



# SNS COLLEGE OF TECHNOLOGY

(An Autonomous Institution)

Coimbatore – 35



## DEPARTMENT OF BIOMEDICAL ENGINEERING

### BIOPOLYMERS:

Biopolymers are polymers that occur in nature. Carbohydrates and proteins, for example, are biopolymers. Many biopolymers are already being produced commercially on large scales, although they usually are not used for the production of plastics. Even if only a small percentage of the biopolymers already being produced were used in the production of plastics, it would significantly decrease our dependence on manufactured, non-renewable resources.

- cellulose is the most plentiful carbohydrate in the world; 40 percent of all organic matter is cellulose!
- starch is found in corn (maize), potatoes, wheat, tapioca (cassava), and some other plants. Annual world production of starch is well over 70 billion pounds, with much of it being used for non-food purposes, like making paper, cardboard, textile sizing, and adhesives.
- collagen is the most abundant protein found in mammals. Gelatin is denatured collagen, and is used in sausage casings, capsules for drugs and vitamin preparations, and other miscellaneous industrial applications including photography.
- casein, commercially produced mainly from cow's skimmed milk, is used in adhesives, binders, protective coatings, and other products.
- soy protein and zein (from corn) are abundant plant proteins. They are used for making adhesives and coatings for paper and cardboard.
- polyesters are produced by bacteria, and can be made commercially on large scales through fermentation processes. They are now being used in biomedical applications.

A number of other natural materials can be made into polymers that are biodegradable. For example:

- lactic acid is now commercially produced on large scales through the fermentation of sugar feedstocks obtained from sugar beets or sugar cane, or from the conversion of starch from corn, potato peels, or other starch source. It can be polymerized to produce poly(lactic acid), which is already finding commercial applications in drug encapsulation and biodegradable medical devices.
- triglycerides can also be polymerized. Triglycerides make up a large part of the storage lipids in animal and plant cells. Over sixteen billion pounds of vegetable oils are produced in the United States each year, mainly from soybean, flax, and rapeseed. Triglycerides are another promising raw material for producing plastics.

These natural raw materials are abundant, renewable, and biodegradable, making them attractive feedstocks for bioplastics, a new generation of environmentally friendly plastics.

- Starch-based bioplastics are important not only because starch is the least expensive biopolymer but because it can be processed by all of the methods used for synthetic polymers, like film extrusion and injection moulding. Eating utensils, plates, cups and other products have been made with starch-based plastics.



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- Interest in soybeans has been revived, recalling Ford's early efforts. In research laboratories it has been shown that soy protein, with and without cellulose extenders, can be processed with modern extrusion and injection moulding methods.
- Many water soluble biopolymers such as starch, gelatin, soy protein, and casein form flexible films when properly plasticized. Although such films are regarded mainly as food coatings, it is recognized that they have potential use as nonsupported stand-alone sheeting for food packaging and other purposes.
- Starch-protein compositions have the interesting characteristic of meeting nutritional requirements for farm animals. Hog feed, for example, is recommended to contain 13-24% protein, complemented with starch. If starch-protein plastics were commercialized, used food containers and serviceware collected from fast food restaurants could be pasteurized and turned into animal feed.
- Polyesters are now produced from natural resources-like starch and sugars-through large-scale fermentation processes, and used to manufacture water-resistant bottles, eating utensils, and other products.
- Poly(lactic acid) has become a significant commercial polymer. Its clarity makes it useful for recyclable and biodegradable packaging, such as bottles, yogurt cups, and candy wrappers. It has also been used for food service ware, lawn and food waste bags, coatings for paper and cardboard, and fibers-for clothing, carpets, sheets and towels, and wall coverings. In biomedical applications, it is used for sutures, prosthetic materials, and materials for drug delivery.
- Triglycerides have recently become the basis for a new family of sturdy composites. With glass fiber reinforcement they can be made into long-lasting durable materials with applications in the manufacture of agricultural equipment, the automotive industry, construction, and other areas. Fibers other than glass can also be used in the process, like fibers from jute, hemp, flax, wood, and even straw or hay. If straw could replace wood in composites now used in the construction industry, it would provide a new use for an abundant, rapidly renewable agricultural commodity and at the same time conserve less rapidly renewable wood fiber.

The widespread use of these new plastics will depend on developing technologies that can be successful in the marketplace. That in turn will partly depend on how strongly society is committed to the concepts of resource conservation, environmental preservation, and sustainable technologies. There are growing signs that people indeed want to live in greater harmony with nature and leave future generations a healthy planet. If so, bioplastics will find a place in the current Age of Plastics.

### **COLLAGEN:**

Collagens are a family of structurally related proteins, which occur in all animals and are most abundant proteins in vertebrates. They are the extracellular proteins that are organized into insoluble fibers of great tensile strength. Collagens provide the insoluble scaffold for the provision of shape and form. Collagens occur as supramolecular assemblies, with the attachment of macromolecules, glycoproteins hydrated polymers, inorganic ions and cells. The range in morphology is from ropelike fibrils that provide the fibrous scaffold maintaining the integrity of tendons, ligaments, bone and teeth to net-like sheets in the basement



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membranes that underline epithelial and endothelial cells. The collagen fibrils in various tissues are organized in ways that largely reflect the functions of various tissues (Table 6.1). Thus, tendons, skin and cartilage must support stress in predominantly one, two and three dimensions respectively and their component fibrils are arranged accordingly. These different forms provide characteristic tensile strength to bones, tendons, teeth, cartilages, ligaments, skin and blood vessels.



Table 6.1 Collagen polymorphism, molecular species, cellular origin, and characteristics of the genetics distinct types of collagen

Type	Molecular species	Major cellular origin	Molecular and supramolecular structures	Tissue distribution
I	$[\alpha_1(\text{I})]_2\alpha_2(\text{I})[\alpha_1(\text{I})]_3$	Fibroblast Osteoblasts	Large cross-banded interstitial fibers. Fiber diameter, 45-180 nm. Heterotypic fibrils composed of type I, type III and type I, type V collagens.	Bone, cornea, dermis, dentin, ligament tendon, heart valves, large vessel, and uterine walls.
I	$[\alpha_2(\text{II})]_3$	Chondroblasts	Fibers of various sizes in different zones of the hyaline cartilage (5-100 nm) or within collagenous matrices. Heterotypic fibrils composed of type II and type XI collagens.	Hyaline cartilage, vitreous body, and nucleus pulposus.
I	$[\alpha_1(\text{III})]_3$	Fibroblasts, reticulum cells	Fine fibrillar reticular networks. 40 nm fiber diameter.	Dermis, gingiva, heart valves, large vessel, and uterine walls. Embryonic collagen.
I	$[\alpha_1(\text{V})]_2\alpha_2(\text{V})[\alpha_1(\text{V})]_3[\alpha_1(\text{V})\alpha_2(\text{V})\alpha_3(\text{V})]$ and other forms	Smooth muscle cells	Globular domain at the N terminal. Pericellular (cell associated) and interstitial filaments. Heterotypic fibers with type I collagen.	Bone, cornea, fetal membranes, large vessel walls, heart valves, and hyaline cartilage [A-B collagen].
I	$\alpha_1(\text{XI})\alpha_2(\text{XI})\alpha_3(\text{XI})$ $[\alpha_1(\text{XI})]_3$ and other forms	Chondrocytes	Fine fibrils of cartilage. $\alpha_3(\text{XI})$ and $\alpha_1(\text{XI})$ product of the same gene with differences in post-translational processing. $\alpha_1(\text{XI})$ constituent of bone type V collagen.	Cartilage, vitreous body, intervertebral disk. I $\alpha_2\alpha_3$ or K-collagen.
I	$\alpha_1(\text{IX})\alpha_2(\text{IX})\alpha_3(\text{IX})$	Chondrocytes	Length of the triple helix: 200 nm. Globular domain at the N terminal. It binds covalently glycosaminoglycans (chondroitin and/or dermatan sulfate). Filaments in cartilage (lateral association to banded fibrils). Heterotrimeric disulfide-bonded collagen with three short triple-helical and two non-triple-helical domains.	Cartilage, vitreous body, intervertebral disk. Only expressed in type II—containing-tissues. Type M or HMW-LMW collagen.
II	$[\alpha_1(\text{XII})]_3$	Fibroblasts	Lengths of the triple helix: 135 nm. Homology of type XII with type IX collagen. Triple-helical region smaller than that of the type IX while nonhelical N-terminal domain is larger.	In type I collagen containing tissues. Tendons, ligaments, perichondrium, and periosteum.

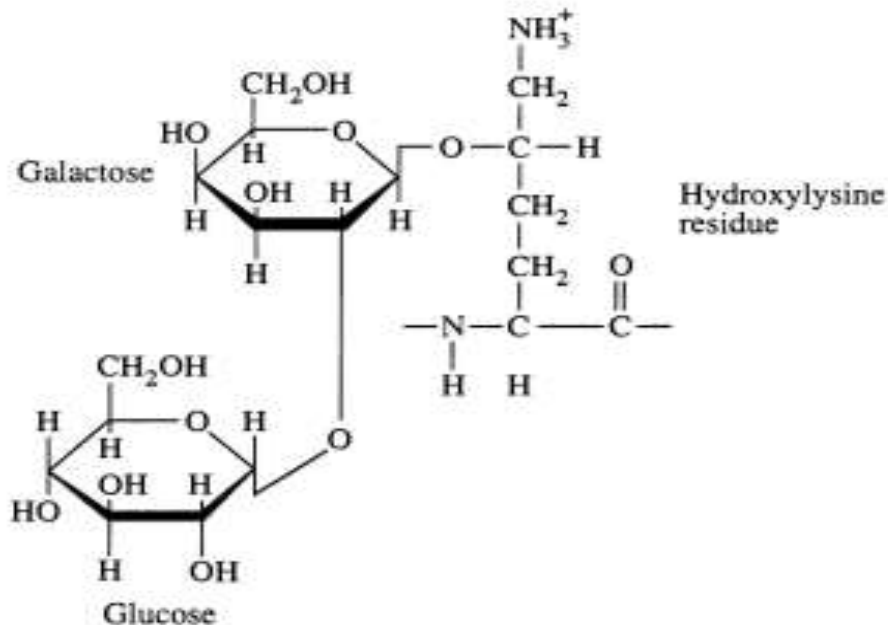
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Collagens are composed of three polypeptide chains wound into a triple helix. To distinguish one collagen type from another they are labeled in the order of discovery (I, II, III, etc.). Chains are designated as  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$  with the collagen type in which they occur in parenthesis. For example, type I collagen, which consists of two identical chains and one dissimilar chain, all of which are unique to type I collagen.

The type I collagen molecule is approximately 300 nm in length and has diameter of 1.4-1.5 nm. An individual polypeptide helix has 3.3 residues per turn and a pitch of 1 nm. Three left handed helical peptide chains are coiled together to give a right-handed coiled helix with a periodicity of 2.86 nm in below figure. This triple super helix named as tropocollagen is crosslinked to form collagen.



**Fig. 6.2 Carbohydrates attached to hydroxylysine residues of collagen.**

Prochains each comprise approximately 1000 residues, collagenous domain (coli domain) which is about 300 nm in length. The prochains also contain amino and carboxyl terminal extension polypeptides, N-propeptide and C-propeptide which are of about 33 nm and 17 nm length respectively. Specific endopeptidases cleave, amino and carboxyl terminal extensions to generate the collagen monomers that are the building blocks of the collagen fibrils. The fibrils are formed by self-assembly of collagen molecules; millions of individual collagen molecules associate by end on and side by side interactions to generate fibrils that are approximately cylindrical with diameters that range from 20 to 500 nm.

Collagens have the general amino acid sequence Gly-Pro-Hyp-Gly-x arranged in a triple helix. The side groups of amino acid (x) may be acidic, basic or hydrophobic. These nonpolar hydrophobic side groups avoid contact with water and seek the greatest number of contacts with the nonpolar side chains. The chains are stabilized through intramolecular hydrogen bonding between  $>\text{C}=\text{O}$  and  $-\text{NH}$  groups; and ionic bonding between side groups of acidic





and basic amino acids. Hydroxyproline (Hyp) confers stability upon collagen probably through intramolecular hydrogen bonds that may involve bridging water molecules. If, for example, collagen is synthesized under conditions that inactivate prolyl hydroxylase, it loses its native conformation (denatures) at 39°C (denatured collagen is called gelatin). The bulky and relatively inflexible pyrrolidine moiety of Pro and Hyp, residues confer rigidity on the entire assembly. Hyp residues appear after collagen polypeptides have been synthesized in which some of proline residues are converted to Hyp residues by the action of enzyme prolyl hydroxylase. This enzyme requires ascorbic acid (vitamin C) to maintain enzymatic activity. In the vitamin C deficiency disease scurvy, the collagen synthesized cannot form fibers properly. This results in the skin lesions, blood vessel fragility and poor wound healing, the conditions which are characteristic of scurvy. Since the presence of Hyp is unique to collagen the determination of collagen content in a given tissue is often achieved by assaying the Hyp content.

Collagen contains covalently attached carbohydrates in amounts that range from 0.4 to 12% by weight depending on the collagen's tissue of origin. The carbohydrates, which consist mostly glucose, galactose and their disaccharide are covalently attached to collagen at its 5-hydroxylysyl residues by specific enzymes. Collagen cross-links are derived from lysine (lys) and histidine (his) side chains through the action of enzyme lysyl oxidase, a copper-containing enzyme that converts lys residues to those of the aldehyde allysine.

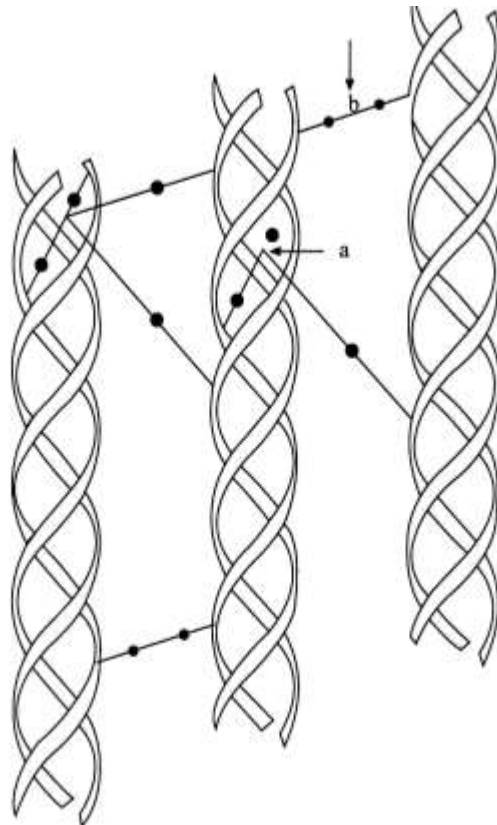


Fig. 6.3 (a) Intra and (b) intermolecular crosslinks in collagen. (Adapted from Tanzer, 1973)



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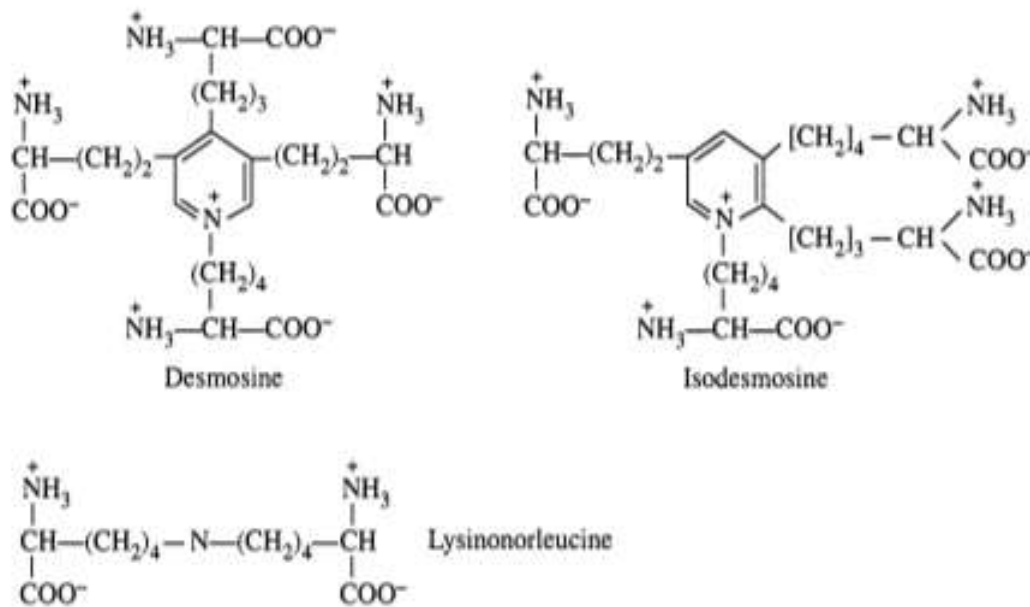
### ELASTIN:

Elastin is another structural protein found in a relatively large amount in elastic yellow connective tissue that occur in ligaments, lung, aortic wall and skin. It is a protein with rubber like elastic properties whose fibers can stretch to several times their normal length. Elastin, like collagens has a distinctive amino acid composition. It consists predominantly of small, nonpolar residues. It has onethird glycine, over one-third Ala. + Val., and rich in proline. It contains little hydroxy- proline, no hydroxylysine and few polar residues. Unlike collagen fibers, elastin is devoid of regular secondary structure. The covalent cross-links in elastin are formed by allylsine aldol and lysinonorleucine, desmosine and isodesmosine. Desmosine and isodesmosine are unique to elastin and are responsible for its yellow color. They result from condensation of three allylsine and one lysine side chains. Elastin fibers are also composed of microfibrillar proteins that form the outer core of elastic fibers. The ratio of elastin to microfibrillar components varies according to the location within the skin. Recently fibrillin has been reported to be one of the molecules that are present in microfibrils (Geesing and Berg, 1991). Elastin is stable to relatively high temperatures and chemical reagents due to low content of amino acids with polar side chains. The enzyme elastase, hydrolyses elastin at peptide bonds after small hydrophobic residues, particularly alanine. The mechanical properties of elastin and collagen fibers.



<i>Amino acids</i>	<i>mol /100 amino acids</i>
Gly	32.4
Hyp	2.6
Asp, Glu	2.1
His, Lys, Arg	1.3
Nonpolar amino acids Pro, Ala, Val, Met, Leu, Ileu, Phe, Tyr	59.5
Cys	0.4

\*Adapted from Chrapil (1967).



**Fig. 6.5 Structures of desmosine, isodesmosine, and lysinonorleucine found in elastin.**

**Table 6.6 Mechanical properties of elastin and collagen fibers\***

<i>Fibers</i>	<i>Modulus of elasticity Mpa</i>	<i>Tensile strength Mpa</i>	<i>Ultimate elongation %</i>
Elastic fibers	0.6	1	100
Collagen fibers	1000	50-1000	10