



## CHAPTER V

### EFFECT OF INTERNAL VOIDS ON INDUCED DIPOLE IN PVC FILMS BY PHASE SEPARATION TECHNIQUE

#### 5.1 Abstract

The voided PVC films with spherical voids were induced by phase separation technique. The shape, and size of voids were controlled by varying types of solvent and polymer concentrations. SEM micrographs showed the spherical voids inside the voided films by DMAc solution. Thermal properties of voided films were not different compared to those of dense films. The dielectric constants of voided films lower than that of dense film due to the dielectric mixing rule. Rayleigh model confirmed the connectivity of 0–3 void–polymer composites describes a cubic array of spherical voids. Piezoelectric coefficient of voided film was not different from dense film indicated that the internal voids did not affect on the piezoelectric properties in PVC.

#### 5.2 Introduction

Porous polymer films have an enhanced charge storage capability, since the charge drift across the film is hindered by the presence of voids (Behrendt, N., et al., 2008). During electrical charging, polarization is generated by charge storage in voids creating upper and lower void surface of opposite charges. Each void can be considered as a macroscopic dipole. Therefore, a novel concept of creating internal voids is introduced in bulk of polymer (Wilson, S.A., et al., 2007).

Dipole moment of PVC comes from the presence of chlorine in the side group (Kocharyan, N.M., *et al.*, 1968). PVC is also known as piezoelectric polymer. The piezoelectric properties are obtained by orienting dipole moments in the polymer by poling (Mark, J.E., 2007). Microporous PVC films are often prepared by immersion precipitation in which, a polymer solution was casted as a thin film on a support and was subsequently immersed in a non-solvent bath. Precipitation could

occur because the good solvent in the polymer solution was exchanged for non-solvent. (van de Witte, P. *et al.*, 1996). After drying, the non solvent was removed out and left the voids inside the structure of film. The variation of size and shape of void and also the porosity of the film were controlled by polymer concentrations and types of solvent.

The objectives of this work were focused on the effect of internal voids induced in PVC film on dipole by phase separation technique. In this method, PVC powder was dissolved with 2 different solvents —*N,N* Dimethylacetamide (DMAc) and Tetrahydrofuran (THF)— at different polymer concentrations. Subsequently, the morphology of voided films was observed using Scanning Electron Microscope (SEM). The dielectric constant and dielectric loss were measured as a function of frequencies range from 1 kHz to 1 MHz at room temperature. Moreover, the dielectric properties were also measured as a function of temperatures. Piezoelectric and ferroelectric properties obtained from voided films were compared to those of dense polymers films. Other physical, thermal and mechanical properties, are herein discussed.

### **5.3 Experimental**

#### **5.3.1 Preparation of Dense Films**

PVC is an easily degraded material so the PVC films cannot be prepared by compression molding. Phase separation technique was used instead.

PVC powder (14 wt% PVC) was dissolved in THF and casted on the Teflon mold. The casted solution was left to solidify at room temperature ( $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ ,  $50\text{ \% RH} \pm 5\text{ \% RH}$ ) for 24 hr and dried in vacuum oven at  $48\text{ }^{\circ}\text{C}$  for 24 hr to remove residual solvent and anneal film.

#### **5.3.2 Preparation of Voided Films**

Solvent cast of PVC films were obtained by casting a DMAc or THF solution of 8, 11 and 14 wt% PVC on the Teflon mold. The films were pre-evaporated for 5 minutes in air ( $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ ,  $50\text{ \% RH} \pm 5\text{ \% RH}$ ) and then immersed in  $25\text{ }^{\circ}\text{C}$  distilled water bath for 24 hr. After that, the films were washed in

the series of distilled water. To ensure that the residual solvent was removed out, these films were dried at 48 °C for 24 hr in vacuum oven. This condition will also be helpful to anneal the films to minimize the swelling of the films.

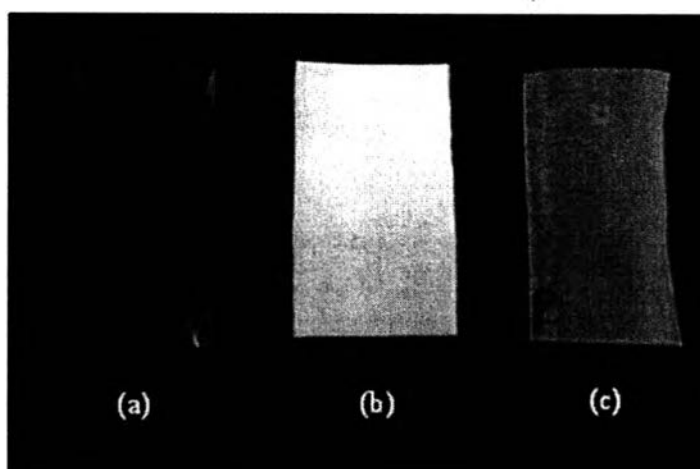
The electrical properties which were dielectric strength, dielectric constant, dielectric loss, piezoelectric coefficient and hysteresis loop were measured. In addition, physical, mechanical and thermal properties of the dense and voided films were also tested.

### 5.3 Results and Discussion

#### 5.4.1 Films Fabrications

Dense PVC film was prepared by solution casting while voided films were prepared by phase separation technique. Dense and voided PVC films of 332-496  $\mu\text{m}$  thickness were obtained.

Figure 5.1 shows the images of PVC films. The voided films were opaque while the dense film was clear due to cloud phenomenon which indicates the occurrence of phase separation of the polymer solution (Xu, J. *et al.*, 2002).



**Figure 5.1** Images of PVC films: (a) dense, (b) voided by DMAC, and (c) voided by THF.

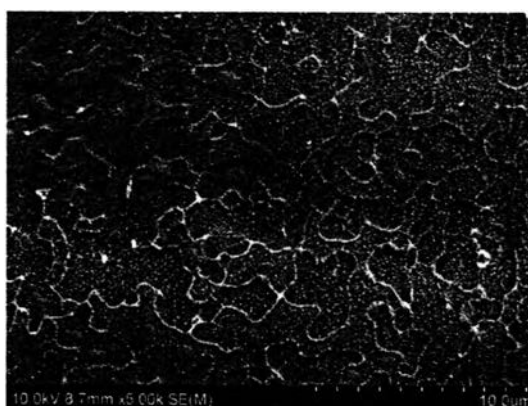
From all images, the colors of the voided films were observed the changes. However, the voided structure and cell sizes cannot be seen clearly from the images. So the Scanning Electron Microscope (SEM) was used to study the morphology.

## 5.4.2 Films Characterizations

### 5.4.2.1 *Physical Properties*

#### *A. Morphology*

Figure 5.2 show the SEM micrographs of cross-section of dense PVC films casted from 14 wt% PVC and THF. The micrograph confirms that there was no void inside the film.



**Figure 5.2** SEM micrographs of cross-section of dense PVC films casted from 14 wt% PVC.

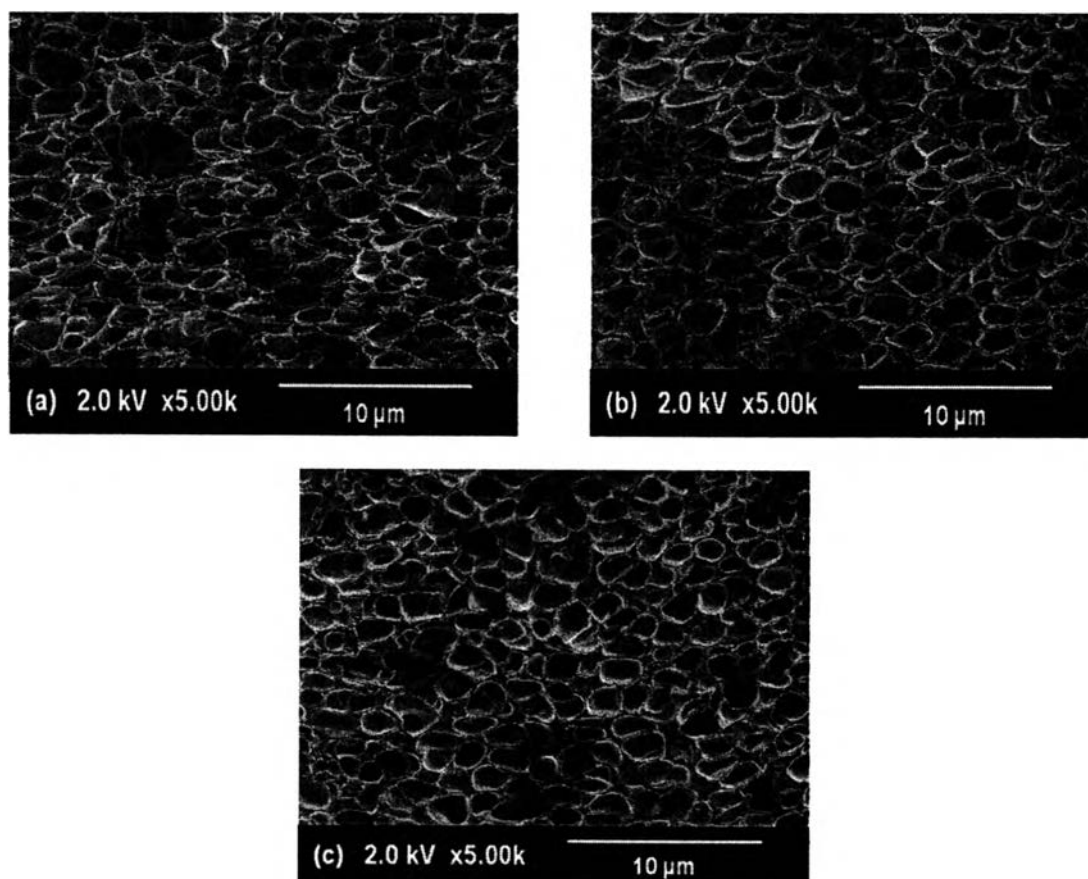
For voided PVC films, the water precipitates the top surface of the cast film rapidly, forming the dense, selective skin. The skin slows entry of water into the underlying polymer solution, which precipitates much more slowly and forms a more porous structure (Baker, R.W., 2004).

For phase separation process, polymer concentration is one of the parameters affected on the structure, void size and porosity of PVC films as presented in Figures 5.3 and 5.4. At higher polymer concentration, the lower void

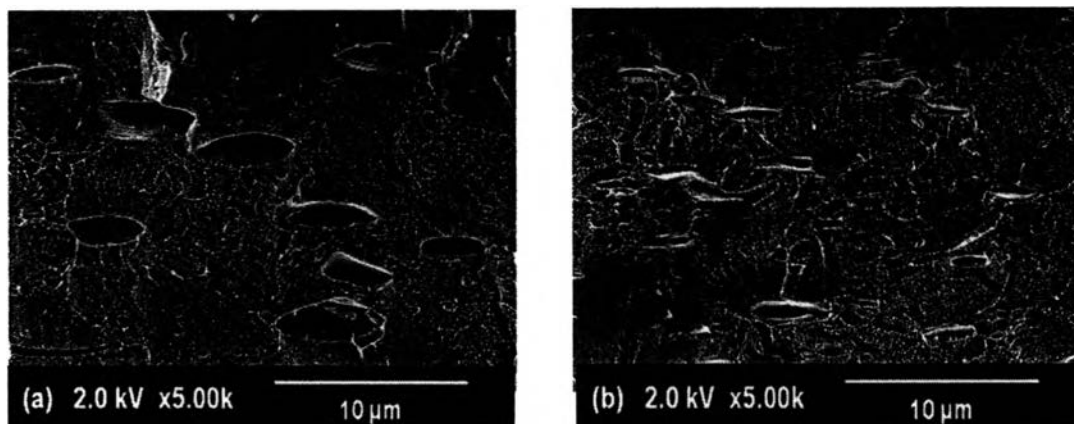
size was exhibited which provided the compact structure of PVC films. Figure 5.3 shows the cross-section of films fabricated from 8, 11, and 14 wt% PVC by DMAc solution. The cellular and rather regular structure of internal voids was obtained. Figure 5.4 shows the cross-section of film casted from 8 and 14 wt% PVC by THF solution. The irregular and lens-like structure of internal voids was obtained.

The structure of void from both solutions was different because DMAc is an aprotic solvent and casting solutions based on it precipitate rapidly when immerse in water to give porous structure while THF makes the casting solutions precipitate slowly and give relatively non-porous structure (Baker, R.W., 2004).

At 8 wt% PVC, some open-cell voids were observed because of too low polymer concentration. And also, lower than 8 wt% PVC, the solution could not been casted on the substrate. At higher polymer concentration than 14 wt% PVC, the interaction between macromolecule starts to interfere and become a gel-like.

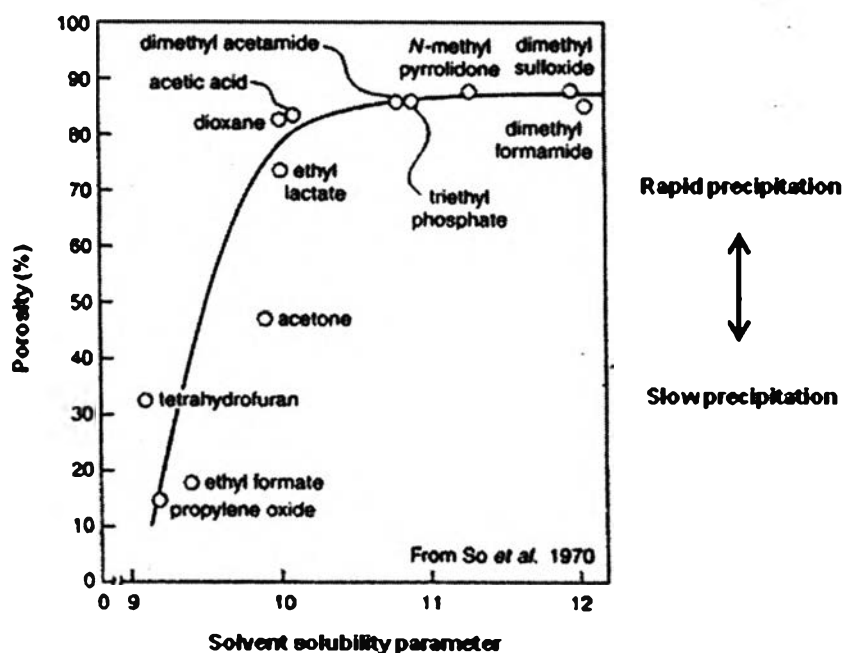


**Figure 5.3** SEM micrographs of cross-section of voided PVC films casted from DMAc: (a) 8 wt % PVC, (b) 11 wt % PVC, and (c) 14 wt % PVC.



**Figure 5.4** SEM micrographs of cross-section of voided PVC films casted from THF: (a) 8 wt % PVC, (b) 11 wt % PVC, and (c) 14 wt % PVC.

Figure 5.5 illustrates the correlation between solvent solubility parameter and porosity. DMAc has higher solubility parameter than THF and make rapid precipitation and high porosity of the solution.



**Figure 5.5** The correlation between solvent solubility parameter and porosity.

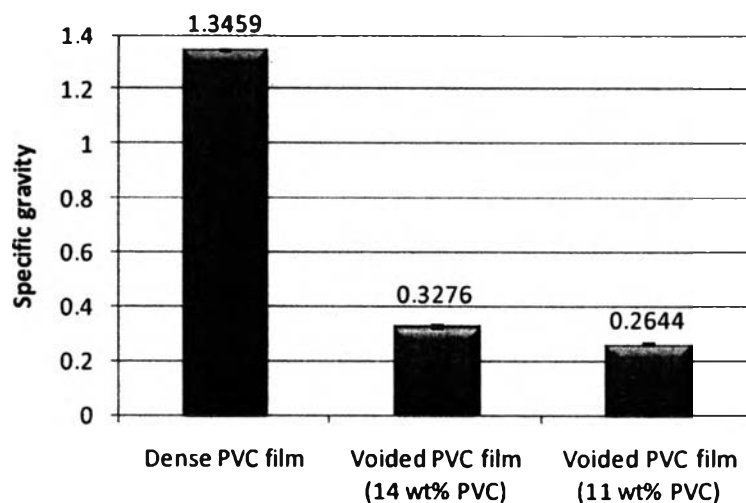
Therefore, voided PVC films of 11 wt% PVC, and 14 wt% PVC by DMAc were chosen for further study.

### B. Density and Porosity

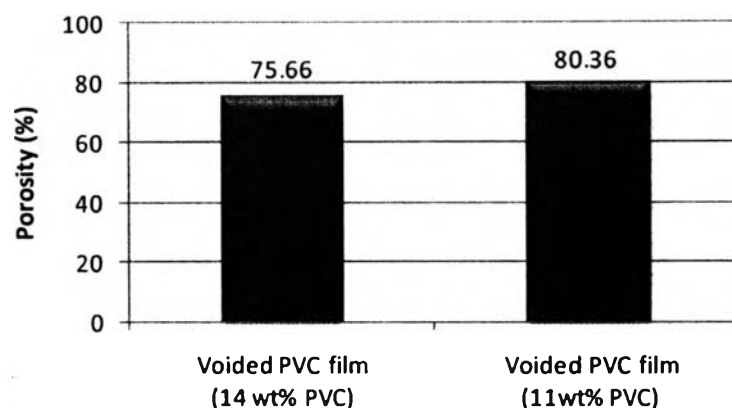
The densities and porosities of dense and voided PVC films are shown in Table 5.1. For voided films, increasing polymer concentration increased the density. The densities of voided films abruptly decreased from dense film due to the creation of voids inside the film. However, the densities and porosities of films fabricated from 11, and 14 wt % PVC were not significantly different from each other.

**Table 5.1** Average specific gravities and porosities of dense and voided PVC films at various polymer concentrations

| Sample                      | Average specific gravity | Porosity (%) |
|-----------------------------|--------------------------|--------------|
| Dense film                  | 1.3459                   | 0            |
| Voided PVC film, 14 wt% PVC | 0.3276                   | 75.66        |
| Voided PVC film, 11 wt% PVC | 0.2644                   | 80.36        |



**Figure 5.6** Average specific gravities of dense and voided PVC films at various polymer concentrations.



**Figure 5.7** Porosities of voided PVC films at various polymer concentrations.

### C. Void Size

The internal voids from phase separation technique gave smaller void size compared to compression molding with blowing agent. The effect of polymer concentration on void size was shown in Table 5.2. It was found that average void size increase with decreased polymer concentration.

**Table 5.2** Average void diameters of voided PVC films at various blowing agent concentrations

| Sample                      | Average void diameter ( $\mu\text{m}$ ) |
|-----------------------------|---|
| Voided PVC film, 14 wt% PVC | 1.58+0.38                               |
| Voided PVC film, 11 wt% PVC | 1.77+0.47                               |

### 5.4.2.2 Thermal Properties

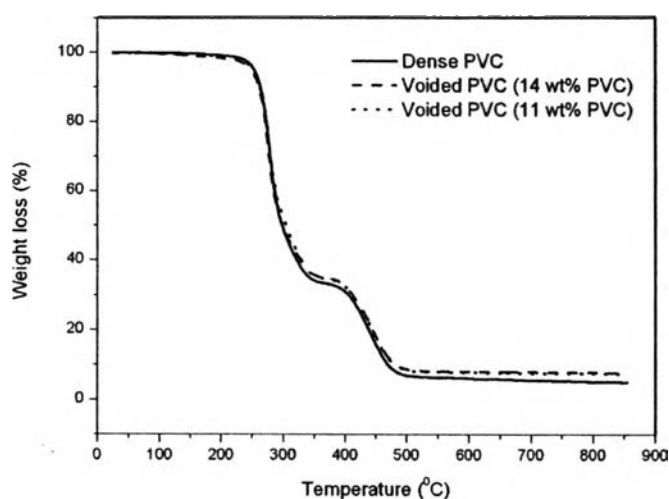
#### A. Thermogravimetric Analyzer (TGA)

TGA thermogram of dense and voided PVC films was shown in Figure 5.8. Thermal decomposition of PVC was a two-stage process. The first stage in inert atmosphere consisted of the progressive dehydrochlorination of the polymer. In the second stage, loss of HCl produced a conjugated polyene structure as a residue, which can undergo further pyrolysis to yield a series of hydrocarbon products



(Wang, Y. *et al.*, 2009). Similar to dense film, voided PVC films reveal two-stage degradation which confirm the complete removal of solvent or distilled water from the voided films.

The first stage decomposition of dense and voided PVC films was in the range of 259.0 °C to 260.1°C and the second stage was 405.7 °C to 407.0°C.

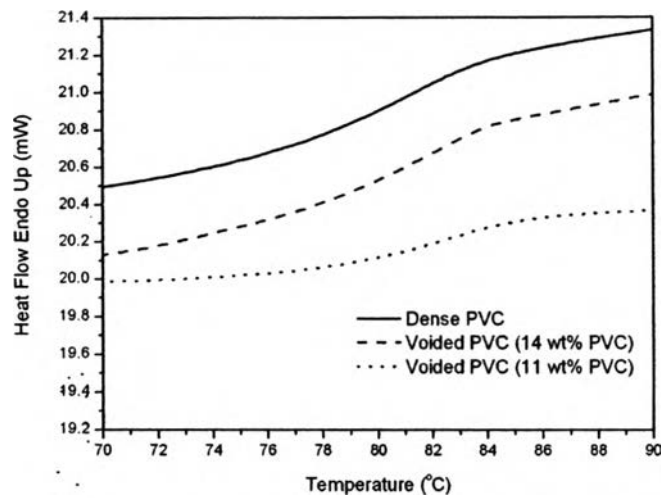


**Figure 5.8** TGA thermograms of dense and voided PVC films at various polymer concentrations.

It can be suggested that the decomposition temperatures of voided films were not depend on the amount of inside air and porosity of the film.

#### *B. Differential Scanning Calorimeter (DSC)*

The DSC graphs of dense and voided PVC films are shown in Figure 5.9. They showed that the onset glass transition temperatures ( $T_g$ ) of voided PVC films were not different from dense film in range 80.9 °C to 81.9 °C.



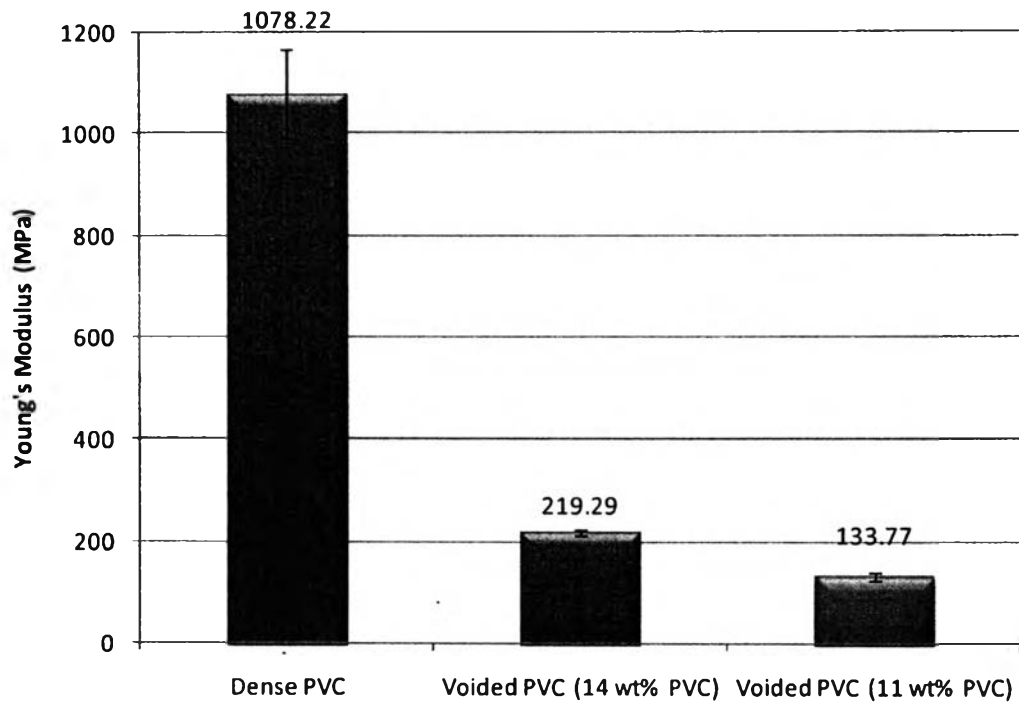
**Figure 5.9** DSC graphs of glass transition temperatures of dense and voided PVC films at different polymer concentrations.

From all DSC graphs, they were obviously found that thermal properties of voided films were not different from dense films because there was no interaction or chemical bonding between voids and polymer matrix.

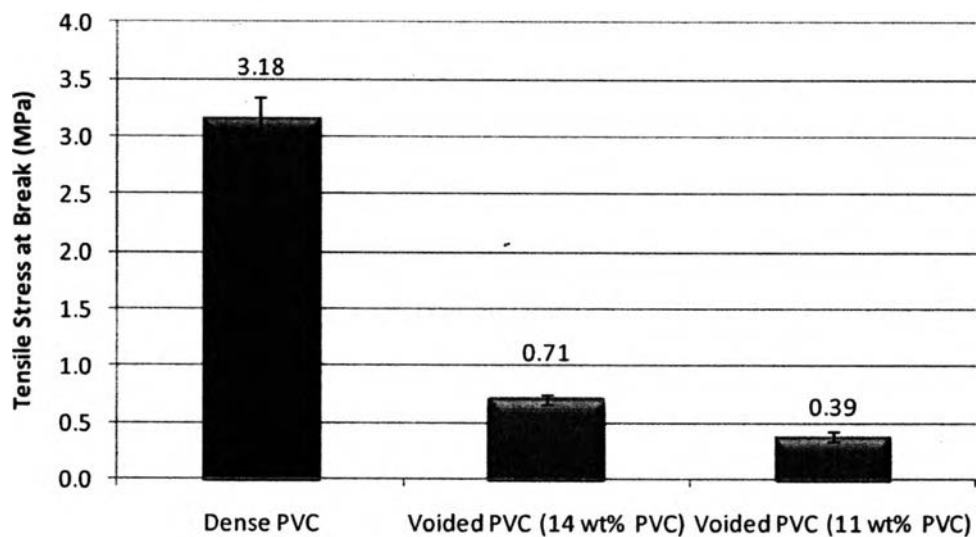
#### 5.4.2.3 Mechanical Properties

##### A. Tensile Testing

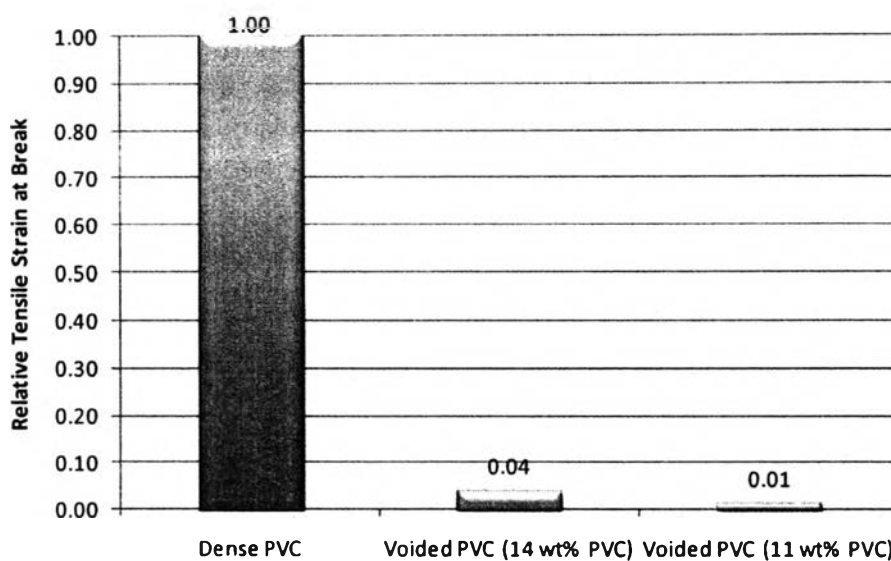
Figures 5.11 and 5.12 show the decreasing in the stress at break and strain at break values in voided PVC films compared to dense film. From Figure 5.10, it was found that the creation of voids also decrease the tensile modulus of the films. The higher the porosity, the lower the tensile properties were obtained.



**Figure 5.10** Young's modulus of dense and voided PVC films at various polymer concentrations.



**Figure 5.11** Tensile stress at break of dense and voided PVC films at various polymer concentrations.



**Figure 5.12** Relative tensile strain at break of dense and voided PP films at various blowing agent concentrations.

#### 5.4.2.4 Electrical Properties

##### A. Dielectric strength

Dielectric strength of voided PVC films abruptly decreased from dense film because high amount of voids inside the films. However, the dielectric strengths of voided films prepared from different polymer concentrations were not significantly different because the porosities were not different.

**Table 5.3** Average dielectric strengths of dense and voided PVC films at various blowing agent concentrations

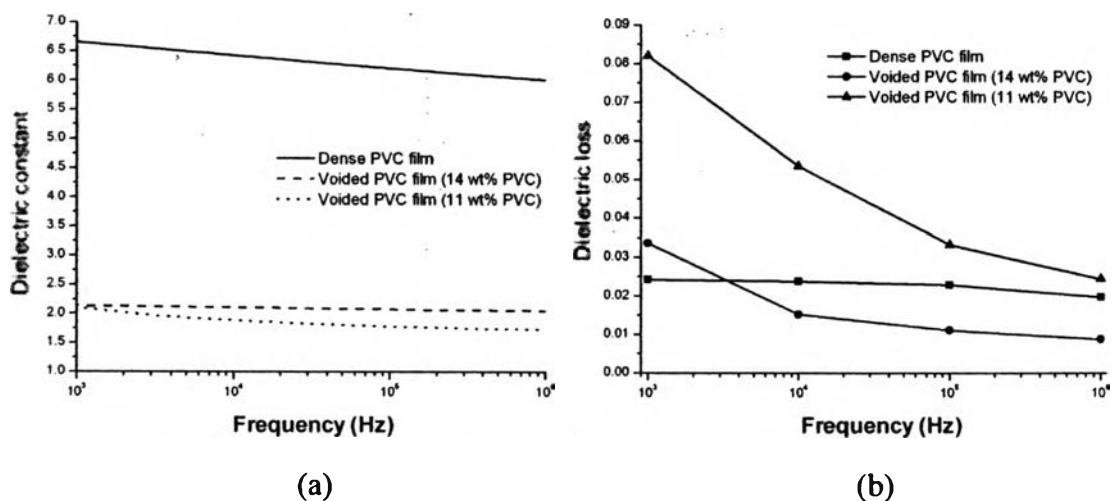
| Sample                      | Average dielectric strength (MV/m) |
|-----------------------------|------------------------------------|
| Dense film                  | $17.99 \pm 0.29$                   |
| Voided PVC film, 14 wt% PVC | $4.74 \pm 0.12$                    |
| Voided PVC film, 11 wt% PVC | $4.34 \pm 0.12$                    |

The breakdown occurred at the border of all dense films but inside of all voided films. The external discharges and surface tracking caused the breakdown in the dense films while the internal discharges and electrical treeing are the mechanism of breakdown in the voided films (Blythe, T., and Bloor, D, 2005).

### B. Dielectric constant and dielectric loss

It was observed from Figure 5.13(a) that as the frequencies increased, the dielectric constant decreased. Because the charge carriers migrated through the dielectric and get trapped against the defect site. They induced an opposite charge in its vicinity, as result of which, motion of charge carriers was slow down and the value of dielectric constant decreased. According to Dissado and Hill theory at high frequency, a single cluster dipole moment relaxation takes place. This reduces the dielectric constant at higher frequency (Shah, S. *et al.*, 2008).

The dielectric loss versus frequency of dense and voided PVC films was shown in Figure 5.13(b). It was observed the dielectric loss of voided films significantly decreased with the increased frequency. However, the dielectric loss of dense film showed a slight frequency dependency.



**Figure 5.13** (a) Dielectric constant and (b) dielectric loss as a function of frequency at room temperature of dense and voided PVC films.

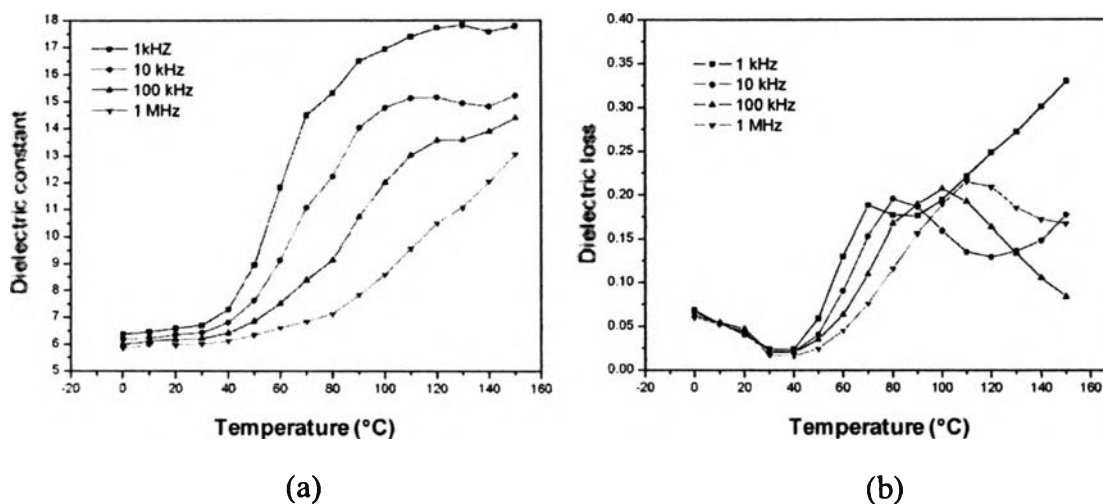
PVC is a polymer that contains a dipolar structure. At very low temperatures, dipolar structures do not have sufficient mobility. The dipolar structure

of PVC is in the form of a pendant group which is attached to the backbone via a flexible bond, the sufficient energy will eventually be present on heating to reach a point at which the pendant group will be able to respond to the electric field. The temperature at which this occurs is usually well below the glass transition temperature. After 40 °C, the dielectric constant values abruptly increased as shown in Figure 5.14(a) for dense film and 5.15(a) for voided films. As the temperature is further increased, the mobility of pendant continues to increase and it would be expected that the dielectric constant would increase with it (Daniels C.A., 1989).

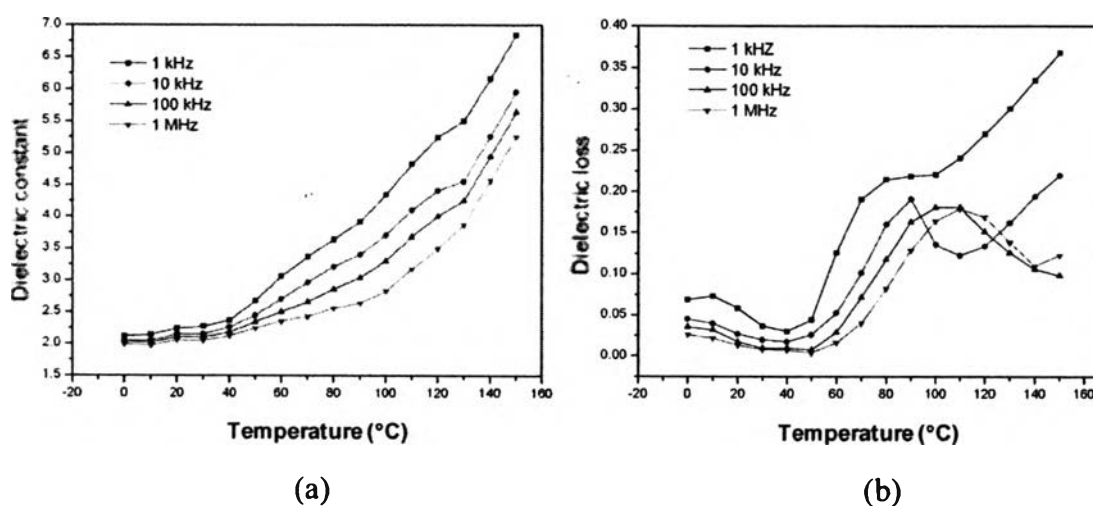
The temperature dependence of the dielectric constant of PVC is determined by the ability of the permanent dipole in the structure to align in the direction of an applied electric field. As the temperature increased, the permanent dipoles become to align more easily with an applied electric field as the molecular mobility increase (Bicerano J. 2002).

The increase of loss factor with temperature, as suggested by Jonscher, is a characteristic of a  $\beta$ -relaxation process. The relaxation temperature depends on intra- and intermolecular interactions. The greater the intermolecular interaction, the less mobile are the molecules; and the higher is the relaxation temperature at which the loss maximum occurs.

In the dielectric loss curves, two relaxation processes were clearly observed as shown in Figure 5.14(b) for dense film and 5.15(b) for voided film. At 0 °C to 25 °C, the weak and broad  $\beta$  process was detected. At 75 °C to 110 °C, the strong and sharp  $\alpha$ -relaxation which was related to the glass-rubber transition of the material was found. Finally, at the temperature above glass transition temperature the material became electrical conductive, resulting in the sharp dielectric loss. The temperature dependence for the  $\beta$  process indicated that the polarization mechanism to the local motion in the polymeric chain. This transition has been attribute to a type of motion of the main of polymeric backbone which a few segment are involved cooperatively. The relaxation strength of the  $\alpha$ -relaxation is much larger than the strength of the  $\beta$ -transition because the rotational mobility of the C-Cl dipoles is only completely liberated at the  $\alpha$ -transition (Salamone J. C., 1996).

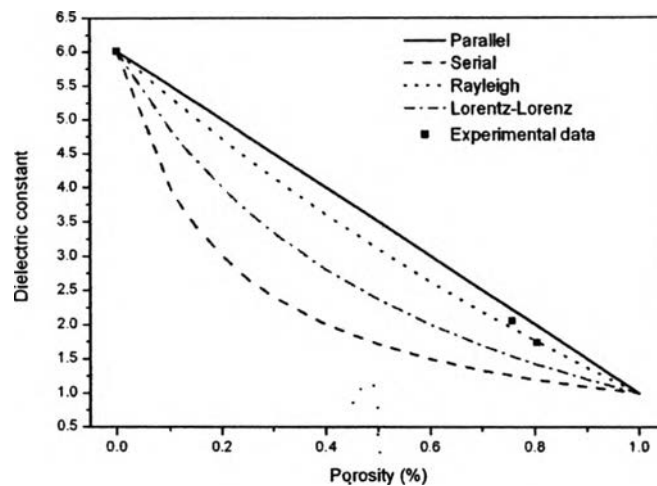


**Figure 5.14** (a) Dielectric constant and (b) dielectric loss as a function of temperatures at different frequencies of dense PVC film.



**Figure 5.15** (a) Dielectric constant and (b) dielectric loss as a function of temperatures at different frequencies of voided PVC film (14 wt% PVC).

As shown in Figure 5.16, the experimental data close to the Rayleigh model. It was in agreement with the SEM micrographs and the Serial's assumptions. Therefore, we ascribe this correlation mainly to the cubic array of spherical voids.



**Figure 5.16** Correlation between the dielectric constant at 1 MHz and porosity of voided PVC films at room temperature as calculated as according to different model.

### C. Piezoelectric coefficient

PVC films can be made to possess piezoelectric properties by aligning the dipoles in an electric field at an elevated temperature above glass transition and subsequent cooling (Bharti, V., *et al.*, 1995). Because PVC has a dielectric relaxation associated with dipole motions at elevated temperatures. When a field was applied at an elevated temperature, the dipole could undergo thermal motions and then cool to room temperature without removing the field. As a result, the remanent polarization was obtained due to frozen-in dipole orientation (Furakawa, T. 1989).

Poling was performed in oil bath at 85°C and applied voltage of 15 kV/mm. Then, the samples were cooled to room temperature without removing the field. The applied voltage higher than 15 kV/mm caused the breakdown in voided samples. Table 5.4 shows the comparison data of  $d_{33}$  between dense and voided films before and after poling. The poling caused the piezoelectric properties in PVC because of dipole orientation under the poling condition. After poling, the piezoelectric coefficient of dense film was equal to that of voided film. It could be summarized that the internal voids did not effect to the piezoelectric coefficient in polar polymers. The results correspond with the information from Mark, J.E. (2007) that the piezoelectric properties in polar polymers such as PVDF and PVC arise from the orienting dipole moment by poling.



**Table 5.4** Piezoelectric coefficients of dense and voided PVC films

| Sample                      | Piezoelectric Coefficient (pC/N) |              |
|-----------------------------|----------------------------------|--------------|
|                             | Before Poling                    | After Poling |
| Dense film                  | 0                                | 3            |
| Voided PVC film, 14 wt% PVC | 0                                | 3            |
| Voided PVC film, 11 wt% PVC | 0                                | 3            |

## 5.5 Conclusions

The microvoid composites of PVC/air bubbles can be prepared by phase separation method. The morphology and porosity of voided films can be varied by different solvents and polymer concentrations. Thermal properties of voided films have not been changed from dense film present that there was no interaction or chemical bonding between voids and polymer matrix. The introduction of voids into the films considerably reduced dielectric constant of mixing phase according to the dielectric mixing rule. The voided films can be described as 0–3 void–polymer composites. The apparent dielectric constants could fit with Rayleigh model indicated a cubic array of spherical voids. The presence of internal voids did not effect to the piezoelectric properties of PVC film.

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