EMAC 276 Final Exam Review

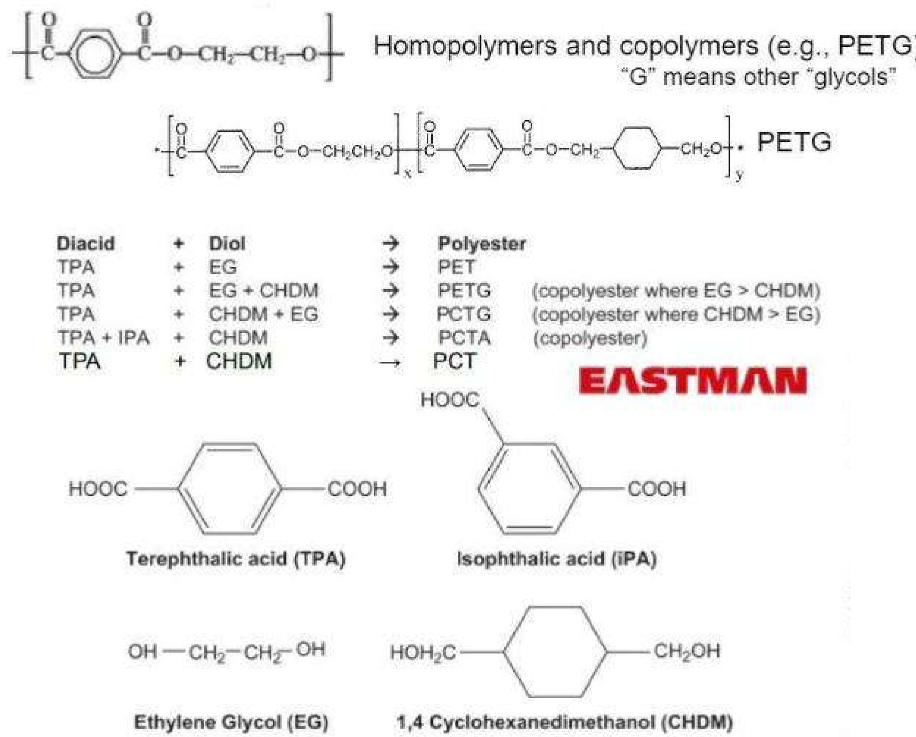
Exam Overview

9 – 11 AM 5/2

- 120 minutes
- Open-Book/Open-Note
- Only material after Midterm
- True/False Questions
- Multiple Choice
- Two short response

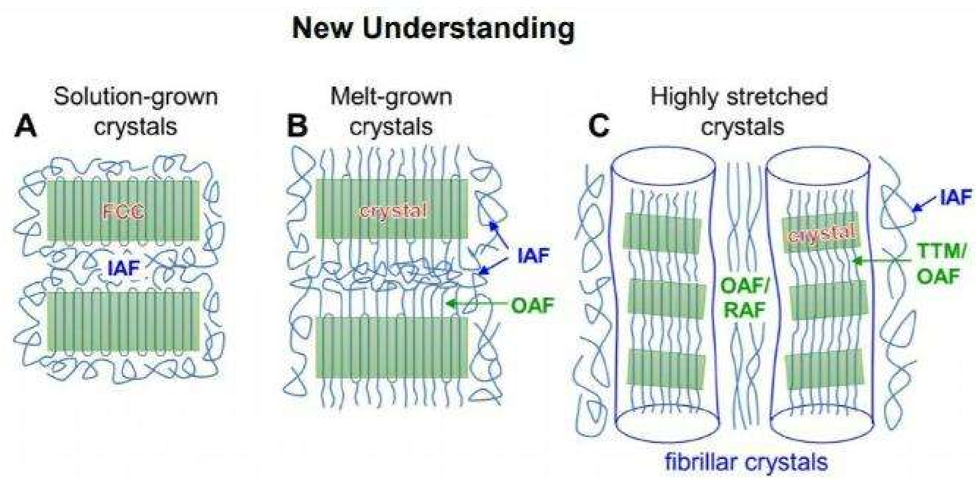
Polyesters - Poly(ethylene terephthalate) (2-6)

- Tg: 72-100 °C
- Tm: 255-265 °C
- Bisphenol-A free PETG to replace PC in teeth aligners, water/milk bottles, medical containers
- PETG contains glycol comonomer and is less brittle that PET
- Applications:
  - Injection molding and bottles
  - Fibers for textiles and tire
  - Films and sheets
  - Multilayer film coextrusion
  - 1D photonic crystals
  - 3M Enhanced Specular Reflection (ESR) films

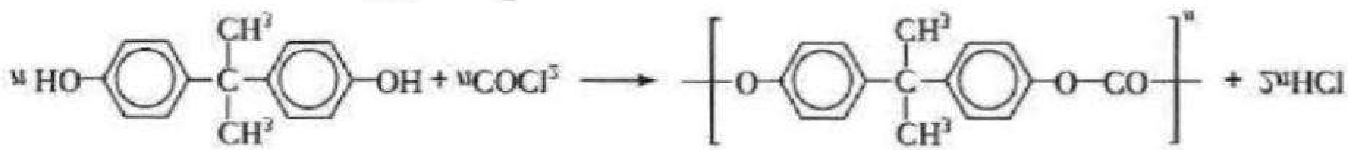


Polyesters - Poly(ethylene terephthalate) (2-6)

- PET has moderate crystallinity (0-40%)
- Isotropic amorphous fraction (IAF)
- Taut-tie molecules (TTM)
- Rigid amorphous fraction (RAF) enhances
    - Mechanical properties
    - Gas barrier properties
    - Electrical properties



Polyesters - Polycarbonate (18-21)



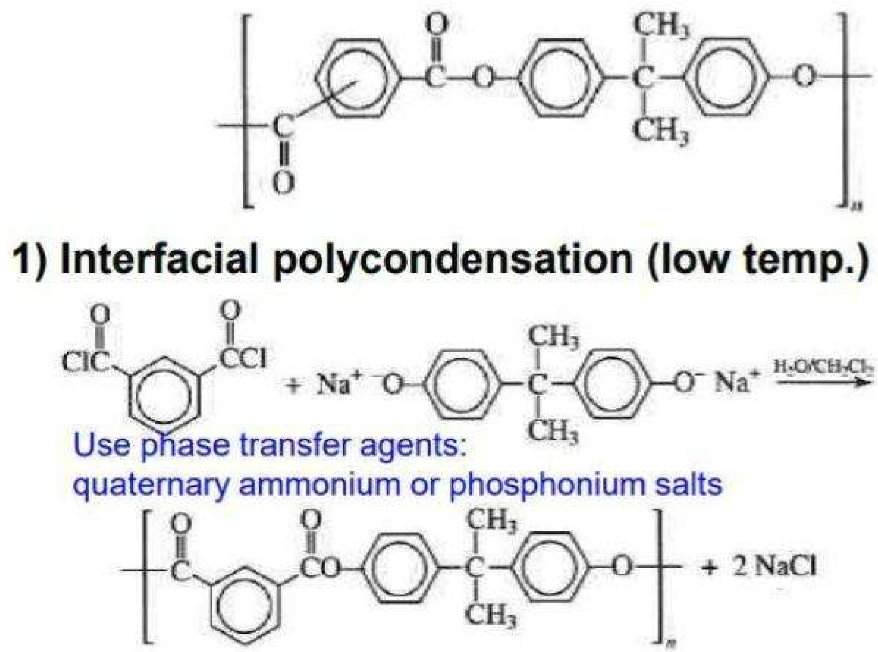
- Synthesis:
    - Ester exchange
    - Phosgenation
- High toughness
- Amorphous
- Tg: 145 °C
- High transparency & Refractive Index
- Applications
    - Construction materials
    - Data storage
    - Automotive, aircraft and security
    - Medical applications





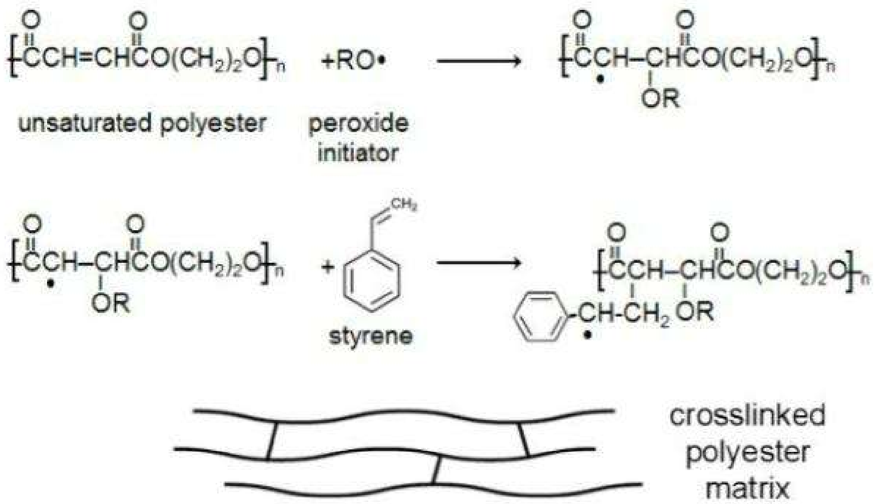

Polyesters - Aromatic Polyesters (22)

- Also called polyarylates
- Amorphous
- Tg: 190 °C
- Tougher and better heat resistance than PC
- Applications
  - Automobiles
  - Electronics
  - 5G antennas
  - Fire helmets/shields



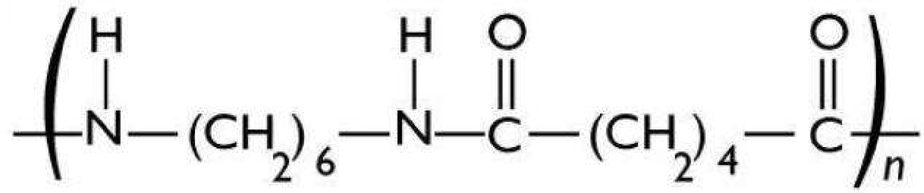
Polyesters - Unsaturated Polyester Resins (27-32)

- Made by curing linear low MW unsaturated polyester, dissolved in vinyl monomer (styrene) with inhibitor
- The unsaturated component in UPRs is maleic/fumaric acid or maleic anhydride
- Rigidity depends on structure of saturated modifying acid
- Thermoset, insoluble and infusible after curing
- Applied hand lay-up or spray-up
- Applications
    - Transportation
    - Construction

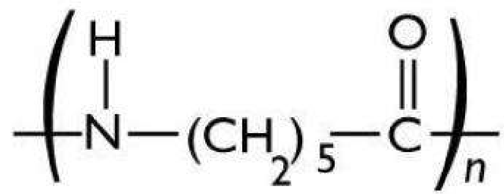


What are Polyamides (PA2)?

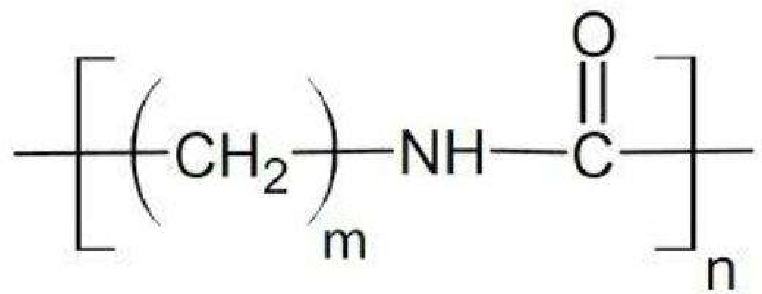
- Chemically (-NH-CO-)
  - n-Nylons
  - Nylon m,n
  - Copolymers
- Common PAs
  - Nylon 6
  - Nylon 11
  - Nylon 12
  - Nylon 6,6,



Nylon 6,6

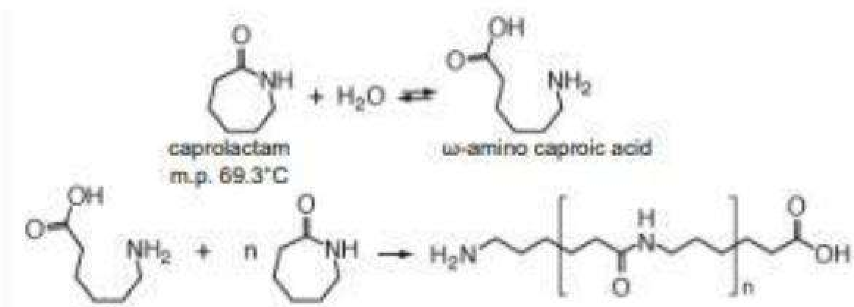


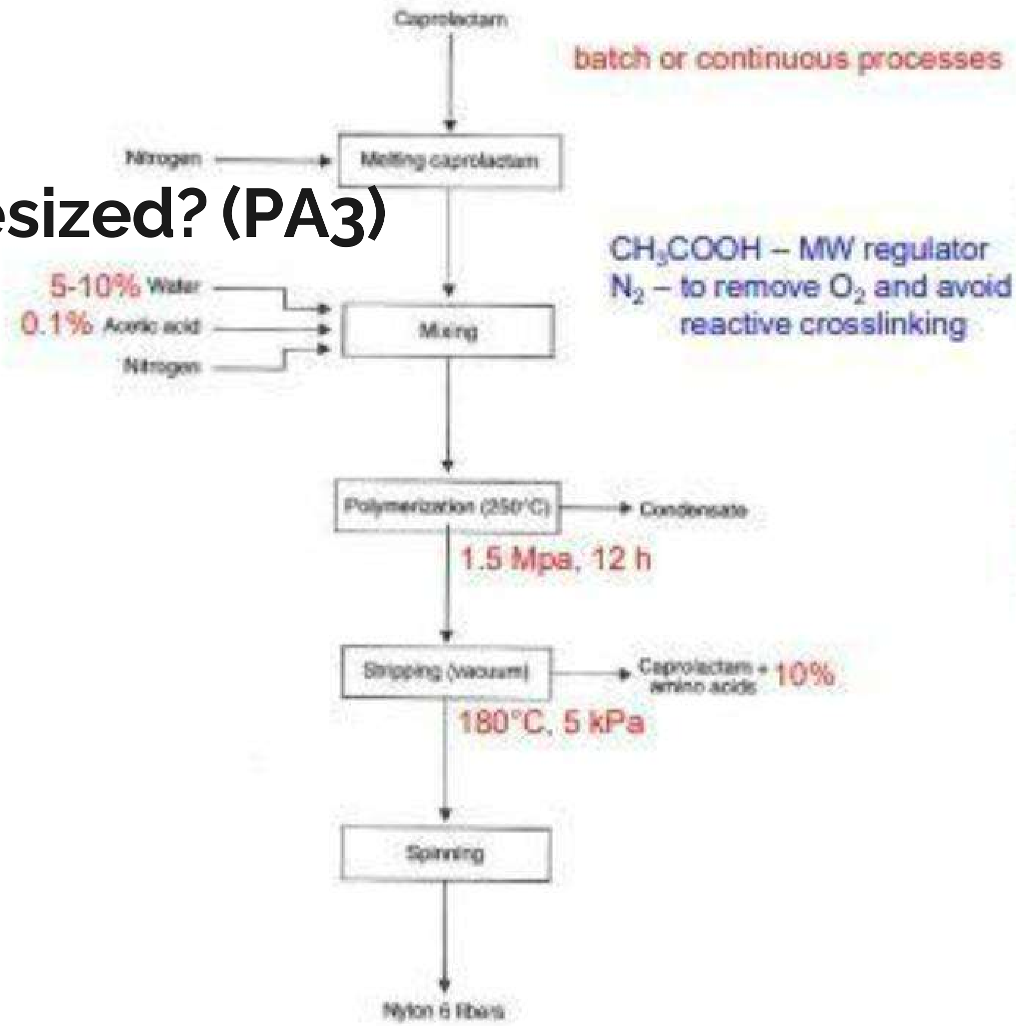
Nylon 6



How are Polyamides Synthesized? (PA3)

- Polycondensation Rxns are common
    - Nylon 6,6 from adipic acid and hexamethylenediamine
- Ring Opening Polymerizations
    - Nylon 6 with caprolactam
- How does this scale up?
    - Hydrolytic Ring Opening Polymerization (Industry) with lactams
    - E.g. Nylon 12 with lauryl lactam





Properties of Polyamides (PA6)

Advantages

- High Tm
- High tensile strength
- High abrasion resistance
- Low linear CTE
- Good solvent resistance
- Good O2 barrier
- Taylored properties with copolymers

Disadvantages

- Absorb moisture
- Low melt viscosity
- Poor UV resistance (need stabilizers)
- Easily oxidized
- Volume shrinkage after crystallization
- Electrical and mechanical properties affected by moisture

Why do we get really nice properties? ⇒ Hydrogen Bonding!

Can we modify Polyamide? (PA8)

YES!

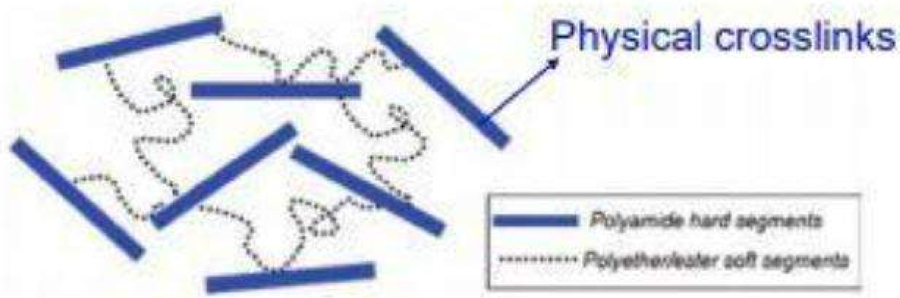
- Nucleating Agents (e.g. silica)
- Heat stabilizers (e.g. copper salts)
- Light Stabilizers (e.g. carbon black)
- Impact Modifiers (e.g. rubber-type materials)
- Other Fillers (e.g. plasticizers)
- Reinforcing Fillers (e.g. glass fibers)

Where can we find Polyamides? (PA9-10)

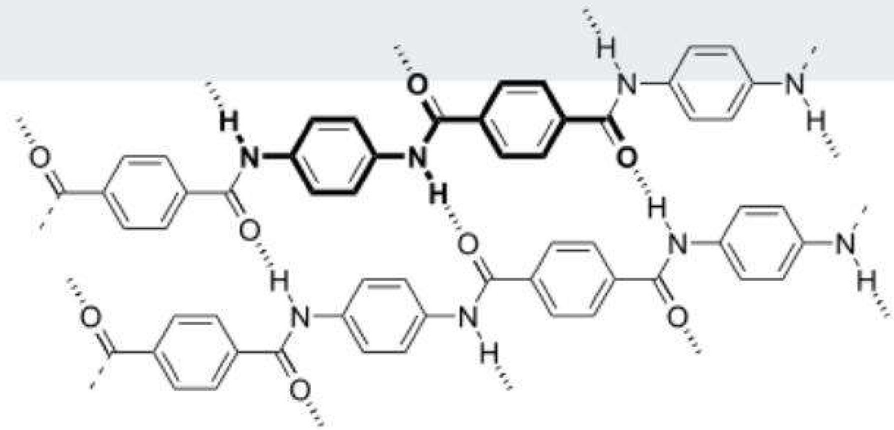
EVERYWHERE

- Fiber applications (e.g. monofilaments)
- Plastics (e.g. clothing or gears)
- Adhesives (e.g. flexible adhesives)
- Appliances (e.g. personal care)
- Automotive
- Consumer Equipment
- Electrical
- Hardware
- Packaging

What are PEBAX/TPEs? (PA11-13)

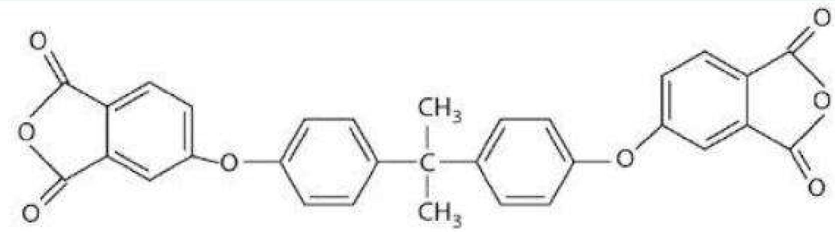


- Polyamide Thermoplastic Elastomers
- Block copolymers
  - Hard segments (e.g. PA 6, PA, 11, PA 12)
  - Soft segments (e.g. PTMO, PEOP, PPO)
- Synthesis = Melt Polycondensation
  - Polyamide + diacid
  - Polyol + polyamide
- High Performance Polymer with High Performance Properties (and $$$)
  - Great Abrasion Resistance and Flexibility
  - Great Chemical Resistance and Mechanical Properties
  - UV Stability
- Multiple Applications



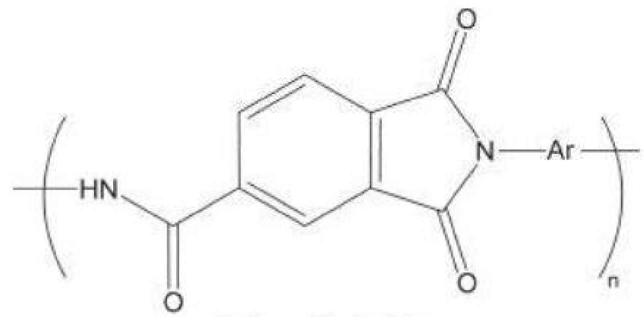
What are Aramids? (PA14-18)

- Aramids = aromatic polyamides
- Can be partially aromatic (multiple copolymers available)
- Example: Kevlar
  - Poly(p-phenylene terephthalamide)
  - Solution Polymerization
  - Great properties (i.e. highest strength among commerical fibers)
  - Highly Crystalline
  - Forms LC in sulfuric acid (Kwolek + Fiber spinning)

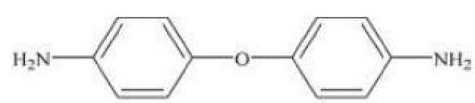


What are Polyimides? (PA19-21)

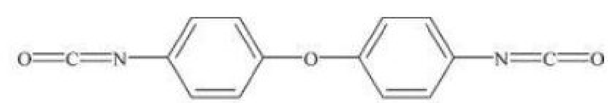
- Chemically (-CO-NR-CO-)
- One or Two step synthesis
- Properties
  - Heat resistance (high Tg)
  - Dielectric Strength
  - Oxidative Resistance
  - Flame Retardant
- Applications
  - Electric motors
  - Jet Engines
  - Flexible Electronics
- Modifications
  - PAIs = Poly(amide-imides)
  - PEIs = Poly(ether0imides)



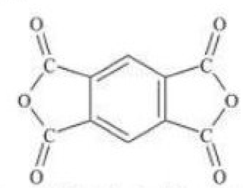
Polyamide-imide



4,4'-diaminodiphenyl ether oxydianiline (ODA)

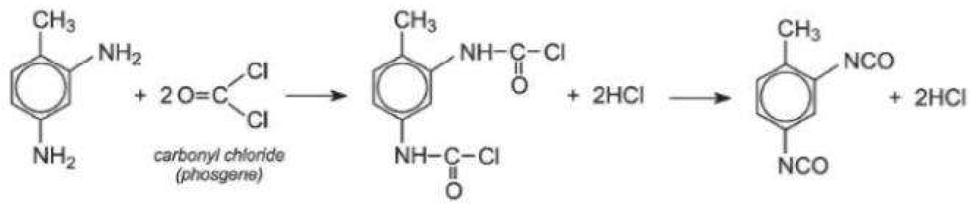


4,4'-Diphenylmethane diisocyanate

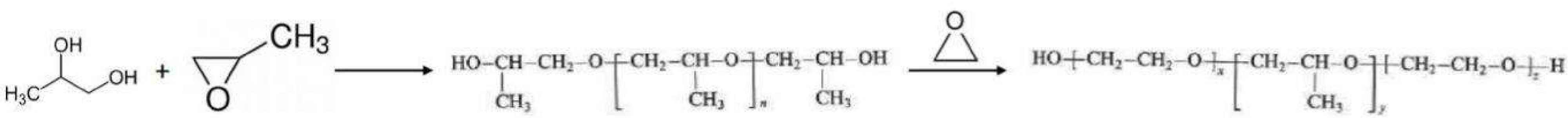


Pyromellitic Dianhydride (PMDA)

Polyurethanes - Formulation (3-11)

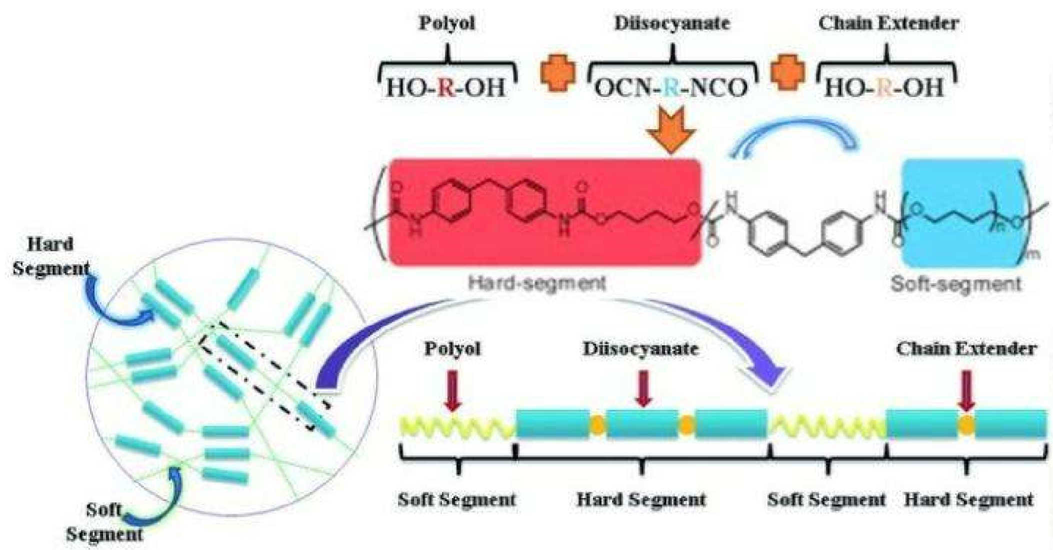


- Made up of urethane groups −NH−(C=O)−O−
- Isocyanates
  - Made via phosgenation
  - Highly reactive from phosgenation
- Polyols
  - Polyethers polyols (PEPs)
  - Polyesters polyols (PESPs)
- Chain Extenders
  - Aromatic diamines and aliphatic or aromatic hydroxyl compounds
- Catalysts



Polyurethanes - Cast PU Elastomers (12-14)

- Diisocyantes + Polyols (soft segment) between Diisocyanates + Chain Extenders (hard segment)
- High abrasion and tear resistance
- Chemical resistance
- Maximum service temp: 120 °C
- Applications: rollers, pipes, molds
- Cannot remelt due to cast and crosslinking



Polyurethanes - Thermoplastic PU Elastomers (15)

- Linear block copolymers
- Can be melted like thermoplastics
- Mechanical strength is temperature sensitive
- Applications:
    - Medical grade catheter,
    - Wire jacketing
    - Adhesives

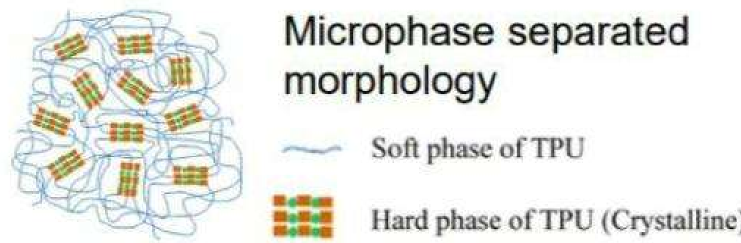


Table 7.6 Some properties of TPUs based on polycaprolactone polyester

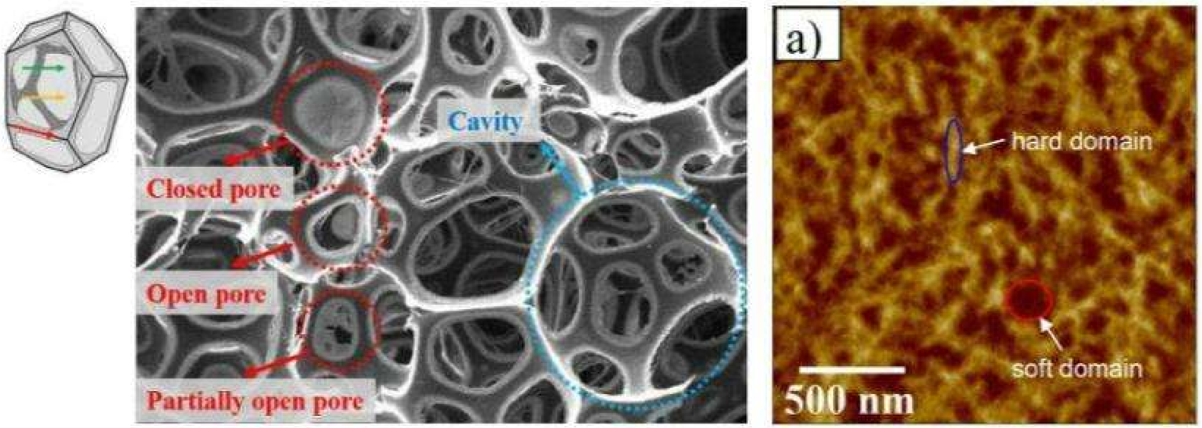
Hardness	80 Shore A	55 Shore D
Tensile strength (MPa)	52	43
Elongation (%)	490	350
Modulus 100% (MPa)	6	20

Polyurethanes - PU fibers & Millable PU Rubbers (16-17)

- PU Fibers (Spandex)
    - Chemical crosslinks through biuret and allophanate structures at elevated temperatures during the curing of fibers.
    - Replaces natural rubber fibers in many applications
- Millable PU Rubbers
    - Crosslinked and processed using conventional rubber roll mills
    - Superior abrasion resistance and mechanical strength

Polyurethanes - PU Foams (18-22)

- Versatile foams, brittle to flexible
- Rigid foams contain more closed cell structure and adds resilience
  - Used for building thermal insulation
- Flexible foams contain more open cell structure
  - Used for cushioning and textiles
- Adding water acts as foaming agent and potential crosslinker



Polym. Adv. Technol. **2018**, *29*, 852-859; *J. Macromol. Sci. Part B: Phys.* 2003, 42, 6, 1125-1139.

Polyurethanes - PU by Reaction Injection Molding (23-24)

- High pressure intensive mixing
- Employs continuous circulation of reactants
- Quick injection into molds
- 1-2 post-curing time
- Can be reinforced with glass (RRIM) to provide a high flexural modulus and low thermal expansion coefficient

Table 7.12 Some properties of PU/urea RIM for automotive applications [68]

Property	*Unfilled*	*15.8% Glass filled*
Density (g/cm^3)	1.02	1.07
Hard segment content (%)	41.1	30.9
Flexural modulus (MPa)		
−29°C	849	618/392*
22°C	405	360/194*
70°C	304	260/137*
Tensile strength (MPa)	26.7	15.2
Elongation (%)	195	125/180*
Coefficient of thermal expansion $\times 10^{-6}/°C$ (from 66°C to 121°C)	170	51/145*

* parallel/perpendicular

Polyurethanes - Coatings, Adhesives, & Sealants (25-28)

Coatings

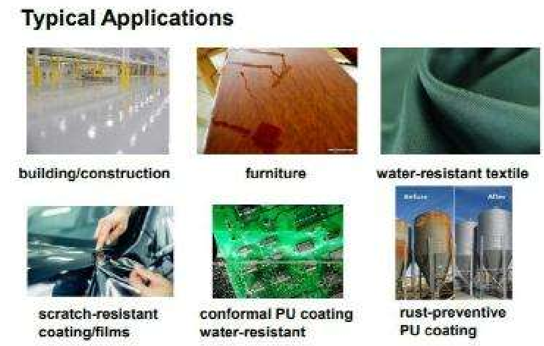
- Strongly adheres to substrate from its polar nature
- Tough and flexible, crack resistant

Adhesives

- Can use water dispersions
- Sticks on most surfaces, whether porous or not
- Not as strong as epoxy adhesives

Sealants

- Stronger adhesion than Si sealants

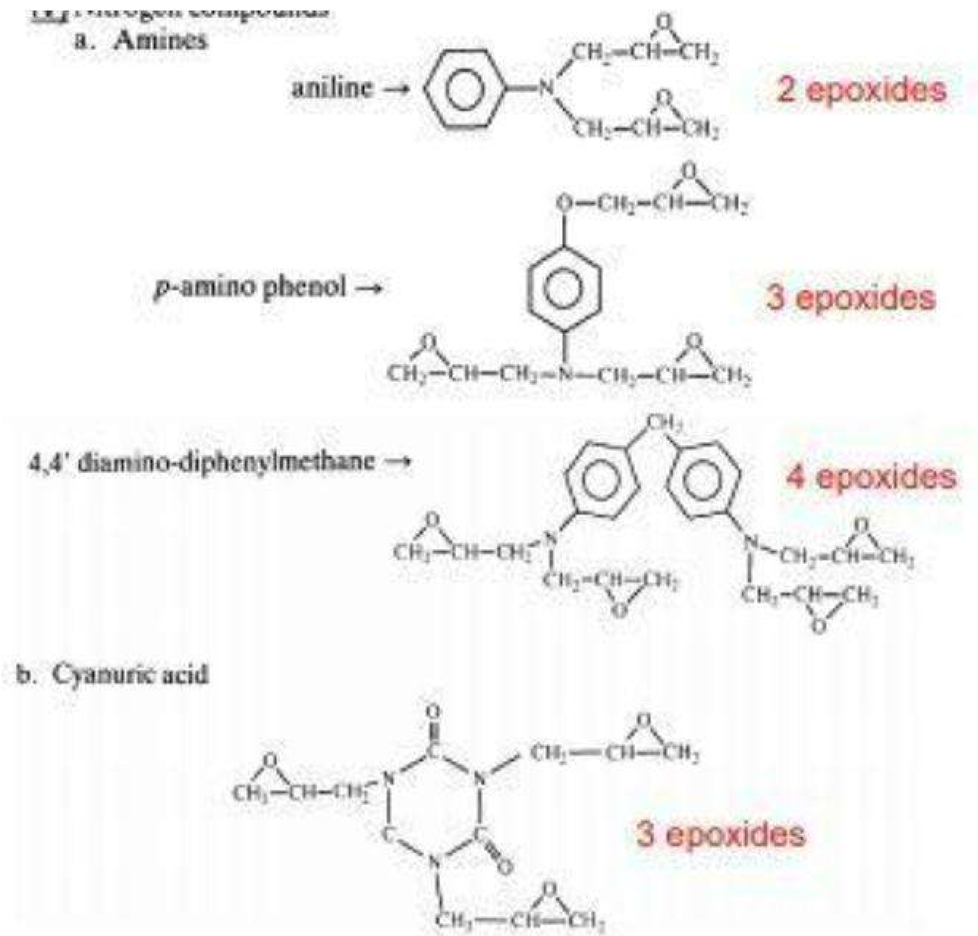


Difference between PU and silicone sealants

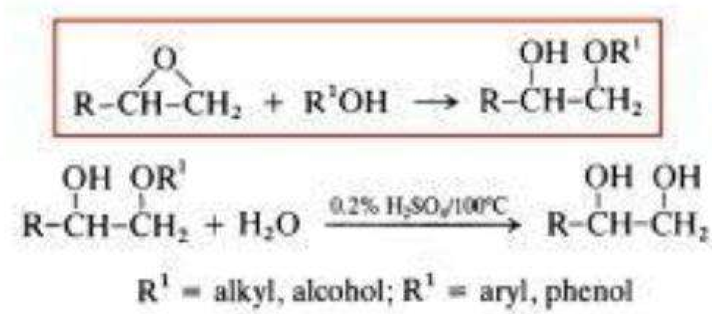
Sealants	PU	Silicone
UV resistance	Not good, need additives	Good
Lifespan	5 years	20 years
Cost	Less expensive	More expensive
Versatility	Less	More
Wood sealing	Good adhesion	Poor adhesion

What are Epoxies? (EP2-3)

- Three-member ring
- Thermoset polymer resin
- General Properties
  - High strength and large cohesive force
  - Good adhesion
  - Excellent stability
  - Flexibility and diversity in design



How do we make Epoxies? (EP4-14)



Variety of ways!

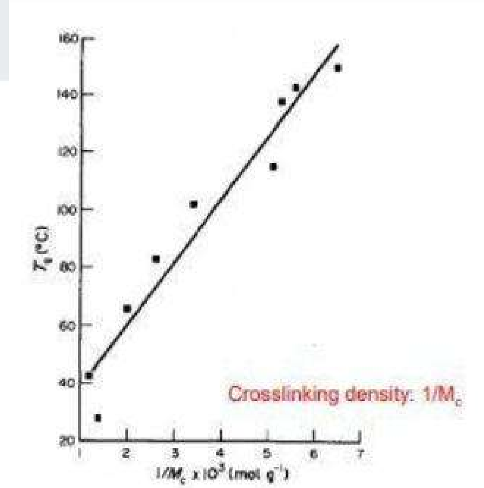
- Phenols, Alcohols, Carboxylic or Fatty Acids, Nitrogen compounds
- Epoxy Prepolymers
  - Bisphenol A Epoxy (Taffy Method)
  - Fusion Method
- Curing
  - Amines (most versatile)
  - Diacids/Anhydrides
  - Various Hardeners have different effects

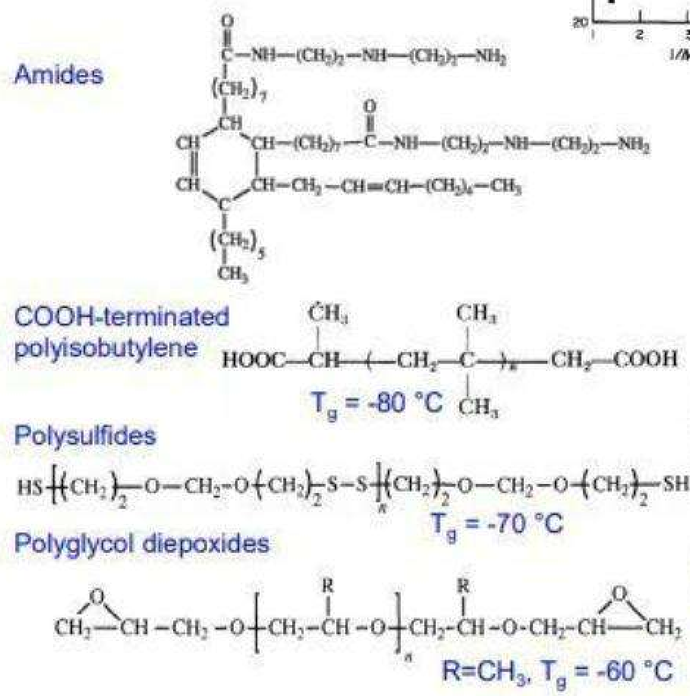
Hardeners	Advantages	Disadvantages
Aliphatic amines	Convenient, low cost, RT cure, low viscosity	Skin irritant and blushes
Aromatic amines	Moderate heat resistance, chemical resistance	Solids at RT, long and elevated cures
Polyamides	RT cure, flexibility, toughness, low toxicity	High cost, high viscosity, low HDT
Anhydrides	Heat and chemical resistance	Long, elevated cures
Polysulfides	Moisture insensitive, quick set	Odor, poor HDT
Catalysts	Long pot life, high HDT	Long, elevated cures, poor moisture resistance
Phenol/formaldehyde	HDT, chemical resistance, hardness	Solid, weatherability

Can we modify Epoxies? (EP17-27)

OF COURSE WE CAN

- Structure Property Relationship
  - Tg is proportional to 1/Mc
- Curing agent affects mechanical properties
- Additives
  - Diluents can be either reactive or unreactive (reduce viscosity, increase wettability)
  - Flexibilizers are reactive (reduce brittleness, increase flexibility)
  - Inorganic fillers (reduce shrinkage and cost)
- Toughening (THINK: airplanes)
  - Resinous additives (i.e. aliphatic polyamides or nylon)
  - Elastomers (BAN, Polysiloxanes, fluoroelastomers)





Applications of Epoxy Composites/Coatings (EP28-30,34)

- Electric Vehicles (Composites)
  - Carbon fiber composites
- Printed Circuit Boards (PCBs) (Composites)
  - Epoxy laminates
  - Need low dielectric constant and low dielectric loss
- Wind Turbine Blades (Composites)
  - Epoxy laminates
- Industrial Flooring (Coating)
- Waterproof Roofing (Coating)
- Concrete Repair (Coating)

- More on Coatings
  - Surface Preparation
  - Solution Coating
    - Control film thickness
  - Dip Coating
    - Good control
  - Water Dispersions
    - Strong mechanical shearing
    - Difficult to achieve uniform dispersions
  - Powder Coatings
    - 100% solid
    - Electrical resistance
    - Corrosion resistance

General Tips for Studying and Last Minute Review

- 120 minutes - pace yourself
- ***Focus on structure-property relationships
- Don’t focus on reaction mechanisms
- Compare types of polymers in each section and how they are processed and applied in industry