**Biopolymer Basics:**

Polymers are long chain molecules with a wide range of physical and chemical properties. One of the main advantages of the polymer materials is the ease of fabrication to produce various shapes (rod, film, fiber, sheet, etc.). The advances in polymer chemistry have made it possible to tailor the properties of polymers for specific application.

**1- Classification of Polymers:**

Polymers can be classified according to their sources, chain structures, thermal

behaviors, stabilities, etc. , as discussed below.

1.1 Source

By source, polymers can be divided into two groups. They are naturally occurring polymers and synthetic polymers.

Table 1 listed some examples of naturally occurring polymers.

|  |  |  |
| --- | --- | --- |
|  | Polymer | Source |
| A. Proteins | Silk  Keratin  Fibrinogen  Elastin  Collagen | Animals  Animals  Animals  Animals  Animals |
| B. Polysaccharides | Cellulose  Starch  Chitin  Alginic  Agar | Plants  Plants  Animals  Brown Seaweeds  Red seaweeds |

Synthetic polymers are synthesized via polymerization reaction using monomers. Some of the commonly used polymers are listed in Table 2.

Table 2 Commonly seen synthetic non-biodegradable polymers.

|  |  |  |
| --- | --- | --- |
| Type of Polymer | Name of Polymer | Polymerization Mechanism |
| Polyolefin  Polyacrylate  Polyamide  Polyurethane  Polyester  Polycarbonate  Poly( ether ether ketone)  Polysulfones | Polyethylene  Polypropylene  Poly( methyl methacrylate)  Nylon 66  Nylon 6  Poly( ether-urethane)  Polyester-urethane  Poly( ethylene terephthalate)  Poly( butylene terephthalate)  Bisphenol a polycarbonate  Poly( ether ether ketone)  Polysulfones | Radical,ionic chainreaction polymerization  Ionic chain-reaction polymerization  Radical polymerization  Step polymerization  Step polymerization  Step polymerization  Step polymerization  Step polymerization  Step polymerization  Step polymerization  Step polymerization  Step polymerization |

**2- Polymer Stability:**

Polymeric materials can be divided into two main classes — biostable and biodegradable polymers according to their stability when they are used in contact with biological systems.

Biodegradable polymer is a polymer in which the degradation is mediated at least partially by a biological system. The biodegradation of a polymer can be caused by hydrolytic, enzymatic or bacteriological degradation processes occurring within a polymer matrix. The degradation process will cause a deleterious change in the properties of a polymer due to a change in the chemical structure.

Most of the biodegradable polymers discovered so far contain hydrolysable linkages, such as ester and amide in their backbone structure. Among them, the flexible ester containing polymers, and in particular aliphatic polyesters, appear to be the most attractive biodegradable polymers because of their useful biodegradability and their versatility regarding physical, chemical and biological properties. Table 3 listed some examples of biostable and biodegradable polymers for biomedical applications.

Table 3 Some commonly seen synthetic biodegradable polymers.

|  |  |  |
| --- | --- | --- |
| Polymer | Physical Characteristics | Applications |
| Poly( glycolic acid) (PGA) | Thermoplastic crystalline polymer  Tg = 22.5°C, Tm = 40°C -45°C | Absorbable suture and meshes |
| 10/90 Poly ( L-lactide-co-gly- colide) | Thermoplastic crystalline polymer  Tg = 43 °C, Tm =205°C | Absorbable suture and meshes |
| Poly( p-dioxanone) (PDS) | Thermoplastic crystalline polymer  Tg = 10°C, Tm=110°C-115°C | Sutures |
| 85/15 Poly ( DL-lactide-co- glycoside) | Amorphous polymer  Tg = 50 °C -55°C | Sutures |
| Poly( e-caprolactone) (PCL) | Thermoplastic crystalline polymer  Tg= -60°C, Tm =59°C-64°C | Sutures |

**Naturally Occurring Polymer Biomaterials:**

Naturally occurring polymers are used as biomaterials largely because their structures are similar to the human tissue they intend to replace. They are also available cheaply and easily in large quantities. Usually, the naturally occurring biomaterials can be degraded by naturally occurring enzymes and therefore they are biodegradable, which offers an additional advantage over the use of synthetic non-biodegradable polymers. However, the use of naturally occurring polymers often has the **problem** to provoke immune reaction of the host tissue. Therefore, many of the naturally occurring polymers have to be chemically modified before they are used as biomaterials.

**1- General Introduction to Proteins:**

Proteins are monodisperse polymers of amino acids. They are essential components of plants and animals. There are twenty different α-amino acids, which can join together by peptide linkages to form polyamides or polypeptides. Polypeptides are often used by biologists to denote oligomers or relatively low molecular weight proteins.



 Because amino acids have both amino and carboxylic groups, they can be ionized. The net ionic charge of an amino acid varies with changes of solution pH. At certain pH an amino acid can be electrically neutral and this pH is called isoelectric point. For simple amino acids which contain only one acid and one amine groups, this isoelectric point occurs at a pH about 6 at which a dipole or zwitterion is formed, as shown below.

Because these amino acids can be ionized, they are water-soluble polar compounds, which migrate toward an electrode at pH values other than that of the isoelectric point in a process called electrophoresis.

**2**- **Collagen:**

Collagen, the most abundant protein in mammalian tissues, accounts for up to one-third of all protein mass in a mammal. Collagen fibers form the matrix or cement material in human bones where bone mineral precipitate. Collagen fibers constitute a major part of tendons and act as a major part of skin. The main function of collagen is the mechanical reinforcement of the connective tissues of vertebrates.

The individual polypeptide chains of collagen contain 20 different amino acids and the precise composition varies between different tissues. The variation in specific amino acid sequence gives rise to the different types of collagen labeled as Type I , Type II up to Type XIX. The most commonly occurring collagens are Types I , and M, which form the long-recognized characteristic fiber bundles seen in many tissues. Type I collagen is mostly found in skin, tendon, and bone, and Type HI in blood vessels.

The basic building block of collagen is a triple helix of three polypeptide chains called the tropocollagen unit. Each chain is about 1,000 amino acid residues long. These three individual a-chains are cross-linked biosynthetically and fold to form a triple helix (tertiary structure) with a molecular weight of approximately 300.000 g/mol, a length of approximately 300 nm and a diameter of 1. 5 nm .



Figure 1 Triple helix structure of collagen molecule.

The collagen molecules possess an axial periodicity that is visible in the electron microscope and pack into lattices with lateral symmetry (quaternary structure). This supramolecular structure is widely accepted as the microfibril containing five collagen triple-helices, with a diameter between 3.5 nm to 4.0 nm. Approximately 1,000 microfibrils can aggregate laterally and end-to-end into a fibril having a diameter of 80 -100 nm (Fig. 2).

Collagen fibers are strong. In tendons, the collagen fibers have strength similar to that of hard-drawn copper wire.

There has been an increased interest in the use of collagen and collagen containing tissues in medical devices during the recent two decades. One way to use collagen-rich tissues is to chemically treat the tissue in order to make them into implantable prostheses. Examples are heart valves, vascular grafts, tendons, ligaments, and pericardium. Another way involves the use of purified collagen obtained from animal tissue, processed in a variety of ways to generate a large number of products that not only have applications in the medical field, but also in the manufacturing of cosmetics. Collagen can be used in the form of native soluble collagen, enzymatically processed native collagen, soluble collagen of reconstituted fibers, etc. Products are used as dermal implants, implantable drug delivery vehicles, sponges, tubes and suture.

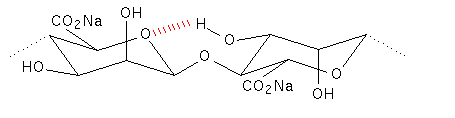


Figure 2 Collagen fibril structure

**3- Alginate:**

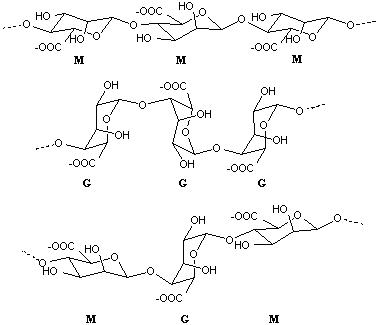
Alginates are cell-wall constituents of brown algae (Phaeophycota). They are chain-forming heteropolysaccharides made up of blocks of mannuronic acid and guluronic acid. Composition of the blocks depends on the species being used for the extraction and the part of the thallus from which extraction is made.





glycosidic linkage

Alginates are linear unbranched polymers containing β-(l→4)- linked D-mannuronic acid (M) and α-(l→4)-linked L-guluronic acid (G) residues. According to the source algae, alginates can consist of blocks of similar and strictly alternating residues (i. e. MMMMMM, GGGGGG and GMGMGMGM), each of which have different conformational preferences and behavior. Alginates may be prepared with a wide range of average molecular weights (50 -100,000 residues) to suit the application.



Because of their abundance in source and low in prices, Alginates have been widely used in the food and pharmaceutical industry as *thickeners*, *emulsifying agents*, *binder and disintegrating agent for tablet and capsule formulations*. Because of their biocompatibility, alginates have been used in medical applications such as *wound dressings*, *scaffolds for tissue engineering* and *hepatocyte culture* and *surgical or dental impression materials*. Alginates are also known to be broken down to simpler glucose type residues and can be totally absorbed.

When used as biomaterials for implantation or tissue engineering scaffolds, alginates have to be cross-linked. Alginate can be easily cross-linked by *calcium ions* to form ionic bonding between alginate molecules. The cross-link is a fast process. As an example, cross-linked alginate beads can be obtained instantly by dripping sodium alginate solution into calcium chloride solution.

Because of these useful characteristics, *living cells*, *growth factors* and other *active ingredients* can be easily encapsulated into calcium ion cross-linked alginate gels. The cross-linked alginate gel can act as an immunoprotection barrier for its encapsulated living cells. Alginates cross-linked with calcium ions (from CaSO4) have recently been used as *cell delivery vehicles* for in vivo tissue engineering research.

Alginate can also be easily fabricated into fibers. The fibers can be used to make non-woven fibers for medical applications. For example, non-woven calcium alginate fiber dressings have been used frequently on both full- and partial-thickness wounds. Many studies have shown that these alginate dressings can accelerate epithelialization.

Alginate can also be covalently cross-linked using ethylenediamine in the presence of water-soluble carbodiimide, as carbodiimide will induce cross-links between carboxylic acid and amine groups without itself being incorporated. The covalently cross-linked membrane is easily biodegradable and can reduce foreign-body reactions after healing skin wounds.

- **Alginate uses:**

The uses of alginates are based on three main properties:

* The first is their ability, when dissolved in water, to thicken the resulting solution (more technically described as their ability to increase the viscosity of aqueous solutions).
* The second is their ability to form gels; gels form when a calcium salt is added to a solution of sodium alginate in water. The gel forms by chemical reaction, the calcium displaces the sodium from the alginate, holds the long alginate molecules together and a gel is the result.
* The third property of alginates is the ability to form films of sodium or calcium alginate and fibers of calcium alginates.

- **Alginate Applications:**

**Textile printing:**

In textile printing, alginates are used as thickeners for the paste containing the dye. Alginates became important thickeners with the advent of reactive dyes. These combine chemically with cellulose in the fabric. Many of the usual thickeners, such as starch, react with the reactive dyes, and this leads to lower colour yields and sometimes by-products that are not easily washed out. Alginates do not react with the dyes, they easily wash out of the finished textile and are the best thickeners for reactive dyes.

**Food:**

The thickening property of alginate is useful in sauces and in syrups and toppings for ice cream. Addition of alginate can make icings non-sticky and allow the baked goods to be covered with plastic wrap. Water-in-oil emulsions such as mayonnaise and salad dressings are less likely to separate into their original oil and water phases if thickened with alginate. Some fruit drinks have fruit pulp added and it is preferable to keep this in suspension; addition of sodium alginate, or propylene glycol alginate ( PGA ) in acidic conditions, can prevent sedimentation of the pulp. In chocolate milk, the cocoa can be kept in suspension by an alginate/phosphate mixture.

Calcium alginate films and coatings have been used to help preserve frozen fish. The oils in oily fish can become rancid through oxidation even when quick frozen and stored at low temperatures.

**Immobilized biocatalysts:**

When used enzymes as biocatalysts for the conversion of *glucose to fructose*, the *production of L-amino acids for use in foods*, the *synthesis of penicillins*, *conversion of starch to ethanol* , and the *continuous production of yoghurt*. To carry out these processes on a moderate to large scale, the biocatalysts must be in a concentrated form and be recoverable from the process for re-use.

This can be achieved by "immobilizing". Beads made with calcium alginate were one of the first materials to be used for immobilization. In use, they are packed into a column and a solution of the substance to be converted is fed into the top of the column and allowed to flow through the bed of beads containing the immobilized biocatalyst in the cells. The conversion takes place and the product comes out at the bottom. A simple example is to immobilize yeast cells, flow a solution of sugar through the beads, and the sugar is converted to alcohol.

**Pharmaceutical and medical uses:**

Good quality stable fibres have been produced from mixed salts of sodium and calcium alginate, and processed into non-woven fabric that is used in wound dressings. They have very good wound healing and haemostatic properties and can be absorbed by body fluids because the calcium in the fibre is exchanged for sodium from the body fluid to give a soluble sodium alginate. This also makes it easy to remove these dressings from large open wounds or burns since they do not adhere to the wound.

Alginic acid powder swells when wetted with water. This has led to its use as a tablet disintegrant for some specialized applications. Alginic acid has also been used in some dietary foods, such as biscuits; it swells in the stomach and, if sufficient is taken, it gives a "full" feeling so the person is dissuaded from further eating. The same property of swelling has been used in products such as Gavisconä tablets, which are taken to relieve heartburn and acid indigestion.

Alginate is used in the controlled release of medicinal drugs and other chemicals. In some applications, the active ingredient is placed in a calcium alginate bead and slowly released as the bead is exposed in the appropriate environment.

**Paper:**

The main use for alginate in the paper industry is in surface sizing. Alginate added to the normal starch sizing gives a smooth continuous film and a surface with less fluffing. The oil resistance of alginate films give a size with better oil resistance and enhances greaseproof properties.

**Welding rods:**

Coatings are applied to welding rods or electrodes to act as a flux and to control the conditions in the immediate vicinity of the weld, such as temperature or oxygen and hydrogen availability.

**Release agents:**

The poor adhesion of films of alginate to many surfaces, together with their insolubility in nonaqueous solvents, have led to their use as mould release agents, originally for plaster moulds and later in the forming of fibreglass plastics.