Chapter 1

Introduction and literature review

1.1 Introduction

Poly(ethylene terephthalate) (PET) is a polymer which is transparent, lightweight, possess good mechanical and gas barrier properties and is easily and widely available. Because of its versatile properties and low cost, it is replacing glass and metals in various fields. It is widely used for various applications such as food packaging, water/soft drink bottles, sports equipment, automobile, construction, and many more. The most attractive quality apart from the above mentioned is the large scale recyclability of PET. It can be recycled indefinitely for primary and safe food packaging purposes. Continued research is going on for making it more usable by enhancing its properties further by making blends and composites. From past few decades, research has been inclined toward nanocomposites. The amount of nanofiller needed for nanocomposite preparation is very less. The nanosize fillers have large surface area to interact with the matrix. Hence, the strong interactions can occur and is considered as the key factor for enhancement of various properties, usually called synergistic effect. The key factors for improving the properties, by incorporating nanofillers in polymer matrix, are homogeneous dispersion, good interactions with the polymer matrix, degree of exfoliation and/or intercalation [1]. All these factors play important role in enhancing the mechanical properties, thermal stability, electrical conductivity, gas barrier properties, and so forth [2]. Only a meager amount of nanofiller can improve the property to a great extent. PET has majorly replaced the glass and metals but still lacks in properties in terms of mechanical strength, gas barrier and thermal stability.

As polymers are an inherent part of our lives today, there is an urgent need to recycle and reuse them and certainly there is a prerequisite to enhance their properties for different applications. Continuous research is going on to produce high performance polymeric materials to incorporate wide array of properties. Plastic plays a crucial role in our day today lives as we are highly dependent on different products made out of it. Massive production of plastics is underway to fulfil the demands of the society every year. The discarded plastic products after use, creates a humongous amount of plastic waste which is increasing day by day. The harmful chemicals present in the plastic waste can disrupt water, soil as well as widely diverse wildlife and create other environmental problems. So, there is a strong necessity to reuse and utilize them in an effective manner to curb the amount of discarded plastic waste. Using them as polymer blends and composites to enhance the properties of some of the existing polymers can prove to be a great way to regulate them again in practical lives.

The useful portion of discarded plastics can also be utilized to enhance the properties of some existing polymers. Poly(acrylonitrile-butadiene-styrene) (ABS) is largely present in the discarded electronic waste. ABS is a preferred polymer in applications in electronics as well as in automotive industry due to its excellent mechanical properties and good surface finish. The properties can be customized by varying its constituents. It provides desirable properties along with ease of processing at a low cost. Low density polyethylene (LDPE), on the other hand, is a widely used polymer in applications such as in packaging, textile, construction and various other household items [3]. Continuous investigation has been going on for the improvement of its properties [4-11]. It can be achieved by making its blend utilizing the already available ABS extracted from the huge amount of existing E-waste. For making polymer blend, two or more polymers are combined to enhance and modulate the existing properties of base polymers in order to achieve the required purpose. Here in this study, a single phase blend of ABS extracted from E-waste and LDPE have been prepared through a single step reactive extrusion. The prepared blend have been characterized for improved mechanical strength to make it practically applicable and commercially desirable.

1.2 Composite:

Composite materials are prepared by combining two or more physically or chemically different materials which are separated by a distinct interface. Composite materials are non-homogeneous at microscopic level. The individual materials combine to result in a material having properties different than the individual elements. The composite materials show synergistic behavior i.e. additional property gain is obtained as opposed to simple additive rule:

$$1 + 1 = 2 + \alpha \tag{1.1}$$

Where α signifies the additional property gain. Composites are preferred due to their exceptional properties such as light weight, heat resistance, corrosion resistance, mechanical strength to name a few. The application of composites is distributed in a various fields such as construction, automotive, packaging, aerospace, biomedical, electrical and electronic etc. Composites primarily have two constitutive elements called matrix and filler. The matrix is the continuous phase and the filler is the dispersed phase. Both the phases have different fundamental properties. The continuous matrix phase is mostly a more ductile phase which works as a binding phase whereas the filler phase is the more rigid reinforcing phase. The filler material is mechanically stronger than the matrix phase.

1.3 Polymer Nanohybrids

Polymer nanohybrids/nanocomposites are the materials where the matrix phase is an organic polymeric material and inorganic filler phase has one of its three dimensions in nanometer range (<100nm) and is called nanofiller. The polymer nanohybrid need very less volumes of nanofillers (1-10%) (compared to the polymeric matrix material) in order to achieve the exceptional properties as opposed to the high filler loading capacity of traditional macrofillers (15-40%). These exceptional properties of polymer nanohybrids are the result of the nanoscale size of the filler materials. The physical manifestations and implications of the nano dimension of filler materials on the properties of polymer nanohybrids is well known [12-20]. At such size reduction, even very less volume of filler achieve a huge surface area. This enormous surface area provides the opportunity for the interactions between inorganic and organic phases to enhance manifold. The key factor for the enhancement of the properties of nanohybrids is polymer-nanofiller interface. The interface truly dominates the properties of polymer nanohybrids. At the interface, the interactions between inorganic nanofiller and organic polymer molecules are molecular level interactions [21]. Polymer nanohybrids were discovered more than two decades before and are being continuously studied for the further improvement. Polymer nanohybrids have become an eminent part of materials research as they exhibit exceptional properties as compared to the traditional composite materials. They also provide multifunctional properties and are preferred in many practical applications. The property enhancement and performance of polymer nanohybrids depends on following factors:

- Process of preparation of polymer nanohybrids
- Type of polymer matrix (e.g. elastomeric, thermoplastic or thermosetting)
- Nanofillers and their surface modifications
- Dispersion and interactions of nanofillers and polymer matrix

On basis of above mentioned factors, polymer nanohybrids can achieve major advantages with some of the limitations mentioned in ***Table 1.1*** and are becoming the favorable choice for a vast variety of applications.

Table 1.1: *Effects of nanoparticles on polymers [21]*

Improved properties	**Drawbacks**
❖ Specific strength	❖ Viscosity increment (results in limiting processability)
❖ Specific stiffness	❖ Difficulty in dispersion of nanofiller
❖ Mechanical properties (e.g. tensile strength, impact strength, toughness)	❖ Compromise in optical property
❖ Gas Barrier Property	❖ Brittleness
❖ Thermal stability	
❖ Thermal conductivity	
❖ Electrical conductivity	
❖ Dimensional stability	
❖ Corrosion resistance	
❖ Chemical resistance	
❖ Flame retardancy	
❖ Biological compatibility	

PET is a thermoplastic material which has a wide spectrum of applications such as textile, automotive, electronics and food and beverage packaging industry. PET has excellent properties such as electrical insulation, chemical resistance, thermal resistance, light weight, high strength and stiffness. PET is the most exploited polymeric material for food packaging and dominates the market of bottled packaging for beverages because of its gas barrier properties. PET has the largest monopolized market of the packaging of carbonated soft drinks (CSD) and water bottle especially. PET replaced glass packaging largely because it is light weight (multifold in comparison to glass), transparent and shatter proof. The weight reduction and excellent strength to weight ratio in comparison to aluminum, glass and other packaging materials, makes it highly energy efficient. The PET water bottles are very light in weight, hence less fuel is needed for the transportation.

1.4 Introduction to PET

Although PET has many favorable properties but in comparison to glass and metals it lags behind in properties such as mechanical strength and gas barrier properties and needs constant improvement. There have been continuous research going on for the improvement of properties of PET.

1.4.1 Applications and demand

PET is one of the largest produced polymeric material globally because it is easily processible, highly economic and recyclable polymeric material. PET is used in packaging, textile, electrical & electronics, industrial machinery, construction, material handling and other applications such as various household items (***Figure 1.1***). In 2016 the total consumption of PET was 23.5 million tons whereas in 2017, the global production of PET was 30.3 million tones. The global PET production capacity of different regions in the world has been shown in ***Fig. 1.2*** [22]. China had the maximum share of PET production (30.8%). The Asian region other than china accounted for 21% of the total PET production. North American region produced 16.9% where United States had the largest produced share of PET. The European region contributed 14.7% of the global PET production.

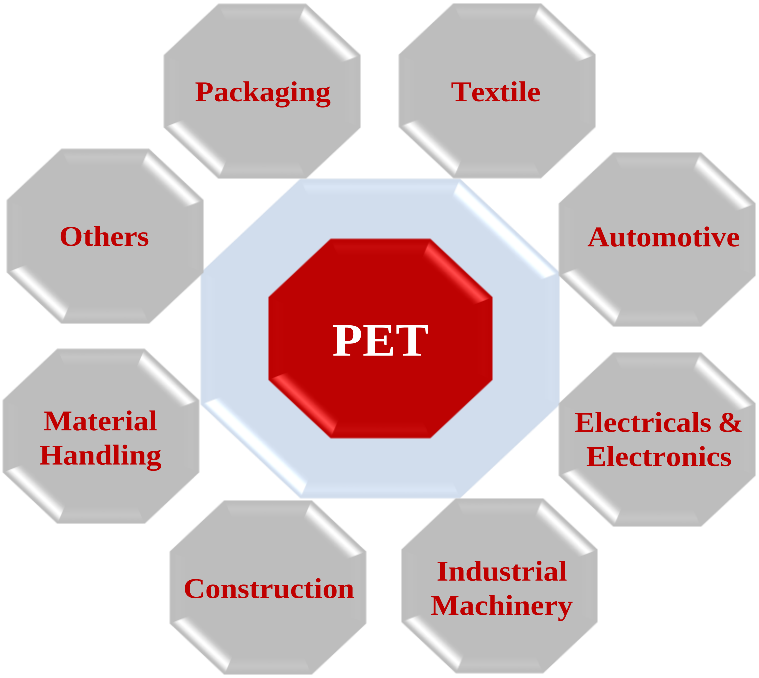

Figure 1.1: *PET applications in different sectors.*

Other than that Middle East, South America and Africa were accounted for 10.2%, 4.1%, and 2.3% global PET production respectively [22]. The global consumption of PET in different applications in food packaging sector has been shown in ***Fig.1.3***.

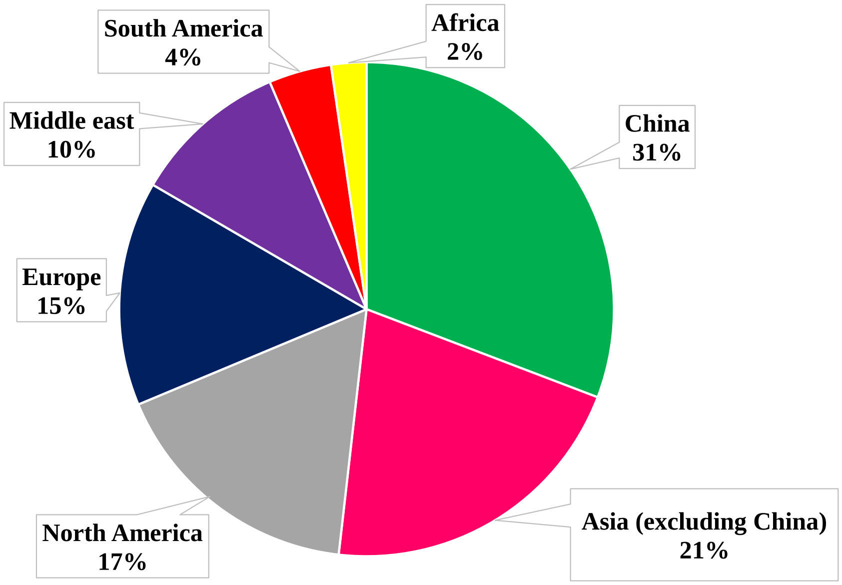

Figure 1.2: *Global PET production capacity in different regions (Total production 30.3 million tons in the year 2017) [22]*

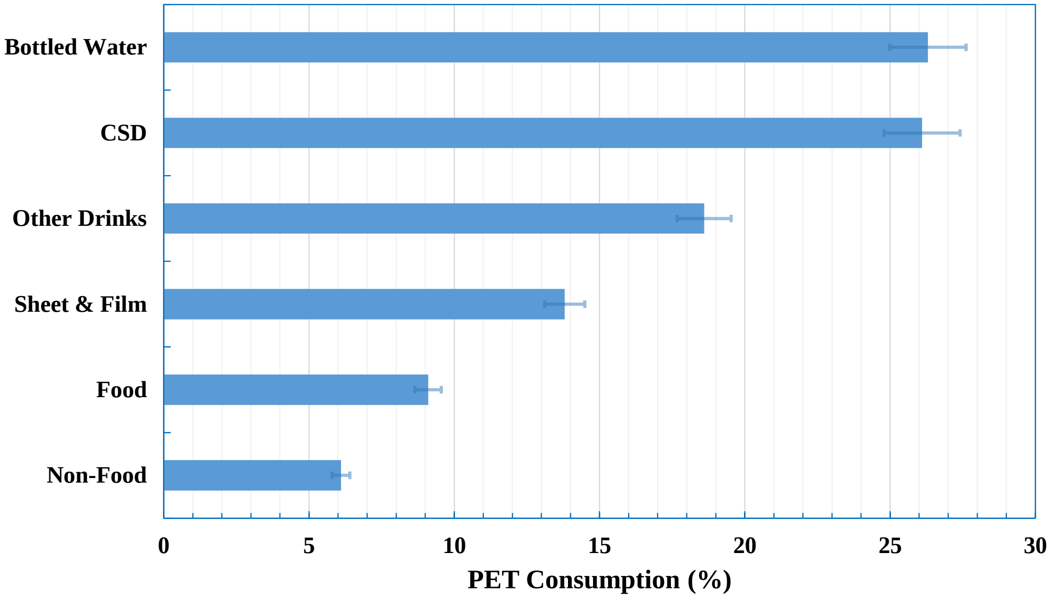

Figure 1.3: *Global PET consumption in packaging sector in different forms of packaging applications (Total consumption 23.5 million tons in the year 2016) [22]*

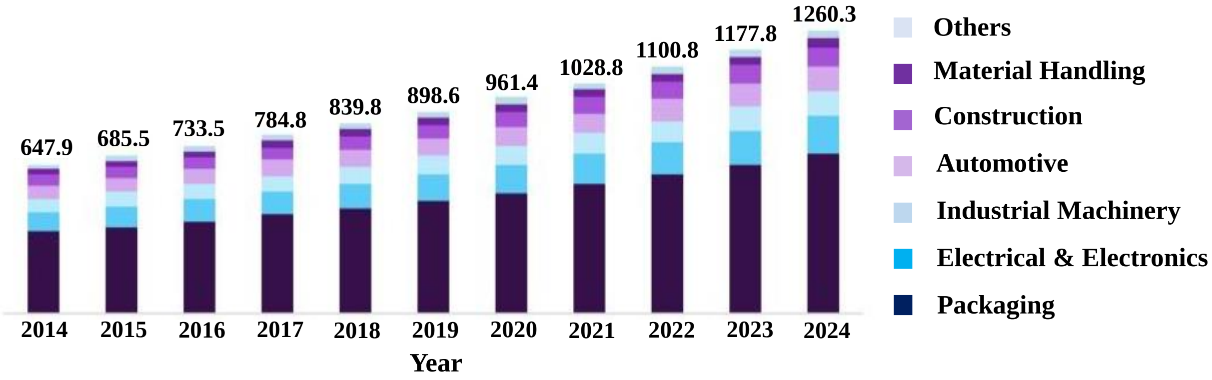

Figure 1.4: *Demand forecast of PET consumption market size in different application sectors in U.S. (values shown are in USD million) between the years 2014 to 2024. The packaging sector was leading segment in the year 2014 and was forecasted to grow with an estimated compound annual growth rate (CAGR) of 7% from year 2016 to 2024 [23].*

The maximum produced PET is used in the bottled drinks with bottled water being at 26.3% followed by CSD at 26.1%. Packaging of other drinks have a share of 18.6% of the total PET production. Sheet and film accounted for 13.8% of total PET followed by food (9.1%) and non-food products (6.1%) [22]. In view of the consumption of PET in different sectors, its future demand is also expected to increase specially in packaging industry as shown in ***Figure 1.4*** [24].

Apart from the desirable properties, PET also has excellent recyclability which makes it a favorable material in terms of sustainability. PET is recycled at a very large scale universally. The recycled PET can be used for the primary applications and it is safe for the food and beverages. According to PETRA (PET resin association), recycling rate of PET in United States is almost 30% and in the European Union, it is about 52% [22]. Many companies are producing bottles containing 50-100% recycled PET and accounted 1.4 million tons of the PET packaging market in 2018 [22]. Recycling industry of PET is very efficient and makes it a desirable material for usage in various sectors especially in packaging industry due to the generation of minimum waste causing landfill.

1.4.2 Preparation and chemistry

Discovery of PET dates back to American chemist W. H. Carothers' (1896-1937) work on linear polymers accomplished at DuPont Company's laboratory. In 1929, W. H. Carothers and American chemist J.W. Hill (1904-1996) prepared polyester by condensation reaction of dicarboxylic acids with diols. However, PET was first synthesized by J. R. Whinfield (1901-1966) and James T. Dickson in the year 1941 at a British textile company called Calico Printers' Association of Manchester. They synthesized PET by condensation reaction of two monomers i.e. ethylene glycol and terephthalic acid. This discovery was first utilized to produce the first PET fibre [25, 26].

PET is an aromatic polyester (***Figure 1.5***), synthesis of which require reaction of bifunctional acids and alcohols. The reaction takes place in presence of metal catalyst [27]. The synthesis of PET is performed using ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT) (dimethyl ester of TPA) by step growth polymerization. These monomers are obtained from petrochemical feedstock obtained from crude oil (petroleum) [28].

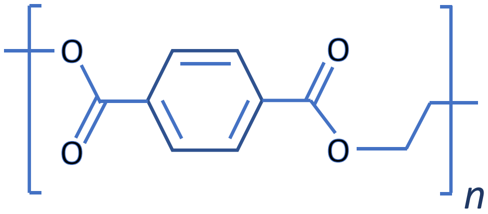

Figure 1.5: *Chemical structure of PET*

The EG is synthesized using ethylene which is obtained by petroleum or natural gas. The chemical reaction involves catalytic oxidation of ethylene. The ethylene is converted in to ethylene oxide (EO) by catalytically oxidizing ethylene with oxygen in the presence of silver catalyst. Then, the hydrolysis of produced ethylene oxide in presence of water results in EG [28, 29]. The reaction mechanism has been shown in ***Figure 1.6***.

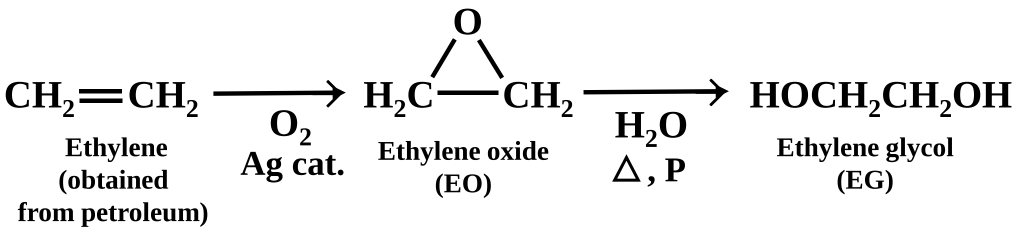

Figure 1.6: *Reaction mechanism of EG production [30].*

TPA is largely produced by AMOCO (American Oil Company) process according to which the para-xylene is oxidized with oxygen in an acitic acid medium. The *para*-xylene is derived from petroleum catalytic reforming. The oxidation process takes place in presence of corrosive Co-Mn-Br catalyst. DMT can be produced by two methods. In first method DMT can be derived from *para*-xylene by means of a multi-step process in which *para*-xylene is oxidized in presence of Co-Mn catalyst followed by esterification using methanol and second method to produce DMT is esterification of TPA by reaction with methanol (reaction mechanism shown in ***Figure 1.7***) [29] [31].

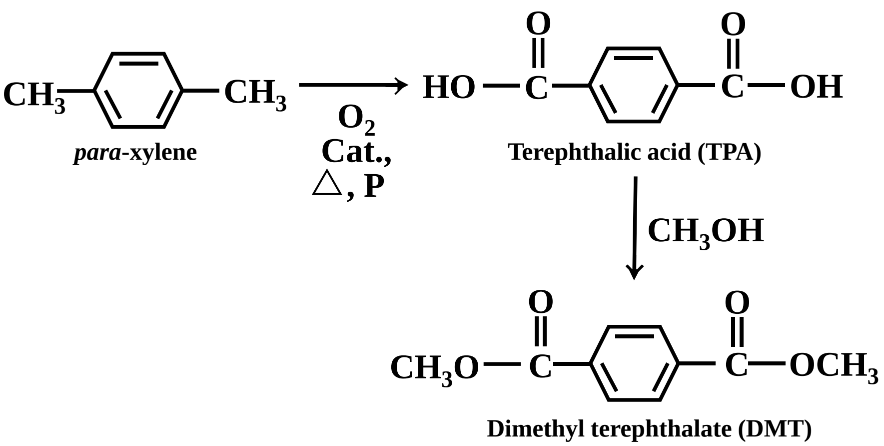

Figure 1.7: *Reaction mechanism of the production of DMT using* para-*xylene [30].*

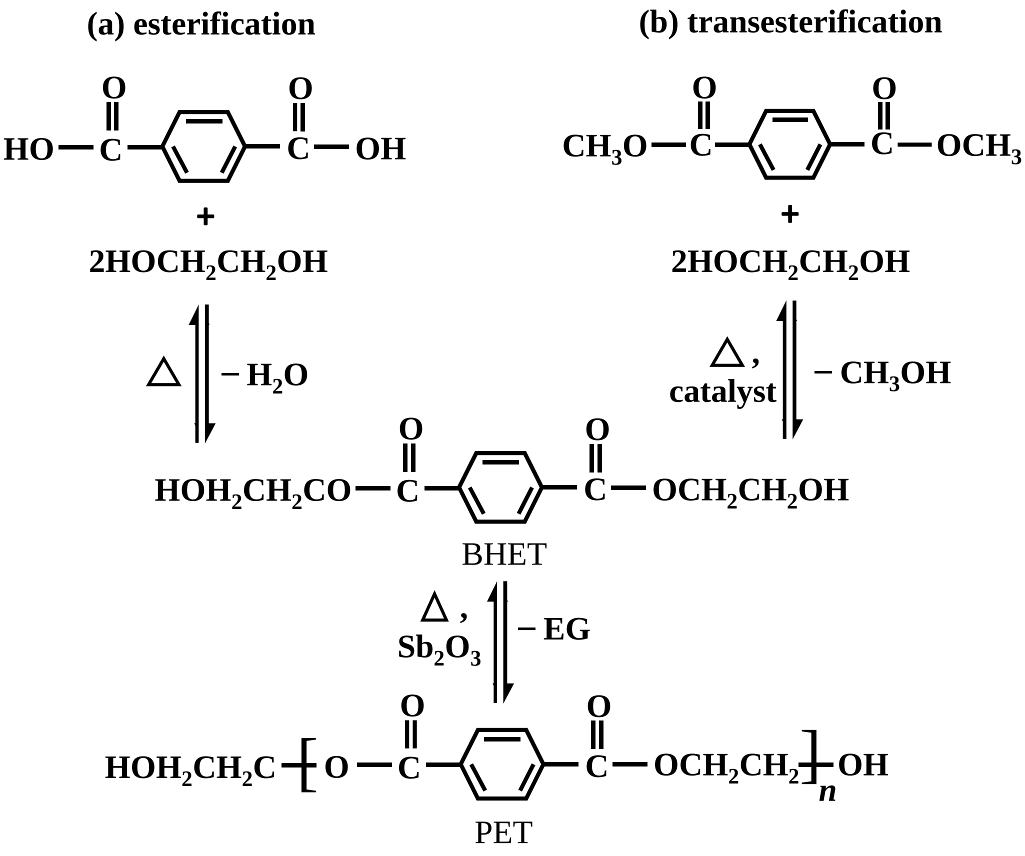

Figure 1.8: ***(a)*** *Esterification and* ***(b)*** *transesterification reaction mechanisms for PET polymerization.*

There are two chemical mechanisms mainly by which the PET can be produced, esterification reaction (by using TPA) and *trans*-esterification (by using DMT) (reaction mechanisms shown in ***Figure 1.8***). In the esterification reaction of PET synthesis, diacid TPA and diol EG are prepolymerized at a pressure of 3-6 bar and temperature of 250°C. This process does not need any catalyst because the diacid functionalities can self-catalyze the esterification reaction. The high temperature given to the reaction helps in solubilizing TPA in EG. Water (H_2O) is produced as a sub-product and bis-(2-hydroxyethyl)-terephthalate (BHET) is produced.

On the other hand, the *trans*-esterification reaction is performed at a comparatively lower temperature (150 to 200 °C). The catalyst commonly used in the reaction is antimony. The sub-product methanol need to be removed via distillation for continuous production of BHET. The second step involves pre-polymerization of BHET for the production of PET. This step involves continuous removal of EG (produced via condensation) from BHET at a temperature of 250-280°C, pressure of 2-3kPa and antimony oxide (Sb_2O_3) taken as catalyst [26, 32-35].

Hence produced PET has a degree of polymerization (DP) up to 30. The third step in PET synthesis is polycondensation to increase the molecular weight. The DP in this stage can be further increased to 100.

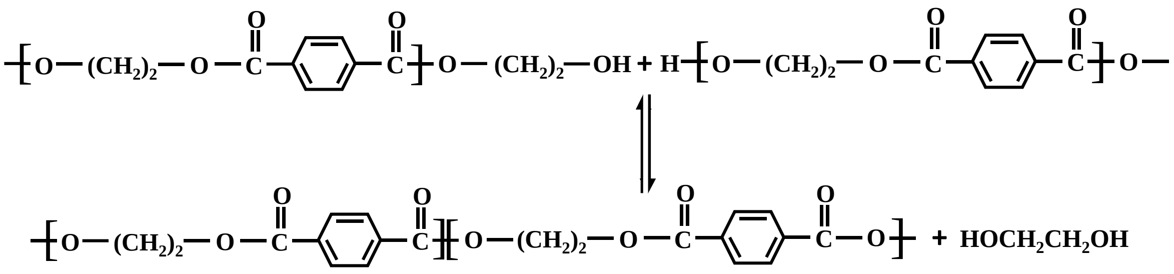

Figure 1.9: Polycondensation reaction mechanism.

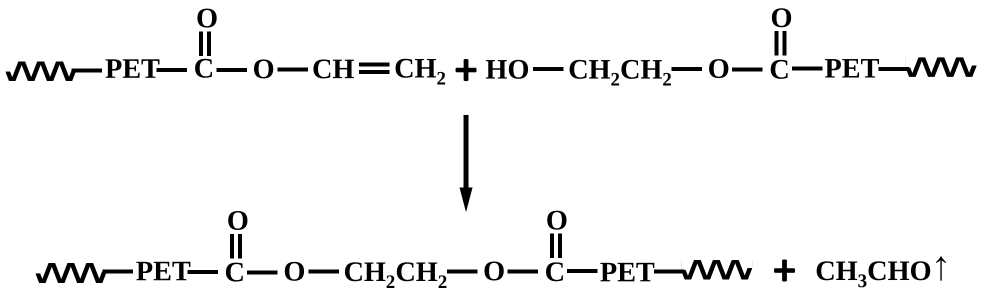

Figure 1.10: Reaction of vinyl ester and hydroxyl end groups.

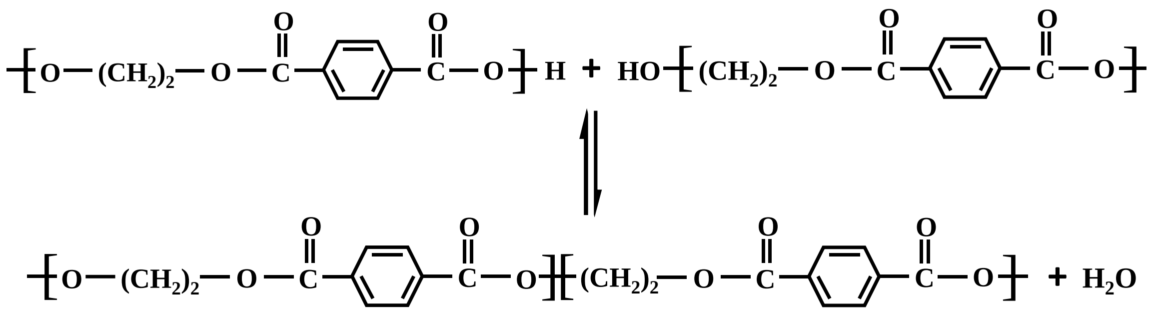

Figure 1.11: Esterification reaction.

The parameters for polycondensation process are 280-290 °C [34], 270-285 °C and 50-100 Pa [26]. Hence produced PET have enough properties to be used for production of sheets and fibres. The applications where high molecular weight PET is required (*e.g*. containers, packaging) having DP in range of 130 to 150, an additional step of solid state polymerization (SSP) process is needed. The SSP is relatively simple process in which molecular weight of the polymer is increased by promoting reactions between polymer end groups. The SSP results in increased side reactions to enhance the DP and it is very efficient in extraction of volatile degradation product in comparison to other processes for molecular weight enhancement. The operating condition for SSP are 200-240 °C at a pressure of 100kPa for a time duration of 5-25 hours [34]. The bottle grade PET is produced by SSP at a temperature of 210°C for 15 to 20 hours [36, 37].

Three main reactions occur during SSP process [30, 37]:

1- The main reaction occurring while SSP process is polycondensation reaction in which two hydroxyl end group of polymer chains interact and enhance the molecular weight of PET. EG is produced as a side product (***Figure 1.9***).

2- The second reaction occurs when hydroxyl end group reacts with vinyl ester end group producing acetaldehyde (AA) as a by-product and results in increment of PET molecular weight (***Figure 1.10***).

3- The third reaction that takes place during SSP is when hydroxyl and carboxyl end group reacts and results in enhancement of molecular weight of PET while producing H_2O as a side product (***Figure 1.11***).

The transparency of PET is an excellent advantage for several applications. The amorphous PET is used in most of the application where transparency is a priority such as bottled packaging of CSD, juice, water etc. The properties of PET such as mechanical thermal and gas barrier are enhanced by biaxial orientation blow molding technique [38].

1.5 Nanofiller

The fillers are classified as "nanofiller" when one of the three dimension of them falls in nano range *i.e.* <100nm. Depending on the desired properties, there are different types of nanofillers available. The commercially available nanofillers can be classified as [24, 39]:

1.5.1 Zero-dimensional (0D) nanofillers (particulates): These fillers have all the three dimensions in nanometer range (*i.e.* <100nm). The examples of zero-dimensional nanofillers are:

- Quantum dots
- Nano-alumina
- Nano-silica
- Nano-titanium dioxide (n-TiO_2)
- Polyhedral oligomeric silsesquioxanes
- Nano-magnesium hydroxide (n-$Mg(OH)_2$)
- Nano-silicon carbide (n-SiC)
- Nano-zinc oxide (n-ZnO)
- Nano-silver (n-Ag)

Apart from the above mentioned nanofillers, particulate filler also include nano-diamond, n-Fe_3O_4, n-Fe_2O_3, n-$CaCO_3$, n-$BaTiO_3$, n-$BaSO_4$, n-ZnS etc [24]

1.5.2 One dimensional (1D) nanofillers: These fillers have two of their dimensions in nanometer range (*i.e.* <100nm). These nanofillers have been studied widely and have been used to enhance various properties. Some of one dimensional fillers are:

- Carbon nanotube (CNT) (single-wall CNT (SWCNT) and multi-wall CNT (MWCNT))
- Carbon nanofiber (CNF)
- Halloysite nanotube (HNT)
- Nickel nanostrand (NiN)
- Aluminium oxide nanofiber (Nafen)

1.5.3 Two dimensional (2D) nanofillers (platelets): This category of nanofiller have one of their dimension in nanometer range (*i.e.* <100nm). The other two dimensions can be two fold or multifold higher. These nanofillers have layered structure. Examples of 2D nanofillers are:

- Nanographene platelet (NGP)
- Montmorillonite clay (MMT)
- Layered double hydroxide (LDH)

1.5.4 Three dimensional (3D) nanofillers: In this category none of the three dimensions of nanofiller falls in nanometer range. All three dimensions are greater than 100nm. Examples of 3D nanofillers include [40-44]:

- Zeolite
- Polycrystals
- Nanoballs (having dendritic structure)

- Nanocoils
- Nanocones
- nanopillers

1.6 Structure and properties of layered silicate:

Polymer clay nanohybrids are mostly prepared with layered silicate as nanofillers. The layered silicates are 2D nanofillers having a 2:1 layered structure and belong to phyllosilicate family. Montmorillonite (MMT) is a largely used layered silicate nanoclay having chemical formula as $Na_{1/3}(Al_{5/3}Mg_{1/3})Si_4O_{10}(OH)_2$. It has silica and alumina as the essential constituents. The structure of layered silicate has been shown in ***Figure 1.12***. A single platelet of the layered structure has one octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The tetrahedral unit of silicate layer comprise of SiO_4 forming a tetrahedral network, single repeating unit of which consists of Si_4O_{10}. Between these two silicate layers there exist an octahedral sheet consists of aluminum oxide in which aluminum atom is embedded by surrounding closely packed hydroxyls or oxygens. In these clay layers isomorphic substitution of tetrahedral or octahedral lower valent metallic cations (*e.g.* Al^{3+} get replaced by Fe^{2+} or Mg^{2+}, or Mg^{2+} by Li^{1+}) cause a negative charge which is distributed along the platelets due to the difference in charge valancy [45]. This negative charge is counter balanced by exchangeable cations (alkaline and alkali earth cations) which are located in the space between the clay platelets called interlayer spacing or gallery. The layered silicates consist of stacks of these platelets hence forming a layered structure. The platelets are stick to one another by weak Van der Waals force. Thickness of the single sheet of layered structure is 0.94nm whereas the space between two platelets is ~1nm in its natural unmodified state whereas the lateral dimensions of the silicate layers may range from 30nm to few microns or larger [2, 45-49]. The lateral dimension of the layered silicates are not well defined and depend on the geological process in which the layered silicates were formed from the solution [46].

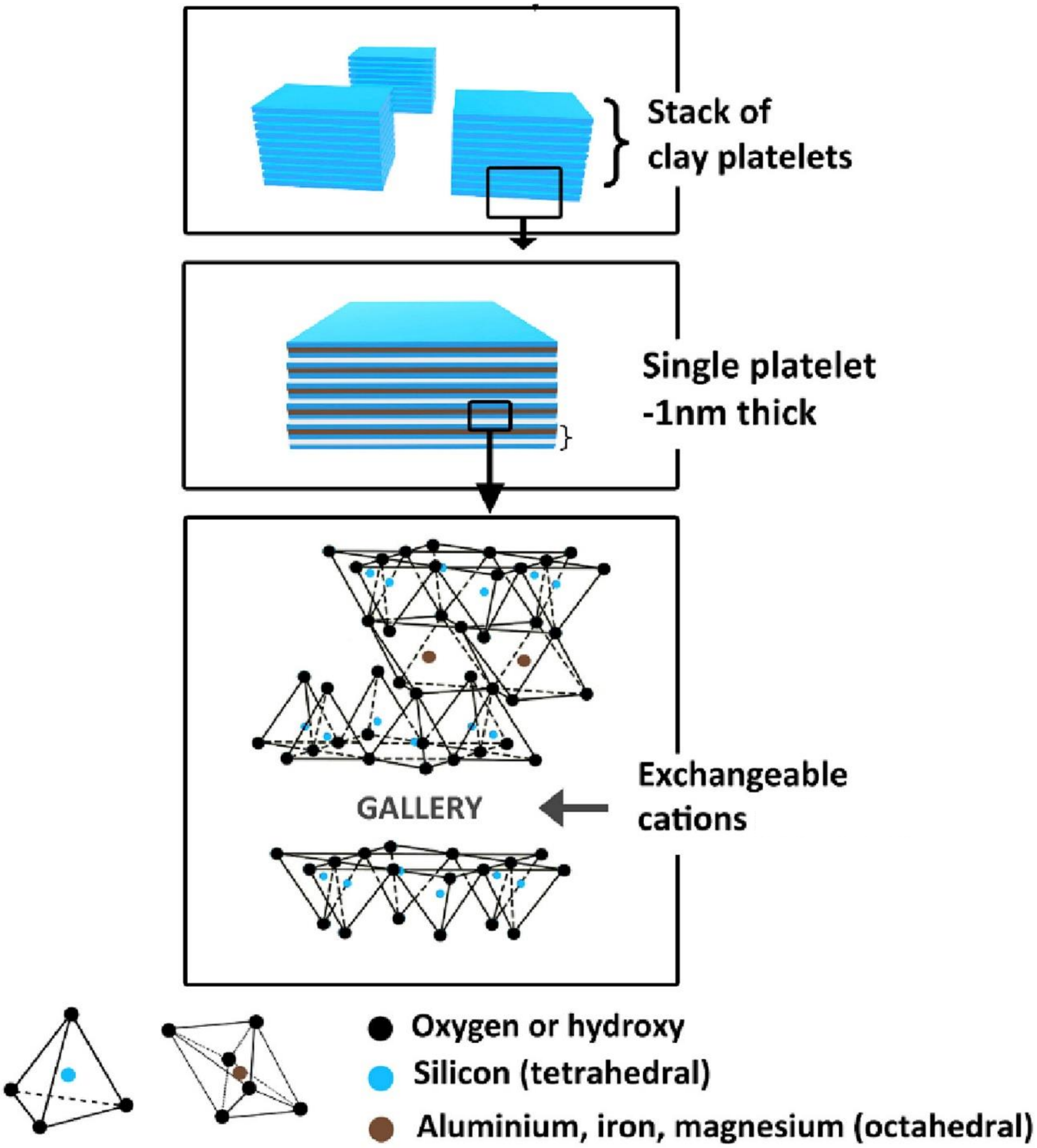

Figure 1.12: *Structure of layered silicate [50]*

The simple physical mixture of unmodified layered silicates and polymer matrix may or may not form a nanohybrid. The poor interfacial interaction between organic (polymer) and inorganic (silicate clay) phases is the key factor due to which poor thermal and mechanical properties are obtained. On the other hand when there is strong interfacial interaction between inorganic and organic phases, individual clay layer dispersion takes place at a nanometer range, achieving the enhanced properties overall in comparison to microcomposites or traditionally filler polymers [2, 51-56]. The pristine layered nanoclay have cations (usually Na^+ or K^+) in their interlayer [57]. In this natural state, the nanoclay exist in stacks of clay platelets as shown in ***Figure 1.12***. There are two specific characteristics of the layered silicate which need to be considered for the formation of the polymer nanohybrids:

- The capability to be dispersed into polymer matrix separating the individual clay layer.
- The capability to modify the surface chemistry by ion exchange reaction between inorganic and organic cations.

The layered silicates, in pristine state are miscible with only hydrophilic polymers (for example poly(vinyl alcohol) (PVA) [58] or poly(ethylene oxide) (PEO) [59]). For layered silicates to be miscible with the polymeric materials, the pristine hydrophilic surface of the silicate layers must be transformed into the organophilic surface so as to ease the intercalation process for the various polymers to synthesize an effective polymer nanohybrid. Without the organic modification of the layered silicate, the clay stacks will be dispersed in the polymer matrix in a phase separated microcomposite structure. This modification can be accomplished by ion-exchange reactions between the inorganic alkali cation present on the surface of the clay with the organic cations (such as alkylphosphonium or alkylammonium). The layered silicates have a moderate charge because of the cation present at the clay surface which is called cation exchange capacity (CEC) expressed in mequiv/100g. The organic cations improves the wetting capacity of the clay platelets by lowering surface energy of the inorganic silicate layers and causes the platelets to swell and gallery to expand resulting in an enhanced interlayer spacing. Also, alkylphosphonium or alkylammonium cations in organically modified layered silicate cater functional groups which can react with polymers. These functional groups can also initiate polymerization of monomer in some cases and enhance the interfacial strength of polymeric matrix and inorganic layered silicate [56, 60].

Table 1.2: *Details of few of surface modified MMT clay (Southern Clay Products, Inc.) [24]*

Nanoclay	**Dry particle size (μm)**	**d-spacing (nm)**	**Surfactant**
Cloisite®Na^+	<25	1.17	None
Cloisite®5	<40	3.27	Bis(hydrogenated tallow alkyl)dimethyl salt
Cloisite®10A	<10	1.9	Benzyl(hydrogenated tallow alkyl)dimethyl salt
Cloisite®11	<40	1.84	Benzyl(hydrogenated tallow alkyl)dimethyl salt
Cloisite®15	<10	3.63	Bis(hydrogenated tallow alkyl)dimethyl salt
Cloisite®20	<10	3.16	Bis(hydrogenated tallow alkyl)dimethyl salt
Cloisite®30B	<10	1.85	Alkyl quaternary ammonium salt
Cloisite®93	<40	2.79	Trialkyl ammonium salt
Cloisite®Ca^{++}	<15	1.55	None

Different organically modified clays which are commercially available are listed in ***Table 1.2***. Southern Clay Products, Inc. supplies MMT clays under commercial name “Cloisite”. The CEC and the surfactant used are listed in Table. Different organic modification and content of the surfactant result in variation in interlayer spacing (d-spacing). Although increased d-spacing is not always the only criteria for getting the exfoliation of nanoclay and the desired properties. In a study, Dennis et al. [61] prepared nylon6 nanocomposite using Cloisite 30B and Cloisite 15A. They found that the Cloisite 30B was comparatively easy to exfoliate and disperse in the nylon6 matrix than the Cloisite 15A whereas the d-spacing of Cloisite 30B is lower. Hence, the exfoliation and interfacial interaction, being the major focus for achieving the desired properties, depend on the surfactant structure and surface chemistry of the layered silicates.

1.7 Structure of polymer-clay nanohybrids

For production of polymer-clay nanohybrid, very low weight percentage of nanoclay is needed. Nanoclays usually have a very high aspect ratio with their intergallery spacing about 1nm and length ranges from 30-1000 nm. Hence, very small amount of clay gives a very high surface area (for one gram of nanoclay, the surface area achieved by dispersed platelets is 700-800m^2) for a strong interaction between polymer and nanoclay in comparison to traditional fillers. This interfacial interaction is responsible for mainly three kinds of polymer clay nanohybrid structures (***Figure 1.13***):

1.7.1 Phase separated (tactoid formation): When the nanoclay stacks are intact and tactoids are dispersed in form of micro-sized fine clay particles in the polymer matrix, the structure is called phase separated. Polymer chains are unable to enter in between the clay gallery.

1.7.2 Intercalated: When polymer chains penetrate the intergallery spacing of nanoclay platelets in a well ordered manner and increase the interlayer spacing between the clay stacks. In this case, the stacking structure of the nanoclay is preserved. Because the adjacent nanoclay platelets get separated (distance between them is increased), this structure also called delaminated structure.

1.7.3 Exfoliated: When the penetration of polymer chains between the nanoclay galleries is so severe that it separates the nanoclay stacks, then the structure is called exfoliated structure. The basic stacking structure of nanoclay is destroyed and the nanoclay layers becomes independent of one another. The nanoclay platelets get dispersed in the polymer matrix in a disordered manner. The exfoliated structure results in generation of the highest amount of surface area of the nanoclay layers. It provides opportunity for the strongest interfacial interaction between nanoclay and polymer matrix. In exfoliated structure much less amount of nanoclay loading is needed to achieve the desired properties. Although, some studied proves that a combination of exfoliated and intercalated structure results in better property enhancement in some polymer nanohybrid system. Svoboda et al [62] prepared polypropylene (PP) nanocomposites with organically modified nanoclay Cloisite 20A and found that the nanocomposites with fully exfoliated structure of nanoclay presented less improved mechanical and crystallization properties as compared to the nanocomposites with a combination of intercalated and exfoliated structure.

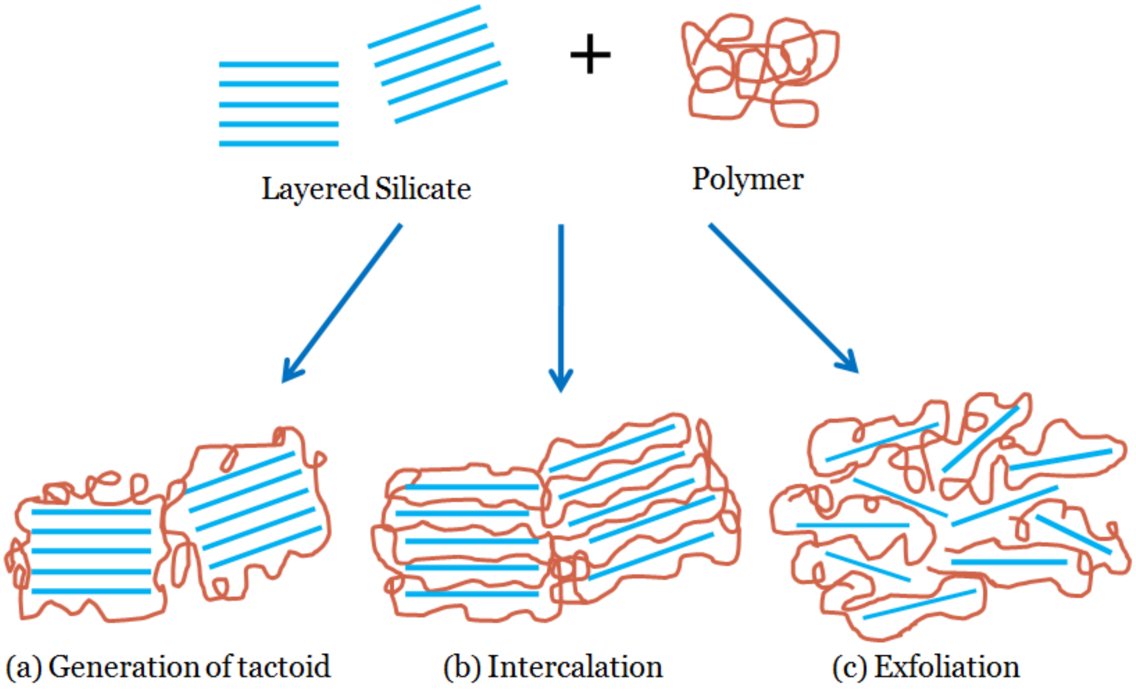

Figure 1.13: *Development of polymer clay nanohybrid (a) tactoid formation results phase separated structure; (b) intercalated structure; (c) exfoliated structure.*

1.8 Polymer nanoclay hybrid preparation techniques

Polymer nanohybrids are prepared by following three methods:

1.8.1 Solution casting

In this preparation technique, a solvent is taken in which the polymer or prepolymer (if the polymer is not soluble such as polyimide) is soluble and the clays are swellable. The polymer is dissolved into the solvent and then the clays are dispersed. The stacks of nanoclay are adhered by weak forces between them hence they are dispersed and delaminated in the solvent or the clay stacks are swelled by the solvent. This allows access to the polymer chains to enter. The polymer then get adsorbed on to the clay layers and polymer chains enter the interlayers of layered nanoclay to intercalate the nanoclay. When the solvent is evaporated the clay stacks reassemble and sandwich the polymer to create a multilayered ordered structure. The polymer is precipitated by solvent evaporation and consequently nanohybrid is obtained. The Toyota research group implemented this method for the very first time to prepare polyimide nanocomposites [12, 63]

1.8.2 In-situ intercalative polymerization

In this preparation method, the layered silicates are swollen into a liquid monomer or the monomer solution. The liquid monomer penetrates the clay interlayers and polymer formation takes place between the intergallery spacing hence creating an intercalated clay structure. The polymerization process can be initiated by external stimulation like heat, radiation, chemical, photochemical activation or by diffusing a suitable initiator into the monomer solution. It can also be induced by organic initiator and/or catalyst inside the clay gallery. When the monomer solution and initiator and/or catalyst are present inside the clay interlayers, the polymerization occurs between the clay layers of the host nanoclay. Subsequently, as the polymer chains grow in between the clay layers, the clay galleries expand and gradually exfoliate. The polymer chains continue to grow leading to distort the ordered structure of inorganic phase by delamination of the nanoclay platelets in the polymer matrix. The success of this exfoliation by delamination of the clay platelets depends on the initiator/catalyst inclusion between the clay galleries to start the sufficient polymerization [64].

1.8.3 Melt intercalation

In this processing technique, the layered silicates are mixed with the polymeric material in a molten state. It is also called melt blending process. The polymer pallets are heated at a temperature above their softening point and mixing nanoclay can be mixed using conventional polymer processing techniques (such as extrusion). The melt intercalation process uses heat and kinetic energy to disperse and separate nanomaterials into distinct nanoparticles and let polymer chains to enter into clay platelets. The successful production of nanocomposite by this process depends on the compatibility between the nanoclay platelets' surface and the polymeric material. To enhance the compatibility between the inorganic nanoclay and organic polymeric matrix, the nanoclay is modified with suitable alkyl ammonium cation by ion exchange reaction before the melt intercalation process [64]. To enhance the properties of nanohybrids by mixing nanoclay into the polymer matrix, the homogeneous dispersion of nanoclay throughout the matrix is the primary goal. The filler agglomerates need to be broken into smaller particles in order to disperse homogeneously. The mixing of hydrophobic polymers and hydrophilic inorganic clays is a challenge for nanocomposite manufacturing. Primarily three factors are responsible for the dispersion of nanoparticle agglomerates: interfacial interaction between polymer matrix and filler (agglomerate particles), cohesive forces between the agglomerate particles; and hydrodynamic forces acting onto the agglomerate particles [65]. When hydrodynamic forces supersedes the cohesive forces among the agglomerate particles and there is a strong interaction between the polymer matrix and filler, the homogeneous dispersion takes place. The dispersion phenomenon has been studied widely using different mechanism [65]. Out of all, rupture and erosion mechanism seem to be the fundamental mechanism of agglomerate dispersion. At first the big agglomerates are broken down into comparatively smaller agglomerates followed by the erosion mechanism, in which the hydrodynamic forces cause the continuous separation of the particles from smaller agglomerates by erosion. Kao et al

[66] proposed a model for the dispersion of spherical particles in the high viscous medium which is given as:

$$\frac{d(\frac{R}{R_0})}{dt} = \check{k}\frac{a}{R_0} \tag{1.2}$$

Where R is the radius of agglomerate, a is the radius of individual spherical particle making the cluster, $\check{k}$ is the proportionality constant which is dependent on volume fraction of the particles forming the cluster, local velocity gradient and the flow field geometry.

1.9 Problem of e-waste

As it is well known that the polymer waste is a humongous problem of present time. The waste causing landfill generates environmental problems. The harmful chemicals leach out from the different kinds of plastics and cause disruption of water, soil as well as all form of wildlife. The amount of discarded polymer waste is increasing day by day. The degradation of every polymer is not feasible or easy. The plastic sustain in the environment for centuries and continue to disrupt the habitat in form of landfills. Because of our dependency on polymeric materials from domestic products to the technological advancements, prominence of the need of plastic predominates which causes gigantic amount of plastic waste every minute. Hence it is a necessity to circulate the used plastic again into useful practical applications. One such area is electronic waste or E-waste. The term E-waste represent the discarded electrical or electronic equipment. E-waste also comprise of the used electronic components which are to be retrieved, reused, recycled, resale or disposed. The E-waste is generated when an electrical or electronic equipment is discarded away from its useful life and discontinued from further usage.

The development and innovations in the electronic industry make people to update to newer equipment and discard the older versions very frequently such as VCRs were replaced by DVD players which then replaced by blu-ray players. These technological advancements cause generation of huge amount of E-waste. The equipment which are no longer in use fill the landfill rapidly. In 2018, only 20% of the total generated E-waste was collected, documented or recycled. The continuous E-waste generation has been growing day by day. According to a report by Platform for Accelerating the Circular Economy (PACE) and United Nation (UN) E-waste coalition report of January 2019, approximately 50 million metric tonnes of E-waste was generated globally. A very small portion of this E-waste (only 20%) was formally recycled [67]. This E-waste is expected to grow further in the upcoming years This E-waste contains many potential materials which can be used for the generation of materials of improved property. Poly(acrylonitrile butadiene styrene) (ABS) is one such material which is abundantly found in the electronic equipment. It has a huge potential to be used for the property modulation of an existing polymer such as low density polyethylene (LDPE).

1.10 Structure and properties of ABS

ABS is an amorphous thermoplastic engineering polymeric material containing three main monomer components: acrylonitrile, butadiene and styrene (***Figure 1.14***). It consist of a substantial category of efficiently producible resin materials used for manufacturing of products manifesting wide spectrum of properties. ABS consists of a thermoplastic matrix (styrene and acrylonitrile copolymer (SAN)) in which particulates of rubber (butadiene copolymer or polybutadiene) are dispersed.

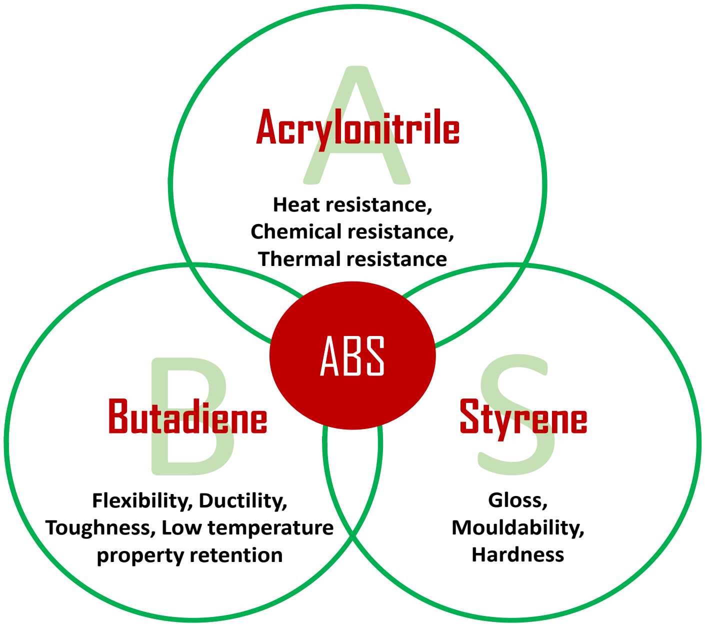

Figure 1.14: *Elements of ABS*

The properties of ABS can be modulated by varying the ratio of three monomer units and the process by which these components are formulated and polymerized (***Figure 1.15***) [24, 68]:

- Acrylonitrile: provides hardness, rigidity, aging resistance, heat resistance, thermal stability and chemical resistance.
- Butadiene: provides flexibility, ductility, melt strength and toughness.
- Styrene: provides gloss, hardness and good processability.

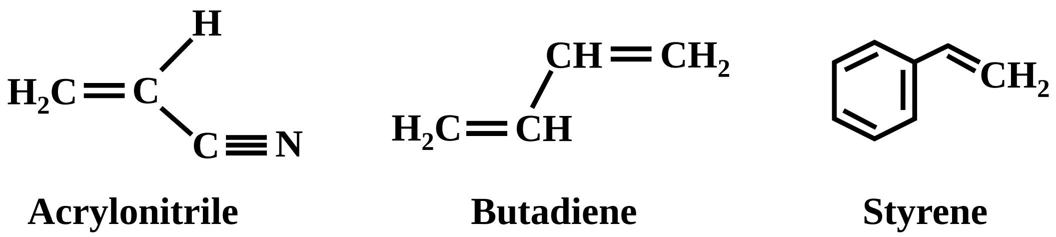

Figure 1.15: *Structures of monomer units of ABS*

General range of these monomer units is taken as 15% to 35% of acrylonitrile, 5% to 30% of butadiene and 40% to 60% of styrene. ABS can be manufactured in two ways [69, 70]:

- The first manufacturing approach, a blend of copolymers of styrene acrylonitrile copolymer (SAN) and acrylonitrile butadiene rubber (NBR) is prepared. Generally the small particles of rubber phase are homogeneously dispersed in the continuous phase of SAN.
- In the second method acrylonitrile is chemically bonded (grafted) onto a butadiene or styrene copolymer or butadiene backbone. This manufacturing process is more viable as it provides better opportunities to modulate the specific properties of ABS.

The different polymerization techniques help in controlling and modulating the SAN structure as a grafted polymer linked to rubber particles, as a continuous phase and as occlusions comprised within rubber particles [71].

Key properties of ABS are:

- High rigidity
- High dimensional stability
- Good impact resistance
- Excellent surface gloss and appearance
- Good abrasion resistance
- Electrical properties: ABS has a sufficiently good dielectric constant and its electrical properties are unaffected by humidity and temperature.
- Fire resistant: It has flame retarding grades which have slow burning properties required for electrical and electronic equipment as well as in other applications such as building and construction.
- Good chemical resistance: resistant to salts, aqueous acids, alkalis, oils, alcohols, concentrated hydrochloric acid etc.

Key properties are achieved by additives, comonomers or by modulating structural alterations (such as constituents' content and composition, extent of rubber crosslinking, size of rubber particulates and distribution, extent of SAN grafting *etc.*). Because of its excellent properties, ABS is used in various electrical and electronic applications such as telephone handsets, monitors, keyboards, computer housings, laptop bodies, home appliances as well as in other fields such as automotive applications, building and constructions, sports instruments etc. The huge production of E-waste generates the discarded ABS which proposes an opportunity to be used and mixed with a polymer which has comparatively inferior properties. One such polymer is LDPE which has comparatively lower rigidity and mechanical strength than ABS. The discarded ABS can be beneficial for the mechanical, thermal property enhancement of LDPE for opening more horizons of application of LDPE/ABS blends.

1.11 Polyethylene (PE)

Polyethylene or polythene is one of the most commonly used plastic worldwide. It is produced by catalytic polymerization of ethylene monomer [72]. To enhance or modify its properties, it is also copolymerized using other materials. The variation in comonomer content and type can manipulate the properties of PE such as density. This comonomer can affect and modulate the frequency, length and type of branching of polymer chains. There are various types of PE are manufactured having a mixture of similar ethylene polymers of chemical formula of $(C_2H_4)_n$ with varying values of 'n'[73]. It is a thermoplastic polymer which can be modified into thermosetting polymer (cross-linked PE). There are several types of PE depending on the density and polymer chain branching. The properties of PE depend on the type and extent of branching, molecular weight and crystal structure. There are various types of PE depending on above mentioned factors:

- Ultra high molecular weight polyethylene
- High molecular weight polyethylene
- Ultra low molecular weight polyethylene
- High density polyethylene (HDPE)
- Crosslinked polyethylene
- Low density polyethylene (LDPE)
- Linear low density polyethylene (LLDPE)

Out of these the most important grades of PE are LDPE, LLDPE and HDPE. The degree of branching which discriminate among the PE types has been shown in ***Figure 1.16***. The polymer chains of HDPE has linear structure and hence the HDPE has closely packed polymer structure with high density. The LLDPE has short chain branching on the main chain and it has lower density than the HDPE. The LDPE has long chain branching and the structure is less closely packed and hence it has lower density than LLDPE.

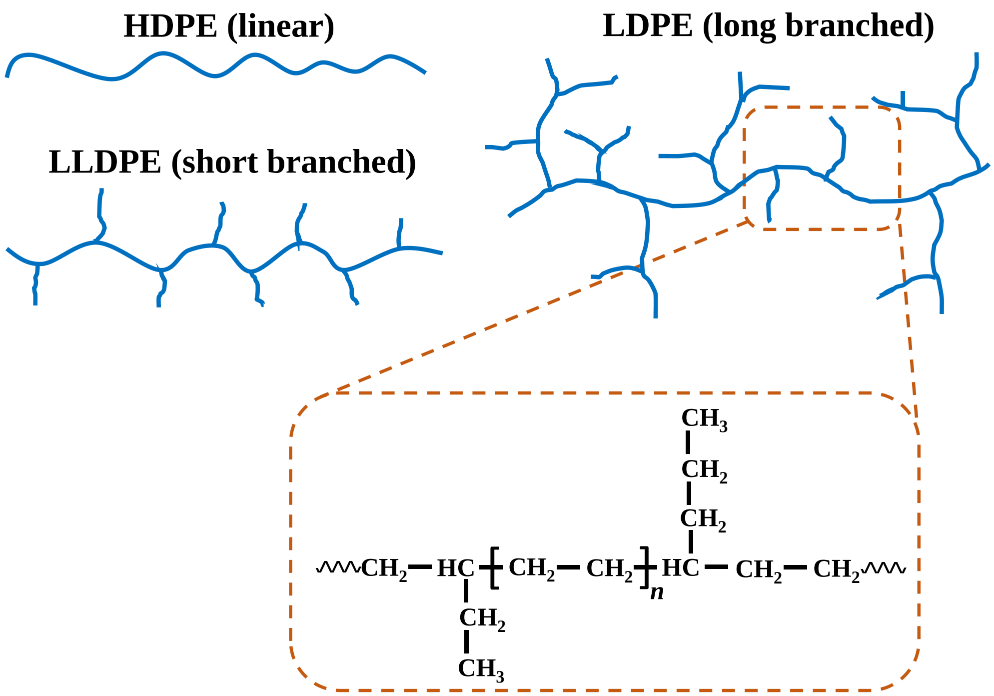

Figure 1. 16: *polymer chain branching in various kinds of PE*

1.12 Low density polyethylene (LDPE) polymer

LDPE is a common commodity polymer which is used widely in numerous applications. It is a thermoplastic material which is manufactured by free radical polymerization of ethylene monomer at high temperature and pressure. Due to its highly branched structure, it does not have a close packed structure and has low density. The branched structure provides toughness and linearity gives strength to the polymer [74]. It has a hazy appearance and it is highly flexible, non-contaminating, nontoxic, and chemically inert and insoluble at room temperature. It is widely used in many general purpose applications such as containers, toys, bags, films, liners, laboratory equipment, agriculture films and various other durable polymer products applicable in daily lives as well as in construction, automotive *etc*. It has high processability and it can be processed by extrusion, blow molding, injection molding *etc*.[75] It has high ductility but has low tensile modulus and tensile strength and lacks in mechanical strength. The limitations of LDPE are:

- Low tensile strength
- Low tensile modulus
- Limited heat distortion temperature
- Poor thermal resistance
- Low hardness, stiffness

Hence it has the need for the improvement of mechanical and thermal properties and the discarded ABS can fill this gap by acting as a strengthening component.

1.13 Polymer blends

Mixing of polymers to form a polymer blend is accomplished in order to obtain the modulated property gain from each of the constituent polymers. Polymer blend is defined as the mixture of minimum two polymers or copolymers where the concentration of each ingredient is above 2%. The polymers when mixed can form a miscible blend or can be immiscible. Miscible blend is formed when its domain size is equivalent to the macromolecular segment and are homogeneous to the molecular level. Immiscible blends contain one of the polymer phase in dispersed form with a distinct interphase and are inhomogeneous at molecular level [76, 77].

In case of immiscible blend systems, the morphology of the blend depends on the concentration of components. The dispersed phase is attained in spherical form for low concentration of either of the component. As the concentration increases the spherical shape of dispersed particles can transform into cylinders, fibers or sheets. The interphase compatibility is a crucial factor for the betterment of the properties. Most of the industrial polymers are immiscible hence form immiscible blends with poor interphase properties. To improve the interphase properties, need of compatibilization arises for:

- Finer dispersion by reduction of interfacial tension.
- Interfacial adhesion in solid state.
- Stabilization of the morphological structure against the shear and thermal effects during processing steps.

Compatibilization process consists of the following general strategies for immiscible polymer blends [78]:

a) The two polymeric phases can be co-crystallized where the immiscible polymeric phase are semi-crystalline and are capable of co-crystallization.

b) The dispersed crosslinkable phase can be dynamically vulcanized during the melt processing while the second phase is a non crosslinkable, immiscible polymeric material.

c) A third component added for the compatibilization. It can be performed in following ways:

  - An additional component is added (0.5 to 2 wt. %) depending on the miscibility with both the phases of blend (either have miscibility for both phases or have one part miscible with one polymer and another part with other polymer)
  - Addition of compatibilizer in form of core shell polymer in large quantity (≤ 35 wt. %) (works as impact modifier).
  - Reactive compatibilization where during the extrusion process, the compatibilizing copolymer formation takes place by heterogeneous reactions across the boundary of melt phase. It is a sub-category of **reactive extrusion** process where chemical reactions resulting interchain copolymer formation takes place during extrusion process at high temperatures [79].

1.14 Reactive extrusion

It is relatively an economical and efficient industrial process to produce polymer blends having a compatibilized structure. It is preferred across the industries for its feasible single step reactive processing. It facilitates the formation of copolymerizing agent whilst the establishment of an immiscible phase structure during a single step melt processing of immiscible polymeric blend. The key factors of this strategy are [78]:

- The primary benefit gain from this strategy is that the copolymer need not to be prepared separately which results in lesser energy consumption.
- The copolymer formation at the boundary surface of immiscible polymeric materials facilitates the direct and immediate compatibilization process. Hence, it diminishes the need to be dependent on the residence time of extrusion for diffusion process to take effect.
- Copolymer has the similar segmental molecular weights as compared to the bulk phase molecular weights in which the segment has to be dissolved during in-situ formation of copolymer. Hence wide range of molecular weight polymer blends can be produced.
- The disadvantage of this strategy is that the immiscible polymers are required to have specific chemical functionality for the interphase reaction in presence of copolymer or third agent formed *in-situ* while reactive extrusion.

The reactive extrusion is dependent on the exposure of the interfacial volume that is available at the phase boundaries. The extruder are designed (screw element sequences, auxiliary conditions) in such a way that the maximum interfacial surface area is exposed in order to promote the chemical reactions. There are two processes which takes place during the *in-situ* formation of crosslinked, block or graft copolymer [78]:

- The immiscible polymer react with each other across interphase boundary directly via reactive functionalities present on each of the polymers called direct process.
- Additional reactive species is added in the immiscible blend during reactive extrusion for formation of copolymer. Hence present three chemical bodies are required to react

during the short extrusion residence time. The additional reactive species can be a catalyst that activates the reactive functionalities on first polymers to react with the reactive functionality on second polymer.

- Most of the times, the added reactive species is a coupling agent which can react with each of the immiscible polymer individually as opposed to reacting with one polymer only. If this coupling agent is soluble in one phase, the homogeneous reaction across the melt interphase boundary predominates instead of copolymer formation (heterogeneous reaction).

1.15 Benefits of polymer blending

The benefits achieved via the polymer blending process include:

- It provides the economic way of achieving the full set of properties.
- Enhances the performance of an existent engineering resin.
- Improves the specific properties such as chemical resistance, impact strength, tensile strength, heat distortion temperature (HDT), dimensional tolerance, hardness, stiffness etc.
- Presents the feasible means for recycling of polymer waste.

1.16 Literature review

1.16.1 Past studies on PET/clay nanohybrids

Enhancement of properties of PET has been the focus of the past studies because of the exceptional implementations of PET in various fields. The numerous present applications and possible usages of PET in other applications present the need of improvement in structural, mechanical, thermal, gas barrier properties etc. There are several work done by researchers which focus on the formation of PET/clay nanocomposites for fulfilment of the same [80-91]. Inducing crystallinity is also a way to improve few properties such as gas barrier. However, it has a drawback of reducing toughness to a greater extent [92]. Hence, there should be a balance among all the properties for the material to make it practically useful. In situ polymerization is an energy consuming process whereas the melt mixing and the solution casting processes are comparatively economical [93]. The melt mixing process is also a widely used process but it could have the disadvantage of degradation of clay modifier at higher temperatures because the modifier present between the clay layers usually has lower degradation temperature [91].

Ghasemi et al. [94] prepared PET/Cloisite 30B nanocomposites by cast extrusion technique. The nanocomposites were uniaxially stretched using chill roll subsequent to cast extrusion. The nanocomposites were prepared using up to 3 wt. % of the nanoclay. The nanocomposites were found to have intercalated and partially exfoliated structure. In stretched nanocomposite samples, the nanoclay platelets were found to be aligned in machine direction as deduced by wide angle X-ray diffraction (WAXD). The nanocomposites were tested for the mechanical, thermal, gas barrier properties. The tensile modulus was enhanced up to 20% and gas barrier was enhanced up to 23% for oxygen gas. The nanocomposites became brittle due to inclusion of nanoclay in polymer matrix as rendered by puncture and tear propagation resistance.

Wang et al. [95] prepared PET/MMT nanocomposite using organic Montmorillonite DK_2 by melt extrusion technique. Good dispersion of nanoclay in the polymer matrix was achieved at 1% of nanoclay concentration. More than 1% clay concentration the dispersion was not ideal and intercalation was not completed. The mechanical properties were improved for 1% of clay concentration because of presence of large surface area for interfacial interaction. The crystallization rate and thermal stability improved. Onset temperature of degradation and peak degradation temperature enhanced. The optimum mechanical properties were improved. Tensile strength was improved up to 25% at 1% of clay loading. Although, for more than 3% clay inclusion, mechanical properties such as flexural strength, impact strength, tensile strength and elongation at break were decreased less than that of pure PET. The elongation at break increased slightly for 1% clay concentration and then started decreasing for higher clay loading.

Yang et al. [96] studied effect of nanoclay treated with super critical carbon dioxide ($scCO_2$). Cloisite®30B nanoclay was used which was processed with $scCO_2$. The nanoclay was mechanically stirred at above the critical temperature (50 ^oC) and pressure (17.2 MPa) of CO_2 in a sealed vessel. Hence treated predispersed Cloisite®30B clay was used for the formation of PET/clay nanocomposites and was compared with the nanocomposites prepared with as-received Cloisite®30B nanoclay by melt extrusion technique. The structural investigation by TEM and WAXD showed that the PET was able to penetrate into the intergallery of predispersed Cloisite®30B and the nanocomposites had homogeneous dispersion. The Young's modulus and tensile strength were improved 24.9% and 12.1% respectively whereas the gas barrier was increased up to 44% at a clay loading of 3wt %. Although, elongation at break reduced drastically from 369% to 66%. The prediction of Young's modulus values were done using Halpin-Tsai model and a micromechanical model proposed by Ji et al. [97]. The range of predicted values was higher than the experimental values of Young's modulus. The reasons for less increment in the Young's modulus of PET/clay nanocomposites using predispersed Cloisite®30B clay $scCO_2$ were contemplated as the lack/low level of exfoliation of the nanoclay, presence of agglomerated particles, weak interfacial interactions between polymer and clay particles, inability of clay particles to rotate in the stretching direction.

Ghanbari et al. [98] focused on to overcome the accelerated thermal degradation during melt extrusion in PET/clay nanocomposites. An epoxy based multifunctional chain extender (Joncryl®) was used to react with the PET chain end groups to compensate the molecular weight loss during the thermal degradation. Two organo-MMT clays were used namely C30B (Cloisite®30B) and N28E (modified with octadecyl ammonium). The presence of Joncryl® resulted in uniform dispersion of nanoclay particles in PET matrix. The molecular weight was increased due to the presence of Joncryl® which was evident from the higher viscosities observed from rheological measurements. The Young's modulus was improved but there was huge reduction in elongation at break and toughness. The gas barrier properties were also improved in presence of Joncryl®.

Zekriardehani et al. [99] focused on biaxially oriented PET films and studied the effect of crystallization, chain dynamics and free volume distribution on the gas barrier properties. Strain-induced crystallized PET was prepared at different stretch ratios. Hence produced crystalline samples were compared to amorphous PET. The gas barrier properties were obviously improved due to the presence of crystalline phase and reduction in average fractional free volume as well as free volume distribution.

Tammaro et al. [100] prepared PET nanocomposite using organically modified layered double hydroxide (LDH). LDH was prepared by co-precipitation method and modified using seven types of organic molecules. The PET nanocomposites were prepared by incorporating LDH into PET using high energy ball milling and obtained milled powder was then compression molded into films. Hence prepared nanocomposites found to have a well delaminated structure as observed by XRD. The nanocomposites showed thermal stability of organic molecules after intercalation was up to 200^{o}C as compared to pristine molecules. The pristine unmodified LDH were observed as irregularly dispersed in the matrix as compared to homogeneous dispersion of organically modified LDH in nanocomposites prepared by ball milling. The permeability was also reduced because of the highly dispersed polar nanoclay platelets. Mechanical properties were not examined.

Shen et al. [101] investigated the effect of biaxial orientation on PET and PET/clay nanocomposites prepared with 6 wt. % addition of synthetic fluoromica clay Somasif MTE which was modified with 31% methyl trioctyl ammonium chloride via melt extrusion. Biaxially stretched (at 95 ^{o}C and 120 ^{o}C) nanocomposite films were investigated and characterized. The compression molded nanocomposites showed higher strain hardening due to the exfoliation of clay platelets and resulted in better mechanical properties as well. The strain hardening parameter was found to be linearly and inversely related to the tensile modulus for PET and PET/clay nanohybrids. Higher strain rates hindered the clay particle rotation and delamination of clay platelets. The TEM images showed that the tactoids were aligned and had higher aspect ratios when samples were stretched at lower temperature (95 ^{o}C). Halpin-Tsai model predicted the modulus of PET and PET nanocomposite and gas barrier properties were also improved up to 27% for 6% clay concentration.

Ghasemi et al. [102] prepared PET/ clay nanocomposite using Cloisite 30B and MMT modified with pyridinium, imidazolium and phosphonium surfactants. Nanocomposites prepared by C30B showed better intercalation level and dispersion than the imidazolium and phosphonium modified MMTs. Nanocomposites with phosphonium modified clay were characterized to have better thermal stability but showed lower level of intercalation.

Kim et al. [103] focused on the dispersion of nanoclays in PET/clay nanocomposites which were prepared by melt extrusion and solid state polymerization. Three types of organo-MMT clays were used namely Cloisite 10A, Cloisite 15A and Cloisite 30B. The melt compounded nanocomposites showed intercalated structure whereas the solid state polymerized nanocomposites showed two interlayer spacing for intercalated structure. Nanocomposites were found to have lower thermal stability and hydrolysis taking place at 275 ^{o}C. Due to presence of clay modifiers, molecular weights of nanocomposites were reduced because of the comparatively high degradation rates of nanocomposites.

Dini et al. [104] also studied the effect of clay concentration on solid state polymerization (SSP) of PET and PET/clay nanocomposites using Cloisite 30B. The water assisted extrusion route was adopted for the nanocomposite production. It was found that the SSP after extrusion process compensated the molecular weight reduction effect caused by hydrolysis in PET and nanohybrids. Nanocomposites showed lower molecular weight than the pure PET because of the restriction in the movement of reactive groups and diffusion of water and ehthylene glycol formed due to SSP because of the nanoclay platelets. In their previous work Dini *et. al.* [105] compared water assisted extrusion process followed by SSP in three nanocomposite system containing Cloisite Na+, Cloisite 30B and Nanomer I28E. Nanocomposites with Cloisite 30B showed better clay dispersion and intercalation than the others. Also, tensile modulus and gas barrier properties of C30B nanocomposites were improved up to 20 and 26% respectively. Rheology studies showed that the effect of SSP was limited in nanocomposites due to the barrier imposed by clay platelets as compared to pure PET.

Vassiliou et al. [106] prepared PET nanocomposites using organomodified MMT with a synthesized modifier based on triphenylphosphine and fumed silica by *in-situ* polymerization process. The nanocomposites were thermally stable and showed better mechanical properties than pure PET.

Xu et al. [107] studied the degradation of PET /clay nanocomposite prepared by melt extrusion. The study was focused on the two primary factors for the degradation of nanocomposites which were hydroxyl group present on the clay edges and the absorbed ammonium on the clay. The MMT clay was modified in five ways having different hydroxyl group present on the clay edges and different amount of ammonium absorbed preparing the PET/clay nanocomposites. Viscosities and molecular weight were determined by dilute solution viscosity. The presence of hydroxyl group accelerated the degradation process because hydroxyl group behaved as Brønsted acidic sites. The absorbed ammonium caused polymer degradation due to Brønsted acidic sites produced by Hofmann elimination reaction occurring in ammonium. Moreover, the nanocomposites with exfoliated structure experienced more degradation due to large surface exposure of clay and PET. The degradation was apparent from the lowered viscosity and molecular weight. Pyromellitic dianhydride (PMDA) was used as the chain extender which resulted in increment of molecular weight and retained the exfoliated structure as well.

Gokkurt et al. [108] prepared PET/clay nanocomposites using 1, 3 and 5 wt. % of Nanomer®I30E (MMT clay organically modified using octadecylamine). The nanocomposites were prepared by a two-step melt processing technique in which a masterbatch was prepared with 20 wt. % of nanoclay via twin screw extruder. After that that the masterbatch was diluted in a single screw extruder to produce nanocomposite film. The structure was found to be exfoliated for 1 wt. % of clay and mix of intercalated and exfoliated for higher clay concentrations. Nanocomposites showed higher storage modulus in glassy region as determined by DMA analysis. The barrier properties were also improved up to 35% for 5 wt. % of clay. The permeability values were predicted using Nielsen model and storage modulus values were fitted in Halpin Tsai model.

Frounchi et al. [109] used two clays namely Cloisite 15A and Nanolin (1 to 4 wt. %) for PET nanocomposite preparation via melt extrusion. The nanocomposites had exfoliated structure for 1% clay concentration and intercalated structure for high clay concentrations. Thermal properties were improved with an improvement in melting temperature from 245 to 251 ^{o}C.

It was deduced that the clay platelets could shield the conduction of heat to an extent until the heat flow at higher temperature was enough for melting the crystals. Although the glass transition temperatures were found to be the slightly lower in Nanolin and same for Cloisite 15A. The reason was the higher exfoliation level in Nanolin as compared to Cloisite 15A. The high exfoliation caused intimate mixing of nanoclay platelets and polymer molecules which lowered the interaction between PET molecules and eased the molecular motions. Tensile and gas barrier properties were improved for low wt % of clay due to nanoclay exfoliation.

Wang et al. [110] prepared nanocomposites of PET and poly(*m*-xylene adipamide) (MXD6) using sodium montmorillonite (Na-MMT) clay up to 5 wt % without any surfactants or additives. Due to the compatibility of water and Na-MMT clay, the Na-MMT water solution was used with polymer in melt extrusion process to achieve the exfoliation of clay platelets at nanometer level. The exfoliation was achieved for lower loadings of clay but at high level of clay loading (3 and 5 wt %), complete exfoliation in PET/Na-MMT was not achieved whereas good level of exfoliation was achieved for all clay loadings of MXD6/Na-MMT nanohybrids as determined by combined TEM and XRD analysis. The thermal properties were improved with increments in glass transition (T_g) and melting temperatures (T_m) in PET nanocomposites due to presence of nanoclay. The rate of crystallization was improved as nanoclay behaved as a nucleating agent in both nanohybrid systems. The oxygen barrier properties were also improved in both nanohybrids where PET hybrids had better gas barrier at 2% of clay than the higher loadings because of the exfoliated structure.

Mahajan et al. [111] studied and determined the effect of oxygen scavengers on PET to improve the oxygen barrier properties. Two scavengers were used namely 3-cyclohexene-1, 1-dimethanol (CHEDM) and monoolein (MO) separately with PET by *in-situ* polymerization. It was found that both scavengers reacted with the hydroxyl group at PET chain ends. The oxygen barrier was improved up to 39% in PET/CHEDM and 26% in PET/MO by using a cobalt octoate catalyst while sheet extrusion for permeability testing. T_g and T_m were found to be decreased in PET/MO copolymer with the increment in MO content (from 1 to 5%) because of the long side chains of MO. In PET/CHEDM, the T_g remained unchanged and T_m decreased. The decrement in melting peak was due to restriction of PET crystallization because of transesterified CHEDM. The rheological measurements determined Newtonian behavior for PET at a range of shear rates whereas the PET/MO copolymers showed Newtonian behavior at 1% MO and non-Newtonian at 5% MO. PET/CHEDM copolymers showed Newtonian behavior at all compositions.

Hayrapetyan et al. [112] focused on a sustainable way to produce ecofriendly sulfonated polyester to be used as clay compatibilizer to promote the polymer mixing during extrusion process to produce of PET/clay nanocomposites. The nanocomposites prepared with MMT modified by sulfonated polyester (MMT-SPE) was compared with imidazolium modified MMT (MMT-MSIm) and commercially modified MMT with ammonium exchanged MMT (MMT-Alk) and Cloisite30B (MMT-OH). The onset degradation temperature was enhanced for MMT-SPE and MMT-MSIm as compared to MMT-Alk and MMT-OH. Sufficient clay matrix mixing was determined by the XRD where no peak was observed whereas TEM images showed the patchy distribution of nanoclay in the matrix and sufficient intercalation taking place in the clay layers. The Young's modulus and elongation at break were not changed duo to the reason that the development of small imperfect crystallites counterbalanced the reinforcement effect provided by the nanoclay. Oxygen gas barrier and water vapor barrier properties were also improved. The UV-transmission rate was decreased in nanocomposites.

Ke et al. [93] synthesize PET/clay nanocomposites by in-situ polymerization. The Na-MMT used was organically modified by a series of steps. Clay content was taken from 1 to 4 wt. %. XRD patterns showed absence of peak in nanocomposites. The T_g decreased for lower clay content because of the plasticization effect but it increased with increasing clay content. The oxygen barrier property was measured on biaxially stretched film and found to be improved compared to PET.

Chen et al. [113] prepared PET/clay nanocomposites via in-situ polymerization technique. For prevention of thermal degradation of nanoclay modifier, the Na^+ MMT clay was modified directly with BHET (monomer of PET) and the nanohybrids were produced via in-situ polymerization. Hence prepared nanohybrids were compared with the nanohybrids prepared via unmodified Na^+-MMT in terms of dispersion of clay, mechanical properties, thermal properties and crystallization kinetics. Unmodified nanoclay was found to be dispersed in the polymer matrix in form of large agglomerates with an average size of 0.5 µm. whereas BHET modified nanoclay was nanodispersed as well as intercalated in the PET matrix. The thermal and mechanical properties were improved with enhancements in glass transition temperature, tensile strength, tensile modulus and storage modulus. Elongation at break reduced drastically.

Costache et al. [114] used thermally stable surfactants for preparation of PET/clay nanocomposites. The nanocomposites were prepared by melt blending technique and were characterized for morphology and thermal stability. Three clays were used namely montmorillonite, magadiite and hectorite. To overcome the problem of organic modifier degradation, the clays were organically modified with the prepared thermally stable surfactants. The investigated organic modifications included vinylbenzyl-ammonium copolymers and alkyl-quinolinium surfactant. These two organic modifiers had high degradation temperature to be used for the melt extrusion processing of PET nanocomposites at high temperatures and had encouraging thermodynamics for the formation of PET clay nanocomposites. The structure of nanocomposites prepared with the modified MMT and hectorite clays were found to have mix morphology of immiscible, intercalated and/or delaminated clay platelets whereas the PET/magadiite showed a mix immiscible microcomposite structure. The peak heat release rate was decreased for the nanocomposites.

Wen et al. [115] studied the effect of silane grafting on the structure of PET/MMT clay nanocomposites. Ammonium intercalated MMT and acid treated MMT were used for the nanocomposite formation by melt extrusion. The acid treated MMT showed better interaction with PET as concluded by mixed intercalated exfoliated structure, increased storage modulus and depressed equilibrium melting point obtained by Hoffman-Wees plots.

Barber et al. [116] studied the effect of PET modification coupled with the organic modification of MMT clay. Three clays were used namely Cloisite®Na$^+$, Cloisite®10A and Cloisite®15A. PET ionomer were prepared via PET sulfonation containing several ionic comonomer incorporations (low levels *i.e.* 1.8-5.8mol% of $-SO_3-Na$ group) in the PET backbone. The nanocomposites of modified polymer as well as filler were prepared via melt extrusion. The incorporation of sulfonate groups in the PET backbone resulted in the better dispersion of organically modified MMT clays as deduced by TEM and XRD. The structure of modified PET/clay nanocomposites was found to be exfoliated and/or largely intercalated. The reason for the better structure was the interaction between the electrostatic interactions between the edges of nanoclay platelets and the sulfonate groups attached to the backbone of modified PET. This interaction promoted the movement of the sulfonate groups along with the PET chains, into the clay galleries. The nanocomposites were found to have increased tensile modulus but were not investigated for the toughness/elongation at break or brittleness. Crystallization rates were found to be decreased for the nanocomposites due to the improved dispersion of nanoclays.

Gurmendi et al. [117] obtained PET/clay nanocomposites via melt intercalation using three kinds of Cloisite®20A, Cloisite®15A and Cloisite®30B. The XRD results showed increment in d-spacing in nanocomposites of 20A and 30B clays concluding the intercalation took place. Although, it was deduced that the unchanged d-spacing in 15A could also have the intercalated morphology present in the nanocomposites by substituting the surfactant present in the interlayer. All three clays showed almost similar dispersion levels in PET matrix. 15A showed slightly better dispersion despite having an unchanged interlayer spacing. The mechanical properties were improved and tensile modulus increment was linear for up to 6% of clay concentrations. It was observed that the level of intercalation was favored by higher polarity (high level of interactions between surfactant and polymer chains) but clay dispersion and modulus increment were independent of the amount and polarity of the surfactant used for clay modification. Elongation at break reduced drastically from 278.6%

for pure PET to ~2% for nanocomposites containing 4 and 6 weight percentage of clay concentrations.

Calcagno et al. [118] used Cloisite Na^+, 10A, 15A and 30B to produce PET nanocomposites via melt extrusion. Clays were found to be dispersed in a mixed intercalated and exfoliated structure and tactoids were found in clay with apolar modifiers (Cloisite 15A). Nanocomposites showed a higher crystallization rate compared to pristine PET.

Farhoodi et al. [119] compared effect of spherical (Titanium dioxide (TiO2)) and platelet shaped nanoparticles in PET/TiO_2 and PET/Cloisite 20A nanocomposites. Mechanical properties improved slightly whereas the ductility of clay nanohybrid system reduced as compared to the addition of TiO_2 nanoparticles. Abdallah et al. [120] studied effect of surface modification of purified bentonite clays using phosphonium salts (benzyl triphenyl phosphonium chloride and tetraoctyl phosphonium chloride). Mechanical properties were slightly improved. Clay system showed better results and improved decomposition temperature. Li et al. [121] studied the chemistry of clay surface by using ethoquad modified MMT, unmodified hectorite, and phenyl hectorite for PET nanocomposites formation via *in-situ* polymerization. The thermal, mechanical and water vapour transmission rate were investigated and PET/MMT showed high storage modulus and water vapour barrier because of the probable strong interaction in nanohybrid due to PET-ethoquad entanglements.

1.16.2 Past studies on polymer blends utilizing ABS

The polymer blends have been studied in the past in various reports where ABS has been used to enhance the properties of different polymers by melt extrusion or reactive extrusion process. ABS is abundantly available in E-waste. Arnold et al. [122] studied the recycling of ABS obtained from different variety of waste electrical and electronic equipment (WEEE) resources. The authors studied the effect of void formation during the recycling of ABS obtained from different E-waste resources. The mechanical properties and optical microscopic studies were performed in order to investigate the extent of effect of void formation to analyze the reusability of ABS polymer. By additional intensive/longer processing, the voids present during processing were reduced and ABS of improved strength was achieved. Wang et al. [123] recycled ABS obtained from WEEE by using a chain extender based on epoxy. The properties lost due to recycling were recovered to an extent by using chain extender. Blends of ABS with different polymers had been studied in the past for improvement of their properties.

Polyamide 6 (PA6, also known as nylon 6) is a polymer which is not compatible with ABS. The blends of PA6 with ABS has attracted many studies for improvement of the blend properties. Zhao et al. [124] prepared the PA6/ABS blends with submicron size particles of ABS dispersed in PA6 matrix via in-situ reactive extrusion. The ABS content of 15% was found to be suitable for the enhanced interfacial adhesion and increased toughness and impact strength of the blends. In another report [125] they also studied the crystallization and rheological properties and found the blends to have heterogeneous nucleation and shear thickening behavior.

Zhao et al. [126] prepared PA6 and ABS blend by using core shell and grafted ABS via an elaborated in-situ reactive extrusion processing. Dispersed phase structure was obtained having ABS droplets in PA6 matrix. The core shell ABS and PA6 blend resulted in homogeneously dispersed ABS in PA6 matrix having improved impact strength whereas the grafted ABS and PA6 blend resulted in agglomerated ABS phase dispersion resulting in lower toughness. The tensile and flexural strength were improved due to presence of rigid particles of grafted ABS.

A triblock copolymer Styrene (ethylene butadiene) styrene (SEBS) grafted MA (SEBS-g-MA) used in the studies to enhance the compatibility of PA6/ABS blends. Essabir et al. [127] used SEBS-g-MA up to 16% concentration by extrusion. The blends of PA6/ABS were found to have enhanced adhesion in the dispersed ABS particles in PA6 matrix. The blends showed two phase structure and enhanced tensile strength. However, Young's modulus decreased upon increasing the SEBS-g-MA content. T_g increased slightly and values of storage modulus and loss modulus also improved.

Kudva et al. [128] prepared nylon6/ABS blends using four types of ABS having different rubber contents. Imidized acrylic polymer was used as compatibilizer in 5 wt% concentration. The morphological investigation revealed that the ABS particles were efficiently dispersed and mechanical properties tests showed increment in low temperature toughness due to presence of ABS with compatibilizer. By increasing nylon6 content, modest enhancement in yield strength and modulus was noticed whereas the impact strength at room temperature was not compromised. In their other report [129] they studied the effect of type of compatibilizer and history of processing on nylon6/ABS blend. Effect of two types of compatibilizer styrene-acrylonitrile-maleic anhydride terpolymer (SANMA) and imidized acrylic polymer was studied. The blends were tested for property change for multiple extrusion cycles. The blends showed high toughness at room temperature and at low temperature, the multiple extrusions compromised the ductility for imidised acrylic polymer. The morphology also changed to larger domain size after number of extrusion cycles. Both low temperature toughness and morphology was unaffected in blends having SANMA. The blends containing SANMA showed better processability and other properties in comparison to imidised acrylic polymer due to the reactive nature of both the compatibilizers. The imidized acrylic polymer had anhydride and acid functionalities which could react with nylon6 whereas SANMA had anhydride functionality only.

Araujo et al. [130] studied the thermal properties of Nylon6 and ABS blends. Nylon6/ABS blend is immiscible and incompatible. Hence, poly(methyl methacrylate)(PMMA)-MA copolymer was used to compatibilize the blend. The MA functional group of copolymer reacted with NH_2 groups resulting grafting of nylon6 molecule with PMMA-MA and enhancing the interfacial adhesion. A two phase structure was achieved. The dynamic mechanical thermal analysis showed no change in T_g. The morphological analysis showed the compatibility between nylon6/ABS blend in presence of PMMA-MA by reduction of dispersed ABS particle size. There are few other studies which have also focused on nylon6/ABS blends using compatibilizer [131-142]

Vadori et al. [143] prepared polylactide (PLA) and ABS blends using a chain extender and an acrylic copolymer by melt blending because PLA and ABS are not compatible with each other. Two phase structure was achieved with comparatively better dispersion of ABS particles in comparison to simple melt extrusion of PLA and ABS. The PLA reacted with epoxide groups of chain extender (Joncryl) and caused the chain extension whereas the ABS remained unchanged. There were no functional reaction between PLA and ABS and the interactions between two polymers were mechanical. Hence prepared blend showed enhanced mechanical properties. Increment in chain mobility allowed chains to slide and caused enhanced elongation at break and impact strength. They deduced that the chain extender also caused the formation of interchain linkages in PLA resulting in increased toughness.

Rigoussen et al. [144] studied the property improvement of PLA by making its blend with ABS. They studied the effect of cardanol on compatibility of PLA/ABS blend and found that the reactive extrusion in presence of cardanol gave improved PLA/ABS blend morphology. Further they [145] used cardanol in modified way to improve the mechanical properties of PLA/ABS blends. The blends were prepared via reactive extrusion of PLA/ABS in two ways. Cardanol is a compatibilizer which reacts with ABS whereas it does not react with PLA. It was used in two ways i.e. in presence of epoxidized cardanol compatibilizer and mixture of unmodified cardanol and epoxidized cardanol compatibilizer. The interfacial adhesion was improved and fine dispersion of ABS was observed. The mechanical properties were significantly improved.

Abt et al. [146] modified the properties of PLA by reactive extrusion with ABS. PLA was first modified by reactive extrusion using Joncryl (multifunctional epoxy reactive agent). A compatibilizer, ABS grafted with maleic anhydride (ABS-g-MA), was also used during the melt extrusion processing of ABS and modified PLA. The addition of modified PLA resulted in reduced ABS particle size as compared to unmodified PLA. The dispersed ABS phase size further reduced when ABS-g-MA was added. The ABS phase was found to be dispersed in rod like particles. The diameter of rod reduced after addition of compatibilizer. The storage modulus values decreased in presence of ABS whereas glass transition temperature found to be unaltered. The presence of ABS particles resulted in reduction in crack propagation speed by diverting its way because of interactions with propagating crack, resulting in higher absorbed energy. The PLA/ABS blends prepared by first reactive extrusion of PLA and then melt extrusion of PLA/ABS with ABS-g-MA by Carrasco et al. [147]. They studied the thermal degradation phenomenon of the blends by determining the kinetic parameters using general analytic equation. The degradation temperature was enhanced in polymeric blend.

Polypropylene (PP) is a polyolefin which has also been used with ABS for its property improvements. Patel at al. [148] used PP-g-acrylic acid to enhance the phase dispersion and interfacial adhesion in PP/ABS blends. The blends were prepared by melt extrusion. Up to 5wt % of the compatibilizer the ABS phase size reduced. The interphase properties compromised for more than 5% of PP-g-acrylic acid content due to formation of compatibilizer aggregates. Morphology as well as tensile modulus was improved for 5wt% compatibilizer concentration. In their other work [149] they used PP grafted with 2-hydroxyethyl methacrylate (2-HEMA) as compatibilizer by a two-step mixing extrusion technique to improve the properties. The ABS concentration was varied from 10 to 90% and 2-HEMA was taken from 2.5 to 7.5 phr. 2.5 phr was found to be optimum for 2-HEMA and PP rich blends showed better enhancement and balance of morphological and mechanical properties.

For PP/ABS blends preparation, PP grafted with MA (PP-g-MA) and/or ABS-g-MA had been used in various studies. Luo et al. [150] prepared polypropylene (PP) and ABS blend and tested their mechanical properties. PP and ABS are immiscible and not compatible with each other so the PP/ABS blend was prepared using two compatibilizers PP-g-MA and ABS-g-MA in a mass ratio of 2:1. These two graft copolymers were added with an epoxy curing agent and reactive extrusion was performed. The blend achieved was of two phase structure with ABS particles dispersed in it. The addition of two graft copolymers only did not improve properties and the size of dispersed ABS was also did not reduce. The addition of epoxy curing agent resulted in decrement of the size of dispersed ABS phase and improvement in interfacial adhesion. Tensile strength and flexural modulus was increased whereas impact toughness could not improve with addition of grafted copolymers and epoxy curing agent.

Lee et al. [151] prepared PP/ABS blends in 70/30 ratio with PP-g-MA as compatibilizer via twin screw extrusion. The morphology improved and two phase blend showed reduced size of ABS dispersed phase PP/ABS (70/30) blend with 3phr PP-g-MA. The impact, flexural and tensile strength were improved the most for 3phr PP-g-MA.

Bonda et al. [152] used SEBS-g-MA, PP-g-MA and an ethylene α copolymer (EAO) in three concentrations (3, 5 and 10phr) with PP/ABS blends to see their effect on property improvement. Blends having 20% ABS concentration showed better properties than other concentrations. Combination of SEBS-g-MAH and EAO, each in 5 phr concentration considered to be ideal combination for compatibilizer concentrations for enhanced mechanical properties. Other studies have also showed the use of separately prepared compatibilizer's usage to gain the property improvements in PP/ABS blends [153-160]

LDPE and ABS blends have very few studies because of their high immiscibility and incompatibility. Peydro et al. [161] studied the effect of LDPE contamination on ABS. The mechanical properties of the ABS degraded due to mixing with LDPE. The low concentrations (1 to 8 wt. %) of LDPE were mixed and extruded with 1 to 8 wt% of SEBS. The mixing of SEBS improved impact strength and elongation at break but could not improve the tensile strength and young modulus. Gupta et al. [162] prepared PP/ABS blends and studied the effect of adding LDPE on the properties of ternary blend. They achieved a finer dispersion of ABS in the PP matrix in presence of LDPE. In their other report [163] they studied the impact and tensile properties of binary (PP/ABS) and ternary blends (PP/ABS/LDPE). Dispersed and elongated ABS particles in PP matrix became less elongated in presence of LDPE. The presence of LDPE caused low impact toughening behavior in ternary blends because of interlock network structure with the PP matrix. The fracture surface of ternary blends showed less coarseness. Young's modulus and elongation at break did not improve by addition of LDPE whereas yield stress and yield strain showed almost similar values as the binary blends.

As we can see that various polymers have been blended with ABS in order to modulate their properties. The past works have used numerous kinds of compatibilizers such as PP-g-MA, ABS-g-MA, SEBS, SEBS-g-MA, SANMA etc for the enhancement of several properties. These compatibilizers are prepared separately and the process is cost and energy consuming. On the other hand, single step reactive extrusion can prove to be beneficial and less energy consuming if no separately prepared copolymer is used in the process.

There is a need for the usage of ABS extracted from large amount of E-waste. This ABS can be utilized by making its blend with an existing polymer to enhance its properties. As LDPE has very minimal studies reported with ABS due to their compatibility issues and is widely being produced and used, it presents an opportunity for the development of their blend with improved properties.

1.17 Objectives of this work:

The polymers being the primary part of our daily lives, there is a need to continuously improve the properties for different applications of polymers. PET is a largely used polymer in various fields as discussed and there have been various studied conducted to improve its mechanical, thermal, morphological and structural properties. PET nanohybrids have attracted great attention over the years to improve the properties. This is a preferable and widely researched field over other methods. Different nanoclays with layered structures have been used for PET nanohybrids' preparations. The environmental and economical aspects of the polymer applications in packaging and other fields require virtues of being light weight and having improved mechanical, thermal and gas barrier properties. Hence there is still a need to improve the mechanical, thermal and gas barrier properties of PET. There is no study of PET nanohybrids with nanotalc and NK75 clay.

The used PET has been widely extracted back from the discarded polymeric waste and being recycled at high rates. Whereas there is still huge scope of extracting useful materials which can be recycled and developed into valuable and useful practical applications. ABS polymer is abundantly found in E-waste and there are numerous studies in which ABS has been widely used to improve the properties of various polymers. Hence, there is an opportunity and large scope for extracted ABS to be reused as a strengthening agent with an existing polymer.

The objectives of this study is to develop PET nanohybrid using three different clays (nanotalc, NK75 and Cloisite 30B) to enhance its mechanical, thermal, gas barrier and structural properties. Further, reuse and recycle ABS extracted from E-waste by making its blend with LDPE polymer to enhance its mechanical properties.

The specific objectives of the thesis are:

- Synthesis of PET nanohybrids using three different nanoclays by solvent casting route.
- Structural, mechanical, thermal and gas barrier property enhancement in PET nanohybrids by addition of nanotalc.
- Improvement in the structural, mechanical, thermal and gas barrier properties by addition of NK75 clay in PET/clay nanohybrids
- Effect of addition of Cloisite 30B nanoclay on structural, mechanical and thermal properties of PET nanohybrids.
- Utilization of ABS extracted from E-waste by single step reactive extrusion process.
- Prepare a blend with extracted ABS having improved mechanical properties for various practical applications.