Biopolymers

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What are biopolymers?

Biopolymers are polymers produced from natural sources either chemically synthesized from a biological material or entirely biosynthesized by living organisms.

Biopolymers include the polysaccharides such as cellulose, starch, the carbohydrate polymers produced by bacteria and fungi and animal protein-based biopolymers such as wool, silk, gelatin and collagen.

Classification Of Biopolymers(Based on sources):

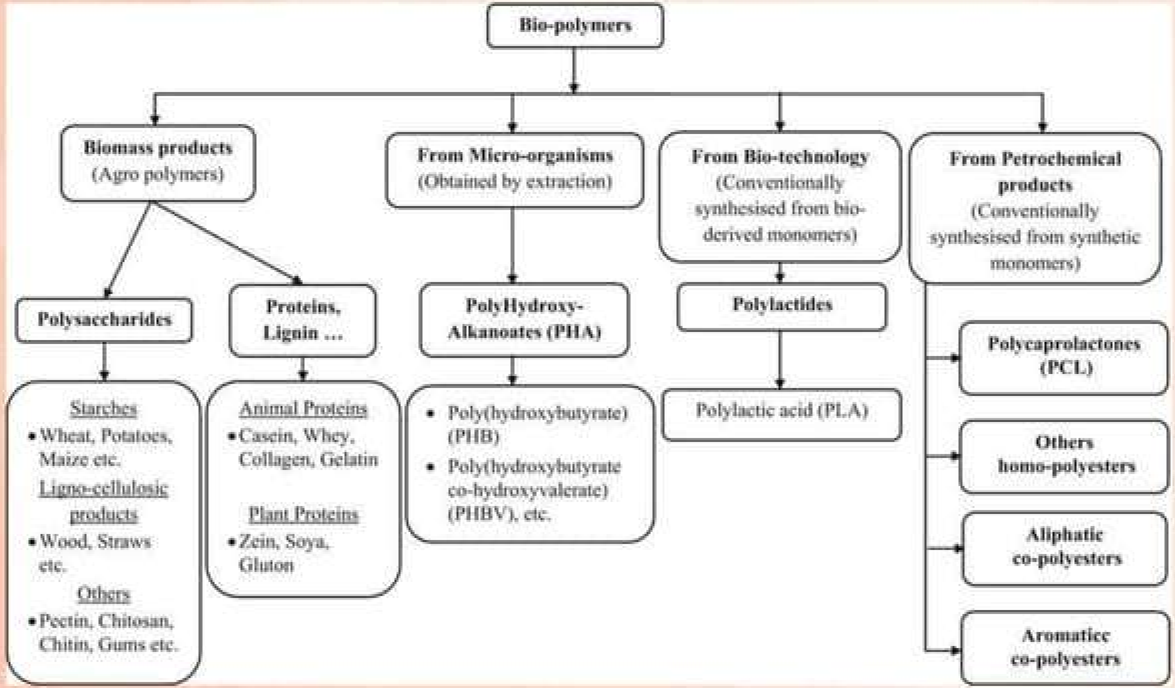

Fig-1 Classification of biopolymers

Source: T.Karthik, R.Rathinamoorthy -Sustainable biopolymers in textiles: An overview (Springer link)

Types Of Biopolymers

There are four main types of biopolymer based respectively on:

1. Starch
2. Sugar
3.Cellulose
4.Synthetic materials

1. Starch based polymers

Starch is a particular form of carbohydrate and is a biopolymer of anhydroglucose units linked by $\alpha \rightarrow 4$ linkages.

It is one of the most abundant, naturally occurring biodegradable polymers made up mainly of two polysaccharides namely amylose (molecular weight of up to 2,000,000) and amylopectin (100- 400,000,000).

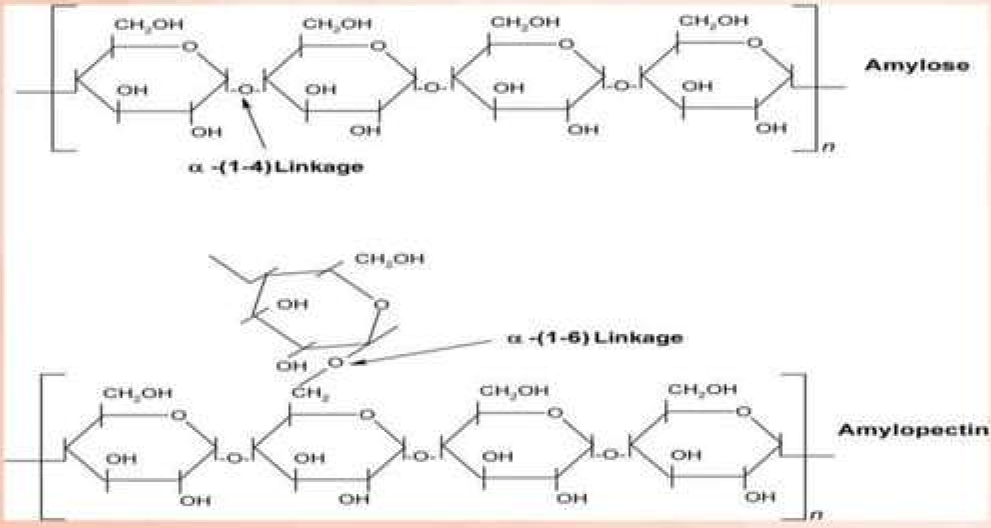

Fig-2 Chemical structure of amylose and amylopectin
Source:Thermoplastic Starch: A Renewable, Biodegradable Bioplastic March 4, 2013 By Jeffrey Gotro

The amylose and amylopectin molecules are in an ordered arrangement within the starch granule and this gives crystallinity to the granule.

Starch granules exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding due to the hydroxyl groups on the granule surface.

This strong hydrogen bonding association and crystallisation leads to poor thermal processing, since the melting temperature is higher than the thermal decomposition temperature and degradation sets in before thermal melting.

The hydrophilicity and thermal sensitivity renders the starch molecule unsuitable for thermoplastic applications.

'Thermoplastic' starch has two main disadvantages when compared to most plastics currently in use

- ✓ It is water-soluble and therefore exhibits poor environmental stability.
- ✓ Poor mechanical properties and processability

To improve some of these properties various physical and chemical modifications of the starch molecule have been considered including blending, chemical derivation and graft copolymerisation .

Its water resistance can be improved by mixing it with certain synthetic polymers and adding cross linking agents such as calcium and zirconium salts and lignin .

Companies such as Novamont, Novon International, and National Starch and Chemical market a range of commercial bioplastics based upon de-structured thermoplastic starch.

2. Sugar based biopolymers

Two types of polyhydroxyalkanoate (PHA) polymers have been developed, namely polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV).

These are based on fermented sugars (sucrose, glucose and lactose) with different starch feedstocks as starting materials.

Polyhydroxyalkanoates are polyoxo-esters produced intracellularly by a wide variety of bacteria for the purpose of carbon and energy storage when they are placed in an environment with limited nutrients, and are thus of biological origin .

Biodegradable copolymers derived from hydroxybutyrate (HB) and hydroxyvalerate (HV) have been prepared that exhibit thermoplastic characteristics suitable for medical applications .

3. Cellulose based biopolymers

The monomer unit in cellulose is β-1, 4 linked glucan chains with hydrogen bonds formed between hydroxyl groups and oxygen atoms both within a single glucose chain and between neighboring chains. Hydrogen bonding and van der Waals forces aggregate glucan chains together side by side to form cellulose microfibrils.

These cellulose microfibrils are then stacked together to form crystalline cellulose [37]. The polar –OH groups present in the cellulose chain form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together. The stacking of chains is so regular that it forms hard, stable crystalline regions, and this gives the bundled chains more stability and strength. The length of the chain varies greatly from a few hundred sugar units in wood pulp to over 6000 for cotton. It is the most common natural organic polymer which is considered as an almost inexhaustible source of raw material for the increasing demand for environment friendly and biocompatible products. Due to the strong hydrogen bonding, it is insoluble in common solvents. As a result, it is chemically modified into ether, ester, and acetal derivatives.

Cellulose, the most abundant biological material on Earth, is also composed of glucose monomers but joined by beta glycosidic bonds, giving it a straighter shape that packs closely and provides mechanical strength in wood [38]. The remarkable strength of wood is due to cellulose which is a long chain of linked sugar molecules. Plant cell walls, which are the basic building block for textiles and paper, also have 58 Recent Advances in Biopolymers cellulose as main component. The purest natural form of cellulose is cotton which is used in many textile applications.

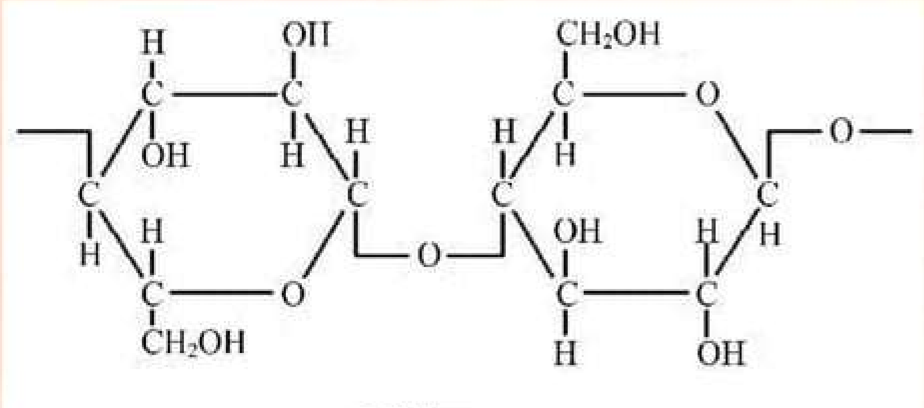

Fig-3 Chemical structure of cellulose
(Source- Google Image)

- ✓Cellulose has been excessively used in the form of nanofibrils.
- ✓Cellulose nanofibrils (CNF) or nanocellulose is typically generated by mechanical grinding or high-pressure fluidization of cellulose to remove its lignin content.
- ✓CNF consists of very thin (5–20 nm) and long (several μm) fibrils with high aspect ratio. At low concentrations, it forms a transparent gel-like material which can be used for producing biodegradable and environmentally safe, homogeneous, and dense films for various applications, especially in biomedical field.

Sources Of Cellulose:

- ✓Coir
- ✓banana
- ✓sugar beet
- ✓Hemp
- ✓softwood
- ✓hardwood pulps

Fig-4- Image showing a. Coir b. Softwood as a source of cellulose (Source-Google images)

4. Synthetic based biopolymers

Synthetic compounds derived from petroleum can also be a starting point for biodegradable polymers, e.g. aliphatic aromatic copolyesters.

These polymers have technical properties resembling those of polyethylene (LDPE). Although these polymers are produced from synthetic starting materials, they are fully biodegradable and compostable.

The relatively high price of biodegradable polymers of synthetic substances, e.g. aliphatic aromatic copolyesters has prevented them from reaching a large scale market. The best known application is for making substrate mats.

Manufacturing Methods For Biopolymers:

The route for manufacturing thermoset articles is slightly different, thermoset components should not react to form polymers until they have been formed into their final shape. As a consequence of this, unreacted thermosets still consist of short chain molecules and therefore are much less viscous than thermoplastic polymer melts

This phenomenon opens up a number of interesting production routes. It now becomes possible to inject (low viscosity) liquid thermosets through reinforcing materials to produce long-fibre composite articles (e.g., vehicle panels).

Additives

When processing a fossil origin polymer melt, the operator has the advantages of having access to a wide Biopolymers 20 range of processing aids and property improvers. These additives are usually added in small quantities, and with the exception of the biocides, are unlikely to have any effect on the gross biodegradation of the polymer. However, the selection of additives for biodegradable polymer systems should be undertaken with care to avoid compromising the biodegradability certification of the finished article, such as the DIN CERTCO standards.

1 .Plasticisers

✓Plasticisers increase the flexibility of the polymer product and also decrease the viscosity of the polymer melt, a role also played by lubricants.

✓In terms of biological origin materials, epoxidised soyabean oil is used as a plasticiser and heat stabiliser in PVC production.

2 .Lubricants

These materials are effective mould release agents but care must be taken to avoid overdosing the mould surface. This will have the consequence of producing greasy bloom on the surface of the moulding.

3. Colourants

Some colourants may be objected to due to inherent toxicity, but environmentally acceptable substitutes of either mineral or vegetable origin are increasingly available. DIN CERTCO ,
lists the following mineral colourants as certified compostable up to levels of 49%:

- carbon black
- iron oxide

4. Crosslinkers

At the moment, crosslinkers are usually the same formulations as those used in fossil origin thermoset formulations. Thus articles made from bio-origin thermosets are not always 100% biological origin. However, some crosslinking agents such as the formaldehyde used in cashew nut origin phenolics are biological in origin, being made from wood alcohol.

5. Fillers

Fillers are the most commonly used additives. Fine mineral powder fillers are added as nucleating agents in small (~1%) quantities to limit the size of crystalline structures. This is of limited application with biopolymers as the complexity of the molecules in most biopolymers limits the degree of crystalline structure formation. DIN CERTCO , lists the following fillers as certified compostable up to levels of 49%:

- aluminium silicates
- ammonium carbonate
- calcium carbonate
- calcium chloride

Commercially available Biopolymers

Polylactic acid (PLA):

✓PLA belongs to the family of aliphatic polyesters with the basic constitutional unit lactic acid.

✓ The monomer lactic acid is the hydroxyl carboxylic acid which can be obtained via bacterial fermentation from corn (starch) or sugars obtained from renewable resources.

✓PLA is a thermoplastic polymer which has the potential to replace traditional polymers such as PET, PS, and PC for packaging to electronic and automotive applications.

✓PLA has similar mechanical properties to traditional polymers, the thermal properties are not attractive due to low Tg of 60°C.

Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are a family of polyesters produced by bacterial fermentation with the potential to replace conventional hydrocarbon-based polymers.

PHAs occur naturally in a variety of organisms, but microorganisms can be employed to tailor their production in cells.

PHA can also be produced by using several renewable waste feedstock. The feedstock include cellulosic, vegetable oils, organic waste, municipal solid waste, and fatty acids depending on the specific PHA required.

PHA and its copolymers are widely used as biomedical implant materials.

These include sutures, suture fasteners, meniscus repair devices, rivets, bone plates, surgical mesh, repair patches, cardiovascular patches, tissue repair patches, and stem cell growth.

PHAs can also be used in drug delivery due to their biocompatibility and controlled degradability.

Polymer vs Biopolymer

More Information Online WWW.DIFFERENCEBETWEEN.COM

	Polymer	Biopolymer
DEFINITION	Polymers are large molecules that have the same structural unit repeating over and over.	Biopolymers are polymer materials that form in living organisms.
DEGRADATION	Mostly non-degradable	Degradable
OCCURRENCE	Some are naturally occurring materials while others are man-made materials.	Occurs inside biological systems.
STRUCTURE	Can be either simple or complex.	Mostly complex structures.
RENEWABILITY	Some are renewable while others are non-renewable	Mostly renewable

Fig-4- Table showing the difference between polymer and biopolymers
Source: (Website-www.differencebetween.com)

Application Of Biopolymers:

Biomedical Application

The biomaterial have shown potential in biomedical application, including tissue engineering, drug delivery, wound dressing , bond substitution and sutures.

For eg; chitosan based nanocomposite as a novel group of biomaterials with the potential to support and facilitate cell growth for controlled drug delivery and as biosensors to detect glucose in the body.

Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials.

Plastic packaging for food and non-food applications is non-biodegradable, and also uses up valuable and scarce non-renewable resources like petroleum.

The current focus on exploring alternatives to petroleum and emphasis on reduced environmental impact, research is increasingly being directed at development of biodegradable food packaging from biopolymer-based materials.

Recent developments in biopolymer-based food packaging materials including natural biopolymers (such as starches and proteins), synthetic biopolymers (such as poly lactic acid), biopolymer blends, and nanocomposites based on natural and synthetic biopolymers.

Automotive Applicatons

Renewable resources based "Green" nanocomposite are the next generation of material which provide a combination of performance and environmental compatibility

It help to replace existing petroleum derived polypropylene pp/tpo based nanocomposite with environmentally friendly nanocomposite produced from bacterial based bioplastic (PHA) reinforced with compatibilised nanoclay for automotive application.
The nanocomposite are sustainable materials since they are recyclable; are stable in use but can be triggered to biodegradable under composting condition.

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Thank You