

OVERVIEW OF POLYMERIC MATERIALS

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OUTLINE

- What are polymeric materials?
- Types of polymeric materials
- Properties of polymeric materials
- Examples of applications
- Market trends and industrial R&D
- Polymer selection and use for products
- Sourcing of materials
- Supply chain considerations
- Modeling, simulations, and data mining
- Conclusions

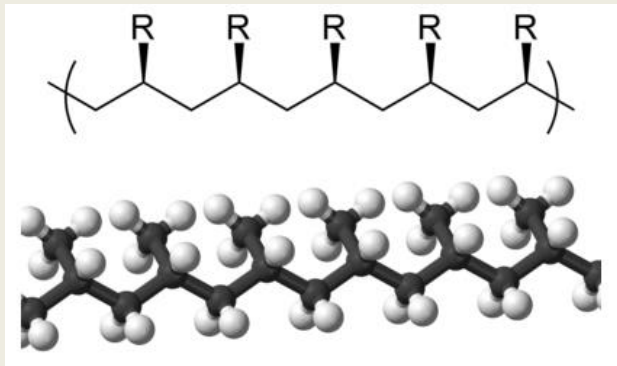
WHAT ARE POLYMERIC MATERIALS?

- Merriam-Webster: A polymer is “*a chemical compound or mixture of compounds formed by polymerization and consisting essentially of repeating structural units.*”
- Wikipedia illustrations of the most common polymer types:
 - 1: Homopolymer with “A” as repeat unit.
 - 2: Alternating copolymer with “A” and “B” as its repeat units.
 - 3: Statistical copolymer (may have some “blockiness” or be completely random).
 - 4: Block copolymer.
 - 5: Graft copolymer.

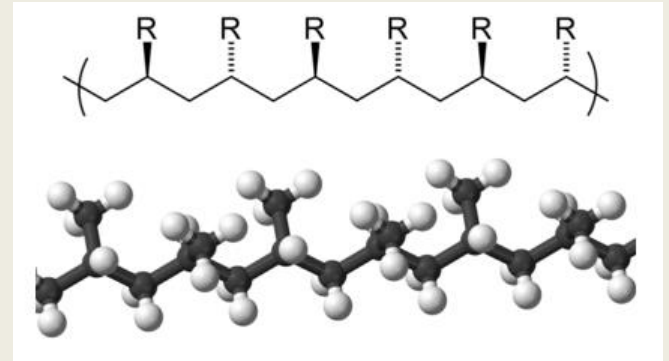


Stereoblock Copolymers

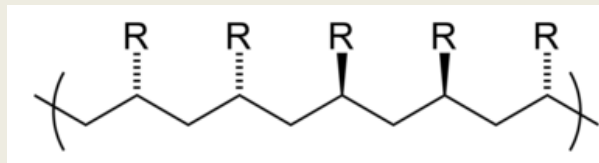
- Some homopolymers have stereoisomeric versions differing in the three-dimensional orientations of their atoms in space.
- Wikipedia illustrations:



Isotactic



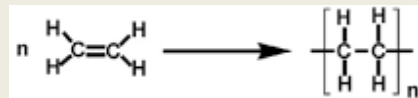
Syndiotactic



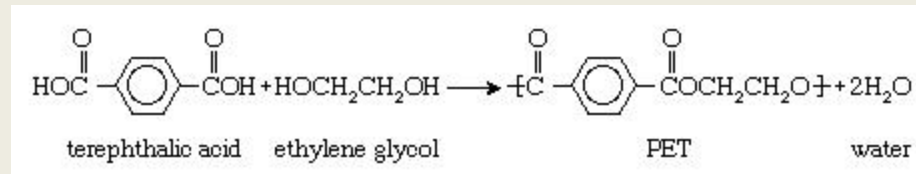
Atactic

Main Classes of Polymerization Reactions

- There are many different polymerization processes.
- These processes can be categorized into two main classes:
 - Addition polymerization.
 - The polymerization of ethylene into polyethylene is an example.
 - All of the atoms present in the monomer are incorporated into the polymer.

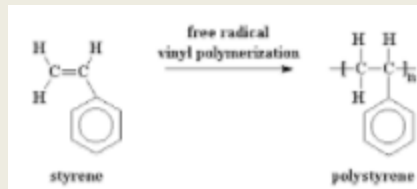


- Condensation polymerization.
 - The reaction of terephthalic acid with ethylene glycol to produce poly(ethylene terephthalate) (PET) is an example.
 - Some atoms present in the monomers are left out of the polymer (in this instance, two H atoms and two $-\text{OH}$ groups which have combined into two H_2O molecules).



Variants Within Same Polymerization Class

- There are many variants, which can produce quite different outcomes, within each class of polymerization processes.
- For example, anionic addition polymerization tends to produce polystyrene chains with much lower variation of molecular weight than free-radical addition polymerization.
 - Free-radical addition polymerization.

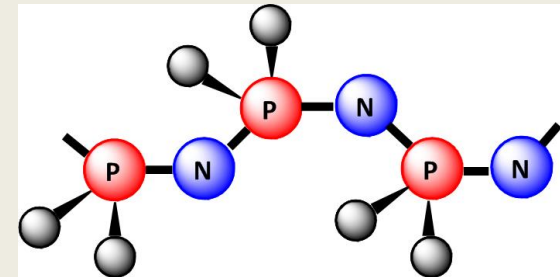
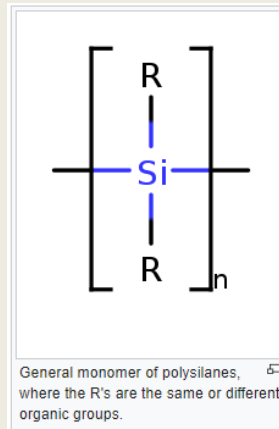
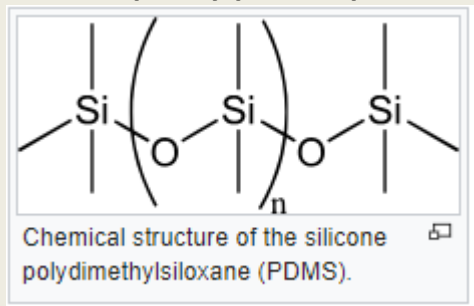


- Anionic addition polymerization.



Some Other Examples of Polymeric Materials

- Those that have covalently crosslinked networks.
- Those that have ionic charges along their chains.
- Those that have inorganic backbones; such as silicones, polysilanes, and polyphosphazenes.



Polyphosphazenes

- Those that are blends of two or more polymers.
- Those that are interpenetrating networks of two or more polymers.
- Those that are composites containing fillers dispersed in a polymer.

TYPES OF POLYMERIC MATERIALS

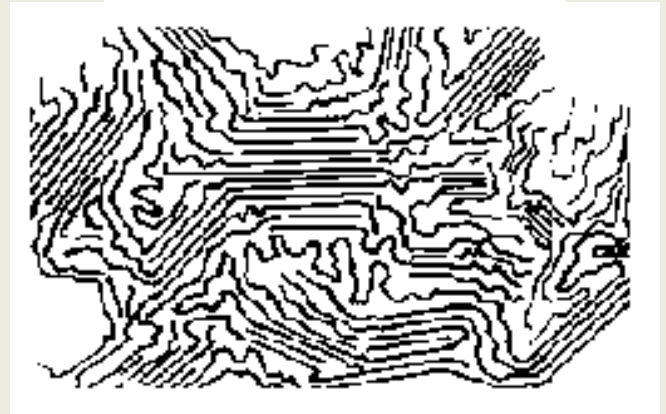
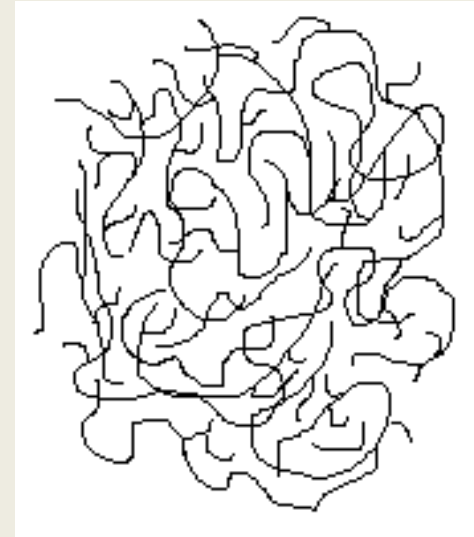
- There are many types of polymers and polymeric composites of commercial interest, as reviewed in the following slides.
- These types of materials span vast ranges of:
 - Monomer sources.
 - Synthesis, compounding, and processing methods used in preparation.
 - Molecular structures.
 - Molecular architectures.
 - Morphologies.
 - Basic material properties.
 - End use performance characteristics.
 - Price and availability.
 - EH&S attributes.

Amorphous and Semicrystalline Thermoplastics, and Their Melts

Schematic illustrations are provided here of typical amorphous random coil (top) and semicrystalline (bottom) morphologies of thermoplastic polymers.

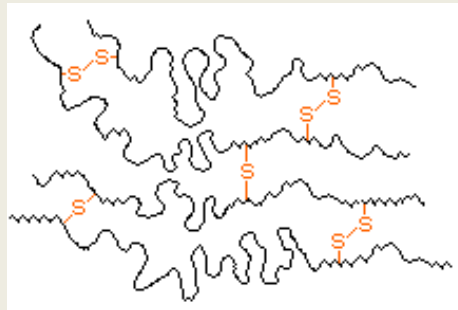
Atactic polystyrene and bisphenol-A polycarbonate are examples of amorphous thermoplastics.

High-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) are examples of semicrystalline thermoplastics. The amorphous and crystalline domains are connected to each other by covalent chemical bonds in a semicrystalline polymer so that a chain may traverse both amorphous and crystalline regions. Chain segments linking two crystalline domains are often called "tie chains". Boundaries between amorphous and crystalline domains are usually diffuse and they are sometimes called "interphase" regions.



Conventional (Thermoset) Rubbers/Elastomers

Covalent crosslinks provide a three-dimensional **elastic network** with "junctions". When the specimen is heated, these junctions survive until their thermal or thermooxidative degradation temperatures are reached. The material is hence a "thermoset", in the sense that once its network structure is formed it can no longer be processed by using melt processing techniques. However, it is also an elastomer (a "rubbery" material) because its glass transition temperature is low and so it has a low stiffness (low elastic moduli, and a lot of "bounce") at typical end use temperatures.



Schematic illustration. The chains of natural rubber (cis-polyisoprene) are crosslinked slightly with sulfur (-S-) linkages by using the "vulcanization" process. There are many other types of elastomers as well, differing from this example by the use of different polymer structures, crosslink types, and preparation processes.

Thermoplastic Elastomers

A three-dimensional **elastic network** is provided by "**physical crosslinks**", such as crystalline and/or rigid glassy amorphous domains in a soft amorphous matrix. Unlike conventional (thermoset) elastomers, thermoplastic elastomers can be processed by using melt processing techniques, since their crystalline and/or rigid glassy amorphous domains can be melted during processing and can then reestablish themselves upon cooling.



Schematic illustration. Evolution of thermodynamic **equilibrium morphology** of a typical AB-diblock copolymer [such as poly(styrene-block-butadiene)] with immiscible A and B components as the volume fraction of the B component (black) is changed. From left to right: spheres of B domains in a matrix of A, cylinders of B domains in a matrix of A, ordered bicontinuous gyroid, lamellar bicontinuous, ordered bicontinuous gyroid, cylinders of A domains in a matrix of B, and spheres of A domains in a matrix of B.

Rigid Thermosets

These materials are, in general, **amorphous** polymers where **covalent crosslinks** provide a three-dimensional **network**. However, unlike conventional (thermoset) elastomers, rigid thermosets are stiff (have high elastic moduli) at their use temperatures (and often up to much higher temperatures) because their particular combinations of chain stiffness and crosslink density characteristics result in a high glass transition temperature. The most familiar examples are the cured epoxy thermosets.



Schematic illustration. Note the similarity to the example of a conventional (thermoset) elastomeric network that was shown earlier. The main practical difference between these two classes of polymers is that rigid thermosets have much higher glass transition temperatures than conventional (thermoset) elastomers.

Gels

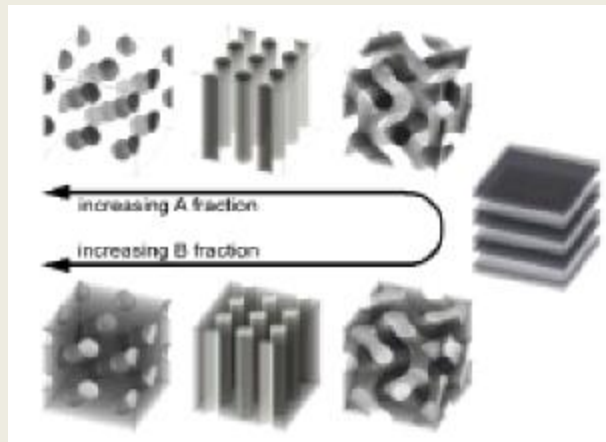
- A gel is a semi-solid jelly-like state of a material, similar to gelatin in its consistency.
- There are many different types of **polymeric gels**. For example:
 - During the synthesis of a crosslinked thermoset from liquid oligomer and curing agent reactants, it increases in stiffness (modulus) rapidly when the "gel point" is reached so that a three-dimensionally percolating network of crosslinks is established.
 - A covalently or physically crosslinked "solid" polymer can form a gel by absorbing a sufficient amount of an appropriately chosen solvent.
 - A **hydrogel** is a gel where water is the solvent.
 - A **smart gel** or **stimuli-responsive gel** (such as certain synthetic polyacrylamide gels) can change its volume (expand or contract), its elastic properties (soften or stiffen), and/or its optical properties (color) rapidly and drastically as functions of small changes in solvent composition, pH, temperature, lighting, electric field, magnetic field, etc.



A gel.

Solutions

Depending on the chemical structure of the solvent and the chemical structure and chain architecture of the polymer, one can find a wide range of behaviors and morphologies, including homogeneous solution, precipitation of the polymer, and a wealth of ordered phases similar to those shown in an earlier slide for block copolymers. An example is shown below.



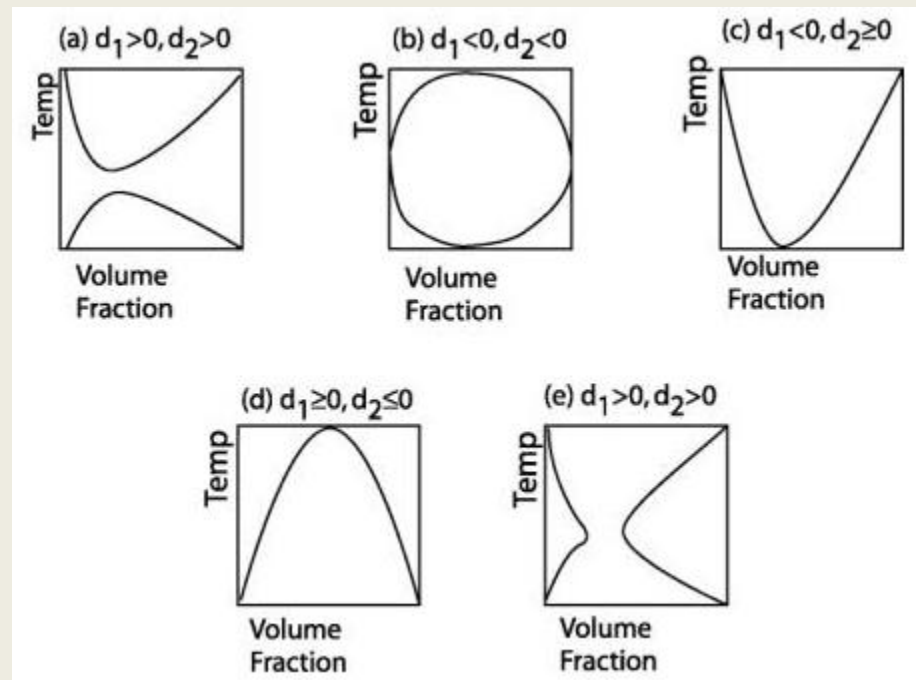
Schematic illustration. Morphologies in mixtures of polyol-based triblock copolymer **surfactants** with water. Going clockwise from the top left, micellar cubic, hexagonal, bicontinuous cubic, lamellar, reverse bicontinuous cubic, reverse hexagonal, and reverse micellar cubic. By definition, the hydrophobic (“oil”) phase domains are enclosed in the continuous water phase in the micellar cubic and hexagonal morphologies, while the water domains are enclosed in the continuous hydrophobic (“oil”) phase in the reverse micellar cubic and reverse hexagonal morphologies.

Blends (1)

- Blends span the entire range from fully **miscible** to completely **immiscible**.
- The thermodynamic drive towards **phase separation** increases with increasing inherent incompatibility and with increasing average molecular weights of polymer chains.
- Unlike block copolymers where highly ordered morphologies (as shown in an earlier slide) are found, one does not normally find ordered arrangements of regularly-shaped domains in a blend since the polymer chains of different blend components are not bonded to each other.
- The blend morphology can be affected significantly by many factors; including:
 - Incorporation of compatibilizers.
 - Kinetic "freezing in" of nonequilibrium morphologies by the application of shear during processing.
 - Annealing at an elevated temperature to release the kinetically frozen-in morphological features and thus approach thermodynamic equilibrium.

Blends (2)

Schematic illustration. Types of possible polymer blend **phase diagrams**, for binary blends where additional complications that can be introduced by competing processes (such as crystallization of a component) are absent. The coefficients d_1 and d_2 refer to a general functional form (as a function of temperature and component volume fractions) of the binary interaction parameter that quantifies deviations from ideal mixing.



Fossil Fuel Based Raw Materials

Polymers spanning the entire range of performance/price balance, from the cheapest **commodity polymers** with low profit margins intended for large volume markets to the most expensive **specialty polymers** intended for niche markets can be obtained from fossil fuel based raw materials by using different polymerization methods.



There is a drive towards enhancing sustainability by replacing fossil fuel based raw materials with biobased raw materials (next slide). While the ideal situation is complete replacement, often only partial replacement is practical due to performance and/or cost constraints.

Biobased Raw Materials

Biobased raw materials are **renewable resources**. Polymers prepared from biobased raw materials include **biopolymers**, such as the polyhydroxyalkanoates and cellulose, which are obtained directly from living organisms such as **plants** and/or **bacteria**. They also include polymers prepared in the laboratory by modifying biopolymers (such as cellulose triacetate) or by polymerizing **biobased monomers** [such as poly(lactic acid)].

The industrial importance of biobased polymers is expected to increase gradually in the future. The main driving forces are the anticipated gradual depletion of petroleum-based raw materials and the potential environmental advantages (possibly resulting in increasing governmental regulations and incentives) of using renewable resources whenever it is cost-effective to do so without sacrificing critical performance attributes.



Examples of biobased sources of polymers. From left to right, a paper birch tree, cotton, soybeans, corn, and a culture of *Wautersia eutropha* bacteria.

Foams

Foams can be **flexible** or **rigid**, **thermoplastic** or **crosslinked**, and **physically foamed** or **chemically foamed**.

- The polymeric structure develops via chemical reactions along with expansion into a foam in a **chemically foamed** system. The most familiar examples of both rigid and flexible chemically foamed materials are polyurethane foams manufactured from different formulations under different processing conditions.
- A previously synthesized molten polymer is expanded into a foam in a **physically foamed** system. The most familiar example is an expanded atactic polystyrene rigid foam.

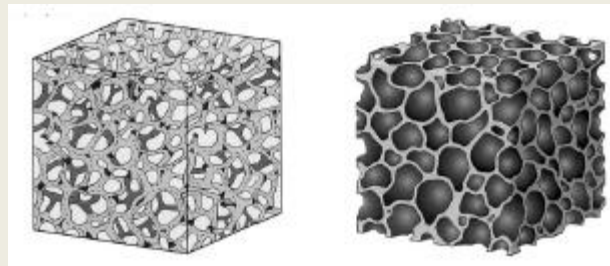
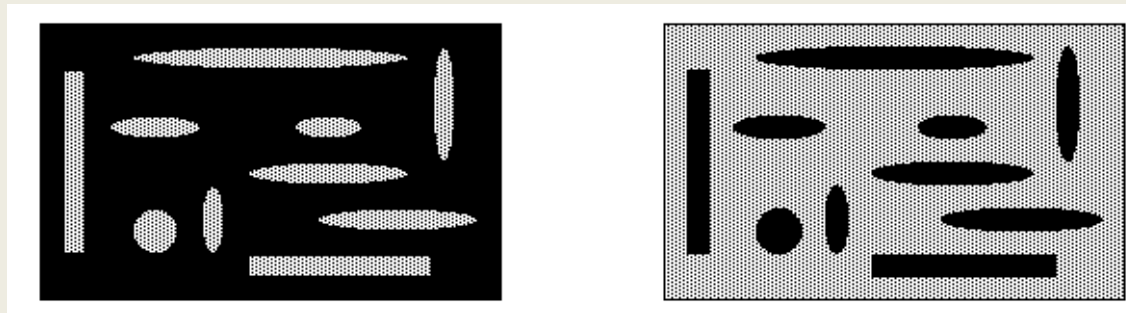


Illustration. Models of slabs of typical **open-cell foams** (left) and **closed-cell foams** (right). The foam cells adopt polyhedral shapes which result from the combination of the physical factors governing the foaming process and the geometrical constraints of packing.

Composites

The term **composite** is often used to describe **matrix** polymers containing conventional **fillers** (such as glass spheres, short fibers, continuous fibers, or talc particles). Composites where (most often highly anisotropic) **nanofillers** (such as carbon nanotubes or "exfoliated" clay platelets) have been dispersed in a polymer are commonly called **nanocomposites**.



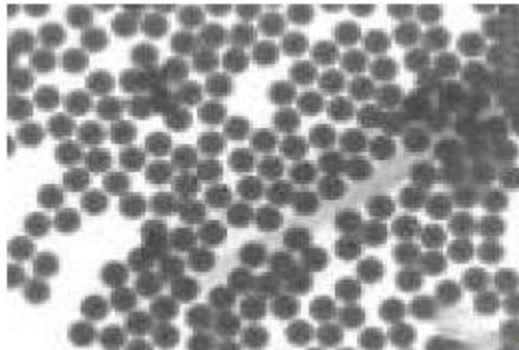
Schematic illustration. A composite consisting of stiff (high-modulus, darkly-shaded) matrix polymer containing flexible (low-modulus, lightly-shaded) discontinuous fillers (left), and a flexible matrix polymer containing stiff discontinuous fillers (right). The properties of a composite depend on the material properties and volume fractions of each component; the shape, orientation and size distributions of each type of filler present in the composite; the strengths of the matrix-filler interfaces, and the sample preparation conditions.

Suspensions

Often also referred to as **dispersions**, the systems of interest most often consist of various types of **particles in ordinary or polymeric fluids**.

The particles can be spherical, fibrous or discoidal in shape. Particles of more than one type of material and/or different shapes may be present in the same suspension.

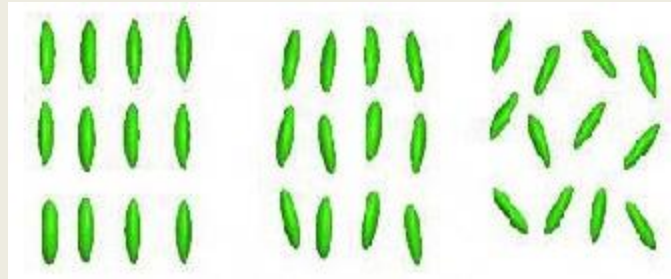
The morphology and the rheological properties of a suspension depend on the same factors as those affecting the properties of composites.



A suspension of monodisperse spherical particles.

Liquid Crystalline Polymers

- From left to right, the key differences between **crystalline order**, **liquid crystalline order**, and **liquidlike disorder** are shown below.



- The molecular arrangement manifests both translational order and orientational order in a crystalline arrangement.
 - Orientational order along a preferred direction is also observed in liquid crystalline arrangements, while the full three-dimensional translational periodicity is lost. There are several types of liquid crystalline order (nematic, smectic, cholesteric and columnar phases), differing in the extent and the details of the order manifested by them.
- Polymers manifesting liquid crystalline order include various "rigid rodlike" aromatic polyamides and polyaromatic heterocyclics. These polymers have very stiff chains which do not readily adopt the random coil conformation found in typical amorphous polymers. But, they also do not pack well into a fully three-dimensionally periodic crystalline lattice because of their molecular shapes. The result is a preference for liquid crystalline order.

PROPERTIES OF POLYMERIC MATERIALS

- The properties of a polymer fall into two general classes:
 - **Material properties** are mainly related to the nature of the polymer itself.
 - **Specimen properties** are primarily consequences of the size, shape and layout of the finished specimens prepared from that polymer, and the process used to prepare these specimens.
- **Morphology** at the microscale and/or the nanoscale plays an especially important role in determining the properties of more complex polymeric materials; such as block copolymers, polymer blends, and polymer matrix composites.
- **Kinetic factors** (determined by fabrication process conditions) can have a major influence on the morphology.

More on Material and Specimen Properties

- Hence the separation of the properties of polymers into these two classes is unfortunately not always straightforward.
- Material properties affect the specimen properties, and fabrication conditions affect the observed material properties.
- Two examples are given below:
 - The density is essentially a material property. The density of a given specimen, however, can be affected by the nature of the specimen. For example, many polymers can be prepared with different percent crystallinities, and hence with different densities, by changing the preparation method or annealing the specimens after preparation.
 - The amount of directional variation ("anisotropy") induced in various physical properties by uniaxial or biaxial orientation ("drawing") is a process-related specimen property. The response of a specimen to a given set of drawing conditions, however, depends on the material properties of the polymer from which it is made.

“Fundamental” Versus “Derived” Material Properties

- **Fundamental properties**, such as the van der Waals volume, cohesive energy, heat capacity, molar refraction and molar dielectric polarization, are directly related to some very basic physical factors.
 - Materials are constructed from assemblies of atoms with certain sizes and electronic structures.
 - These atoms are subject to the laws of quantum mechanics.
 - They interact with each other via electrical forces arising from their electronic structures.
 - The sizes, electronic structures and interactions of atoms determine their spatial arrangement.
 - Finally, the interatomic interactions and the resulting spatial arrangements determine the quantity and the modes of absorption of thermal energy.
- **Derived properties**, such as the glass transition temperature, density, solubility parameter and modulus, are more complex manifestations of the fundamental properties, and can be expressed in terms of combinations of them.
- It is not, however, always straightforward to decide if a property is “fundamental” or “derived” since such a determination can depend on one’s perspective.

Polymer Properties (1)

- **Volumetric properties;** such as van der Waals volume, molar volume, and density.
- **Thermodynamic properties;** such as heat capacity and properties that can be calculated from it (enthalpy, entropy, and Gibbs free energy).
- **Cohesive properties;** such as cohesive energy density and solubility parameter.
- **Transition and relaxation temperatures;** such as glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), heat distortion temperature (HDT), and softening temperature.
- **Interfacial properties;** such as:
 - Surface tension.
 - Interfacial tension, adhesion, and coefficients of friction when in contact with other surfaces.
- **Optical properties;** such as refractive index, optical losses, and stress-optic coefficient.
- **Electrical properties;** such as dielectric constant, dissipation factor, and dielectric strength.
- **Magnetic properties;** such as diamagnetic susceptibility.

Polymer Properties (2)

- **Mechanical properties:**
 - Small-deformation properties; such as moduli (tensile, compressive, flexural, shear, and bulk) and compliances under various modes of deformation, and surface hardness.
 - Abrasion (scratch, mar) resistance.
 - Large-deformation properties; such as yield stress, fracture stress, and fracture toughness.
 - Residual stresses due to thermal expansion coefficient mismatch, such as stresses caused by shrinkage during curing.
 - Long-term properties affecting durability; such as creep resistance, stress relaxation, dynamic fatigue resistance, chemical resistance, ultraviolet (UV) light resistance, and resistance to microorganisms.
 - ✓ The preference for a given type of behavior may depend on the application. For example:
 - ✓ We would want a polymer to have high resistance to microorganisms if it is expected to continue to retain its mechanical properties for a very long time in an application where it is buried under soil.
 - ✓ On the other hand, if we want the polymer to be compostable, we would want it to undergo relatively rapid biodegradation when exposed to microorganisms in a compost pile.
- **Dilute solution properties;** such as steric hindrance parameter, characteristic ratio, persistence length, radius of gyration, statistical chain segment length, and intrinsic viscosity.

Polymer Properties (3)

- **Rheological properties;** such as:
 - Viscoelastic properties under shear or extension.
 - Shear viscosity.
 - Extensional viscosity.
- **Heat transport properties;** such as thermal conductivity and thermal diffusivity.
- **Properties quantifying transport of small molecules;** such as:
 - Solubilities of small molecules in a polymer.
 - Extent of swelling and/or dissolution by small molecules.
 - Diffusivities of small molecules through the polymer.
 - Overall permeabilities of a polymer to different small molecules.
- **Heat resistance properties;** such as:
 - Thermooxidative stability (measured in an environment containing oxygen, most commonly air).
 - Thermal stability (measured in a non-oxidative environment, such as under a nitrogen blanket).
 - Fire resistance.

Price Versus Performance

J. Bicerano, "A Practical Guide to Polymeric Compatibilizers for Polymer Blends, Composites and Laminates", SpecialChem, December 2005.



Figure 1: Schematic illustration of the "commodity trap"; namely, the empirical rule² that, if a polymeric product remains a commodity material competing for use in commodity-type applications, then the price that the average customer is willing to pay for this material will only increase proportionally to the logarithm of the improvement in its performance

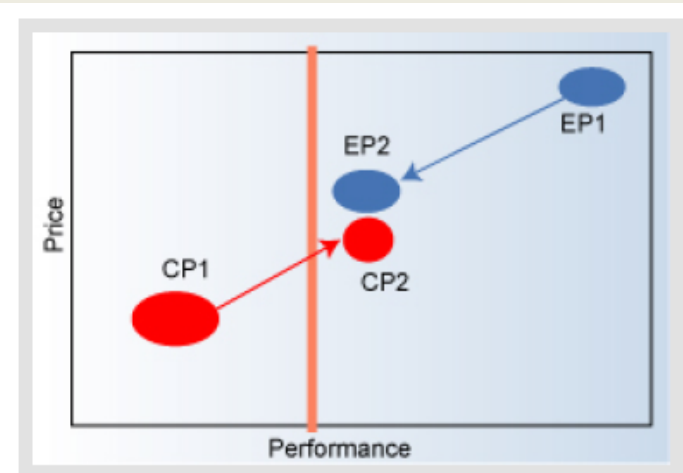


Figure 2: Schematic illustration of two situations where blending and/or compounding are especially attractive from a commercial viewpoint. The thick vertical brown line represents the minimum acceptable performance required to qualify a material for a certain application. The ellipses represent regions on the "price-performance plane". EP1 is an expensive engineering polymer that far exceeds the performance requirements of the application. EP2 is a cheaper blend or composite of EP1 with less expensive ingredients, still exceeding the minimum performance requirements. CP1 is a commodity polymer that does not meet the performance requirements of the application. CP2 is a blend or composite of CP1 that exceeds the minimum performance requirements and can thus be sold at a substantially higher price.

Tradeoffs and Optimization (1)

- The fundamental factors affecting various polymer properties make it difficult to obtain some combinations of properties simultaneously.
- For example, requiring a thermoset to have extremely high stiffness, strength, and heat resistance simultaneously tends to increase its brittleness, so that price-versus performance tradeoffs are often made.
- There tends, therefore, to be a price premium on polymeric materials which combine exceptional characteristics that are difficult to attain simultaneously.

Tradeoffs and Optimization (2)

- There are many ways in which optimum combinations of performance attributes can be obtained, such as:
 - Selection of monomer(s) which polymerize into repeat unit(s) providing optimum property combinations.
 - Consideration of molecular architecture optimization along with optimum repeat unit selection. For example:
 - ✓ Rubber-toughenable thermosets with high T_g are more readily obtained if the high T_g is attained by enhancing the chain stiffness than if it is attained by increasing the crosslink density.
 - ✓ Thermosets prepared from “crosslinkable epoxy thermoplastic” resins are consistently tougher at room temperature than conventional epoxy thermosets of equal T_g .
 - ✓ The next slide provides a schematic illustration of how increasing T_g mainly via increased crosslinking has a detrimental effect on the toughness of an epoxy thermoset.
 - Incorporation of any one or a combination of a broad range of formulation ingredients; such as plasticizers, rigid fillers, and/or elastomeric (rubbery) domains.
 - Optimizing fabrication processing conditions; for example, to induce orientation and/or to take advantage of kinetic effects to “freeze in” an optimum morphology.

Example: Effects of Crosslinking on Thermoset Strength and Toughness

J. Bicerano, *Prediction of Polymer Properties*, third edition (2002).

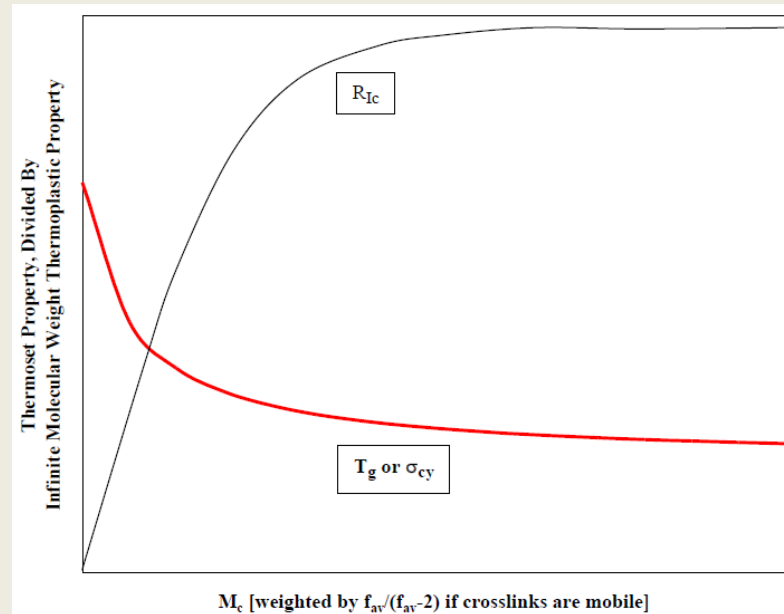
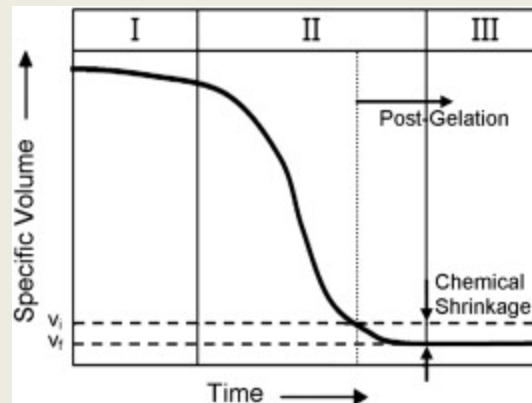


Figure 11.19. Schematic illustration of dependences of glass transition temperature (T_g), compressive yield stress (σ_{cy}), and fracture energy R_{Ic} (G_{Ic} for brittle networks and J_{Ic} for ductile networks), on average molecular weight between crosslinks (M_c). If the crosslinks are mobile, then the variable along the x-axis becomes $M_c \cdot f_{av}/(f_{av}-2)$, where f_{av} is the average crosslink functionality. The depiction of a single curve for the normalized values of T_g and σ_{cy} is for simplicity, since the curve for T_g may lie above or below the curve for σ_{cy} depending on the value of b in Equation 11.44 for a given family of thermosets. The normalized R_{Ic} typically begins to decrease catastrophically with further crosslinking beyond the crosslink density at the rapid upturn in T_g and σ_{cy} , and varies over a much wider range than the normalized T_g and σ_{cy} .

Example: Shrinkage as a Source of Residual Stress (1)

- Thermosets are often used in intimate contact with materials of much lower coefficient of linear thermal expansion. For example:
 - A thermoset film may be coated on a surface, or sandwiched between two surfaces as an adhesive.
 - A thermoset matrix may be filled with high-modulus fibers in aerospace structural materials and in other composite materials.
- A residual stress can build up in all such systems because of shrinkage caused by the different volumetric responses of the thermoset and the other material(s) to changes in temperature.
 - This residual stress typically reflects the balance between the driving force to produce residual stresses due to differential shrinkage upon cooling and the temperature-dependent capacity to relax these stresses.
 - The worst such effects usually occur as the temperature drops below the T_g of the thermoset during or after curing.



Example: Shrinkage as a Source of Residual Stress (2)

- Residual stresses resulting from shrinkage during curing can cause specimens to warp and distort, and sometimes even to fail during use.
- The shrinkage in the glassy temperature region and the internal stress both depend on the difference between T_g and the measurement temperature.
- The following equation provides a crude approximation based on a general theory for the elastic interactions in a composite plate of layers with different relaxed planar dimension :

$$\sigma_r = \frac{E_1 \cdot E_2 \cdot t_2 \cdot (T - T_g) \cdot (\beta_2 - \beta_1)}{E_1 \cdot t_1 + E_2 \cdot t_2}$$

- σ_r : Residual stress.
- E_1 and E_2 : Tensile (Young's) elastic moduli of the thermoset (Material 1) and the substrate (Material 2).
- t_1 and t_2 : Thicknesses of the layers of thermoset and substrate.
- $(\beta_2 - \beta_1)$: Difference between the coefficients of linear thermal expansion ($\beta_2 < \beta_1$, and in many cases $\beta_2 \ll \beta_1$).
- $(T - T_g)$: Difference between the use temperature (T) and the glass transition temperature of the thermoset (T_g); with $(T - T_g) < 0$, and in many cases $(T - T_g) \ll 0$.
- The increasingly more accurate estimation of such residual stresses caused by shrinkage and the development of approaches for their reduction is a very active area of experimental, theoretical, and computational materials science.

EXAMPLES OF APPLICATIONS

- Polymers are ubiquitous, with literally no industry in which they are not used extensively.
- Here are some of the vast range of applications of polymers:
 - Textiles (cotton, polyester, polyamide, acrylic, spandex, etc.).
 - Footwear.
 - Plastic pipes.
 - Rubber hoses.
 - Rubber tires.
 - Rubber gloves.
 - Foam insulation used in appliances and construction.
 - Vinyl (PVC) siding for buildings.
 - Polyurethane foam seat cushions.
 - Polycarbonate eyeglass lenses.
 - Plastic and rubber toys.
 - Personal care products (such as combs, toothbrushes, components of shavers, etc.).
 - Adhesives (glues) of various polymeric compositions.
 - Polyester (PET) bottles.
 - Structural components used by the transportation industry (in cars, trucks, boats, airplanes, etc.).
 - Under-the-hood components used in cars and trucks (as in electric power steering systems).
 - Casings, enclosures, and boxes for electronic devices.
 - Applications of conductive polymers as antistatic materials, and in displays and batteries.
 - Catheters and stents.
- Some additional interesting applications will be discussed next in more detail.

Crop Growth and Protection

- Plastic containers and pots (mostly manufactured from molded polystyrene or polypropylene) as replacements for clay containers and pots.
- Greenhouses, farm buildings, and agricultural equipment using a wide variety of thermoplastic polymers as materials of construction.
- Soil conditioners (polymeric surfactants and flocculants, such as many types of water-soluble polymers and hydrogels).
- Seed coatings (such as hydrogels).
- Mulch films (such as polyethylene as well as other types of polymer films).
- Nettings for plant and crop protection.
- Various types of superabsorbent polymers used in controlled irrigation:
 - Absorb water and swell (but do not dissolve) when the water concentration in soil is high.
 - Release the absorbed water when the water concentration in soil is low.
 - Can go through many reversible cycles of water absorption and release over a very long time.

Polymeric Delivery Systems

- Polymeric media are used widely in delivery systems for flavors, fragrances, and drugs.
- My own experience includes much work on tablets used for the controlled release of drugs.
 - Hydroxypropyl methylcellulose (HPMC) was used as the sustained release medium in the oral delivery of drugs.
 - Lactose was included in the HPMC matrix to improve tablet compaction (crushing) properties.
 - Statistically designed experiments were used to optimize the HPMC/lactose tablet composition.
 - A theoretical model was implemented and applied to predict the release kinetics of various drugs from such tablets.

Figure 1. Model requirements.

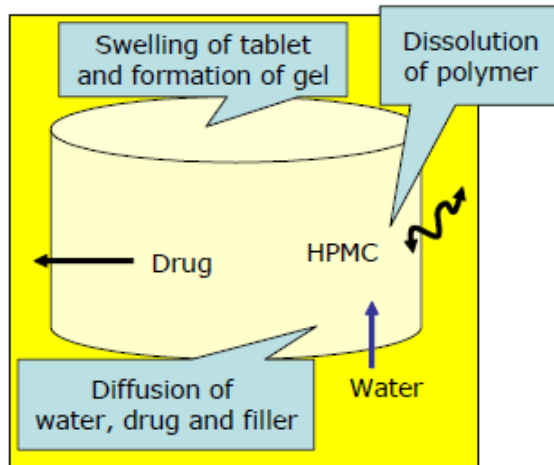
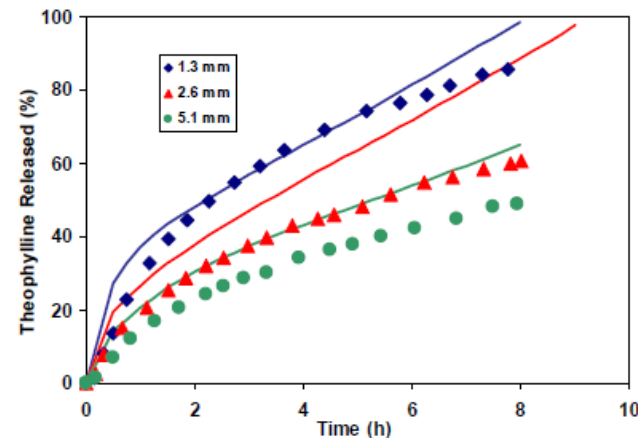


Figure 6. Predicted and experimental theophylline release.



Paints and Coatings


- Polymers are used in a vast range of paints and coatings.
- Acrylic polymers are most commonly used in polymeric paints.
 - Fast-drying.
 - Made of a pigment suspended in an acrylic polymer emulsion.
 - Water-soluble, but become water-resistant when dry.
- Coatings are sometimes used on textiles to modify their surface characteristics (such as comfort, water vapor transmission, liquid water absorption resistance, etc.)
- Polymeric coatings to protect metal components from corrosion:
 - Fluoropolymer coatings.
 - Epoxy coatings.
 - Phenolic coatings.
 - Polyurethane coatings.
 - Poly(phenylene sulfide) coatings.
- Some corrosion-resistant coatings contain pigments and hence also function as paints.
- There are countless other examples of polymeric coatings.




A Unique High-Value Application of Elastomers

- Ultrasoft thermoplastic elastomers of various compositions can be used to construct anatomically realistic ultrasound training models for medical personnel.
- For example, the picture below shows some such deservedly expensive products offered by CAE Healthcare which is one of the leaders in this technology area.


By Anatomy - Heart




[FAST Exam Real Time Ultrasound Training Model](#)
Starting at: \$27,040.00



[Vimedix Cardiac Echo Simulator](#)



[Transthoracic Echo and Transthoracic Echo Training Model](#)
Starting at: \$24,440.00



[Transthoracic Echocardiography and Pericardiocentesis Ultrasound Training Model](#)
Starting at: \$17,160.00

Additives

- Polymeric materials are used as additives in a vast range of applications.
- One major class of a very broad range of such applications involves the use of polymeric additives as formulation ingredients for the compatibilization of incompatible components in multicomponent systems: J. Bicerano, "*A Practical Guide to Polymeric Compatibilizers for Polymer Blends, Composites and Laminates*", SpecialChem, December 2005.
- Other important examples include the use of polymeric additives as impact modifiers and as lubricants.

MARKET TRENDS AND INDUSTRIAL R&D

- The trend of innovative technology leaders is to:
 - Divest from “cash cow” commodity markets involving product line extensions in existing markets by spinning off, selling, or shutting down commodity businesses.
 - Investing increasing amounts of R&D funding towards product line extensions into new markets, new product launches in existing markets, and most ambitiously new product launches into new markets.
- The next six slides will provide examples in three specific areas.

Biopolymers (1)

- See my presentation titled “*Environmentally Sustainable Polymer Development Through Feedstock Selection*” (2014) for a more detailed discussion of this topic.
- The following were the industry statistics as of 2014:
 - Global plastics industry:
 - ~ \$ 830 billion annual revenues.
 - ~ 2.8% annual growth rate.
 - Biobased industry:
 - ~ \$ 2.6 billion annual revenues.
 - ~ 15% annual growth rate.
- Many plants and microorganisms are biobased feedstock sources for obtaining and/or deriving monomers, oligomers, polymers, and/or biofibers.

Biopolymers (2)

The following are some significant agricultural sources of biobased feedstocks:

- Starch: Corn, sugar cane, sugar beets.
- Glucose: Corn, sugar cane, sugar beets.
- Cellulose: Switch grass, bamboo, eucalyptus.
- Vegetable Oil: Corn, soy, castor, rapeseed (canola), cottonseed, palm, algae.
- Vegetable Protein: Soy.
- Cellulosic Biofibers: Cotton, jute, kenaf, hemp, flax, sisal, ramie, corn, wheat, rice, sorghum, barley, sugarcane, pineapple, banana, coconut.

Biopolymers (3)

The following are some examples of biobased polymers [from R. P. Babu, K. O'Connor, and R. Seeram, “*Current Progress on Bio-based Polymers and Their Future Trends*”]:

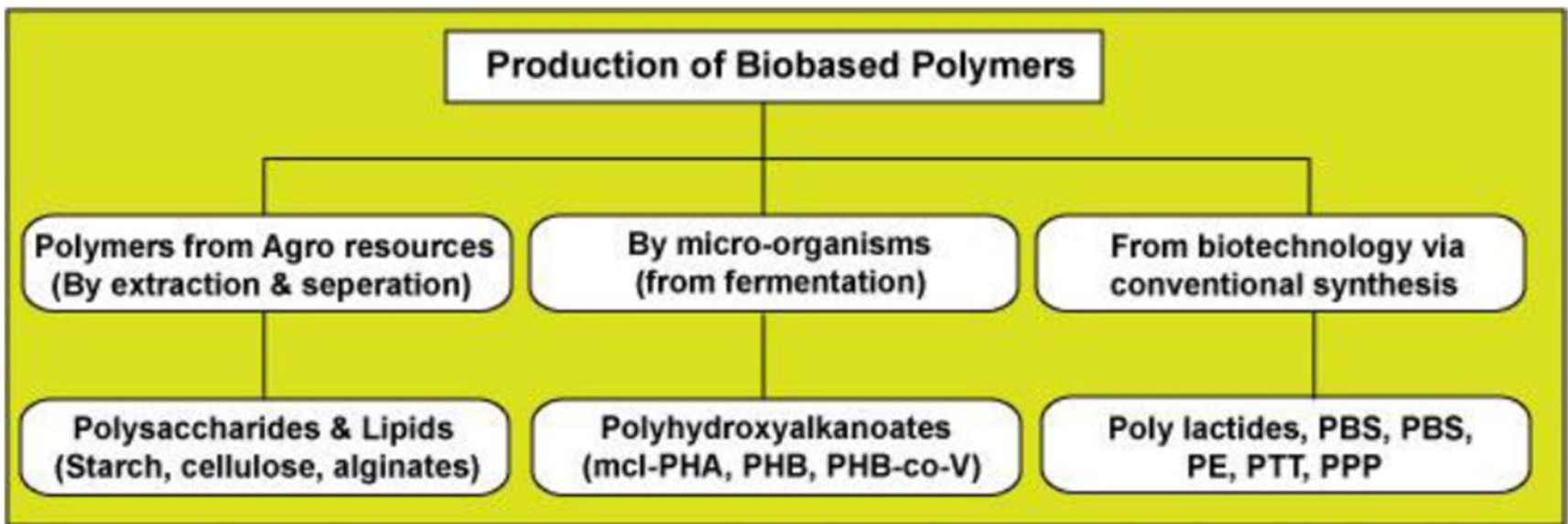


Figure 2: Most Common Categories of Bio-based Polymers Produced by Various Processes

New Formulations

- The most important frontier in new formulations is the development of nanoparticle-containing formulations that provide increasingly more exceptional combinations of performance characteristics while remaining processable during product fabrication.
- Carbon black, single-wall or multi-wall carbon nanotubes, boron nitride nanotubes, carbon nanofibers, graphene nanoplatelets, fumed silica, fumed alumina, cellulosic nanofibers, fly ash, polyhedral oligomeric silsesquioxanes, metal nanowhiskers, and metal nanoclusters are some examples of nanoparticles that may be used.
- Nanoparticles may be dispersed either in liquids or in polymers, as in:
 - Fluids possessing unique magnetic properties as a result of the incorporation of magnetic nanoparticles.
 - Fluids containing nanoparticles that are either coated onto or absorbed by textile products to improve their properties and in some instances to even impart the textile product with new attributes.
 - Fluids containing nanoparticles in a reactive precursor mixture that polymerizes, to form a thermoplastic or thermoset (which may be either rigid or elastomeric) polymer matrix nanocomposite.
 - Moldable and/or extrudable compounds of nanoparticles in thermoplastic polymers.
- Usually the main challenge is to disperse the nanoparticles very well in the desired medium, since otherwise the nanoparticles will not provide the desired level of improvement.
 - Higher nanoparticle anisotropy provides greater potential of obtaining exceptional improvements at the same volume fraction, but at the expense of making the achievement of excellent dispersion more difficult.

Polymerization Processes

- Addition and condensation polymerization continue to remain the two main classes of polymerization processes.
- Advances in polymerization processes mostly involve the development of increasingly more effective formulations and processing conditions for specific processes within these two classes to obtain precisely targeted products of higher quality at higher yield and lower cost.
- The following are selected examples:
 - The development and coming of age of metallocene catalyst technology for olefin polymerization was one of the most important developments of the last 30 years.
 - Progress continues to be made incrementally in suspension polymerization (an area where I hold many patents) and emulsion polymerization processes.
 - Various existing polymerization approaches are being improved (quantitatively significantly but qualitatively mostly incrementally) to enhance the effectiveness of plastics recycling efforts.
 - Solid state shear pulverization (SSSP) is emerging as a method that operates near ambient conditions and that may contribute significantly both to the recycling of polymers such as PET and to the more cost-effective manufacturing of various engineering plastics with higher quality and performance.
 - The development of [Molecularly Imprinted Polymers \(MIPs\)](#) is an exciting new polymerization technology frontier, with [Ligar Polymers](#) as a company whose leading-edge MIP technology I have previously studied in some detail during the course of a past project for another client.

Applications

- A vast amount of industrial R&D is in progress to achieve product line extensions into new markets, new product launches in existing markets, and most ambitiously new product launches into new markets.
- This industrial R&D is pushing the frontiers of the applications of polymeric materials in every industry where such materials are used; namely, in every industry in the world.
- It is difficult to justify singling out just one or two of such application development efforts as being of uniquely greater interest than all others.
- Perhaps this topic merits a separate full lecture of its own to cover in a meaningful way.

POLYMER SELECTION AND USE FOR PRODUCTS

Selection Process:

- The required processing behavior during fabrication and the end use performance characteristics are defined as precisely as possible.
- Price is also usually an important consideration.
- Potential candidate materials are selected based on these criteria.
- Samples are obtained from material suppliers and evaluated.

Anonymous Case Studies (My Work):

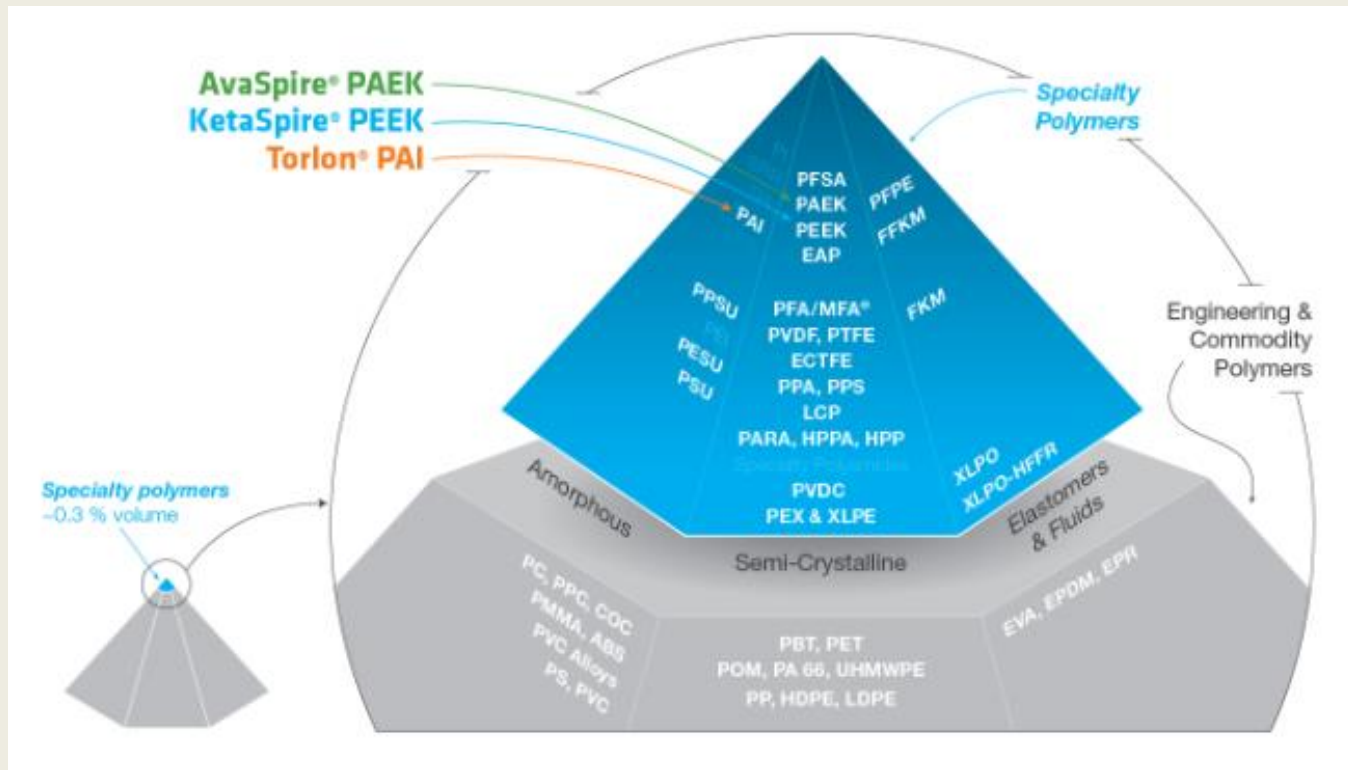
- A thermoplastic product.
- A thermoset product.
- A product that needed additives to achieve its performance targets.

Thermoplastic Material Selection (1)

- The client was interested in FDA-compliant, non-outgassing, and chemical-resistant material selection for a molded thin-walled thermoplastic product that would need to withstand long-term use at a temperature of 250 °C.
- The cost of the material could not exceed \$ 10/lb for large volume purchases because of the assumed limit to how much customers are likely to be willing to pay for the molded product.
- Online databases (Omnexus, MatWeb, UL Prospector, CAMPUS) of thermoplastic materials were searched to obtain preliminary ideas on potential candidate materials.
- More detailed product literature provided online by material suppliers was studied to refine these preliminary ideas.
- Customer technical service personnel at each company manufacturing a potential candidate material were contacted to discuss the need in detail and obtain recommendations of their specific commercial product grades that they recommend for evaluation.
- These recommendations were put together into a report.
- The client molded product prototypes from each of the recommended thermoplastic polymers and evaluated these prototypes to determine the best thermoplastic to use for the targeted application.

Thermoplastic Material Selection (2)

The chart pasted below was copied from the website of Solvay which is the world's leading supplier of high-performance thermoplastic polymers. It illustrates some of the vast variety of available choices for selecting a polymer that meets the desired performance and price targets.



Thermoset Material Selection

- The client was interested in a high-performance monolithic machine part, to be cast in place at room temperature within a cavity in the machine from a suitable thermosetting resin.
- It was determined that the versatility of epoxy resin chemistry provides the best design space to seek suitable ingredients for use in manufacturing this product.
- Customer technical service personnel at the three leading global providers of epoxy resins and related intermediates (Hexion, Huntsman, and Olin) were contacted to discuss the need.
- Each provider recommended a short list of combinations of its epoxy thermoset precursors (resin, curing agent, and in some formulations also a reactive diluent) to evaluate.
- These recommendations were put together into a report.
- The client evaluated the recommended formulations in laboratory experiments on smaller-scale samples to determine the optimum formulation for use in the machine part.

Polymeric Additive Selection

- The product under development was a nanocomposite wherein a reinforcing nanofiller was dispersed in a thermoset polymer matrix.
- The manufacturing method involved the dispersion of the nanofiller within the unreacted monomer liquid followed by heating up the dispersion while stirring vigorously to polymerize the monomer and thus convert the liquid into a rigid thermoset matrix.
- The main challenge was that the nanofiller and the monomer liquid were quite incompatible with each other so that the nanofiller dispersion was poor, resulting in poor mechanical properties for the finished thermoset nanocomposite product.
- It was determined that the best way to solve this problem would be to include two types of additives in the formulation:
 - A polymeric dispersant which will situate itself between the monomer and the nanoparticles to render the thermodynamics of the system more favorable to providing improved dispersion.
 - A polymeric coupling agent which will react both with the polymer and with the nanoparticles, thus improving the load-bearing performance by grafting the nanoparticles unto the thermoset network.
- Recommendations were obtained from the leading suppliers of polymeric additives for which ones among their vast ranges of such products to evaluate.
- The recommended additives were evaluated to determine the best dispersant and coupling agent to use and the optimum percentage of each additive to use in the formulation.

SOURCING OF MATERIALS

- There are three different general approaches for selecting and sourcing materials for use in formulations and compounding:
 - Internal sourcing of materials.
 - Sourcing of materials from suppliers.
 - Use of formulation and compounding service providers.
- Companies often use a combination of at least the first two resources, and some companies use all three resources.
- These approaches will be discussed in the next three slides.

Internal Sourcing of Materials

- Companies sometimes practice vertical integration of their supply chain by sourcing the key building blocks used in producing their polymeric products internally. For example:
 - Dow Chemical once produced both styrene monomer and polystyrene made from this monomer.
 - It [sold or shut down many styrene manufacturing plants](#) and also [spun off its styrenic polymers business and some other businesses as Trinseo](#) in divesting itself of low-value commodity businesses.
- Dow Chemical is [the world's leading supplier of polyether polyols](#) while also providing (through Dow Automotive Systems) [polyurethane foam technologies for automotive use](#).
 - Dow Chemical provides the technology and some of the key precursor formulation ingredients for its implementation, but foaming is normally done at a customer's automotive manufacturing facility.
 - In other words, in this case, selling the precursors and the technology is both more convenient and of greater value than selling the finished product.
- On the other hand, [Avantium](#) (a small entrepreneurial company) manufactures both the furanics family of biobased monomers and poly(ethylene furanoate) which is a completely biobased thermoplastic polymer intended to serve as a more sustainable alternative to PET.
- Hence companies pursue whichever strategy is likely to generate the greatest value.
- This strategy may involve any one or any combination of:
 - Internal or external sourcing of key polymer building blocks.
 - Licensing or teaching of polymerization technologies for using those building blocks.
 - Preparing the polymers in their own facilities.

Sourcing of Materials from Suppliers

- It was seen in the previous slide that:
 - Producers of finished polymeric products (such as polystyrene or an automotive polyurethane foam) will very often (but not always) purchase the key building blocks (such as styrene monomer or polyether polyol) from other suppliers.
 - Sometimes one company will produce both a building block and a finished polymeric product made from that building block.
- Polymeric products often also contain additives used to enhance processability (catalysts, surfactants, rheology modifiers, etc.) and/or end use performance (plasticizers, impact modifiers, dispersants, coupling agents, fire retardants, etc.).
 - Most often, the manufacturer of a finished polymeric product will purchase most or all of the additives it needs from companies that specialize in manufacturing additives.
 - There are a few different leading suppliers specializing in the manufacture and sale of product families of each of the major different types of additives.

Formulation and Compounding Service Providers

- Another approach sometimes used by polymeric product manufacturers is to work with formulation and compounding service providers to obtain either complex combinations of ingredients used in manufacturing their products or to obtain the products themselves.
- For example:
 - [Clariant](#) is a global leader in color and additive concentrates and performance solutions for plastics. It produces masterbatches for six separate market segments (Packaging, Consumer Goods, Medical Pharma, Fiber, Automotive, and Agriculture), each of which focuses on the customer's individual needs.
 - [RTP Company](#) is a leading thermoplastic compounder. It offers a wide range of technologies, available in pellet, sheet, and film forms, that are designed to meet challenging application requirements.
 - [Adhesives Technology Corporation](#) is a contract manufacturer of epoxies, polyurethanes, polyureas, polyesters, methacrylates, and their hybrids for its clients.

SUPPLY CHAIN CONSIDERATIONS

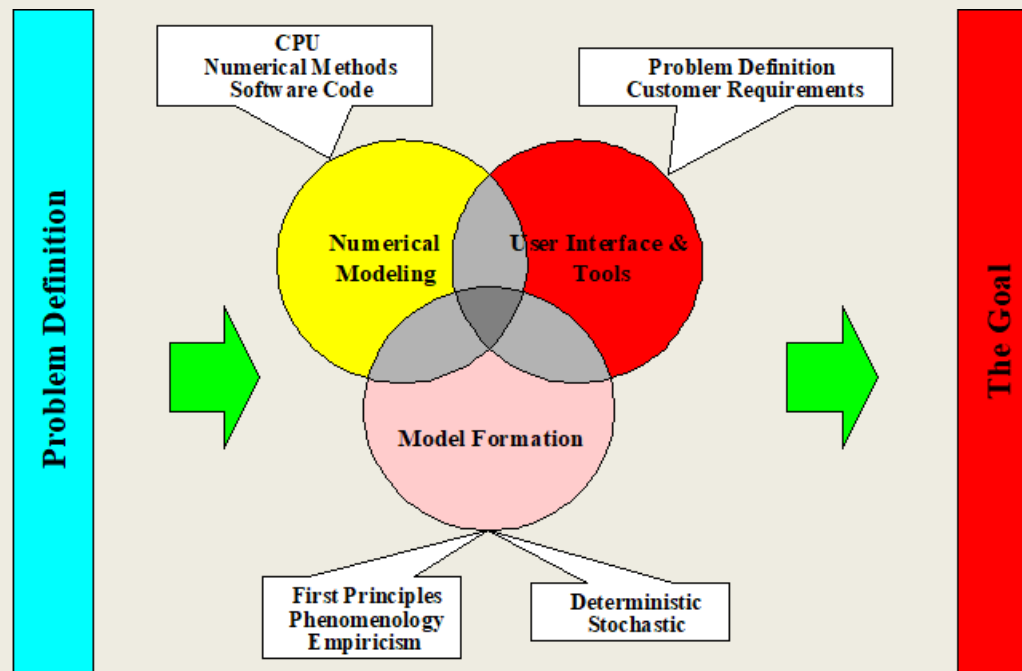
- There is an elaborate supply chain in industries involved in the production and distribution of polymeric products.
- The preceding section of this talk, which covered the sourcing of materials used in manufacturing polymeric products, also provided some insights related to supply chain management.
- It is common for material producers to exist in a state of collaborative competition.
- For example, Dow Chemical and DuPont were among each other's major customers for decades and now are merging.
- Some additional thoughts are provided on the next slide.

Optimized Supply Chain Management

- Optimized management of supply chains is a specialized field of its own.
- Polymer supply chain management applies the general principles and techniques of supply chain management to this specific product area.
- Aspen Technologies (AspenTech, a leading chemical engineering software company) provides the best tools that I am aware of for polymer supply chain management.
 - Their industry white paper titled [Polymer Supply Chain Management](#) provides valuable insights on the general considerations that are involved.
 - Their [aspenONE](#) supply chain management software can be used to help in the optimization of process manufacturing supply chains.

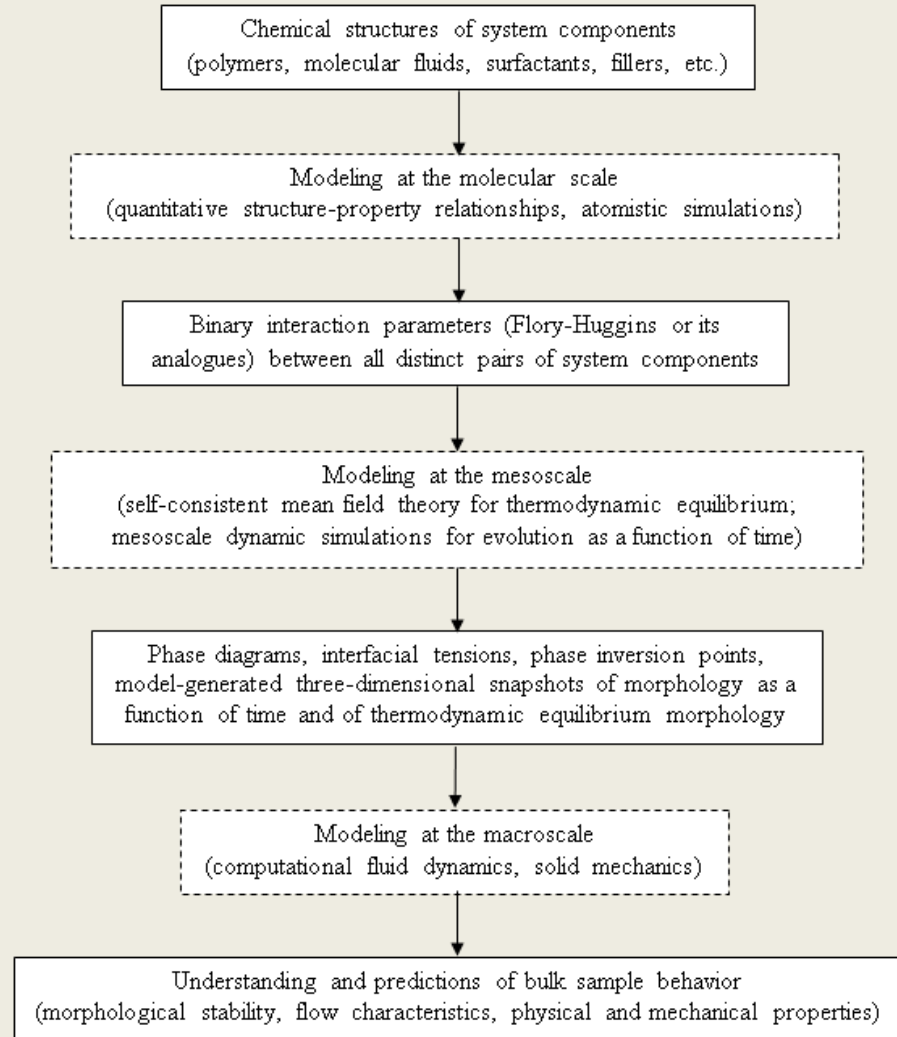
MODELING, SIMULATIONS, AND DATA MINING

- Finally, it is worthwhile to also discuss briefly the growing role of modeling, simulations, and expert systems in industrial R&D.
- A schematic illustration is provided below (Bicerano *et al.*, 2004, full citation on next slide) of the multidisciplinary nature of industrial modeling.



Multiscale Modeling

A schematic illustration (Bicerano *et al.*, "*Polymer Modeling at The Dow Chemical Company*", J. Macromol. Sci. - Polymer Reviews, 44, 53-85, 2004) is provided on this slide of the multiscale modeling paradigm for predicting the morphologies and properties of many types of polymeric materials.



Data Mining

- Data mining goes far beyond searching for information in databases such as Omnexus, MatWeb, UL Prospector, and CAMPUS.
- It involves the analysis of large datasets using sophisticated algorithms to discover patterns that can then be used in a predictive manner.
 - For example, a large dataset may comprise information on the effects of monomer purity, catalyst attributes expressed in terms of several quantitative descriptors, reaction temperature profile, and stirring rate on the percent conversion as a function of time, product purity, and product yield during a polymerization process.
- Data mining tools are especially valuable in the development of expert systems because the mathematical models expressing the discovered patterns evolve as additional data are incorporated so that these models can be said to “learn”.
 - Dataset sparseness, due to the fact that many of the input parameters are often missing, is a frequently encountered challenge during data mining.
 - Model parsimony, whereby a desired level of explanation or prediction is achieved with as few predictor variables as possible, is an important objective of model development since it is essential for achieving a robust model.
- The [DataModeler](#) package of Evolved Analytics is an example of a highly effective data mining tool.
 - The original version was developed by a team led by Dr. Mark Kotanchek at Dow Chemical.
 - He was later allowed to further develop and commercialize it by forming his own company.

CONCLUDING REMARKS

- This lecture merely provided a quick introduction to the most essential aspects of polymeric materials, to the extent that it is possible to summarize such a vast subject in two hours.
- The coverage of each of the topics introduced in this lecture can be easily expanded into an entire lecture by itself.