Chapter 1
Chapter 1

Introduction

1.1 POLY (ETHYLENE-CO-VINYL ACETATE) (EVA)

EVA copolymer represent the largest volume segment of the ethylene copolymer market. The commercial success of EVA is due to its transparency and ease of fabrication. Moreover, these copolymer are heat processible, flexible, have better UV and ozone resistance and are relatively inexpensive. It is a semi-crystalline polymer and offers excellent weather resistance, toughness, chemical resistance, solvent resistance. EVA has no specific fragrance or odour. It is mainly recognized for its flexibility and toughness (even at low temperatures), adhesion characteristics and stress-cracking resistance. EVA is one of the most widely used high barrier family of materials due to its low permeability to gases and organic vapors. The polymer can be made into end product by various processing techniques such as coating, solvent evaporation technique, molding, melt extrusion and a variety of emulsion and solution mixing.

EVA is highly resistant to dilute mineral acids, alkaline substance, fats, oil and detergents but not to concentrated mineral acids, ketones and aromatic or chlorinated hydrocarbons and strong oxidizing agents. Halogen attack on EVA leads to embrittlement, although dilute solutions of chlorine and bleaching agent have little effect.

EVA is a high molecular weight copolymer obtained in the form of free flowing, solid pellets. It can be produced commercially by three different basic methods - solution, emulsion and continuous bulk polymerization techniques. It is the copolymer of ethylene and vinyl acetate (Scheme. 1.1). The weight percentage of vinyl acetate usually varies from 10 to 40%, with the remainder being ethylene. The properties of EVA depend on the vinyl acetate content - the amount of vinyl acetate in the copolymer controls its character. At very low proportions of vinyl acetate, the copolymer resembles low density polyethylene but exhibits the processing behaviour and physical properties of a tough thermoplastic. Initially, EVA with lower percentage of vinyl acetate comonomer was available in market. By varying the vinyl acetate content, EVA copolymers can be tailored for applications as rubbers, thermoplastic elastomers and plastics (Yin et al (2006)). Increase in the vinyl acetate content results in increased flexibility; amorphous nature of EVA increases by decreasing the crystalline nature and it becomes more elastic in nature. An increase in polarity gives rise to a number of interesting properties such as compatibility with other polymers, increased adhesion, printability and electrical properties.
1.1.1 APPLICATIONS OF EVA

EVA is a widely used copolymer in a variety of industrial applications. It is used as barrier sheets, packaging films, adhesives/paper coatings, carpet backing, shoe foams, tyres, different types of foams, sound damping/ sound barrier sheet, surfboard and skim board, traction pads, for making decorative flowers, as cold flow improver in diesel fuel and a separator in HEPA filters. EVA copolymer is a biocompatible polymer and is used in various biomedical applications such as drug delivery systems and medical implants. It is used in pharmaceutical fields as disposable surgical gloves, orthodontia products, contact lens holders, anaesthetic face masks and floating eyewear.

EVA foam is used as padding for various sports equipment such as bicycle saddles, hockey pads, boxing and mixed martial arts gloves and helmets, wakeboard boots, ski boots, water-ski boots, fishing rods and fishing reel handles. It is used as a shock absorber in sports shoes. It is also used in manufacturing of floats for fishing gear such as purse seine (seine fishing) and gillnets because of its resilience properties. EVA slippers and sandals had become very popular now a days because of its unique properties like low cost, light-weight, easy to process and mold, odorless, glossy finish. EVA is widely used in coatings formulation for interior water-borne paints.
1.1.2 EVA IN FOOD PACKAGING

EVA is being used in food packaging as shrink wrappers, ice bags, stretch wraps for refrigerated meat and poultry, gaskets, freezer doors, ice cube trays, disposable feeding bottle teats etc. The copolymer is used in manufacturing various films for fresh meat packaging, horticultural films and cling films.

LDPE is the most widely used low cost polymer in food packaging. EVA is superior to polyethylene due to its clarity, toughness, stretch properties, low temperature properties, low heat seal temperatures, low toxicity and flexibility. Single layer films of EVA are used in bags, intravenous pouches, stretch-cling film and bag-in-box packages. EVA is also used as a coating on polyvinylidene chloride (PVDC), metalized film, and polyester (PET) to form the heat seal layer for cheese wrap, cereal packaging, and meat packaging. Some of the advantages of using EVA film or coatings in place of LDPE are: (Robert and Peter (1992))

a) good sealing properties

b) low temperature flexibility which allows use in frozen food packaging

c) ease of coating heat-sensitive substrates containing oriented polypropylene (OPP)

   or metalized film

d) broad and low heat sealing range.
Table. 1.1.2: Some of the food product packaging based on EVA copolymer

<table>
<thead>
<tr>
<th>Food products</th>
<th>Packaging material</th>
<th>Form of usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channa, Khoa, cheese</td>
<td>Biaxially oriented nylon/EVA</td>
<td>Films</td>
</tr>
<tr>
<td>Ground spices</td>
<td>PE/EVA, BOPP/EVA</td>
<td>Bags with barrier films</td>
</tr>
<tr>
<td>Ginger, curry powder and</td>
<td>PET/EVA, BOPP/EVA</td>
<td>Bags or Pouches</td>
</tr>
<tr>
<td>Chillies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biscuits, breads and corn</td>
<td>Coating of EVA</td>
<td>Bags</td>
</tr>
<tr>
<td>flakes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiled sweets, chocolate</td>
<td>EVA</td>
<td>Wrap</td>
</tr>
<tr>
<td>Liquid milk</td>
<td>EVA</td>
<td>Cartons coated on board</td>
</tr>
<tr>
<td>Vegetables</td>
<td>EVA</td>
<td>Pouches on laminates</td>
</tr>
</tbody>
</table>

1.2 COMPOSITES

Composites are man-made material formed by the combination of matrix which is often called as continuous phase and fillers or fibers which is in dispersed phase. The composite materials have received tremendous importance since the overall properties of the composites are superior to those of the individual components - very strong and stiff, light in weight, fatigue properties, do not corrode like steel, and their ability to be used in high performance structural application and faster assembly. More and more researchers are now focusing their attention onto these materials due to their possible wide spectra of applications.
1.2.1 CLASSIFICATION OF COMPOSITES

Composites materials can be grouped into three major categories based on the matrix constituent - metal-matrix composites, and ceramic-matrix composites, polymer-matrix composites.

1.2.1.1 METAL MATRIX COMPOSITES

In metal matrix composites, the matrix is metal. Aluminium, magnesium and titanium are metals generally used for making composites. The reinforcement phases in metal matrix composite systems are generally silicon carbide, carbon, boron, alumina and glass.

1.2.1.2 CERAMIC MATRIX COMPOSITES

Ceramic matrix composites are developed using alumina, calcium alumina silicate glass, glass-ceramic and oxide ceramic as matrices. These matrices are reinforced by silicon carbide, silicon as fillers. Ceramics are strongly bonded materials which results in high strength and hardness. High temperature tolerance of super alloys is also offered by these composites.

1.2.1.3 POLYMER MATRIX COMPOSITES

The polymer matrix composites are very common and are considered as advanced composites. Great strength and stiffness along with resistance to corrosion is provided by this material. They are characterized by low cost, high strength and simple manufacturing principles. The polymeric matrices are mainly classified as shown in Scheme 1.2.

![Scheme 1.2: Classification of polymer matrices](image)

The materials with thermo-reversible cross-links are termed as thermoplastics. Thermoplastic polymers soften and eventually melt when heat is applied. Thermoplastics have a wide range of applications as they can be fabricated and re-fabricated in so many shapes. Some examples are food packaging, insulation, automobile bumpers and credit cards. Commonly used commercial thermoplastics are
polyethylene, poly (vinyl chloride), polypropylene, polystyrene etc. Polymers that get cured irreversibly through chemical reaction, irradiation or heating are called thermoset polymers. Thermosets are strong and durable. They are primarily used in automobiles and construction. They are also used to make toys, varnishes, boat hulls, and glues. The major advantages of thermoplastic matrix composites over thermosets are the low processing cost, design flexibility and ease of moulding complex parts of the former etc.

1.2.2 COMPONENTS OF COMPOSITES

1.2.2.1 MATRIX

Matrix is generally the continuous phase which provides the composite system with toughness and ductility. The main role of the matrix in the composites is to transfer and distribute the applied stresses along the reinforcement phase. They protect the reinforcing phase from abrasion and degradation. They also adhere the dispersion phase together and cause them to act as a team in resisting failure or deformation under an applied load.

1.2.2.2 FILLER

Fillers are fine particles added to polymer matrices to reduce the consumption or uptake of more expensive binding material or to improve some physical and chemical properties of the material. They are relatively inexpensive, solid substances that are added into polymer matrices to adjust volume, weight, cost, colour, processing behaviour, shrinkage, conductivity, permeability, mechanical properties etc. Fillers are classified mainly into two types - fillers which helps in reducing cost are called extenders or inactive filler and the filler which changes the properties are called functional or active fillers so that the compound meets the requirements. The reinforcing filler can be defined as the material capable of increasing the mechanical properties, abrasion resistance etc. Some reinforcing fillers function by forming chemical bonds with the polymer. The properties of the composites are based on reinforcing fillers geometry, reinforcing characteristics and fiber orientation.

1.2.2.2.1 NATURAL FIBERS

Government’s plastic waste control legislations and the growing interest among the customers in sustainable and environmentally friendly products have driven the retailers and manufacturers towards their investment on the development of sustainable materials with
acceptable cost. The public awareness of increased un-decomposable solid wastes and their impact to the environment has awakened a new interest in the area of developing biodegradable polymers.

Natural fiber reinforced polymer composites is considered as an alternative to overcome this issue. Natural fibers have gained popularity as fillers in composites due to their availability, wide range of applications, attaining higher strength, flexibility and less weight and biodegradability. Polymer composites based on natural fillers are currently receiving great attention as innovative materials for industrial applications in several sectors such as automotive, building appliance, packaging and biomaterials. The main advantage of employing natural fibers is that these are biodegradable, renewable, exhibit low cost, low density and high toughness.

1.2.2.2 ADVANTAGES OF NATURAL FIBER REINFORCEMENT

The development of cellulose reinforced composite material as a replacement for synthetic plastic provides many advantages - utilization of an abundant supply of cellulose, thereby providing economic benefit to poor rural people, reducing the existing dependency on non-renewable resources, reducing plastic waste and associated harmful substances from the process of plastic incinerations and less energy requirement. The light-weight of natural fiber composites improves the fuel efficiency and reduces emissions in the usage of the component, especially in auto-applications. At the end of life, incineration of natural fibers results in recovered energy and carbon credits. Some of the basic advantages of natural fibers in comparable to synthetic fibers are following reasons: These fibers are mainly based on cellulose, which is the most abundant material on our planet and are inexpensive, easy availability, renewable, consume very less fuel. Natural fibers are amenable to physical, chemical and mechanical modifications, possess low density, high flexibility and their breaking resistance is high, have no health hazards and are susceptible to microbial decomposition and hence biodegradable.

1.2.2.3 DRAWBACKS OF NATURAL FIBER AS REINFORCEMENTS

Though natural fibers have enormous advantage certain drawbacks are there based on their chemical composition and structure. For example: the diameter of natural fibers is about 10 times larger than that of synthetic fibers. This shows an increased aspect ratio in short fiber reinforced composites and thus decreases the load bearing capability. Natural fibers have a moisture absorption tendency which results in swelling of the fibers. They have high degree of porosity due to the empty lumens of the ultimate cells which account for the moisture
absorption by capillary action. The waxy materials present on the fiber surface helps to retain
the water molecules on the fiber (Li and Matuana (2003)). Low impact strength is another
disadvantage of natural fibers. They create points of stress concentrations, thus providing sites
for crack initiation and potential composite failure (Nakai and Hosomi (2007)).

1. 2.2.2.4 STRUCTURE OF NATURAL FIBERS

Natural fibers are made up of three major units namely cellulose, hemicelluloses and
lignin, along with other small compounds like wax, pectin and lipids (Mussig (2010)). The
cellulose microfibrils act as rebar, lignin acts as the aggregate, and hemicelluloses acts as the
binder. Cellulose is the primary unit of linear polymer chain made up of 1,4-β glucan units.
The linear polymers form sheets that are held together with hydrogen bonds followed by
Vander Waals bonds generating microfibril crystalline structures.

Hemicelluloses is a branched polymer with molecular weight lower than cellulose. It
is an amorphous carbohydrate made of a group of heterogeneous polymers with different
types of sugar moiety. Hemicellulose is highly hydrophilic in nature. They may act as an
adhesive binder between cellulose and lignin. In the cell wall, hemicellulose is made up of
polysaccharides by forming a bond between 5- and 6-carbon of sugars.

Lignin is a high molecular weight phenolic compound which acts as a structural
support in natural fiber. It is less polar than cellulose and thus it improves adhesiveness
between fibers. It is found in the middle lamella. The secondary wall of the natural fiber is
made of lignin. In the secondary wall, lignin acts as a matrix surrounding the cellulose fibers.
It is a complex heterogeneous high molecular weight material made up of aromatic and
aliphatic constituents.

1. 2.2.2.5 PAST WORKS ON NATURAL FIBER/POLYMER COMPOSITES

Polymer composites with natural fibers such as hemp (Khoathane et al (2008)); sisal
(Joseph et al (1999)); coir (Haseena et al (2004)); jute (Khondker (2005)); kenaf (Ribot et al
(2011)); flax (Li et al (2009)) have been well studied. Ali et al (2011) developed kenaf
reinforced polyurethane composites. Tensile strength, flexural strength and impact strength of
the composites has been studied. Tensile strength and flexural strength of the composites has
been improved for 125 and 300 μm fiber size. The impact strength increases as the fiber size
increases. Girones et al (2012) studied the physical-chemical properties of natural fiber
reinforced thermoplastic starch composites. The report showed increased mechanical and
thermal properties of the composites. Anuar and Zuraida compared the mechanical properties
of polypropylene composites reinforced with kenaf fiber/ natural rubber and ethylene – diene
monomer in the presence of the maleic anhydride polypropylene. The reinforcements with kenaf fiber improved the mechanical properties of the composites. Fuentes et al (2013) studied the mechanical behaviour of bamboo fiber reinforced thermoplastic composites such as polypropylene, maleic anhydride grafted polypropylene, polyvinylidene fluoride and polyethylene terephthalate. The mechanical behaviour was higher in the bamboo fiber/polyvinylidene fluoride composites. Bajpai et al (2013) studied the wear and friction characteristic of three different natural fibers reinforced poly lactic acid composites. The three different natural fibers were nettle, Grewia optiva and sisal. The experimental result indicated an improvement in both the characteristic when compared with PLA matrix. The mechanical and thermal behaviour of wheat flour thermoplastic matrix reinforced cotton fiber was studied by Dobircau et al (2009). The mechanical behaviour of the composites increases whereas the thermal properties show negligible effect on fiber loading. Curvelo et al (2001) used cellulosic fibres from *Eucalyptus urograndis* pulp as reinforcement for thermoplastic starch matrix. They found an increment of 100% in tensile strength and more than 50% in modulus for the composites with respect to non-reinforced thermoplastic starch. Sapuan et al (2013) studied the mechanical properties of soil buried kenaf fiber reinforced thermoplastic polyurethane composites. Tensile strength of the composites dropped down after soil burial. Pothan et al (2003) studied the dynamic mechanical properties of banana and glass polyester composite. Increasing the number of layers made the second relaxation peak visible and damping values were found to be lowered by the incorporation of more number of layers. The tensile and flexural properties of green composites with different weight percentage of pineapple fiber content in polyester were compared with the virgin resin by Luo and Netravali. The mechanical properties of the jute fabric-reinforced polyester composites compared with wood composites (Klemm et al (2005)). From this evaluation it has been concluded that the jute fiber reinforced composite has better strengths than wood composites. The mechanical properties of abaca fiber reinforced PP composites with different fiber lengths and a different compounding process was studied by Bledzki et al (2008). The results showed the tensile and flexural properties of the composites increasing with increasing fiber length. When comparing with three different compounding processes, the mixer-injection molding process resulted in better mechanical performance. The same author (2007) compared the mechanical properties of the polypropylene composites by reinforcing abaca /jute/flax fibers. Among the three natural fibers, abaca fiber composites showed better notched charpy and falling weigh impact properties. Sastra et al (2005) mentioned the flexural properties of *Arenga pinnata* fibers reinforced epoxy composites. From the results, they concluded that *Arenga pinnata* fibers can be used as reinforcing filler in epoxy composites. Joseph and Carvalho (2000) studied the effect of hybridisation on the tensile properties of jute – cotton woven fabrics reinforced polyester composites. The tensile strength of the composites has been increased up to 50 %
fiber content than pure polyester composites. Alper et al (2010) studied the effect of filler on the mechanical, thermal and rheological properties of celluloses filled thermoplastic composites. The tensile strength of the composites increased with particle size of fillers. The thermal degradation does not have much effect on particle size.

1.2.2.6 INTERFACE

The region between matrix and reinforcement/filler is known as interface. Interfacial interaction is one of the most important factors determining the properties of polymer composites. The presence of pendant hydroxyl and polar groups in natural fillers lead to poor adhesion between fibers and hydrophobic matrix (John et al (2008); Kalia et al (2009)). Interfacial interaction between fiber and matrix surfaces can be achieved through a number of adhesive mechanisms, including adsorption and wetting, electrostatic interactions, chemical bonding, diffusion, mechanical interlocking (Hull and Clyne (1996)). If there are no specific interactions between the matrix and reinforcing phase, the interface adhesion will be very poor. The interfacial interactions between polymer and fibers can be achieved either by physical/chemical treatment of fibers, by surface modification of the fibers, polymer functionalization, addition of compatibilizers, addition of interfacial additives. The few well known chemical treatments of the fibers are silane and isocyanate, glycidyl methacrylate (George et al (2001), acetic anhydride, stearic acid (Zafeiropoulos et al (2002)), maleic anhydride (Mwaicambo et al (2000)); Machado et al (2003)). In the fiber reinforced composites, different kinds of coupling agents has been used for improving binding capacity between the polymer matrices and natural fibers (Patel and Parsania (2010); Pickering et al (2007); Paul et al (2010)).

1.3 FABRICATION OF THE COMPOSITES

Fabrication of the composite materials has an important impact on the final properties of the composites. The techniques that are used should consider the intrinsic properties of the filler particles, their interfacial characteristics, the nature of the polymeric matrix, and the desired final properties such as its geometrical shape. Polymeric materials are formed by different techniques depending on (a) whether the material is thermoplastic or thermoset, (b) melting/degradation temperature, (c) atmospheric stability, and (d) shape and intricacy of the product. Polymers are often formed at elevated temperatures under pressure. The most widely
used processing technique for fabrication of thermoplastic composites is injection molding and compression molding. A few of the processing techniques are discussed below.

1.3.1 EXTRUSION

Extrusion is the most widely used commercial techniques for the preparation of polymer composite. Most of the films are prepared through extrusion which is considered as the single most accepted process for forming composites film. Polymer and the reinforcing fillers are combined and loaded into a heated tubing barrel by means of a single screw or two co-rotating screws, depending on the type of extruder. The polymer is melted and mixed with the filler to form a composite melt, which is then drawn forward through the extruder barrel and further mixed and compressed to improve the melt homogeneity. The composite formulation is first warmed up on a mill and then fed directly to the twin screw extruder, which extrudes the composites to a shape and size given by the die placed on the front of the pressure barrel with nip gap roller. The extrudate or processed composites is cooled and solidified as it is passed through the die or water tank. In some cases, the extrudate or sample is pulled through a very long die, in a process called pultrusion.

Figure. 1.3.1: Schematic representation of extrusion molding
1.3.2 INJECTION MOLDING

Injection molding is a process for producing polymer related parts by injecting or feeding the material into a mold. Thermoplastic and thermosetting polymers can be performed through injection molding. Host material is fed into a heated barrel, mixed, and forced into a mold cavity, delivering a homogeneous melt to the machine nozzle, and injecting the melt into a closed mold. The mold unit, which contains of a fixed section and a movable section, encloses the shaped cavity into which the composite is injected and cooled. Polymer to be injection molded must be very carefully designed to facilitate the molding process; the material used for the part, the desired shape and features of the part, the material of the mold, and the properties of the molding machine must all be taken into account. Injection molding is widely used for manufacturing a variety of parts, from the smallest component to entire body panels of cars.

Figure. 1.3.2: Schematic representation of injection molding machine
1.3.3 BLOW MOLDING

Blow molding technique is generally used for manufacturing hollow thermoplastic articles. Blow molding is a discontinuous process involving extrusion as well as blowing the molten polymer extrudate by air. Blow molding technique started with the production of a molten tube of polymer called a parison, using an extruder or injection molding. This parison is then placed between a split mold and is then closed while sealing the parison tube. An air blowing device is fitted at one end of the parison, which will blow air into the parison and inflate it into the mold cavity. The mold is cooled with water, solidifying the part inside, to form the final product. The mold is then opened and part is ejected and trimmed.

1.3.4 HAND LAY-UP TECHNIQUE

Hand lay-up technique is the most common, simple and widely used methods for fiber reinforced polymer composites production. Hand lay-up molding is carried out by laying down fibers made for reinforcement and brushing or painting with the matrix resin layer by layer until the desired thickness is obtained. Most of the aerospace particles are made by hand layup technique by combining with the autoclave method. Since hand assembly is involved in the lay-up procedure, one can align long fibers with controlled orientation. Another advantage of this technique is the ability to accommodate irregular-shaped products. The mold can be as simple as a flat sheet or can have infinite curves and edges. To obtain different shaped product, molds must be joined in sections so they can be taken apart after curing. Before starting lay-up processes, the mold is prepared with a release agent to ensure that the product will not adhere to the mold. Resin must then be catalyzed and added to the fibers. A brush, roller or squeegee can be used to impregnate the fibers with the resin. The lay-up technician is responsible for the quality of saturation and controlling the amount of resin. Other fabrication processes such as vacuum bagging, vacuum resin transfer molding and compression molding can be used with hand lay-up to improve the quality of the finished part or save time.
1.4 FOOD PACKAGING

1.4.1 COMMONLY USED FOOD PACKAGING MATERIALS

Paperboard package is a cardboard box, which has been used for dry milk powder. It is lightweight and low cost but is susceptible to moisture and tearing. Glass bottles are heat resistant but heavy and fragile. Aluminium and tin are still used for food packaging. Another common packaging material is polymer. Most commonly used polymers for food product packaging are polyethylene (high density polyethylene, low density polyethylene, linear low density polyethylene), poly styrene, poly ethylterphthalate, starch, polyamide, ethyl vinyl acetate, ethyl vinyl alcohol, resin etc.

1.4.2 POLYMERS IN FOOD PACKAGING

All food packaging product need to meet strict requirements for food safety. The shelf life of the product in a polymer based packaging depends on the type of raw materials and the processing technology used. A large number of works have already been carried out on the preservation of food products. However, works on polymer based food packaging is very limited. Cinelli et al (2006) evaluated the effect of corn fibers on foam plates prepared by baking aqueous mixtures of potato starch, corn fibers, and poly(vinyl alcohol) (PVA) inside a hot mold. The tensile strength and
flexibility was found to be decreasing with increasing fiber content. The mechanical and barrier properties of wheat straw and starch reinforced LDPE composites were investigated by Eleni et al (1997). The performance of the composites decreases as the starch content increased but the rate of the biodegradation increased. Melissa et al (2009) studied the anaerobic degradability of starch/polyvinyl alcohol blends as potential biodegradable food packaging materials. They measured the rate and extent of solubilisation for the composites. The solubilisation data showed that PVOH remained at the end of the digestion and the starch was entirely degraded. Gajdos et al (2001) studied the gas permeability and differential scanning calorimetry characteristics of polymer used in food packaging. The permeabilities of polymers to oxygen and nitrogen were measured at different temperatures using the manometric method. The tested polymers showed great structural stability for temperatures up to 200 °C. Tripathi et al (2010) prepared chitosan/poly (vinyl alcohol)/pectin ternary film for food-packaging applications. SEM studies indicated that the surface of the ternary film is rough and heterogeneous. The reports affirmed the chitosan/poly (vinyl alcohol)/pectin ternary film as a universal antimicrobial food-packaging material. Salgado et al (2008) developed biodegradable food packaging trays made from cassava starch, sunflower proteins and cellulosic fibers obtained by baking process. The composites containing starch, 20% cellulosic fibers and 10 % sunflower protein exhibited maximal resistance and reduced water absorption.

1.4.3 SUITABILITY OF PLASTICS FOR FOOD PACKAGING

Use of plastics for food packaging applications is increasing both in quantum as well as in variety. Plastics are available in various forms such as monofilms, co-extruded films, laminates, sachets, jars, bottles, jerry cans, trays, cups and containers of all shapes and sizes. Realising the versatility of plastic packaging which has prompted its wide usage in food packaging in the country, it was considered expedient by the BIS (IS: 10171-1982, guidelines on suitability of plastics for Food) to formulate standard on this subject. The standard, however, does not provide guidance on the actual design of the food packaging system or cover the shelf-life requirements for various food products but it gives general idea about the polymers in packaging. EVA for food packaging is covered under - IS: 13449-1992: Positive list of constituents of ethylene vinyl acetate (EVA) copolymers in contact with foodstuffs,
pharmaceuticals and drinking water and IS: 13601-1993: Ethylene vinyl acetate (EVA) co-polymers for its safe use in contact with foodstuffs, pharmaceuticals and drinking water.

1.4.4 BASIC PROPERTIES EXPECTED FOR FOOD PACKAGING

Some of the basic properties required for the food packaging application are mechanical properties such as tensile strength, elongation at break, high glossiness and clarity, good puncture and flex–crack resistance over a wide range of temperature, good barrier to water vapour, oils and greases, moisture, CO$_2$ and O$_2$.

1.5 CHARACTERIZATION OF POLYMER COMPOSITES

1.5.1 MORPHOLOGY

Different instruments or methods generally used to analyse polymer morphology are SEM, optical microscope, FTIR, AFM and TEM. The optical or light microscope use visible light as a source of illumination and glass lenses are used for the magnification of the specimens in the range between approximately 10 to 1,000 times their original sizes. The optical microscopes capture the image from the sample by normal light-sensitive cameras to generate a micrograph. SEM is a type of electron microscope in which SEM produces images of a composite by scanning it with a focused beam of electrons, the electrons from the source interact with the electrons on the composites and shows the images. TEM projects high energy electrons in which the electron beam behaves like a wave front with wavelength about a million times shorter than light waves.

1.5.2 MECHANICAL PROPERTIES

The mechanical properties of composites are one of the most important aspects in determining the end-use applications of the materials. Composite mechanical properties can be affected by combination of many factors such as shape, relative volume, and orientation of the reinforcing material and the length of the fillers. The mechanical properties of the composites are determined from the intrinsic properties of the matrix and the filler. Thus the composite properties are mainly governed by factors such as the fiber architecture and the fiber–matrix interface. The
adhesion between the fiber and the matrix affect the mechanical properties of fiber-
reinforced polymer composites. In particular, the tensile strength of the composite is
affected by efficiency of load transfer from the matrix to fiber. A number of
mechanical tests have been developed to measure the capacity of the interface to
transfer stress from the matrix to the fiber in a composite such as tensile strength,
elongation at break, tear strength, flexural strength and compression strength.

1.5.2.1 TENSILE STRENGTH

The ability of a material to resist breaking under stress is called as tensile
strength. Tenacity or tensile strength is the stress at the breaking point of the
materials. It is one of the most widely measured mechanical properties for materials
used in applications. The breakage of material can differs based on the material type
and design methodology. Ultimate tensile strength is defined as the force per unit area
required to break a material.

\[
\text{Tensile strength} = \frac{\text{Load at failure}}{\text{Area of cross section}} \quad ---- (1.1)
\]

1.5.2.2 TEAR STRENGTH

Tear strength is the force required to tear a specimen of given thickness. The tear strength shows the withstand ability of the material on the
growth of any cuts when the material is stressed.

1.5.2.3 DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA is a technique used to study and characterize materials under periodic
stresses. These analysis are carried out to measure the mechanical and viscoelastic
behavior of polymers. The viscoelastic property of composites is studied using DMA
by applying a force to a polymer and the strain is measured. Storage modulus (E')
determines material elasticity or the storage energy of the composites. Loss modulus
(E'') gives the idea about the dissipate energy or energy loss in the form of heat from
the composites. Tan δ is attributed to physical interaction between the polymer and
filler.

1.5.3 SOLVENT TRANSPORT STUDIES
The unavoidable application of polymer composites in various fields as membranes has paved a way of curiosity among the researchers about the solvent transport phenomenon through the polymer membranes. Transport of solvents and vapours in polymers is an important subject from technological or scientific point of view and it is a key step in designing and manufacturing of commercial products. The diffusion and solvent transport phenomenon through filled composites depend on the nature of the filler, degree of the cohesion provided by the host polymer matrix to the filler, compatibility of the polymer to the filler and the nature of the penetrant. Selective permeable membranes of the matrix are enormously used in the field of reverse osmosis, pervaporation, electrodialysis and drug delivery. In order to examine the suitability of a membrane, it is essential to acquire a thorough understanding of its interactions with liquids and vapours. Diffusion behaviours can be classified into three categories: (i) Fickian diffusion, in which the rate of diffusion is much less than that of sorption and the sorption equilibrium is rapidly established. (ii) sorption, in which the diffusion rate is anomalous. (iii) Non-Fickian diffusion which occurs when the diffusion rate and the sorption rate are comparable.

These phenomena can be described in terms of Fick’s first law of diffusion according to which the diffusive flux \( J \) (the amount of penetrant passing through a plane of unit area normal to the direction of flow during unit time) in the \( x \)-direction of flow is proportional to the concentration gradient \( \frac{\partial c}{\partial x} \) as

\[
J = -D \frac{\partial c}{\partial x}
\]

----- (1.2)

Where \( D \) is independent of distance, time and concentration and depending on the boundary conditions.

On the other hand, Fick’s second law describes the unsteady state transport process, which is given by the rate of change of the penetrant concentration at a plane within the membrane, as

\[
D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}
\]

----- (1.3)
This is an ideal case in which the membrane is isotropic and $D$ is independent of distance, time and concentration.

1.5.4 THERMAL STUDIES

Thermal analysis is becoming an increasingly useful tool in evaluating thermal stability of individual polymers with other polymers or reinforcement with fibers. It has the potential to provide quick information of elastomer composition and is often an important quality control requirement for elastomer industry. Composites usually have better thermal stability in comparable with the polymer matrix and the reinforcing filler in the system. This synergism is usually attributed to the interface adhesion of the polymer and natural fiber. The thermal degradation of natural fibers has received considerable attention in the past. The thermal degradation of the natural fiber depends on the crystallinity, orientation and crosslinking of cellulose fiber. Optimization of the processing temperature and time with an understanding of the matrix, the reinforcing element and the interface can lead to the best balance of composite properties. The thermal properties of the composites have to be evaluated by TGA and DSC. The TGA data provides thermal breakdown stages and weight loss of the composites in each stage. DSC can explore the heterogeneous or homogenous nature of composites. DSC analysis can give the $T_g$ of the polymeric material and the fiber phases.

1.6 BIODEGRADATION STUDIES

Biodegradable plastics normally refer to an attack by microorganisms on non water-soluble polymer-based materials. This indicates that the biodegradation of plastics is usually a heterogeneous process (Okada (2002); Mohanty et al (2000)). Several different definitions have been published by national and international standardization bodies and organizations. Few definitions used in correlation with biodegradable plastics are: According to ASTM standard D20-96, biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae. According to ISO 472 definition, biodegradable plastics are plastics designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification. The change in the chemical structure results from the action of naturally
occurring microorganisms. According to CEN, biodegradable polymers is a degradable material in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass. Biodegradation can be determined using several methods that range from direct incubation in an environment with an undefined biocenosis and in highly nurtured synthetic media with specific cultures. Various methods for evaluating biodegradation have been described by several researchers (Lotto et al (2004); Luo and Netravali (2003); Kim et al (2005); Singh et al (2003)).

1.7 LITERATURE REVIEW AND EXISTING GAP

The development of a biodegradable, low cost, light weight cellulose micro/nano fiber reinforced composites are the long term objective of the research. This will lead industries such as the food packaging company to green environment by decreasing gases emission during incineration and enhances the biodegradation. Extraction of cellulose micro/nano fibers and their composites has gained lots of momentum in the last few years. The concept of micro/nano structured polymer material design is gaining widespread importance among the scientific research community. Several studies have been reported on the properties of cellulose micro/nano reinforced polymer composites/blends. However, natural filler reinforced polymer composites for food packaging applications is relatively new concept. The replacement of these natural fillers with micro or nano sized fillers is emerging as the new research arena with much expectation.

The reinforcement of natural fiber in EVA has not been studied much. The hydrophilic nature of natural fiber and the hydrophobic EVA matrix gives rise to incompatibility factor (Mydul et al (2009)). The author reported decreased mechanical properties of EVA with natural fiber incorporation. The work carried out by Staël et al (2001) on the deformation property of bagasse/EVA composites showed reduced deformation capacity of EVA with bagasse incorporation. Malunka et al (2006) reported that dicumyl peroxide increases the grafting between sisal and EVA in sisal/EVA composites. Recently Haque and pracella (2010) studied the structure-property relationships of EVA composites with maleic anhydride and glycidyl methacrylate modified cellulose fiber. The fracture surfaces of samples with functionalized components displayed good interfacial adhesion. The fiber surfaces were coated with a layer of polymer indicating an improved compatibility of modified fiber with EVA copolymers.

The extraction of nano/micro fibrils and their application in EVA has been studied. These micro nano fibers has been found to be excellent reinforcements for
many polymers. Susana et al (2010) prepared chitosan composites with different percentage of nanofibrillated celluloses. The composites showed better mechanical and thermal properties than the unfilled chitosan. Sanchez et al (2008) studied the morphology, thermal and transport properties of poly (lactic acid), polyhydroxybutyrate-co-valerate (PHBV) and polycaprolactones (PCL) containing micro cellulose fibers as a function of filler content. SEM, optical microscopy and Raman imaging results indicated a good dispersion of the fibers in the matrix. Taniguchi and Okamura (1998) evaluated the films obtained from microfibrillated natural fibers. The composites showed uniform morphology and increased mechanical properties. Okubo et al (2005) developed bamboo/PLA/MFC composite which showed improvements in fiber-matrix interactions and toughness. Zheng et al (2012) prepared sisal microfibrill/gelatine biomass composites. The morphology, mechanical and water absorption behaviour of the composites were evaluated. The water sorption behaviour of the composites decreases whereas the tensile strength increased. SEM analysis showed good interfacial adhesion between fiber and matrix. As discussed earlier EVA is one of the commonly used food packaging material. However the application of natural fiber reinforced EVA composites for food packaging has not been studied yet.

1.7.1 OBJECTIVES OF THE WORK

The main objective of the present work was

Extraction of CMF from *Hibiscus sabdariffa* by steam explosion technique

i) Development of CMF/EVA composites by melt extrusion with different percentage of CMF loading

ii) Analyze the following characteristics of the composites keeping unfilled EVA as the standard - this gives an idea about the effectiveness of CMF as filler in EVA

   a) Mechanical properties b) Effect of gamma and thermal ageing c) Barrier to gas and solvents d) thermal properties e) biodegradation f) microbial growth
Since EVA is widely used in food packaging applications, most of the characterization studies were carried out keeping in mind the requirement of food packaging materials.