

Chapter-1

Chapter 1

Introduction

1.1 Biomaterial

Biomaterials are the materials of natural or man-made origins that are used to direct, supplement, or replace the functions of living tissue of the human body [Black (1995)]. They are used to make devices to replace a part or a function of the human body in protected, cost-effectively, and biologically acceptable mode.

“A biomaterial is a nonviable material used in a medical device, intended to interact with biological systems” (Williams, 1987).

Medical implant materials have history more than 2000 years ago, Romans and Chinese used gold in dentistry. Although, most of the biomaterials in the early years were not so successful due to unclear important concept related to infection and the biological reaction with materials. Over the centuries, these factors were firstly observed by British ophthalmologist Harold Ridley, while examining Spitfire fighter pilots who had remains of canopy plastic unintentionally implanted in their eyes from enemy machine gunfire, he observed these shards seemed to heal without ongoing reaction in 1940. His first implantation of such a lens was in 1949. At that same time, Harold Ridley was innovating Intraocular lens (IOLs), Charnley was developing the hip implant, Vorhees invented the vascular graft, Kolff was revolutionizing kidney dialysis, and Hufnagel invented the ball and cage heart valve. These innovators were accomplished biomaterials without understanding the relation of these materials with living system and saved lives and developed the platform for today's biomaterial [Ratner et al. (2004)].

Different varieties of biomaterials and implants are being used in the medical area. Several implants such as sutures, bone plates, joint replacement, ligaments vascular grafts, heart valves, intraocular lenses, dental implants etc. and devices are used in the biomedical area such as pacemakers, biosensors, artificial hearts, blood tubes etc. They replace or repair the function of traumatized or degenerated tissue or organs to help in healing, to recover function, to correct abnormalities and therefore recover the life of the patients [Ramakrishna et al. (2001)].

Biomaterials are important because they replace impaired organs, for better performance and increase the functionality. Biomaterials are of two types natural and synthetic material. Natural biomaterials are further categorized in two types: one is gelatin while another one is polysaccharides based. Synthetic biomaterials are categorized in Polymer (nylon, silicone, poly(vinyl chloride), polyester, polyurethane, polystyrene etc.), metals (Ti and its alloy, Co-Cr alloys, Au-Ag stainless steels etc.), Ceramics (alumina, zirconia, calcium phosphate including hydroxyapatite, carbon) and Composites (carbon-carbon, wire or fiber-reinforced bone cement).

1.1.1 Polymeric Biomaterials

One of the important class of biomaterial is polymeric materials that are extensively used in the biomedical field. The word “polymer” word is derived from the Greek term poly or meros, which means “many parts.” This term is accepted for a huge group of natural and synthetic materials with a wide range of properties [Carragher (2008)].

There are a large number of polymeric materials that have been used as implants or part of implant systems. The polymeric systems include acrylics, polyamides, polyesters, polyethylene, polysiloxanes, polyurethane, and a number of reprocessed biological materials. Some examples of polymeric materials having applications in biomedical fields are: artificial heart, kidney, liver, pancreas, bladder, bone cement, catheters, contact lenses, cornea and eye-lens replacements, external and internal ear repairs, heart valves, cardiac assist devices, implantable pumps, joint replacements, pacemaker, encapsulations, soft-tissue replacement, artificial blood vessels, artificial skin, and sutures. As bioengineers search for designs of ever increasing capabilities to meet the

needs of medical practice, polymeric materials alone and in combination with metals and ceramics are becoming increasingly popular for incorporation into devices used in the body.

Some unique properties of polymers are:

- 1- Flexibility;
- 2- Resistance to biochemical attack;
- 3- Good biocompatibility;
- 4- Light weight;
- 5- Available in a wide variety of compositions with adequate physical and mechanical properties;
- 6- Can be easily manufactured into products with the desired shape

Most of the polymers are simply synthesized and could be used as biomaterials while some polymers are mainly used in medical device fabrications from throwaway to long lasting implants [Lee et al. (2000)]. The main advantages of the polymeric biomaterials over the metal or ceramic materials are easy synthesis procedure to produce different shapes (due to easiness of secondary processability), cost effective, and accessibility with required mechanical and physical properties. The necessary properties of polymeric biomaterials are summarized in Table 1.1.

Table 1.1: Required properties in polymer for use as implant [Ratner et al. (2004)].

Requirements for Biomedical Polymers	
Properties	Description
Biocompatibility	Noncarcinogenesis, nonpyrogenicity, nontoxicity, and nonallergic response
Sterilizability	Autoclave, dry heating, ethylenoxide gas, and radiation
Physical property	Strength, elasticity, and durability
Manufacturability	Machining, molding, extruding, and fiber forming

As developments took place in biology and materials science, polymer researchers were quick to incorporate these new ideas into biomaterials [Ratner et al. (2004)]. Some frequently used polymers are listed below (Table 1.2) with their applications.

Table 1.2: Different type of polymers used in medical field [Ratner et al. (2004)].

Biomedical Application of Polymeric Biomaterials	
Synthetic Polymers	Applications
Polyvinylchloride (PVC)	Blood and solution bag, surgical packaging, IV sets, dialysis devices, catheter bottles, connectors, and cannulae.
Polyethylene (PE)	Pharmaceutical bottle, nonwoven fabric, catheter, pouch, flexible container, and orthopedic implants.
Polypropylene (PP)	Disposable syringes, blood oxygenator membrane, suture, nonwoven fabric, and artificial vascular grafts.
Polymethylmetacrylate (PMMA)	Blood pump and reservoirs, membrane for blood dialyzer, implantable ocular lens, and bone cement.
Polystyrene (PS)	Tissue culture flasks, roller bottle
Polyethyleneterephthalate (PET)	Implantable suture, mesh, artificial vascular grafts, and heart valve.
Polytetrafluoroethylene (PTFE)	Catheter and artificial vascular grafts.
Polyurethane (PU)	Film, tubing, and components.
Polyamide (Nylon)	Packaging film, catheters, sutures, and mold parts.

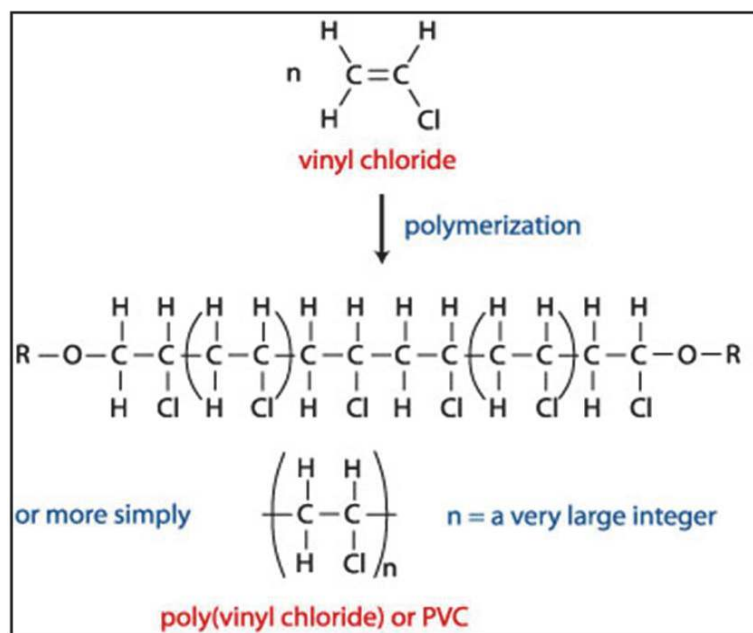
1.1.2 Poly(vinyl chloride) (PVC)

Poly(vinyl chloride), commonly known as PVC, is one of the oldest synthetic material. PVC was discovered unintentionally in the 19th century. French physicist and chemist Henri Victor Regnault in 1838 and German Eugen Baumann in 1872 discovered polymer which appeared as a white solid within flasks of the newly discovered vinyl chloride gas that had been left exposed to sunlight. The material was complicated to work with and no one mastered the challenge of commercial applications [Mallakpour et al. (2013)].

In the continuation of PVC history, German inventor Friedrich Heinrich August Klatte prepared PVC by polymerization of vinyl chloride in the presence of sunlight and patented it in 1913. Industrial scientist Waldo Semon developed synthetic PVC for replacement of the increasingly costly natural rubber in 1920 [Mallakpour et al. (2013)]. PVC is a colourless, rigid and amorphous in structure containing polar chlorine group in the structure with glass transition temperature of 115-135 °C. It is produced by polymerization of vinyl chloride by free-radical mechanisms in suspension and emulsion, bulk and solution processes [Mallakpour et al. (2013)]. Other applications in the medical field include blood storage bags, endotracheal tubes, dialysis tubing, and intravenous catheters.

Free radical polymerization is one of the most common and useful reaction for making polymers. It is used to make polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds (Scheme 1.1) [Odian et al. (2004)]. Free radicals are independently-existing species that have unpaired electron. Normally they are highly reactive with short life time. Free radical polymerizations are chain polymerizations in which each polymer molecule grows by addition of monomer to a terminal free-radical reactive site known as active centre. After each addition the free radical is transferred to the chain end.

In the long use of PVC in medical field, it causes some health problems due to leaching of plasticizer which has potential carcinogens leading to the pathogenesis of endocrine, pulmonary and hepato-toxicity. Other than this, PVC has poor biocompatibility due to its hydrophobic surface which attracts unwanted protein adsorption and cell adhesion.



Scheme 1.1: Schematic representation of polymerization of PVC.

To resolve these problems, considerable fundamental and applied research has been dedicated to the functionalization of PVC. The polymer surface chemistry plays an important role in contact of material in biological environment. By functionalization of polymer with different functional group, the performance of the polymer can be altered for biological compatibility.

1.1.3 Biomedical applications of PVC

PVC is most widely used plastic resin in medical devices. Approximately 25% of all plastic medical products are made of PVC. The main reason for this is the resin's low cost, ease of processing, and the ability to tailor its properties for a wide range of applications [Ramakrishna et al. (2001)]

The medical articles made from PVC are many folds: blood and solution bags, ventilation tubes, blood transfusion tubes, indwelling catheters, artificial prosthesis such as cardiovascular implants, orthopaedic replacements, intraocular implants, intravascular

and urinary catheters, surgical packaging, IV sets, dialysis devices, catheter bottles, connectors, cannulae etc. [Lee et al. (2000) and Chen et al. (2011)].

The following is a more thorough list of reasons for the popularity of PVC in medical devices [Ramakrishna et al. (2001)]:

- ❖ Used successfully for over 50 years in various medical devices with no known adverse or toxic effects.
- ❖ Plasticized PVC has good clarity and transparency retention so that tubes and other products allow for continual monitoring of fluid flow.
- ❖ PVC can be manufactured in a range of flexibilities and its resistance to kinking in tubing reduces the risk of fluid flow being interrupted.
- ❖ PVC can be used in a wide range of temperatures, and it retains its flexibility, strength, and durability at low temperatures.
- ❖ PVC formulations exhibit excellent strength and toughness.
- ❖ PVC exhibits very good chemical resistance and stability and is also biocompatible for applications in blood bags and drug delivery.
- ❖ Plasticized PVC maintains its product integrity under various sterilization environments like steam, radiation, and EtO.
- ❖ PVC can be easily welded to various other plastics by a wide range of methods.
- ❖ It's relatively lower cost and high-performance value maintains its position as the number one plastic used in medical devices.
- ❖ PVC has safety and cost advantages for a wide variety of medical applications, especially for single-use disposable devices.

1.1.4 Merits and Demerits associated with PVC

Most biomaterials and medical devices perform satisfactorily, giving better quality of life for the receiver or patient by saving lives. However, synthetic materials are never perfect leading to failure of the material. Other than this, every human is different from other in respect of genetics, gender, body chemistries, living environment, and physical movement. Moreover, physicians also differ in their "talent" for implanting devices. The

other side to the medical device success story is that there are problems, compromises and complications that occur with these devices. Like other biomaterial, PVC also suffers such type of problem. PVC is a rigid polymer; plasticizers are incorporated into increase its flexibility. The esters of phthalic acid, particularly di(2-ethylhexyl)phthalate (DEHP), are the most preferred plasticizers for medical grade PVC. However, because these additives are not bound to the base polymer by covalent bonds, their component may leach out when come in contact with biological system [Hanawa et al. (2000); Inoue et al. (2003); Ito et al. (2006); Faouzi et al. (1999); Allwood (1986); Tickner et al. (2001)].

Matsumoto et al. (2008) described in detail about phthalic acid esters used as plasticizers and their adverse effect on reproduction in humans. Hauser et al. surveyed phthalate effect on human from 1973 to 2005. Other than this, another factor for its failure is microbial adhesion on PVC surface observed when it used as catheters which causes major complications. After adhesion and growth of infectious microorganisms on a biomaterial surface, the biofilm mode of growth protects the organisms against the host defense system and antibiotics. However infection related problems can be overcome by immobilizing antibacterial agent on PVC surface but that cannot be a permanent solution.

Above problems can be improved by functionalization of PVC or its ionomers and through making their composites. Because surface charge can decrease the hydrophobicity of material and increase their functionality.

1.1.5 Functionalization of PVC

Polyvinyl chloride (PVC) faces many problems due to hydrophobic nature of its surface. The existing estimation is that the surface hydrophobicity may carry onward severely unfavourable consequences, in particular when such materials are exposed to biological systems. This has enthused extensive research during recent decades seeking efficient means to figure out the problem [Asadinezhad et al. (2012)]. An obvious solution of this problem is to take advantage of functionalization of polymers.

Functionalization in polymer science is necessary because material itself cannot produce a covet polymer but through modification it may be possible. Modification of

PVC has received greater attention as it brings specific properties to be acquired for various application, such as, PEG was used by Balakrishnan et al. (2005) and DEHP was used by Zhao et al. (2008) to enhance blood compatibility. PEG was also used by Chen et al. (2011) Zha et al. (2009) used Iron, heparin and dextrin sulfate to enhance hydrophilicity of PVC, Asadinezhad et al. (2010) used antibacterial agent for PVC functionalization, Balazs et al. (2003) modified PVC by oxygen glow discharge, Kameda et al. (2011) and James et al. (2003) functionalized PVC by thiocynate group to acquire antibacterial surface, Lakshmi et al. (2002) used thiosulphate to prevent plasticizer migration. Other than this, PVC was functionalized for packaging materials by Pearson et al. (1982), Sadat-Shojai et al. (2001) and Zhang et al. (2009) for recycling of waste and water treatment.

In view of the given structure-property relationship of polymer modification, PVC is motivated for alteration in its properties. The modification of PVC leads to change in surface properties such as, surface chemistry, surface energy, surface topography, etc. that could be critical for assessing the biocompatibility for consideration in medical applications [Kameda et al. (2011), Zha et al. (2009)].

1.1.6 Methods for Modification of PVC

Generally, PVC functionalizes (Figure 1.5) by chemical and surface modification methods [Kameda et al. (2009); Ratner (1995); Hoffman (1995); Reyes-Labarta et al. (2003); Moulay (2010)]. Further, surface modification categorized by three types: physical methods [Oehr (2003)], chemical methods or reagent treatment [Sacristn et al. (2000); Bigot et al. (2013)] and physical-chemical methods.

1.1.6.1 Surface modification

As the Figure 1.5 describes, surface modification of PVC can occur by three routes. There are several reports available for PVC modification. However, all different methods used for surface modification have more or less common interests from chemical and physical viewpoints. In the subsequent paragraphs, a short background is specified for different techniques employed for the surface modification method [Asadinezhad et al. (2012)].

Physiochemical covers firstly plasma treatment, which is widely used method for surface modification because partially ionized gas containing free electrons, ions, and radicals, as well as neutral particles used for this treatment, different type of reaction occur between these molecules and the surface of polymer.

a) Physical method

Physical method describes the adsorption of Langmuir-Blodgett films. Several reporters described detailed reports about surface chemical modification, which has been performed by the functionalization of gaseous reagents, liquid reagents, by the vapour phase chemical grafting and liquid phase chemical grafting. Other than two, in physiochemical modification, several sub type of modification also occur such as plasma discharge, corona discharge, UV irradiation, laser ion beam, electron beam and γ irradiation for several application.

Different types of modification possible in the plasma treatment such as plasma polymerization in which an organic monomer in solution or vapor phase is polymerized, plasma functionalization in which various chemical groups gets attached to the surface, and plasma etching develops a coating on the surface [Asadinezhad et al. (2012)]. Zhang et al. (2013) used oxygen and argon for plasma treatment to examine effect of diethyl phthalate (DEP) and dibutyl phthalate (DBP) plasticizer migration from the PVC surface. Khorasani et al. (2007) also used this method on PVC blood bags with the result that their surface becomes more hydrophilic and gets negative charge which reduces fibroblast cell growth. Asadinezhad et al. (2012) used physiochemical method to graft antibacterial molecule on medical grade PVC for generating antibacterial surface.

b) Physiochemical modification (Grafting)

This method is corona discharge; ozone is put directly on the polymer surface and consequently O_3 formation-decomposition combined reactions occur there. Dumitrascu et al. (2000) used this method for the enhancement of wettability and porosity of PVC surface without affecting bulk properties of polymer surface. Same procedure occurs with

UV irradiation (Figure 1.1) including γ -radiation, β -irradiation (electron beam), and ion radiation method which support the reaction kinetics rather than decomposition phenomenon on the surface. Hydrogen ions, noble gases, gold particle etc. are also used for this modification, which act as high energy photons and deliver surface radicals who act as initiating sites for subsequent functionalization. These techniques are easy and preferably used for surface grafting of polymers. The extent of surface modification may be well controlled by fine-tuning the irradiation time, monomer concentration, photoinitiator, and solvent. The solvent selection is very critical in this context, as the treatment can be run in vapor phase also (Figure 1.2) [Asadinezhad et al. (2012)]. Dumitrascu et al. (2000) compared the two methods of PVC modification, chemical grafting of hydrophilic molecules and corona discharge with helium on medical grade PVC. The result proved that, both the methods increases the hydrophilicity of the modified PVC surface compared to that of pure PVC but cracks appear on chemically grafted polymer surface [Dumitrascu et al. (2000)].

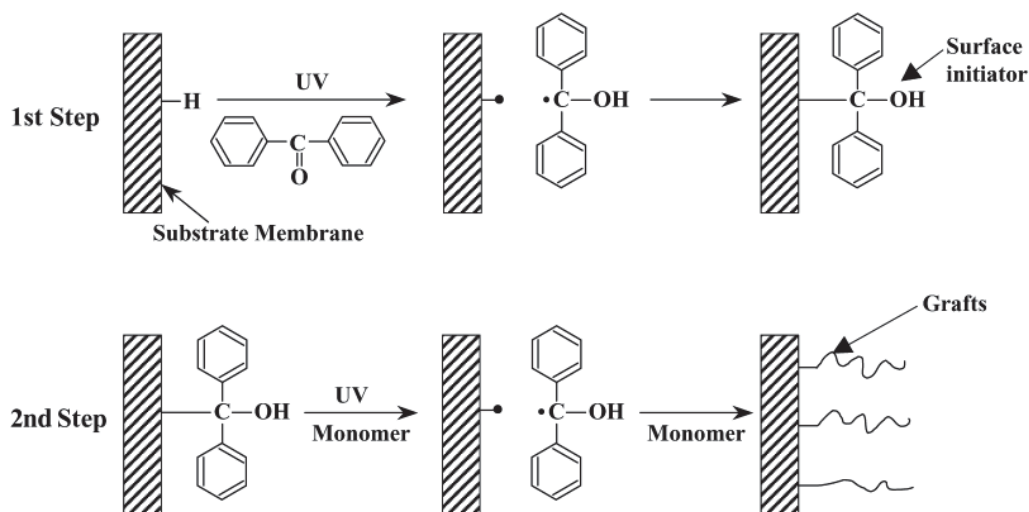


Figure 1.1: Schematic diagram of a novel photo-induced living graft polymerization method [Ma et al. (2000)].

Another approach for PVC modification is Langmuir-Blodgett (LB) films, in which

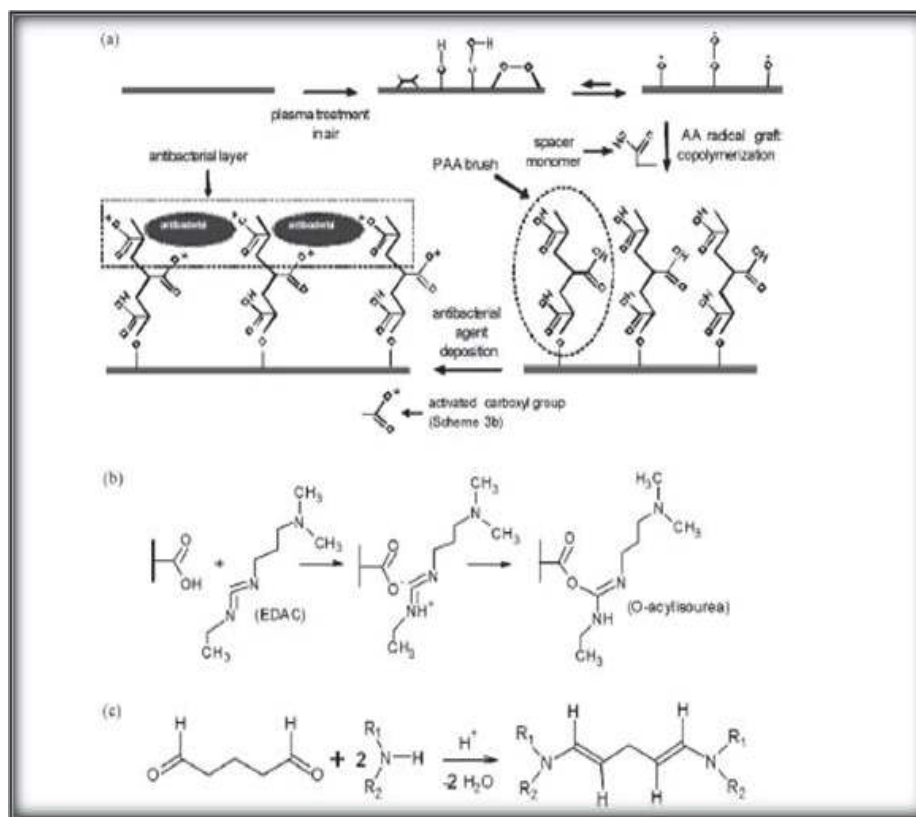


Figure 1.2: Schematic representation for multistep strategy for deposition of antibacterial agent on PVC surface in physiochemical approach (a), carboxyl group activation mechanism by EDAC (b), and enamine formation following secondary amine and glutaraldehyde reaction [Asadinezhad *et al.* (2012)].

polymer film is immersed in one or more monolayer of organic solution to obtain the homogeneous layer over the polymer surface. Preininger *et al.* (2000) used this for immobilization of Ig G antibody on the PVC surface and Gönen *et al.* (2010) used Langmuir-Blodgett (LB) films method for obtaining calcium stearate film.

c) Surface chemical modification

The last method of surface modification is chemical surface modification, in which a nucleophile is dissolved in aqueous solvent with a polymer film and substitution, elimination reaction occur on the surface of polymer film. This is also popular method for

surface modification of polymer film. A number of literatures are also available for surface modification of PVC by different functional groups. Sacristán et al. (2000) modified sodium azide and amino thiophenol by phase transfer catalyst. Lakshmi et al. (2002) used thiosulphate to reduced plasticizer migration and sodium sulphide for enhancing biomedical application for medical grade PVC [Lakshmi et al. (2003)]. Chen et al. (2011) functionalized plasticized PVC with poly(ethylene) glycol to increase wettability and Kameda et al. (2011) used thiocyanate to achieve antibacterial surface.

1.1.6.2 Modification by atom transfer radical polymerization

Atom-transfer radical polymerization (ATRP) has been one of the most efficient controlled/living-radical polymerization (CLRP) methods for the modification of PVC. The controlled chain growth and living nature of ATRP make it very useful for the preparation of well defined block and graft copolymers. Another advantage of this method over common radical initiation methods is that only negligible homopolymer formation is observed when it is employed in graft copolymerizations. Liu et al (2006) graft the functional polymer poly(hydroethyl acrylate) (PHEA) from commercial cross-linked PVC beads and then to hydrolyze the ester groups into carboxyl groups to yield poly(acrylic acid)-grafted cross-linked poly(vinyl chloride) (PAA-PVC) (Figure 1.3) beads for the extraction of heavy metal ions such as Cu(II), Zn(II), Cd(II), and Hg(II) from aqueous solutions.

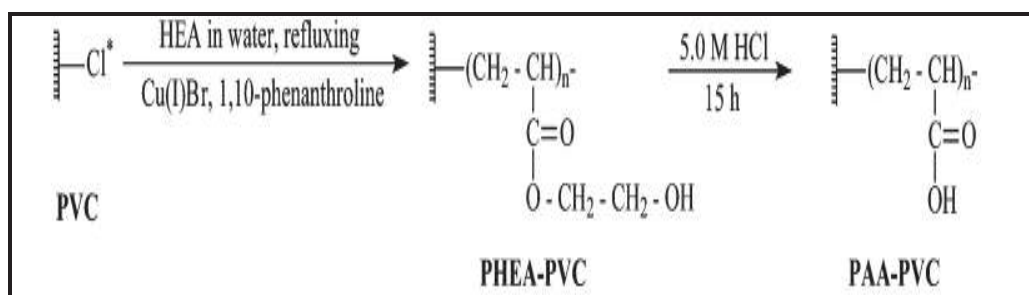
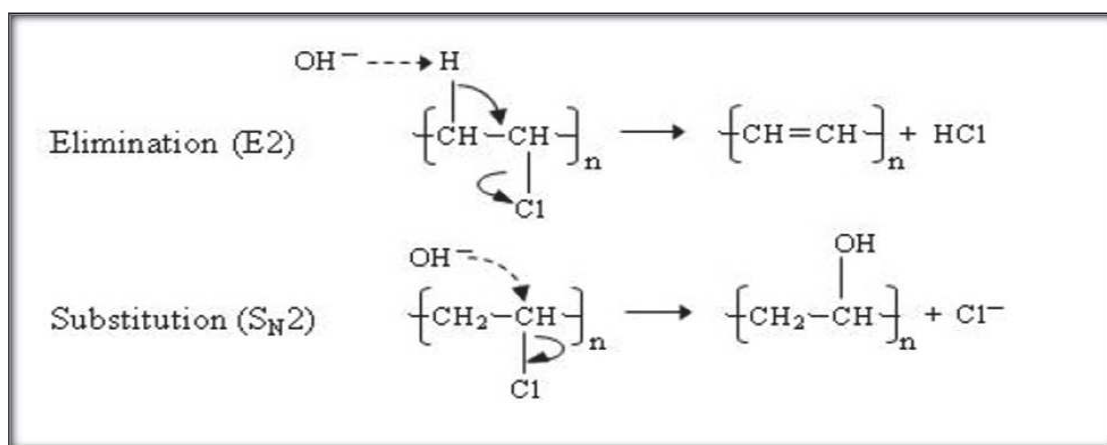


Figure 1.3: Modification of PVC by atom transfer radical polymerization [Liu et al. (2006)].

1.1.6.3 Chemical modification of PVC

Although, all the above methods are good for modification of PVC but they may lose transparency of the polymer films due to the treatment over the surface which can be overcome by the chemical modification of PVC resin. Chemical modification of PVC resin has been reviewed by a number of authors with a series of functional groups [Reinecke et al. (1997); Lpez et al. (1997); Hidalgo et al. (1997); Bicak et al. (2001)].

As previously reported, the properties of PVC can be altered by replacing the chlorine atom as shown in Scheme 1.2 in PVC chain by other atom or groups without any side reaction because chlorine atom is responsible for all the properties such as, the high value of the glass transition temperature, T_g interactions of the polymers with, solvents, dielectric response etc. [Lpez et al. (1997); Bicak et al. (2001)].

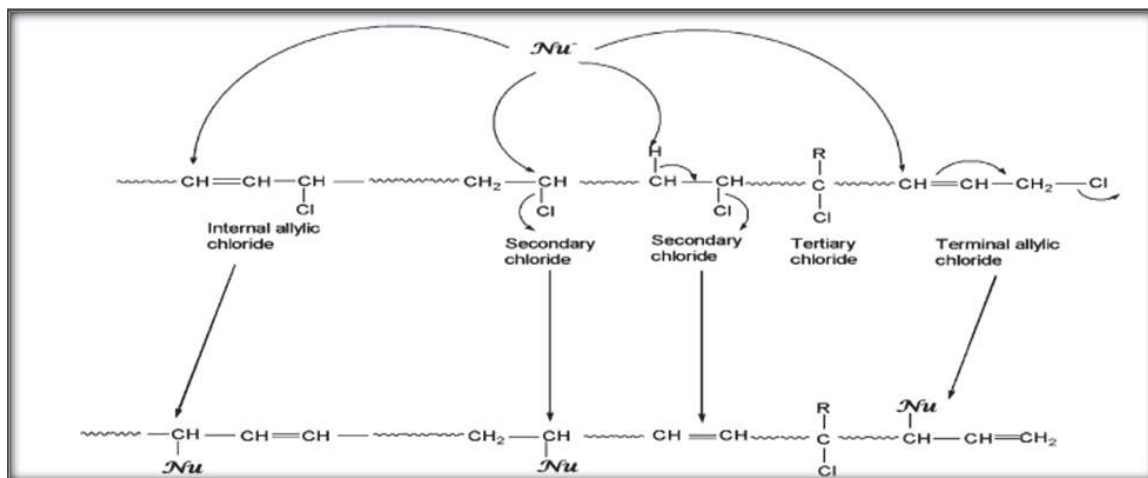


Scheme 1.2: Schematic representation of the mechanism involves in chemical modification of PVC [Kameda et al. (2010)].

The main principle behind the modification of PVC is a nucleophilic substitution reaction that provides an opportunity for steady replacement of chlorine atoms through desired atoms or groups without any side reactions (Scheme 1.2).

Considerably, nucleophilic substitution has been the most studied reaction. However, when the basicity of the nucleophile (Nu⁻) prevails over its nucleophilicity, β

elimination of HCl may strongly compete with substitution, as illustrated in Scheme 1.3 [Moulay (2010)]. Modification of PVC have been carried out in both wet and dry processes and in various circumstances for example organic media, aqueous solutions, aqueous suspensions, phase transfer catalyses, solvent/non-solvent systems. The nature of the nucleophile is not the only parameter that affects the degree of modification, but there are several other factors such as, the nature of solvent, the temperature, and the duration of the reaction in wet method. Kameda and co-workers [Kameda et al. (2010)] examined this effect with five different nucleophiles, Iodide ion (I^-), thiocyanate ion (SCN^-), hydroxide ion (OH^-), azide ion (N_3^-), and phthalimide anion, in two different solution, Ethylene glycol (EG) and N, N -dimethylformamide (DMF) as solvents. At 190 °C, nearly 95% dechlorination occurred with N_3^- and OH^- in 1 hour, however, it was slower for the remaining nucleophiles, and the degree of dechlorination was observed to be 98 and 60% after 6 h for SCN^- and I^- , respectively in EG.



Scheme 1.3: Schematic representation of possible reaction site in PVC [Moulay 2010].

When the reactions were performed in DMF the reaction temperatures had to be changed dependent on the nucleophile to get hold of a sensible reaction rate: room temperature for OH^- , 60 °C for I^- and phthalimide anion, and 100 °C for SCN^- and N_3^- . Unlike the result

with EG, the dechlorination outcome was not good for all of the nucleophiles with DDs (or DSs) of 11 (3.6), 30 (18.7), 14 (0), 98 (66.1), and 55% (10.5%), respectively. Elimination predominated, but not as completely as in EG solvent, because DMF is known to be a good solvent for nucleophilic substitution. In addition, they also observed the effect of phase transfer catalyst (PTC) tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogen sulfate (TBAHS) with SCN^- nucleophile and EG used as solvent. TBAB performed slightly more substitute compare to TBAHS and no modification occurred without the PTC. While, adding together of nitrobenzene with TBAB to $\text{SCN}^- / \text{H}_2\text{O}$ increased substitution [Kameda et al. (2010)].

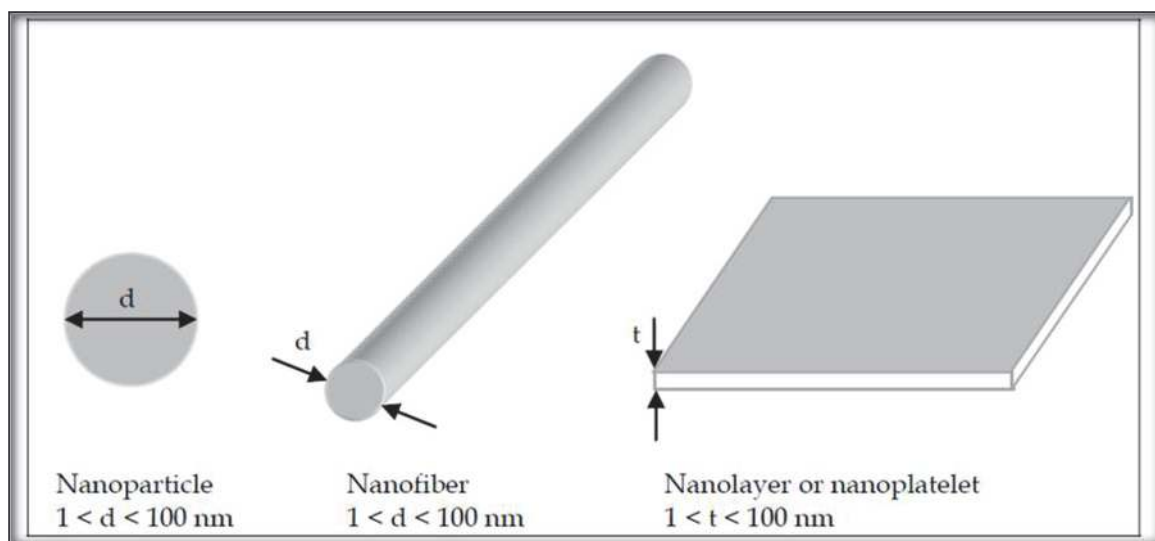
An extra approach, to make material better is polymer nanocomposites synthesis. Various types of natural and synthetic nano clay are available for this purpose.

1.2 Composites

A composite material is prepared by combining two or more materials – which have very different properties. The two materials work together to give the composite its distinctive properties. The major benefit of composite materials is to give flexibility because many of them can be moulded into complex shapes and without showing any increase in their weight and provide strength. The aspect ratio of the filler is very important and crucial for many properties of better composite such as electrical [Al-Saleh & Sundararaj (2010); Grossiord et al. (2008)], mechanical [Zhang et al. (2007)] and thermal [Meneghetti et al. (2006)] properties. Polymer composites with the high aspect ratio of nano-fillers such as platelet clays, carbon nanotubes and nanofibers are receiving considerable attention due to their unique multifunctional and highly enhanced properties. Combination of filler nanoscale dimension and high aspect ratio with its nanoscale dispersion within polymer matrix leads to significant improvements in the polymer properties at very low filler volume fractions. As a result using filler in lower amount, the macroscopic homogeneity and low density of primary polymer retains as well as its opacity in the final nanocomposite system is also retained.

This is well-known as nano-effect. In other words the effect of nanofillers on the polymer properties is different from that predicted by using thermodynamical studies for

reduced particle size fillers [Gacitua et al. (2005)]. Studies and modelings using continuum mechanics reveal that the enhanced properties of nanocomposites are strongly dependent on features of nanofiller system, in particular, its content, aspect ratio and the ratio of filler particles in the matrix (Sheng et al. 2004). The nanoscale is considered where the dimensions of filler particles (diameter), platelets (thickness) or fibers (diameter) are in the size range of 1-100 nm (Scheme 1.4).



Scheme 1.4: Schematic representation of various types of nanofillers with nanoscale dimension [Olad et al. (2011)].

1.2.1 Types of reinforcement in polymer composite

Polymer nanocomposites are the new class of hybrid materials in this category (Mittal 2009). Wu et al. (2010) described various types of layered silicates nanoclay for synthesis of polymer nanocomposites. Paul et al. (2008) observed different polymer nanocomposites, their structure, properties and application in various fields and discussed about different nanoclay such as, SWCNT (single-walled carbon nanotube); MMT (montmorillonite); MWCNT (multi-walled carbon nanotube) and other inorganic clay example LDH (Layered double hydroxides). LDH is one of the most favourable inorganic clay for polymer nanocomposites due to cost effective method.

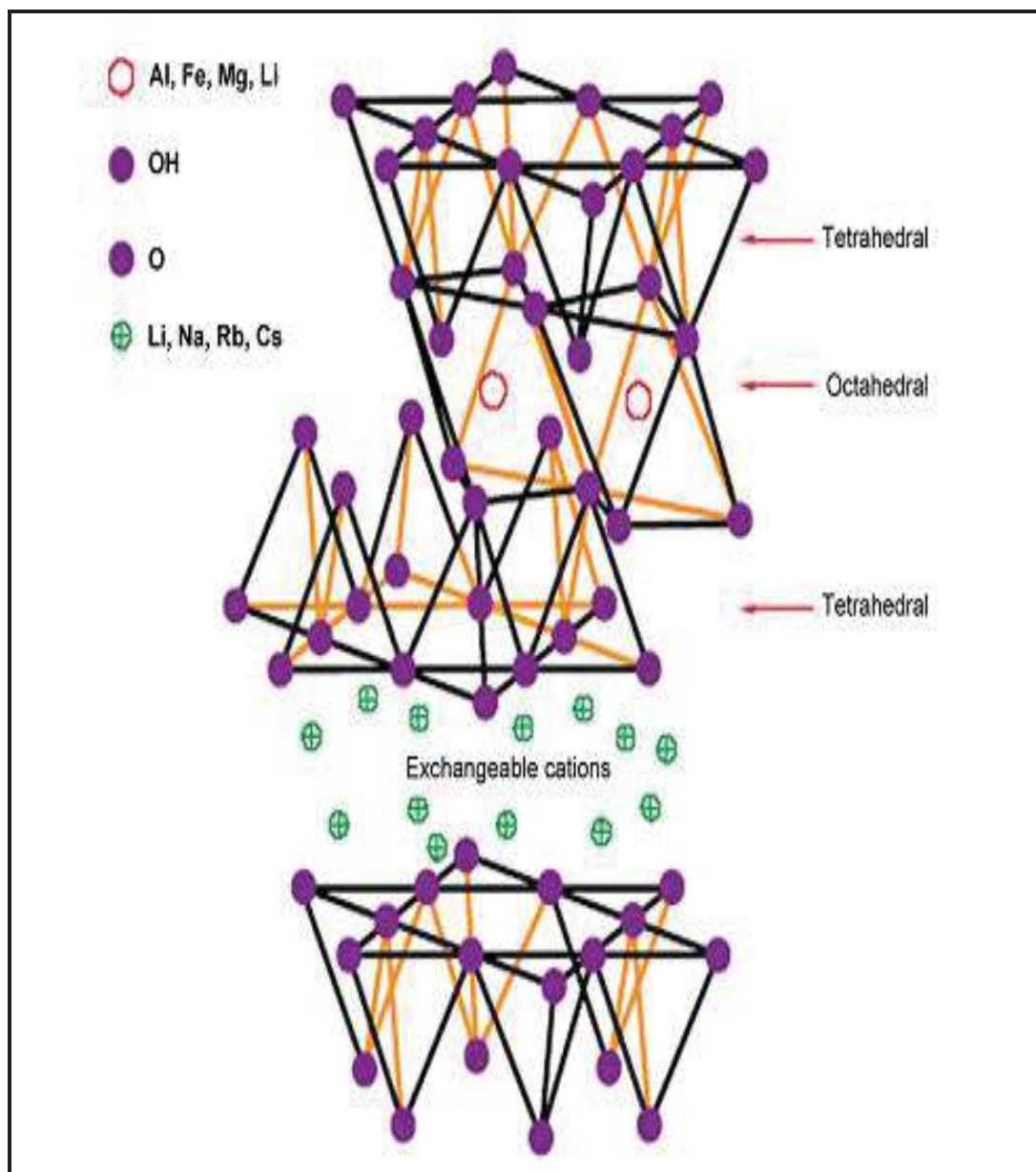


Figure 1.4: The structure of a 2:1 layered silicate [Pavlidou et al. (2008)].

1.2.1.1 Layered silicates:

The layered silicates are natural or synthetic minerals consisted of the regular stacks of aluminosilicate layers with a high aspect ratio and high surface area. Layered silicates are easily available and have low cost. The current most popular layered silicates used in polymer nanocomposites preparation are clays [Olad (2011)]. Their basic building blocks

are tetrahedral sheets in which silicon is surrounded by four oxygen atoms, and octahedral sheets in which a metal like aluminum is surrounded by eight oxygen atoms [Pavlidou et al. (2008)].

a) Kaolinite:

It is a very simple 1:1 structure. It is only tetrahedral sheet is combined with an octahedral sheet, and both the sheet bounded by the oxygen atoms are shared [Pavlidou et al. (2008)].

b) Phyllosilicates:

It is the crystal lattice of 2:1 layered silicates consists of two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets, as shown in Fig. 1.4. The basic 2:1 structure with silicon in the tetrahedral sheets and aluminum in the octahedral sheet, without any substitution of atoms, is called pyrophyllite [Pavlidou et al. (2008)].

c) Montmorillonite (MMT):

If in the original pyrophyllite structure the trivalent Al-cation in the octahedral layer is partially substituted by the divalent Mg-cation, the structure of montmorillonite is formed, which is the best-known member of a group of clay minerals, called “smectites” or “smectite clays”. In this case the overall negative charge is balanced by sodium and calcium ions, which exist, hydrated in the interlayer. A particular feature of the resulting structure is that, since these ions do not fit in the tetrahedral layer, as in mica, and the layers are held together by relatively weak forces, water and other polar molecules can enter between the unit layers, causing the lattice to expand [Pavlidou et al. (2008)]. Montmorillonite, hectorite and saponite are the layered silicates that are most commonly used in nanocomposite materials. Their chemical formula is given in Table 1.3 [Pavlidou et al. (2008)].

1.2.1.2 Modified layered silicates

The direct physical mixture of a polymer and layered silicate (in natural form) may not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation has takes place into discrete phases. Nano level dispersions are existed when polymers and layered silicates have been strongly interacted in polymer/layered silicate nanocomposites and this phenomenon leads to the organic and inorganic phases. The nano level dispersions exhibit unique properties are not obtained in micro counterparts or conventionally filled polymers. Generally, pristine state layered silicates are only miscible with hydrophilic polymers, in order to render layered silicates miscible with other polymer matrices, layered silicates must be hydrophobic or organophilic. One can achieve this property to layered silicates by ion-exchange reactions with long chained cationic surfactants including primary, secondary, tertiary, and quaternary alkyl ammonium or alkyl phosphonium cations shown in Figure 1.5. During ion-exchange reactions the organic surfactants with positively charged ends, are tethered to the surface of the negatively charged silicate layers, resulting in an increase of the gallery height [Kim et al. (2001)].

Table 1.3: Chemical formal of 2:1 phyllosilicates (layered silicates) [Pavlidou et al. (2008)].

2:1 Phyllosilicates	General formula
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$

M: monovalent cation; x: degree of isomorphous substitution (between 0.5 and 1.3).

Additionally the organic surfactants can provide functional groups that can react with polymer matrix and sometimes they initiate polymerization [Chin et al. (2001)]. Suitable

gallery spacing and microchemical environment are available for intercalation of polymer molecules when layered silicates are modified with organic surfactants [Huang et al. (2001)]. Conclusively, the surface modification process is enhance the basal spacing of clays and made compatible as hydrophilic clay to hydrophobic polymer [Zerdaet al. (2001)].

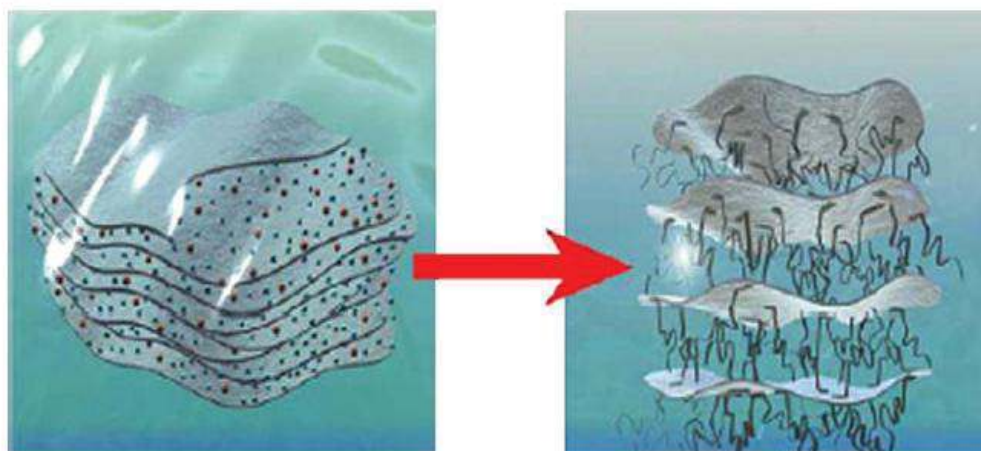


Figure 1.5: Schematic picture of ion-exchange reaction in layer structured silicates [Pavlidou et al. (2008)].

1.2.1.3 Graphene

It is a two-dimensional, sp^2 bonded carbon atoms, and has a higher surface-to-volume ratio. This makes graphene potentially more favorable for improving the properties of polymer matrices, such as electrical properties. Therefore, graphene-based polymer composites have attracted both academic and industrial interest [Khanam et al. (2015)]. By using conventional processing methods, graphene composites can be easily fabricated into intricately shaped components with excellent preservation of the structure and properties. This is very important to make full use of the outstanding properties of graphene. Tapan et al. (2013) prepared different grapheme/polymer composites (Poly (Polyaniline/Graphene, 3,4-Ethyldioxythiophene)/Graphene, Epoxy/Graphene, Polyurethane (PU)/Graphene, Polyvinyl Alcohol (PVA)/Graphene, Poly Vinylidene

Fluoride (PVDF)/Graphene, Polyethylene Terephthalate (PET)/Graphene, Nanocomposites, Polycarbonate (PC)/Graphene, Nafion/Graphene Nanocomposites) for electronic devices, sensor, energy storage and biomedical applications.

1.2.1.4 Carbon nano tube (CNT)

It is well established that structural perfection is more and more nearly reached as the reinforcing elements become smaller and that the ultimate properties of reinforcing composite elements may be expected if their dimensions reach atomic or molecular levels. Larger is their internal surface and hence their tendency to agglomerate rather than to disperse homogeneously in a matrix [2]. Carbon nanotubes can be classified into single-walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs) and carbon nanofibers (CNFs). SWNT with a diameter of 1–2 nm consists of a single graphene layer wrapped into a cylindrical shape, and hemispherical caps seal both ends of the tube. SWNT can be further divided into three classes, i.e. armchair, zigzag and chiral depending on the arrangement of hexagons in their structures (Figure 1.6) [Tjong (2006)].

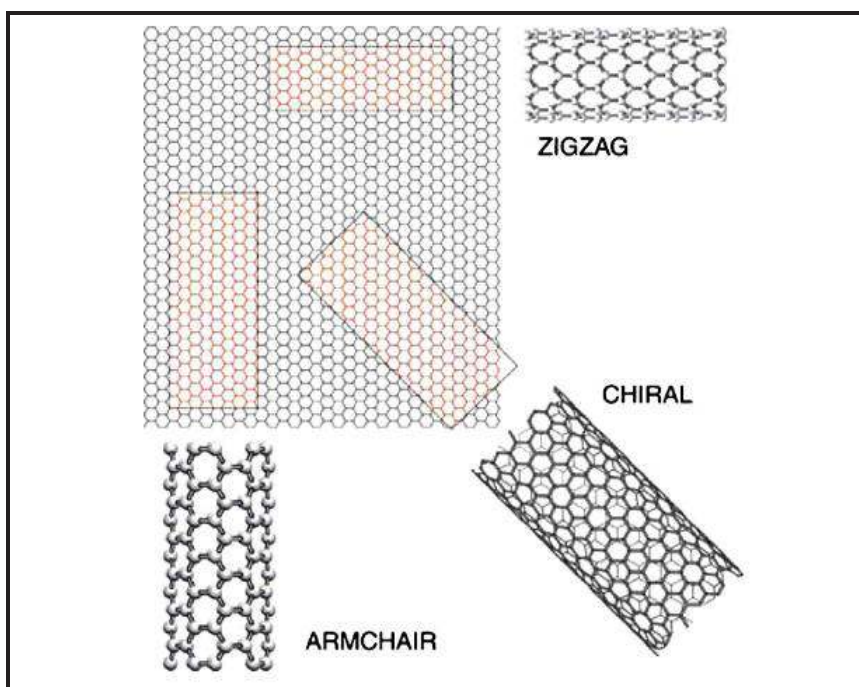


Figure 1.6: Different types of CNT structure [Tjong (2006)].

1.2.2 Polymer nanocomposites structure

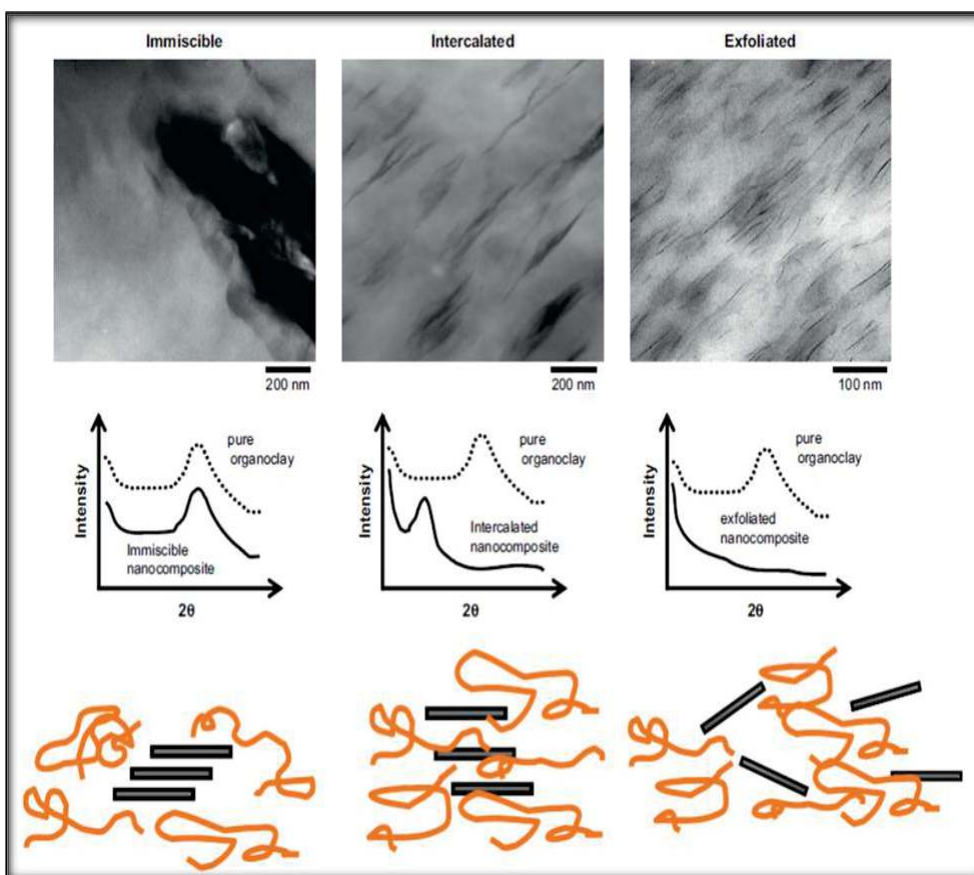
Polymer nanocomposite is one of the most fascinated extensive areas for current research for enhancing polymer properties and extending their applications in various fields, by using nanoscaler materials support [Ishida et al. (2000)]. A nanocomposite is made up of two materials in which one material is in the nano size (Figure 1.4). The term nanocomposite signifies a new and exciting field which combine many fields together such as biology, chemistry and nanotechnology etc. The nanocomposite technology has emerged as an efficient and powerful strategy to upgrade the structural and functional properties of synthetic polymers as well as natural polymer [Olad et al. (2011)].

Polymer nanocomposites have attracted great attention worldwide academically and industrially due to the exhibition of superior properties such as modulus, strength, toughness and barrier far from those of conventional micro composites and comparable with those of metals. However polymer nanocomposites have added advantage of lower density and ease of processability. In polymer nanocomposites, the filler has at least one dimension in the nanometer scale and its nanoscale dispersion within the polymer matrix leads to the tremendous interfacial contacts between the polymer and inorganic filler which causes to the superior properties than those of bulk polymer phase. When the dimensions of filler particles are decreased to the nanoscale, their properties also change significantly (Kumar et al. 2009).

Generally, the structure of polymer nanocomposites is based upon the level of intercalation and exfoliation of polymer chains into the interlayer space between the clay. Intercalation and exfoliation depends on diverse factor such as clay nature, organic modifier, and polymer matrix and also on preparation method through which different composite micro-structures can be obtained [Olad et al. (2011)].

Incorporation of nanoparticles to thermosets and thermoplastics polymers have been shown to greatly increase the final nanocomposite properties. A key component to achieve these improvements in properties lies in the proper dispersion of the nanoparticles in the polymer matrix. Some of the most commonly used methods for dispersing nanoparticles in polymers include: mechanical mixing, magnetic stirring, and sonication. It has been reported by many researchers that poorly dispersed nanoparticles

could degrade the mechanical properties of polymers. Depending on the mixing technique used, conventional nanoclay reinforced composites can take the form of phase-separated microcomposite, intercalated nanocomposites, or exfoliated nanocomposites (Scheme 1.5) [Agubra et al. (2013)].



Scheme 1.5: Schematic representation of different states dispersion of organoclay in polymers [Paul et. al. (2008)].

1.2.2.1 Immiscible structure

In this, organic polymer is not capable to enter into the interlayer space of nano material and the clay is dispersed as aggregates or particles with layers stacked together within the polymer matrix. The obtained composite structure is considered as immiscible or “phase separated”. The properties of phase separated polymer/clay composites are in the range of

traditional micro composites [Olad (2011)]. The d -spacing of the layers structures remains nearly identical to their perfect state. Therefore, properties of composite remain the same as that of traditional microcomposites [Liu et al. (2006)].

1.2.2.2 Intercalated structure

When polymer chains penetrate into the galleries of nano clay and enhance their inner layer spacing, without effecting the periodic arrangement of the clay layer resultant intercalated nanocomposite is formed. This combination provides a well-organized multilayer hybrid structure with high interference relations between the polymer and nanoclay [Olad (2011)]. Subsequently, the interlayer d -spacing is also expanded, but only to a limited extent (usually on the order of 20-80 Å) [Liu et al. (2006)].

1.2.2.3 Exfoliated structure

When the layers of nano clay separated after incorporation of polymer chains in it, exfoliated structure formed and individual layers are dispersed within the polymer matrix. Due to the enhancement of interlayer spacing more than 80-100 Å, and well dispersion of individual clay layers, significant improvement in polymer properties is obtained due to the large surface interactions between polymer and clay [Olad (2011)].

1.3 Layered double hydroxides (LDH)

Layered double hydroxides (LDHs) have been known for over 150 years since the discovery of the mineral hydrotalcite. Layered double hydroxides (LDHs) belong to a general class called anionic clay minerals. They can be of both synthetic and natural origin [Costa et al. (2008)]. LDHs can be structurally characterized as containing brucite- (magnesium hydroxide-) like layers in which some divalent metal cations have been substituted by trivalent ions to form positively charged sheets. The metal cations occupy the centres of octahedral whose vertices contain hydroxide ion. These octahedra are connected to each other by edge sharing to form an infinite sheet. The cationic charge created in the layers is compensated by the presence of hydrated anions between the stacked sheets.

LDHs have the general formula $M^{II}_{1-x}M^{III}_x(OH)_2(A^{n-})_{x/n} \cdot m H_2O$, where M^{II} is a divalent cation (Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , or Ca^{2+}); M^{III} is a trivalent ion (Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} , or La^{3+}) and A^{n-} is the gallery anion such as Cl^- , CO_3^{2-} , NO_3^- , etc. [Costa et al. (2008)]. Figure 1.7 schematically illustrates the LDH structure.

There are several methods for synthesizing LDH compounds such as co-precipitation, sol-gel synthesis, salt-oxide reaction, hydrothermal growth and electrochemical synthesis. However, all of these methods are not appropriate and equally efficient for every combination of metal ions [Costa et al. (2008)]. The co-precipitation method describes the immediate precipitation of a selected pair of metal ions from their mixed aqueous solution by dilute NaOH and/or $NaHCO_3$, Na_2CO_3 , or NH_4OH solution at the pH range 8–10 of the reaction.

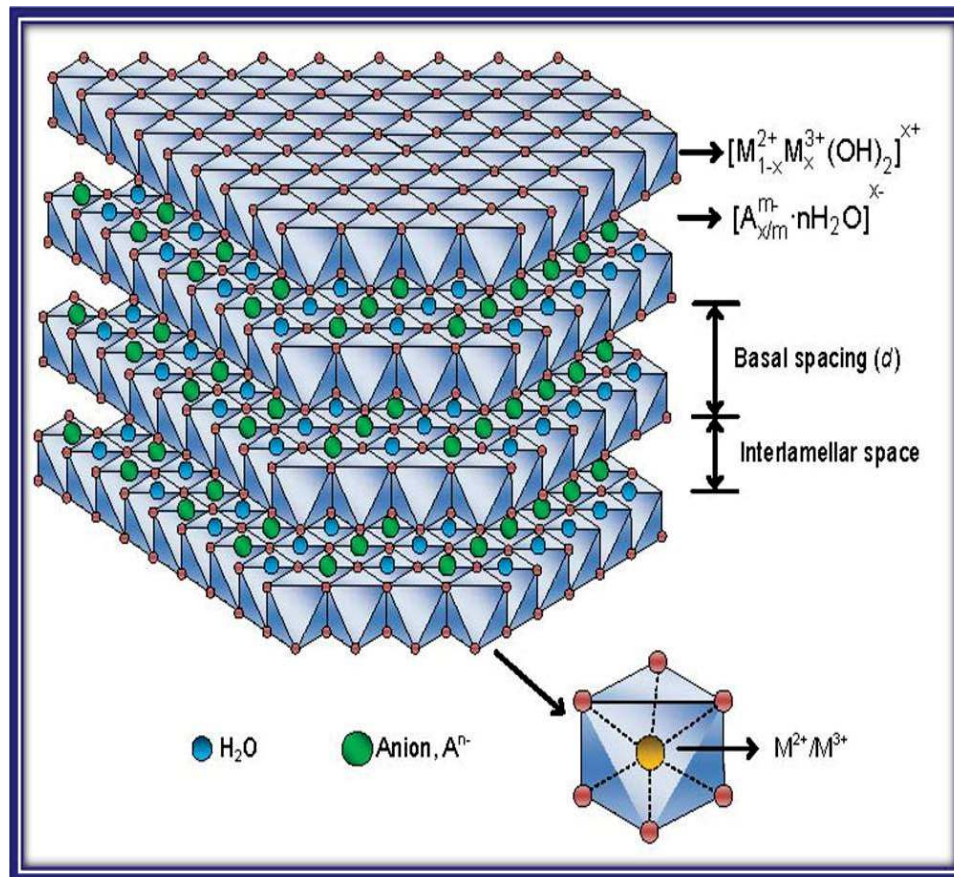


Figure 1.7: Atomic structure of layered double hydroxides (LDH) [Tronto et al. (2013)].

In hydrothermal process, final suspension is usually carried out to obtain well-crystallized sample. One more method is “Urea hydrolysis” method, where an aqueous solution of desired metal ions and urea in proper molar ratio is heated at 90 °C to reflux temperature for 24–36 h. Resultant urea molecules undergo decomposition producing ammonium carbonate and a fine distribution LDH of particle size containing CO_2^{-3} as the intercalating anion is also formed. In the ion exchange method, the interlayer anions in LDHs are replaced by other anionic species [Costa et al. (2008)].

1.3.1 Properties of LDHs

The aim for addition of clay minerals to the polymers is to improve the polymer properties and to produce the polymer/clay nanocomposites with demand characteristics for desired applications. It is desired to obtain a nanocomposite with demand properties and characters or overcome the drawbacks of polymers while remaining the intrinsic advantages of primary polymer matrix. Because of the low price, availability, high aspect ratio as well as desirable nanostructure and interfacial interactions, clays can provide dramatic and adjustable improved properties at very lower loadings along with retaining the original useful properties of the polymer. The nature and properties of material components as well as preparation methodology and conditions effects the final properties of polymer/clay nanocomposite [Olad et al. (2011)].

In this section the various improved properties of polymer/clay nanocomposites as well as the mechanism and effective parameters are discussed. The most interesting properties of these layered double hydroxides may be summarized as follows: [Del Hoyo et al. (2007)].

- ❖ High specific surface area ($100\pm 300 \text{ m}^2/\text{g}$).
- ❖ Homogeneous dispersion of the metal ions thermally stabilizes the reducing conditions, with formation of very small and stable metal crystallites
- ❖ Impregnation procedures for the preparation of metal catalysts normally cannot achieve such a high degree of metal dispersion.

- ❖ Synergetic effects between the elements, due to the intimate dispersion favours, the development of unusual basic or hydrogenating properties. It is worth noting that basic properties depend significantly on the composition and the calcination temperature.
- ❖ Good anion exchange capacities.
- ❖ “Memory effect”, which allows reconstruction (after calcination until 500 °C) of the original structure by contact with solutions containing various anions.

1.3.2 LDHs in biology and medicine

LDHs are positive charge layer and have the capability to exchange their interlayer anions with another. Various research studies have been reported on the basis of anion exchange Changwen et al. (2001) reported that the sheets of LDHs are the host species, and the interlayer anions and water molecules are the guest species. The host and the guest are combined to form a two-dimensional super molecular layered system via electrostatic and hydrogen bonding interactions, and can be assigned to the research field of supermolecule chemistry (Figure 1.8).

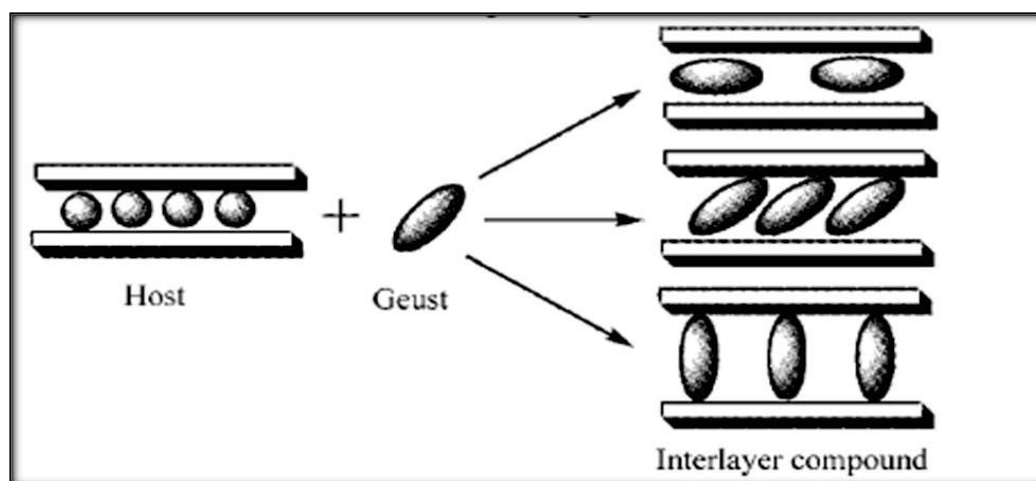


Figure 1.8: Diagrammatical model of anion exchange for layered compounds [Changwen et al. (2001)].

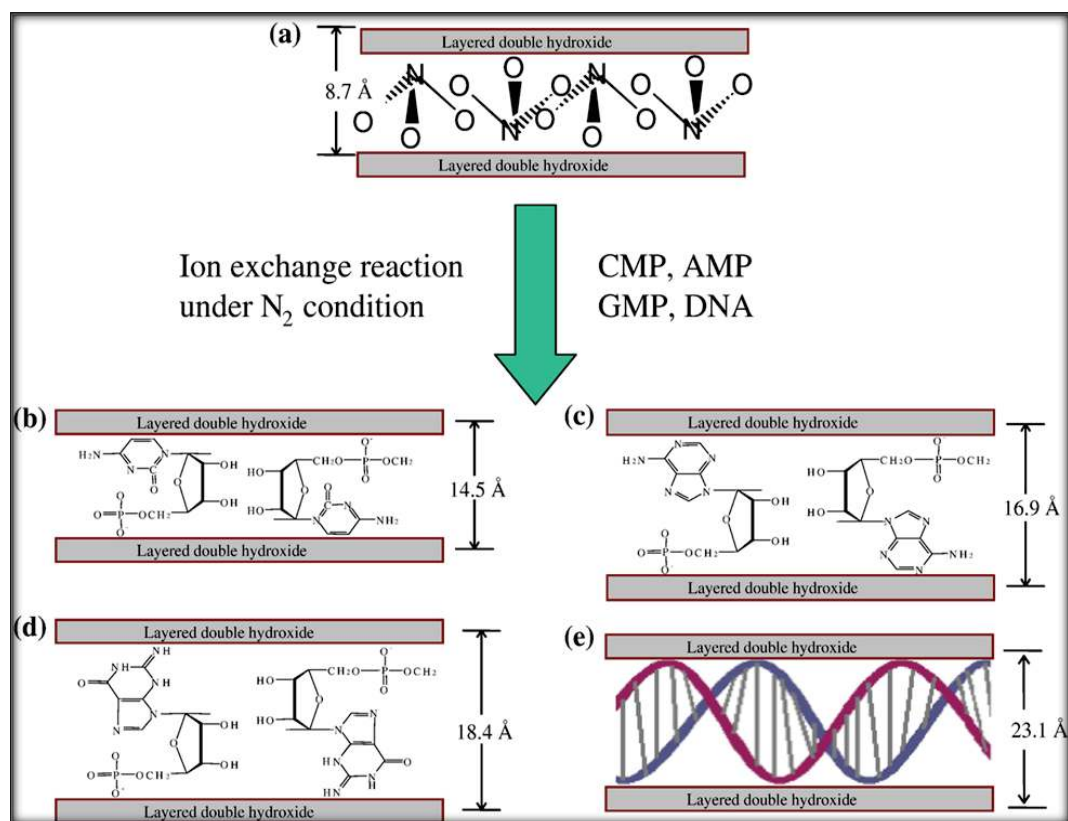


Figure 1.9: Various biomolecule–LDH hybrids obtained by intercalation reaction (a) the pristine MgAl–LDH, (b) CMP–LDH hybrid, (c) AMP–LDH hybrid, (d) GMP–LDH hybrid, and (e) DNA–LDH hybrid [Choy et al. (2007)].

Hence, we name this kind of LDHs as the supermolecular layered double hydroxides. Choy et al. (1999), (2000), (2001) focused on synthesis of bio-LDH, in which DNA, nucleotide, fluoresceine 5-isothicyante, antisense oligonucleotide as anion exchanger. Particularly, the single or double stranded DNAs (Figure 1.9) have huge applications in different biological areas [Choy et al. (2007)] such as gene therapy; biosensing etc., Choy et al. (2000), (2007) also developed vectors for delivery of antisense oligonucleotides.

A promising potential advantage of using LDH over other molecule is that it can be also recovered very easily by exposing DNA-LDH hybrids to an acidic condition due to the solubility of LDHs in acidic medium found in cytoplasm of cell (Figure 1.10),

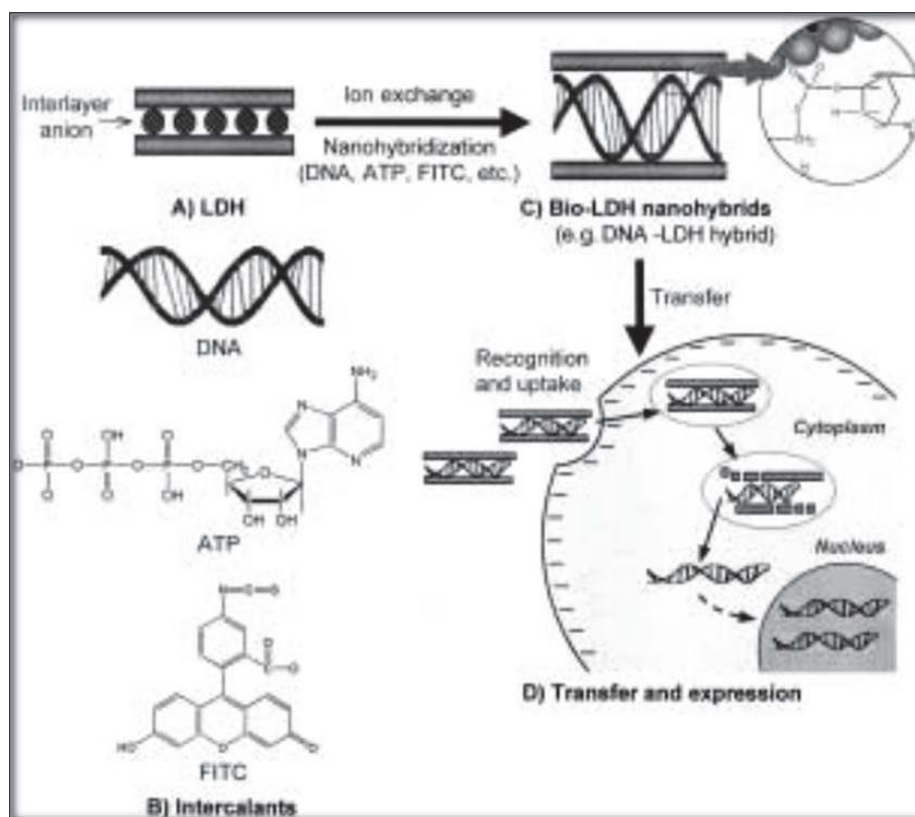


Figure 1.10: Hybridization of bio-LDH molecule and their expected transfer mechanism [Choy et al. (2000)].

where LDH separate with their host molecule and degrades. LDHs also have other possible applications in pharmaceuticals over biology and medicine field. In addition, Hwang et al. (2001) prepared two type of inorganic molecule, hydrozincite and layered double hydroxide for the intercalation of functionalized organic molecule such as retinoic acid, ascorbic acid, indole acetic acid, citric acid, salicylic acid, acidic dye by co-precipitation method for the pharmaceutical, cosmeceutical and nutraceutical functions. Pharmaceuticals technology requires formulation to be able to maintain pharmacologically active drug levels for long periods avoiding repeated administration and to localize the drug release at its pharmaceutical target. The interlayer region of LDHs may be considered as microvessel in which an anionic drug may be intercalated and released via deintercalation process [Evans et al. (2006)].

1.3.3 LDHs as additives in polymers

LDH can be used for chemical addition in several polymers for required applications. The addition of nano clay as fillers in polymer has recently strained vast consideration due to its capability to get better properties of neat polymers with comparatively in low amount [Olad (2011)]. Several authors reported about LDH and its potential use as non-halogenated, non-toxic flame-retardant nanofiller for polymers [Kim et al. (2004); Pereira et al. (2009); Wypych et al. (2005)]. For instance, Costa et al. (2008) reported that addition of LDH in larger amount facilitate polymer to acquire flame-resistant composition.

To obtain polymer with improved properties, it is necessary that nanomaterial should be well mixed throughout the polymer. A recently proposed way of improving dispersion of metal hydroxide nanolayers on polymer matrices regards the organic modification of the LDH. In addition, reported flame-retardant characteristics of Mg–Al LDH in nylon 6 was obtained via organic modification and melt intercalation of LDH, especially when 5 wt.% LDH was incorporated into the polymer [Becker et al. (2011)].

So we have seen that PVC is very common polymer with varied applications in medical field. But due to its short comings, it faces many challenges leading to disadvantages. This produces hindrances for its use in medical devices. So there arises a need to alter some of its unwanted properties. It is also studied that LDH/nanoclay when mixed with polymer, alter its properties. So in the present work it was planned to alter some of the properties of PVC, both by functionalization and addition of LDH, to get polymer with desired properties.

1.4 PVC/LDHs composites

Polymers cover wide range of products which are used in our daily life. A large number of polymers are widely used in various applications. This is mainly because they are available in wide variety of compositions, properties, and forms (solids, fibers, fabrics, films, and gels), which can be fabricated readily into complex shapes and structures [Ramakrishnan et al. (2001)]. However they tend to be too flexible and too weak to meet

the some specific properties such as thermal and mechanical demands of certain applications. Also they may absorb liquids and swell, leach undesirable products such as their monomers, fillers, plasticizers and antioxidants depending upon the application and usage of polymer [Ramakrishnan et al. (2001)].

PVC is one such polymer which finds wide applications in different fields especially in medical field [Lee et al. (2000)]. PVC faces numerous challenges due to hydrophobic nature of their surface. The current opinion is that surface hydrophobicity may bring forth several adverse consequences, in particular when such materials are exposed to biological systems [Asadinezhad et al. (2012)]. It is used to make some medical devices such as ureter prosthesis and catheters without much long-term success. PVC is not very successful in ureter prosthesis due to lack of joint of a fluid-tight prosthesis to the living system. Besides microbial infection and calcification creates blockage in urine passage. PVC is also used to make tubes for catheters to supply glucose, medications, blood & other products like fluids. For the fulfillment of above application the material should have better properties such as blood compatibility, nonthrombogenicity and resistant to microbial growth. In fact, several studies have investigated the relationship between hydrophobicity and electrical surface charge with the complex process of cell adhesion onto biomaterial, and their subsequent influence on the attachment and spreading of cells that finally conclude the success or failure of the implant in service [Mao et al. (2004)], Still more work need to be done.

This has encouraged extensive research during current decades in search to solution of the problem. The poor biocompatibility of the hydrophobic PVC surface leads to unnecessary protein adsorption and cell adhesion due to their hydrophobicity. To resolve this difficulty substantial fundamental and applied research has been dedicated to the modification of PVC. The most common and primary route to enhance the properties of material is functionalization of polymer. The functionalization of PVC leads to change in surface properties such as, surface chemistry, surface energy, surface topography, etc. that could be critical for assessing the biocompatibility.

Modification reactions on PVC are carried out with different purposes, such as the preparation of polymers which cannot be directly obtained by polymerization.

Functionalization of the polymer leads to improvement of the chemical properties of the original polymer and the gradual variation of the original polymer structure [López et al. (1997)]. Therefore, such modifications of polymer play crucial role in revealing their antimicrobial efficacy and thus their selection for consideration in medical applications [Kameda et al. (2011); Zha et al. (2009)]. One of the important applications of biocompatibility is blood compatibility of PVC that can be improved by adsorption of biological molecules such as heparin [Balakrishnan et al. (2005)], PEG [James et al. (2003)], fibronectin [Yu et al. (1997)] and self-assembled hemocompatible coating on its surface. In addition, various reported methods [Mouley (2010)] including surface modification by specific chemical groups [Jagur-Grodzinski (1999)] reveals an enhancement in hydrophilicity of the PVC surface that is vital in governing their biocompatibility.

The synthesis and applications of polymers nanocomposites have drawn serious interest in research by developing new kinds of hybrid materials which influence new materials properties such as dynamic mechanical, rheological, electrical, and thermal behaviour. At present different range of layered inorganic material, commonly called layered double hydroxide (LDH), is also gaining significance as nanofiller for the synthesis of polymer nanocomposites. These materials have a possibility to develop a very wide range of chemical compositions based on diverse metal species, interlayer anions [Costa et al. (2008)]. The other possible applications of LDHs and their presence either as polymer composites or any other modified forms contain biomedical applications e.g., controlled release of various drugs and biomolecules, gene therapy [Changwen et al. (2001); Choy et al. (1999); (2000); (2001); Hwang et al. (2001)], improvement of heat stability of PVC/LDH composites [Liu et al. (2008)], controlled release or adsorption of pesticides [Cardosa et al. (2006)], UV/photo stabilization [Guo et al. (2006); Tian et al. (2007)] and magnetic nanoparticle synthesis [Lukashin et al. (2003)], or in wastewater treatment [Frederick (2012)].

Among all the metal ion combinations, the Mg – Al pair is one of the most widely reported components for polymer nanocomposite preparation. The specialty of the LDHs based on this ion pair is their natural occurrence, biocompatible nature, comparatively

more easy synthesis in highly crystalline and small particle-sized form, etc. In fact, one of the primary objectives for the use of Mg – Al LDH as nanofillers for polymer is to explore its potential as flame retardant for the polymer matrix. The major driving force in this regard is to develop a nontoxic and environmentally friendly flame retardant [Costa et al. (2008)].

1.4.1 Thermal stability

Thermal degradation is a process where temperature imposed on a material causes loss of physical, mechanical or electrical properties and usually studied by thermogravimetric analysis (TGA). The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature. Generally, the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition [Costa et al. (2008)].

Several types of compounds are used as stabilizers or additives for polymers or PVC for preventing degradation because without them, polymer rapidly degrades during processing turns dark coloured and loses its properties. Besides this a better way to prevent degradation is to make polymer composites.

Li et al. (2006) described that Japanese Chemical Industries were the first to prepare PVC/LDH composites in mixture with other additives such as zinc stearate and tin maleate leading to enhancement in thermal stability of the resin. Gu et al. (2010) synthesized zinc-magnesium-aluminum-layered double hydroxide (ZnMgAl-LDH) by one-step coprecipitation method and their thermal stability time of PVC containing 8 wt% ZnMgAl-LDH-stearate loading is 12 times more compared to pure PVC. In addition, different PVC composites such as, PVC/LDH-nitrate (PVC/LDH-NO₃) composite, PVC/LDH-dodecyl sulfate (PVC/LDH-DS), and PVC/LDH-stearate (PVC/LDH-st) nanocomposites also exhibit improved thermal properties (Figure 1.11) [Liu et al. (2010)].

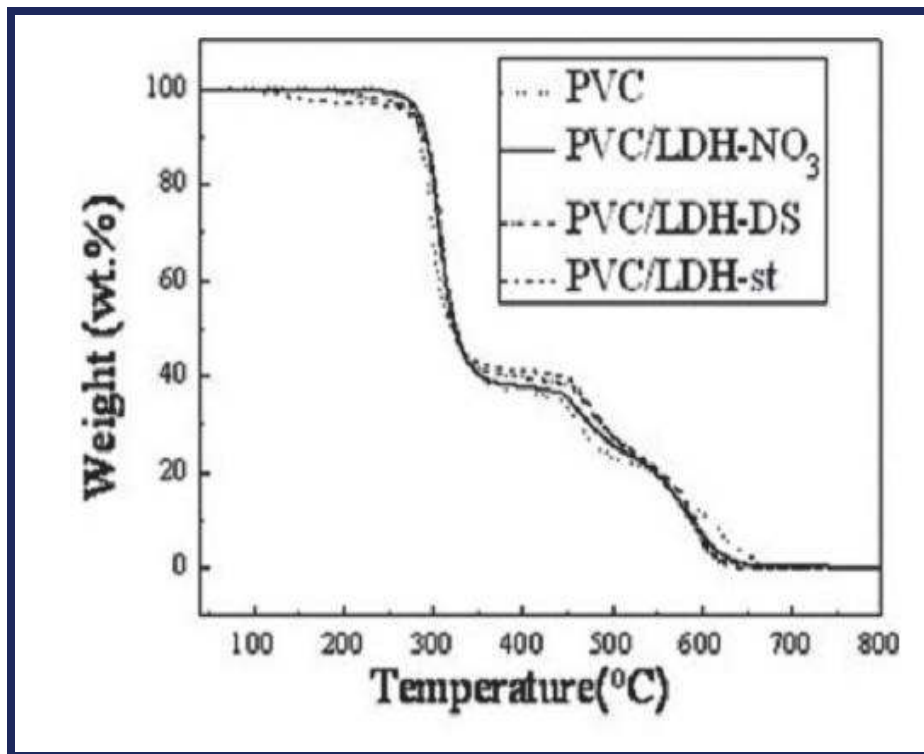


Figure 1.11: Thermal behaviour of PVC and its nanocomposites [Liu *et al.* (2010)].

Thermal degradation of PVC occurs by an autocatalytic dehydrochlorination reaction with the consequent arrangement of conjugated double bonds. After the loss of first HCl molecule, the subsequent unsaturated structure created in a PVC chain is an allylic chlorine structure. However, this allylic chlorine stimulates the next loss of an HCl molecule and repeated process leads to the chain dehydrochlorination [Folarin *et al.* (2011)].

The process starts at the glass transition temperature (70°C) by elimination of HCl, which is the main volatile product up to about 330°C [Klaric *et al.* (1996)]. However, traces of benzene have been reported at temperatures as low as 150 to 160°C [Levchik and Weil (2005)] and at 200 to 360°C, about 15% of the polyene is converted to benzene [Grimes *et al.* (2007)]. The formation of benzene in this temperature range results from an intra-molecular process involving cyclization of polyene segments (Starnes 2002). The primary process of thermal degradation includes three main steps viz:

- (1) initiation of dehydrochlorination
- (2) elimination of HCl and simultaneous formation of conjugated double bond and
- (3) termination of dehydrochlorination

The evolution of HCl takes place by elimination from the polymer backbone and discolouration is due to the formation of conjugated polyene sequences of 5 to 25 double bonds [Hjertberg et al. (1988); Minsker et al. (1989); Ivan et al. (1990)]. The limited length of the polyene sequence could be due to resonance stabilization or due to the presence of blocking groups such as chain branches. The instability of PVC is related to its structure. Impurities are unlikely to be a cause of degradation, because the stability does not increase after reprecipitation. The chain end groups of PVC are quite stable. Chloromethyl groups are stable because C has not bonded to carbon having tertiary chlorine atom in the main chain. The two groups believed to be the cause of instability are the chlorines adjacent to internal double bonds and the tertiary chlorines of branch carbons. The instability of the two groups is similar, but the concentration of tertiary chlorine is greater, and thus its effect is believed to be more significant. Although conjugated systems are known to be unstable, the effect is unlikely to be significant because of the low concentration. The main contribution of different vinyl chloride defective structures to dehydrochlorination is tertiary chlorine, (70–80%) [Kiyoshi (2002)].

Because of their technological relevance and intrinsic scientific significance, the thermal degradation and stabilization of PVC have been the subjects of much research. Unfortunately, they also have attracted an uncommon amount of mechanistic speculation that frequently has not been informed by a comprehension of well-known chemical facts [Starnes (2002)]. The problem of thermal instability of PVC can be overcome through thermal stabilizers; LDH is a non-toxic, environmentally friendly compound, which is a type of thermal stabilizer inorganic material.

Kyowa chemical industries of Japan were the first to demonstrate that adding Mg-Al LDHs to PVC in combination with other additives such as zinc stearate and tin maleate leads to an enhancement in thermal stability of the resin (Evans and Duan, 2006).

Several researchers have reported [Liu et al. (2008), Evans et al. (2005), Turhan et al. (2010)] that PVC-LDH composite has much better thermal stability than does PVC, probably because the hydroxides can absorb the HCl as it is evolved. Nonetheless, the HCl is still evolved with concomitant degradation of the PVC and this has not been examined.

Huang et al. (2009) investigated the thermal behaviour of PVC/LDH composites with 2 and 5 weight % of nano clay by weight. They compared the thermal behaviour of PVC with their composites as well as LDH and the result showed (Figure 1.12) improved PVC/LDH nanocomposites with 2 and 5% LDH at 650 °C which are significantly increased from 6.84 to 11.61, 15.05%, respectively.

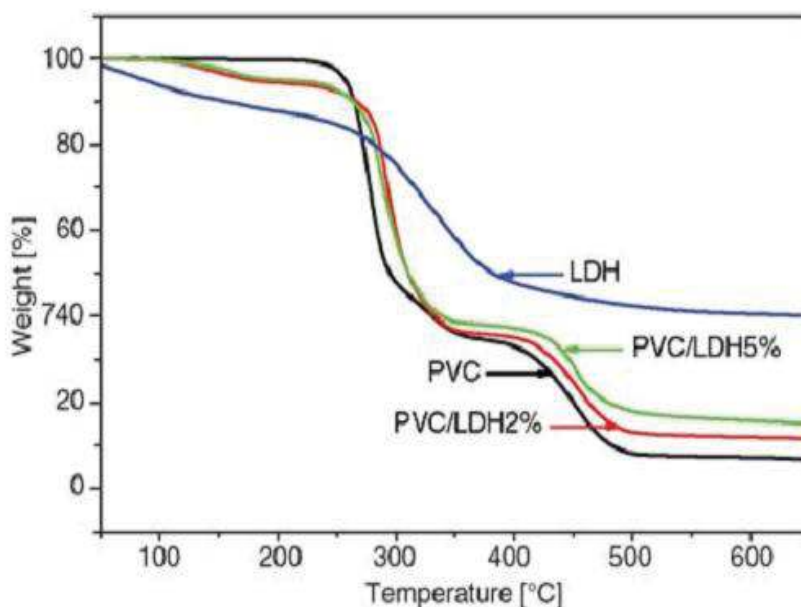


Figure 1.12: Thermal behaviour of PVC and its nanocomposites [Huang, *et al.* (2009)]

Lin et al. (2005, 2006) studied the effect of varying the composition, structure and added amounts of LDH hydrotalcite on the thermal stability of PVC. The investigation further confirms the stabilizing effect of hydrotalcite on PVC. Thermal aging test was used to evaluate the effect of the additives. The results showed enhanced long-term stability. The effect of nano-sized LDH on the thermal stability of PVC was investigated by Liu et al. (2008) through solution intercalation process.

The nanoscale exfoliated LDH particles were homogeneously dispersed in the polymer matrix. Thermal stabilizing effect of this particles increased dehydrochlorination time of samples containing LDH particles. The results indicated increased stabilization with increased loading of LDH.

1.4.2 Mechanical Properties

The first and essential objective of nano clay added to the polymer is enhancement in the mechanical properties and as a result nano clay is frequently called as reinforcement material [Jiang et al. (2005)]. The method of the reinforcement is based on the higher resistance of rigid filler materials against straining due to their higher module. When rigid filler is added to the soft polymer matrix, it will carry the major portion of applied load to the polymer matrix under stress conditions, if the interfacial interaction between filler and matrix is adequate [Tortora et al. 2002; Gorrasi et al. 2003].

Therefore, larger the interface between filler and matrix, and also more strong interfacial interactions, the greater the reinforcement effect will be. Also the modulus increases by increasing the filler ratio in the composite or nanocomposite composition. Because of the rigid structure of clay layers and their high aspect ratio, they have proven to be very effective in increasing modulus and stiffness of the polymer matrix in well dispersed condition. In fact, due to very higher aspect ratio of nano-clay fillers compared to that of regular fillers such as glass fibers, dramatic improvements in the mechanical properties of nanocomposites are achieved even at very lower nanoclay additions [LeBaron et al., 1999)].

In another approach, polymer chains, adhesived by strong physisorption forces onto the rigid clay mono layers, become equally a portion of rigid material and dramatically exhibit high modulus. Considering the very large interfacial area in well dispersed nanocomposite structures, significant improvement in the modulus can be expected. However any enhancement in the polymer-clay interfacial contact leads to better stress transfer in the nanocomposite. It has been well demonstrated that the enhancement in the interfacial adhesion properties between clay and polymer by surface modification of polymer chains using a suitable polar compatibilizer causes to the

increase the mechanical properties of nanocomposite [Osman et al. (2005); Mittal (2008)]. It should be noticed that in higher loadings of compatibilizers, may cause some degree of plasticization due to their lower molecular weight, which negatively effects the modulus of nanocomposite [Mittal (2008)].

Also use of organically modified clay filler increases both the modulus and stiffness of nanocomposite because of more intercalation/exfoliation achieved. At all, any parameter which helps to the intercalation of polymer molecules within the clay galleries and consequently causes to the more exfoliation and interfacial interactions, results in greater improvement in the modulus. However, it is difficult to achieve the complete exfoliation of clay layers and there are varieties of platelet structures with different thicknesses (depending on the number of layers stacked together) in polymer matrix. Fornes and Paul (2003) have analytically formulated the effect of incomplete exfoliation on the nanocomposite properties. Also it has been reported that tensile modulus increases by increasing the filler volume fraction in nanocomposite [Mittal (2007)]. However clay loading more than threshold limit value, causes leveling-off in the increasing period of Young's modulus, which is due to the formation of partially exfoliated/intercalated structure after that fully exfoliated structure, after that fully exfoliated formation [Ray and Okamoto (2003); Alexandre and Dubois (2000)].

Also the incorporation of clay minerals usually improves the tensile strength of polymers [Fornes et al. (2001); Shelley et al. (2002); Kojima et al. (1993)]. However the tensile strength is influenced by the final morphology of nanocomposite. There are number of reports on the reduction of tensile strength by the addition of clay minerals [(Alexandre and Dubois (2000); Finnigan et al. (2004)]. Similar to modulus, any factor affecting the degree of intercalation/exfoliation has an impact on the tensile strength of nanocomposite.

The effect of clay fillers on the stress at break values for polymer nanocomposites depends on the interfacial interactions between polymer and clay layers. Stronger interfacial interaction causes increase of stress at break and the weak interfacial forces may lead to some decrease of stress at break for nanocomposite. The polymers with more polarity such as nylon and rubber based polymers have more strong interfacial

interactions with polar clay layers and their nanocomposites represent improved stress at break values compared to that of pure polymer [Wang et al. (1998)]. Polyamide/clay nanocomposites have shown highly improved stress at break values, because of their higher degree of exfoliated structures based on the presence of strong ionic bonds between polymer chains and clay layers [Alexandre and Dubois (2000)]. The nanocomposites of non-polar polymers such as polyolefines with clays exhibit weak interfacial interactions and low degree of exfoliation and consequently show decreased or slightly improved stress at break values. However the modification of polymer chains or clay layers may cause improved stress at break characteristics for non-polar polymers.

Elongation at break for polymer/clay nanocomposites is similarly dependent on the interfacial interactions of polymer/clay system. There are both increasing and decreasing reports of elongation at break for polymer/clay nanocomposites in literature [Finnigan et al. (2004); Yao et al. (2002)]. The impact strength of polymer/clay nanocomposites was also studied and compared with that of pure polymer systems. The reports usually emphasised on the increase of impact strength by the addition of very low fraction of clay loadings such as 0.1 wt% [Zhang et al. (2000); Oya et al. (2000)]. In these studies organic modified clay fillers were added to the compatibilized polyolefines. There are also reports on the decrease of impact resistance by the addition of clay materials [Phang et al. (2005)]. Dynamic mechanical analysis studies on polymer/clay nanocomposites have shown that usually storage modulus and glass transition temperature (T_g) are improved by the addition of clay nanofillers [Nam et al. (2001); Laus et al. 1997; Krikorian and Pochan (2003); Ray et al. (2002)].

Gu et al. (2010) synthesized zinc-magnesium-aluminum-layered double hydroxide (ZnMgAl-LDH) by one-step coprecipitation method and their thermal stability time of PVC containing 8 wt% ZnMgAl-LDH-stearate loading is 12 times more compared to that of pure PVC. In addition, tensile strength of the nanocomposites increases with the increase of ZnMgAl-stearate content and exhibits excellent mechanical properties.

1.5 Anti Bacterial Activity

The adhesion of bacteria to surfaces has been analyzed in terms of surface charge, surface energy, and the characteristics of polymers on bacteria, to understand the factors that control bacterial adhesion [Speranza et al. (2004)]. Even though some properties of bacteria such as hydrophobicity and surface charge have been used to explain bacterial adhesion to a surface [Wang et al.(1993)]. Biomaterial related infections are serious problem associated with the use of biomaterial implants and devices. Bacterial cell surface molecules containing a variety of functional groups, exhibit repulsive and attractive interactions with the surface, and mediate bacterial adhesion [Gottenbos et al. (2008)]. After adhesion and growth of infectious microorganisms on a biomaterial surface, the biofilm mode of growth protects the organisms against the host defense system and antibiotics. Consequently, an infected biomaterial implant has to be replaced, at the expense of considerable costs and patients discomfort. A comparative study of early surface development rate of *Staphylococcus epidermidis*, *Pseudomonas aeruginosa* and *Escherichia coli* on different orthopedic implant materials in a parallel plate flow chamber has been done a relationship was investigated among the free energy of *P. aeruginosa* and different synthetic biomaterials but this type of connection was not established for *S. epidermidis* and *E. coli*. Pavithra et. al. (2008) described the modification route for bacterial adherence reduction. Various techniques have been used, such as oxygen plasma treatment [Balazs et. al. (2001)], wet chemical methods using organic reactions [Herrero et. al. (2006)], Ni-P-PTFE (Nickel-phosphorus-polytetrafluoroethylene) coatings [Liu et. al. (2005)], and have proven to be effective in reducing bacterial adhesion and biofilm formation.

1.6 Biocompatibility

Biocompatibility is the most important and supreme necessity for all biomaterials used in biomedical diagnosis. The lack of biocompatibility usually causes many undesirable physiological response, which can lead to more serious problems such as haemolysis, thrombogenicity and cytotoxicity etc. Thus, for biomedical applications, it is essential for polymers or polymer composites to own good biocompatibility. The

single most important factor that distinguishes a biomaterial from any other material is its ability to exist in contact with tissues of the human body without causing an unacceptable degree of harm to that body. It was therefore considered that the very basic edict that biocompatibility, which was equated with biological safety, meant that the material should do no harm to the patient, was no longer a sufficient pre-requisite. Accordingly, biocompatibility was redefined in 1987 as follows:

“Biocompatibility refers to the ability of a material to perform with an appropriate host response in a specific situation” [Williams (1987)].

Biocompatibility is a word that is used extensively within biomaterials science, but there still exists a great deal of uncertainty about what it actually means and about the mechanisms that are subsumed within the phenomena that collectively constitute biocompatibility. As biomaterials are being used in increasingly diverse and complex situations, with applications now involving tissue engineering, invasive sensors, drug delivery and gene transfection systems, the medically oriented nanotechnologies and biotechnology in general, as well as the longer established implantable medical devices. This uncertainty over the mechanisms and conditions for, biocompatibility is becoming a serious impediment to the development of these new techniques. This review of biocompatibility attempts to address some of these uncertainties and provides a proposal for a unified theory of biocompatibility mechanisms [Williams (2008)].

1.6.1 Blood Biocompatibility

Blood compatibility is the single most important characteristics feature for blood-interfacing implant. Although blood coagulation is the most essential necessity factor for blood compatibility, the implant should not damage the proteins, enzymes, and formed elements of blood included red blood cell rupture process (haemolysis) following initiation of platelet release reaction which accelerates clotting and thrombus formation. Blood biocompatibility depends upon the surface roughness and wettability. More the rough surface, the more it is exposed to blood which promotes faster blood coagulation.

Wettability is another important factor which means hydrophilicity (wetable or water loving) or hydrophobicity (non-wetable or water hating).

1.6.1.1 Hemolysis

Hemolysis is phenomenon of destruction of red blood cells (RBC) where the resultant contained haemoglobin is freed into the surrounding medium. The hemolysis of blood cells is directly related to the bioincompatibility of a material. In general, the breaking of RBCs starts when cells come in contact with water. This problem may be aggravated in the presence of an implant material.

PVC is a blood contacting biomaterial of so much attention because of its extensive application in blood and blood contact with the surface of PVC triggers a complex series of interacting events, such as protein adsorption [Wendel et al. (1999)], platelet reactions [Forbes (1981)], activation of the intrinsic coagulation with complement systems [Bouma et al. (1997); te Velthuis et al. (1997); Yu et al. (1997)]. To minimize these interactions, various methods for PVC surface modification have been attempted (Figure 1.12), such as modification by coating or immobilization with heparin, hirudin and albumin [Zha et al. (2009)].

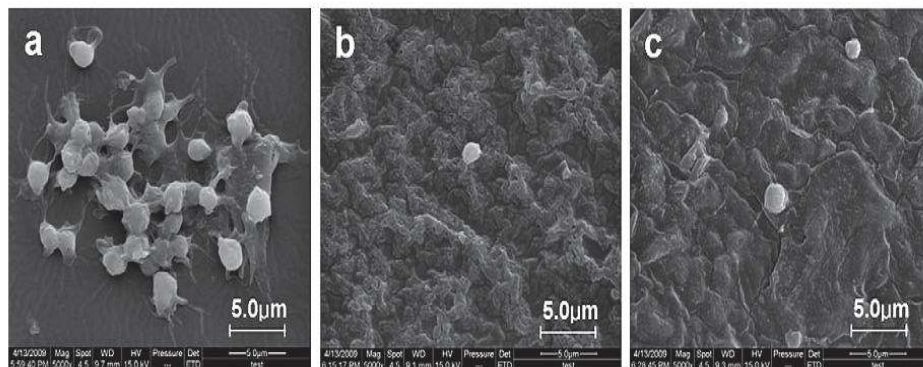


Figure 1.13: SEM micrographs of PVC surface after being contacted with fresh platelet enriched plasma: (a) control PVC, (b) CTAB/Hep/(Fe³⁺ /Hep)₇coated PVC and (c) CTAB/DS/Fe³⁺/Hep(Fe³⁺/DS/Fe³⁺/Hep)₃coated PVC [Zha et al. (2009)].

1.6.2 Cell adhesion cell viability

Approaches to biomaterial include reduction of unspecific protein adsorption, non-fouling properties, enhancement of adsorption of specific protein and material modification by immobilization of cell recognition motives to obtain control interaction between cells and synthetic substrates. In this context polymers can be modified by attaching peptides such as RGD (Arginine, Glycine and Aspartic acid) containing the cell recognition motif which not only triggers the cell adhesion effectively but can also be used for selectively certain cell lines [Hersel et al. (2003)]. On the other hand, a highly hydrophobic surface may expel any protein molecule and inhibit protein adsorption [Volger et al. (1998)], highly hydrophilic surface also shows the same properties and to overcome this problem polymers can be chemically modified to show moderate hydrophilic properties.

1.7 Objectives

There has been extensive research on PVC to improve blood and cellular biocompatibility for biomedical applications. Preparing functionalized polymer composite is an innovative technique for developing new materials for advance polymer especially in biomaterials area.

The main objective of the present research work is to synthesize new functionalized polymer by chemical modification method with the help of phase transfer catalyst to develop the next generation high performance material for biomedical applications. This will be accompanied by the following-

- To critically assess the merits and demerits of existing synthesis technique for functionalization of PVC.
- To critically assess the merits and demerits of existing functional group for functionalization of PVC.
- To develop new functionalize polymer with hydrophilic nature.
- To develop new hybrid polymeric nano materials for enhancing their thermal and mechanical properties.
- To examine the blood biocompatibility of functionalized polymer and functionalized polymer composites.
- To examine the cellular biocompatibility of functionalized polymer and functionalized polymer composites with mouse mesenchymal stem cell line.