1. POLYMERS

1.1 GENERAL INTRODUCTION AND ITS SCOPE

Polymers form a very important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from greek words, poly= many and mers= parts or units of high molecular mass each molecule of which consist of a very large number of single structural units joined together in a regular manner. In other words polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as polymerization [1]. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

1.2 HISTORICAL DEVELOPMENT OF POLYMERS

Polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. However, the origin of today's polymer industry is commonly accepted as being the nineteenth century when important discoveries were made concerning the modification of certain natural polymers. In eighteenth century, Thomas Hancock gave an idea of modification of natural rubber through blending with ceatrain additives. Later on, Charles Goodyear improved the properties of natural rubber through vulcanization process with sulfur. The Bakelite was the first synthetic polymer produced in 1909 and was soon followed by the synthetic fiber, rayon, which was developed in 1911. The systematic study of polymer science started only about a century back with the pioneering work of Herman Staudinger. Staudinger has given a

new definition of polymer. He in1919 first published this concept that high molecular mass compounds were composed of long covalently bonded molecules.

1.3 CLASSIFICATION OF POLYMERS

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless form and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in different ways, which are summarized in Table 1.1, whereas, important and broad classification of polymers are described in the next section.

Table1.1: Classification of Polymers

Basis of Classification		Polymer Type
Origin	-	Natural, Semi synthetic, Synthetic
Thermal Response	-	Thermoplastic, Thermosetting
Mode of formation	-	Addition, Condensation
Line structure	-	Linear, Branched, Cross-linked
Application and Physical Properties	-	Rubber, Plastic, Fibers
Tacticity	-	Isotactic, Syndiotactic, Atactic
Crystallinity	-	Non crystalline(amorphous), Semi-crystalline, Crystalline
Polarity	-	Polar, Non polar
Chain	-	Hetro, Homo-chain

1.3.1 Origin

On the basis of their occurrence in nature, polymers have been classified in three types [2]:-

A. **Natural polymer:-** The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc..

B. Semi synthetic polymer:- They are the chemically modified natural polymers such as hydrogenated, natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc.

C. Synthetic polymer:- The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc..

1.3.2   Thermal Response

On the basis of thermal response, polymers can be classified into two groups [3]:-

A. Thermoplastic polymers:- They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing wax etc..

B. Thermosetting polymers:- Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic, resins, urea, epoxy resins, diene rubbers, etc.

1.3.3   Mode of Formation

On the basis of mode of formation, polymers can be classified as [2]:-

**A. Addition polymers:-** They are formed from olefinic, diolefnic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

B. Condensation polymer:- They are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules having reactive functional groups such as –OH, -COOH, -NH₂, -NCO, etc..

1.3.4 Line Structure

On the basis of structure, polymers are of three types.

A. Linear polymer:- If the monomer units are joined in a linear fashion, polymer is said to be linear polymer.

——X——X——X——   ——X ——Y ——X——
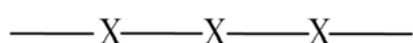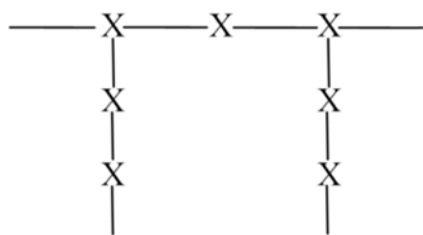
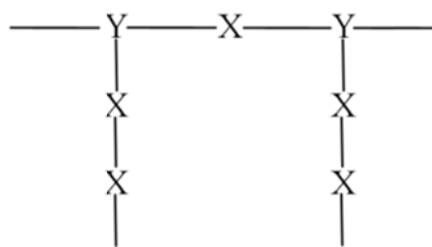Linear Homopolymer   Linear Copolymer

B. Branched polymer:- When monomer units are joined in branched manner, it is called branched polymer.
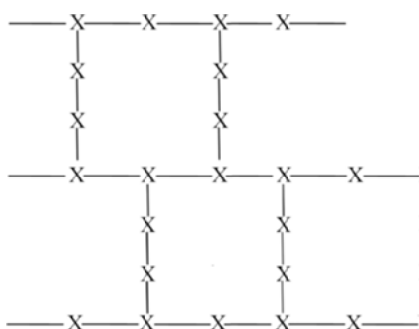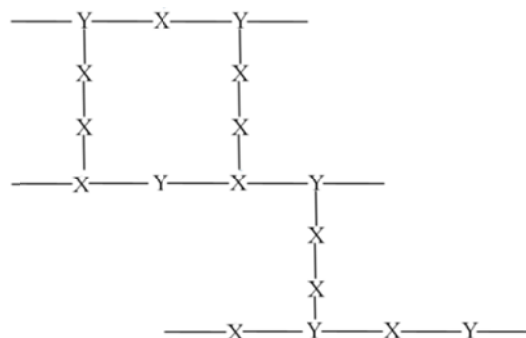
Branched Homopolymer   Branched Copolymer

C. Cross linked polymer:- A polymer is said to be a cross linked polymer, if the monomer units are joined together in a chain fashion.

Cross linked Homopolymer   Cross linked Copolymer

1.3.5 Application and Physical Properties

Depending on its ultimate form and use a polymer can be classified as [2]:-

A. **Rubber (Elastomers):-** Rubber is high molecular weight polymer with long flexible chains and weak intermolecular forces. They exhibits tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000% . Examples are natural and synthetic rubber.

B. **Plastics:-** Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubbers. They exhibit tensile strength ranging between 4000-15000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene, etc.

C. **Fibers:-** Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000- 150,000 psi., are light weight and possess moisture absorption properties.

1.3.6 Tacticity:-

It may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

A. **Isotactic polymer:-** It is the type of polymer in which the characteristic group are arranged on the same side of the main chain.
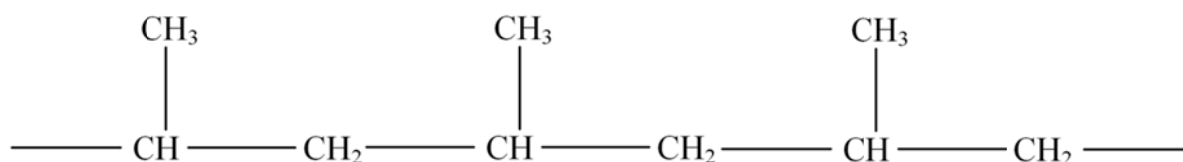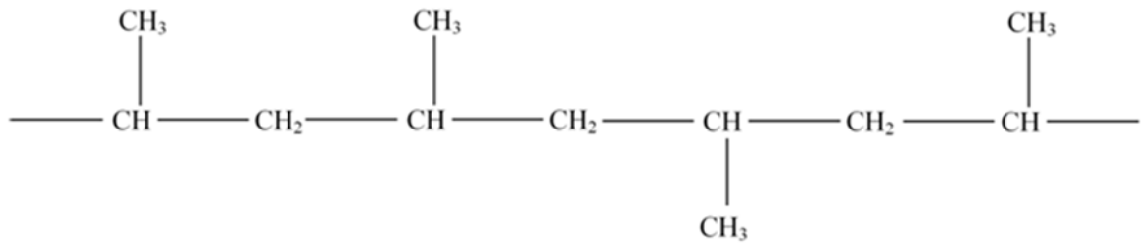

Isotactic Polypropene

B. Syndiotactic polymer:- A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.
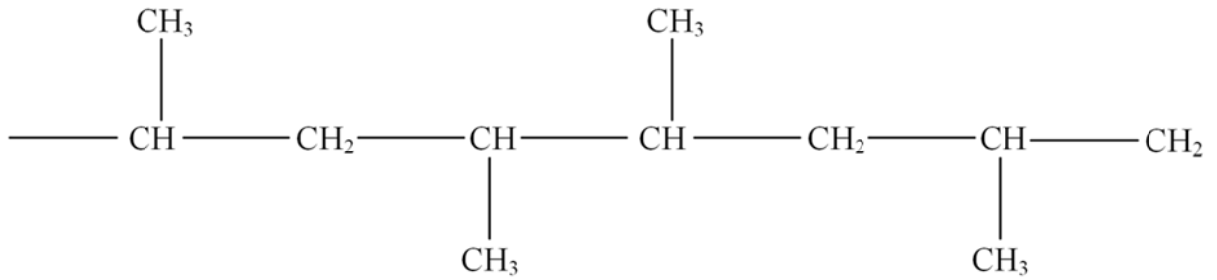
Syndiotatic Polypropene

C. Atactic polymer:- A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.

Atactic Polypropene

1.4 BIOCOMPOSITES

Composite are attractive materials because they combine material properties in ways not found in nature. Such materials often result in lightweight structures having high stiffness and tailored properties for specific applications, thereby saving weight and reducing energy needs [4-6]. Fiber-reinforced plastic composites began with cellulose fiber in phenolics in 1908, later extending to urea and melamine, and reaching commodity status in the 1940s with glass fiber in unsaturated polyesters. From guitars, tennis racquets, and cars to microlight aircrafts, electronic components, and artificial joints, composites are finding use in diverse fields.

Composite materials derived from biopolymer and synthetic fibers such as glass and carbon also come under biocomposites. Biocomposites derived from plant-derived fiber (natural/biofiber) and crop/bioderived plastic (biopolymer/bioplastic) are

likely to be more ecofriendly, and such biocomposites are sometimes termed "green composites" [4].

1.4.1 Natural/Biofibers as Reinforcements in Biocomposites

The world's supply of natural resources is decreasing and the demand for sustainable and renewable raw materials continues to rise. Biofiber-reinforced composites represent a potential nontraditional, value-added source of income to the agricultural community.

Jute is from India and Bangladesh; coir is produced in the tropical countries of the world, with India accounting for 20% of the total world production; sisal is also widely grown in tropical countries of Africa, the West Indies, and the Far East, with Tanzania and Brazil being the two main producing countries; kenaf is grown commercially in the United States; flax is a commodity crop grown in the European Union as well as in many diverse agricultural systems and environment throughout the world, including Canada, Argentina, India, and Russia. Flax fiber accounts for less than 2% of world consumption of apparel and industrial textiles, despite the fact that it has a number of unique and beneficial properties. Hemp originated in Central Asia, from which it spread to China, and is now cultivated in many countries in the temperate zone. Ramie fibers are the longest and one of the strongest fine textile fibers mostly available and used in China, Japan, and Malaysia.

Most of the polymers by themselves are not suitable for load-bearing applications due to their lack of sufficient strength, stiffness, and dimensional stability. However, fibers possess high strength and stiffness. Unfortunately, they are not suitable for use in load-bearing applications by themselves because of their fibrous structure. In fiber-reinforced composites, the fibers serve as reinforcement by giving strength and stiffness to the structure while the plastic matrix serves as the adhesive to hold the fibers in place so that suitable structural components can be made. A broad classification (nonwood and wood fibers) of natural fibers is represented schematically in Fig. 1.1.

Currently several nonwood fibers (e.g., hemp, kenaf, flax, and sisal) are being utilized commercially in biocomposites in combination with polypropylene for

automotive applications. Now from need of society and research point of view it is much important to work on leaf based nonwood fibers [4].
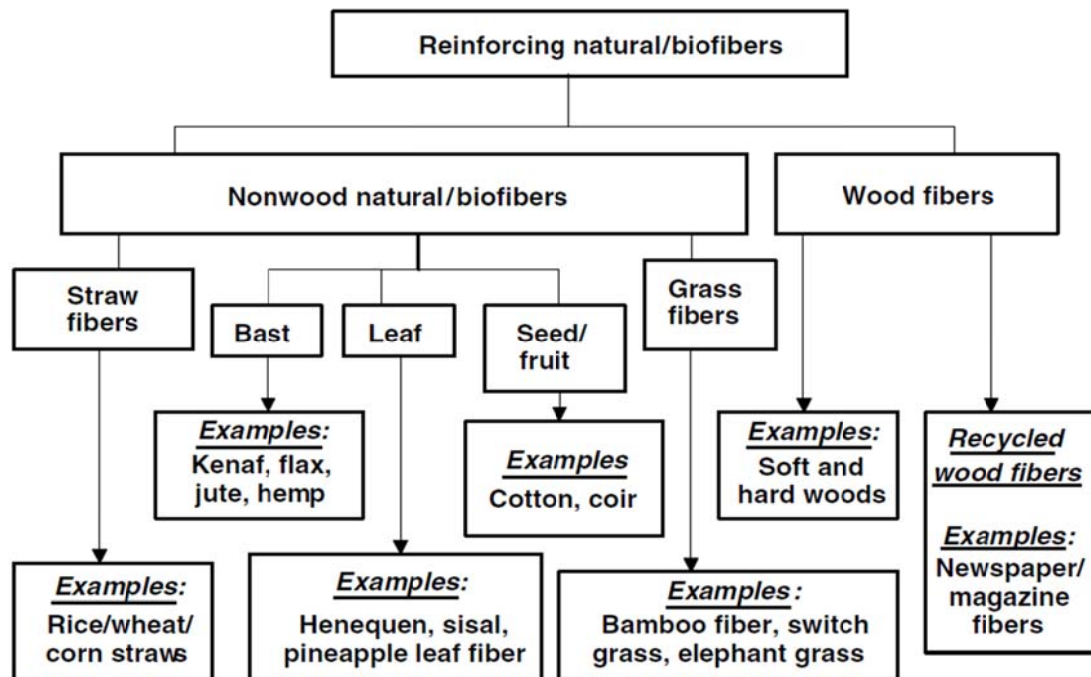

Fig 1.1: Schematic representation of reinforcing natural/biofibers classification [4]

1.5 MECHANISM OF POLYMERIZATION

The linking together of a large number of small molecules termed as monomers with each other to form a macromolecule or polymer molecule through chemical reactions is termed as polymerization. It can also be defined as the fundamental process by which low molecular weight compounds are converted into high molecular weight compounds. In addition to the structural and compositional differences between polymers Flory stressed the very significant difference in the mechanism by which polymer molecules are build up. Although Flory continued to use the terms "addition polymerization" (polymerization by repeated addition processes) and "condensation polymerization" (polymerization by repeated condensation processes, i. e., with the elimination of small molecules) in his discussion of polymerization mechanism. The current terminology classifies polymerization into step growth polymerization and chain growth polymerization [7].

The degree of polymerization is related to the molecular mass (M) of the polymer and is given by the equation,

$$D_p = \frac{M}{m} \hspace{4cm} 1.1$$

where, m is the mass of the monomeric unit.

1.5.1 Condensation Polymerization or Step-growth Polymerization

Condensation Polymerization is a chemical reaction in which polymer is formed and a small molecule of by-product with a lower molecular weight is released. The by-product eliminated is called as condensate. The reaction can take place between two similar or different monomers. It is also called as step-growth polymerization [8-9].

1.5.2 Addition Polymerization or Chain Polymerization

In addition polymerization, two or more molecules of monomers attach together to form a polymer. In this polymerization, there is no elimination of any molecule. It is a chain reaction and no by product is released. It is obtained by linking together the monomer molecules by a chain reaction to give a polymer whose molecular weight is exactly an integral multiple of that of the monomer as in the case of polyethylene obtained by polymerization of ethylene. Only a single monomer is involved in addition polymerization and hence the polymer is homopolymer and contains the same monomer units. Addition polymerization reaction is usually induced by light, heat or a catalyst for opening the double bond of the monomer and creating the reactive sites [9].

1.6 CHARACTERIZATION OF POLYMERS

It is comparable to the synthesis of organic compound, composites, biocomposites without a subsequent characterization of its various properties Synthesized material characterization is therefore of very great importance. Some of the important aspects related to characterizations have been described in this section.

1.6.1 Molecular Weight and its Distribution

The molecular weight of a polymer is of prime importance in the polymer's synthesis and application. It is important because it determines many physical properties. The term molecular weight is a ratio of the average mass per formula unit of substance to 1/12 th of an atom of ^{12}C. Molecular weight (MW) and its distribution (MWD) has a considerable effect on macroscopic properties of polymer such as toughness, tensile strength, adherence and environmental resistance, etc. [10]. A simple chemical has fixed molecular weight but when we discuss about the molecular weight of polymer, we mean something different from that which applies to small sized compounds. Since polymers are mixture of molecules of different molecular weight, the molecular weight is expressed in the term of "average" value. This average molecular weight is basically based on either average number of repeating units, known as number average molecular weight, or average weight, known as weight average molecular weight. The number average molecular weight is obtained from the number n_i of macromolecules for each degree of polymerization P_i by taking for each degree of polymerization the product of the number of polymer molecules and their degree of polymerization $n_i\, p_i$ and dividing the sum of these product by the total number of monomers N_o:

$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} n_i p_i}{N_o}$$

$\hspace{10cm}$ 1.2

The weight average molecular weight $\overline{M}_w$ is obtained in a similar manner from mass m_i of each degree of polymerization P_i according to the following equation:

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} m_i p_i}{M_o}$$

$\hspace{10cm}$ 1.3

When the molecular weight distribution is very narrow, the number average and weight average molecular weights are essentially equal. When the distribution is broad, the weight average molecular weight is considerably greater than the number

average molecular weight and broader the distribution, the greater the difference between them as shown in Figure 1.2. From these molecular averages the molecular weight distribution is represented by their ratio $\dfrac{\overline{M}_w}{\overline{M}_n}$
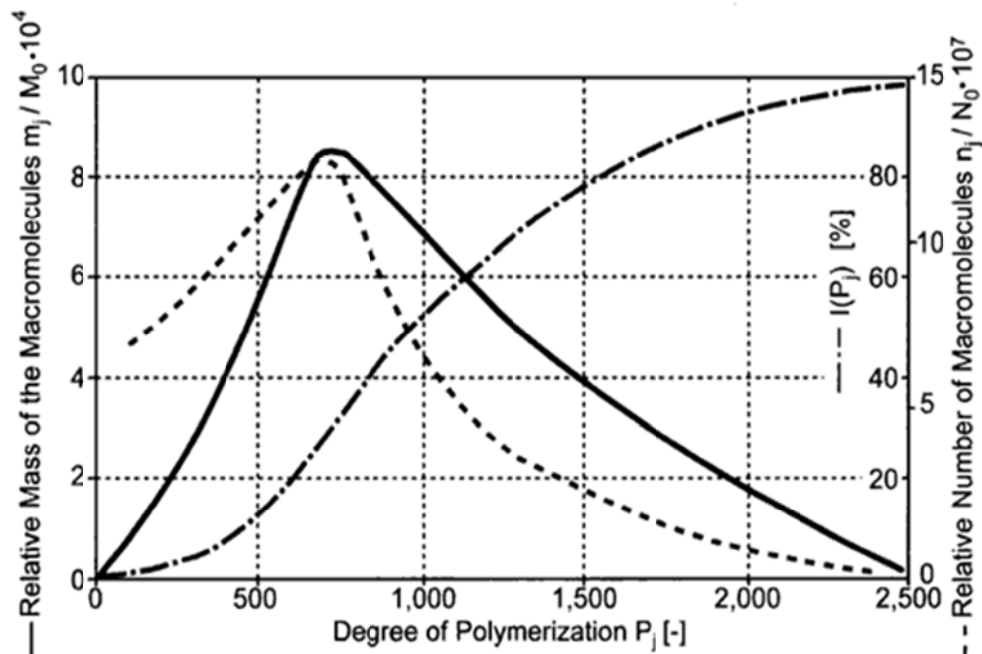
Fig1.2: Schematic representation of the weight average and number average molecular weight distribution as a function of the degree of polymerization [11].

Tensile and impact strengths increase with molecular weight. The melt viscosity of the polymer, however, shows a different trend. At very high molecular weights, the melt viscosity rises more steeply than at low molecular weights. Molecular weight distribution also affects properties of polymers. To know of a polymer properly, we must have a good knowledge of both the average molecular weight as well as its dispersion patterns.

1.6.2 Crystallization

Crystallization in polymer has always been the subject of great scientific and academic interest, since polymers are known to exhibit a variety of structures at various length scales, such as unit cell, lamella, and spherulites. It is an interesting property related to phase transition which determines the final properties of many technologically relevant and scientifically exciting systems [12, 13]. Polymer

crystallization controls the structural formation process of polymeric materials and thereby dominates the properties of final polymer product. Polymer crystallization is usually divided into two separate processes : primary nucleation and crystal growth [14].

In general, a crystalline phase must primarily nucleate. The fundamental kinetics of nucleation are often complicated to determine because the rate of heterogeneous nucleation at defects, impurities, and surfaces is much faster than the homogeneous rate of nucleation within the pure bulk liquid. After a nucleus forms, the kinetics of crystal growth determines the overall rate of the phase transformation. For growth from solid or liquid solutions, the rate limiting step in the kinetics is often mass diffusion. For crystal growth from a melt, heat transfer plays an important role for metals, ceramics, and semiconductors, but for large molecules and polymers, the microscopic kinetics associated with attaching a large molecule or polymer segment to the growing crystal are typically the most important consideration [14].

The crystalline and amorphous components influence polymer properties. Actually, crystallinity of a polymer sample is expressed in terms of that fraction of the sample which is crystalline. The definition of degree of crystallinity is, of course, based on the premise that crystalline and non-crystalline components of a polymer can co-exist". The highest crystallinity is generally associated with polymers which have a simple unit cell structure and a relatively high degree of molecular order. The overall property (Q) of a partially crystalline polymer can be expressed as a sum of its two components as:

$$Q = Q_c + Q_a \qquad\qquad 1.4$$

where Q_c and Q_a are contributions of the crystalline and amorphous components of the sample, respectively. A number of methods can be used to detect crystallinity and estimate its degree: X-ray diffraction, infrared-absorption spectroscopy, polarized light microscopy, density, differential thermal analysis and nuclear magnetic resonance spectroscopy, etc.. Accurate and undisputed measurement of the volume fraction of crystallinity in a polymer is not easily accomplished because each of the method of measurement mentioned above is concerned with a different physical aspect of material. Nevertheless, the great practical consequences of crystallinity and

orientation on mechanical properties dictate that at least relative changes in these factors be observed by whatever means are applicable, and that these be correlated with changes in processing and fabrication methods and with end-use behaviour. It was found that the preparation method of samples influence the morphology and crystallization behaviour of blends.

1.6.3   Glass Transition Temperature

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature Tg. The glass transition is a phenomenon observed in linear amorphous polymer. It occurs at fairly well defined temperature when the bulk material ceases to be brittle and glassy in character and become less rigid and more rubbery. The knowledge of Tg is essential in the selection of materials for various applications.

Many Physical properties change profoundly at the glass transition temperature, including mechanical properties and electrical properties. All of these are dependent on the relative degree of freedom for molecular motion within a given polymeric material and each can be used to monitor the point at which the glass transition occurs [15-17].

1.7 MECHANICAL PROPERTIES OF POLYMERS

To study the necessary set of valuable properties, polymers differing from one another by their chemical structure and properties are usually mixed together, either homogeneously or heterogeneously. The mechanical properties of inhomogeneous mixture are worse than those of individual polymers, while the mechanical properties of homogeneous mixture are good.

Polymers can exhibit the features of glassy, brittle solid or an elastic rubber, or that of a viscous liquid, depending on the temperature and time scale of measurement. The studies on mechanical properties of polymer can, therefore, be carried out by subjecting them to some form of mechanical stress either continuous or in a periodic manner at different rate. Some of the important properties of polymers with regard to their use as engineering material are tensile strength, compressive and flexural strength, hardness, creep, fatigue resistance and impact resistance.

Toughness of a polymer is the ability to absorb mechanical energy without fracturing. The property such as tensile strength is the maximum amount of tensile load per unit area a material can withstand, while the tensile elongation gives the measure of increase in length in response to a tensile load expressed as a percent of the original length. Elongation at break is the maximum elongation the plastic can undergo.

Engineering applications of polymers are governed to a great extent by strain hardening considerations. The designer using polymeric materials must, therefore, understand their mechanical behaviour with respect to the maximum permissible strains to avoid failure. As for most materials, a simple tensile stress-strain curve provides a good start towards understanding the mechanical behaviour of a particular polymer. This curve is usually established by continuously measuring the force developed as the sample is elongated at constant rate of extension until it breaks. Portions of the curve in Fig.1.3 represent the stress-strain behaviour of any polymer and are used to define several useful quantities. The initial slope provides a value for Young's modulus (or the modulus of elasticity) which is a measure of stiffness. The curve also gives yield stress, strength and elongation at break. The area under the curve or work to break is a rough indication of the toughness of the polymeric material. The stress at the knee in the curve (known as the yield point) is a measure of the strength of the material and resistance to permanent deformation. The stress at the breaking point, commonly known as ultimate strength, is a measure of the force required to fracture the material completely.

A hard, brittle material such as an amorphous polymer far below its Tg, usually has an initial slope indicative of very high modulus, moderate strength, a low elongation at break, and a low area under the stress-strain curve (Fig. 1.4). Polymeric materials showing hard brittle behaviour at room temperature or below are polystyrene, poly (methyl methacrylate) and many phenol-formaldehyde resins.

Hard and strong polymers have high modulus of elasticity, high strength, and elongation at break of approximately 5 percent. The shape of the curve often suggests that the material has broken where a yield point might be expected. This type of curve is characteristic of some rigid poly(vinyl chloride) formulations and polystyrene polyblends. Hard, tough behaviour is shown by polymers such as cellulose acetate,

cellulose nitrate and nylons; they have high yield points and high modulus, high strengths and large elongations. Most polymers of this group show cold-drawing or "necking" during the stretching process. Cold-drawing is important in synthetic fiber technology, and is used to develop strength. Polymeric materials that are soft and tough show low modulus and yield values, moderate strength at break, and very high elongation ranging from 20 to 100 per cent. This type of stress-strain curve is characteristic of plasticized PVC and rubbers (elastomers).

The two mechanical performances creep and stress relaxation are related to each other. In creep, elongation takes place under the application of constant stress, while in stress relaxation, decrease in stress occur when a specimen is held at constant and essentially instantaneously induced strain. The varying stress or strain is measured as a function of time. Repeated flexing of a sample through a given distance often causes a sample to fail at a lower stress than it could for a single flexure. This feature is referred to as fatigue.
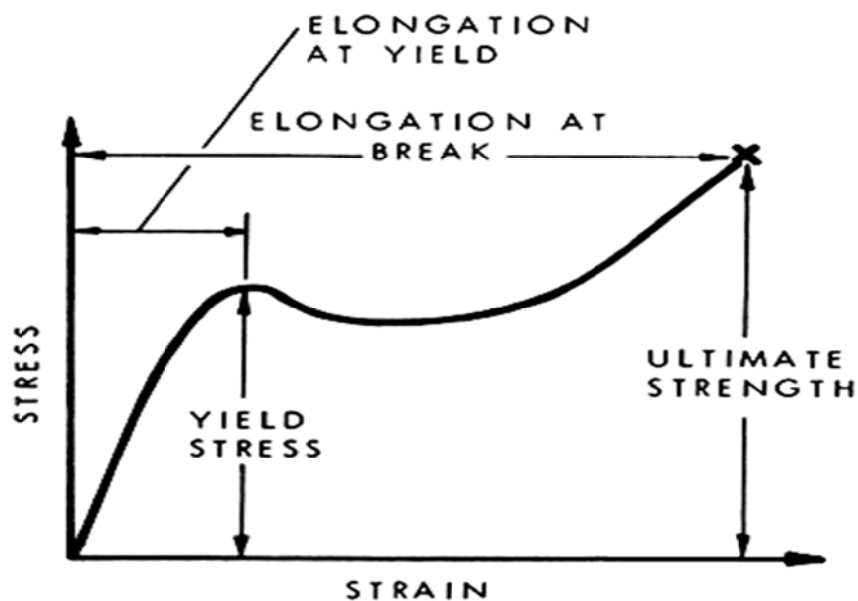
Fig 1.3:   Generalized tensile stress-strain curve for some polymeric materials
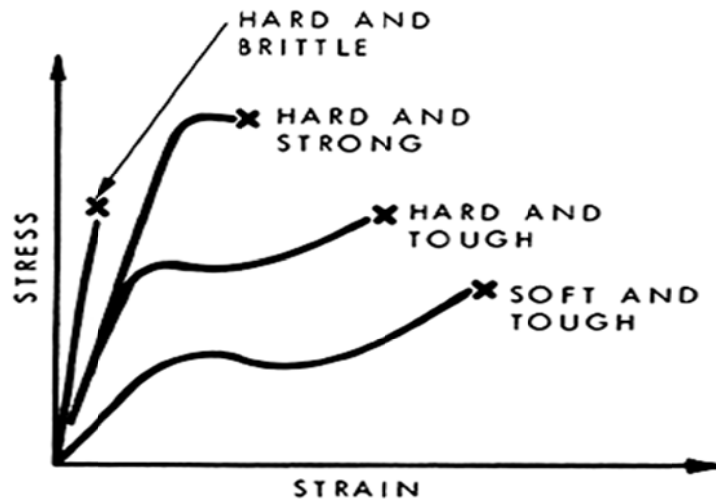
Fig 1.4: Tensile stress-strain curves for four types of polymeric material.

Fatigue testing may be carried out by subjecting the sample to alternating tensile and compressive stress. The fatigue resistance usually decreases with increase in rigidity.

Impact strength is a measure of toughness or resistance to breakage under high velocity impact conditions. From this point of view, polymeric materials under normal conditions of use are thought to be either brittle or tough. For example, polystyrene, poly(methyl methacrylate) and unmodified, non plasticized PVC are usually rated as brittle, breaking with a sharp fracture; plasticized PVC's are considered to be tough. In general, polymeric materials are either brittle or tough, depending on the temperature and rate of impact, i.e. rate of deformation. Impact strength of polymers and derived plastics depends on the position of the glass transition temperature (T_g) with respect to room temperature and ease of crystallization. Far below the glass-transition, amorphous polymers break with a brittle fracture, but they become tougher as the service temperature approaches T_g. Above T_g, amorphous polymers are in a rubbery state so that the term impact ceases to have any significance

1.7.1 Mechanical properties of a thin film Polymer

The mechanical properties of any polymer blend and composite also depend on its dimensional size weather it is thinner or thicker in appearance. The size of the blend makes it usable in various fields. Today polymers are used extensively in many applications in thin film form, like film coating, adherent epoxy under fills to localize

the stress concentration during thermal expansion, in electronic packaging etc.. The mechanical state within the polymer necessarily varies from point to point within the thin film, as can the strength of the adhesion between the polymer and the substrate. In most practical cases, even in thin film applications such as found in electronic packaging applications, the typical dimensions of the polymer component are much larger than the dimensions of individual molecules. At scales much larger than this, the material can be considered as continuum and the usual mechanics can be invoked to model the deformation behavior, and bulk tensile properties (which will vary with resin and processing) can accurately describe the time dependent properties of the thin film.

1.7.2   Microhardness of a Polymer

If we discuss the mechanical properties of polymer and biocomposites, hardness of the material is one of the most important aspects in its mechanical characterization; it is generally defined as "resistance of a material to plastic deformation, usually by indentation". It is the property of a material, which gives it the ability to resist permanent deformation (bend, break, or have its shape changed), when a load is applied. The greater the hardness of the material, the greater is the resistance it has towards deformation. The one of the best available definition is given by Ashby [18], which states "hardness is a measure of the resistance to permanent deformation or damage".

Microhardness is the hardness of a material measured at low loads as determined by forcing an indenter such as Vickers or Knoop into the surface of the material under 5 g to 160 g load. Usually the indentations are so small that they must be measured with a microscope. Micro indenters work by pressing a tip into a sample and continuously measuring applied load, penetration, depth and cycle time. Nano-indentation tests measure hardness by indenting with very small (of the order of 1 nano-Newton) indentation forces and measuring the depth of the indention that is made.

The hardness test measures the mean contact pressure, when an indenter is pressed onto the surface of a flat specimen. It provides the simple and non-destructive means of assessing the resistance of material to plastic deformation. In this present work Vickers's microhardness indentation testing has been utilized to

study various properties of polymer and polymer biocomposite blends, which has also been utilized by various workers. This typical hardness test involves applying a fixed load to the indenter, and measuring the resultant size of indentation. This has been related empirically to the yield stress of the material. This work presents the results of micro-indentation testing on electrically stressed polymer thin films [19-26].

1.8 ELECTRICAL PROPERTIES OF POLYMER

Materials such as glass, ceramics, polymers and biocomposites are non conducting materials. They prevent flow of current through them. When these types of non-conducting materials are placed in an electric field, they modify the electric field and they themselves undergo appreciable changes as a result of which they act as stores of electrical charges. When charge storage is the main function, the materials are called dielectrics. For a material to be a good dielectric, it must be an insulator. As good insulators, polymers posses excellent dielectric properties. Many authors have reported theoretical and experimental work related to these properties [29-52]. The common electrical properties of interest are discussed below:

1.8.1 Dielectric polarization

Polarization with the application of an electric field, due to the displacement of charge particles inside the material forming dipoles, is known as internal polarization. Some of the internal polarizations are electronic, orientational (dipolar), space charge and barrier polarization.

Dielectric can also be charged by direct injection of charge carriers, when high electric field ($\approx 10^5$ V/cm) is applied between the electrodes in intimate contact with it. Charges get sprayed or deposited due to corona discharge or dielectric breakdown in the thin air gap between the electrode and the dielectric. If the injected charge in the surface is of same sign as that of electrode in contact, it is called homo-charge; if it is opposite in sign then it is called hetero-charge.

The total polarization is the resultant of both internal and external polarization.

$$P = P_{int} + P_{ext} \qquad\qquad 1.5$$

Polymers as dielectrics are known to store charge permanently when subjected to field - temperature treatment; such quasi permanently charged dielectrics are known as Electret.

1.8.2 Dielectric strength

It measures the highest current that can be applied to a plastic before it allows current to pass. It is expressed as the voltage just before this happens divided by the thickness of the sample (in volts/m). It is affected by temperature, thickness, how the sample was conditioned, rate of voltage increase, test duration and contamination etc.

1.8.3 Electrical conduction

The electrical conductivity of polymer, x, measures the presence of free ions not connected chemically with the macromolecules. It also depends on presence of low molecular weight impurities that can serve as source of ions. The chemical constitution has only an indirect effect on the mobility of the ions.

In glassy state the conductivity of the polymer is approximately 10^{-13} to 10^{-19} ohm^{-1}. With increasing temperature, the conductivity of polymer increases according to the exponential law as,

$$x = A\ e^{-\Delta U/RT} \qquad\qquad 1.6$$

where, A is a Coefficient mainly dependent on temperature, R is Universal gas constant, and ΔU is the Activation energy

1.8.4 Dielectric constant (or permittivity)

Dielectric constant, ε^{l}, indicates how easily a polymer/plastic can be polarized relative to vacuum. It is defined as the ratio of the capacity of an electric capacitor filled with the substance to that of the same capacitor in vacuum, at a definite external field frequency. This dimensionless number which is important in high frequency applications varies with temperature, moisture, frequency and thickness.

1.8.5 Dissipation factor

This measures the energy dissipated during rapid polarization reversals, as with an alternating current. It can be seen as the ratio of energy lost as heat to current

transmitted. It is usually measured at 1 MHz. This factor should be low when polymers are used as insulators in high-frequency applications such as radar and microwave equipments.

1.8.6 Dielectric loss

Dielectric loss, ε^{ll}, measures the part of the energy of an electric field that is dissipated irrecoverably as heat in the dielectric. Dielectric loss in polymeric materials is due to the independent movement of chain sections consisting of large number of monomer units.

1.8.7 Volume resistance

A standard measure of conductivity when a direct current potential is applied across a material is volume resistivity (measured as ohm × area of the smaller electrode/ specimen thickness). Materials measuring volume resistance above 10^8 ohm-cm are insulators.

1.8.8 Surface resistance

This expresses how well current flows over the surface of a material between electrodes placed on the same side of a specimen. While volume resistance is a property of the material, surface resistance measures how susceptible a plastic is to surface contamination, especially moisture. It is useful when surface leakage may be a problem but since it is not measurable exactly it should be used with wide margin of safety.

1.9 STATEMENT OF THE PROBLEM

Composite materials are attractive because they combine material properties in ways not found in nature. Such materials often result in lightweight structures having high stiffness and tailored properties for specific applications, thereby saving weight and reducing energy needs [4,54-55]. Typically, a manmade composite would consist of a reinforcement phase of stiff, strong material, frequently fibrous in nature, embedded in a continuous matrix phase. The advantage of such a coupling is that the high strength and stiffness of the fiber may be exploited.

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include

plant fibers such as cotton, flax, hemp and fibers from recycled wood or waste paper, or even by-products from food crops. Biocomposites offer a significant non-food market for crop-derived fibers and resins.

Considerable growth has been seen in the use of biocomposites in the automotive and decking markets over the past decade or so, but application in other sectors has hitherto been limited. Nevertheless, with suitable development, the potential exists for biocomposites to enter new markets and thus stimulate an increase in demand for non-food crops. Fibers provide strength and stiffness and act as reinforcement in fiber-reinforced composite materials; ultimately the properties of a composite are governed by the inherent properties of these fibers. Natural fibers can be subdivided into vegetable, animal and mineral fibers [55].

Biodegradation is the process by which organic substances are broken. The term is often used in relation to ecology, waste management and environmental remediation (bioremediation). Biodegradable composite which can be easily degraded in natural environment are gaining public interest. Biodegradable plastics and biocomposites are being developed in number of research laboratories concerned about the persistence and ecological effect of synthetic plastic in the environment worldwide including applications such as waste management, recycling, sustainability, packing, automotive, construction, etc [54-56].

Wide range of bio-based biodegradable polymers which are utilized to prepare biodegradable polymer and biocomposite such as Polyhydroxyalkanoates (PHAs), Polylactides (PLA), Cellulose esters, Starch plastics which are Renewable resource-based and Aliphatic polyesters, Aliphatic-aromatic polyesters, Poly ester amide, Poly vinyl alcohol are Petroleum/fossil fuel-based. Poly vinyl alcohol (PVA) is one of the best biodegradable polymers and it is widely utilized to prepare the biocomposites.

The characterization of biocomposite can be made on the basis of structural, mechanical, electrical, thermal and biodegradation. The study of the surface structure of biocomposite can be made with the help of various characterization techniques like FTIR, XRD, SEM, TEM, AFM, STM, etc [56-62]. The surface structure is also responsible for the biodegradation of the biocomposites. The mechanical behavior of various types of biodegradable materials depends, mainly, on their chemical composition and the application conditions. Various additives are added into the bio-

blends to improve their properties, which sometimes even reach the levels of the conventional plastics. It is well known that the environmental conditions during production, storage, and usage of these materials influence their mechanical properties. The mechanical characterization can be made with the help of Microhardness and Tensile Stress, tensile strength [56,58,59,63]. The study of thermal properties like thermal stability, thermal expansion of biocomposites can be made with the DSC and TGA [64-66]. Biodegradation of polymeric materials affect a wide range of industries; information on degradability can provide fundamental information facilitating design and life-time analysis of materials. The common tests to check the Biodegradability of biocomposites are Weight Loss Test, FT-IR Technique and 1H NMR Spectroscopy [67]. The TSDC technique is a basic tool to identify and evaluate the polarization and charge storage and decay phenomena, so it can be utilized to check the electrical behavior of biocomposite films [29-52].

With the view to have a sufficiently good knowledge of structural, mechanical, electrical, and thermal behaviour and to characterize the material for such applications a detailed investigation has been under taken on biocomposite of PVA and palm leaf. The measurement techniques employed include:

1.   IR/XRD/DSC/AFM and SEM studies on samples to investigate the structural, morphological, thermal aspects of the film specimens.

2.   Microhardness measurement to study the effect of composition and load on the pure PVA film and PVA incorporated palm leaf biocomposite film specimens.

3.   Tensile strength and elongation studies on samples to investigate the mechanical properties of the specimens.

4.   Short circuit thermally stimulated depolarization current measurement on samples polarized under varying field and temperature conditions.

1.10 SELECTION OF MATERIAL

1.10.1 Polyvinyl Alcohol (PVA)

Many authors have studied biocomposites; some of the studies are based on the composition of PVA with agro-industrial waste, corn fiber starch, glycerol, cellulose.

The sample has been prepared with different techniques. The structural, thermal and mechanical characterization has been carried out. The effect of various types of thermal pretreatment on the properties of biocomposites has been investigated.

Chiellini et al have studied composite films based on biorelated agro-industrial waste with PVA and reported that the mechanical properties of prepared agro-industrial based biocomposite films were found to be dependent upon the nature and environmental conditions [56]. Cinelli et al have studied the properties of injection molded composition containing corn fiber and PVA and reported that the addition of starch moderately reduces tensile properties of composite, lowering the elongation and increasing Young's modulus while tensile strength remains constant. Yun et al have studied the mechanical properties with the functional group of additives for starch/ PVA films and reported increase in flexibility and strength of films and degree of swelling (DS) of films[68].

Mao et al have studied the mechanical properties, morphology and biodegradability of Extruded Cornstarch- Glycerol PVA blends and reported that addition of PVOH to blends slows down the biodegradation process and improves physical and mechanical properties[59]. Jayshekara et al have studied biodegradation by composting of surface modified starch and PVA blended films and reported that PVA can be facilitate as biodegradation of composite films[69].

Imam et al have widely studied the composites based on PVA and reported that the FTIR based biodegradation and hexamethoxymethyl-melamine (HMMM) based composite for improving water resistance of PVA based biocomposite[64]. Rudnik has studied the thermal properties of biocomposite and reported increase in thermal stability of modified starch[70]. The thermal stimulated discharge current in polymer composite films has been reported by many authors on polymeric films [29-52,71,72].

PVA is one of the most important polymeric materials to prepare composites of biomaterials. The chemical structure of Polyvinyl alcohol is shown in Fig 1.5. The general properties of PVA are appearance as white granule or powder, specific gravity of 1.25~ 1.32, bulk density of above about 0.4 ~ 0.7, ph value is about to 5 ~ 7 with glass transition temperature (Tg) = 85^0C, melting point of 210 ~ 230^0C, thermally stable, gradual discoloration at about 100^0C, darkens rapidly above 160^0C, gradual

decomposition above 180^0C as melting point is similar to decomposing temperature and is soluble in water and resist to oil, animal, plant and grease oils. The different type of biocomposites of PVA have been studied with corn-starch, lingo-cellulosic fiber, agro-industrial waste, starch, glycerol with different aspect of study like mechanical, surface structure and thermal properties.
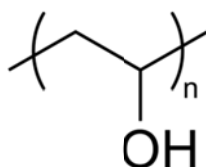
Fig 1.5: Chemical Structure of PVA.

The different types of biodegradable biocomposites have been prepared for various biological applications including packing, agriculture, waste management, recycling, sustainability, automotive, construction, contact lenses, bio-medical field, etc[55-60]. Application of hexamethoxymethyl-melamine (HMMM) with PVA reduces its water sensitivity[56].

1.10.2 Alexander Palm Leaf

The other names of this palm are; Alexandra palm, Kind palm, King Alexander palm, Aalexandrae palm. It has a medium sized, gray trunk (1 – 1.5 feet in diameter). Crownshaft is a bright green colour (a woody shaft at the top of the trunk composed of tightly wrapped leaf base). The type of the leaf is pinnate. It is a fast growing solitary single trunk palm of height of near about 40 feet. Palm leaf contains fibers inside the leaf and it has many potential applications in agriculture and villages.

1.10.3 Bio Composites of PVA and Palm Leaf

The world's supply of natural resources is decreasing and the demand for sustainable and renewable raw materials continues to increase. Biofiber-reinforced composites represent a potential nontraditional, value-added source of income to the agricultural community. Due to the above mentioned properties of Polyvinyl Alcohol and Palm leaf powder the biocomposite of PVA and Palm Leaf can be developed. In present study the biocomposite of PVA avd Palm leaf powder has been successfully prepared and this biocomposite can be the potential material with conducive

structural, mechanical and electrical properties for various applications like automobile, agriculture and industries sectors.

1.11   Possible Outcome

The developed biocomposite may definitely exhibit the properties incorporating the individual qualities of PVA and Palm Leaf powder. It may lead to develop a green material with higher mechanical properties, improved microhardness, improved structural morphology, improved thermal properties and improved charge storage properties, providing high strength to weight ratio, for various applications as biodegradable and environmental friendly material.

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