

Influence of Silane Additive Agent on the Polymer-Based Dielectric Material

by

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Abstract

The dielectric material, a kind of material whose polarization will change with the applied external electric field. With the development of technology, there comes a higher requirement for energy storage material. For the request on the nowadays electronic devices, it's necessary for the energy storage material to have a high dielectric constant, low dielectric loss and a high breakdown field.

In this thesis, the 1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane was used as the silane additive agent and mix with P(VDF-CTFE) 91/9 mol.% polymer matrix. We study the frequency dependence dielectric property, temperature dependence dielectric property, dielectric property under a high electric field and its breakdown process of the mixture sample with different content of silane additive agent. From the experiment result, it's easy to see that the dielectric property and dielectric breakdown strength is improved by the adding of silane additive agent.

For the first part, this thesis will briefly introduce the dielectric material, dielectric property and the mechanism behind dielectric breakdown; the second part will focus on the sample preparation process, the test of dielectric property and the test of dielectric breakdown strength; the third part showed the experiment result and discussion of the phenomenon; the fourth part will show the discussion of this thesis and the work of the future.

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Chapter 1

Introduction

Electrical energy storage plays an important role in the fields of mobile electronic devices, electric vehicles, and electrical pulse devices ^[1-3]. In the development of the fields which was talked above, there comes a requirement for an energy storage material which has the property such as high energy storage, rapid release, and small density. Therefore, the polymer based dielectric material with low density, high dielectric constant, low loss factor, and a high dielectric breakdown strength comes into the researcher's sight. Nowadays, high dielectric constant materials which have been commercialized today are inorganic material. Inorganic material always has a large dielectric constant, but generally, have high density and poor toughness. What's more, the preparation process of inorganic material requires a large amount of energy which is uneconomical. Therefore, the polymer materials such as polypropylene (PP), polyester (PET), etc. come into industrially used as the material of capacitors. Although their breakdown strength is high, loss factor is low, and density is small, but their low dielectric constant makes them have low energy storage ability. Therefore, many researchers hope to be able to utilize the advantages of the above two materials to prepare a polymer-based composite material which has a high dielectric constant.

At present, there are two main methods for preparing high dielectric constant composite materials. One is to incorporate ceramic particles with high dielectric constant, such as barium titanate (BT), calcium copper titanate (CCTO), titanium dioxide, etc. into the polymer matrix with the appropriate method. For the composite sample, the dielectric constant is improved by the mixing effect. The other method is the mixture of the conductive filler and polymer matrix, and the dielectric constant of the composite material is greatly increased when the content of the conductive filler reaches the percolation threshold. These two methods we talked above are currently used as main methods to obtain a high dielectric constant composite materials and it's important to make the inorganic filler distribute well in the composite. Therefore, the silane coupling agent comes into our sight.

Silane coupling agent always has two special end group, one of them can react with some structure on the surface of the inorganic filler, and another end group can interact with our polymer. Then the interface condition and the distribution was improved by the silane coupling agent. Form our previous research, we found that the silane coupling agent can affect the dielectric property and dielectric breakdown strength by itself. Therefore, this thesis will treat the silane coupling agent as the additive agent and research its effect on the dielectric property and dielectric breakdown strength.

1.1 Dielectric Property

1.1.1 Dielectric Constant

For the dielectric material, the charge carrier such as electrons, ions, etc. is limited by the microstructure and cannot move freely. When the external electric field was applied to the material, the bond charge will be reoriented and separated slightly. When an external electric field created by a stable DC voltage is applied to the material, the dielectric constant can be defined as flow equation [4, 5]:

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \quad (1-1)$$

$$\vec{D} = \epsilon \vec{E} = \epsilon_0 \epsilon_r \vec{E} \quad (1-2)$$

In equation (1-1) and (1-2), D is the electric displacement field which shows how the external field E affect the movement and reorientation of the charge carriers and dipoles; ϵ , ϵ_0 , ϵ_r is the dielectric constant of sample, vacuum ($\epsilon_0 = 8.854187 \times 10^{-12}$ F/m) and relative permittivity of sample respectively; P is polarization.

For the polarization, there four mechanisms to explain the polarization which are electronic polarization, ionic polarization, orientation polarization, and space charge polarization. The applied external electric field will cause the movement of the electron cloud, changing in the relative distance in between ionic, reorientation of dipoles and separating of the positive and negative space charges, and these are the reason for electronic polarization, ionic polarization, orientation polarization, and space charge polarization respectively [4, 5]. The influence of the polarization of different mechanisms with changing frequency was shown in Figure 1-1. The polarization P was defined as equation (1-3):

$$\vec{P} = \frac{\sum_{i=1}^N \vec{p}_i}{dV} \quad (1-3)$$

In equation (1-3), p is the induced dipole moments.

What's more, equation (1-4) shows the polarization under a stable DC electric field which was calculated by the equation (1-1) and equation (1-2):

$$\vec{P} = (\epsilon_r - 1)\epsilon_0\vec{E} = \chi\epsilon_0\vec{E} \quad (1-4)$$

In equation (1-4), χ is the dielectric susceptibility which can be calculate by the equation (1-5)

$$\chi = \epsilon_r - 1 \quad (1-5)$$

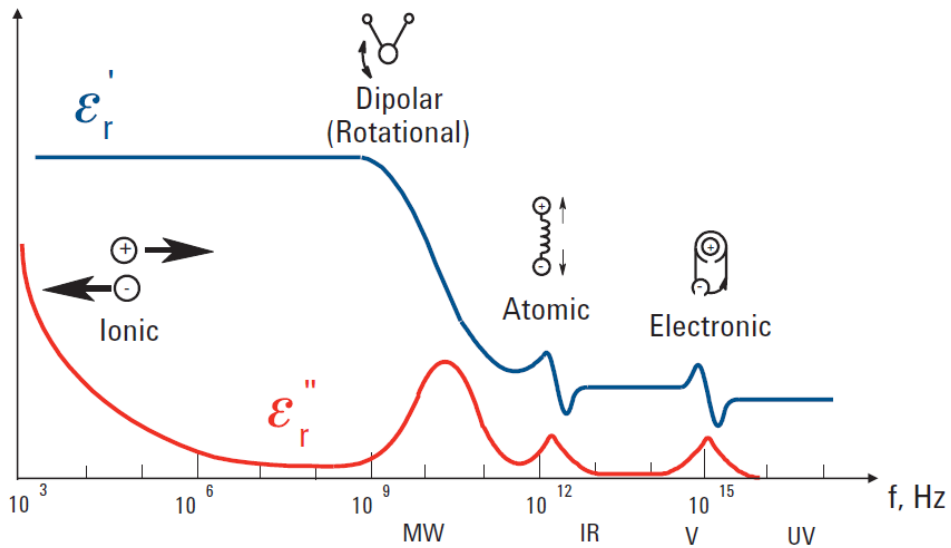


Figure 1-1 Frequency response of dielectric mechanisms

The calculation which was talked above is under a stable DC electric field. However, when a time-varying electric field was applied to the sample, the displacement current will be observed. Therefore, electric displacement D and polarization P became complex and can be defined by the equation (1-6) and equation (1-7):

$$\vec{D}^* = \varepsilon_0 \vec{E} + \vec{P}^* \quad (1-6)$$

$$\vec{P}^* = (\varepsilon_r^* - 1) \varepsilon_0 \vec{E} \quad (1-7)$$

In equation (1-6) and equation (1-7), ε_r^* is the complex permittivity, D is complex electric displacement and P is complex polarization. In these two equations, the complex permittivity shows the complex nature of electric displacement and polarization.

1.1.2 Dielectric Loss

For a normal dielectric material, its response to a time-varying (AC) electric field depended on the applied external electric field's frequency. Under an AC electric field, the dielectric constant will be complex and shown in equation (1-8):

$$\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r'' \quad (1-8)$$

In equation (1-8), j is the imaginary unit, ε_r' is the real part of dielectric constant and ε_r'' is the imaginary part of dielectric constant. The real part of dielectric constant reflects the energy storage in the material and the imaginary part of dielectric constant represent the energy loss for the material. Therefore, the dielectric loss was defined for calculating the energy lost.

The dielectric loss can be represented as loss angle δ , and the loss angle δ was defined by the loss factor $\tan \delta$ which was shown equation (1-9):

$$\tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'} \quad (1-9)$$

From Kramers-Krong relations ^[5], the relationship between ε_r' and ε_r'' can be obtained by equation (1-10) and equation (1-11):

$$\varepsilon'_r(\omega) = \varepsilon_{r\infty} + \frac{2}{\pi} \int_0^{\infty} \frac{u \varepsilon''_r(u)}{u^2 - \omega^2} du \quad (1-10)$$

$$\varepsilon''_r(\omega) = \frac{2}{\pi} \int_0^{\infty} [\varepsilon'_r(u) - \varepsilon_{r\infty}] \frac{\omega}{u^2 - \omega^2} du \quad (1-11)$$

In equation (1-10) and equation (1-11), ω is the angular frequency; $\varepsilon_{r\infty}$ is the dielectric constant at high-frequency limit. If $\omega = 0$, the equation (1-8) can be calculated as equation (1-12):

$$\int_0^{\infty} \varepsilon''(\omega) d(\ln \omega) = \frac{2}{\pi} (\varepsilon_{rS} - \varepsilon''_{r\infty}) \quad (1-12)$$

In the equation (1-12), ε_{rS} is static dielectric constant.

1.1.3 Dielectric Relaxation

When a time-varying (AC) electric field was applied to the dielectric material, there was an instantaneous delay on the response of the material to the change of the external electric field. This phenomenon was defined as dielectric relaxation. Dielectric relaxation shows dielectric material's relaxation process under a time-varying electric field and many theories were developed to illustrate it. If we suppose the dipoles in the material will not interact with each other under an AC electric field, the Debye equation can be used to illustrate the dielectric relaxation phenomenon and the Debye equation was shown in equation (1-13) to (1-16):

$$\varepsilon^*_r(\omega) = \varepsilon_{r\infty} + \frac{\varepsilon_{rS} - \varepsilon_{r\infty}}{1 + j\omega\tau_0} \quad (1-13)$$

Or

$$\varepsilon'_r = \varepsilon_{r\infty} + \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{1 + \omega^2\tau_0^2} \quad (1-14)$$

$$\varepsilon''_r = \frac{(\varepsilon_{rs} - \varepsilon_{r\infty})\omega\tau_0}{1 + \omega^2\tau_0^2} \quad (1-15)$$

$$\tan \delta = \frac{\varepsilon''_r}{\varepsilon'_r} = \frac{(\varepsilon_{rs} - \varepsilon_{r\infty})\omega\tau_0}{\varepsilon_{rs} + \varepsilon_{r\infty}\omega^2\tau_0^2} \quad (1-16)$$

In equation (1-13) to (1-16), τ_0 is so-called characteristic relaxation time.

The characteristic relaxation time can be defined as the relaxation time under the relaxation frequency which can be described as $f_0 = \omega_0/2\pi = 1/2\pi\tau_0$; ε_{rs} is the static relative dielectric constant (When $\omega=0$); $\varepsilon_{r\infty}$ is the relative dielectric constant at the high-frequency limit (when $\omega=\infty$). In the equation, which was talked above, $\varepsilon_{rs} - \varepsilon_{r\infty}$ can be used to illustrate how the relaxation processes affect the static relative dielectric constant.

From equation (1-12) and equation (1-13), we can get equation (1-17):

$$\left(\varepsilon'_r - \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{2}\right)^2 + \varepsilon''_r{}^2 = \left(\frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{2}\right)^2 \quad (1-17)$$

From the equation (1-17), the ε''_r and $\tan \delta$ reached the maximum value at ω_0 and ω_δ respectively and it can be described as equation (1-18) and equation (1-19):

$$\omega_0\tau_0 = 1 \quad (1-18)$$

$$\tan \delta_{\omega=\omega_\delta} = \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{2(\varepsilon_{rs}\varepsilon_{r\infty})^{\frac{1}{2}}} \quad (1-19)$$

Figure 1-2 and **Figure1-3** show the relation between ε'_r and ε''_r .

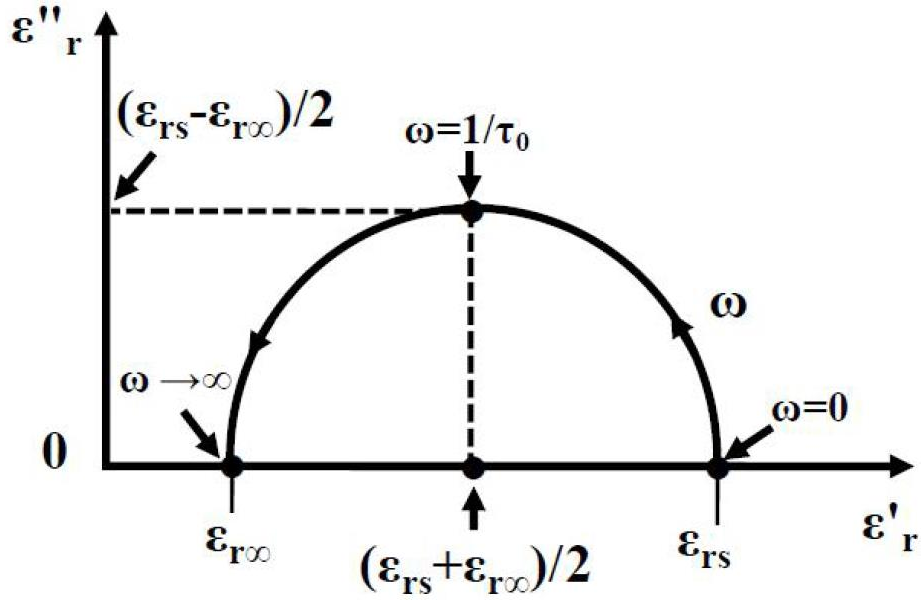


Figure 1-2 The Debye relation between ϵ'_r and ϵ''_r when one relaxation time was existed.

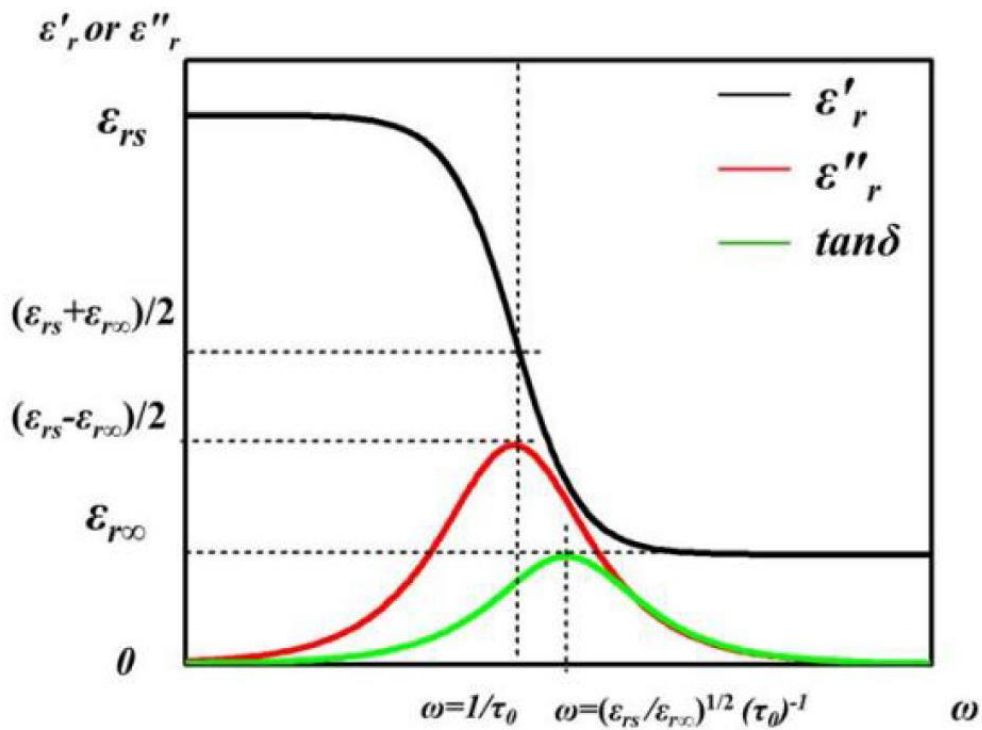


Figure1-3 The result of frequency dependence of ϵ'_r , ϵ''_r and $\tan \delta$ calculate by Debye equation.

From what was talked above, it's easy to see that the calculation based on Debye equation was under an ideal assumption which has only one relaxation process existed in the material system. Obviously, this theory will not fit for most of the dielectric material system which has multiple relaxation processes existed in the material system. For the real case, the dielectric constant's frequency dependence is complicated. Therefore, many empirical theories came out to illustrated the dielectric relaxation process, and the Cole-Cole equation is one of them. Equation (1-20) showed the Cole-Cole equation:

$$\varepsilon_r^*(\omega) = \varepsilon_{r\infty} + \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{1 + (j\omega\tau_0)^{1-\alpha}} \quad (1-20)$$

In the equation (1-20), α is the parameter, with $0 < \alpha < 1$. When $\alpha=0$, the material system is under ideal Debye mode. Similar to Debye equation, Cole-Cole equation cannot fit all the material system. Therefore, many other modifications on the Cole-Cole equation was introduced to fitting others material systems. But right now, no relation was found which can fit all the material systems.

1.1.4 Energy Storage

In an electric circuit, a capacitor made by dielectric material always be used as a temporary electric energy storage component. Therefore, the energy storage capability was another important property for the dielectric material. For a dielectric material, its energy storage density can be calculated by the applied electric field and electric displacement, and the equation was shown in equation (1-21) [6,7]:

$$W_E = \int E dD \quad (1-21)$$

In the equation (1-20), W_E is the energy storage density (J/m^3). If we combine the equation (1-2) and equation (1-21), the relationship between dielectric constant, external electric field and energy storage density for the linear material will be got ^[6]:

$$W_E = \frac{1}{2} \epsilon_0 \epsilon_r \vec{E}^2 \quad (1-22)$$

Figure 1-4 showed the relation between dielectric constant, external electric field and energy storage density for the linear material with different curvature:

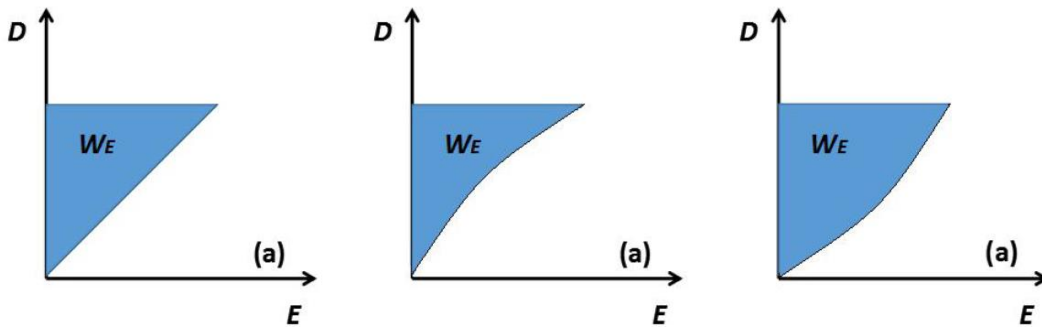


Figure 1-4 The relation between dielectric constant, external electric field and energy storage density for the linear material with different curvature: (a) linear; (b) positive curvature; (c) negative curvature

Form what has been talked above, it's easy to see that for the linear material if we want to have a higher energy density, a higher dielectric constant and higher dielectric breakdown strength is required. **Figure 1-5** showed the relationship

between dielectric constant, external electric field and energy storage density for different kinds of material.

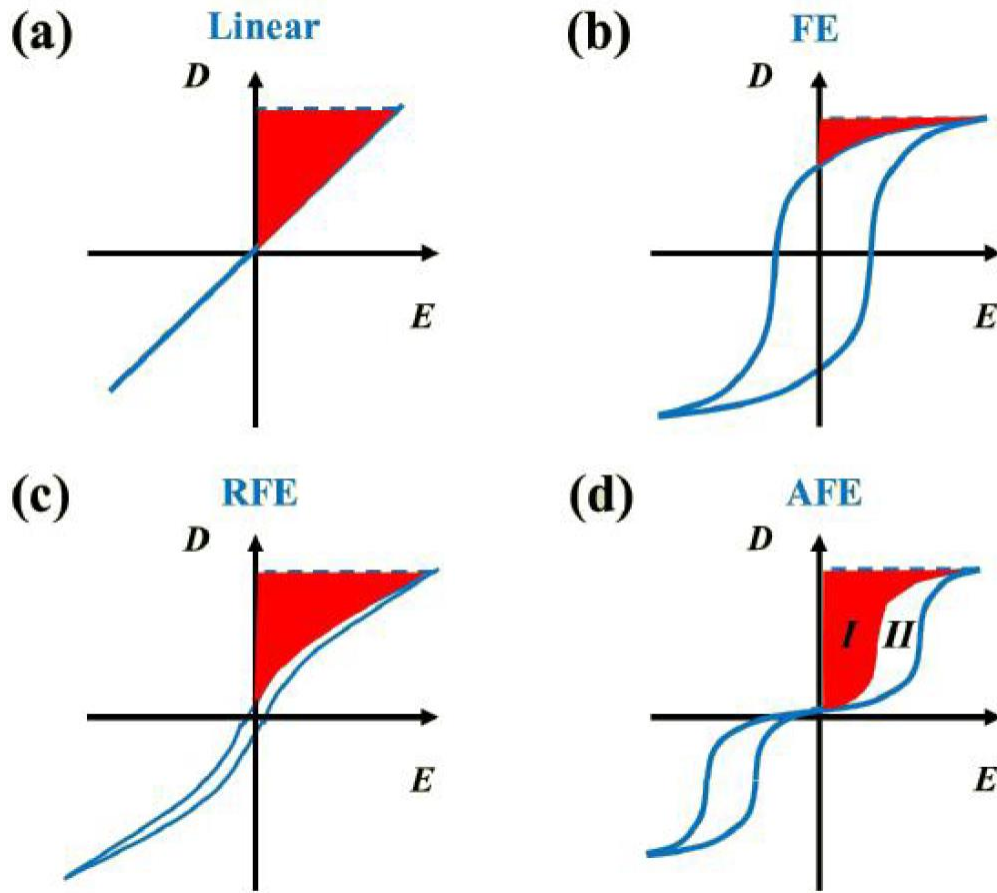


Figure 1-5 The relationship between dielectric constant, external electric field and energy storage density for (a) linear dielectrics material, (b) ferroelectrics, (c) relaxor ferroelectrics, and (d) antiferroelectric ^[8].

From figure 1-5, it's easy to see that under the same dielectric constant and electric field, the linear material is more suitable for the use of energy storage. For the linear material, although it has a high dielectric breakdown strength, it always has a relatively low dielectric constant. Therefore, if the linear material wants to be

used to make the electric energy storage component, the dielectric constant of it should be improved.

For some inorganic material, it has a very high dielectric constant and a very low dielectric breakdown strength^[9]. For the organic material, some of them have a very high dielectric breakdown strength and a small dielectric constant^[5]. Therefore, the research on the composite made by mixing of the organic and inorganic material and tried to combine both advantages of them become popular in this field.

1.2 Dielectric Breakdown Strength

Dielectric breakdown refers to the phenomenon that the dielectric changes from a dielectric state to a conductive state under the effect of an external electric field and the dielectric breakdown strength limit the energy storage density of dielectric material^[10]. In the parallel plate, the dielectric breakdown strength (E_b) can be calculated by the equation (1-23):

$$E_b = \frac{V_b}{d} \quad (1-23)$$

In equation (1-23), V_b is the voltage applied between the parallel plate; d is the thickness of the parallel plate. For the thin film sample with small electrodes on both side of the sample, the calculation of dielectric breakdown strength can use the parallel plate.

For the research on the dielectric breakdown process, most of them are focus on the solid or inorganic materials^[11] and many mechanisms have also been introduced to understand it.^[12] But for the dielectric breakdown process of

polymer-based materials, many problems remained for the researcher to solved. In this part, the mechanisms of breakdown process of polymer-based dielectric material will be discussed. Next, the measurement of dielectric breakdown strength will be talked.

For most of the polymer material, the rang of dielectric breakdown strength was 100 to 900 MV/m at 20 °C which was higher than most of ionic crystals materials who has a dielectric breakdown strength range from 50-100 MV/m at 20 °C. What's more, most of the maximum values of the dielectric breakdown strengths of polymer material was test under a low temperature, and the dielectric breakdown strength of the polar polymer is higher the nonpolar polymer.

1.2.1 The Mechanism of Breakdown Process

The first theory which was introduced to illustrate the breakdown process of inorganic material was proposed in 1922 by Wagner ^[13]. In his theory, the dielectric break down was caused by the imbalance between the Joule heating (caused by the current) and thermal dissipation. Wagner's theory illustrated the breakdown process in the high-temperature region ($\partial E_b/\partial T < 0$).

However, when the temperature change to the low-temperature region ($\partial E_b/\partial T > 0$), Wagner's theory (thermal breakdown theory) was difficult to explain the experiment result. Therefore, the research about the electronic conduction current in the solid material was proposed.

Through the research on the time lag ^[14] and the path of dielectric breakdown ^[15], the dielectric breakdown process of solid material was caused by

the electronic process, for example, the collision ionization caused by the high-speed electrons, and the collision ionization will cause the multiplication on the electric current. Therefore, the researchers think that the electronic process played an important role in dielectric breakdown process. Although, the thermal breakdown theory was used to illustrate the dielectric breakdown process in the high-temperature region, based on what has been talked above, thermal breakdown process was not the only dielectric breakdown process in this region.

Through the experiment, it finds that the combination of thermal breakdown theory and simple collision ionization theory was not suitable for the dielectric breakdown phenomenon in the low-temperature region. Therefore, the modification of simple collision ionization theory by the space charge effect was introduced ^[16], the new theory also put the interaction between the conduction electrons and the electrons trapped by the impurity component into consideration ^[10].

What's more, the dielectric breakdown characteristics of polymer material shows at glass transition temperature (or viscous flow temperature) is similar to its mechanical property. Therefore, the electromechanical breakdown theory was introduced ^[17]. This theory the mechanical deformation caused by Maxwell stress contribute to the dielectric breakdown process. This theory is only suited for the polymer material and successfully explain some polymer's dielectric breakdown process at the high-temperature region. Another theory which suitable for the polymer material's dielectric breakdown process is the free volume theory, this

theory is used to illustrate the polymer material's dielectric breakdown process near the glass transition temperature.

Figure 1-6 is a summary of the dielectric breakdown theories which was mentioned above.

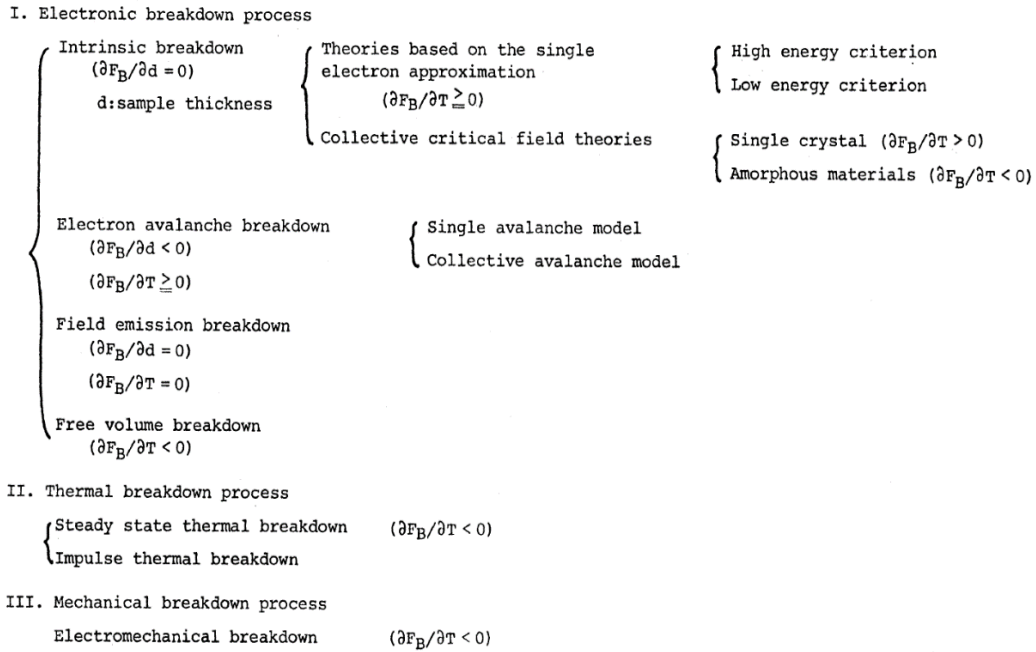


Figure 1-6 Dielectric breakdown theories ^[10]

For the dielectric breakdown mechanisms, there is no theory can be used to illustrate all the dielectric breakdown process, and in one dielectric breakdown process, many mechanisms may contribute to the dielectric breakdown process and it's hard to tell which mechanisms play a main role in the dielectric breakdown process.

1.3 Microstructure and Dielectric Breakdown Strength

1.3.1 The Effect of Chemical Structure

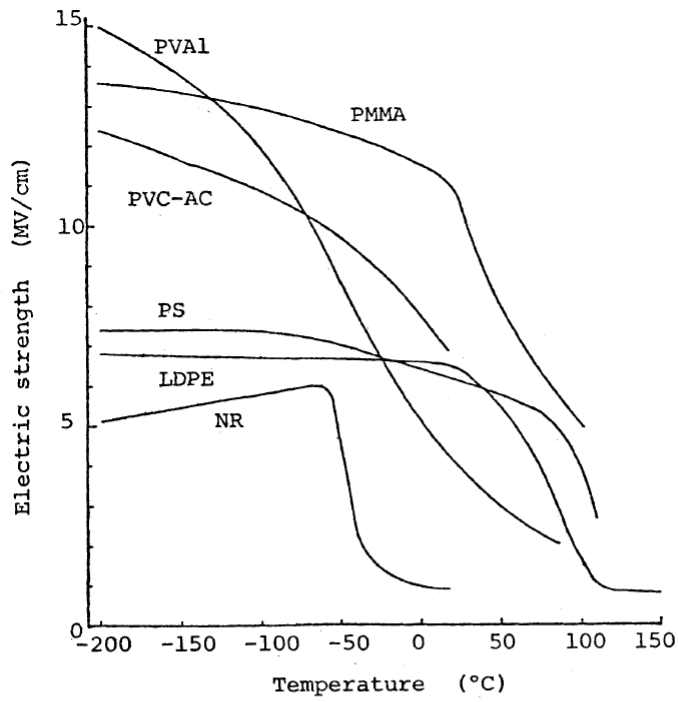
(1) Polar group

From **Figure 1-7**, it's easy to see that the introduction of the polar group will increase the dielectric breakdown strength in the low-temperature region. For all the polymer shown in the figure, they have a high dielectric breakdown strength in the high-temperature region and a low dielectric breakdown strength in the low-temperature region. This phenomenon was caused by the changing of the free volume and it will be discussed later in this thesis.

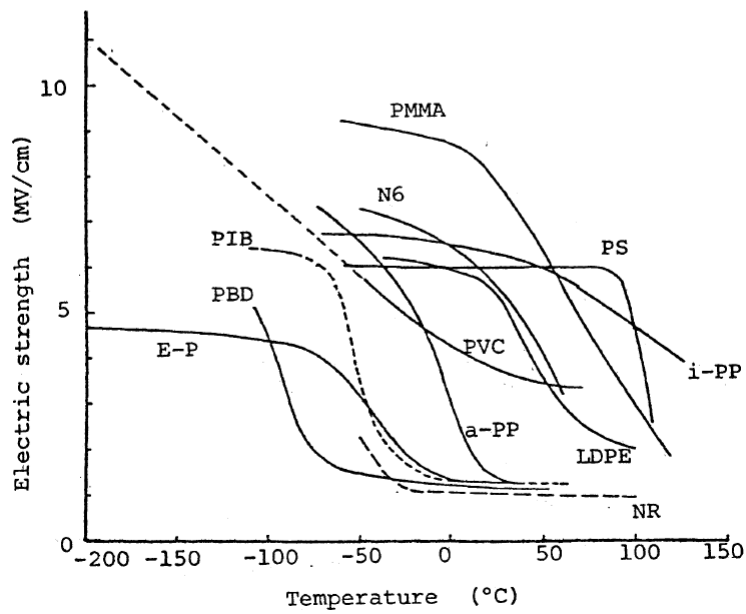
For the nonpolar material, there will be a temperature in which the dielectric breakdown strength will sharply decrease at this point, this temperature is defined as critical temperature (T_c). For the polar material, there was no critical temperature was observed in the test region.

The reason for dielectric breakdown strength's improvement was considered as the contribution of the dipoles created by the polar group. At the low-temperature region, the breakdown process of polymer material was dominated by the electron process. The existence of dipoles will interrupt the energy transmit process and improve the dielectric breakdown strength ^[18].

However, when the temperature enters the high-temperature region, the thermal breakdown mechanism, electromechanical breakdown mechanism, and others mechanism will domain the dielectric breakdown process and how the polar group worked in this region was not clear right now.



(a)



(b)

Figure 1-7 The temperature dependence of dielectric breakdown strength of different polymer material ^[10].

(2) Molecular weight

Figure 1-8 showed how the molecule weight affects the dielectric breakdown strength at room temperature. From the figure, it's easy to see that the breakdown strength will increase with the increasing molecular weight. However, from **Figure 1-7** we can see that the critical temperature of PE is near to the room temperature. Therefore, it's hard to analyze the mechanism of this phenomenon.

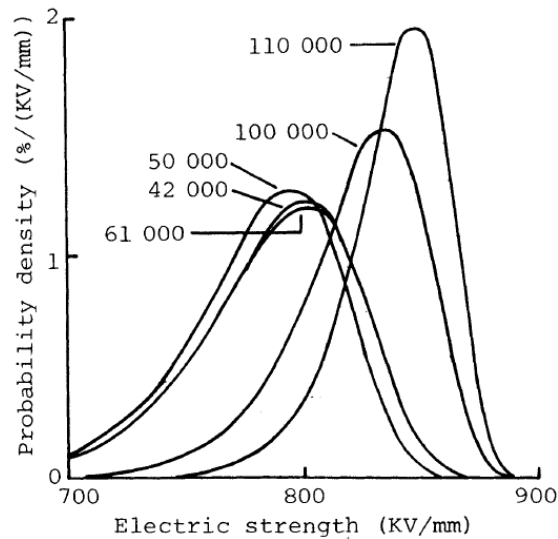


Figure 1-8 The molecular weight dependence of dielectric breakdown strength of polyethylene ^[19]

(3) Molecular conformation

Form **Figure 1-7**, we can see that at the low-temperature region, the atactic polypropylenes have a higher dielectric breakdown strength; at the high-temperature region, the isoatactic have a higher dielectric breakdown strength ^[10]. This phenomenon may be caused by the acceleration process of the electron was interrupted by the atactic PP's irregular conformation.

(4) Crosslinking structure

From previous research, the dielectric breakdown strength will increase with the crosslinking structure of the polymer [21]. This phenomenon mainly caused by the increase of the viscous flow transition temperature indicates the reduced of the free volume of polymer material. The high-energy electron beam will cause the crosslinking reaction in polyethylene, and **Figure 1-9** showed how the crosslinking structure will affect the dielectric breakdown strength of polyethylene.

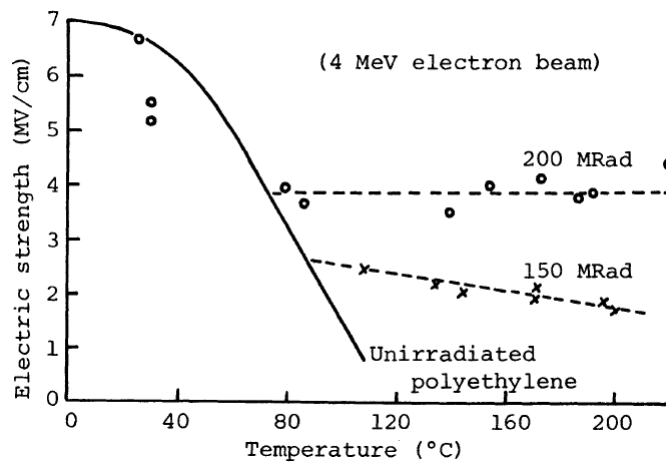


Figure 1-9 The relation between the high-energy radiation and dielectric breakdown strength of polyethylene [21]

1.3.2 The Effect of Solid Structure

(1) Crystallinity

For the crystalline polymers, it has both the crystalline phase and the amorphous phase. Previous research showed that the dielectric breakdown strength was related to the crystalline structure and the degree of crystallinity. **Figure 1-10**

showed the effect of degree of crystallinity on the dielectric breakdown strength of polyethylene. From the figure, it's easy to see that the dielectric breakdown strength will decrease with the increasing degree of crystallinity when the temperature is lower than 80 °C, however, when the temperature was higher than 80 °C, the trend was reversed. When the temperature is lower than 80 °C, the depth of shallow trap levels will increase with the decreasing degree of crystallinity and interrupt the electron's collision process, therefore the dielectric breakdown strength was improved. When the temperature was higher than 80 °C, the electromechanical breakdown mechanism will domain the dielectric breakdown process.

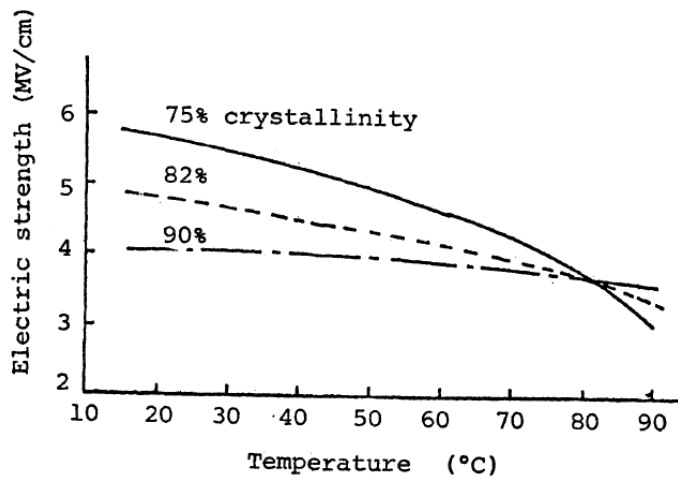


Figure 1-10 The relation between the degree of crystallinity and dielectric breakdown strength of polyethylene

Figure 1-11 shows the dielectric breakdown strength of the bends of polyethylene (PE) and ethylene-vinyl acetate (EVA) and pure EVA with different content of vinyl acetate (VA) at the low-temperature region. From the figure, the dielectric breakdown strength will increase with the increasing content of VA, this

phenomenon caused by the adding VA united decrease the degree of crystallinity and introduce the polar group. According to what was talked above, these two factors will improve the dielectric breakdown strength. What's more, the dielectric breakdown strength of EVA and PE-EVA blender is similar at same content of VA was added in, that shows at the low-temperature region, the dielectric breakdown strength not only influences by the degree of crystallinity but also influenced by the size of micro-crystallites [22].

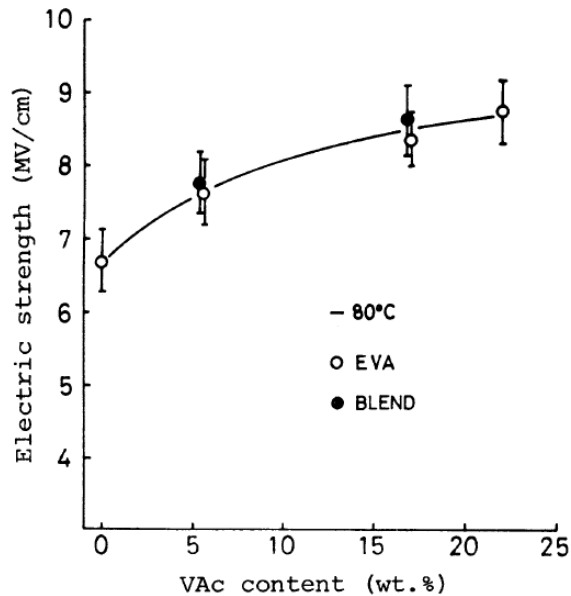


Figure 1-11 Dielectric breakdown strength of the blends of PE and EVA and pure EVA with different content of VA at the low-temperature region [22]

(2) Molecular motion

The molecular motion of the polymer was related to free volume. The free volume theory was introduced by Fox and Flory in 1950 [23]. It indicates that the molecular motion of polymer is domain by the free volume which is not occupied by the molecule chain. With the increasing temperature, the free volume will

increase and increase the ability of motion of polymer chain and the polymer material will change from glass-like state to rubber-like state, finally to the viscosity flow state. **Figure 1-12** showed the dielectric breakdown strength's temperature dependence of PE thin film ^[22]. In this figure, both of LDPE and HDPE under DC field and pulse field, the dielectric breakdown strength will decrease around the glass transition temperature. This indicates that the free volume will contribute to the energy transmit process between electron.

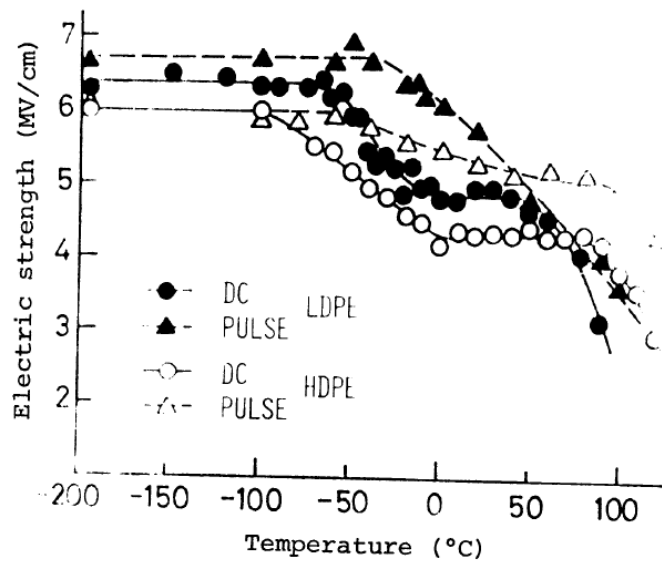


Figure 1-12 Dielectric breakdown strength's temperature dependence of polyethylene ^[22]

(2) Microdefect

Compare to the traditional dielectric material which is made by the inorganic material, the polymer material has many internal defects such like, atomic vacancies, interstitial and atoms, impurity atoms, grain boundaries, and etc. The interaction between microdefect and the dielectric breakdown process is complicated. Based on the recent research result, the microdefect of polymer material will significantly reduce the dielectric breakdown strength ^[24].

(3) Additive agent (impurities)

The different additive agent will make a different effect on the dielectric breakdown strength of the polymer. **Figure 1-13** showed the effect of the different additive agent on the dielectric breakdown strength of PE ^[17]. From the figure, we can see that the conductive additive agent (AS-1) will decrease the dielectric breakdown strength. The conductive filler will supply the charge carriers in the material system and caused an increase in the conductivity of the material system, then reduce the dielectric breakdown strength ^[25]. For the Pyrene additive agent, it has some π electrons which will affect free electron's accelerate process ^[17]. What's more, it may improve the dielectric breakdown strength by decreasing the free volume of the material system ^[26].

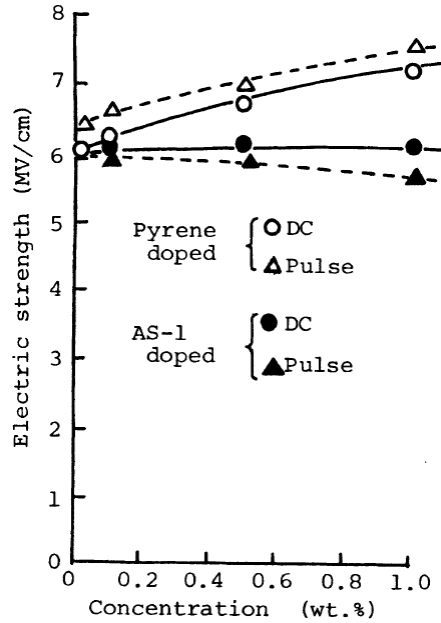


Figure 1-13 Influence of different additive agent on the dielectric breakdown strength of PE at -196°C ^[17].

(4) Summary

Expect the solid structure which was talked above, there are many different kinds of solid structure of polymers will influence the dielectric breakdown strength-for example, rigid skeleton structure, crystalline interface and internal strain ^[10]. Different microstructure will have a different influence on the dielectric breakdown process with different dielectric breakdown mechanism. Compare to the traditional ceramic dielectric material, the dielectric breakdown process of polymer-based dielectric material still needs to be well researched in the future.

1.4 The Test of Dielectric Breakdown Strength

For the test of dielectric breakdown strength, the experimental condition will significantly affect the result. For example, when the external electric field was applied to the material, the surrounding's partial discharge phenomenon mainly happens in the edge of the electrode before the dielectric material's complete breakdown. This phenomenon is called the edge effect. When the edge effect happens, the test result of dielectric breakdown strength will be lower than the value. Therefore, several methods were introduced to eliminate this effect, such as use the DC voltage to create the electric field and increase the voltage carefully [10].

For the analysis of dielectric breakdown strength, the 2-parameter Weibull distribution was considered as the most appropriate statistic method [27, 28] and can be described in equation (1-24):

$$P = 1 - \exp \left[- \left(\frac{E}{E_0} \right)^\beta \right] \quad (1-24)$$

In the equation (1-24), P is the cumulative breakdown probability, β is the shape parameter (e in this case), E_0 is the dielectric breakdown strength when the cumulative breakdown probability is 63.2%.

With equation (1-24), if the cumulative breakdown probability under different is known, as what was shown in **Figure 1-14** we can put all the electric field strength and its Weibull Parameter ($\ln[-\ln(1 - P)]$) into one straight line [29], then with the equation of this straight line, we can calculate the dielectric breakdown strength when the cumulative breakdown probability is 63.2% which was seen as the breakdown strength.

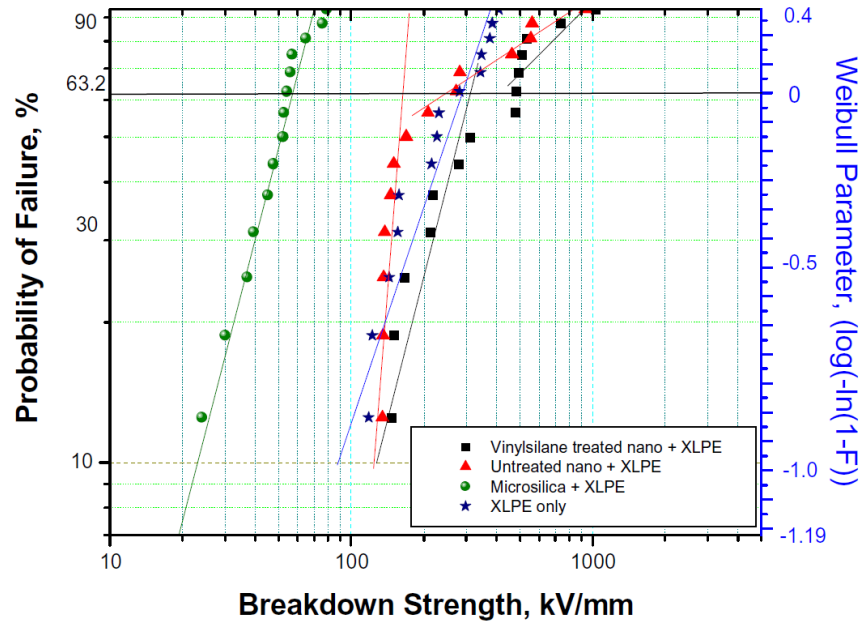


Figure 1-14 Weibull plot for the dielectric breakdown strength ^[29].

Chapter 2

Research Setup and Experiment Procedure

2.1 Experiment Methodology and Property Test Process

For the Polymer based dielectric material we have talked above, the sample's preparation and measurement about research are presented in this chapter. For this thesis, P(VDF-CTFE) 91/9 mol.% copolymer was utilized as the object because its good dielectric property and effect of silane adding were mainly studied for the improvement of P(VDF-CTFE)'s dielectric property.

The different weight concentrations (0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0 wt. %) of silane were added into P(VDF-CTFE) matrix to improve the dielectric property. The thin film samples were prepared by solution casting from N, N-Dimethylformamide (DMF). Glass slides were used as the substrate for the solution casting process. After the casting process, tweezers were used to peel the thin film samples off from the glass substrates.

The noble metal such as gold was used as the electrode for the dielectric property test, and physical vapor deposition was used to coat the electrode on the thin film sample's top and bottom sides. After the electrode was coated, the impedance analyzer can be used to test the capacitance, dielectric loss, relaxation time, etc. The precision materials analyzer system was used to test the Polarization-Electric field loop (P-E loop), P-E loop can be used to calculate the energy storage density.

The dielectric breakdown strengths or breakdown field of the polymer was tested under an external electric field which is created by a DC voltage to avoid the edge effect. As talked before, the dielectric breakdown strength of the material was related to the material's micro defect. In this thesis, the test of dielectric breakdown was repeated 10 times for each sample, and the results were put into the 2-parameter Weibull distribution to analyze the Weibull statistics result of dielectric breakdown.

2.2 Silane Additive Agent

For the nowadays research, silane was used mainly as a kind of coupling agent to improve the distribution of nonorganic filler in the polymer matrix. The reason why silane was used as the coupling agent can be illustrated as follow: many kinds of silane has two special end group which can form bridge-linked action between the nonorganic filler and polymer matrix.

But according to the previous experiment, some kinds of silane could improve the dielectric property and dielectric breakdown strength by itself. So, this thesis used silane as an additive agent to study its effect on the polymer based dielectric material. The detail information about the silane additive agent was shown in **Table 2-1**.

Table 2-1 The detail information about the silane additive agent

Chemical Name	1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane
Molecular Formula	C ₈ H ₄ Cl ₃ F ₁₃ Si
Synonyms	Trichloro-1 H, 1H, 2H, 2H-Perfluorooctylsilane
CAS Number	78560-45-9
Company	Alfa Aesar
Boiling Point	84-85 °C
Flash Point	54 °C
Density (g/ml)	1.638
Molar Mass (g/mol)	481.55
Solubility in water	Reacts

2.3 Preparation of Thin Film Sample

This thesis use solution casting as the method to prepare the Silane-P(VDF-CTFE) thin films sample and P(VDF-CTFE) 91/9 mol% (VC91) was used as the polymer matrix for this thesis.

N, N-Dimethylformamide (DMF) was used as our solvent to dissolve P(VDF-CTFE) matrix. The mixture of P(VDF-CTFE) and DMF will be blended about 12 hours by the magnetic stirring under 340 RPM's rotating speed. The silane additive agent was dissolved in ethanol, the mixture of silane additive agent and ethanol will be sonicated for 1 hour to make the silane well distributed in the ethanol solvent. Then the silane solution will be added into the polymer matrix solution by pipette with different volume. The mixture of P(VDF-CTFE) matrix and silane additive agent solution will be blended about 12 hours by the magnetic stirring under 340 RPM's rotating speed.

After the silane additive agent solution is well distributed in the P(VDF-CTFE) matrix, the silane-P(VDF-CTFE) solution was cast on the glass substrate at 70 °C for 8 hours. For reader's convenient, the flowchart was shown in **Figure 2-1**.

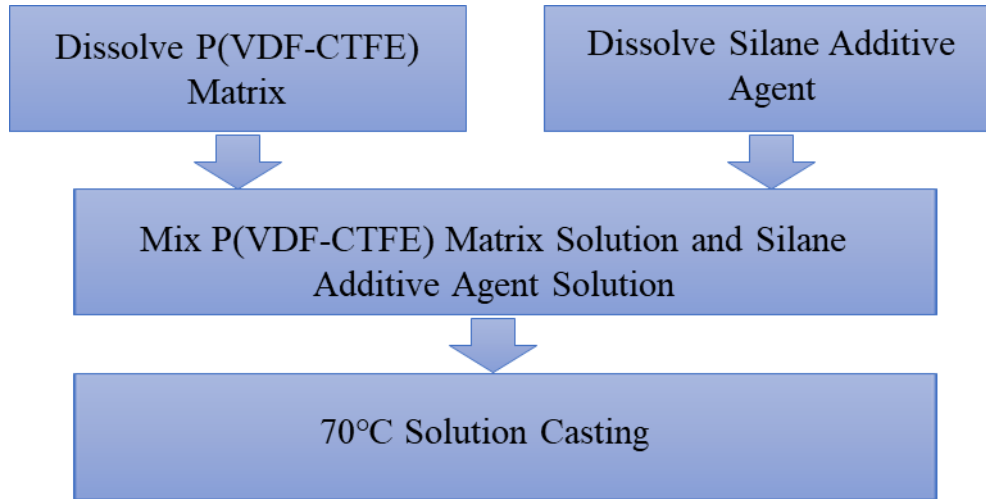


Figure 2-1 The flowchart of preparation of silane-polymer thin film sample

2.4 Annealing of Thin Film Sample

After the solution casting process, the uniform and translucent thin film samples are obtained. The next step is to remove all the DMF and ethanol from the sample because the remaining solvent will significantly influence the microstructure of the sample, increased the number of microdefect, and then reduced the dielectric property. Therefore, the annealing process is needed for the material which is made by the solution casting process and it will significantly improve the dielectric property of the thin film sample.

For the annealing process, the most important factor is the annealing temperature. Based on the previous experiment, the crystallization temperature of

P(VDF-CTFE) 91/9 is around 160 °C. Therefore, the sample which was obtained from the solution casting process was kept in the oven at 160 °C for 12 hours.

2.5 The Test of Dielectric Property

2.5.1 The Made of Electrode

For the electrode on the thin film sample's top and bottom sides, we choose SC-6 sputter (shown in **Figure 2-2**) and a mask (shown in **Figure 2-3**) which have several round holes with 3mm diameter on each side of the mask. The thin film sample was put between the mask's upper part and lower part. Then, the mask and the sample will be put into the chamber of the sputter. The sputter will coat a thin layer of gold on the thin film sample's surface which is not covered by the mask.



Figure 2-2 Pelco SC-6 sputter



Figure 2-3 Mask for gold coating

2.5.2 The test of dielectric constant and dielectric loss

After the electrode was sputtered on the thin film sample's top and bottom sides, the Agilent 4294A impedance analyzer was used to test the dielectric property. The dielectric property was tested under a frequency range from 100Hz to 1MHz and Cp-D function. The figure of Agilent 4294A impedance analyzer was shown in figure 2-4. The permittivity of the thin film sample can be calculated by using the parallel plate mode with the capacitance data obtained from the impedance analyzer. The Equation is shown as follow:

$$C = \frac{\epsilon S}{4\pi k d} \quad (2-1)$$

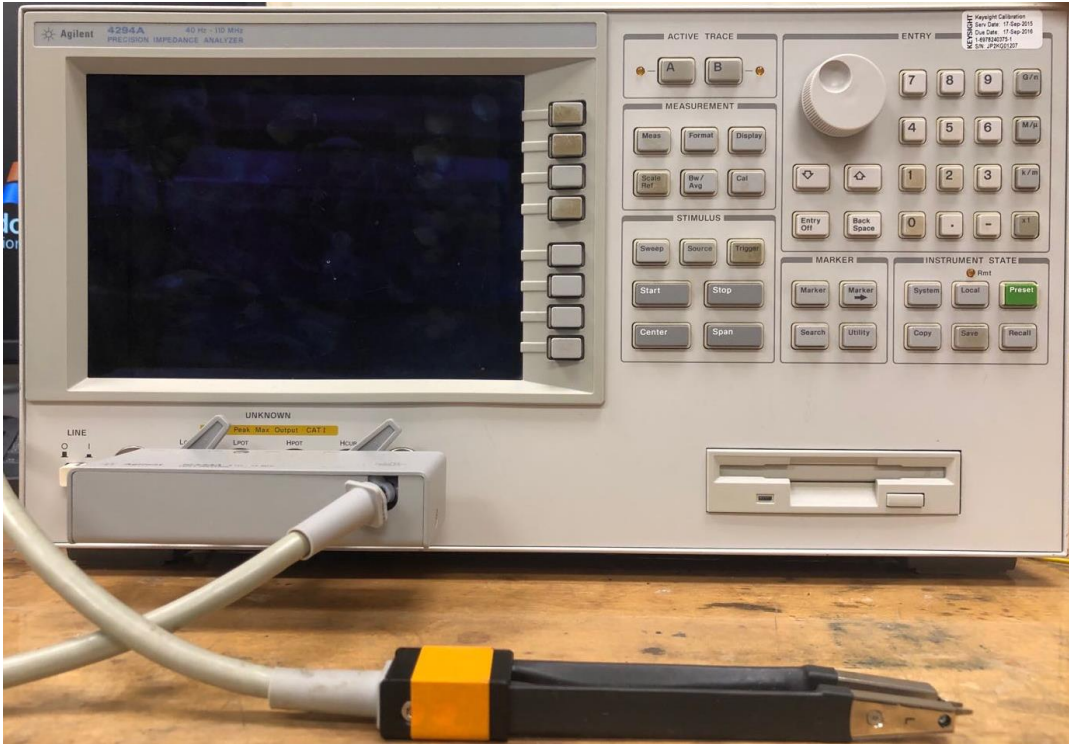


Figure 2-3 Agilent 4294A impedance analyzer

2.5.3 The Test of Energy Density

The test of the Polarization-Electric field loop (P-E loop) was finished by the Precision-LC100 system (shown in **Figure 2-4**). And the energy density is calculated from the P-E loop, and the definition of dielectric material's energy density is shown as Equation (2-2):

$$W_e = \int_0^{D_{max}} E dD \quad (2-2)$$

In Equation (2-2), W_E (J/m^3) is energy density, E is the electric field and D is electric displacement. For the dielectric materials, which has a high dielectric

constant, the electric displacement can be replaced by polarization, therefore, the Equation (2-2) can be convert as Equation (2-3) which is shown as follow:

$$W_e = \int_0^{P_{max}} EdP \tag{2-3}$$

Based on Equation (2-3), we can calculate energy density W_E from the P-E loop.

During the test, the sample with a round electrode ($d=3\text{mm}$) was clamped by the holder and submerge in the silicone oil. Then, the test of P-E loop was begun after the whole system is set up well.



Figure 2-4 Precision-LC100 system and H.V. Supply Amplifier/Controller

2.5.4 The Test of dielectric breakdown strengths

The test of dielectric breakdown strengths was finished under the electric field created by DC voltage. The DC voltage is created by TREK MODEL610D H.V. Supply Amplifier/Controller (shown in **Figure 2-5**). During the test, the sample with a round electrode ($d=3\text{mm}$) was clamped by the holder and submerged in the silicone oil. After the sample links with the system, the voltage between two sides of the thin film sample begins to increase. At the meantime, the voltage meter which was built into the H.V. Supply Amplifier/Controller will begin to test the voltage between two sides of the thin film sample. When the thin film sample is broken down, the circuit will short, and the biggest voltage shown in the voltage meter is breakdown voltage (V_b) for the tested sample, the **Figure 2-6** showed the structure of the testing circuit. The dielectric breakdown strengths or breakdown field (E_b) can be simply calculated by Equation (2-4) which is shown as follows:

$$E_b = \frac{V_b}{d} \quad (2-4)$$

In Equation (2-4), d is the thickness of the thin film sample.

The test result was analyzed by the 2-parameter Weibull distribution. This statistical method was concerned as the best method for the dielectric breakdown strengths analysis [30-31]. And the 2-parameter Weibull distribution can be described as equation (2-5):

$$P = 1 - \exp \left[- \left(\frac{E}{E_0} \right)^\beta \right] \quad (2-5)$$

In Equation (2-5), β is the shape parameter, E_0 is the dielectric breakdown strength when the cumulative failure probability is 63.2%, and P is the cumulative

failure probability. By using Equation (2-5), we calculate the Weibull dielectric breakdown strength.



Figure 2-5 TRek MODEL610D H.V. Supply Amplifier/Controller

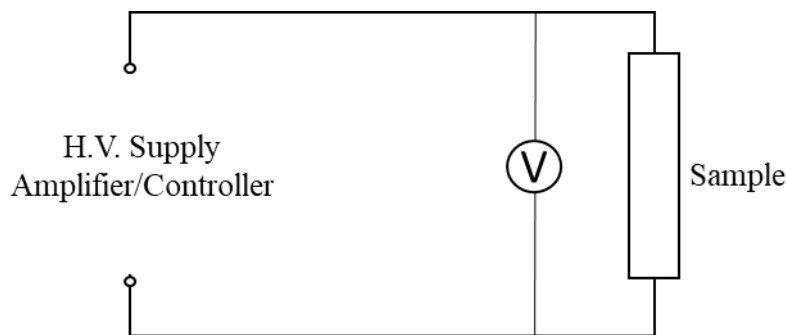


Figure 2-6 Schematic of the Test Circuit

The reason why this thesis used DC voltage to test dielectric breakdown strengths was for avoiding the edge effect. Edge effect can be illustrated as the partial discharge happened at the edge of the electrode before complete breakdown [32]. For eliminating the edge effect, the dielectric breakdown strengths should be carefully measured with DC voltage. [33]

Chapter 3

Silane-Polymer Thin Film

In this chapter, the Silane-Polymer composite with high dielectric constant and a dielectric breakdown strength was made by direct mixing the 1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane solution with P(VDF-CTFE) 91/9 mol% polymer matrix solution by traditional solution casting process. Based on the experiment result, the dielectric constant was increased by about 10%, and the Weibull breakdown strengths were increased by about 60%. Therefore, this composite may have great potential on the commercial application such as the generation of pulse power, capacitors with high permittivity, etc.

3.1 Test Condition

As what has been talked in **Chapter 2**, P(VDF-CTFE) 91/9 mol% was used as the polymer matrix and different weight concentrations (0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1 wt.%) of 1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane were added into P(VDF-CTFE) matrix as additive agent. Traditional solution casting was used to obtain composite thin film. The condition of preparation of the thin film sample was listed in **Table 3-1**.

Table 3-1 The condition of preparation of the thin film sample

Conditions	Value
Silane Additive Agent Contents	0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1 wt.%
Casting Temperature	70 °C
Annealing Temperature	160 °C
Testing Frequency	100 Hz ~ 1 MHz

3.2 Dielectric Properties at Room Temperature

3.2.1 Frequency Dependency of Dielectric Constant

Figure 3-1 shows the frequency dependency of the dielectric constant of 1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane-P(VDF-CTFE) composite thin film samples. From **Figure 3-1**, It's easy to see that in the test range, the dielectric constant was increased with the increasing content of the silane additive agent before 0.3 wt.%. With the content of silane additive agent further increased, the dielectric constant will decrease with the increasing content of silane additive agent. For all tested sample, the dielectric constant shows a similar trend with the increasing frequency. And from **Figure 3-2**, It's easy to see that the sample with relatively low content of silane additive agent shows a stronger frequency dependence, in other words, the dielectric constant decrease more with the increasing frequency. When the content of the silane additive agent at 0.3 wt.%, the dielectric constant shows the strongest frequency dependence. When the content of silane additive agent bigger than 0.3 wt.%, the frequency dependence of dielectric will decrease with the increasing content of silane additive agent, finally, very similar with the pure P(VDF-CTFE) sample.

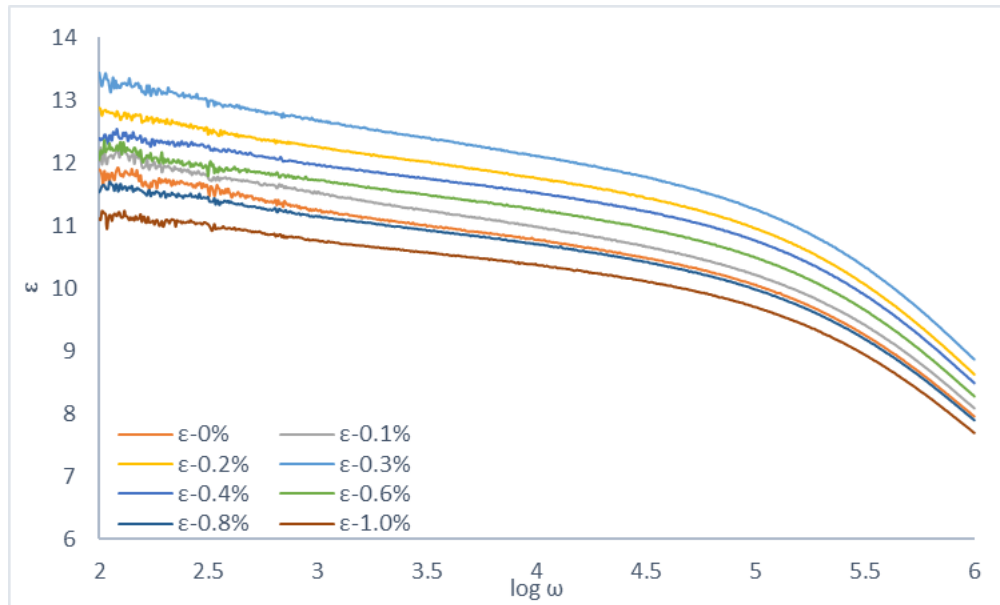


Figure 3-1 Frequency dependency of dielectric constant with different content of silane additive agent

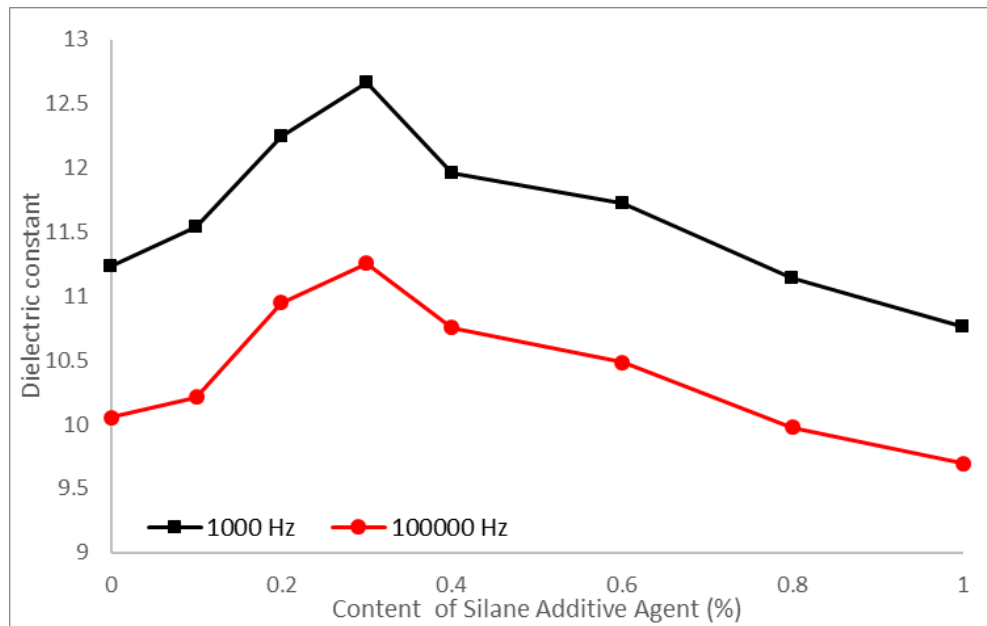


Figure 3-2 Dielectric constant with different content of silane additive agent at 10^3 Hz and 10^5 Hz

3.2.2 Frequency Dependency of Dielectric Loss

Figure 3-3 shows the frequency dependency of the dielectric loss of 1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane-P(VDF-CTFE) composite thin film samples. Based on **Figure 3-3** It's easy to see that at all test frequency range, all the tested sample's dielectric loss shows a similar trend which is increasing with the increasing frequency. Also, it's easy to see that all the tested sample has an almost same value at the high frequency.

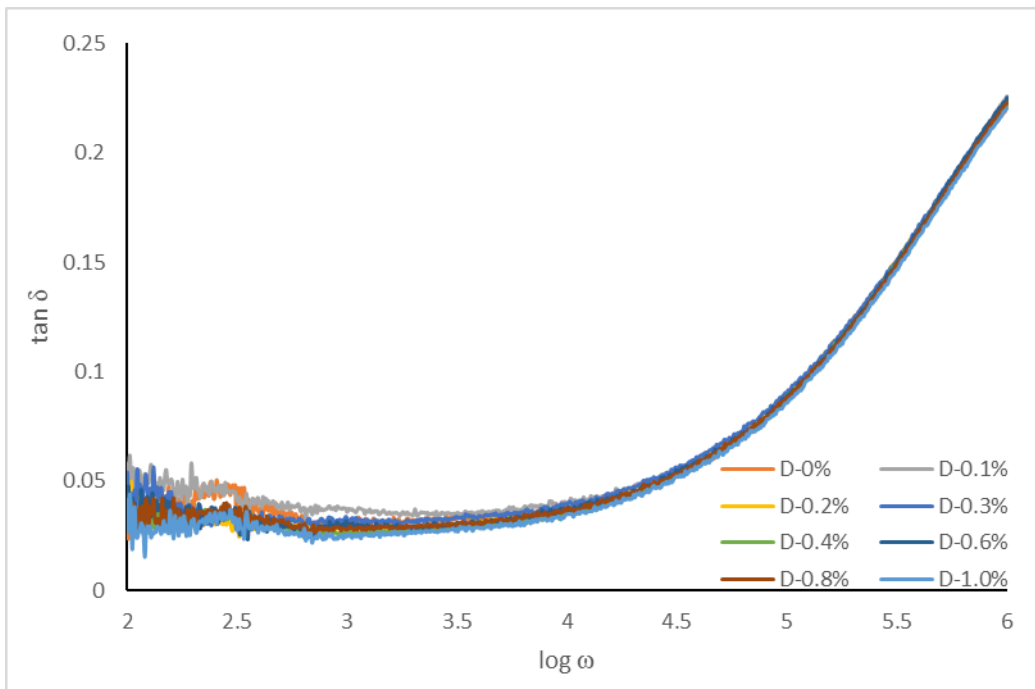


Figure 3-3 Frequency dependency of dielectric loss

3.3 Dielectric Breakdown Strengths

Figure 3-4 shows the Weibull plot for the dielectric breakdown strength of the samples with different amount of silane additive agent. If we consider the electric field which material will have a 63.2%'s cumulative failure probability is the dielectric breakdown strengths, we can obtain **Figure 3-5** from **Figure 3-4**.

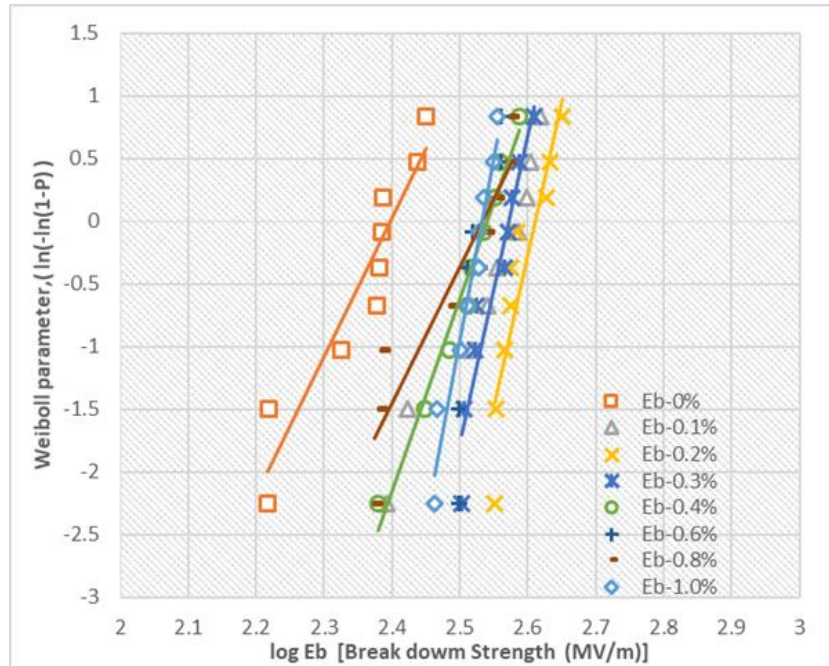


Figure 3-4 Weibull plot for the dielectric breakdown strength of the samples with different amount of silane additive agent

From **Figure 3-5** It's easy to see that the dielectric breakdown strength will increase with the increasing content of silane additive agent before 0.2 wt.%. After 0.2% wt.%, the dielectric breakdown strength will decrease with increasing content of silane additive agent. Finally, the dielectric breakdown strength is stable at 340 MV/m.

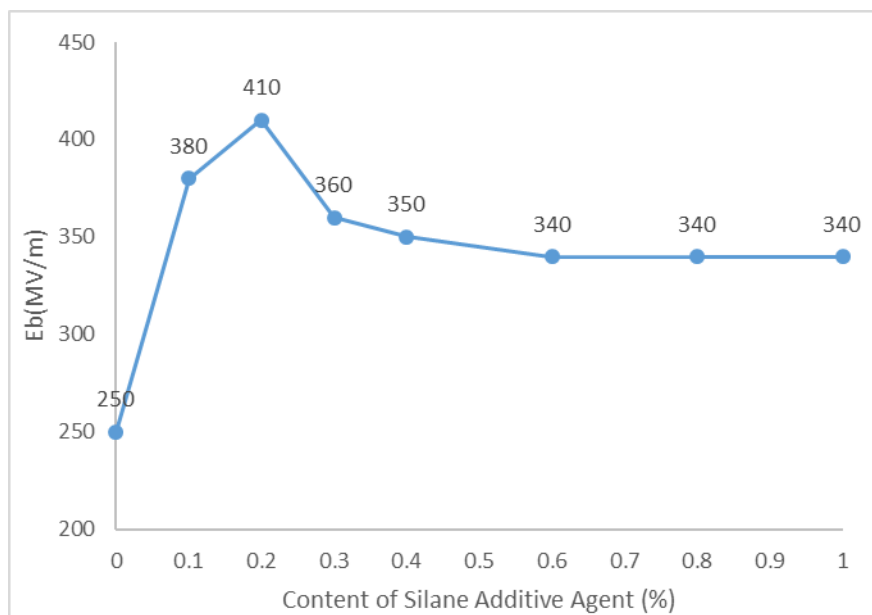


Figure 3-5 The dielectric breakdown strength of the samples with different amount of silane additive agent

3.4 Dielectric Properties under High Electric Fields

Figure 3-6 shows the P-E loop of the thin film samples with different amount of silane additive agent at 1500 kV/cm's electric field. From **Figure 3-6**, It's easy to see that the P_{max} is increased with the increasing content of the silane additive agent before 0.3 wt.%. After 0.3% wt.%, the P_{max} will decrease with increasing content of silane additive agent. The trend of P_{max} changed with the content of silane additive agent is similar to the trend of dielectric constant changed with the content of the silane additive agent. From what has been talked above, the relationship between polarization and dielectric constant is direct Proportion. Therefore, this result also proves that the dielectric constant is improved by the silane additive agent.

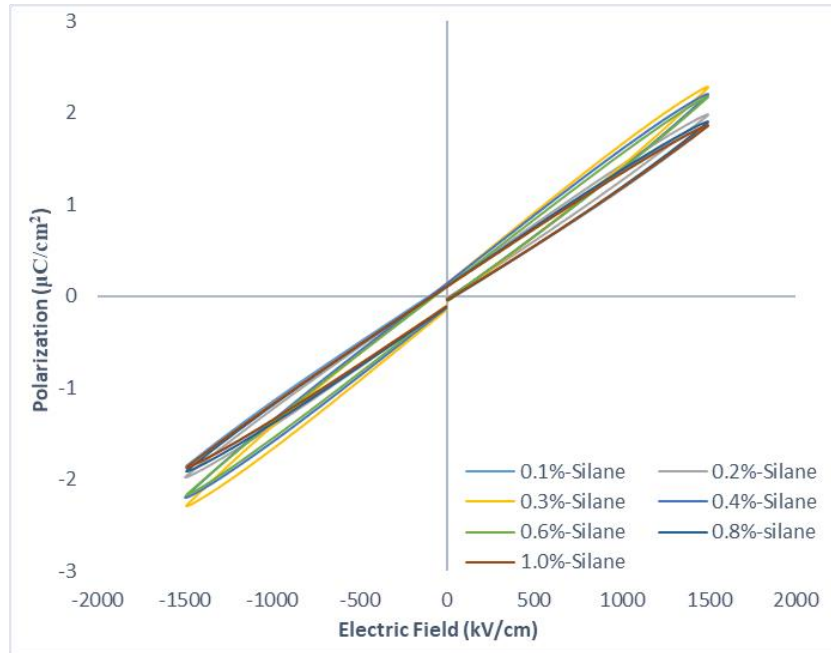


Figure 3-6 The P-E loop of the samples with different amount of silane additive agent at 1500 kV/cm's electric fields.

Figure 3-7 (a) shows the P-E loop of the samples with different amount (0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1 wt.%) of silane additive agent at maximum electric field. From **Figure 3-7 (a)**, the maximum polarization ($4.667 \mu\text{C}/\text{cm}^2$) was reached by the sample with 0.2 wt.% silane additive agent under 280 MV/m's electric field. **Figure 3-7 (b)** shows the P-E loop under the different electric field of the sample (0.2 wt.% silane additive agent) which have the greatest energy density.

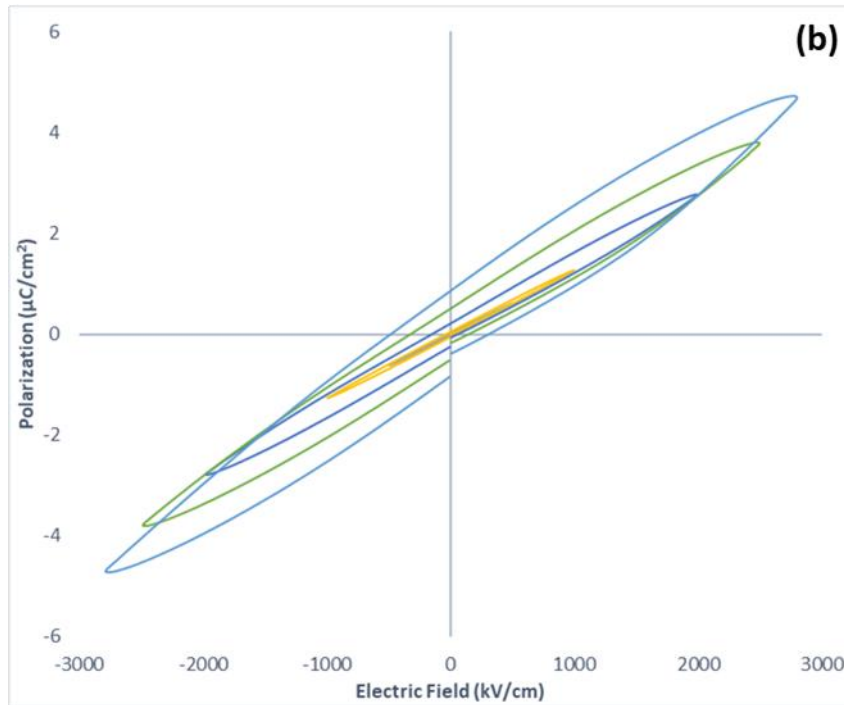
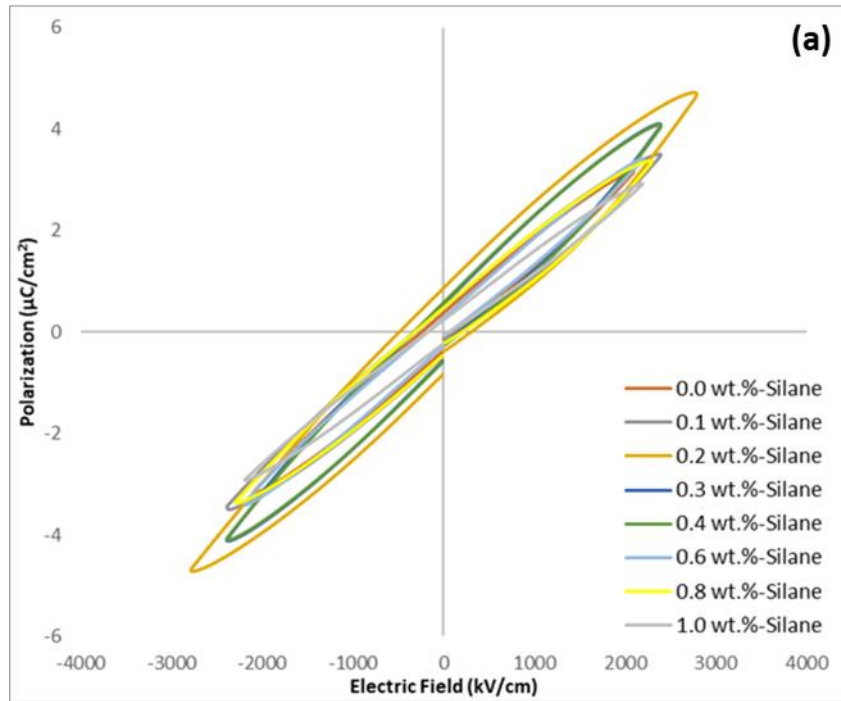


Figure 3-7 (a) The P-E loop of the samples with different amount of silane additive agent at maximum electric field and **(b)** The P-E loops of the sample with 0.2 wt% of silane additive agent under different electric fields.

Based on this P-E loop of the samples with different amount of silane additive agent at the maximum electric field, we can calculate the energy density of each sample which is shown in **Figure 3-8**. From **Figure 3-8**, it is easy to see that the energy density will increase with the increasing content of silane additive agent until the content reaches the 0.2 wt.%. From **Figure 3-8**, the maximum energy density (7.0731 J/cm^3) was reached by the sample with 0.2 wt.% silane additive agent under 280 MV/m 's electric field.

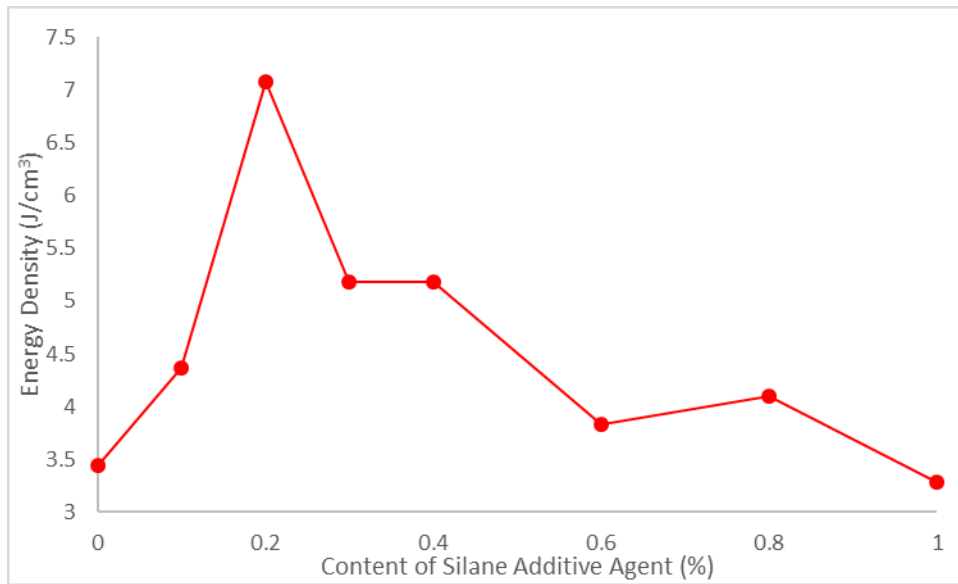


Figure 3-8 The energy density of the samples with different amount of silane additive agent at maximum electric field

3.5 Temperature Dependence of Dielectric Properties

Figure 3-9 to **Figure 3-15** shows the temperature dependence of the dielectric properties. For the reader's convenience, we show the trend of the dielectric constant and dielectric loss under 10^3 Hz , 10^4 Hz , 10^5 Hz , 10^6 Hz with

changing temperature. For this experiment, we choose 4 very representative samples which are pure polymer matrix sample (0.0 wt.%), the sample with 0.2wt.%, 0.3 wt.% and 0.8 wt.% silane additive agent.

From **Figure 3-9** to **Figure 3-12**, it's easy to see that the overall trend of the dielectric property change with the temperature is similar no matter what the content of the silane additive agent was added in. From the peak of dielectric loss and the step of dielectric constant, it's easy to see that there is a relaxation process from -40 °C to 40 °C, this phenomenon is caused by the glass transition process. Therefore, the glass transition temperature should be in this range.

Figure 3-13 and **Figure 3-14** showed that the peak of dielectric loss and the step of dielectric constant will shift to a higher temperature with the increasing content of silane additive agent until 0.3 wt.%. When the content of silane additive agent is higher than the 0.3 wt.%, the peak of dielectric loss and the step of dielectric constant will shift back to a lower temperature.

From **Figure 3-15 (a)**, it's easy to see that the dielectric constant at low frequency will increase until the content of the silane additive agent reach 0.2 wt.%, then it will decrease. For the dielectric loss showed in the **Figure 3-15 (b)**, the dielectric loss at low frequency will increase with the increasing content of silane additive agent, but for the sample with 0.3 wt.% of silane additive agent, it will show a relatively lower dielectric loss.

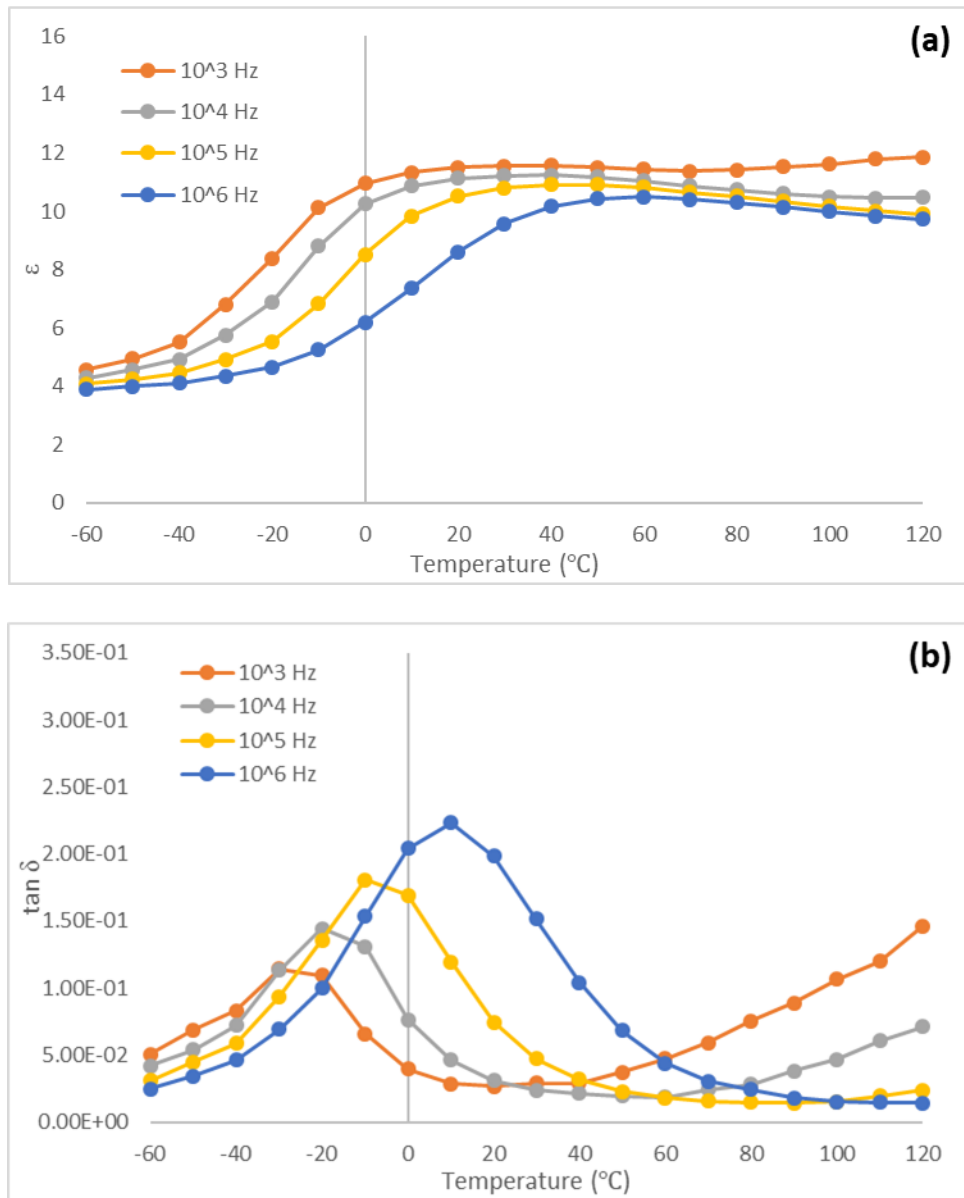


Figure 3-9 (a) Temperature dependence of dielectric constant with different frequency for P(VDF-CTFE) with no silane additive agent. (b) Temperature dependence of dielectric loss with different frequency for P(VDF-CTFE) with no silane additive agent.

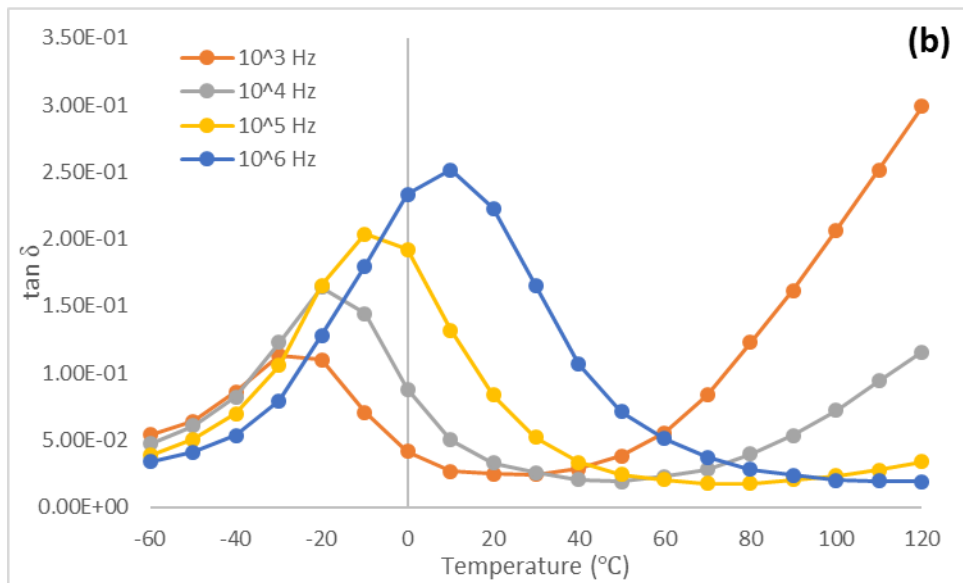
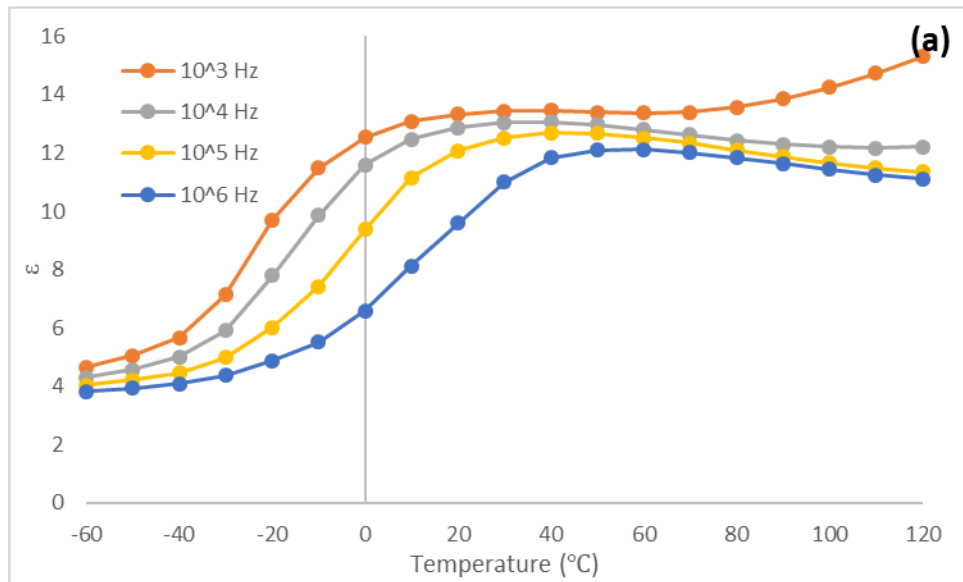


Figure 3-10 (a)Temperature dependence of dielectric constant with different frequency for P(VDF-CTFE) with 0.2 wt.% of silane additive agent.

(b)Temperature dependence of dielectric loss with different frequency for P(VDF-CTFE) with 0.2 wt.% of additive agent.

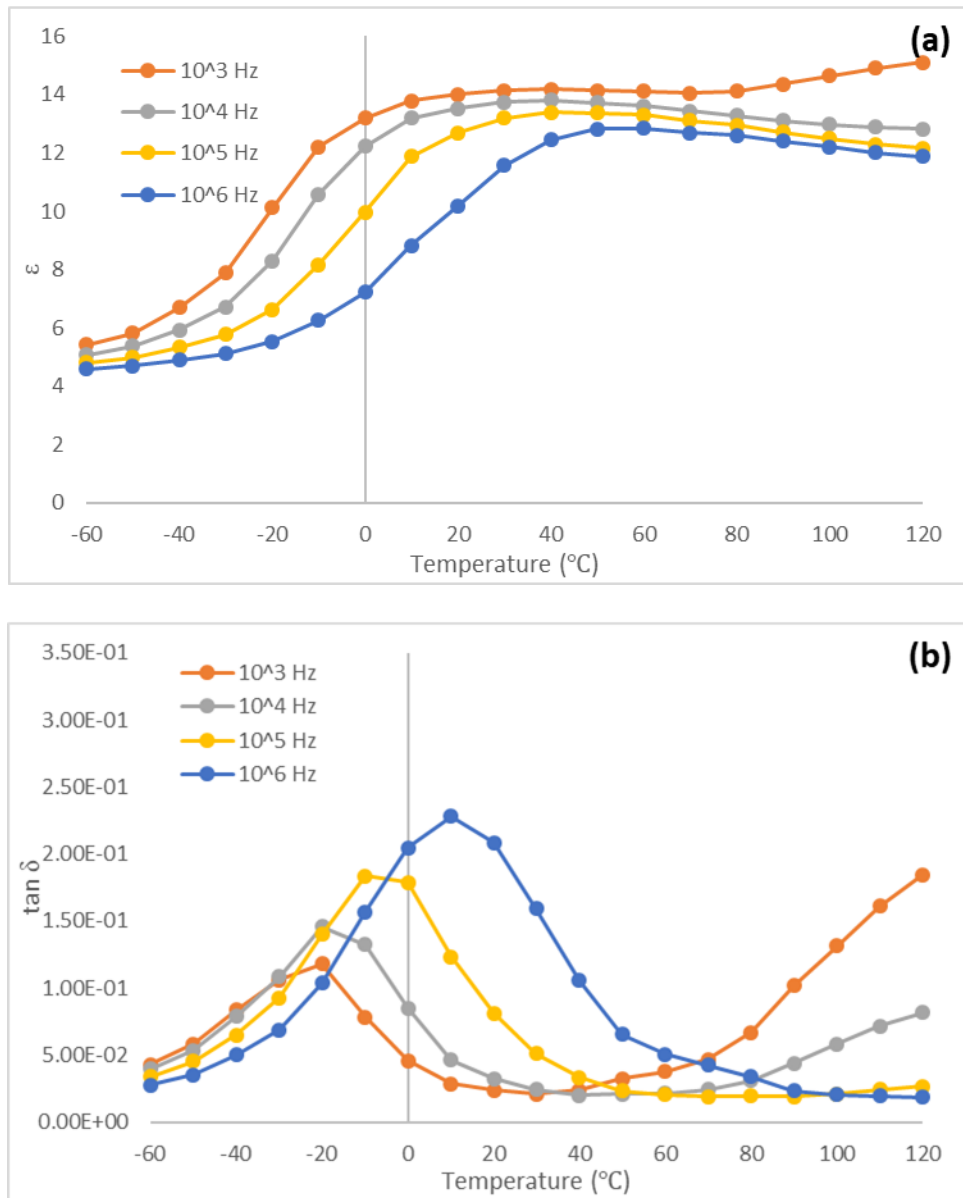


Figure 3-11 (a)Temperature dependence of dielectric constant with different frequency for P(VDF-CTFE) with 0.3 wt.% of silane additive agent.

(b)Temperature dependence of dielectric loss with different frequency for P(VDF-CTFE) with 0.3 wt.% of additive agent.

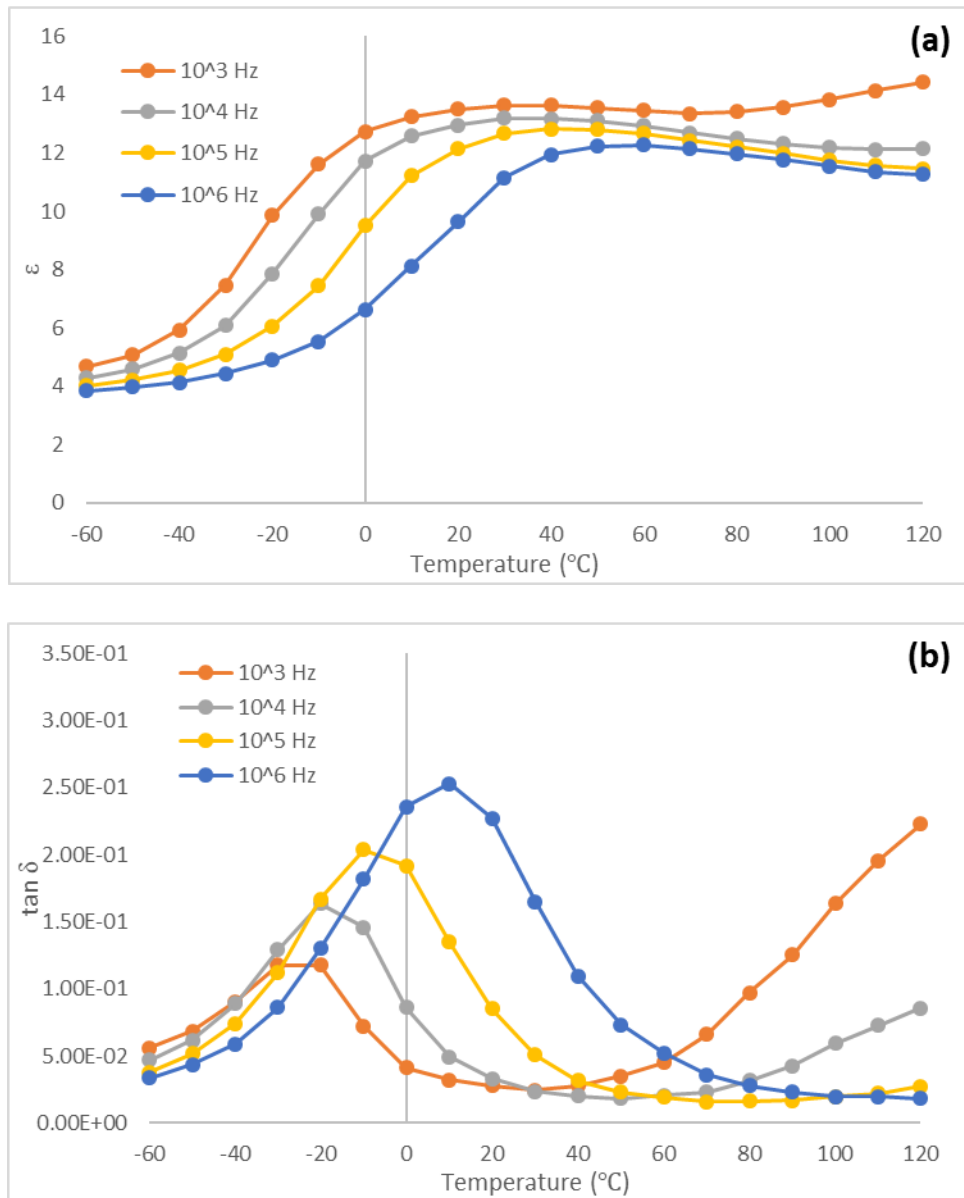


Figure 3-12 (a)Temperature dependence of dielectric constant with different frequency for P(VDF-CTFE) with 0.4 wt.% of silane additive agent.

(b)Temperature dependence of dielectric loss with different frequency for P(VDF-CTFE) with 0.4 wt.% of additive agent

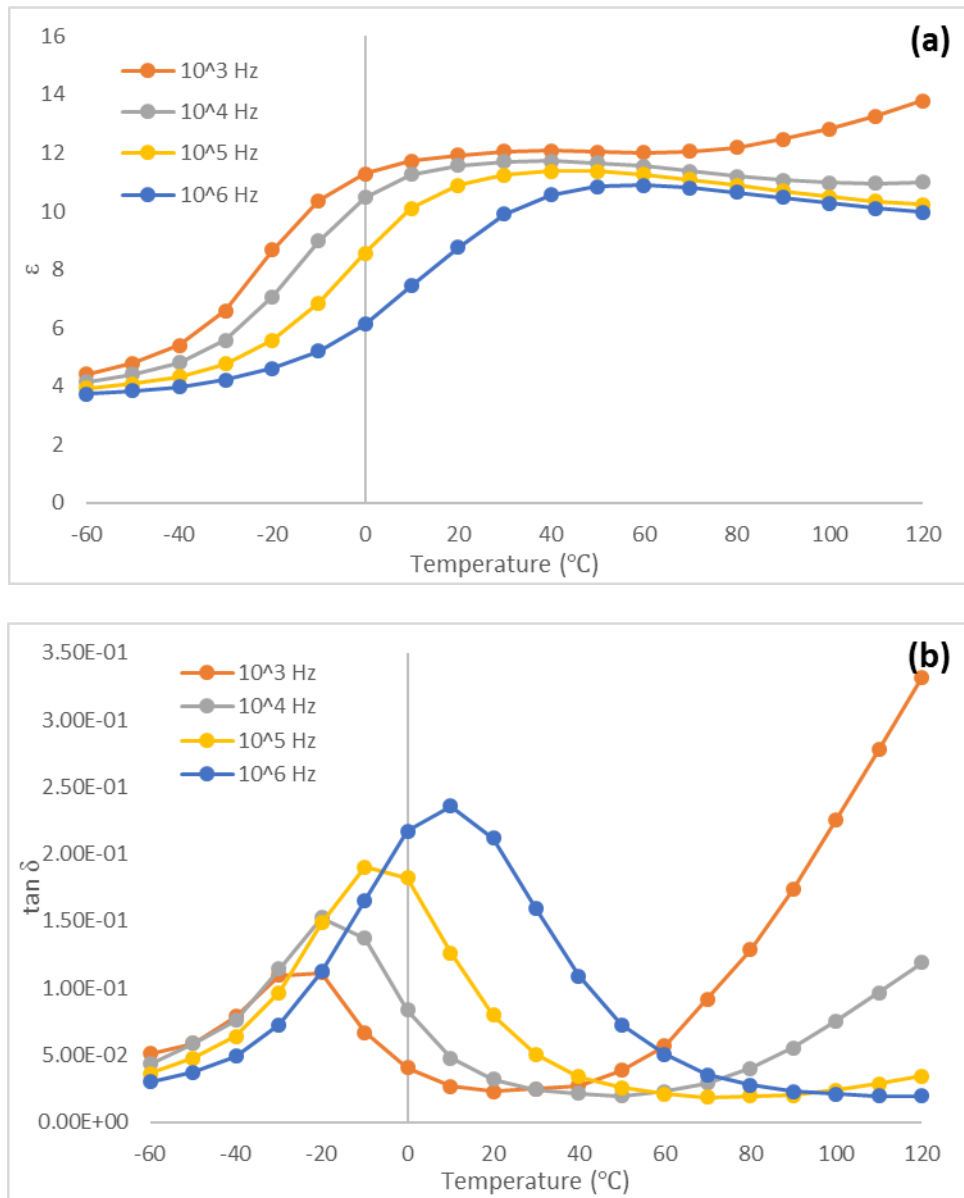


Figure 3-13 (a)Temperature dependence of dielectric constant with different frequency for P(VDF-CTFE) with 0.8 wt.% of silane additive agent.

(b)Temperature dependence of dielectric loss with different frequency for P(VDF-CTFE) with 0.8 wt.% of additive agent.

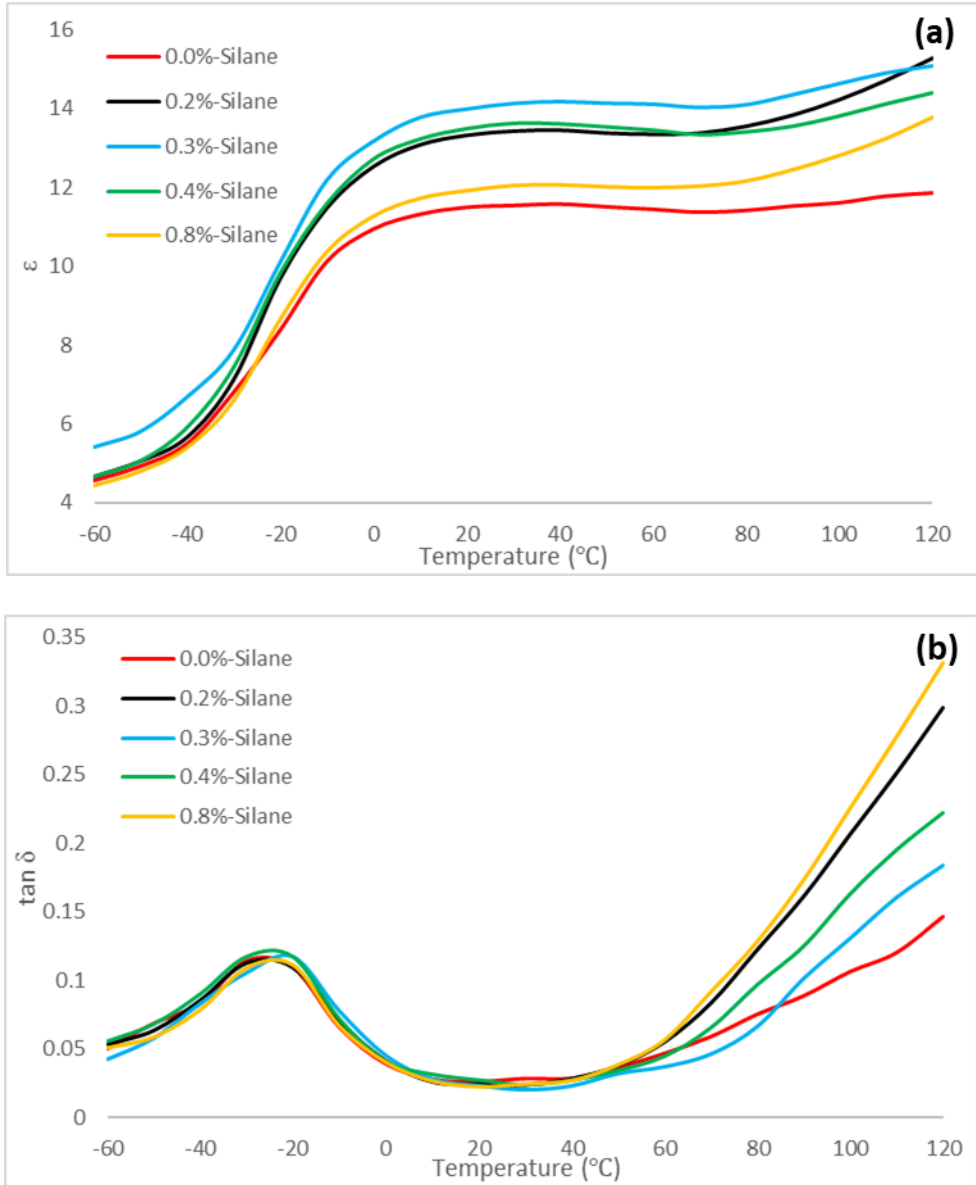


Figure 3-14 (a)Temperature dependence of dielectric constant with different content of silane additive agent at 1000 Hz. (b)Temperature dependence of dielectric loss with different content of silane additive agent at 1000 Hz.

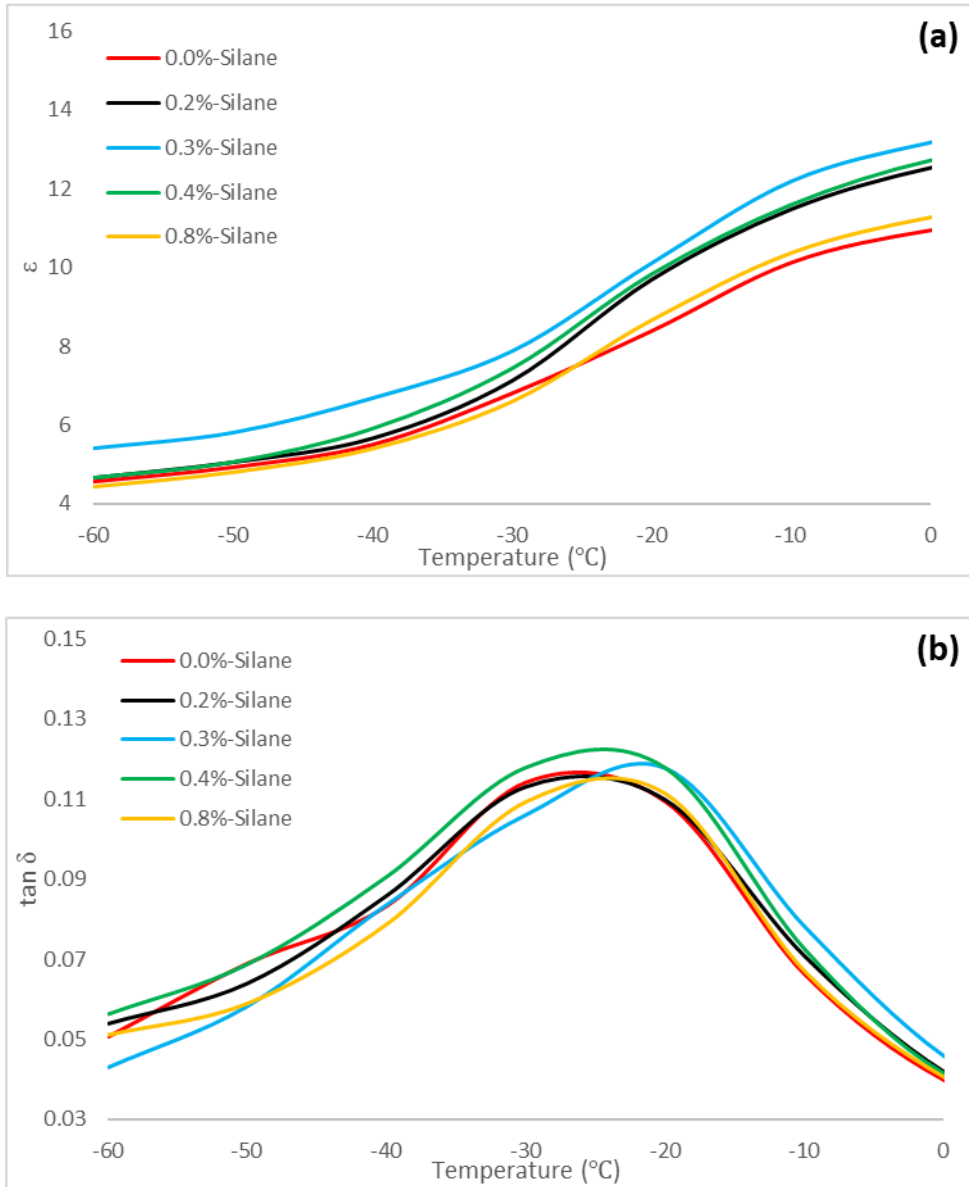


Figure 3-15 (a)Temperature dependence of dielectric constant with different content of silane additive agent at 1000 Hz. (b)Temperature dependence of dielectric loss with different content of silane additive agent at 1000 Hz.

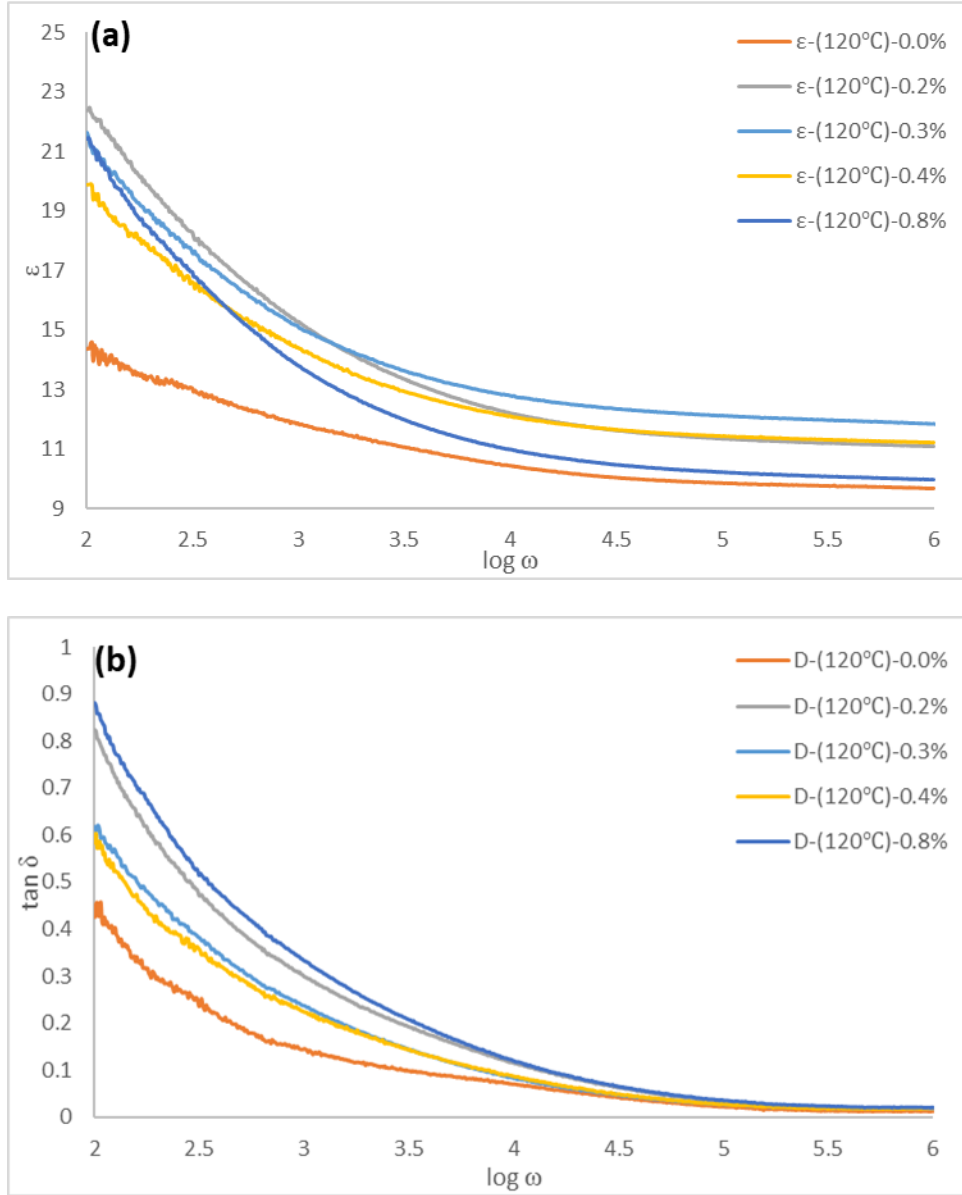


Figure 3-16 (a) Frequency dependence of dielectric constant with different content of silane additive agent at 120°C. (b) Frequency dependence of dielectric loss with different content of silane additive agent at 120°C.

3.6 DSC Result

Through the cooling and heating process of the DSC results, there was only one large crystallization peaks and melting peaks can be observed. That means our sample was well annealed. What's more, in the heating process of the DSC, there was one small melting peaks right behind the main melting peaks for the pure polymer matrix sample, that shows there was one more crystalline phase in the pure sample and sample with silane additive agent doesn't have this crystal phase. Therefore, the adding of silane additive agent help the crystalline process.

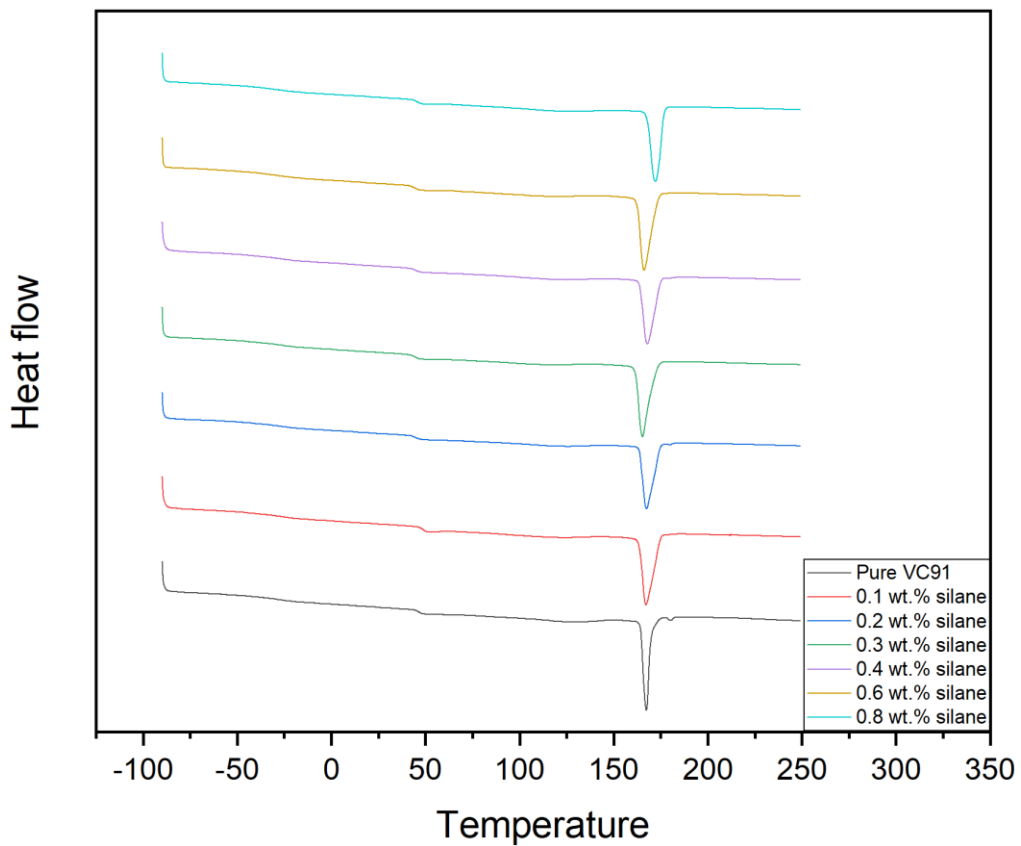


Figure 3-17 DSC result of heating process with different content of silane additive agent

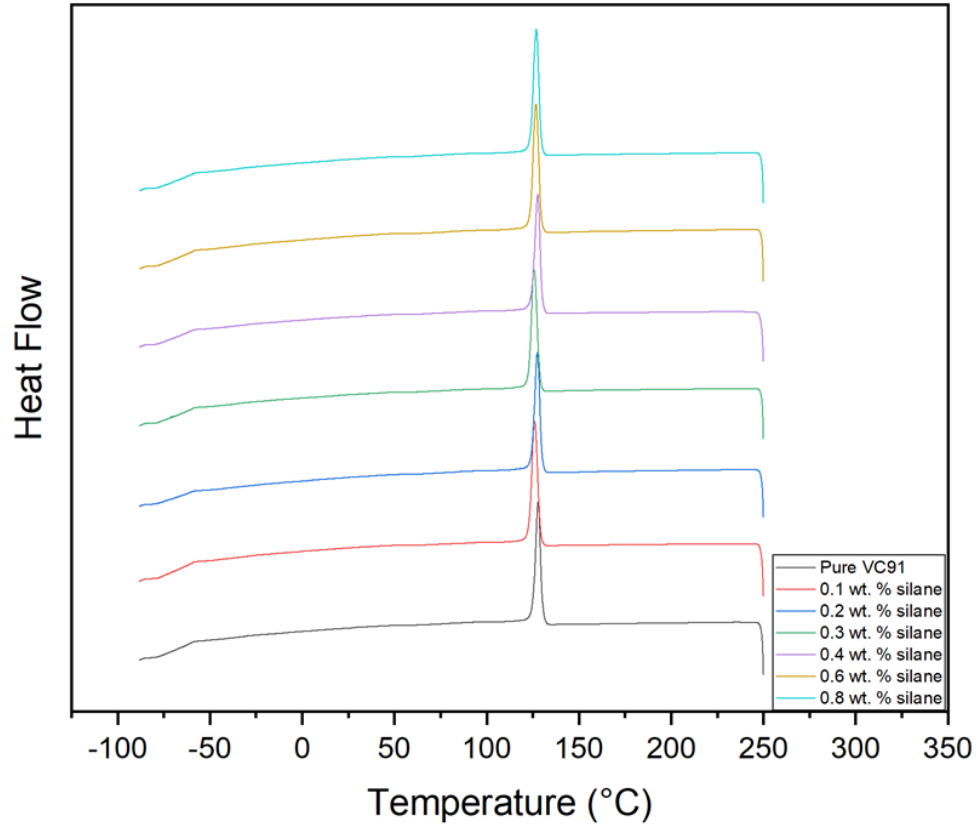


Figure 3-18 DSC result of cooling process with different content of silane additive agent

3.7 Discussion

From what has been talked in part 3.2, It's easy to see that the dielectric property of P(VDF-CTFE) was significantly improved by adding the silane additive agent. The reason why the silane additive agent can improve the dielectric constant and dielectric breakdown strength of P(VDF-CTFE) polymer matrix should be talked separately.

3.7.1 The Improvement of Dielectric Constant

For the dielectric constant, the participate of silane additive agent can improve the uniformity of thin film sample and this is the reason why silane always be used as the coupling agent between the nonorganic filler and polymer matrix. The interaction between the silane additive agent and P(VDF-CTFE) polymer matrix is shown in **Figure 3-10**.

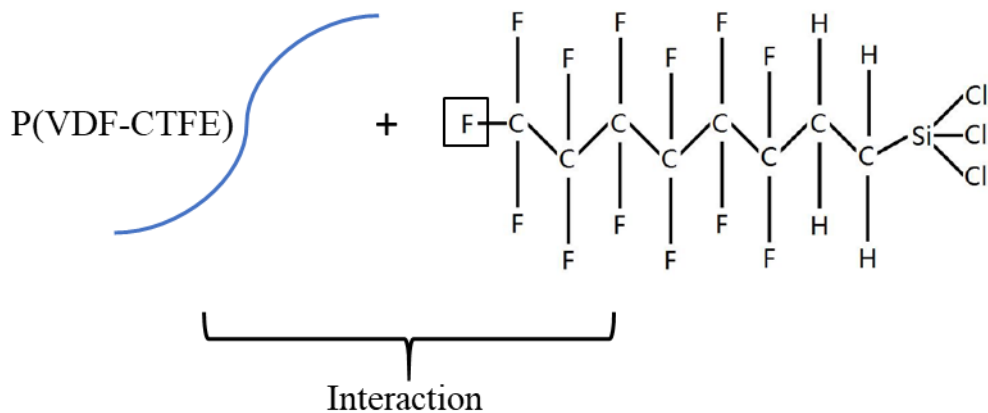


Figure 3-19 The schematic of interaction process between silane additive agent interaction and P(VDF-CTFE) polymer matrix

The interaction between the silane additive agent and P(VDF-CTFE) polymer matrix helped the polymer matrix's crystallization process and made the thin film samples denser and more uniform. What's more, from **Figure 3-3**, It's easy to see that the dielectric loss doesn't change much with changing content of the silane additive agent, that means the Silane-P(VDF-CTFE) thin film samples mainly shows the property of P(VDF-CTFE) matrix. That means the main chemical structure and crystal structure of the P(VDF-CTFE) doesn't change much with the adding of silane additive agent. So, the dielectric constant was improved by the uniformity of the thin film sample. When the content of the silane additive agent was bigger than the 0.3 wt.%, the silane additive agent may form some microphase and these microphases will reduce the dielectric constant.

From Figure 3-13 and Figure 3-14, we can see that the peak of dielectric loss and the step of dielectric constant will shift to a higher temperature with the increasing content of silane additive agent until 0.3 wt.% and then move to a lower temperature. From what has been talked in Part 3.5, this phenomenon was caused by the glass transition process. So, this trend showed the glass transition temperature will increase with the increasing content of silane additive agent until 0.3 wt.% and then move to a lower temperature. Based on the free volume theory (showed in Part 1.3.2 (2) Molecule motion), for one polymer system, a higher glass transition temperature means a lower free volume. Free volume is some parts of the material which were not occupied by the molecule chain. The decrease of the glass transition temperature when the content of silane additive agent is higher than 0.3

wt.%, is caused by the formation of silane's microphase, the existence of microphase will decrease the glass transition temperature and increased the number of microdefect.

So, if we consider the free volume is occupied by the air which has a dielectric constant around 1, the existence of free volume will reduce the dielectric constant. Therefore, the dielectric constant will increase with the increasing content of silane additive agent until 0.3 wt.% and then move to a lower position.

3.7.2 The Improvement of Dielectric Breakdown Strengths

For the dielectric breakdown process, the dielectric breakdown strengths can be seriously reduced by the micro-defects ^[34]. As what has been talked at part 3.6.1, the uniformity of the thin film sample will be improved by the adding of silane additive agent, and the number and size of the micro-defects will be reduced. Therefore, the dielectric breakdown strength will be improved by the adding of silane additive agent. What's more, the addition of silane with a low molecular weight into the P(VDF-CTFE) may reinforce the volume between lamellae. ^[35] So, the number and size of micro-cracks/voids were further reduced. When the content of silane additive agent was bigger than the 0.2 wt.%, the silane additive agent may form some microphase and these microphases can be seen as microdefect, and it will reduce the dielectric constant.

From the molecular structure diagram (shown in Figure 3-11) of our silane additive agent, it's easy to see that there is a big dipole structure in the molecule of silane additive agent. For the breakdown process, when a high electric field is

applied on the dielectric material, the charge carriers such like ions, electrons will reorientation, move and accelerate by the external field, then the movement of charge carriers will deflect the others charge carriers and finally caused the dielectric breakdown. The big dipole structure in the molecule of silane additive agent may stop the movement passing process, therefore, the dielectric breakdown strengths will be improved.

What's more, as what has been talked in the Part 1.3.2 (2) Molecule motion, the dielectric break down strength will decrease with the increasing of free volume. From Figure 3-13 and Figure 3-14 and Part 3.6.1, we know that the free volume will decrease with the increasing content of silane additive agent until 0.3 wt.%. So, the dielectric break down strength will increase first and then decrease.

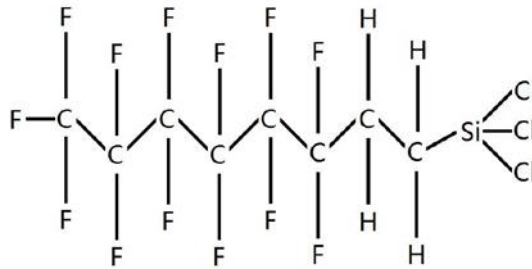


Figure 3-20 Molecular structure diagram of silane additive agent

3.7.3 The Improvement of Energy Density

From equation 3-1, it's easy to see that with the increase of dielectric constant and the dielectric breakdown strengths, we can easily obtain an increasing trend on the energy density and the experiment result (shown in **Figure 3-6**) already

proved that the energy density was improved by the adding of the silane additive agent.

$$U = \frac{1}{2} \varepsilon_0 \varepsilon E_b \quad (3-1)$$

In equation 3-1, U is the energy density of the liner material; ε_0 is the dielectric constant of the vacuum or vacuum permittivity; ε is the dielectric constant of samples; E_b is the dielectric breakdown strengths.

What's more, from what was shown in equation 1-4, we know that the polarization is directly proportional to the $(\varepsilon_r - 1)$. **Figure 3-4** showed that the maximum polarization will increase with increasing content of silane additive agent until 0.3 wt.%, then it will decrease. This phenomenon also indicates that the dielectric constant will increase with the increasing content of silane additive agent until 0.3 wt.%, and then, it will decrease.

For the test of dielectric breakdown strengths, one thing should be mentioned. For the test of P-E loop, the probability of partially breakdown happened at the edge of the electrode before complete breakdown was higher than the test of the dielectric breakdown strength under a DC voltage, which means the dielectric breakdown strengths we obtained from the P-E loop may be lower than the dielectric breakdown strengths which are tested under a DC voltage. This phenomenon is caused by the edge effect ^[36]. In the test of the P-E loop, the changing of the electric field was too fast for the test of the dielectric breakdown strength, and it may cause the edge effect and caused the partial breakdown. This is the reason why we obtain a lower dielectric breakdown strengths result from the test of P-E loop.

Chapter 4 Conclusion and future work

4.1 Conclusion

From what has been talked above, P(VDF-CTFE) 91/9 mol.% copolymer was used as the polymer matrix and mix with different amount of silane additive agent. The thin film samples were made by tradition solution casting process. The N, N-Dimethylformamide (DMF) and ethanol were used as the solvent of P(VDF-CTFE) and silane additive agent respectively. The gold electrode with 3mm's diameter was deposited on the two sides of the thin film sample. A DC voltage dielectric breakdown test system was established to test the change of dielectric breakdown strength with the addition of the silane additive agent. Based on the experimental data we can get several conclusions:

1. The dielectric constant and dielectric breakdown strengths of P(VDF-CTFE) could be improved by the addition of 1H, 1H, 2H, 2H-Perfluorooctyltrichlorosilane.
2. The dielectric constant reached the highest point when 0.3 wt.% of the silane additive agent was added into the P(VDF-CTFE). Compared to the P(VDF-CTFE) sample, the dielectric constant was increased by about 10%.
3. The energy density of our sample was improved by the adding od silane additive agent. The energy density reached the highest point when 0.2 wt.% of

silane additive agent was added into the P(VDF-CTFE) matrix, and the energy density was increased about 40% compared with the pure P(VDF-CTFE) sample.

4. The dielectric breakdown strengths reached the highest point when 0.2 wt.% of the silane additive agent was added into the P(VDF-CTFE). Compared to the P(VDF-CTFE) sample, the dielectric breakdown strength was increased by about 60%.

4.2 The Work of the Future

1. From part 3.6.1, It's easy to see that one of the reasons why silane additive agent can improve the dielectric property of the P(VDF-CTFE) matrix is it has an end group which can interact with P(VDF-CTFE) polymer matrix and a relatively lower molecular weight. So, we can find a chemical which has two end group both can interact with P(VDF-CTFE) matrix and a relatively lower molecular weight. We can use this kind of chemical such as VDF oligomer and PEG as our new additive agent. We believed it will be better than the silane additive agent we used in this thesis.

2. For the solution casting sample, we already got a significant improvement on the dielectric property. But we must see that the sample which is prepared by the traditional solution casting process will have more micro-cracks/voids and non-uniform structure compared with other thin film sample preparation method. As what was talked before, one of the reasons why the dielectric property is improved by silane additive agent is the improvement of the

uniformity of the thin film sample. So, the dielectric property of Silane-P(VDF-CTFE) thin film sample which is prepared by other methods such as spin coating should be tested to prove the universality of the silane additive agent.

Reference

- [1] Arbatti, Milind, Xiaobing Shan, and Z-Y. Cheng. "Ceramic-polymer composites with high dielectric constant." *Advanced Materials* 19.10 (2007): 1369-1372.
- [2] Qi, Lai, et al. "High-Dielectric-Constant Silver-Epoxy Composites as Embedded Dielectrics." *Advanced Materials* 17.14 (2005): 1777-1781.
- [3] Yuan, Jin-Kai, et al. "High dielectric permittivity and low percolation threshold in polymer composites based on SiC-carbon nanotubes micro/nano hybrid." *Applied physics letters* 98.3 (2011): 032901. [4] Kao K C. Dielectric phenomena in solids[M]. Elsevier, 2004.
- [4] Kao, Kwan Chi. *Dielectric phenomena in solids*. Elsevier, 2004..
- [5] Barsoum, Michel, and M. W. Barsoum. *Fundamentals of ceramics*. CRC press, 2002.
- [6] Chu, Baojin, et al. "A dielectric polymer with high electric energy density and fast discharge speed." *Science* 313.5785 (2006): 334-336.
- [7] Arbatti, Milind, Xiaobing Shan, and Z-Y. Cheng. "New high-dielectric-constant polymer-ceramic composites." *MRS Online Proceedings Library Archive* 847 (2004).
- [8] Gregorio, R., M. Cestari, and F. E. Bernardino. "Dielectric behaviour of thin films of β -PVDF/PZT and β -PVDF/BaTiO₃ composites." *Journal of Materials Science* 31.11 (1996): 2925-2930.
- [9] Branwood, A., J. D. Hurd, and R. H. Tredgold. "Dielectric breakdown in barium titanate." *British Journal of Applied Physics* 13.10 (1962): 528.
- [10] Barsoum M, Barsoum M W. Fundamentals of ceramics[M]. CRC press, 2002.
- [10] Ieda, Masayuki. "Dielectric breakdown process of polymers." *IEEE Transactions on Electrical Insulation* 3 (1980): 206-224.
- [11] Whitehead, S. "Dielectric Breakdown of Solids, Chap." (1953).
- [12] O'Dwyer, John Joseph. *The theory of electrical conduction and breakdown in solid dielectrics*. Clarendon Press, 1973.
- [13] Wagner, Karl Willy. "The physical nature of the electrical breakdown of solid dielectrics." *Journal of the American Institute of Electrical Engineers* 41.12 (1922): 1034-1044.
- [14] Rogowski, W. "Der elektrische Durchschlag von Gasen, festen und flüssigen Isolatoren." *Electrical Engineering (Archiv für Elektrotechnik)* 23.5 (1930): 569-578.
- [15] Von Hippel, Artur. "Electric breakdown of solid and liquid insulators." *Journal of Applied Physics* 8.12 (1937): 815-832.
- [16] Inuishi, Y., et al. "Secondary factors in dielectric breakdown of solids." *J. Inst. Elect. Engrs. of Japan* 76 (1956): 913-918.
- [17] Miyairi, K., et al. "Dielectric breakdown of polyethylene at low temperature." *J. Inst. Elect. Engrs. of Japan* 91 (1971): 1962-1968.

- [18] Ball, Ian David Leonard. "The intrinsic electric strength of polyvinyl alcohol and its temperature variation." *Proceedings of the IEE-Part I: General* 98.110 (1951): 84-86.
- [19] Fischer, Peter HH, and Kurt W. Nissen. "The short-time electric breakdown behavior of polyethylene." *IEEE Transactions on Electrical Insulation* 2 (1976): 37-40.
- [20] Amakawa, K., et al. "Electric conduction and dielectric breakdown of polyethylene films." *J. Inst. Elect. Engrs. of Japan* 84 (1964): 129-135.
- [21] Stark, K. H., and C. G. Garton. "Electric strength of irradiated polythene." *Nature* 176.4495 (1955): 1225.
- [22] Nagao, Masayuki, et al. "Dielectric Breakdown of Ethylene-Vinyl Acetate Composit Polymers in Low-Temperature Region." *The transactions of the Institute of Electrical Engineers of Japan. A* 97.12 (1977): 617-622.
- [23] Fox Jr, Thomas G., and Paul J. Flory. "Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight." *Journal of Applied Physics* 21.6 (1950): 581-591.
- [24] Chen, Shuting, et al. "Comparative investigation of the structure and properties of ferroelectric poly (vinylidene fluoride) and poly (vinylidene fluoride–trifluoroethylene) thin films crystallized on substrates." *Journal of applied polymer science* 116.6 (2010): 3331-3337.
- [25] Ieda, M., et al. "Dielectric Breakdown of High Temperature Polymers." 3rd Int. Symp. on High Voltage Eng.. Vol. 21. 1979.
- [26] Shinohara, U., and M. Kimura. "Effects of various additives on dielectric breakdown of plasticized polyvinyl-chloride resin." *J. IEE of Japan* 77.829 (1957): 1300-1306.
- [27] Khalil, M. Salah. "The role of BaTiO₃ in modifying the dc breakdown strength of LDPE." *IEEE Transactions on Dielectrics and Electrical Insulation* 7.2 (2000): 261-268.
- [28] Ueki, M. M., and M. Zanin. "Influence of additives on the dielectric strength of high-density polyethylene." *IEEE Transactions on Dielectrics and Electrical Insulation* 6.6 (1999): 876-881.
- [29] Roy, M., et al. "Polymer nanocomposite dielectrics-the role of the interface." *IEEE transactions on dielectrics and electrical insulation* 12.4 (2005): 629-643.
- [30] Roy, M., et al. "Polymer nanocomposite dielectrics-the role of the interface." *IEEE transactions on dielectrics and electrical insulation* 12.4 (2005): 629-643.
- [31] Khalil, M. Salah. "The role of BaTiO₃ in modifying the dc breakdown strength of LDPE." *IEEE Transactions on Dielectrics and Electrical Insulation* 7.2 (2000): 261-268.
- [32] Ieda, Masayuki. "Dielectric breakdown process of polymers." *IEEE Transactions on Electrical Insulation* 3 (1980): 206-224.
- [33] Nagao, M., M. Kosaki, and Y. Mizuno. "On temperature dependence of electric strengths of polar polymeric films in low-temperature region." 1992., *Sixth International Conference on Dielectric Materials, Measurements and Applications*. IET, 1992.

- [34] Chen, Shuting, et al. "Comparative investigation of the structure and properties of ferroelectric poly (vinylidene fluoride) and poly (vinylidene fluoride–trifluoroethylene) thin films crystallized on substrates." *Journal of applied polymer science* 116.6 (2010): 3331-3337.
- [35] Rahimabady, Mojtaba, et al. "High electric breakdown strength and energy density in vinylidene fluoride oligomer/poly (vinylidene fluoride) blend thin films." *Applied Physics Letters* 99.14 (2011): 142901.
- [36] Ieda, Masayuki. "Dielectric breakdown process of polymers." *IEEE Transactions on Electrical Insulation* 3 (1980): 206-224.