Contact Lens Materials

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The Ideal Lens Material

- meets cornea’s oxygen requirements
- physiologically inert
- excellent in vivo wetting
- resists deposition
- dimensionally stable
- durable
- optically transparent
- requires minimal patient care
- easily machineable
Materials Types

- **Rigid**
  - PMMA (late 1930’s)
  - RGP (late 1970’s)

- **Hydrogel**
  - Low water content (WC - late 1960’s)
  - High water content (HWC - late 1970’s)
  - Silicone hydrogel (late 1990’s)
Material Categories

- **Natural**
  - Collagen

- **Modified natural**
  - CAB (butyrate of cellulose acetate)

- **Synthetic**
  - PMMA (polymethylmethacrylate)
  - HEMA (poly-2-hydroxyethyl methacrylate)
Fundamentals

- All materials formed from repeating short units (monomers) joined to form long chains (polymers)
Fundamentals

- **Single monomers joined (homopolymer)**
  - poly (methyl methacrylate) - PMMA
  - poly (2-hydroxyethyl methacrylate) - polyHEMA

- **Two or more monomers joined**
  - copolymers
Simplest Synthetic CL Polymers

PMMA (rigid) + hydroxyl groups (OH) to increase hydrophilicity = HEMA (soft)
Crosslinking

- polymer chains connected to each other by side chains
- affect the tensile strength
- affect the oxygen permeability
- greater cross links, less water, smaller pore size
Polymer Physical Characteristics

- Hardness → Shore D
- Index of refraction → refractometer
- O₂ Permeability → Fatt method
- Impact Resistance → ASTM D256-78 Impact test
- Light Transmittance → Hoffman
RGP Physiochemical Properties

- light transmission
- refractive index
- specific gravity
- oxygen permeability
- hydration
- adsorption/absorption
- wettability
- tensile strength
- scratch resistance (Shore hardness)
Important Material Properties

- rigidity
- durability
- deposit resistance
Hydrogel Physiochemical Properties

- hydration
- refractive index
- light transmission
- linear expansion (swelling factor)
- oxygen permeability/transmissibility
- pervaporation tendencies (SCL’s)
- absorption/adsorption
- stability in aqueous environments
- tensile strength
Hydrogel Physiochemical Properties

- **tensile strength**
  - “how strong is it?”

- **modulus of elasticity**
  - “how flexible is it?”

- **coefficient of elongation**
  - “how far can it be stretched?”

- **tear strength**
  - “how does it resist tearing?”
Hydrogel Physiochemical Properties

- Biocompatibility
- Cytotoxicity
- Ocular irritation 21-day rabbit test
- Resistance to microbial growth
- Absorption of Preservative/Disinfectants
- Stability in Solutions
- Protein Deposition
Oxygen Transport
Oxygen Transport

- **Material Permeability (P)**
  - $D$ (diffusion component) $\times k$ (Oxygen permeability)
  - Value $\times 10^{-11}$

- **Oxygen Transmissibility**
  - $Dk/t$ (lens thickness)
  - Value $\times 10^{-9}$
Corneal Oxygenation (SCL)

- Transmissibility related to Dk and t
  - EWC
  - BVP & design

- Reduced thickness increases oxygenation linearly

- Increased equilibrium water content (EWC) increases oxygenation logarithmically

- Minimum thickness related to EWC
  - handling
  - dehydration

Oxygen Permeability related to amount of H₂O that O₂ can diffuse through

Holden et al; CEO 1986
McNally et al; CEO 1987
Orsborn & Zantos; CLAO J1988
Rigid (thermoplastics)

- PMMA (polymethyl methacrylate)
- GP

1. CAB (cellulose acetate butyrate)
2. Silicone-acrylate copolymers
3. Fluorinated polymers

Oxygen permeability related to cross-linking of the material and ability to bond with \( O_2 \) physically within the materials
Poly (methyl methacrylate) [PMMA]

- patented as perspex in 1934
- used in contact lenses late ‘30s
- readily machined and polished
- low cost
- fairly wettable when clean
- easy to care for
- zero $O_2$ permeability
- used up to 1970’s
RGP lens materials

- Early attempts to replace PMMA:
  - cellulose acetate butyrate (CAB)
  - siloxane acrylates (SA)
Cellulose Acetate Butyrate (CAB)

- introduced by Eastman, mid 1930s
  - derived from polysaccharide (cellulose)
- more flexible than PMMA
- can be moulded or lathed
- hydroxyl groups result in 2% $H_2O$ content
  - material stability lower than PMMA
- $Dk$ range 4-8
- incompatible with BZK chloride
Siloxane Methacrylates
(Silicone Acrylates)

- MMA backbone
- Si-O-Si bond
- Dks 12-60 (low - medium)
- wetting agent added
- surface negatively charged
Silicone Acrylates

- Advantages
  - *higher Dk than any previous materials*
  - *reduced rigidity*
  - *allowed larger lens diameters*

- Disadvantages
  - *more deposit prone*
  - *surface easily scratched*
  - *higher breakage rate*
  - *can craze*
  - *flexure problems*
  - *parameter instability*
Silicone Acrylates

Dk values

- Boston II 12
- Boston IV 19
- Optacryl 60 18
- Paraperm O₂ 16
- Paraperm EW 56
- Silperm 100 100
Fluorosilicone Methacrylates
Fluorosilicone Acrylates (FSA)

- *same basic structure as silicone acrylate copolymer*
- *has fluorinated side chains added*
- *early attempts to surpass siloxane acrylates include:*
  - Alberta N; Equalens; FluoroPerm
- *lower surface charge*
- *better wetting (?)*
- *reduced deposits (?)*
Fluorosilicone Acrylates

- DKs 40 to 100+ (med - high)
- EW potential
- surface easily scratched & greater lens flexure compared with PMMA
- next generation
  - Fluorex; FluoroPerm
  - Equalens II; Alberta N-FL
- NB Boston RXD
  - Dk 45, tough material, approaching PMMA
Modern “Boston” family of RGP materials

- Patented AerCor technology
  - fluorosiloxane methacrylates
  - use low silicone content
    - typically SA 10-20%; AerCor design 5-7%
- Boston EO (extra oxygen) - Dk 82
- Boston ES (extra stiffness) - Dk 31
- Boston 7 - Dk 73
- Boston XO - Dk 100
Menicon Materials

- Menicon Z
  - Fluorosilicone acrylate with silylstyrene
  - Dk 163; Dk/t 125
  - Approved for up to 30 nights wear

- Menicon Super Ex (SF-P)
  - Dk 145; Dk/t 81
Silicone Rubber (Elastomers)

- High molecular weight cross-linked poly (dimethyl diphenyl vinyl siloxanes)
  - eg Silsoft
- polymerized at high temp and pressure
- moulded lens
- high permeability (Dk=250)
- very hydrophobic
  - poor wettability
  - lipophilic
- surface plasma irradiated or chemically coated to wet
Soft (Hydrophilic) Materials
Hydrogels (Thermosetting Plastics)

- copolymer of hydrophilic and hydrophobic monomers
- xerogel - rigid
- hydrophilic
  - interacts with water
- hydrophobic
  - backbone
  - mechanical strength
- cross-linking agents for increasing strength and stability
Soft Contact Lens Polymers

- **PolyHEMA**
  - hydroxyethyl methacrylate
  - original material
  - polyHEMA crossed linked by EGDMA
    - ethylene glycol dimethacrylate
  - close relative of PMMA
  - 38% water content

- **Wichterle**
  - molded PHEMA lenses (1956)
  - developed spin-casting (1961)
  - developed lathing of the xerogel (1963)
Advantages of HEMA

- Cheap
- Easily machinable
- Long life
- Dimensionally stable
  - pH
  - Tonicity
  - Temperature
Disadvantages of HEMA

- Reduced thickness
  - poor handling

- Low Dk
  - increased edema
  - increased vascularisation
  - “CL Exhaustion Syndrome”
### Examples of Typical Dk/t

<table>
<thead>
<tr>
<th>Hydrogels</th>
<th>Dk/t</th>
<th>RGP’s</th>
<th>Dk/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>LWC (38%)</td>
<td>15</td>
<td>SA</td>
<td>27</td>
</tr>
<tr>
<td>MWC (55%)</td>
<td>27</td>
<td>FSA</td>
<td>60</td>
</tr>
<tr>
<td>HWC (70%)</td>
<td>22</td>
<td>F</td>
<td>130</td>
</tr>
</tbody>
</table>

Measured at -3.00D

**Min required Dk/t** – Daily Wear 24; Extended Wear 87
How to Increase WC?

- Take base material
  - MMA
  - HEMA

- Copolymerise with monomer with increased hydrophilicity
Principal Backbone:

HEMA - hydroxyethyl methacrylate
MMA - methyl methacrylate

Neutral (non-ionic)

- N-vinyl pyrrolidone
- Polyvinyl alcohol
- Phosphoryl-choline
- Glyceryl methacrylate

Negatively charged (ionic)

- Methacrylic acid
- Carboxylic acid
- Acrylic acid
Advantages of HWC

- **Increased Dk**
  - longer WT
  - improved physiology

- **Increased thickness**
  - improved handling
Disadvantages of HWC

- **Reduced**
  - life-span
  - reproducibility

- **Increased**
  - dehydration
  - discolouration
  - cost
  - deposition
### FDA lens materials categories

#### Soft (hydrophilic) material groups ("-filcon")

<table>
<thead>
<tr>
<th>Group</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>Low water content (~50%), non-ionic</strong> (having an ionic content of 1% mole fraction at pH = 7.2)</td>
</tr>
<tr>
<td>2</td>
<td><strong>High water content (↑50%), non-ionic</strong></td>
</tr>
<tr>
<td>3</td>
<td><strong>Low water content (~50%), ionic</strong> (having an ionic content of ↓1% mole fraction at pH = 7.2)</td>
</tr>
<tr>
<td>4</td>
<td><strong>High water content (↑50%), ionic</strong></td>
</tr>
</tbody>
</table>
Soft Contact Lens Polymers

- Ionic Materials
  - net negative charge on surface

- Non-ionic materials
  - still have charged sites within polymer matrix
  - no net surface charge
Ionic versus Non-Ionic

- Lenses containing MA (ionic)
  - more free water molecules
  - wetting agents attract more water and thus can release more water

- Lenses containing nPVP (non-ionic)
  - more bounded water molecules
  - loses ability to hydrate ions thus limited amount of hydration energy: thus limited water loss

Pusch and Walch, Science 1982 10:325-60: independent of $[\text{H}_2\text{O}]$, varies with temperature
Collagen

- High tensile strength
- May be antigenic unless very pure
- Used in other body sites
  - sutures
  - dressings
  - tendons
  - vessels
  - scleral buckles
Collagen

- Porcine scleral tissue
- 63% water
- Dissolvable
  - 6 hrs - 72 hrs
- Bandage lenses
  - corneal trauma
  - keratoplasty
  - drug delivery
    - now superseded by SiH lenses
Hybrid

- **Synergize®**
  - initially Saturn / Saturn II
  - SoftPerm (Synergicon A)
- **Rigid centre**
  - Previous: low Dk siloxane-styrene (14 x 10^{-11})
  - Now: high Dk (100 x 10^{-11})
- **Soft skirt**
  - 25% EWC HEMA-based (5 x 10^{-11})
- **Distorted corneas**
  - post-Rk; post graft; post trauma; keratoconus
    - good vision; good comfort
    - physiological problems
    - very little movement
Proclear (Omafilcon A)

- Based on HEMA + phosphorylcholine (PC)
- Synthetic analogue of a natural phospholipid
- EWC = 60%
- Mimics cell surfaces
  - biocompatibility ?
  - low dehydration ?
  - low deposition ?

Young et al, Optician 1996
Silicone-Hydrogels

- Silicone-containing hydrogels
  - surface treated
- Low water content
- High Dk
- Released 1999
  - CIBA-Vision and B&L
- Monthly continuous wear (CW), biweekly extended wear (EW)
- Advantages
  - reduced hyperaemia
  - minimal oedema
  - no myopic shift
Dehydration

- All SCL materials dehydrate on eye
  - initial loss rapid then slows

Clinically relevant
- fit
- comfort
- Dk
- staining

Zadnik & Mutti; ICLC 1985
Collins et al; CEO 1989
Little & Bruce; OVS 1994
Dehydration:
Relevant Factors

- Polymer characteristics
  - water content
  - ionicity

- Thickness
  - design
  - BVP

- Subject
  - tear film
  - occupation

- Environment
  - air temperature
  - humidity
  - wind velocity

Andrasko - various
Brennan & Efron - various
Increased Dehydration:

**Rules of Thumb**

- **Environment**
  - low humidity (<25%)
  - high temperatures
  - windy conditions

- **Lens**
  - thin lens designs
  - low prescriptions
  - high water content materials
  - ionic materials

- **Subject**
  - poor blinking
Contact Lens Deposits

Module 5 (IACLE)
Prepared by: L. Jones PhD FCOptom DipCLP DipOrth FAAO (DipCL) FIACLE & L. Sorbara OD MSc FAAO (Dip C&CL)

Presented by: M. Steenbakkers OD FAAO
Lens Deposits and Coatings

- primary reason for lens replacement
- aggravated by non-compliance
- must identify onset of the problem (time)
- must direct cleaning towards type and extent of deposit
- source of food for bacteria
  - adhered to lens/coating surface
Lens Deposits and Coatings

- **Sources:**
  - tears, handling, cosmetics, care regime, environment

- **Patient Factors:**
  - ocular temp., osmotic gradient, pH, altered tear chemistry, poor blinking (infrequent)

- **Surface Chemistry:**
  - ionicity, wettability, smoothness of surface, elasticity
Lens Deposits and Coatings

- Dependent on (SCL):
  - lens material
    - methacrylate (MA)=protein
    - n-vinyl pyrrolidone (NVP)=lipid
  - water content (dehydration rate)
  - ionicity (charge of surface)
  - age of the lens (disposable, planned replacement, conventional.)
  - tear film (dry eye)
  - wearing schedule (overnight wear)
  - care system (enzyme use)
Dependent on (GP):

- lens material
  - *silicone acrylate* (SA) = protein
  - *fluoro*-silicone acrylate (FluoroSA) = lipid
- ionicity (charge of surface)
- age of the lens
- tear film (dry eye)
- wearing schedule (overnight wear)
- care system (enzyme use)
Lens Discolouration

- Caused by: (SCL)
  - preservatives: chlorhexidine and thimerosal
  - topping up
  - eye drops
  - make up
  - organic and inorganic substances
  - smoke, nicotine
  - increased adrenaline secretion
Lens Discolouration

- yellow-brown.......chlorhexidine
- yellow-orange.......sorbic acid
- yellow-green.......fluorescein
- orange-red.........ferric oxide
- pinkish...............epinephrine, vasoconstrictors
- grey....................mercurial
- black....................eye makeup, mercury
- milky white..........Ca\(^+\)phosphate
Types of Deposits

- Organic

- Inorganic
  - Ca\(^+\) Carbonate or Ca\(^+\) Phosphate
  - Mercury
  - Lipid and Calcium Combo
Types of Deposits

- **Organic Deposits (GP & SCL)**
  - *protein* from tears
  - lysozyme (+ve charge) or albumin
  - thin colourless film
  - when **denatured**, white film
    - non-reversible change to protein structure due to heat, pH change and chem. reagents
  - forms in layers and cracks
  - *lipids* from Zeiss or Moll glands
  - greasy film or spots (GP-pearlescence)
Types of Deposits

- **Organic Deposits (SCL)***
  - *pigments*
  - yellow to brownish
  - from various contaminants
  - protein binds to chlorhexidine causing pink/yellow deposit
  - see lens discolouration
Types of Deposits

- **Organic Deposits (SCL)**
  - *microorganisms*
  - fungi or yeast eg, Candida, Aspergillus
  - in discrete patches
  - dark brown or black, white mycelia and feathery hyphae
  - bacteria (eg. Strep) also adhere to GP (small amount) and pseudomonas to SCL (especially group IV)
  - white to brown star shaped
  - related to non-preserved solutions, infrequent replacement of storage solution
Fungi

- Fungi use contaminants on lens surface
  - *Aspergillus*
  - *Candida*
- Coloured
- Filamentary
- Inadequate disinfection
- Replace lens
Protein

- Most common
- Clinically - thin, translucent appearance
- Visible versus denatured
- Deposition is complex issue
  - protein type
    - size
    - charge
  - material type
    - water content
    - charge
## Protein Size & Charge

<table>
<thead>
<tr>
<th></th>
<th>Molecular Weight (kD)</th>
<th>Relative Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lysozyme</strong></td>
<td>14.6</td>
<td>+ve (+++)</td>
</tr>
<tr>
<td><strong>Lactoferrin</strong></td>
<td>60 - 80</td>
<td>+ve (+)</td>
</tr>
<tr>
<td><strong>Albumin</strong></td>
<td>65</td>
<td>-ve (-)</td>
</tr>
</tbody>
</table>
Deposited Protein Types

<table>
<thead>
<tr>
<th></th>
<th>GII</th>
<th>GIV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysozyme</td>
<td>33%</td>
<td>90%</td>
</tr>
<tr>
<td>Albumin</td>
<td>33%</td>
<td>5%</td>
</tr>
<tr>
<td>Lactoferrin</td>
<td>33%</td>
<td>5%</td>
</tr>
</tbody>
</table>

Sariri, 1995
Protein Appearance
Protein Film (GP)
Surface Plaque (GP)
Tx: Protein

- Must be removed or lens replaced
  - reduces acuity
  - promotes inflammatory response

- Techniques
  - surfactant cleaning
    - 50-60% removal
  - enzyme removers
    - 50-60% removal
Lipid

- Greasy, shiny appearance
- Many types
- Patient dependent
- Usually combine with other tear film components
- Derived from
  - meibomian glands
  - extraneous sources
- Particular problem with
  - GP’s with Fluorine
  - NVP-containing Group II SCL
Lipid Appearance (SCL)
Lipid Deposition on GP’s

- Lipid attached to lens surface
- If lenses *new* then due to failure to remove polish from lens surface during manufacture
- If *old* then due to poor maintenance
- Often worse in patients with MGD
- Use alcohol-containing surfactants
  - occasionally AM & PM cleaning required
Tx: Lipid

- Must be removed
  - interferes with acuity
  - reduces wettability

- Remove with surfactants
  - Surfactants containing isopropyl alcohol are most effective
  - Eg. Miraflow or Aoflow (CibaVision)
Mucin

- Produced by goblet cells of conjunctiva
- Mainly complex carbohydrates
- Usually base layer for other deposits
- Occasionally a problem with GP’s
  - Part of the GP “plaque”
GP Plaque
Types of Deposits

- Inorganic Deposits (SCL)
  - deposition of salts within lens matrix
  - calcium (white), iron (red), mercury (from thimerosal, complex of protein + sulphide, black discolour), magnesium and silica
  - $\text{Ca}^+$ phosphate (white sheet, related to buffer in solution)
  - common with aphakics and pathological corneae, non-ionic, NVP
  - from non-softened water and external sources
Types of Deposits

- Lipid and Ca\(^+\) Carbonate combo (SCL)
  - white crystalline deposit
  - into lens surface
  - called a "lens calculi"
  - related to calcium in tears
  - covered by lipid spot on the surface
  - called a "jelly bump"
Calculi = Lipid + Ca$^+$ Carbonate

- Discrete, elevated deposits
- Anterior surface of SCL only
- Round or oval
- Grow beneath lens surface

Synonyms
- jelly bumps
- calcium spots
- white spots
- mulberry spots
Gross Calculi Appearance
Calculi-Jelly Bumps

- 90% lipid
- 10% calcium, mucin and protein mixture
- Majority on NVP-containing Group II lenses
- Inter patient differences
  - particularly in dry-eyed subjects
- Removal leaves pit
- Replacement necessary
Calcium

- Derived from tears and/or buffer agents
- Calcium
  - carbonate (white crystals or film)
  - phosphate (white film)
- Remove with chelating agents (EDTA)
Calcium
Iron

- Metallic FB become embedded
- Oxidize to form “rust-spot”
- Building sites common problem
- Replacement necessary
Iron Deposits
Management of Deposits

- Organic:
  - protein
    - enzyme specific for protein
  - lipid
    - surfactant specific to lipid
  - pigment
    - throw out lens
  - microorganisms
    - throw out the lens
Management of Deposits

- Inorganic:
  - rust
    - throw out lens
  - Ca\(^+\) (calculi, jelly bumps)
    - throw out lens
  - mercury
    - throw out lens
Management

Keep lens clean

- Maximise cleaning regime
  - surfactants
  - enzyme cleaners
- Change material
  - from HWC to LWC
  - from ionic to non-ionic
  - from NVP to non-NVP
  - use deposit resistant material

Frequent Replacement !!!
1 - 28 day Replacement Of Group II & Group IV Materials

Clinical Trial

- Group II lens (Soflens 66) vs Group IV lens (Acuvue)
- Replaced every 1, 7, 14, 21 or 28 days
- Randomised, cross-over
- n = 22
Total Protein

Days Of Wear

1 7 14 21 28

g of Protein

Group IV

Group II

Days Of Wear

g of Protein

Group IV

Group II
Conclusions

- **Significant differences exist between and within FDA groups**
  - **Protein related to**
    - methacrylate (MA) concentration & EWC (greater in Group IV)
  - **Lipid related to**
    - n-vinyl pyrrolidone (NVP) concentration & EWC (greater in Group II)
Conclusions

- Lipid and protein deposition follow different kinetics
  - **Protein**
    - *almost immediately in Group IV, then plateaus*
    - *slowly accumulates in Group II, no plateau*
  - **Lipid**
    - *inconsequential in non-NVP Group IV*
    - *slowly, progressively accumulates in Group II, no plateau*
Deposition on SiH

Lysozyme and Lipid Deposition on Silicone Hydrogel Contact Lens Materials

Lyndon Jones, Ph.D., F.C.Optom., Michelle Senchyna, Ph.D., Mary-Ann Glasier, M.S., Jillian Schickler, B.S., Ian Forbes, B.S., Derek Louie, M.S., and Christopher May, B.S.

Jones et al, 2003
Lipid Deposition

○ a problem for certain individuals...
SiH Deposition Summary

- Reduced wettability
- Little protein
- Lots of lipid
- Removal of lipid critical
  - current care systems optimised for protein removal
  - rub vs no-rub?
  - additional cleaner?
    - Miraflow ideal