



CHAPTER II LITERATURE REVIEW

2.1 Electrical Behavior

2.1.1 Dipole Moment and Polarization

Dipole moment (p) is a measure of electrostatic effect in a pair of separated opposite charge. If there are more than one pair of separated opposite charges, they will be polarization (P) that is,

$$P = np \quad (1)$$

2.1.2 Dielectric Constant, Dielectric Loss, and Piezoelectric Coefficient

Dielectric constant or relative permittivity (ϵ) shows the ability of material to store the electric potential energy under the influence of an alternative electric field (Sui, G. *et al.*, 2008). It is the ratio of the capacitance of a capacitor filled with the given material to the capacitance of an identical capacitor in a vacuum without the dielectric material. Low ϵ materials are known as insulators while high ϵ materials are used as capacitors. Dielectric constant relates to polarization as equation (2).

$$P = \epsilon_0 E(\epsilon - 1) \quad (2)$$

Dielectric loss or $\tan \delta$ of a polymer is one of the key electrical properties. When some of the energy of an applied electric field is lost due to the internal motions of the material, dissipation occurs. The lossy component of the response of a material to an electric field is expressed in terms of the imaginary component of the complex quantity ϵ^* as equation (3).

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (3)$$

where ϵ'' quantifies the energy lost due to the internal motions. The real component ϵ' of ϵ^* has the same significance as the ordinary dielectric constant ϵ , which is a measure of the polarization of the medium between two charges when this medium is subjected to an electric field. ϵ' quantifies the energy from the applied alternating electric field that is elastically stored in the material during each cycle, to be returned to the electric field at the end of the cycle. The dissipation factor $\tan \delta$ is defined as equation (4).

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad , \quad (4)$$

The dissipation factor $\tan \delta$ of a polymer is the function of frequency, temperature, and material properties (Yu, X. *et al.*, 2008). The loss tangent of polar polymers are generally much greater than nonpolar polymers (Das-Gupta, D. K., 1994).

Piezoelectric coefficient (d) is the ability to converse mechanical stress to electric charges which is direct piezoelectric effect. Conversely, it can convert an electric field to mechanical strain which is converse piezoelectric effect as Figure 2.1. Piezoelectric coefficient relates to dielectric constant as equation (5).

$$d = \epsilon \kappa E \quad (5)$$

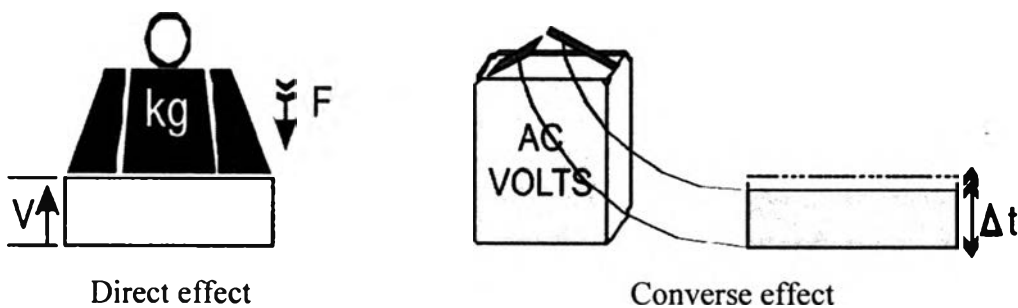


Figure 2.1 Direct and converse piezoelectric effects (Ueberschlag, P., 2001).

These are the direct and converse piezoelectric effects which can be expressed in tensor notation:

$$P_i = d_{ijk} T_{jk} \quad \text{Direct effect} \quad (6)$$

$$S_{ij} = d_{ijk} E_k \quad \text{Converse effect} \quad , \quad (7)$$

where P_i is the polarization generated along the i -axis (Kohpaiboon, K., and Manuspiya, H. 2007) under the action of stresses, T (Bauer, S., 2004) and d_{ijk} (C/N) is a third-rank tensor of piezoelectric coefficients (Damjanovic, D., 1998). For the converse effect, S_{ij} is the strain generated in a particular orientation of the crystal on the application of the electric field E_i , along the i -axis (Kohpaiboon, K., and Manuspiya, H. 2007). The units of the converse piezoelectric coefficients are m/V (Damjanovic, D., 1998).

The piezoelectric coefficients d for the direct and converse piezoelectric effects are thermodynamically identical. The sign of the polarization P_i and strain S_{ij} depends on the direction of the mechanical and electric fields, respectively. The piezoelectric coefficient d can be either positive or negative. It is common to call a piezoelectric coefficient measured in the direction of applied field the longitudinal coefficient and that measured in the direction perpendicular to the field the transverse coefficient. Other piezoelectric coefficients are known as shear coefficients (Damjanovic, D., 1998).

The d coefficients are obtained by measuring the electrical charge density (Coulomb/m²), which appears at the surface of the film when a mechanical stress of 1 Newton/m² is applied. The value is then given in C/N. These constants also correspond to the mechanical strain of the element (m/m) compared with the electrical field applied (V/m). They are then also given in m/V (Ueberschlag, P., 2001). The equation of d coefficients is expressed as:

$$d_{ij} \text{ (C/N)} = \frac{\text{electrical charge density}}{\text{applied stress}} = \frac{Q_i/A_i}{F_j/A_j}, \quad (8)$$

where A_x is area according to axis x , F is force, Q is charge and

$$d_{ij} \text{ (m/V)} = \frac{\text{strain}}{\text{applied electric field}} = \frac{\Delta L_j/L_j}{V_i/L_i}, \quad (9)$$

where L_x is length according to axis x , V is voltage (Ueberschlag, P., 2001).

The axes of the material are numbered 1 to 3. Number 1 corresponds to the machine direction, 2 to the perpendicular planar direction, and 3 to the thickness of the element which is shown in Figure 2.2. According to this, a 31 index will characterize an electrical value considered between the two sides of the film (according to axis number 3), associated with the mechanical stress applied along axis number 1 (Ueberschlag, P., 2001).

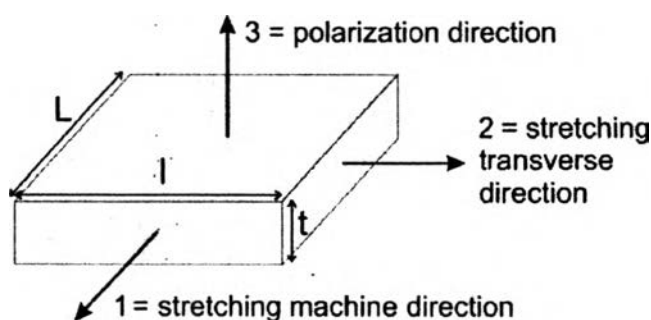


Figure 2.2 Axis definition of piezo elements (Ueberschlag, P., 2001).

2.2 Ferroelectrets

Ferroelectrets are a new class of polymers that consist of non-polar space-charge electrets with cellular foam structures. As most of voids are closed, cellular ferroelectrets may be described as 0–3 void–polymer composites in the connectivity notation (Mellinger, A. *et al.*, 2006). An electret is a material which can exhibit an internal polarization due to trapped charges in non-polar space-charge electrets. 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. An applied mechanical stress leads to the decrease of void size accompanied by the generation of an electrical signal. Therefore, piezoelectricity in ferroelectrets results from changes of dipole sizes (Wilson, S.A. *et al.*, 2007). Because the materials do not contain molecular dipoles, their behavior is sometimes called quasi-piezoelectric, quasi-pyroelectric or quasi-ferroelectric (Altafim, R.A.C. *et al.*, 2006).

2.2.1 Pyro- and Piezoelectricity

The pyroelectric vector of ferroelectrets consists of one element p_3 , oriented along the poling axis, since the macroscopic dipoles are perfectly oriented along the 3-axis. The piezoelectric tensor of cellular space-charge electrets is similar to that of ferroelectric polymers and consists of the shear coefficients d_{15} and d_{24} , the longitudinal piezoelectric coefficients d_{31} and d_{32} , and the transverse piezoelectric coefficient d_{33} . Due to the extremely large anisotropy of the investigated systems, d_{33} is the dominant piezoelectric coefficient (Bauer, S. *et al.*, 2002). Ferroelectrets display piezo- and pyroelectric properties that are significantly different in mechanism from traditional ferroelectric polymers (Bauer, S. *et al.*, 2003).

The piezoelectric coefficients of cellular polymers have the same sign as those of typical ferroelectric ceramics, like lead zirconate titanate (PZT) (Bauer, S. *et al.*, 2003). The different sign is observed when compared with ferroelectric polymers which are shown in Table 2.1.

Table 2.1 The sign of the piezoelectric coefficients, d (Bauer, S. *et al.*, 2003)

Material	d_{31}	d_{32}	d_{33}
Ferroelectric polymers	positive	positive	negative
Cellular Polymers and Ferroelectric ceramics	negative	negative	positive

In applications, a high d_{33} coefficient is essential since the performance of piezoelectric devices generally increases with its value (Zhang, X. *et al.*, 2007). Some properties including d_{33} coefficients of some polymers are shown in Table 2.2.

Table 2.2 Electrical properties in polymer materials (Lushcheikin, G.A., 2006)

Polymer	Permittivity, ϵ	Elastic modulus (GPa)	σ_{eff} or P_0 (mC/m ²)	d_{33} (pC/N)
Nonpolar polymers [poly(tetrafluoroethylene), poly(propylene), poly(ethylene), rubbers]	2.0–2.5	1–3	$\sigma_{\text{eff}} \leq 6$	0.1–1.0
Polar polymers [polycarbonate resin, poly(vinyl chloride)]	3–10	2.3–3.5	$P_0 \leq 63$	0.1–3.0
Ferroelectric polymers [poly(vinylidene fluoride), vinylidene fluoride–trifluoroethylene copolymer C]	≤ 12	1.5–2.2	$P_0 \leq 220$	20–40
0–3 and 1–3 composites	10–200	3–50	-	≤ 400
Porous poly(propylene) and poly(tetrafluoroethylene)	1–2	6×10^{-6} – 1×10^{-3}	$\sigma_{\text{eff}} \leq 2000$	≤ 300

The piezoelectric modulus d_{33} is determined by the surface charges and the Young's modulus E_y of the polymer that is,

$$d_{33} = \frac{2\eta\sigma_{\text{eff}}}{E_y} \quad (10)$$

Piezoelectric polymer materials based on electrets prepared from porous polymers, such as poly(propylene) and poly(tetrafluoroethylene) have a low Young's modulus of approximately 0.006 MPa, which ensures high values of the piezoelectric modulus (Lushcheikin, G.A., 2006). Bauer, S. *et al.* (2003) showed that ferroelectrets offer very high d_{33} transducer coefficients, comparable with ferroelectric ceramics and typically 20 times larger than that of ferroelectric polymers like PVDF. Orders of magnitude can be gained in material properties by

foaming. Due to their low density and small Young modulus, ferroelectrets provide extremely lightweight and soft transducer materials as indicated in Figure 2.3.

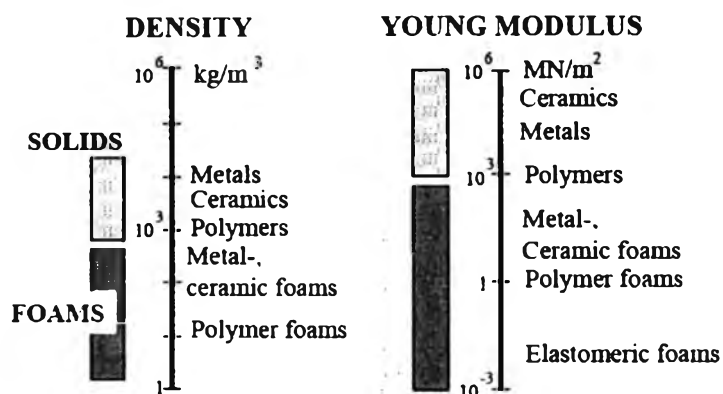


Figure 2.3 Density and elastic modulus of solid materials and foams (Bauer, S. *et al.*, 2003).

2.2.2 Ferroelectric-like Properties

Ferroelectrets exhibit hysteresis in dielectric displacement versus applied voltage (Figure 2.2). Polarization switching is achieved by destroying and recreating the macrodipole by means of dielectric barrier microdischarges at atmospheric pressure (Bauer, S. *et al.*, 2003). The figure shows only one void with its top and bottom charge layers of opposite polarity. In contrast to the Figure 2.4 (idealized figure), real polymer–foam electrets seem to have narrower hysteresis curves which is to be expected because of the large variation of void sizes and shapes in a real cellular film (Gerhard-Mulhaupt, R., 2002).

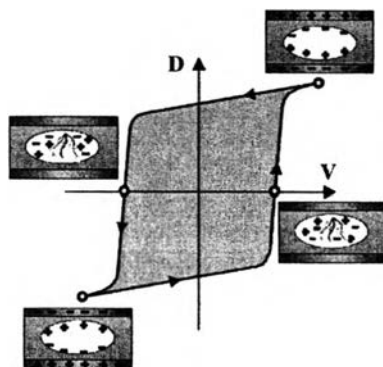


Figure 2.4 Schematic hysteresis in dielectric displacement versus applied voltage (Gerhard-Mulhaupt, R., 2002).

2.2.3 Foam Preparations

Different foaming procedures with separate preparation steps were developed in order to obtain optimized cellular structures. The first step is the initial foaming obtained either by extrusion of filler loaded polymers or by treatment in gases or supercritical fluids (SCF). The extrusion method often leads to cracks and void formation during the manufacturing process. The latter treatment utilizing gases, e.g. in carbon dioxide or supercritical carbon dioxide, during or after the extrusion leads to diffusion of the gas into the polymer. When the pressure is suddenly released, the gas expands violently, which leads to a voided structure. This process is supported by a heat treatment (Wilson, S.A. *et al.*, 2007).

For PP ferroelectrets, the optimized void length and height ratio is approximately 4–5, which corresponds to lens-like voids as shown in Figure 2.5 (Wilson, S.A. *et al.*, 2007). Wegner, M. *et al.* (2005) found from experiments on voided PP films 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 do therefore do not show significant piezoelectricity.

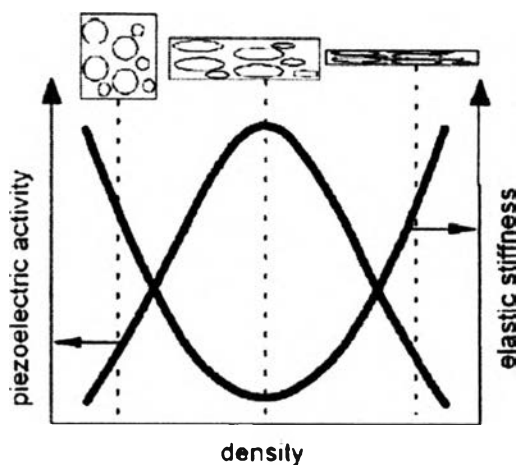


Figure 2.5 Schematic sketch and experimental data (obtained on PP ferroelectrets) of piezoelectric d_{33} coefficient and elastic stiffness c_{33} as function of the foam density (Wegner, M. *et al.*, 2005).

2.2.4 Applications of Ferroelectret

A number of applications have been developed and commercialized such as push buttons for keyboards, keypads and control panels with small areas. It can also be used as a fall sensor. Various types of microphones and musical pickups can be constructed. Other applications include orthopedic diagnostics, sports studies, pressure distributions between vocal chords (Lang, S.B., and Muensit, S., 2006). Ferroelectrets are thus promising as active materials for numerous transducer applications, in particular in headphones and loudspeakers (Wegener, M. *et al.*, 2004). Some examples of applications are quasi-static sensors for motion detection used in factory buildings for safety reasons, as well as for traffic control of cars and other vehicles (Wilson, S.A. *et al.*, 2007). Because of their low mass and almost arbitrary shape, polymer-foam electret transducers are very suitable for measuring movement in biomedical application. For example, breathing movement of laboratory animals. A respiration detector that can be placed between the patient and the supporting mattress (Gerhard-Malthaupt, R., 2002).

2.3 Polyethylene, Polypropylene and Poly(vinyl chloride)

2.3.1 General Description

High density polyethylene (HDPE) has $-(CH_2)_n-$ repeat unit. It is chemically the closest in structure to pure polyethylene. It consists primarily unbranched molecules with very few flaws to mar its linearity. Due to its very low level of branching, HDPE is sometimes referred to as linear polyethylene (LPE) (Peacock, A.J., 2000). The density and mechanical properties of HDPE show the higher values when compared with low density polyethylene (LDPE) and linear low density polyethylene (LLDPE).

Polypropylene (PP) has $-(CH_2-CH(CH_3))_n-$ repeat unit. There are three main types of steric isomer of PP which are isotactic, syndiotactic and atactic PP. Isotactic PP (i-PP) is a semi-crystalline solid with good physical, mechanical and thermal properties. Atactic PP (a-PP) produced in much lower volumes as a by-product of semi-crystalline PP and have very poor mechanical and thermal properties (Karian, H.G., 1999).

Poly(vinyl chloride) (PVC) has $-(\text{CH}_2-\text{CHCl})_n-$ repeating units. PVC has higher hardness and stiffness when compare with PE. It also has more polarity than PE and PP because of C-Cl dipole (Brydson, J.A., 1995). The polarity of the side group makes the chain stiff. For PVC, the effect of side group is strong so the rigidity affects the piezoelectric properties of PVC (Kocharyan, N.M., and Pachadzhyan, Kh.B., 1968).

PE and PP are semicrystalline polymers while PVC is amorphous or slightly crystalline polymer. Some principal properties of HDPE, PP and PVC are shown in Table 2.3.

Table 2.3 Principal properties of different types of polymers (Peacock, A.J., 2000)

Property	HDPE	PP	PVC (unplasticized)	PVC (plasticized)
Density (g/cm^3)	0.94–0.97	0.90–0.91	1.30–1.58	1.16–1.35
Melting temperature ($^{\circ}\text{C}$)	125–132	160–175	75–105*	75–105*
Flexural modulus (psi at 73°F)	145,000–225,000	170,000–250,000	300,000–500,000	-
Tensile modulus (psi)	155,000–200,000	165,000–225,000	350,000–600,000	-
Tensile strength at break (psi)	3,200–4,500	4,500–6,000	5,900–7,500	1,500–3,500
Tensile elongation at break (%)	10–1,500	100–600	40–80	200–450

* Glass transition temperature

2.3.2 Electrical Properties

The principal electrical characteristics can be defined in terms of its resistivity, permittivity, dissipation factor, dielectric strength and arc resistance. The

first three characteristics are important at low electrical stress, while the latter two are more important at electrical stress (Peacock, A.J., 2000).

Resistivity may be defined in term of the bulk or surface conduction of current. In both cases it is a measure of the resistance to electrical flow exerted by the material. Bulk resistance depends on thickness and is inversely proportional to cross-sectional area. It is defined in term of volume resistivity, which is the resistance of a cube of a material, typically 1 cm or 1 m per side, quoted in term of ohms per cubic centimeter or ohms per cubic meter. Surface resistivity is defined as the resistance between two electrodes that form opposite sides of a square and is quoted in units of ohms per square. The volume resistivities of HDPE, PP and PVC are given in Table 2.4 (Peacock, A.J., 2000).

Table 2.4 Volume resistivities of various types of polymers (Peacock, A.J., 2000)

Material	Volume resistivity (ohm-cm at 50% relative humidity and 23°C)
High density polyethylene	$>10^{16}$
Polypropylene (isotactic)	10^{16}
Poly(vinyl chloride) (unplasticized)	10^{15}

The dielectric constant (K), also known as the (relative) electric permittivity or the electric inductive capacity, is a measure of the electrical inertness of a material to an applied electric field. It strongly depends on the polarizability of the dielectric material; the lower the polarizability of the constituent bonds, the lower the permittivity. The dielectric constant of the material is defined as the ratio of the capacitance of a capacitor in which the insulator is replaced by a vacuum. The dielectric constant of polymers is approximately inversely proportional to the logarithm of the volume resistivity. The dielectric constants of HDPE, PP and PVC are given in Table 2.5 (Peacock, A.J., 2000).

Table 2.5 Dielectric constants of various types of polymers (Peacock, A.J., 2000)

Material	Dielectric constant (at 1 MHz)
High density polyethylene	2.3–2.35
Polypropylene (isotactic)	2.2–2.6
Poly(vinyl chloride) (unplasticized)	2.8–3.1

The dissipation factor (D , DF), also known as $\tan d$ or $\tan \delta$ (loss tangent) usually express:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad , \quad (11)$$

where ϵ'' is dielectric loss factor, ϵ' is ac capacitivy (Johnson, G.L., 2008).

Low values are desirable i.e. low power losses due to conversion of electric energy to heat, and are particularly important at high frequencies. The dissipation factor has been shown to decrease as a function of increasing crystallinity. The dielectric constants of HDPE, PP and PVC are given in Table 2.6 (Peacock, A.J., 2000).

Table 2.6 Dissipation factors of various types of polymers (Peacock, A.J., 2000)

Material	Dissipation factor (at 1 MHz)
High density polyethylene	> 0.0005
Polypropylene (isotactic)	0.0005–0.0018
Poly(vinyl chloride) (unplasticized)	0.006–0.019

As the voltage applied is increased, there comes a point at which a catastrophic breakdown of electrical resistance occurs. The voltage at which a breakdown occurs is known as the dielectric strength or breakdown voltage. It is normally quoted as a voltage gradient, e.g., volts per mil (Peacock, A.J., 2000), where 1 mil = 0.001 inch (Johnson, G.L., 2008). The dielectric strength is influence

by the presence of contaminants such as catalyst residues, moisture and dirt, by voids and by polarizable species (Peacock, A.J., 2000).

The arc resistance of a material is the length of time its surface can be subjected to an electric arc (discharge) before it breaks down and conducts current. Arc resistance is normally measured in seconds. There is no correlation between the arc resistance of a polymer and its chemical composition. The arc resistances of PP and PVC are given in Table 2.7 (Peacock, A.J., 2000).

Table 2.7 Arc resistances of various types of polymers (Peacock, A.J., 2000)

Material	Arc resistance (sec)
Polypropylene (isotactic)	136–185
Poly(vinyl chloride) (unplasticized)	60–80

2.4 Preparation of Voided Films

2.4.1 Blowing Agent Compression Molding

Nowadays, the using of foam-enhancing additives or blowing agents to produce foamed or cellular plastics are growing in applications. Small amount of blowing agent can produce the bubbles in a wide range of polymers. So another interesting method to make porous films is mixing blowing agent with polymers by compression molding.

In this research, azodicarbonamide (ACA, AZDC) was used as chemical blowing agent. It enjoys the most widespread use in commercial polyolefin and PVC foam production. It decomposes in a narrow temperature range (approximately 200-210°C). The evolved gas is 65% nitrogen, 32% carbon monoxide and 3% other gases, including ammonia and carbon dioxide (Quinn, S., 2001).

2.4.1.1 Effect of Amount of Blowing Agent

Mechraoui, A. *et al.* (2008) produced polypropylene foams using 1.5, 2, 2.5 and 3% of azodicarbonamide by compression molding. They found that mechanical properties, cell density, skin thickness and foam density decreased, while cell size increased with increasing amount of blowing agent. Similar to the experiment from Klempner, D. and Frish, K.C. (1991), they showed that the density of foam is controlled by the blowing agent level. Foam density is approximately inversely proportional to the blowing agent level. Sahagún, C.Z. *et al.* (2006) found that the foams mainly have a closed cell structure due to the low amount of azodicarbonamide used.

Not only the amount of azodicarbonamide that can affect the structure of the cell, but also the pressure of the processing. Therefore, foamed polymers can be made as either a closed-cell or an open-cell product. In the former case bubbles of gas expand to a limited extent within a molten polymer constrained by pressure. The product comprises cells completely bounded by solidified polymer walls. Open-cell products form when bubbles are allowed to expand in a relatively unconstrained manner. The cell so formed have only partial walls and are thus interconnected like those of sponge (Peacock, A.J., 2000). Therefore, the closed-cell can be produced from the compression molding technique.

2.4.2 Phase Separation Technique

Phase separation processes sometimes called phase inversion or the polymer precipitation process (Baker, R.W., 2004). It can be divided into four main techniques—thermally induced phase separation (TIPS), air-casting of a polymer solution, precipitation from the vapour phase and immersion precipitation. In this research, the immersion precipitation was used. 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. A schematic representation of membrane formation by this technique is presented in Figure 2.6 (van de Witte, P. *et al.*, 1996).

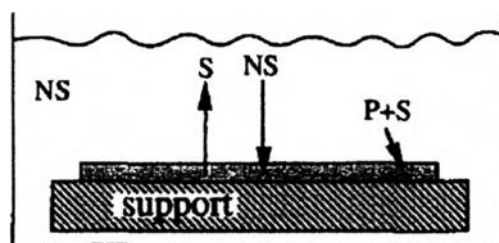


Figure 2.6 Schematic depiction of the immersion precipitation process: P, polymer; S, solvent; NS, nonsolvent (van de Witte, P. *et al.*, 1996).

The variation of porous films was controlled by polymer concentration and types of solvent.

2.4.2.1 Effect of Polymer Concentration

The amount of liquid used should allow the resulting microporous structure to have sufficient minimum handling strength to avoid collapse of the micro porous or cellular structure. Moreover, the amount of polymer use should not be so great as to result in closing off the cells or other areas of micro porosity (Castro, A.J., 1981). van de Witte, P. *et al.* (1996) found that the polymer concentration of the casting solution determined which morphology was obtained. Increasing polymer concentration will decrease the porosity of the membrane and the interconnectivity of the pores. Nunes, S.P., and Peinemann, K.V. (2001) found that the sponge-like or a macrovoid structure is favored by increasing the polymer concentration of the casting solution.

2.4.2.2 Effect of Types of Solvent

Poly(vinyl chloride) (PVC) membranes were prepared from different solvents which were N,N-dimethylacetamide (DMAc), Dimethylformamide (DMF) and Tetrahydrofuran (THF). It was found that the morphology of the PVC membrane was significantly affected by the character of the casting solution (Okuno, H. *et al.*, 1993).