Biomedical Polymers

(I). • Contact Lens – A contact lens is an optical device that is placed over the cornea of the eye in such a manner that the lens remains on the eye's surface throughout blinking. The main purpose of wearing a contact lens is to correct vision deficiencies; in this application they are called cosmetic lenses. Contact lenses can also be used medically for the treatment of certain disease. In such cases they are called therapeutic or bandage lenses.

There are basically three types of lenses:
(a) Soft (b) Hard (c) Gas permeable

Contact lenses range from hard to soft. Hard lenses contain mainly poly (methyl methacylate) (PMMA) and are impermeable to oxygen. Hard and semirigid lenses permeable to oxygen are made from copolymers of siloxanes and methacrylates. Flexible, oxygen gas permeable lenses are made of silicones. Soft contact lenses are prepared from polymers that absorb large quantities of water to become hydrogels. The aqueous phase of the hydrogel is oxygen permeable. Hard and soft hydrophobic lenses require a relatively thick tear film between their posterior surface and the cornea of the eye. Soft hydrogel lenses adhere closely to the cornea with a tear film of only capillary thickness between the lens and the corneal surface. With any kind of contact lens, the cornea's surface must be wet and oxygenated at all times to remain transparent and healthy.

• History of Contact Lens

The first concept of contact lens was developed by Leonardo Da Vinci in the year 1508. In his 1508 "Codex of the Eye", Italian inventor Leonardo da Vinci speculated that submerging the head in a bowl of water could alter vision. He even created a glass lens with a funnel on one side so that water could be poured into it, but the device was impractical. In 1636, after reviewing Leonardo's work, French scientist Rene Descartes proposed another idea; placing a glass tube filled with liquid in direct with the cornea. In case we were wondering, this is the reason they are called "contact" lenses - because they make direct contact with the surface of the eye. Descartes' invention worked somewhat to enhance vision; however, using it made blinking impossible. Improvements in the design of contact lenses would not be seen again for nearly two centuries.

In 1801, English scientist Thomas Young made a basic pair of contact lenses based on Descartes' idea. He changed Descartes' contact lens design by reducing the size of the glass tube to 1/4 inch and then using wax to stick the water-filled lenses to his eyeballs. He was also the first to accurately describe astigmatism, greatly advancing the field of eye care. English physicist Sir John Herschel was the first to hypothesize that taking a mold of the cornea might produce lenses that could correct vision.

The early 1880's were a revolutionary period for contact lenses. New glass production, cutting and shaping technologies made thin lenses possible for the first time. Designs for glass contact lenses that fit in the eye, allowing the wearer to blink, were independently invented by three men: Dr. Adolf Fick, Eugene Kalt, and Louis J. Girard. Credit for the discovery usually goes to Dr. Fick, a Swiss physician who wrote a treatise entitled "A Contact Spectacle", in which he described the first contact lens with refractive power for visual improvement. The first physical example of the lens was made by artificial eye maker F. A. Mueller in 1887. These types of contact lenses were called scleral lenses, and they covered the entire eye, not just the cornea. In 1888, Dr. Fick constructed and fitted the first successful contact lens.

By the late 1920s, technological advances in both anesthesiology and materials is finally allowed Sir John Herscel's ideas about creating molds of the cornea to be tested. In 1948, an English optical technician named

Kevin Touhy was sanding down a plastic lens when the part that covered the white of the eye fell off. Rather than start over, he decided to try the smaller lens. In 1950, George Butterfield came up with the idea of a curved, rather than flat, corneal lens design. Later in the 1950s, Frank Dickenson, Wilhelm Sohnjes, and John Neil created thinner lenses, of about 0.20 millimeters. Even thinner lenses, of about 0.10 millimeters, were introduced in the early 80s. However, even with all these improvements, corneal lenses still hindered oxygen flow to the eyes and couldn't be worn for long periods or overnight.

That was soon to change beginning in 1958. At that time, Czechoslovakian chemist Otto Wichterle was developing a new type of plastic, called hydrogel, that was soft pliable when wet, yet could be shaped and molded.

In 1960, Bausch and Lomb was granted access to the hydrogel and took the material to new levels, including creating a refined casting technique that produced consistent lens surfaces, as well as a process for mass production. Ciba Vision's introduction of Silicone hydrogels in 1998 offered extremely high oxygen permeability. Both hard and soft contact lenses continued to improve over the next 25 years, especially in terms of oxygen permeability, to allow the eyes to breathe.

- Raw materials for contact lenses

The raw material for contact lenses is a plastic polymer. (A polymer is a blend of materials created by linking the molecules of different chemical substances.). Hard contact lenses are made of some variant of polymethyl methacrylate (PMMA). Soft contact lenses are made of a polymer such as polyhydroxyethyl methacrylate (PHEMA) that has hydrophilic qualities, that is, it can soak up water and still retain its shape and optic functions. The science of lens material is always being updated by lens manufacturers, and the specific material of any contact lens may differ depending on the maker.

Manufacturing of Contact Lenses

Contact lenses may be produced by cutting a blank on a lathe, or by a molding process. The forming of the lens involves shaping the plastic into specified curvatures. The major curves ~~(CAC)~~ of the lens are named the central anterior curve (CAC) and the central posterior curve (CPC). The CAC refers to the overall curve of the side of the lens that faces out. This outer contour produces the correct refractive change to fit the patient's visual needs. The CPC is the concave inner side of the lens. This conforms to the measurements of the patient's eye. Usually these two curves are formed first, and the lens is then called semi-finished. The lens is deemed finished when peripheral and intermediate curves are formed, and the edge is shaped.

(1) molding method – molding the lens can be carried out in several different ways. The lenses first developed in prague were spin-cast. Three different fluids were poured into open rotating molds. The outside curvature of the lens was shaped by the mold, and the inside curvature was formed according to the speed of the rotation of the mold. The centrifugal force of the spinning ~~mold~~ mold led to the polymerization of the fluids so that the molecular chains linked to form the required hydrophilic plastic. A more reliable mass-production method is injection molding. In injection molding, the molten plastic is injected into the mold under pressure. Then the lens is removed from the mold and cooled. The lens is then finished on a lathe. It is also possible to produce lenses entirely through molding, that is, they need no lathe cutting. This is a recent development, made possible through highly automated, computer controlled mold production.

(2) Lathe process - The initial forming of the lens can also be done by cutting on a lathe. First a blank is made. The blank is a circle only slightly larger than the size of the finished lens. This can be cut from a plastic rod, or stamped from a plastic sheet. Next the blank is fastened to a steel button with a drop of molten wax. The button is then centered on a lathe, which begins to spin at high speed. A cutting tool, which may be a diamond or a laser, makes concave cuts in the blank to form the CPC. Indicators on the lathe measure the depth of the cuts to guide the lens operator.

The button holding the blank is next moved to a lapping machine. The lapping machine holds the blank against a lapper, which is a revolving disk coated with an abrasive compound. The shape of the lapper machine spins the blank in one direction, and the lapper in the other. It also moves the blank in a small figure eight motion. The abrasion polishes the lens surface.

The polished lens is then mounted on a steel shaft called an arbor. The end of the arbor has been ground to match the CPC so the lens will fit on the shaft. The arbor is installed in a lathe, and the operator makes convex cuts in the lens to form the other major curve, the CAC. Now this side of the lens is polished and the lapper is modified to fit the convex CAC. When this second side of the lens is polished, the lens is considered semi-finished.

(3) Finishing - The contact lens requires several more curves to be ground before the lens will fit exactly on the patient's eye. The final curves are the peripheral anterior and posterior curves and the intermediate anterior and posterior curves, which govern the shape of the lens nearest and next-nearest the edge. The lens is mounted on an arbor again by suction or with

double-sided tape. The arbor is installed in the lathe or grinding machine. These shallower cuts may be ground with emery paper or cut with a razor blade. The diameter of the lens may also be trimmed at this time.

(4) Quality control- Quality control is very important for contact lenses, since they are medical devices and they must be custom fit. The lenses are inspected after each stage of the manufacturing process. The lenses are examined under magnification for anomalies. They are also measured by means of a shadow graph. A magnified shadow of the lens is cast on a screen imprinted with a graph for measuring diameter and curvature. Any errors in the lens shape show up in the shadow. This process may be automatically performed by computer.

(5) Packaging - After the lens has passed inspection, it is sterilized. Lens are boiled in a mixture of water and salt for several hours to soften the lens. Next, the lens are packaged. Standard packaging for lenses is a glass vial, filled with a saline solution and stoppered with rubber or metal. The hydrophilic material of soft contact lenses soaks up the saline solution, which is similar to human tears, and becomes soft and pliable. The lenses in this state are ready to wear.

• Current Developed Polymer : Different chemical recipies which may give plastic in more desirable characteristics are investigating by the researchers. One polymer currently being developed is a silicon-oxygen compound called siloxane. Siloxane forms a thin, flexible film and admits oxygen through the eye about 25 times more better than current standard soft lens materials. However, siloxane does not wet easily, and it attracts lipids (fats) to its surface, producing clouds.

It is a new attempt to introduce flourine molecules to the siloxane compound, causing the material to resist from lipids.

Then they chemically attach a wetting agent, which changes its molecular shape when boiled in a saline solution, so that this material can soak up water like traditional soft lens.

Investigations into new materials are focusing on more oxygen-permeable lenses.

- Working of contact Lenses - A soft contact lens molds to the shape of the eye covering both the cornea and limbus. This is possible because the lens is soft and flexible. The lens floats in the layer of tear that is present on top of the eye. The eyelid and attraction between the polymer and tear film hold the lens in place.

Hard contact Lenses are not flexible and this means that they must be ground to precisely fit the eye. They only cover the cornea, and not the limbus. If hard contacts are not fit precisely to the eye they will move and not work correctly. They are held in place by precise fitting and their attraction to the tear film.

Work - Hard and soft contacts work similarly in that as light is refracted as it passes through the polymer. By varying the thickness and the shape of the lens the amount of refractions can be varied to produce different amounts of visual correction.

- Desirable Properties in polymers : Polymers are the most suitable materials available now for manufacturing the contact lenses. The following properties should be there in a ideal polymer for contact lenses:

(a) A polymer should be transparent, flexible, having low density and tough.

(b) It should be unreactive to chemicals on the eye surface

(c) Polymer should be easy to making the contact lenses.

(d) An ideal polymer should be made from that raw materials which is available in abundance. It should also be easy to mould.

(e) The polymer must consist of hydrophilic nature, its should be suitable for bending light rays and the oxygen gas should be passed through the eye surface.

(f) The polymer should produce lenses which are easy to insert, remove, clean and store.

• Types of Contact Lenses

• Hard Contact Lenses:- Current fifteen percent of the thirty million contact lens users wear hard contact lenses. There are several kinds of hard contact lenses, the most historic being impermeable hard contact lens, and now the most common are the rigid gas permeable (RGP) lens, and silicone acrylate based lenses. All of these lenses consist of an amorphous three dimensional polymer matrix (typically a MMA derivative) that is below its glass transition temperature. The lenses are typically very stiff and have a high modulus of elasticity. This gives them a high tear strength and makes them very easy to handle.

The impermeable contact lens was the first type of hard contact to be developed. It consists of PMMA only. The MMA monomer is polymerized via ultra-violet or infrared radiation in the presence of cross-linkers and initiators. The lenses were then made by the lathe cutting manufacturing process.

PMMA is an ideal polymer to be used for hard contact lenses because it is cheap and easy to make. It is moderately hydrophobic, which also contributes to it repelling proteins effectively. It has a typical oxygen permeability of 0.5 Dk, which makes it effectively an impermeable membrane to oxygen and carbon dioxide. This impermeability is what restricts PMMA lenses from being used more than about 8 hours at a time.

This restriction has caused tremendous research in the area in hard contact lens permeability. It is possible to make theoretical calculations with respect to contact lenses by applying a modified version of Henry's law, and Fick's law. The modified version of Henry's law for polymers below their glass transition temperature can be Simplified as followed:

$$C = k_D p + C_H (bp/1+bp)$$
$$C = k_D p + C_H bp + (bp << 1)$$
$$C = (k_D + C_H b)p$$
$$C = k_D p$$

Units for Henry's Law for polymers below their Glass Transition temperature

C	Concentration of penetrant gas dissolved in polymer
k_D	Solubility coefficient for penetrant
p	Gas pressure at solution equilibrium
C_H	Langmuir mode concentration of sorbed gas
b	Gas affinity parameter

Fick's law for glassy polymers is given as:

$$N = -D_D (dC_D/dx) - D_H (dC_H/dx)$$

This can be simplified as follows:

$$N = -D'_D (d/dx)(C_D + C_H)$$
$$N = D'_D (dC'/dx)$$

Symbols used in Fick's for Glass Polymers

N	rate of gas transfer per unit area
D_D	Fick's diffusion Coefficient
C_D	Henry's Concentration of sorbed gas
D_H	diffusion coefficient for gas tapped
C_H	gas population ($C_H < C_D$)

These equations yield results that are reasonable, and that are in good agreement when applied to hard contact lenses. To gain the necessary data however one must know the free volume fraction of the polymer.

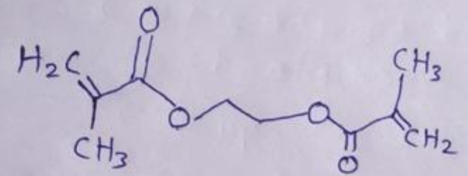
Diffusion is heavily dependent upon the free volume because it is a measure of the polymers porosity. One possible way of finding this is by positron annihilation spectroscopy.

- Soft Contact Lenses

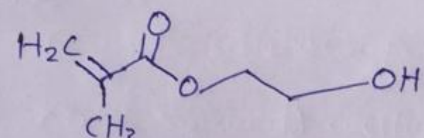
The most popular type of contact. Lens is a soft lens. Soft contact lenses are made of thermo-set polymer hydrogels. Like hard contact lens polymers, these gels are made up of a three dimensional, amorphous network with cross-links. The lenses are soft because the polymer is above its glass transition temperature. Soft contacts are typically formed using cast molding or the spin cast method. They can be produced by the lathe cutting process, but this is less common.

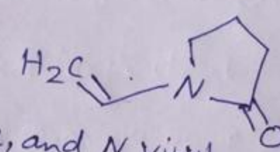
In soft contact lenses the water content affects many things. The permeability of the lens is proportional to the amount of water in the lens. As the percent weight of water increases in the lens, the permeability increases relatively linearly. The lenses ability to absorb various amounts of water also makes them highly hydrophilic. These attributes give soft contact lenses the ability to achieve permeability that allows them to be used for extended wear without damage to the eye. The increased permeability does not come freely however. As the water content is increased the polymers lose their strength. This can lead to tearing or scratching of the lens. A softer lens also offers the cornea less protection.

The first hydrogel contacts consisted of HEMA that was cross-linked with either ethylene dimethacrylate (EDMA) or ethylene glycol monogethacrylate (EGDMA). Future models of hydrogel lenses added the surfactants, methacrylic acid (MAA) and N vinyl pyrollidone (NVP) to increase water content. MMA is undesirable however because it makes the polymer ionic, which attracts proteins. HEMA has also been substituted with such monomers as glycerol methacrylate (GMA) that shows a higher resistance biofilm formation. Typical HEMA/MAA soft contact lenses have oxygen permeabilities of about 15-25 Barriers.



Ethylene glycol monogethacrylate





Hydroxyenthyl methacrylate, and N vinyl pyrollidone

Seeking to improve soft contact lens permeability scientist started to make hydrogels from silicone based polymers like polydimethylsiloxane (PDMS). The silicone hydrogel contact lens, also known as siloxane lenses, show impressive permeability (PDMS has a DK of 600 Barres), while retaining the comfort, wetability, and biofilm resistance of non-silicone based hydrogels. Unlike hydrogel lenses however, the oxygen permeability of silicone hydrogels decreases exponentially as water content increases. As discussed in hard contact lenses, silicone is hydrophobic, so the wetability decreases as water content decreases. This led scientist to researching ways of making siloxane based lenses more wetable.