

SYNTHESIS AND CHARACTERIZATION OF BIO-COMPOSITE MATERIAL

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CERTIFICATE

This is to certify that the report entitled “Synthesis and characterization of bio-composite material” being submitted by **Usha Gracy Kispotta, Roll. No: 409PH2093, Physics Department, National Institute of Technology, Rourkela** in partial fulfillment for the requirements of the Master of Science degree in physics department at National institute of technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

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(Usha Gracy Kispotta)

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ABSTRACT

An eco-friendly biodegradable bio-composite were prepared using sisal fiber and cassava starch by using handmade mould. Bio-composites are finding applications in many fields ranging from construction industry to automotive industry, so we have synthesized and characterized such composites. Surface morphology, glass transition temperatures were investigated by SEM study and TGA study respectively. XRD patterns confirm crystallite size and degree of crystallinity is found to be maximum for S1.5 composite as compared to other two composites and that may be due to properly wetting the fiber by the matrix for S1.5 composite. SEM image shows roughness surface structure of composites. TGA/DTA analysis shows with increase in starch concentration in the composite glass transition temperature increases. So higher the percentage of starch in composite increases the free volume and molecular mobility, which results in increasing of Tg.

INTRODUCTION

COMPOSITE

The composite materials have got a widely applications in all cutting-edge ranges of advanced materials as aeronautics, automotives, boats, sports parts and medical devices.

Definition-

A composite is a structural material that consists of two or more combined constituents that are combined at a macroscopic level and are not soluble in each other. One constituent is called reinforcing phase and one in which it is embedded is called the matrix. The reinforcing phase material may be in the form of fibers, particles or flake. The matrix phase materials are generally continuous. Examples of naturally found composites include wood, where the lignin matrix is reinforced with cellulose fibers and bones in which the bone-salt plates made of calcium and phosphate ions reinforce soft collagen. The roles of matrix in composite materials are to give shape to the composite part, protect the reinforcements to the environment, transfer loads to reinforcements and toughness of material, together with reinforcements. The aims of reinforcements in composites are to get strength, stiffness and other mechanical properties, dominate other properties as coefficient of thermal extension, conductivity and thermal transport. As a comparison between composites and metals, the composites materials are some advantages as:

- Light weight
- High specific stiffness and strength
- Easy moldable to complex forms
- Easy bondable
- Good damping
- Low electrical conductivity and thermal expansion
- Good fatigue resistance
- Part consolidation due to lower overall system costs
- Low radar visibility
- Internal energy storage and release

Such as disadvantages of composites are the followings:

- Cost of materials
- Long development time

- Difficulty manufacturing
- Fasteners
- Low ductility
- Temperature limits
- Solvent or moisture attack
- Hidden damages and damage susceptibility

All of these have made those composites to change more and more the metals, in special in aircrafts, automotives, marines, constructions, etc.

Classification- Composites are classified by geometry of the reinforcement-particulate, flake, fibers, filled, whiskers and directionally solidified eutectics or by the type of matrix-polymer, metal, ceramic and carbon. Polymer matrix material is classified as thermosets and thermoplastics. Again thermosets and thermoplastics are divided by epoxy, phenolic polyamide resin, polyester and polyethylene, polystyrene, polyamides, nylons and polypropylene respectively.

1. Particulate composites consist of particles immersed in matrices such as alloys and ceramics. They are usually isotropic because the particles are added randomly. Particulate composites have advantages such as improved strength, increased operating temp, oxidation resistance, etc. Typical examples include use of aluminium particles in rubber, silicon carbide particles in aluminium, and gravel sand, and cement to make concrete.

2. Flake composites consist of flat reinforcements of materials. Typical flake materials are glass, mica, alumina and silver. Flake composites provide advantages such as high out-of-plane, flexural modulus, higher strength and low cost. However flakes cannot be oriented easily and only a limited no. of materials are available for use.

3. Fiber composites consist of matrices reinforced by short (discontinuous) or long (continuous) fibers. Fibers are generally anisotropic and examples include carbon and aramides.

Polymer Matrix Composites (PMCs)

The most common advanced composites are polymer matrix composites. These composites consist of a polymer thermoplastic or thermosetting reinforced by fiber (natural carbon or boron). These materials can be fashioned into a variety of shapes and sizes. They provide great strength and stiffness along with resistance to corrosion. The reason for these being most common is their low cost, high strength and simple manufacturing principles.

Metal Matrix Composites (MMCs)

Metal matrix composites, as the name implies, have a metal matrix. Examples of matrices in such composites include aluminum, magnesium and titanium. The typical fiber includes carbon and silicon carbide. Metals are mainly reinforced to suit the needs of design. For example, the elastic stiffness and strength of metals can be increased, while large coefficient of thermal expansion, and thermal and electrical conductivities of metals can be reduced by the addition of fibers such as silicon carbide.

Ceramic Matrix Composites (CMCs)

Ceramic matrix composites have ceramic matrix such as alumina, calcium, aluminosilicate reinforced by silicon carbide. The advantages of CMC include high strength, hardness, high service temperature limits for ceramics, chemical inertness and low density. Naturally resistant to high temperature, ceramic materials have a tendency to become brittle and to fracture. Composites successfully made with ceramic matrices are reinforced with silicon carbide fibers. These composites offer the same high temperature tolerance of super alloys but without such a high density. The brittle nature of ceramics makes composite fabrication difficult. Usually most CMC production procedures involve starting materials in powder form. There are four classes of ceramics matrices: glass (easy to fabricate because of low softening temperatures, include borosilicate and aluminosilicates), conventional ceramics (silicon carbide, silicon nitride, aluminum oxide and zirconium oxide are fully crystalline), cement and concrete carbon components.

Carbon-carbon composites (CCMs)

CCMs use carbon fibers in a carbon matrix. Carbon-carbon composites are used in very high temperature environments of up to 6000°F, and are twenty times stronger and thirty times lighter than graphite fibers.

Constituents of composites

1. Matrices

2. Reinforcing Fibers

Matrices

The role of matrix in a fiber-reinforced composite is to transfer stress between the fibers, to provide a barrier against an adverse environment and to protect the surface of the fibers from mechanical abrasion. The matrix plays a major role in the tensile load carrying capacity of a composite structure. The binding agent or matrix in the composite is of critical importance. Four major types of matrices

have been reported: Polymeric, Metallic, Ceramic and Carbon. Most of the composites used in the industry today are based on polymer matrices. Polymer resins have been divided broadly into two categories: Thermosetting and Thermoplastics.

Thermosetting

Thermoset is a hard and stiff cross linked material that does not soften or become moldable when heated. Thermosets are stiff and do not stretch the way that elastomers and thermoplastics do. Several types of polymers have been used as matrices for natural fiber composites. Most commonly used thermoset polymers are epoxy resins and other resins (Unsaturated polyester resins (as in fiber glass) Vinyl Ester, Phenolic Epoxy, Novolac and Polyamide). Unsaturated polyesters are extremely versatile in properties and applications and have been a popular thermoset used as the polymer matrix in composites. They are widely produced industrially as they possess many advantages compared to other thermosetting resins including room temperature cure capability, good mechanical properties and transparency. The reinforcement of polyesters with cellulosic fibers has been widely reported. Polyester-jute, Polyester-sisal, polyester-coir, polyester-banana-cotton, polyester-straw, polyester-pineapple leaf, and polyester- cotton-kapok, are some of the promising systems.

Thermoplastics

Thermoplastics are polymers that require heat to make them processable. After cooling, such materials retain their shape. In addition, these polymers may be reheated and reformed, often without significant changes in their properties. The thermoplastics which have been used as matrix for natural fiber reinforced composites are as follows:

- High density polyethene (HDPE)
- Low density polyethene (LDPE)
- Chlorinated polyethylene (CPE)
- Polypropylene (PP)
- Normal polystyrene (PS)
- Poly (Vinyl chloride) PVC)
- Mixtures of polymers
- Recycled Thermoplastics

Only those thermoplastics are useable for natural fiber reinforced composites, whose processing temperature (temperature at which fiber is incorporated into polymer matrix) does not exceed 230°C. These are, most of all, polyolefinnes, like polyethylene and polypropylene. Technical

thermoplastics, like polyamides, polyesters and polycarbonates require processing temperatures $> 250^{\circ}\text{C}$ and are therefore not useable for such composite processing without fiber degradation.

Reinforcing fibers

The three most common types of reinforcing fibers include fiberglass, carbon and Aramid.

Carbon fibers-Carbon fibers are used for reinforcing certain matrix materials to form composites. Carbon fibers are unidirectional reinforcements and can be arranged in such a way in the composite that it is stronger in the direction, which must bear loads. The physical properties of carbon fiber reinforced composite materials depend considerably on the nature of the matrix, the fiber alignment, the volume fraction of the fiber and matrix, and on the molding conditions. Several types of matrix materials such as glass and ceramics, metal and plastics have been used as matrices for reinforcement by carbon fiber. Natural fiber reinforced composites. Carbon fiber composites, particularly those with polymer matrices, have become the dominant advanced composite materials for aerospace, automobile, sporting goods and other applications due to their high strength, high modulus, low density, and reasonable cost for application requiring high temperature resistance as in the case of spacecrafts.

Glass fibers-

Glass is the most common of all reinforcing fibers for polymeric (plastic) matrix composites (PMCs). The principal advantages of glass fiber are low cost, high tensile strength, high chemical resistance and excellent insulating properties. The two types of glass fibers commonly used in the fiber reinforced plastics industries are E-glass and S-glass. Another type known as C-glass is used in chemical applications requiring greater corrosion resistance to acids than is provided by E-glass.

Kevlar fibers-

Kevlar belongs to a group of highly crystalline aramid (aromatic amide) fibers that have the lowest specific gravity and the highest tensile strength to weight ratio among the current reinforcing fibers. They are being used as reinforcement in many marine and aerospace applications.

Boron fiber-

The most prominent feature of boron fiber is their extremely high tensile modulus. Boron fibers offer excellent resistance to buckling, which in turn contributes to high compressive strength for boron fiber reinforced composites.

Natural Fibers Reinforced Composite-

The use of natural fiber for the reinforcement of the composites has received increasing attention both by the academic sector and the industry. Natural fibers have many significant advantages over synthetic fibers. Currently, many types of natural fibers have been investigated for use in plastics including flax, hemp, jute straw, wood, rice husk, wheat, barley, oats, rye, cane (sugar and bamboo), grass, reeds, kenaf, ramie, oil palm empty fruit bunch, sisal, coir, water, hyacinth, pennywort, kapok, paper mulberry, raphia, banana fiber, pineapple leaf fiber and papyrus. Thermoplastics reinforced with special wood fillers are enjoying rapid growth due to their many advantages; lightweight reasonable strength and stiffness. Some plant proteins are interesting renewable materials, because of their thermoplastic properties. Wheat gluten is unique among cereal and other plant proteins in its ability to form a cohesive blend with viscoelastic properties once plasticized. For these reasons, wheat gluten has been utilized to process edible or biodegradable films or packing materials. Hemp is a bast lingo cellulosic fiber, comes from the plant *Cannabis sativa* and has been used as reinforcement in biodegradable composites. Composites based on biologically degradable polyester amide and plant fiber (flax and cottons) with good mechanical properties, such as sufficient water resistance and biodegradability, have also been investigated. Kenaf, *Hibiscus cannabinus* L, a member of hibiscus family is also a biodegradable and environmentally friendly crop. It has been found to be an important source of fiber for composites and other industrial applications. Aziz *et al.* studied the mechanical properties of composites manufactured from polyester resin with Kenaf fiber that blows to a height of at least 10 meter. Traditionally, hemp has been used to make ropes but these days its fiber is used to make items such as clothing, toys and shoes. The fiber is fully biodegradable, is non-toxic and may be recycled.

Natural fibers are renewable resources in many developing countries of the world; they are cheaper, pose no health hazards and, finally, provide a solution to environmental pollution by finding new uses for waste materials. Furthermore, natural fiber reinforced polymer composites form a new class of materials which seem to have good potential in the future as a substitute for scarce wood and wood based materials in structural applications. Fibers obtained from the various parts of the plants are known as vegetable fibers. These fibers are classified into three categories depending on the part of the plant from which they are extracted.

1. Bast or Stem fibers (jute, mesta, banana etc.)
2. Leaf fibers (sisal, pineapple, screw pine etc.)

3. Fruit fibers (cotton, coir, oil palm etc.)

Properties of plant fibers depend mainly on the nature of the plant, locality in which it is grown, age of the plant, and the extraction method used. For example, coir is a hard and tough multicellular fiber with a central portion called “lacuna”. Sisal is an important leaf fiber and is very strong. Pineapple leaf fiber is soft and has high cellulose content. Oil palm fibers are hard and tough, and show similarity to coir fibers in cellular structure. The elementary unit of a cellulose macromolecule is anhydro-d-glucose, which contains three alcohol hydroxyls (-OH) (Bledzki et al., 1996). These hydroxyls form hydrogen bonds inside the macromolecule itself (intramolecular) and between other cellulose macromolecules (intermolecular) as well as with hydroxyl groups from the air. Therefore, all plant fibers are of a hydrophilic nature; their moisture content reaches 8-13%. In addition to cellulose, plant fibers contain different natural substances. The most important of them is lignin. The distinct cells of hard plant fibers are bonded together by lignin, acting as a cementing material. The lignin content of plant fibers influences its structure, properties and morphology. An important characteristic of vegetable fiber is their degree of polymerization (DP). The cellulose molecules of each fiber differ in their DP and consequently, the fiber is a complex mixture of polymer homologue $(C_6H_{10}O_5)_n$. Bast fibers commonly show the highest DP among all the plant fibers (~10,000). Traditionally these fibers have been used for making twines, ropes, cords, as packaging material in sacks and gunny bags, as carpet-backing and more recently, as a geotextile material.

Advantages of natural fiber-

Natural fibers, as reinforcement, have recently attracted the attention of researchers because of their advantages over other established materials. They are environmentally friendly, fully biodegradable, abundantly available, renewable and cheap and have low density. Plant fibers are light compared to glass, carbon and aramid fibers. The biodegradability of plant fibers can contribute to a healthy ecosystem while their low cost and high performance fulfils the economic interest of industry. When natural fiber-reinforced plastics are subjected, at the end of their life cycle, to combustion process or landfill, the released amount of CO₂ of the fibers is neutral with respect to the assimilated amount during their growth. The abrasive nature of fiber is much lower which leads to advantages in regard to technical process and recycling process of the composite materials in general. Natural fiber-reinforced plastics, by using biodegradable polymers as matrices, are the most environmental friendly materials, which can be composed at the end of their life cycle. Natural fiber composites are used in place of glass mostly in non-structural applications. A number of automotive components

previously made with glass fiber composites are now being manufactured using environmentally friendly composites. Although natural fibers and their composites are environmental friendly and renewable (unlike traditional sources of energy, i.e., coal, oil and gas), these have several bottlenecks. These have: poor wettability, incompatibility with some polymeric matrices and high moisture absorption. Composite materials made with the use of unmodified plant fibers frequently exhibit unsatisfactory mechanical properties. To overcome this, in many cases, a surface treatment or compatibilizing agents need to be used prior to composite fabrication. The properties can be improved both by physical treatments (cold plasma treatment, corona treatment) and chemical treatments (maleic anhydride organosilanes, isocyanates, sodium hydroxide permanganate and peroxide). Mechanical properties of natural fibers are much lower than those of glass fibers but their specific properties, especially stiffness, are comparable to the glass fibers.

Disadvantages of natural fiber composite-

The performance of biocomposites depends on the properties of the natural fibers used in them. However, using natural fibers in building materials has also some disadvantages such as low modulus elasticity, high moisture absorption, decomposition in alkaline environments or in biological attack, and variability in mechanical and physical properties. To understand these problems, it is necessary to study fibers precisely. Generally, cell wall polymers and their matrices are the reason for chemical and physical properties of natural fibers. For instance, dimensional stability, flammability, biodegradability, and degradation are attributed to acids bases and UV radiation that alters the biocomposites back into their basic building blocks (carbon dioxide and water). However, the properties of natural fibers that result from the chemistry of the cell wall components make some main problems in biocomposites. Therefore, to address these problems, improving the natural fiber properties by modifying the basic chemistry of the cell wall polymers has been recommended.

LITERATURE SURVEY-

Bio-composite-

The history of mankind has witnessed several surges in the field of research and development. The rampant use of petroleum products has created a twin dilemma; depletion of petroleum resources and entrapment of plastics in food chain and environment. The increasing pollution caused by the use of plastics and emissions during incineration is affecting the food we eat, water we drink, air we breathe and threatening the greatest right of human beings, the right to live. The exhaustive use of

petroleum based resources has initiated the efforts to develop biodegradable plastics. This is based on renewable biobased plant and agricultural products that can compete in the markets currently dominated by petroleum based products. The production of 100% biobased materials as substitute for petroleum based products is not an economical solution. A more viable solution would be to combine petroleum and biobased resources to develop a cost-effective product having immense applications. Biopolymers or synthetic polymers reinforced with natural or biofibers (termed as biocomposites) are a viable alternative to glass fiber composites. Scientists are looking at the various possibilities of combining biofibers such as sisal, flax, hemp, jute, banana, wood and various grasses with polymer matrices from non-renewable and renewable resources to form composite materials to make the biocomposite revolution a reality.

The term 'Biocomposites' refers to those composites that can be employed in bioengineering. The constituents of the composite retain their identities in the composite. Namely, they do not dissolve or otherwise merge completely into each other although they act in concert. In composites, properties such as the elastic modulus can be significantly different from those of the constituents alone, but are considerably altered by the constituent structures and contents. From a structural point of view, composites are anisotropic in nature. Biocomposites are composite materials, that is, materials formed by a matrix (resin) and a reinforcement of natural fibers (usually derived from plants or cellulose). Biocomposites are the combination of natural fibers (biofibers) such as wood fibers (hardwood and softwood) or non-wood fibers (e.g., wheat, kenaf, hemp, jute, sisal, and flax) with polymer matrices from both of the renewable and nonrenewable resources. Biofibers are one of the major components of Biocomposites. The fibrous material derived from the tree, plant, or shrub sources is defined as biofiber. Biocomposites often mimic the structures of the living materials involved in the process, in addition to the strengthening properties of the matrix that was used, but still providing bio-compatibility, e.g. in creating scaffolds in bone tissue engineering. The degree of biodegradability in bio-based polymers depends on their structure and their service environment. Natural/Biofiber composites are emerging as a viable alternative to glass fiber composites, particularly in automotive, packaging, building, and consumer product industries, and becoming one of the fastest growing additives for thermoplastics. Further, research into biological-inorganic interfaces focuses on the design, synthesis, and characterization of novel amalgams that fuse biological and inorganic materials. The integration of "soft" biological and organic molecular assemblies with "hard" inorganic nano-architectures is of special interest because of the opportunity

to combine normally disparate chemical and physical properties within a single system. Broadly defined, biocomposites are composite materials made from natural/biofiber and petroleum derived non-biodegradable polymers(PP,PE) or biodegradable polymers(PLA,PHA).The latter category i.e. biocomposites derived from plant derived fiber(natural/biofiber) and crop/bio-derived plastic(biopolymer/bioplastic) are likely to be more eco-friendly and such composites are termed as green composites.The best known renewable resources capable of making biodegradable plastics are starch and cellulose.Starch is one of the least expensive biodegradable materials available in the world market today.It is a versatile polymer with immense potential for use in non-food industries.Cellulose from trees and cotton plants is a substitute for petroleum feedstocks to make cellulose plastics.Another aspect that has gained global attention is the development of biodegradable plastics from vegetable oils like soybean oil, peanut oil, walnut oil, sesame oil and sun flower oil.Green composites from soy protein based bioplastics and natural fibers show potential for rigid packing and housing and transportation applications.

One of the major applications for biocomposites that recently has also gained a lot of attention in the North America is in building materials. Nowadays, biocomposites are being used to make products such as decking, fencing, siding, window, door, and so on. Use of bio-composites in building materials offers several advantages such as they are cheap, lightweight, environmental friendly, biorenewable, and more durable. However, in addition to these advantages, they have some disadvantages as well, such as moisture absorption and photochemical degradation because of the UV radiations. For this purpose, some research is going on to address these issues.

Starch-

As well known, synthetic polymer materials have been widely used in every field of human activity during last decades, i.e. post-Staudinger times. These artificial macromolecular substances are usually originating from petroleum and most of the conventional ones are regarded as non-degradable. However, the petroleum resources are limited and the blooming use of non-biodegradable polymers has caused serious environmental problems. In addition, the non-biodegradable polymers are not suitable for temporary use such as sutures. Thus, the polymer materials which are degradable and/or biodegradable have been paid more and more attention since 1970s. Both synthetic polymers and natural polymers that contain hydrolytically or enzymatically labile bonds or groups are degradable. The advantages of synthetic polymers are obvious, including predictable properties, batch-to-batch uniformity and can be tailored easily. In spite of this, they are

quite expensive. This reminds us to focus on natural polymers, which are inherently biodegradable and can be promising candidates to meet different requirements. Among the natural polymers, starch is of interest. It is regenerated from carbon dioxide and water by photosynthesis in plants. Owing to its complete biodegradability, low cost and renewability, starch is considered as a promising candidate for developing sustainable materials. In view of this, starch has been receiving growing attention since 1970s. Many efforts have been exerted to develop starch-based polymers for conserving the petrochemical resources, reducing environmental impact and searching more applications.

Structure and properties of starch-

Starch is mainly composed of two homopolymers of D glucose: amylose, a mostly linear α -D (1, 4')-glucan and branched amylopectin, having the same backbone structure as amylose but with many α -1, 6'-linked branch points (Figure1). There are a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked. Evidently, starch is hydrophilic. The available hydroxyl groups on the starch chains potentially exhibit reactivity specific for alcohols. In other words, they can be oxidized and reduced, and may participate in the formation of hydrogen bonds, ethers and esters. Starch has different proportions of amylose and amylopectin ranging from about 10–20% amylose and 80–90% amylopectin depending on the source. Amylose is soluble in water and forms a helical structure. Starch occurs naturally as discrete granules since the short branched amylopectin chains are able to form helical structures which crystallize. Starch granules exhibit hydrophilic properties and strong inter-molecular association via hydrogen bonding formed by the hydroxyl groups on the granule surface. Owing to its hydrophilicity, the internal interaction and morphology of starch will be readily changed by water molecules, and thereby its glass transition temperature (T_g), the dimension and mechanical properties depend on the water content. T_g of native starch can be as low as 60 to 80°C when the weight fraction of water is in the range 0.12 to 0.14, which allows starch to be successfully injection moulded to obtain thermoplastic starch polymers in the presence of water. On the other hand, the hydrophilicity of starch can be used to improve the degradation rate of some degradable hydrophobic polymers. Starch is totally biodegradable in a wide variety of environments. It can be hydrolyzed into glucose by microorganism or enzymes, and then metabolized into carbon dioxide and water. It is worth noting that carbon dioxide will recycle into starch again by plants and

sunshine. Starch itself is poor in processability, also poor in the dimensional stability and mechanical properties for its end products. Therefore, native starch is not used directly.

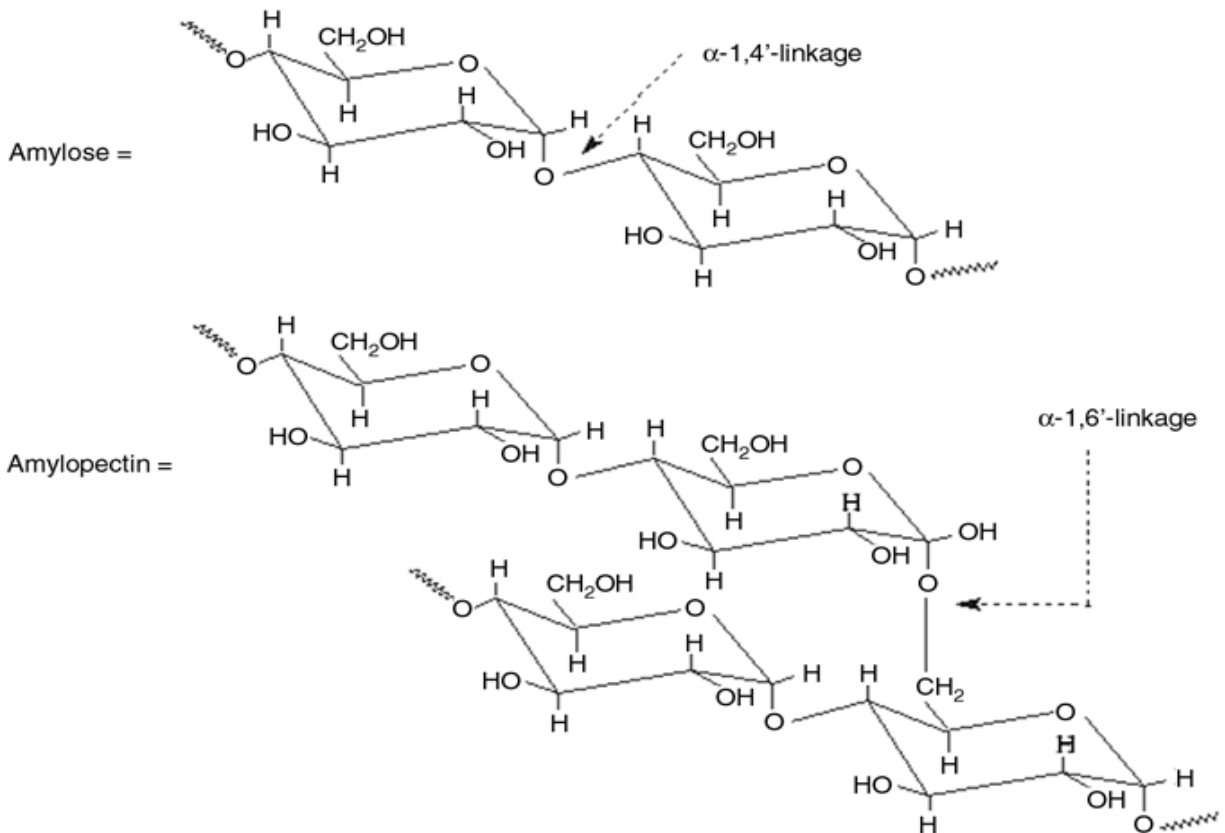


Figure 1. Molecular structure of starch

Applications of starch-based biodegradable polymers-

In food industry-

Food packaging and edible films are two major applications of the starch-based biodegradable polymers in food industry. The requirements for food packaging include reducing the food losses, keeping food fresh, enhancing organoleptic characteristics of food such as appearance, odor, and flavor, and providing food safety. Traditional food packaging materials such as LDPE have the problem of environmental pollution and disposal problems. The starch based biodegradable polymers can be a possible alternative for food packaging to overcome these disadvantages and keep the advantages of traditional packaging materials. However, the components in the conventional starch-based polymer packaging materials are not completely inert. The migration of substances into the food possibly happens, and the component that migrates into food may cause harm for the human body. In view of this, new starch-based packaging materials are being developed. For instance, a

starch/claynanocomposite food packaging material is developed, which can offer better mechanical property and lower migration of polymer and additives. Starch-based edible films are odorless, tasteless, colorless, non-toxic, and biodegradable. They display very low permeability to oxygen at low relative humidity and are proposed for food product protection to improve quality and shelf life without impairing consumer acceptability. In addition, starch can be transformed into a foamed material by using water steam to replace the polystyrene foam as packaging material. It can be pressed into trays or disposable dishes, which are able to dissolve in water and leave a non-toxic solution, then can be consumed by microbic environment. Evidently, the starch-based biodegradable polymers are attractive for food industry and will make great progress in the future.

In agriculture-

Starch-based biodegradable polymers have found three major applications in agriculture: the covering of greenhouse, mulch film and fertilizers controlled release materials. The consumption of agriculture films is abundant. Generally, the disposal methods of tradition films are landfill, recycling or burning. But they are time-consuming, not economic and lead to environmental pollution. On the other hand, the utilization efficiency of fertilizers is the key element of the development of agricultural productions. However, due to surface runoff, leaching and vaporization, the fertilizers escape to environment to cause diseconomy and environmental problems. The development of starch-based biodegradable polymers offers a possibility to overcome the mentioned problems. They can be used as the fertilizers controlled release matrices to release the fertilizers slowly or in controlled way. As a result, the loss of fertilizers and environment pollution can be avoided or reduced. After using, starch-based films can be ploughed into soil and disposed directly. Moreover, no toxic residues formed after the degradation of starch based biodegradable polymers. Thus, the development of starch-based materials for agriculture applications is being continued. For example, to enhance the mechanical properties and solvent or gas resistance, starch-based biodegradable materials are mixed with some nano-grade additives such as TiO_2 , layered silicate and MMT to form bio-nanocomposites.

In medical field-

Starch-based biodegradable polymers have some advantages to be medical polymer materials:

- a) Good biocompatibility
- b) Biodegradable and its degradation products are non-toxic
- c) Proper mechanical properties

d) Degradation as requirement

Starch-based biodegradable polymers have been widely investigated in bone tissue engineering. Starch-based biodegradable bone cements can provide immediate structural support and degrade from the site of application. Moreover, they can become binned with bioactive particles, which allow new bone growth to be induced in both the interface of cement-bone and the volume left by polymer degradation. In addition, starch-based biodegradable polymer can also be used as bone tissue engineering scaffold. Starch-based biodegradable polymers, in the form of microsphere or hydrogel, are suitable for drug delivery. There is no need for surgical removal of the device after drug depletion. The unique properties, such as hydrophilicity, permeability, biocompatibility, and to some extent similar to soft biological systems, of starch-based hydrogels make them useful for various biomedical applications. The 3D structure of starch-based hydrogels enable them absorb and reserve a plenty of water and keep good enough mechanical property at the same time. Starch-based hydrogels have received growing interest for biomedical applications. In our lab, physically cross-linked starch-g-PVA and starch-g-PVA/hydroxyapatite hydrogel are obtained via repeated freezing/thawing circles and hydroxyapatite (HA) can be well dispersed in such a matrix. The water content in the fresh starch-g-PVA/HA hydrogel is comparable to that of PVA/HA hydrogel and the dried starch-g-PVA/HA films can re-adsorb water soon and reach swelling equilibrium within 12 minutes.

Materials and method-

For the synthesis of biocomposite, materials are required-

- a) Sisal fiber
- b) Cassava starch

Sisal fiber-

Sisal fiber is obtained from the leaves of the plant *Agave sisalana*, which was originated from Mexico and is now mainly cultivated in East Africa, Brazil, Haiti, India and Indonesia Nilsson. It is grouped under the broad heading of the “hard fibers” among which sisal is placed second to manila in durability and strength. The name “sisal” comes from a harbor town in Yucatan, Maya, Mexico (Nilsson, 1975). It means cold water. Agave plants were grown by the Maya Indians before the arrival of the Europeans. They prepared the fibers by hand and used it for ropes, carpets and clothing. Some clothes were called “nequen”, and this is where the present name of Mexican agave, henequen, probably originates. It is one of the most extensively cultivated hard fibers in the world

and it accounts for half the total production of textile fibers (Lock, 1962; Wilson, 1971). The reason for this is due to the ease of cultivation of sisal plants, which have short renewing times, and is fairly easy to grow in all kinds of environments. A good sisal plant yields about 200 leaves with each leaf having a mass composition of 4% fiber, 0.75% cuticle, 8% other dry matter and 87.25% moisture. Thus a normal leaf weighing about 600g yields about 3% by weight of fiber with each leaf containing about 1000 fibers (Kallapur, 1962). The fiber is extracted from the leaf either by retting, by scraping or by retting followed by scraping or by mechanical means using decorticators (KVIC, 1980). The diameter of the fiber varied from 100 μ m to 300 μ m.



Cassava starch-

Cassava starch has very good properties that are highly desirable for the paper manufacturer. Cassava starch, as a dominant source of starch in Nigeria, possesses a strong film, clear paste, good water holding properties, and stable viscosity. It should be the most suitable material for the paper industry in West Africa. Cassava starch has been widely used as a tub size and beater size in the manufacture of paper, in the past mainly on account of its low price. A high color (whiteness), low dirt and fiber content and, above all, uniformity of lots are needed in this instance. An important new application of starch is in the machine-coating of magazine paper, formerly done exclusively with caseins. There are indications that cassava is particularly well-suited to the purpose; however, definite specifications for the starch still have to be worked out.

Experimental details-

The composite was prepared by solution mixing technique. At first, very small pieces of sisal fiber had been cut i.e. as small as possible. Then required amount of starch is dissolved in 10 ml water and stirred using stirrer. After 10 minute, the mixture was then dried in a microwave oven at 160W temperature for 1 minute and 30 second. When the mixture turns into semi-liquid state then cutting fiber was put in handmade rectangular shape mould and mixture was poured into mould and pressure

was given from all the sides. Then again the sample was completely dried up in an oven at 80⁰ Celsius for 4 hour .Composites were made by maintain constant fiber concentration and with varying starch concentration. Water concentration kept remains same for all composites. Composites containing 100, 83.3, and 71.4 percent by weight of starch, where as fiber were kept 1.25 gm by weight. All the composites are made in same process by maintaining heating time in microwave oven for 1 minute 30 second and drying time in oven for 4 hour at 80⁰ Celsius.

Results and discussions-

XRD- XRD analysis was studied using the room temperature powder X-ray diffraction (Model: PW 1830 diffractometer, Phillips, Netherland) with filtered 0.154 nm Cu K α radiation. Samples are scanned in a continuous mode from 10^o-80^o with a scanning rate of 2^o per minute except for fiber, for which scanning range is 5^o-45^o. From XRD analysis crystallite size and degree of crystallinity is calculated. XRD plot of S1.25, S1.5, S1.75 are shown in the fig.1.

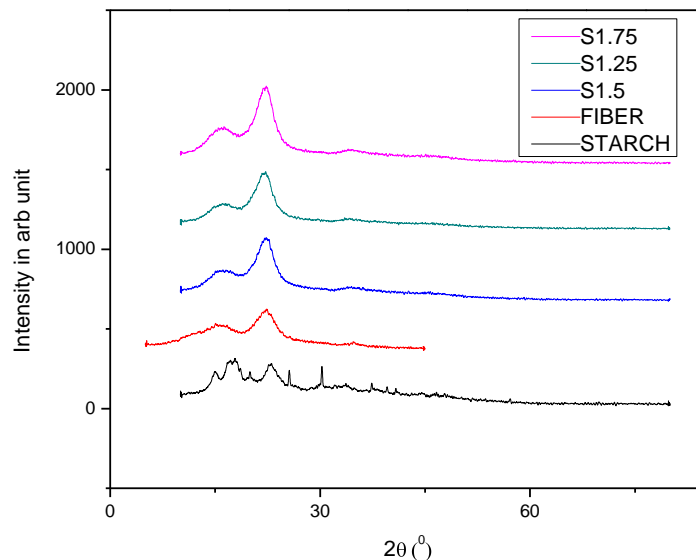


Fig.1: XRD ANALYSIS

- From XRD analysis we found that crystallite size of S1.25 is 9.9982nm and degree of crystallinity is 59.89
- The crystallite size of S1.5 is 12.997nm and degree of crystallinity is 65.476
- The crystallite size of S1.75 is 10.038nm and degree of crystallinity is 64.436

From the above result, it shows that for S1.5 composite crystallite size and degree of crystallinity is maximum as compare to other two composites which shows that proportion of fiber and starch is equal and percentage of starch is properly wetting the fiber. Hence S1.5 composite is the best composite. It may be concluded that with the more matrix (starch), the orientation of fiber is lowered which results in the decrease in the crystallinity.

SEM- Microstructure features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). The SEM microstructure of all samples is shown below. The changes in the morphology of bio-degradable matrix surfaces were studied with different concentration of cassava starch with cross linked fiber matrix. It was observed that the surfaces of matrix undergoing biodegradation. Here the fracture surface of the composite has been examined by SEM analysis.

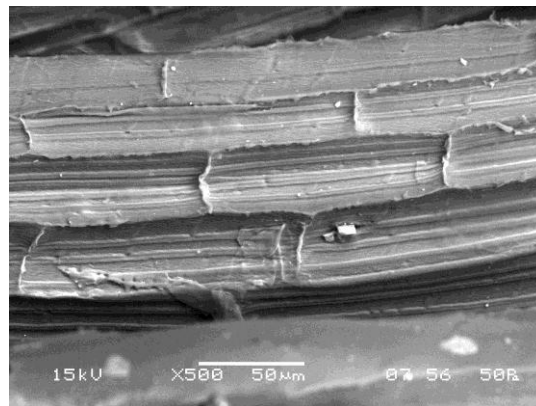


Fig 1.1 SEM OF S1.25

In this figure shows the roughness of the composite. Here surfaces become very heterogeneous and rough. It was observed that surfaces of the matrix undergoing bio-degradation which was highly roughness.

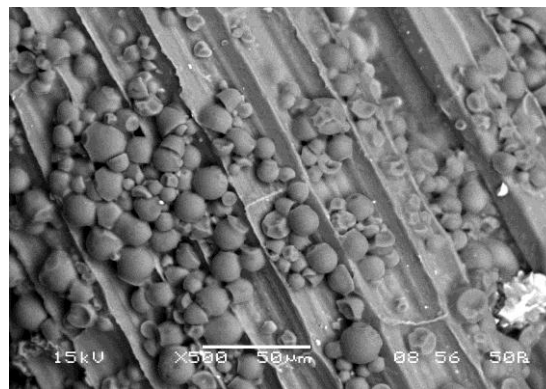


Fig1.2 SEM OF S1.5

In figure1.2 shows the best reinforcement of the fiber in the matrix of the starch. Here some starch has been found to be attached with the fiber and shows good adhesion of fiber with the matrix.

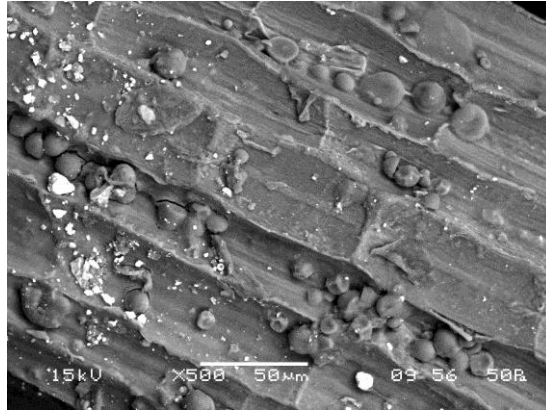


Fig.1.3 SEM OF S1.75

In the figure1.3 indicates some starch is attached in the composite. Here starch concentration is maximum and hence starch is tightly adhering with fiber, which results cracks in the composite.

TGA- The TGA/DTA analysis of all the three samples is carried out using DTG-60H by heating the sample at 5°C/min from 0⁰cto 80⁰c. The plots of S1.25, S1.5 and S1.75 are shown in the figure 1, 2 and 3 respectively.

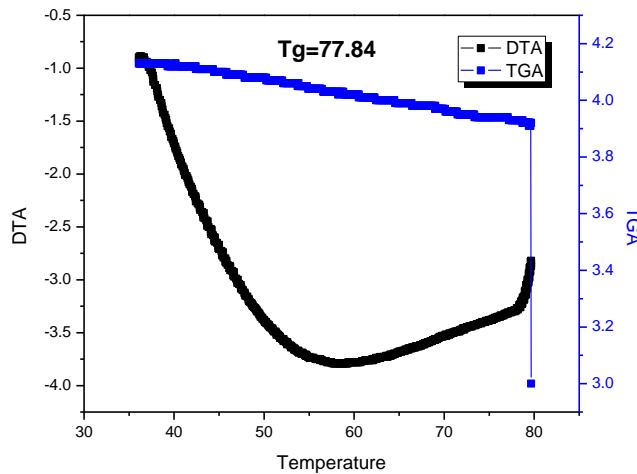


Fig.1: S1.25

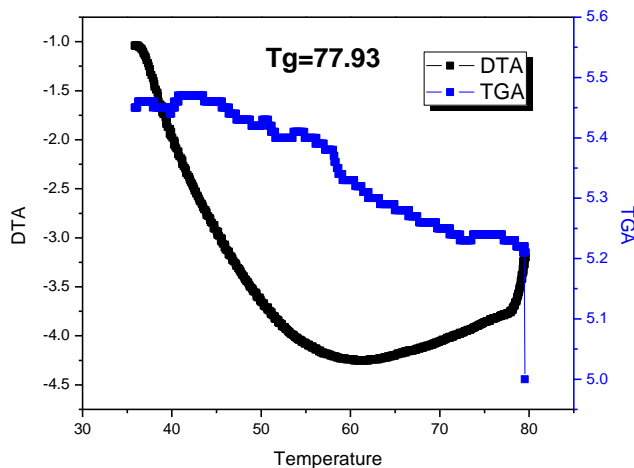


Fig.2: S1.5

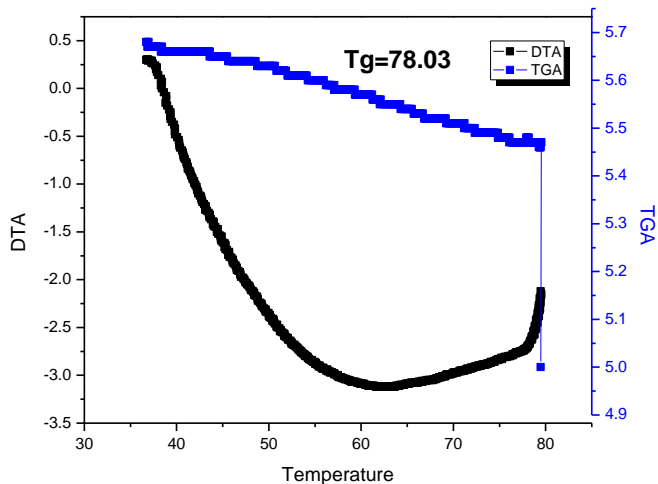


Fig.3: S1.75

From the figure the glass transition temperature increases with increase of starch concentration in the composite. From the above figure the observed value of Tg is influenced by the distribution and percentage of starch in composites. The observed behavior could be explained by the dependence of Tg on molecular mobility and free volume in polymer. In fact, higher the percentage of starch in sample increases the free volume and molecular mobility, which results

in increasing of Tg. Increase in Tg indicates that composites change from rubbery to crystalline phase.

CONCLUSION

In this study, we synthesized starch based bio-composite materials and studied the structural parameter of the fiber with the correlation to morphological and thermal properties of the composites by varying starch concentration with fixed fiber concentration. Bio-composites were prepared with the help of sisal fiber and cassava starch using handmade mould. XRD patterns confirm that for S1.5 composite crystallite size and degree of crystallinity has been found to be maximum as compared to other two composites, which indicate starch is properly wetting the fiber for S1.5 composite. SEM microstructure for S1.5 composite shows good adhesion of fiber with the matrix (starch). TGA/DTA analysis conforms that with increase in the starch concentration in the composite the glass transition temperature increases. Higher the percentage of starch in composite increases the free volume and molecular mobility, which results in increasing of Tg. Increase in Tg indicates that composites change from rubbery to crystalline phase.

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