CHAPTER II
LITERATURE REVIEW

2.1 Piezoelectric Materials

2.1.1 Principle of Piezoelectric Material

Piezoelectric materials are a Greek term for pressure electricity that mean generation of electrical polarization in a material in response to a mechanical stress. This phenomena is known as the direct effect. Piezoelectric materials also display converse effect; mechanical deformation upon application of electrical charge or signal. Piezoelectricity is a property of many non-centrosymmetric ceramics, polymer and other biological systems (Harrison *et al.*, 2001). Piezoelectric materials exhibit unique property; when they are subjected to external strain by applying pressure/stress, the electric dipoles in the crystal get oriented such that the crystal develops positive and negative charges on opposite faces, resulting in an electric field across the crystal. This is exactly the reverse of the above mentioned indirect piezoelectric effect. Jaques and Pierri Curie. first observed those effect in quartz crystal in 1880 and called this piezoelectricity; “piezo” meaning pressure. The effect is called direct piezoelectric effect (Vijaya, 2013).

When a dielectric material belonging to noncentrosymmetric class is subjected to an external electric field, there will be asymmetric movement of adjacent ions that resulting in significant deformation of the crystal and the deformation is directly proportional to the applied electric field. These materials show an electrostrictive effect due to anharmonicity of bonds, but is marked by more significant asymmetric displacement. The materials are called piezoelectric materials. The classification of dielectric materials based on their response to external stimuli is shown in Figure 1.

Vijaya (2013) studied the piezoelectric in piezoelectric materials and devices, the direct and indirect piezoelectric effects are illustrated in Figure 2. and Figure 3. In the direct effect when a poled piezoelectric material is subjected to tensile stress, in the direction parallel to the poling direction, a positive voltage is generates across the face (Figure 2b). When the material is subjected to compressive stress in the direction, a negative voltage is generated across the faces (Figure 2c). In the indirect effect, When an external voltage is applied to the material, the material gets extended if the polarity of the voltage is the same as that of the field applied during poling (Figure 3b) and, when the voltage is applied in the reverse direction, the material gets compressed (Figure 3c)

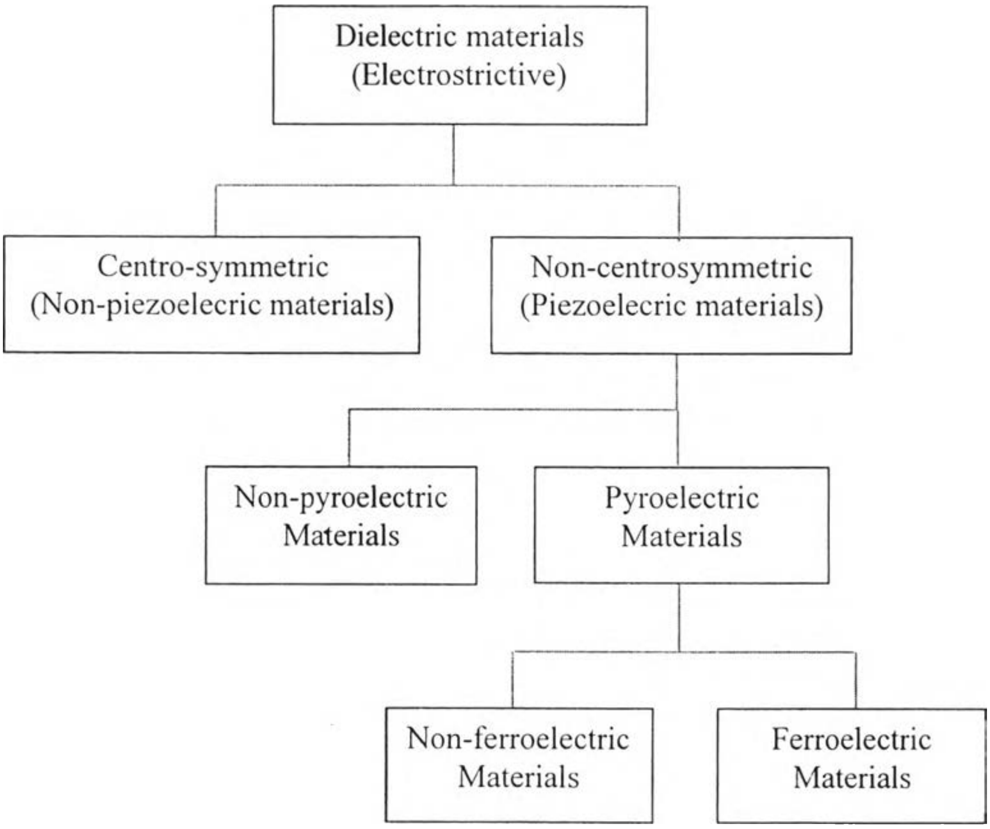

Figure 2.1 Classification of dielectric materials

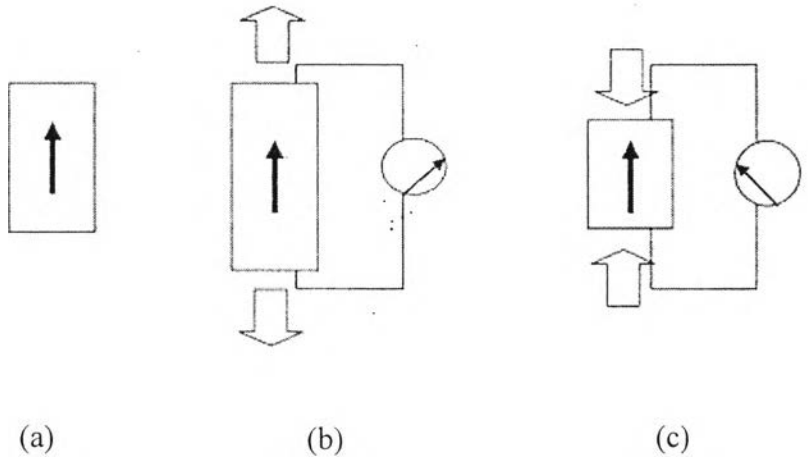

Figure 2.2 Direct piezoelectric effect: (a) Poled piezoelectric material. (b) Positive voltage is generated when apply tensile stress to the material. (c) Negative voltage is generated when apply tensile stress to the material.

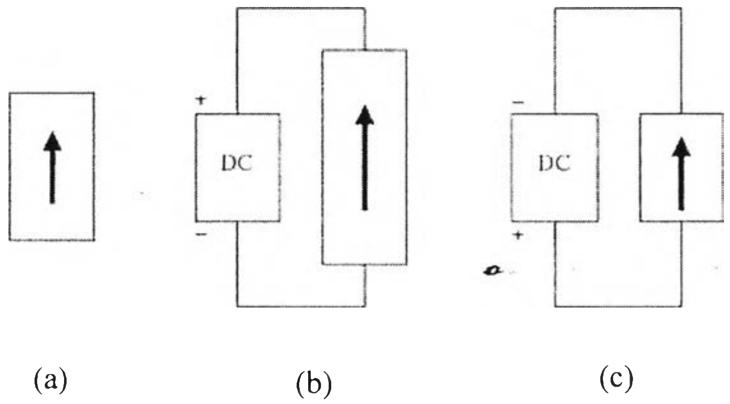

Figure 2.3 Indirect piezoelectric effect: (a) Poled piezoelectric material. (b) Tensile strain is generated when apply DC voltage to the material. (c) Compressive strain is generated when apply DC voltage to the material.

2.1.2 Structure Requirements for Piezoelectric Polymer

In the simplest term, both of semi-crystalline and amorphous polymer require 4 essential elements. The detail of each element was presented as follow ;

- The presence of permanent molecular dipoles

- The ability to align the molecular dipoles
- The ability to sustain the alignment of molecular dipole
- The ability of the material to undergo large strain when apply stress

2.1.3 Characteristics of Piezoelectic Polymers (Harrison *et al.*, 2001)

The piezoelectric properties of polymer are so different from piezoelectric ceramic as exhibited in Table 1. The piezoelectric strain constant (d_{31}) for the Lead Zirconium Titanate (PZT) is higher than PVDF. However, piezoelectric polymer have much higher piezoelectric stress constants (g_{31} = 240 mV-m/N) than piezoelectric ceramic. Mean that polymers are suitable in sensor applications than ceramics. Moreover, polymers have other properties like light weight, tough, high strength, high impact resistances and easy to process in complex shape.

Table 2.1 Properties comparison of common piezoelectric polymer and ceramic

Materials	d_{31} (pm/V)	g_{31}(mV/m/N)
PVDF	28	240
PZT	175	11

In many years ago, piezoelectric materials have been developed so rapidly, Poly(vinylidene fluoride) (PVDF) is a famous piezoelectric polymer that always in electrical devices and it exhibited higher piezoelectric coefficient compare to other polymer. Polyamide have been investigated an the piezoelectric and ferroelectric activity more than 20 years. At room temperature, polyamide exhibited lower piezoelectric constant than PVDF, however, when temperature was elevated above T_g, PA exhibited the superior piezoelectric constant compare with PVDF. There are many polymers that have been studied such as polyureas, polyacrylonitrile, polyvinylidene chloride, and biopolymer. Table 2 shows piezoelectric constants for several semi-crystalline polymers and biopolymer.

Table 2.2 Piezoelectric properties of polymers

Polymer	*d_{31} (pC/N)*
Semicrystalline polymer	
Polyamide11	14
PTrFE	12
Polyamide7	17
PVDF	20-28
Amorphous polymer	
PVC	5
PAN	2
P(VDCN-VAc)	10

Eiichi Fukada, (2000) studied piezoelectric effects in biopolymer, the experiment verification of both direct and inverse piezoelectric effects and determine the piezoelectric of biopolymer matrix. Only the shear piezoelectric constants $-d_{14} = d_{25}$ are finite without cancellation and other components are zero. Due to this symmetry relation, most biopolymer with fibrous configurations may show the shear piezoelectric effects. Most biological polymer including polysaccharides, proteins, and polynucleotides have been found an excellent of shear piezoelectricity as shown in Table3. They are the fibrous from, in which uniaxial symmetry exists.

Table 2.3 Shear piezoelectricity of biopolymer

Polymer	*$-d_{14}$ (pC/N)*
Polysaccharides	
Cellulose	
Wood	0.1
Ramie	0.2
Chitin	
Crab shell	0.2
Lobster apodeme	1.5
Amylose	
Starch	2.0
Proteins	
Collagen	
Bone	0.2
Tendon	2.0
Skin	0.2
Keratin	
Wool	0.1
Horn	1.8

2.1.4 Application

Piezoelectric polymer has several applications, it has been used in sensor and actuator devices for a wide array application. Typical applications include devices in medical instrumentation, optics, touch screen, computers, and ultrasonic. One important application is in biomedical field where polymer are being explored as potential artificial muscle actuators, this polymer has to match with body fluid and human body.

2.2 Polyamide

Polyamide is mainly formed by condensation reaction between diamines and dicarboxylic acids or ring-opening of lactam ring. Polyamide is available in various type depending on the monomer structure, which different grade exhibiting its own properties. In all polyamides, the amide (-CONH-) group is always repeated (Tulsyan, K, 2007).

2.2.1 Structure and properties

polyamide is typically named after the number of carbon atom along the backbone of their monomer unit. The chemical structure of a monomer of polyamide is shown in figure 4. Polyamide has a polar hydrogen bond structure in which the molecular dipole are formed by the N-H and C=O group in the polymer chain (Sampsan *et al.*, 2012).

There are many types of polyamide or polyamide that use in wide application. The properties of polyamide always depend on structure of monomer of polyamide. For example, in topic of dipole moment, the density of N-H and C=O dipoles per unit volume of polyamide is larger for lower numbered polyamide. Therefore, polyamide 5 is expected to exhibit a larger net dipole moment than polyamide7 and polyamide11 (Lewis *et al.*, 1997). For mechanical properties, it depend on structure of monomer unit too. The comparison of mechanical properties is shown in Table 4. These polyamide is always use as engineering plastic that can replace metal because some mechanical properties in some polyamide has higher than metal and it also has light weight.

Table 2.4 Comparison of mechanical properties (Page, 2000)

Polyamide type	Specific gravity (g/cm^3)	Tensile strength (MPa)	Tensile modulus (GPa)	Flxtural modulus (GPa)	Elogation at break (%)	Izod impact strength (kJ/m^2)
Polyamide 6	1.13	70	2.8	2.2	15	45-65
Polyamide 11	1.03	38	1.4	1.2	250	100
Polyamide 12	1.02	45	1.4	-	200	50-200
Polyamide 66	1.14	85	3.0	2.8	5	40-60
Polyamide 69	1.08	70	-	2.3	50	35
Polyamide 610	1.07	55	2.1	-	70	50
Polyamide 612	1.06	61	2.1	2.3	10	50
Polyamide 46	1.18	100	3.3	3.0	-	10

Polyamide or nylon is known to be hydrophilic. Since the water absorption is associated with hydrogen bonding to the polar amide groups, the hydrophilicity increases as the density of amide group increases. The comparison of water absorption properties is shown in Table 5 , water absorption in polyamide11 and polyamide has been shown to be as high as 4.5%, and more than 12% for polyamide5,and less than 0.02% for PVDF. The dielectric and piezoelectric properties can be interrupted by water absorption. However, water does not interrupt the crystallinity or orientation in thermally annealed films. Therefore, polyamide films was be dried to restore their original dielectric and piezoelectric properties (Harrison *et al.*, 2001).

Table 2.5 Comparison typical materials properties for odd-numbered and PVDF (Lewis *et al.*, 1997)

Property	Polyamide 11	polyamide7	polyamide5	PVDF
Dipole density, (D/100 Å^3)	1.34	2.06	2.94	3.90
Tm, (°C)	185	210	260	175
Tg, (°C)	68	83	95	-55
Density (Kg/m^3)	1023	1115	1200	1780
H_2O Absorption (%)	≤ 3.5	≤ 4.5	≤ 12.3	≤ 0.02

Lewis *et al.*, (1997) studied the different between even and odd- numbered polyamide, the result is shown in Figure 2.5. In the even-numbered polyamide the dipoles alternate in their alignment, all amide group dipoles are oriented in anti-parallel, resulting in no net dipole moment. In odd-numbered polyamide all of the dipoles are aligned in the similar direction, all amide group dipoles are oriented in parallel, resulting in a large net dipole moment. As seen in Figure 2.5, the arrows represent the orientation of each N-H and C=O dipole and show how in even-numbered polyamide the dipoles alternate, resulting in no net dipole moment.

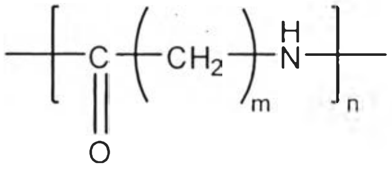

Figure 2.4 polomer repeating unit of polyamide

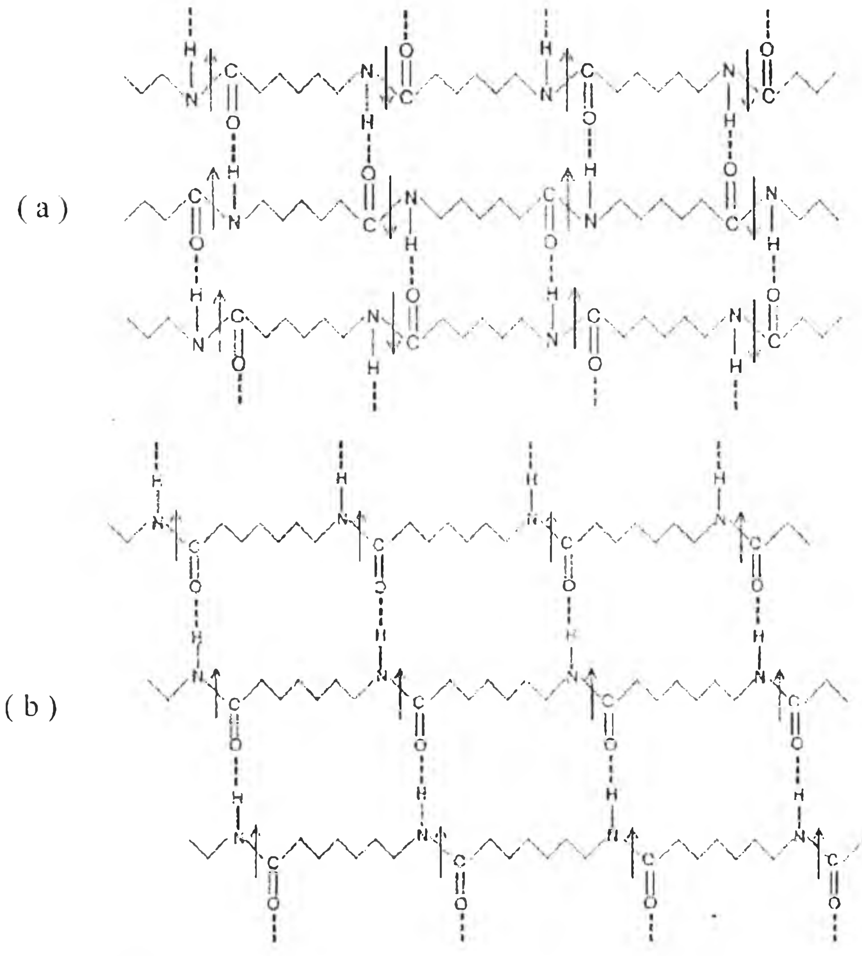

Figure 2.5 Schematic view of the hydrogen-bonded sheet structure of (a) nonpolar polyamide6 and (b) polar polyamide7

2.2.2 Piezoelectric and ferroelectric properties of polyamide

Dielectric and piezoelectric properties of polymers are closely related to the chemical and crystalline structure of materials and the dipole density in the crystalline unit cell (Gang *et al.*, 1985). Sampson *et al.*, (2012) studied piezoelectric and ferroelectric properties of odd-numbered polyamide. the piezoelectric responses of odd-numbered polyamide has higher than the piezoelectric responses of PVDF at higher temperature above their transition temperature, T_g. The piezoelectric constant increase rapidly with temperature maximum stable d_{31} value of 17pC/N and 14 pC/N are reported for polyamide7 and polyamide11 as shown in figure 6. Odd-numbered polyamide, such as polyamide7 and polyamide11 are interested due to their piezoelectric and ferroelectric properties, making them suitable for applications in sensors and actuator.

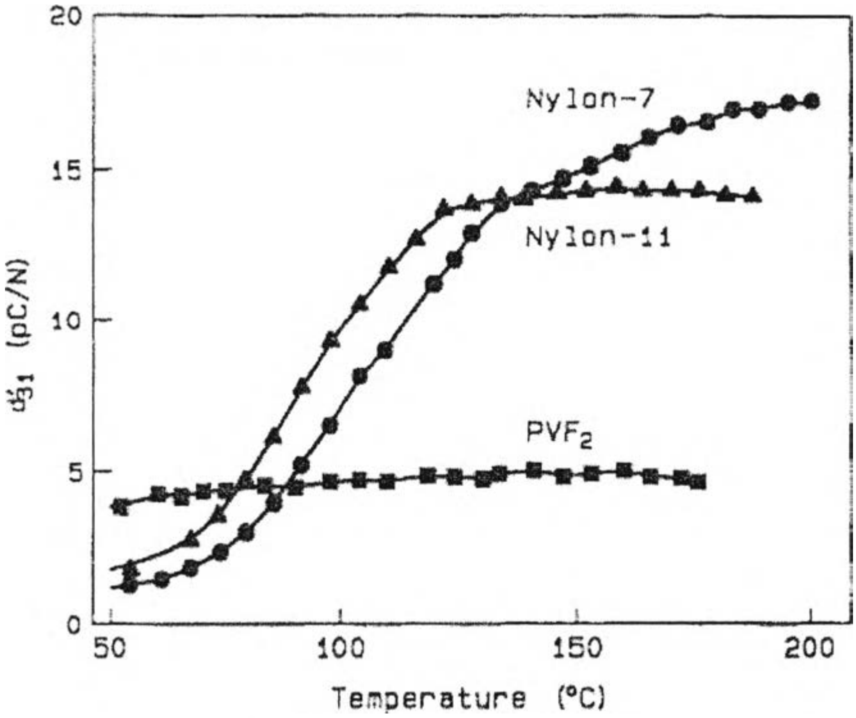

Figure 2.6 Piezoelectric strain constant, d_{31}, for polyamide11 and polyamide7 and PVDF samples measured at 104 Hz from 50°C to temperature close to their melting point (Takase *et al.*, 1991).

Beside the temperature dependence of piezoelectric response of odd-numbered polyamide, it also depends on poling and preparation techniques. There are several factor that can enhance the piezoelectric properties, that are the degree of crystallinity and the level of water absorption. These factors show very little enhancement in the piezoelectric response of polymer.

Moreover, Annealing after poling below the melting temperature, that decrease the spacing between the hydrogen-bonded which results in an increased difficulty for amide group to reorient with increasing thermal motion, giving rise to a superior thermal stability of the piezoelectrical activity as shown in Figure 7, d_{31} of annealed polyamide7 is more stable at high temperature than unannealed polyamide11 (Peter *et al.*, 2004).

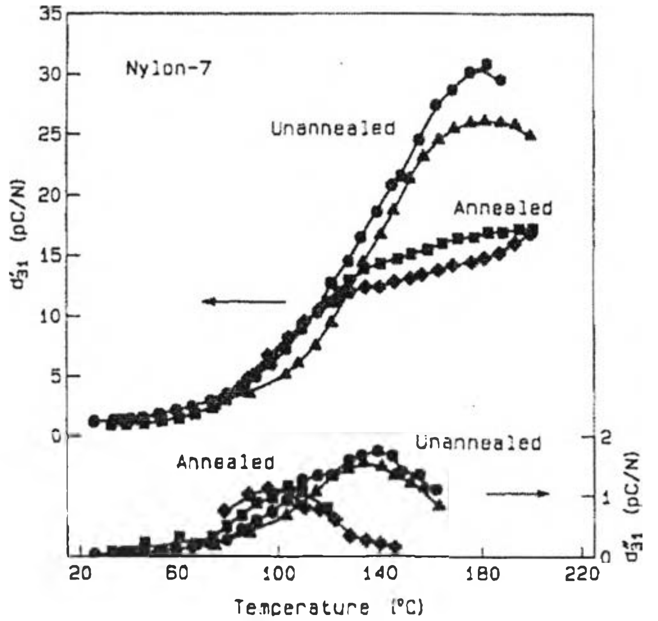

Figure 2.7 Anealing effect (after poling) on the d_{31} versus T characteristics of polyamide7. The measurement frequency was 104Hz.

2.3 Nanocomposite (Tulsyan, 2007)

Nanocomposites system which are thermodynamically stable have the ability to exhibit mechanical, thermal and barrier properties without losing other important properties. Tulsyan et al., (2007) observe and develop conventional composites are able to reach better mechanical peoperties. For compatible, nanocomposite require only 3-5 wt% loading to get desired properties. The cost of nanofillers is higher than microfillers, and require only 3-5 wt% loading of nanofillers is used on nanocomposites. However, the cost of nanocomposite is high. These nanocomposites suitable for engineering application and it's also low weight.

Nano fillers have several forms. They are characterized by dimension and aspect ratio. There are 3 forms of nanofillers which are spherical, rod shape and platelet-like as shown in Figure 2.8. The important properties of nanofillers are high surface area and high aspect ratio. High surface and aspect ratio produce high interfacial interactions, and increase stiffness, thermal, fire and barrier properties, when a good dispersion is obtained.

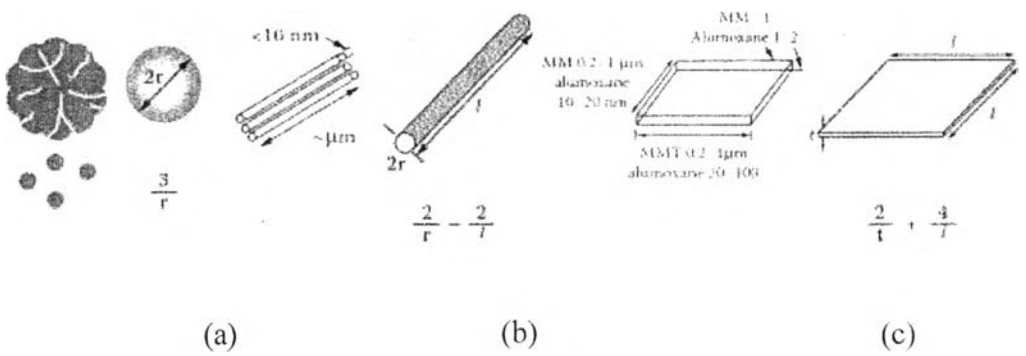

Figure 2.8 Surface area/volume ratios for various reinforcement filler geometries. (a) Spherical (b) rod-like (c) platelet-like (Goddard *et al.*, 2007).

Nanocomposites can be produced by at least three methods. The First method is in-situ polymerization,that means add nanofiller and swell in monomer, and then polymerized leading to nanocomposites, which may or may not have good properties, depening on initial dispersion. Second method is solvent casting, the nanofillers are dispersed in a polar solvent suitable to dissolve the polymer matrix, and on evaporation of the silvent a nanocomposite may be formed. Lastly, this method is melt blending, this method is popular technique to form nanocomposites. The fillers is dispersed in polymer matrix by using screw in extruder.

2.4 Bacterial Cellulose

Bacterial cellulose (BC), a polysaccharide synthesized by various species of bacteria, can be used as a reinforcing material due to its large surface area per mass unit that allows the formation of extensive hydrogen bonds with other hydrophilic polymers (like PVA). The strength of interfaces between BC and PVA leads to a very strong composite. BC has unique properties such as: highly hydrophilic nature, elasticity, biocompatibility, high purity and superior mechanical properties (Ramona *et al.*, 2014).

Bacterial cellulose, known as nata de coco, is used in sweetened form as dessert. It is produced at the surface of coconut water and other suitable media by a gram-negative rod- shaped bacterium, Acetobacter xylinum (Peter *et al.*, 2000).Acetobacter xylinum produce two forms of cellulose: (i) cellulose I, the ribbon-like polymer, and (ii) cellulose II, which is thermodynamically more stable amorphous form of polymer. Cellulose I composed of parallel β, 1-4 glucan chains which are arranged uniaxially with van der Waals forces whereas β. 1-4 glucan chain of cellulose II are arranged in random manner. They are mostly antiparallel and with large number of hydrogen bands that results in more stable form. Bacterial cellulose does not require remedial processing to remove unwanted polymers and comtaminants (e.g. lignin, hemicellulose) and therefore, retains a greater degree of polymerization. This give bacterial cellulose superior unidirectional strength (Bhavna *et al.*, 2014).

Since its discovery, bacterial cellulose (Nasrullah *et al.*, 2013) has shown great potential as an effective biopolymer in various fields. The structural features of BC are far superior to those of plant cellulose, which impart it with better properties (Ul-Islam *et al.*, 2012). Fibril networks consisting of well arranged three dimensional nanofibers enable production of BC sheets with high surface area and porosity (Ul-Islam *et al.*, 2012). Moreover, the crystallinity and mechanical strength of BC are higher than those of plant cellulose, which has increased its utilization in biomedical and other related fields. Specifically, BC has been applied for wound dressings, burn treatments, tis-sue regeneration, skin substitutes, catalyst sensing materials, and electronic devices (Czaja *et al.*, 2005).

Bacterial cellulose has been investigated by Bhavna *et al.*,(2014). Bacterial cellulose compose by 64% of $I\alpha$ and 36% of $I\beta$ phase which $I\alpha$ structure is prevalent in cellulose produced by algae and bacteria whereas $I\beta$ is dominant in cellulose obtained from wood. The crystallinity index was found to be 81.2% and crystal size of <200> crystal plane remained the same around 5.2 nm. The maximum load was 11.95 ± 0.2 N and maximum displacement was 9.71383 ± 0.11 mm. The maximum stress applied was 14.94 ± 0.08 N/mm^2 that results into maximum strain of 97.13 ± 0.18%. Theoretically Young's modulus is 173 GPa and tensile strength in order of 2 GPa. The water absorption capacity for bacterial cellulose was calculated a 400%. The Z-average partical size was 1.44 μm having maximum particals of 0.7419 μm. The particle size distribute between 0.4777μm and 1.152μm. The porosity of bacterial cellulose was calculated as 181.81%.

Now a day, bacterial cellulose is suitable used in electronic devices. Due to their thermal expansion co efficient is low as 0.1 ppm/K, so, it suitable to be used as reinforcement with polymer to produce nanocomposites that have low thermal expansion coefficient. This nanocomposites can use in high temperature and it is also transparence (Nogi *et al.*, 2008).