temperature related.

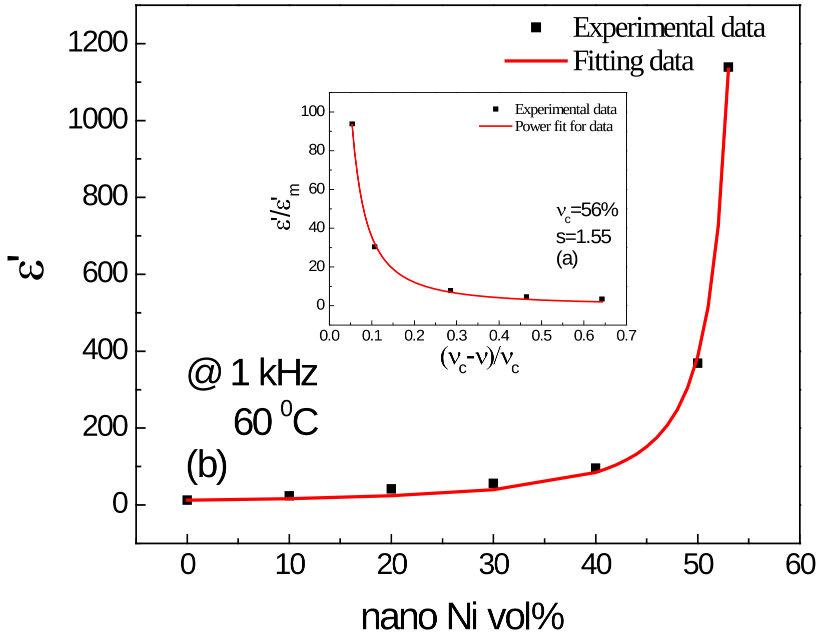


Figure 4.16. (a) The best fit of the dielectric data to equation (4-4); (b) Variation of the dielectric constant of the Ni-P(VDF-TrFE) composite with Ni volume fraction in comparison with best model fitting at 60^0C and 1kHz.

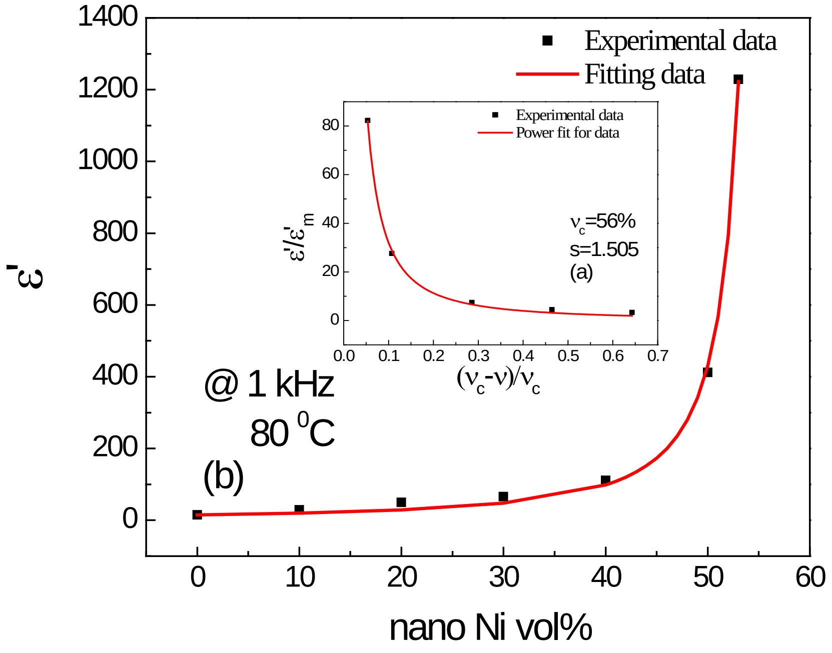


Figure 4.17. Figure 4.18. (a) The best fit of the dielectric data to equation (4-4); (b) Variation of the dielectric constant of the Ni-P(VDF-TrFE) composite with Ni volume fraction in comparison with best model fitting at 80^0C and 1kHz.

Table 4.5. Power fit results at different temperature

Frequency	Temperature	Best Fit Results	
		ν_c	s
1 kHz	40 ^{0}C	0.56	1.571
	60 ^{0}C	0.56	1.550
	80 ^{0}C	0.56	1.505
	100 ^{0}C	0.56	1.447
10 kHz	40 ^{0}C	0.57	1.526
	60 ^{0}C	0.57	1.501
	80 ^{0}C	0.57	1.456
	100 ^{0}C	0.58	1.513

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References

[1] H. P. Xu, H. Q. Xie, D. D. Yang, Y. H. Wu, and J. R. Wang, "Novel Dielectric Behaviors in PVDF-Based Semiconductor Composites," *Journal of Applied Polymer Science,* vol. 122, pp. 3466-3473, Dec.

[2] M. Panda, V. Srinivas, and A. K. Thakur, "On the question of percolation threshold in polyvinylidene fluoride/nanocrystalline nickel composites," *Applied Physics Letters,* vol. 92, Mar 2008.

CHAPTER 5

CONCLUSION AND FUTURE WORKS

5.1 Summary of Results and Conclusions

1. Composites based on nano Ni particles and P(VDF-TrFE) 70/30 mol% copolymer were prepared by hot-pressed solution casting processing. Uniform dispersion of nanoparticles in nanocomposite materials is achieved by improvement of processing conditions. The microstructures were identified by SEM.
2. The percolation threshold of the composite is relatively large, 53 vol%. Compared to the composites with low percolation threshold, composites with high percolation threshold have a wider volume fraction range of the percolation threshold concentration, making the material reproducible for practical applications.
3. It was found that the dielectric constant increased gradually with increasing filler contents in the composites and then increased abruptly at the percolation threshold. For example, the dielectric constant steeply rises from 373 to 1791 that is about 140 times higher than the dielectric constant of pure P(VDF-TrFE), when the volume fraction increases from 50% to 53% at 100 Hz .
4. A higher loading of the nano Ni at the percolation threshold gives the higher value of dielectric constant for Ni-P(VDF-TrFE) composite, but moderate loss. The dielectric loss for the composite film containing 50 vol% Ni is about 0.17 at 100 Hz and maintains a value under 0.28 irrespectively of the frequency, which is attractive for practical use.
5. Percolation theory in Metal-polymer composite was investigated. It is noted that the value of critical exponent s and percolation threshold in the percolation equation depends on frequency.

5.2 Future Works

1. Temperature dependence of dielectric properties has been demonstrated within Ni-P(VDF-TrFE) 70/30 mol% composites due to the temperature dependence of polymer matrix. In order to develop different composites for various applications, decreasing the temperature dependent

instability of dielectric constant is a very important challenge. Different polymer matrix can be used to prepare the metal-polymer composite.

2. In this work, the dielectric properties of Ni-P(VDF-TrFE) composites based on the nano-size were studied. In order to understand the effects of the size on dielectric properties and percolative phenomenon, micro-size composites need to be made.