

2. Review of past works

2.1 General description about used materials

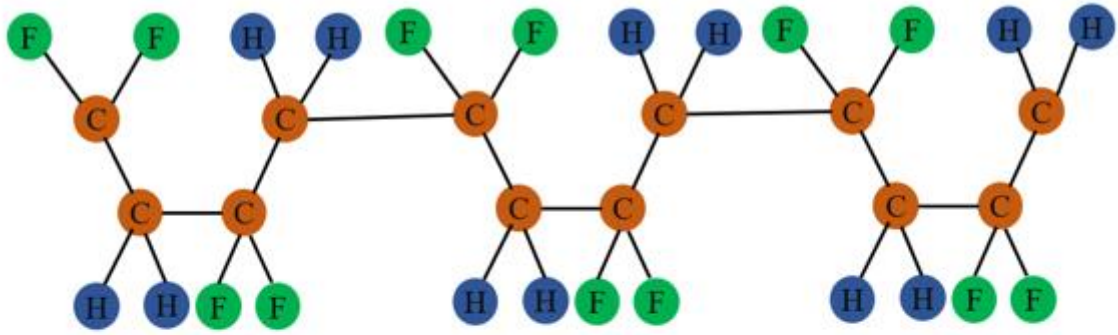
2.1.1 Polyvinylidene fluoride (PVDF)

Polyvinylidene fluoride (PVDF) is an attractive organic, thermoplastic, fluoropolymer with many excellent features like high dielectric, ferroelectric, piezoelectric and pyroelectric properties compared to other biocompatible polymers. It was discovered in 1969 with 10 times higher piezoelectricity compared to any other known polymer then [58]. It belongs to fluoropolymer group with distinct properties due to strong bonding between its fluorine and carbon atoms and their fluorine shielding. Permanent dipole moment between carbon – hydrogen (C – H) (δ^+) and carbon – fluorine (C – F) (δ^-) in opposite direction is the cause of emergence of ferroelectricity in it [59]. It is a semi-crystalline material with crystallinity varying in the range of 35 - 70 % depending upon multiple factors like molecular weight, polymerization procedure and thermal history [60]. It can be synthesized by polymerization of vinylidene difluoride. There are different phases of PVDF depending upon their configuration and synthesis process. These polymorphs are α , β , γ , δ and ϵ phases. However δ -phase is considered to be the polar version of α -phase [61]. Although ϵ -phase is reported to exist but substantial information about it is not present [62]. Out of these different phases β , γ and δ -phases are electrically active because of their non centrosymmetric structure while α and ϵ phases appear to be electrically inactive due their antiparallel packing of dipoles in the unit cell [63]. Out of these many phases, β -phase is the one that exhibits best ferroelectric nature whereas α - phase is the most stable one. Dipole moment of β -phase is found to be 8×10^{-30} C.m per unit cell [64]. However in order to obtain better ferro and piezo responses, they must be oriented in a preferred direction which can be done by external polling [65].

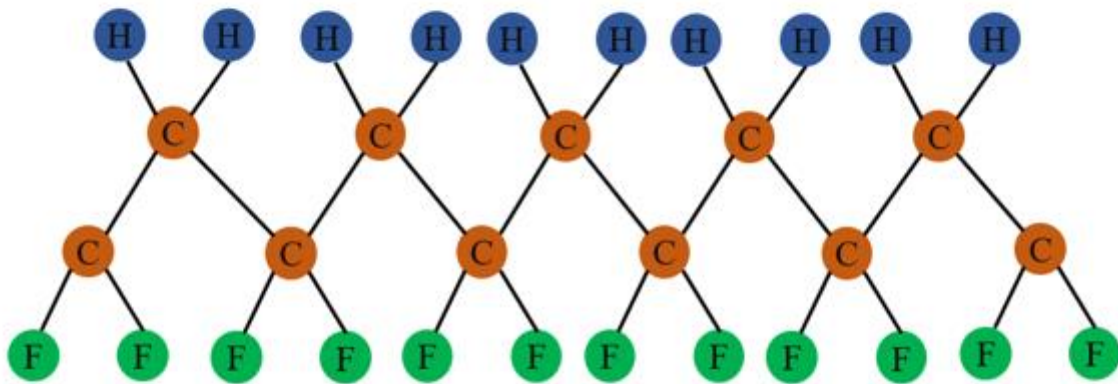
Out of these phases α -phase is the most common one, which can be identified as trans–gauche–trans–gauche' (TGTG') configuration of macromolecular chains as shown in fig. 2.1. Due to antiparallel orientation of dipoles arising from C-H and C-F bonds, it is non-polar in nature and does not exhibit any kind of ferroelectric nature. Although it is non-polar in normal condition but external stress can also generate ferroelectricity in it due to strain gradient [66]. Thus α -phase can be transformed into other 3 polar polymorphic phases by application of external action like mechanical stress, heat or electric field. Thus β -phase can also be obtained from deformation of α -phase by drawing it to very low temperature, annealing at very high pressure or applying high electric field [67]. It has an all trans (TTT) molecular configuration as shown in fig. 2.1 which responsible for emergence of its outstanding ferroelectric and piezoelectric properties. Although report suggests that they are not simply follows the trans- configuration but slightly distorted from their c-axis to form slight zig-zag arrangement [68]. The polar γ -phase is reported to be obtained by annealing of α -phase at very high temperature which is arranged in TTTGTTTG' configuration [68]. Although it is also polar in nature, but not as much compared to its β -phase [59]. It may be considered as an intermediate phase between α and β -phases. The fourth phase also called δ -phase is polar form of α -phase can be processed by applying high electric field [69]. This form of PVDF is identical to α -phase in chain configuration but the difference appears in inter-chain packing. The final phase is called ϵ -phase packed in TTTGTTTG' configuration similar to that of γ -phase, but arranged in anti-polar manner making it electrically neutral [62]. Different properties like lattice parameters, mechanical, thermal and electrical properties measured by previous studies are presented in Table – 2.1 and Table – 2.2 [70-74].

Table – 2.1 Different lattice parameters of β -phase PVDF [70]

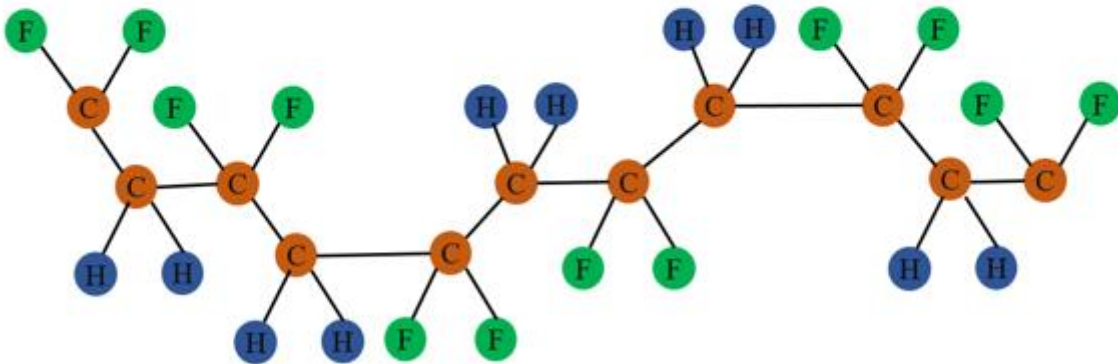
Crystal structure (Space group)	Orthorhombic Cm2m	Monoclinic Cc	Orthorhombic P21cn	Monoclinic P21/c
a (Å)	8.691	4.829	5.011	5.029
b (Å)	9.568	9.568	9.999	9.976
c (Å)	2.568	9.226	4.645	4.646
β (°)	-	94.06	-	90.40



α – phase (TGTG' configuration) (non – polar)



β – Phase (TTT configuration) (polar)



γ – phase (T3GT3G' configuration) (polar)

Fig. 2.1 Atomic configurations of different phases of PVDF

Table – 2.2 Different properties of PVDF at room temperature measured by previous studies [71-74]

Mechanical properties	
Tensile strength	9 – 120 Mpa
Compressive strength	13.8 – 172 Mpa
Elongation	3.5 – 40%
Strength	4.8 – 120 Mpa
Elastic modulus	0.03 – 17.1 Gpa
Flexural modulus	0.07 – 20.9 Gpa
Coefficient of friction	0.2 – 0.4
Density	0.7 – 1.89 g/cm ³
Water absorption	0.01 – 0.5 %
Electrical properties	
Dielectric constant	10.2
Volume resistivity	$>10^{14}\Omega\text{-cm}$
Dipole moment	$5 - 8 \times 10^{-30} \text{ C.m}$
d ₃₃	49.6 pm/V
Thermal properties	
Melting point	175 - 185 ⁰ C
Glass transition temperature	-32 ⁰ C
Thermal conductivity	0.2 W/m. K
Specific heat	1.2 – 1.6 kJ/Kg/K
Coefficient of linear expansion	$12 - 14 \times 10^{-5}\text{K}^{-1}$
Other properties	
Refractive index	1.41 – 1.42
Specific gravity	1.78
Curie temperature	170 ⁰ C

2.1.2 Zinc oxide (ZnO)

Zinc oxide is an inorganic whitish powder compound used as additive nanomaterial to many host compounds. It is a multifunctional material owing to its many physical and chemical properties. It has many excellent features like chemical stability, appropriate band gap to absorb wide band of radiation and piezoelectric property [75]. It is a wide band gap semiconductor with band gap ~ 3.37 eV and bond energy ~ 60 MeV with thermal and mechanical stability making it suitable for many electronic and opto-electronic applications [76]. Moreover, the piezo- and pyroelectric properties further make them useful to be used in sensor, transducer and energy harvesting devices [77]. Recently, ZnO in nanoparticle form has been utilized excessively as reinforcement to many host materials to modulate their many properties [78-79]. Recently, ZnO has been synthesized in many nanoshapes like nanowire, nanoplate, nanosphere, nanotube, nanoring, nanoflower etc [80 – 83]. But ZnO nanoparticles have diameter less than 100 nm and large specific surface area is believed to be one the most produced nanomaterials [84]. Numerous synthesis processes like chemical vapor deposition (CVD), aqueous solution growth, electro-deposition, sol-gel methods have been applied to produce ZnO nanoparticles. ZnO is a group II – VI compound semiconductor which crystallizes in cubic zinc-blend, hexagonal wurtzite or rock salt shape [84]. At natural condition, the stable phase is wurtzite. In this structure, an anion is surrounded by four cations in form of tetrahedron and vice-versa. Although, this tetrahedron is a typical sp^3 bonding, but it also exhibits considerable ionic character. This structure possess hexagonal unit cell with lattice parameters a and c such that $c/a = 5/3$. It belongs to space group of C_{6v}^4 or $P6_3mc$. This structure contains two inter-penetrating hexagonal-close-packed (hcp) sublattices. In an ideal wurtzite crystal, each type of atom in different sublattices are displaced from one another along their c -axis by an amount of $u=3/8=0.375$. Each inter-penetrating sublattice contains 4 atoms per unit cell such that one atom is surrounded by four atoms of other type and vice versa. However in real ZnO crystal the structure slightly deviates either by changing c/a ratio or u parameter. It can be noted that c/a ratio and u parameter are correlated in such a way that if one parameter changes, the other one also changes in such a way that the tetrahedral distance remains almost unchanged due to polar interactions. Different properties like structural, mechanical, physical and thermal properties are presented below in Table – 2.3.

Table – 2.3 Different properties of wurtzite ZnO at room temperature measured by previous studies [85]

Property	Value
Lattice parameters	
Stable phase (at 300 K)	Wurtzite
Space group	P6 ₃ mc
a=b	3.24 Å
c	5.21 Å
c/a	1.602 (1.633 for ideal hexagonal structure)
u	0.345
Physical properties	
Density	5.6 gm/cm ³
Molar mass	81.406 gm/mol
Thermal properties	
Melting point	1975 °C
Boiling point	2360 °C
Heat capacity	40.3 J/K-mol
Linear expansion coefficient	6.5×10^{-6} (for a), 3.0×10^{-6} (for c) /°C
Electrical properties	
Exciton binding energy	60 MeV
Static dielectric constant	8.65
Intrinsic carrier concentration	$< 10^6$ /cm ³
Electron effective mass	0.24
Hole effective mass	0.59
Electron hall mobility at 300 K for low n-type conductivity	200 cm ² /V-s
Hole hall mobility at 300 K for low p-type conductivity	5 – 50 cm ² /V-s

Table – 2.3 Different properties of wurtzite ZnO at room temperature measured by previous studies [85]

Other properties	
Band gap	3.37 eV (direct)
Refractive index	2.01

2.1.3. Graphene oxide (GO)

Graphene is naturally a two-dimensional sheet of sp^2 hybridized carbon atoms arranged in hexagonal honeycomb structure going through extensive research due to their many desirable properties like mechanical strength, high electron mobility, good thermal conductivity, optical transparency and high specific surface area [86]. For these reasons, it has been tried to incorporate into many polymers to fabricate graphene based nanocomposites with beneficial applications [87]. But pristine graphene as a dopant has many problems like difficulty in bottom-up synthesis, agglomeration and poor solubility [88-89]. Therefore, compounds having structure similar to that of graphene synthesized from graphite by top-down approach possess many of those advantageous properties of graphene [90]. Oxidation of graphite in solvent leads to formation of graphene oxide (GO) which consist of many stacked layers of two-dimensional GO sheets [91]. GO has similar hexagonal structure to that of graphene, but contains many other functional groups like hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), carboxylic acid (-COOH) and other oxygen based functional groups [92]. Moreover this GO can be used in formation of reduced graphene oxide (rGO) containing less functional groups and has properties closer to that of pristine graphene. Typical structures of graphene, GO and rGO are presented in fig. 2.2. Recently graphene derivatives like GO, rGO and graphene quantum dots (GQD) are emerging as efficient fillers to be incorporated in host polymer substances to modulate their many properties [93]. GO is a material with extremely hard mechanical structure whose Young modulus is found to be in the

range of 380 – 470 GPa depending upon its oxygen functional groups [94]. Therefore, addition of GO into host material has positive outcome on tensile, hardness and fatigue properties of host substances [95-97]. This improvement in mechanical hardness is utilized in fabrication of polymer based nanocomposites so that they can undergo enough mechanical stress to convert it into usable electrical energy [98]. GO also has remarkable optical properties depending upon their electronic configuration [99 - 100]. Recently GO as a filler material has been used excessively to modulate optical properties of many host materials [101 –102]. GO has the capability of tuning band gap of semiconducting materials useful in many optoelectronic applications [103 – 106]. Owing to its exceptional electrical conducting property, GO has been reinforced as conducting nanofiller to many polymers to modulate their high resistive nature [107-108]. High specific surface area of graphene derivatives is also advantageous in surface modification of many polymers [109]. Different properties of GO are presented in Table – 2.4 [94, 110 – 114].

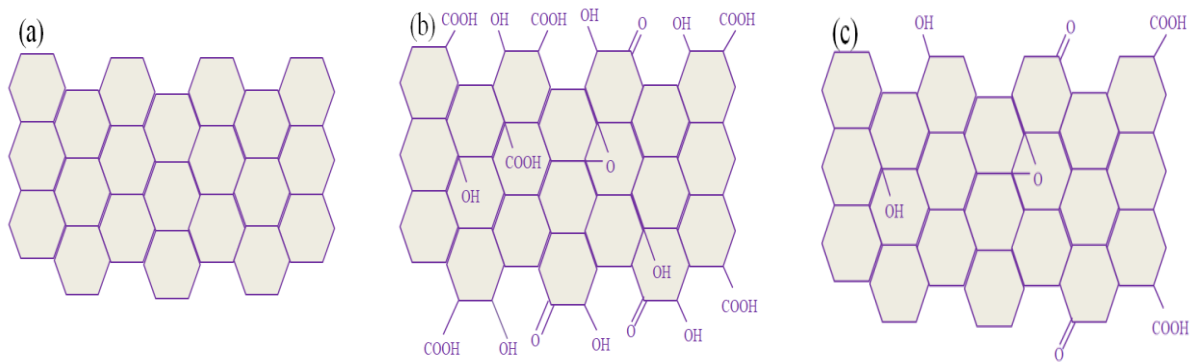


Fig. 2.2 Schematic structure of (a) pristine graphene (b) graphene oxide and (c) reduced graphene oxide

Table – 2.4 Different properties of graphene oxide (GO) measured by previous studies

Mechanical properties	
Density	3600 kg/m ³
Young modulus	380- 470 GPa
Intrinsic strength	38.6 – 46.3 GPa
Thermal properties	
Melting point	4510 K
Specific heat	765 J/kg-K
Thermal conductivity	3000 W/m-K
Thermal expansion coefficient	$1.25 \times 10^{-5} \text{ K}^{-1}$
Electrical properties	
Conductivity	$4.57 \times 10^{-8} \text{ s/cm}$
Dielectric constant	10^6 (at 1 kHz)
Other properties	
Band gap	3.84 eV

2.2. PVDF as a flexible ferroelectric layer

Recently PVDF garnered immense interest of researchers owing to its distinctive ferro, piezo and pyroelectric properties [115-117]. They have been utilized in a large scale for scientific researches and industrial applications due to having thermal stability, chemical resistance and membrane forming capability [118]. Moreover, they possess stable molecular dipole orientation in thermal equilibrium, closely packed crystal structure along with flexibility [119]. This stable permanent dipolar orientation of PVDF makes them ferroelectric substance. Their multifunctional abilities make them fruitful stuff in application in many electronic devices like, transducers, electronic skin, data storage and memory devices due to their non-volatile nature of memory [120].

They have also been widely used in switching devices owing to their polar nature [121]. But future microelectronic technology demand fast switching speed, low energy dissipation, compact size and long retainivity. Thus incorporation of various nanomaterials becomes inevitable. Recently, GO modified polar β -PVDF has shown great switching ratio maintaining high resistive state [122]. To achieve longer durability β -PVDF polymer has been blended by semiconducting polythiophene or organosilicate (OS) to retain its organic ferroelectricity based non-volatile memory [123-124]. They have also turned out to be a superior dielectric material as well with huge energy storing capacity [125-126]. But still solo PVDF has many disadvantages for their dielectric applications like extremely high resistance, high power dissipation, low mobility and slow response [127-128]. Nanomaterials like TiO_2 , ZnO , rGO, Zn , BaTiO_3 , MnO_2 , MgO are few among the dopant materials incorporated into this host polymer for betterment of its dielectric properties [129-135]. Recently polarization of PVDF has further improved along with its breakdown strength by inclusion of $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZCT) nanofibers [136]. Dielectric constant of PVDF has improved maintaining its loss factor by adding two dimensional $\text{Bi}_2\text{Te}_3@ \text{Al}_2\text{O}_3$ hexagonal nanoplates [137]. Again low loss ceramic dielectric like MgTiO_3 has been mixed with PVDF to achieve advantages of both of its components [138]. Moreover many tri-phase composites of PVDF have been developed to overcome inadequacies in these composites [139-142]. Surface structure modification of the polymer by these nanofillers is the key to modulation of these electrical properties.

Also large ferroelectric hysteresis in PVDF causes higher power dissipation obstructing in path for its device application. Thus in recent times PVDF has been loaded with numerous inorganic dopants to overcome this shortcoming. Many creative approaches like surface modification, core modulation, high dielectric material inclusion and layer structure techniques have been utilized. Ferroelectric nature of PVDF has also been improved by inclusion of various nanomaterials like BiFeO_3 , Fe_3O_4 , cobalt ferrite etc. [143-146]. Also P-E loop area of PVDF has also been modified by incorporation of nanomaterials, which in turn increases its energy storage capacity [147]. All such tremendous features of the ferroelectric polymer make it crucial for flexible electronic systems.

2.3 PVDF as piezoelectric nanogenerator

In recent time huge advancement has been made to fulfill necessity of energy from renewable sources to overcome energy crisis and also has an environmental aspect. Piezoelectric energy harvesting technique is one of such mechanism having potential to convert mechanical strain into usable electric energy. There are many discarded energy sources which can be used for transformation into usable electrical energy [148]. Recently PVDF and its copolymers are gaining immense attention because of their flexibility, chemical stability, sustainability and mechanical strength [59]. Out of many phases of PVDF, β , γ and δ phases possess a permanent polar structure results in non-zero dipole moment which leads to emergence of piezoelectricity [149]. Currently PVDF and its copolymer based flexible nanogenerators have emerged as a promising source of sustainable energy utilizing abandoned mechanical energy sources [150-151]. Many abandoned energy sources like acoustic energy, human motion, wind motion, ocean tides have been recycled into usable electrical energy by such piezoelectric nanogenerators [152-155]. Moreover, their piezoelectric nature enables us to use them in many electronic devices like pressure sensors, actuators, energy conversion devices and biomedical equipments [156 – 158].

But being an organic polymer, its piezoelectric energy harvesting capability is nowhere close to its inorganic counterparts like ZnO, BaTiO₃, PZT etc. [159–161]. But being brittle in nature, they cannot undergo enough mechanical stress. So composition of these inorganic materials with flexible PVDF arises out to be advantageous for betterment of piezoelectric capacity thereby providing flexibility. Currently PVDF has been used as host layer in development of many composite based nanogenerators by incorporating nanomaterials like ZnO nanoparticles, ZnO nanorod, GO, BTO etc. [162–165]. These PVDF based composite nanogenerators are exhibiting potential of delivering higher output power compared to that of pristine PVDF.