CHAPTER VI
EFFECT OF INTERNAL VOID SHAPES ON DIELECTRIC BEHAVOIRS OF VOIDED HDPE, VOIDED, PP, AND VOIDED PVC FILMS

6.1 Abstract

In this research, the investigation of the effect of internal void shapes which were spherical and ellipsoidal induced in voided films on dipole was focused. The voided HDPE and PP films were fabricated by blowing agent compression molding (azodicarbonamide or ACA) while the voided PVC films were produced by phase separation technique. Then, the voided films were uniaxilly stretched for changing from spherical to ellipsoidal shape. The dielectric, piezoelectric and ferroelectric properties of both shapes were investigated. The results showed higher dielectric constants from ellipsoidal voided films compared to those of spherical shape. Also the stretching can enhance piezoelectric coefficients and ferroelectric properties in voided films.

6.2 Introduction

Ferroelectrets are a new class of piezoelectric polymers. They consist of non-polar space–charge electrets with cellular foam structures which can exhibit an internal polarization due to trapped charges. In ferroelectrets charge separation exists, effectively creating upper and lower void surfaces that are oppositely charged. This is the origin of the breakdown of symmetry, which is required for piezoelectric characteristics to emerge. Each void can be considered as a macroscopic dipole (Wilson, S.A., *et al.*, 2007). Moreover, gas breakdown and charge trapping inside the voids also cause ferroelectric properties in non-polar film with internal voids (Bauer, S., *et al.*, 2002). Therefore, the study of internal void on electrical properties in non-polar polymers is of interest of many researchers.

The voids heights which represent the size of macroscopic dipole were studied and adjusted because the void structure influence on the piezoelectric properties. For PP ferroelectrets the optimized void length and height ratio is approximately 4–5, which corresponds to lens-like voids (Wilson, S.A., *et al.*, 2007). Some researchers known from experiments on voided PP films and from numerical simulations that lens-like voids with a/b ratios (a: void width, b: void height) in the range between about 2 and 6 are required for high piezoelectric activity. Nearly spherical voids with an a/b ratio of less than 1.5 are usually too stiff to allow deformation and therefore do not show significant piezoelectricity (Wegener, M., *et al.*, 2005).

The objectives of this work are to study the effect of void shapes on dielectric, piezoelectric and ferroelectric properties. The internal voids were created in HDPE and PP films by compression molding with azodicarbonamide or ACA (blowing agent). The voided PVC films were produced by phase separation technique. The voided shape were changed from spherical and ellipsoidal by stretching. Subsequently, internal void shapes were observed by using Optical Microscope (OM) and Scanning Electroc Microscope (SEM). The dielectric constants and losses were measued as a function of frequency in the range of 1 kHz to 1 MHz at room temperature. The piezoelectric coefficient and ferroelectric properties of both void shapes were investigated.

6.3 Experimental

6.3.1 Preparation of Voided Films by Blowing Agent Compression Molding

The voided HDPE and PP films were produced by a compression molding method. The polymer–blowing agent compounds were blended with the Brabender mixer. The dried ACA was ground into powder and screened through a sieve (mesh #325) before using. ACA has decomposition temperature range 200-210 °C and gas volume is 215-225 ml/g.

6.3.1.1 Voided HDPE films

ACA and HDPE pellets were homogeneously blended with the Brabender mixer which set the rotor speed at 45 rpm and temperature at 145 °C.

The temperature of molten compounds was 138.5-141 °C. Concentration of 0.5% was used on the basis of the total weight of HDPE. Compounds were pre-heated and compressed at the same condition as dense HDPE film.

6.3.1.2 Voided PP films

ACA and PP pellets were homogeneously blended with the Brabender mixer which set the rotor speed at 45 rpm and temperature at 175 °C. The temperature of molten compounds was 167.2-170.5 °C. Concentration of 1 % was used on the basis of the total weight of PP. Compounds were pre-heated and compressed at the same condition as dense PP film.

6.3.2 Preparation of Voided Films by Phase Separation

Solvent casting of PVC films were obtained by casting a DMAc solution of 14 wt% PVC on the Teflon mold. The films were pre-evaporated for 5 minutes in air (25 °C $\pm$ 2 °C, 50 % RH $\pm$ 5 % RH) and then immersed in 25 °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.

6.3.3 Preparation of Stretched Voided Films

A uniaxial stretching by the stretch ratio 1:1 was performed by the Universal Testing Machine (LLOYD LRX) and heater chamber in Figure 6.1. The temperatures during stretching were controlled at 120 °C for HDPE, 135 °C for PP, and 75 °C for PVC.

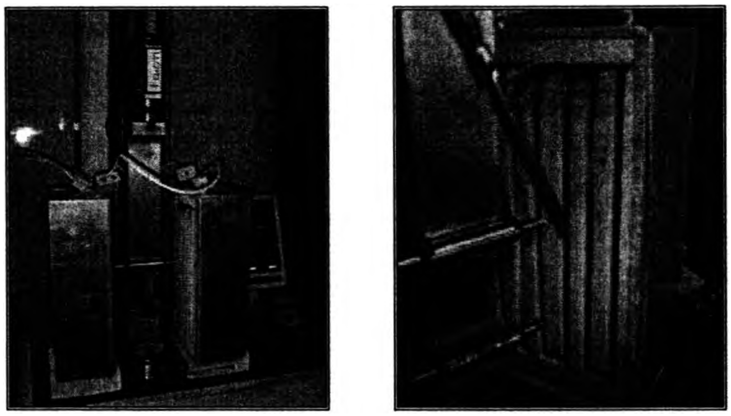


Figure 6.1 The heater band equipment for stretching voided films.

The ellipsoidal voided films of HDPE of 0.5 % ACA, PP of 1 % ACA and PVC (14 wt% PVC) were obtained.

6.4 Results and Discussion

6.4.1 Films Characterizations

6.4.1.1 Physical Properties

A. Morphology

The OM micrographs in Figures 6.2 and 6.3, and also the SEM image in Figure 6.4 confirm that the ellipsoidal structures were generated in stretched voided HDPE, PP and PVC, respectively.

The stability of ellipsoidal voids in stretched films was monitored by Optical Microscope (OM) after the stretched films were aged 1 week, 2 weeks, 1 month, 2 months, and 3 months. OM micrographs of stretched voided films at all periods confirmed that the ellipsoidal shape was stable and did not change with time.

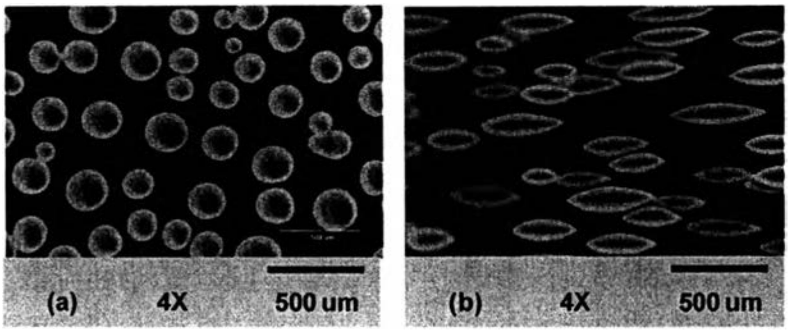


Figure 6.2 OM micrographs of (a) unstretched, and (b) stretched of voided HDPE films.

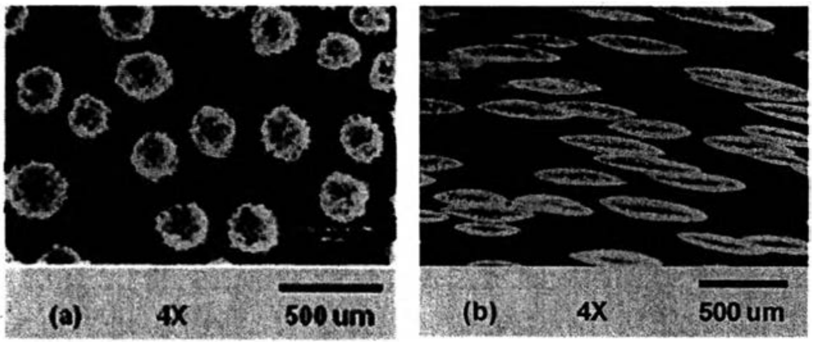


Figure 6.3 OM micrographs of (a) unstretched, and (b) stretched of voided PP films.

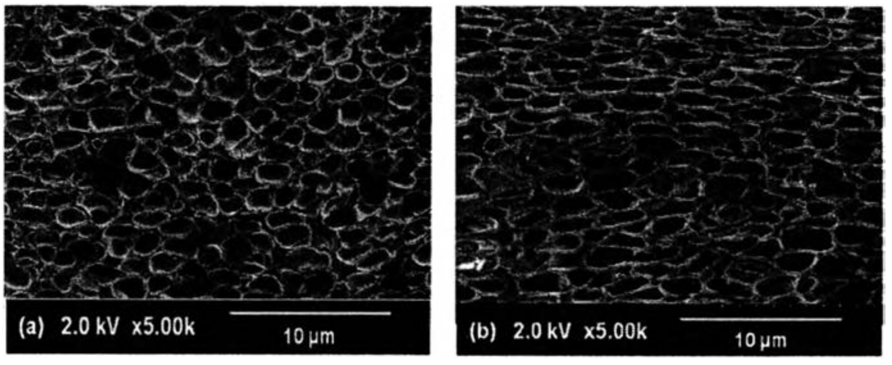
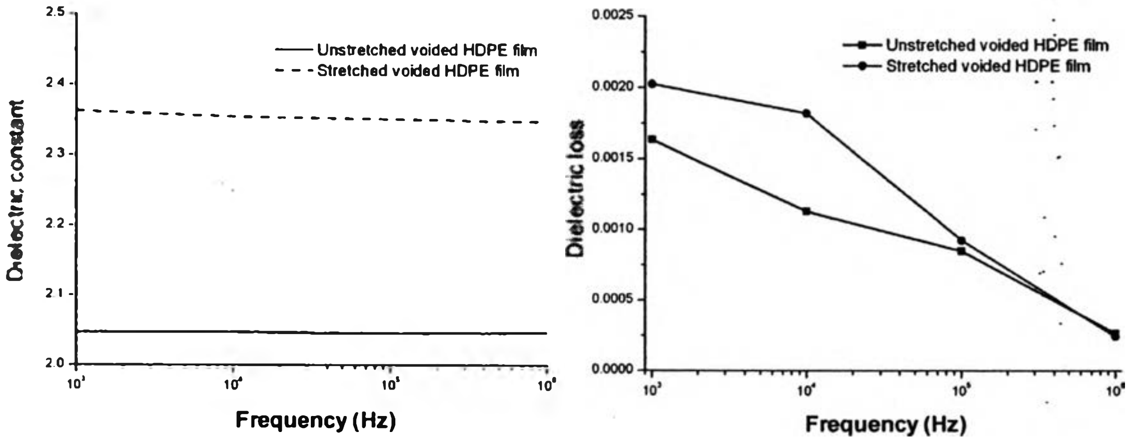


Figure 6.4 OM micrographs of (a) unstretched, and (b) stretched of voided PVC films.

6.4.1.2 Electrical Properties

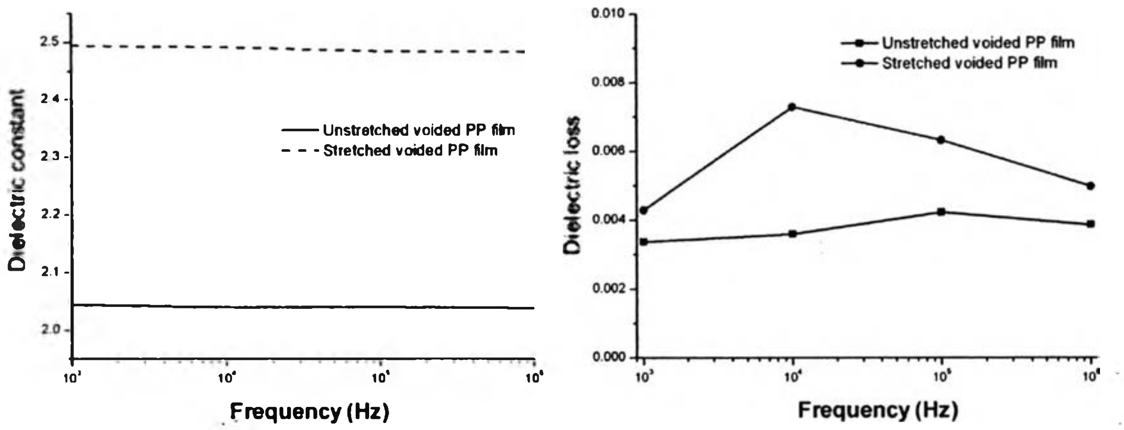
A. Dielectric constant and dielectric loss

Figures 6.5-6.7 show the comparison of dielectric behaviors between ellipsoidal and spherical voids in HDPE, PP, and PVC, respectively. The dielectric constants of ellipsoidal voided film were higher than those of spherical shape in all materials. This was related to charge displacement generated in the ellipsoidal shape and also, higher charge density than spherical voids (Suwansumpan, D., *et al.*, 2008). The higher dielectric losses in ellipsoidal voids were also observed but they were not significantly different from spherical shape.



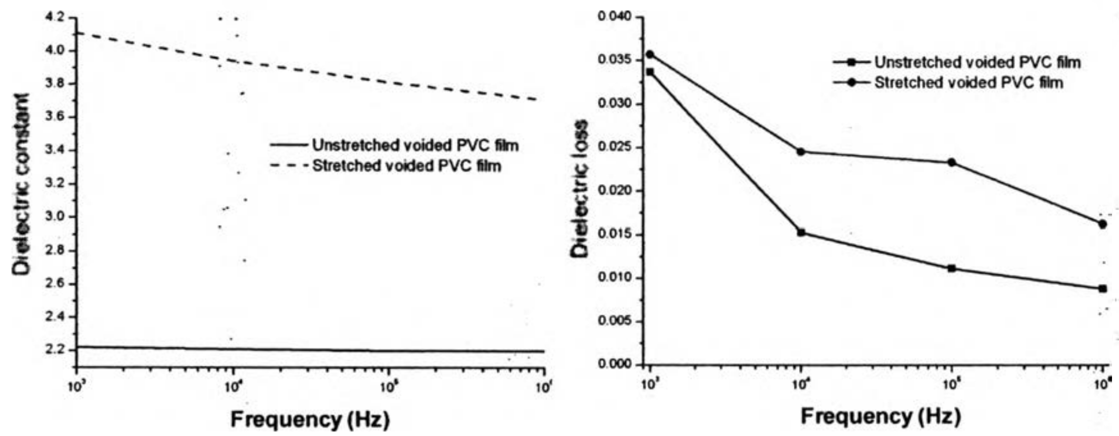
(a) (b)

Figure 6.5 (a) Dielectric constant and (b) dielectric loss as a function of frequency at room temperature of unstretched and stretched voided HDPE films.



(a) (b)

Figure 6.6 (a) Dielectric constant and (b) dielectric loss as a function of frequency at room temperature of unstretched and stretched voided PP films.



(a) (b)

Figure 6.7 (a) Dielectric constant and (b) dielectric loss as a function of frequency at room temperature of unstretched and stretched voided PVC films.

B. Piezoelectric coefficient

Piezoelectric coefficients in stretched HDPE and PP films are shown in Table 6.1. The results show the increasing values from unstretched films due to lower Young's modulus lead to higher d_{33}. The comparison data between unstretched and stretched voided HDPE and PP films are shown in Table 6.2.

Table 6.1 Piezoelectric coefficients of unstretched and stretched of voided HDPE, PP, and PVC films

Sample	Piezoelectric Coefficient (pC/N)	
	Unstretched	Stretched
Voided HDPE film	2	4
Voided PP film	2	4
Voided PVC film	3	7

Table 6.2 Young's modulus of unstretched and stretched of voided HDPE, and PP films

Sample	Young's modulus (MPa)	
	Unstretched	Stretched
Voided HDPE film	310.81	155.23
Voided PP film	314.29	157.29

Higher value of d_{33} in stretched PVC film was also observed. To confirm an effect of void shape on piezoelectric properties, the dense PVC film was stretched and measured the value of d_{33}. The result showed that 7 pC/N was also obtained. So the void shape was not affected on piezoelectric coefficient in PVC. Higher values of d_{33} in stretched PVC film caused by more dipolar orientation takes place. In all probability this is possible due to relatively easy alignment of dipoles when the polymer was stretched. Many chain segments inside the amorphous regions get oriented parallel to the stretching direction and their C-Cl dipoles tend to become parallel to the field applied during poling. Therefore the chain segments will remain frozen in the positions assumed during the production.

PVC contains a low level of crystallinity. When PVC is oriented, anomalous X-ray patterns are obtained, which indicative of both oriented crystallinity, as well as a mesomorphous structure. The determination of the crystal structure of PVC used X-ray diffraction to investigate the behavior of both crystallites and free chains. To obtain information about the crystallite orientation, the X-ray peak at $2\theta = 16.5°$ corresponds to the (200) plane, that at $2\theta = 18.5°$ corresponds to the (110) plane, and that $2\theta = 24°$ corresponds to the (201), (210) and (111) planes were investigated (Kim, H.C., and Gilbert M., 2004).

Figures 6.8 and 6.9 show the XRD diffractograms between unstretched, and stretched voided PVC films. The intensities at these 3 angles which represent to crystallite orientation show higher value from stretched films.

The piezoelectric coefficient of voided PVC film was also found to increase with stretching. Therefore the crystallinity seems to have an important role in determining the piezoelectric properties of the PVC films (Bharti, V., *et al.*, 1995).

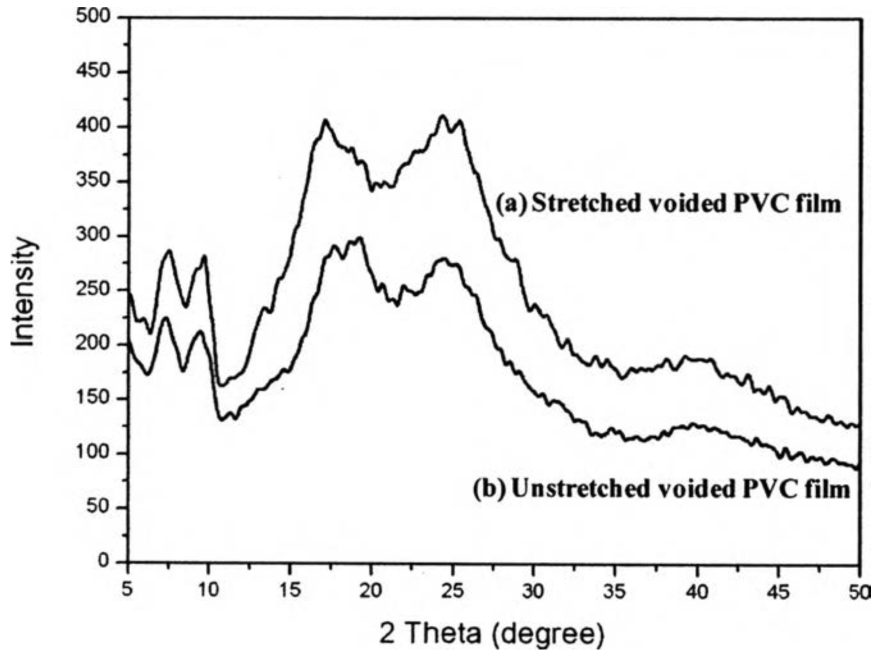


Figure 6.8 XRD diffractograms of voided PVC film: (a) stretched, and (b) unstretched.

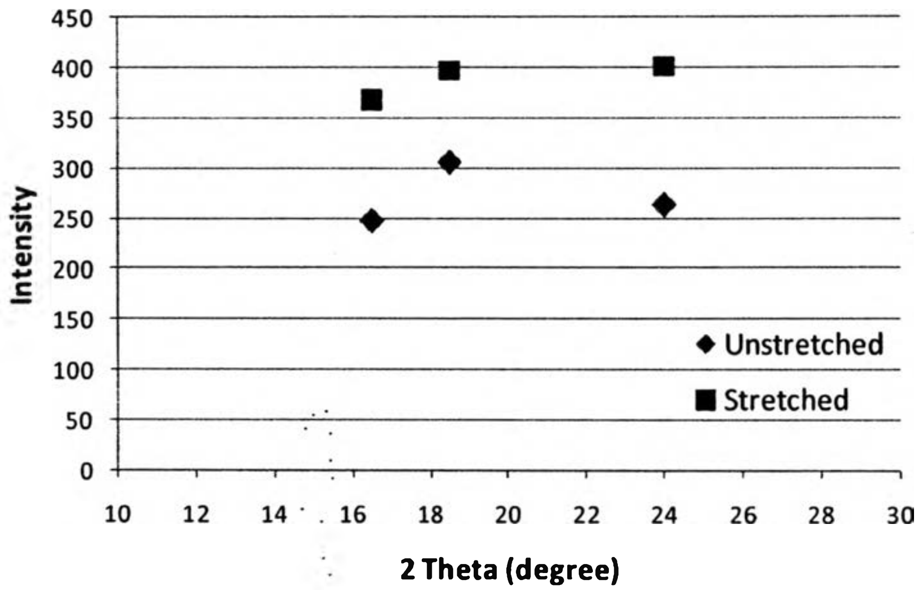


Figure 6.9 Comparative intensities in XRD diffractograms of unstretched, and stretched voided PVC films at $2\theta = 16.5°$, $2\theta = 18.5°$, and $2\theta = 24°$.

C. Ferroelectric properties

As shown in Figures 6.10-6.12, The hysteresis loops can be suggested that these materials have ferroelectric properties and can be classified as soft ferroelectric materials when compare with other polymers. The remanent polarization (P_r) and saturation polarization (P_s) of stretched voided films were higher than those of unstretched voided films which provided higher piezoelectricity (Suwansumpan, D., *et al.*, 2008). Higher P_s in stretched voided HDPE and PP films results from the increasing of the distance between positive and negative charges lead to higher polarization. For stretched voided PVC film, more dipolar orientation occurred during the stretching lead to the increasing of polarization.

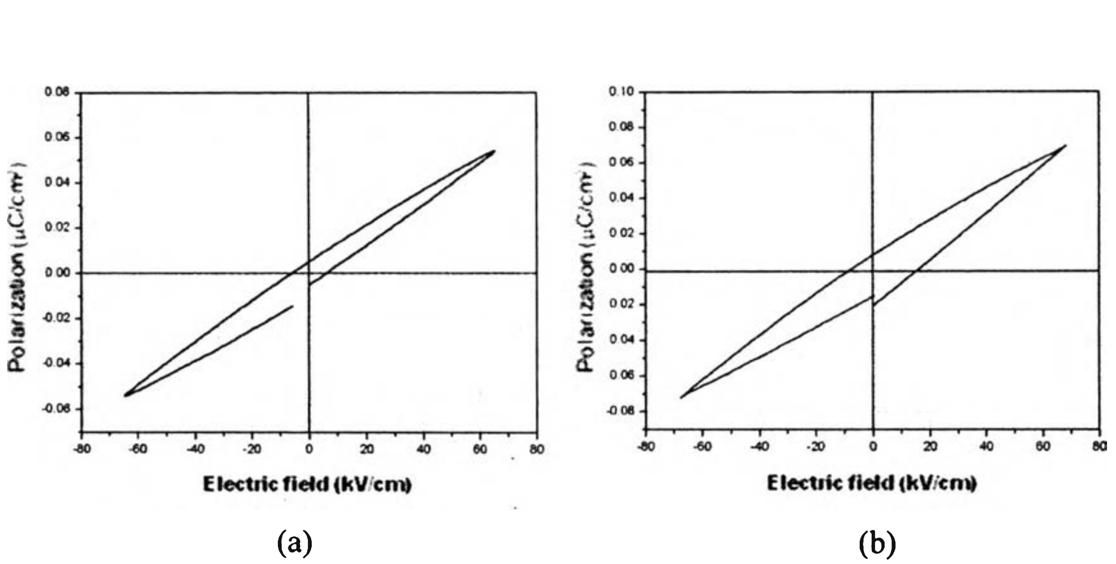


Figure 6.10 Comparative hysteresis loop of voided HDPE between: (a) unstretched, and (b) stretched.

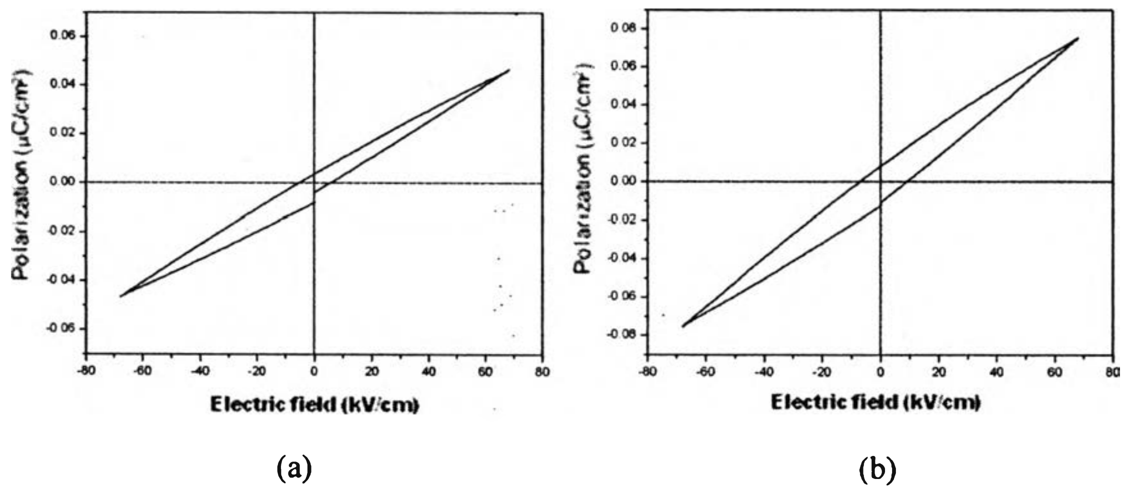
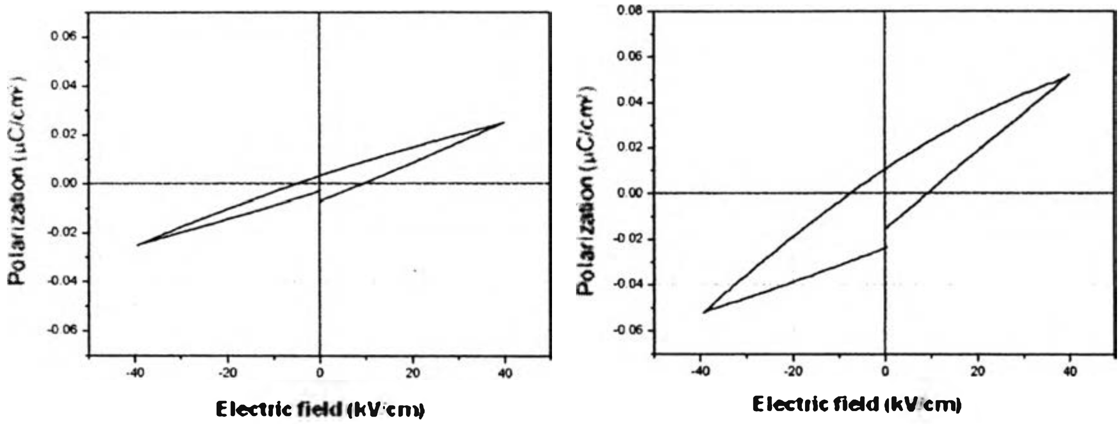


Figure 6.11 Comparative hysteresis loop of voided PP between: (a) unstretched, and (b) stretched.



(a) (b)

Figure 6.12 Comparative hysteresis loop of voided PVC between: (a) unstretched, and (b) stretched.

6.5 Conclusions

The effects of internal voided shapes on dipole have been studied in this part. OM and SEM images confirmed the ellipsoidal structure in stretched films. It was found that the ellipsoidal void shape can enhance dielectric properties than spherical shape because the ellipsoidal voids created the charge displacement in voids and their lower air gap increasing dipole density in voided films. The increasing of piezoelectric coefficients and ferroelectric properties was also observed in stretched voids films. The higher remanant polarization (P_r) and saturation polarization (P_s) of stretched voided film confirmed the improvement of piezoelectricities.

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6.7 References

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