Overview of Medical Polymers
Polymer Pyramid
Crystalline & Amorphous Polymers

Crystalline polymers
• Chemical structure that allows the polymer chains to fold on themselves and pack together in an organized manner
• Regularly defined pattern

Amorphous polymers
• Plastics without the above crystalline regions
• Having no defined shape

Semi-crystalline polymers
• All of the crystalline plastics have amorphous regions between and connecting the crystalline regions
• Almost all “crystalline” polymers are actually “semi-crystalline”
Molecular Structures

MELT

CRYSSTALINE

CRYSSTALS

SOLID

AMORPHOUS

Confidential
Characteristics

Amorphous
• Soften over a broad temperature range
• Easy to thermoform
• Tend to be transparent
• Bond well using adhesives and solvents
• Prone to stress cracking
• Poor fatigue resistance
• Structural applications only (not for bearing and wear)

Crystalline
• Sharp melting point
• Difficult to thermoform
• Tend toward opacity
• More difficult to bond using adhesives and solvents
• Good resistance to stress cracking
• Good fatigue resistance
• Good for bearing and wear
• Good for structural applications
• Good for higher heat applications
## Property Comparison

<table>
<thead>
<tr>
<th>Property</th>
<th>Crystalline</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Stiffness</td>
<td>More Stiff</td>
<td>Less Stiff</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Ductility Elongation</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Resistance to creep</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Impact</td>
<td>Less Impact</td>
<td>Better Impact</td>
</tr>
<tr>
<td>Max Usage Temp</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Shrink and Warp</td>
<td>More</td>
<td>Less</td>
</tr>
<tr>
<td>Flow</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>Higher</td>
<td>Lower</td>
</tr>
</tbody>
</table>
# Examples by Class

<table>
<thead>
<tr>
<th>Type</th>
<th>High Performance</th>
<th>Engineering</th>
<th>Commodity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>Polysulfone, Polyetherimide, Polyethersulfone, Polyarylsulfone</td>
<td>Polycarbonate, Modified PPO, Modified PPE, TPU</td>
<td>Acrylic, Polystyrene, ABS, PVC, PETG, CAB</td>
</tr>
<tr>
<td>Crystalline</td>
<td>PVDF, PTFE, ECTFE, FEP, PFA, PPS, PEEK</td>
<td>Nylon, Acetal, PET, PBT, UHMW-PE</td>
<td>Polyethylene, Polypropylene</td>
</tr>
</tbody>
</table>
Polarity of Polymers

Another key component of a polymers innate functionality is its “polarity”; which has a big effect on adhesion characteristics

Polar molecules
• Electrons are not equally shared
• One part of the molecule is more negative than another part of the molecule
• Molecules thus have negative and positive “poles” like a battery
• This makes them hydrophilic (water loving)

Nonpolar molecules
• Electrons are equally shared
• No one part of the molecule is distinctly negative or positive…no poles
• This makes them hydrophobic (water hating)
### Examples & Characteristics

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Examples</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polar</strong></td>
<td>Nylon, POM, PC, PMMA, PEI, Water soluble polymers, PVC, TPU, Polyesters, ABS</td>
<td>Generally higher surface energy; good wettability (hydrophilicity); easier to bond and adhere to</td>
</tr>
<tr>
<td><strong>Nonpolar</strong></td>
<td>PE, PP, SEBS, PS</td>
<td>Generally lower surface energy; poor surface wettability (hydrophobicity); more difficult to bond and adhere to</td>
</tr>
</tbody>
</table>
Amorphous Polymers
Poly Vinyl Chloride (PVC)

- Long positive history in medical applications
- Dispersion & Suspension resins
- Rigid and flexible grades (phthalate and non-phthalate plasticizers)

Properties
- No drying
- Good UV resistance
- Good innate fire resistance
- Low melt
- High performance with low cost
- Excellent clarity
- Can degrade when processed too hot
- Excellent bondability to a wide variety of substrates by a wide variety of bonding methods
- Very good physical property matrix

Sterilization
- EtO – yes but must be out-gassed for 7 to 14 days
- Gamma – yes but must be specially formulated

Regulatory
- USP Class 6
- FDA
Acrylic (PMMA)

**Properties**
- Excellent transparency – up to 92% light transmittance
- Good mechanical strength and dimensional stability
- Good chemical resistance
  - Alcohol promotes crazing
  - Attacked by organic solvents
  - Resistant to inorganic acids and alkalis
- Inert
- Good UV resistance
- Excellent dimensional stability
- Good bondability and printability

**Sterilization**
- EtO – yes
- Gamma – yes but discolors if not modified

**Regulatory**
- USP Class 6
- FDA
Styrenics (ABS, SAN, PS)

Properties
- Lower melt point
- Easily fabricated
- Good dimensional stability
- Low to moderate price
- Adequate physical property matrix
- Transparency
  - PS and SAN – transparent
  - ABS – opaque or transparent
- Fair bondability

Sterilization
- EtO – yes, but avoid repeated cycles
- Gamma – yes, but may lose some impact

Regulatory
- ISO 10993 (ABS, SAN)
- USP Class 6
- FDA
**PETG** (Polyethylene Teraphthalate Copolymer)

**Properties**
- Excellent clarity and gloss
- Good impact resistance
- Excellent alcohol and lipid resistance
- Good barrier properties
- Excellent bondability & joinability
- Lower cost than PC
- Fair weatherability

**Sterilization**
- EtO – yes
- Gamma – yes

**Regulatory**
- USP Class 6
- ISO 10993
- FDA
Polycarbonate (PC)

Properties
Moderately priced
Good dimensional stability
High temperature resistance polymers
  Good in alcohols & acids
  Poor in hydrocarbons, phenols, esters, ketones, and alkalis
Excellent clarity
High stiffness, impact, and toughness
Excellent scratch resistance
Poor weatherability
Good bondability and joinability
Contains BPA

Sterilization
EtO – yes
Gamma – yes but some discoloring can occur
Autoclave – limited

Regulatory
USP Class 6
ISO 10993
FDA
Modified PPO/PPE (polyphenylene oxide/ether w/HIPS)

**Properties**
- High temperature resistance
- Good chemical resistance
  - good to acids & bases
  - attacked by some hydrocarbons
- Excellent dimensional stability and stiffness
- Good toughness
- Low moisture absorbance

**Sterilization**
- Gamma – yes
- EtO – yes
- Autoclave – yes w/limitations
Cellulosics (Acetate, Butyrate, Propionate)

Properties
- Good impact
- Transparent glossy surface
- Good resistance to UV
- Fair bondable and joining
- Chemical resistance
  - Good in aromatic hydrocarbons, greases, oils, lipids
  - Fair in alcohols
  - Poor in acids, alkalis, ketones

Sterilization
- EtO - yes
- Gamma – yes

Regulatory
- USP Class 6
- ISO 10993
Sulfones (Polysulfone, Polyethersulfone, Polyarylsulfone)

**General Properties**
- Good clarity (brownish tint)
- High stiffness & dimensional stability
- High heat resistance
- Low shrink
- Chemical inertness and resistance
- Good fire resistance
- Higher cost
- Good bondability & joinability
- Universally sterilized

**Sterilization**
- EtO – yes
- Gamma – yes
- Autoclave – yes

**Regulatory**
- USP Class VI
- ISO 10993
- FDA
Crystalline Polymers
Polyethylene (Low & High Density)

Properties
- Moderate melt point
- Low COF
- Good physical property matrix
- Difficult to bond to anything
- Low moisture absorption
- High thermal expansion
- Excellent chemical resistance
- Good ductility
- Very low cost
- No drying
- Non-toxic
- Minimal clarity

Sterilization
- EtO – yes
- Gamma – yes

Regulatory
- USP Class 6
- FDA

Confidential
Polypropylene

Properties
- Moderate melt point
- Low COF
- More rigid than PE
- Good physical property matrix
- Difficult to bond to anything
- Low moisture absorption
- High thermal expansion
- Excellent chemical resistance
- Very low cost
- No drying
- Non-toxic
- Some clarity

Sterilization
- EtO – yes
- Gamma – yes but must be stabilized version

Regulatory
- USP Class 6
- FDA
Polyesters (PBT, PET)

Properties
- Materials are ester based so hydrolization could be an issue
- Moderately priced
- Very good chemical resistance
- Must be dried
- Good creep and fatigue resistance
- Fairly high melt
- Good dimensional stability
- Transparency
  - PET, PBT – opaque unless crystallized quickly
- High stiffness

Sterilization
- EtO – yes
- Gamma – yes

Regulatory
- USP Class 6
- ISO 10993
Polyamides (Nylons)

**Types**
- Diamine and diacid (66, 69, 610, 612)
- Amino acid (6, 11, 12)

**Properties**
- Low/moderate price
- Absorbs moisture
- Should be dried
- Excellent physical property matrix
- Very tough with some flexibility (PA 11, 12)
- Good chemical resistance except in strong acidic environments
- Most grades are opaque, some amorphous grades available
- Low COF

**Sterilization**
- EtO – yes
- Gamma – under 5 Mrad

**Regulatory**
- USP Class 6
- ISO 10993
Acetal

Properties
Highly lubricious material
Good physical properties
Good chemical resistance
Good solvent resistance
Good dimensional stability & stiffness
Low moisture absorption
Good fatigue resistance
Tricky Processing, formaldehyde generation
  Can’t process near PVC

Sterilization
EtO – yes
Gamma – no

Regulatory
USP Class VI
ISO 10993
Fluoropolymers (FEP, PFA, ECTFE, PVDF, MFA, THV)

DEFINED: paraffinic polymers where some or all hydrogen groups have been replaced by fluorine

Properties
Chemically inert materials/excellent chemical resistance
Very low COF
High to very high priced
High specific gravity
Fire resistant
UV resistant
High temperature resins
Expensive materials with high specific gravity
Can get clarity
Flexible to rigid material selection
Highly inert material

Sterilization
EtO – yes
Gamma – depends on material
Autoclave – depends on material
Liquid Crystal Polymers (LCP)

Properties
- Very high modulus
- Low/no shrinkage
- Excellent dimensional stability
- Excellent chemical resistance
- High priced
- High temperature
- Outstanding mechanical properties
- Very difficult to extrude

Sterilization
- EtO – yes
- Gamma – yes
- Autoclave – yes

Regulatory
- USP Class VI
Polyetheretherketone (PEEK)

Properties
- Great for metal replacement
- Very high priced
- High specific gravity
- Very high heat resistance & processing temps
- Very high modulus
- Extraordinary mechanical properties
- Very low shrink
- Great chemical resistance except in some acids
- Can be implanted

Sterilization
- EtO – yes
- Gamma – yes
- Autoclave – yes

Regulatory
- ISO 10993
- Material used for implants
Advanced Biomaterials

**Bioabsorbable and drug delivery polymers**
- Implantable and bioabsorbable
- Can be engineered to degrade or release drug at a controlled rate
- Natural or synthetic
- Good processability
- Sterilizable – gamma or e-beam
- Extremely high priced (up to thousands of dollars per pound)
- Properties are “programmable”: molecular weight variation via copolymerization or compounding
- Include polylactides, polyglycolides, polycaprolactones, etc
Thermoplastic Elastomers (TPE’s)

Diverse family of “rubber-like” elastomeric materials that, unlike vulcanized rubbers (thermoset), can be processed and recycled like traditional thermoplastic processing equipment

Chemistry - Block copolymers and alloys
  Hard segments – provides thermoplastic properties
  Soft segments – provides elastomeric properties

Materials contain crystalline and amorphous segments
Thermoplastic Elastomers Categories

**Engineering TPE’s**
- PEBA—Polyether Block Amides
- COPE—Copolyesters
- TPU—Thermoplastic Polyurethanes

**Specialty TPE’s**
- DVA—Dynamically Vulcanized blends
- SBC—Styrenic Block Copolymers
- TPO—Thermoplastic Olefins
- PVC—PVC Blends (continuous & discontinuous) and Alloys (co-continuous)
Value vs. Performance

High Cost
- Engineering TPE's
  - PEBA
  - COPE
  - TPU
  - DVA
  - SBC
  - TPO
  - PVC

Low Cost
- Commodity
- High Performance
- Specialty TPE's
  - PVC
  - TPO
  - SBC
  - DVA
  - TPU
  - COPE
  - PEBA

Commodity High Performance
Polyether Block Amide (PEBA)

Properties
Thermoplastic elastomer made up of soft polyether mid-block with hard polyamide (nylon 11, 12) end-blocks
Premiere catheter shaft material for vascular therapy...enables outstanding operator control
Excellent torqueability
Easy to process
Some clarity
Maintains modulus in body temps
Good chemical resistance
Weak alcohol resistance
Very good physical property matrix
Durometer range
75 A – 72 D

Sterilization
Gamma – yes
EtO - yes

Regulatory
USP Class VI
Thermoplastic Polyurethane (TPU)

Properties
Great history in medical applications
Durometer range (55A – 75D)
Many vendors
Can be highly filled
Good dynamic properties
Excellent physical properties especially tensile and abrasion
Changes modulus in body
Excellent clarity
Stable to most sterilization techniques
Very good bondability and secondary processability

Sterilization
Gamma – yes but may yellow
EtO – yes

Regulatory
USP Class VI
ISO 10993
Copolyester Elastomers (COPE)

**Properties**
- Durometer range (85A – 75D)
- Excellent dynamic properties
- Excellent physical property matrix
- Clarity depends on processing technique
- Bondable but not as easy as PEBA and TPU
- Polyester backbone so it may hydrolyze over time

**Sterilization**
- Gamma – yes
- EtO - yes
Styrenic Block Copolymers (SBC)

**Properties**
- Very wide durometer range
- Bondability and bonding methods can be an issue
  - Functionalized bondable grades available
- Weak dynamic properties
- Good physical properties
- Lower cost
- Compounded product
  - Many formulation options
- Good for static parts on devices and grips
- Excellent elastomeric properties
- Easily processed

**Sterilization**
- Gamma – yes
- EtO – yes
- Autoclave – yes but limited

**Regulatory**
- USP Class VI and ISO 10993
Dynamically Vulcanized Allows (DVA)

Properties
- Physically cross-linked TPE’s
  - Reaction extrusion of EPDM rubber with PP
- Durometer range 45A – 90A
  - Below 55A are alloys with SBC’s
- Low compression set
- Physical properties are lower than most TPE’s
- Opaque
- A little higher service temperature than SBC’s
- Good chemical resistance to acids, bases
- Difficult to bond without additive bonding agents

Sterilization
- EtO - yes
- Gamma – yes

Regulatory
- USP Class VI and ISO 10993