

MATERIALS ENGINEERING - SYLLABUS

OVERVIEW

Interdisciplinary science and engineering are recognized as essential to making progress as systems of interest become more complex. This is certainly true of soft materials, which require us to bring together chemistry, physics, and biology. Soft materials surround us – in fact we are even made of them! Examples include the foods we eat, the personal products we use (creams, lotions, shampoos, soaps, ...), and plastics. These are materials that are characterized by modest mechanical properties. For example, unlike hard materials such as steel with a modulus over 200 giga-pascals, plastics are about 100 times softer and room temperature butter is 400,000 times softer. This means that soft materials are easily deformed. Another important characteristic is that they respond and relax more slowly. If the stress on a steel part is removed, it restores its shape quickly (assuming the stress is below its yield value) but a soft material, such an elastomer may take many seconds to relax. Soft materials are usually viscoelastic with behavior that is intermediate between a viscous liquid and an elastic solid.

This course explores the design of soft materials through many different applications. For example, how does one stabilize a foam in a food product (did you know that ice cream is a foam?)? Why do polyethylene chains need to be branched in order to successfully make plastic bags for shopping? How do you design polymers for flexible and wearable electronics? What are the considerations that need to be controlled when designing medical implants?

TOPICS OF STUDY IN THIS COURSE

The prerequisites for this course are high school level chemistry, physics, and mathematics. Since soft materials are classified by their mechanical properties, the course begins with an introduction of the concepts of stress and deformation or, in the case of liquids, with the rates of deformation. Both shearing deformations and elongational (or stretching) deformations are described and these lead to the definition of strain and strain rate. These deformations cause stress (force per area) in materials and the relationships between stress and deformation are the foundation of the science of rheology. Broadly, materials respond to deformation in two extreme limits: as perfect, elastic bodies or as perfect, viscous liquids. Purely elastic materials obey Hooke's law where the stress is proportional to strain and this

defines the elastic modulus. In the other limit, we have viscous liquids, which follow Newton's law of viscosity. Real materials, however, are viscoelastic, with reactions that are intermediate between simple liquids and pure elastics. This course will explore viscoelasticity and describe this behavior and how it is measured.

Polymers

Following this introduction to the mechanics of soft materials, attention is then turned to descriptions of the major classes of these systems. Polymer materials are a most important example and the basics of polymer chain architecture (linear chains, branching, copolymers, ...) will be explored. Molecular weight and its distribution controls many of the properties of polymer materials and the methods of measuring this important variable are described. This variable has a very strong influence on the viscoelastic properties of polymers and the concept of chain entanglements is explained. On the other hand, polymer chains can self-assemble into crystalline materials, which profoundly affects mechanical properties and permeability to gases. Crosslinking of polymers is also a very important method of modifying these materials and makes it possible to transition from a sol (solution) to a gel. In this way, important products, such as hydrogels can be produced. Finally, copolymers, fashioned from chemically different monomers have the remarkable ability to undergo microphase separation into a variety of structures.

Surfactants

Many soft materials, such as foams, suspensions, and emulsions are characterized by very large amounts of surface area. Special molecules, called surfactants, are used to stabilize these systems by their unique structure where hydrophilic (water-loving) head groups are attached to hydrophobic (water-hating) aliphatic tails. In addition to strongly decreasing surface tension, these molecules have the ability to self-assemble into intricate structures called micelles. These assemblies, with geometries that include spherical shapes, lamella, and long wormlike threads, are the basis for the cleaning power of detergents and the thick feeling of shampoos. Their ability to attach onto surfaces helps to stabilize emulsions, foams, and suspensions.

Lipids, phospholipids, the cell membrane and vesicles.

When the aliphatic, hydrophobic tails of surfactants become very long, they become “insoluble surfactants” that self-assemble in striking ways and, in the case of phospholipids, form bilayers, the building blocks of cell membranes. Other examples of insoluble surfactants are fatty acids and fatty alcohols that find wide spread use in the foods we consume and the personal products we apply to our bodies. These molecules pack together on liquid interfaces to form highly regular lattices with their tails tilting in specific directions. This results in responses to deformations that can range from very fluid-like to liquid crystalline behavior. In the case of cell membranes, the bilayers formed from ordered phospholipids are combined with membrane proteins that help to regulate the transport of small molecules back and forth from within and outside of the cell.

Dispersed Systems: Emulsions, Foams, and Suspensions

Emulsions, foams and suspensions are commonly found in foods and personal products. For example, toothpaste is a suspension of small abrasive particles that are necessary to rub food particles away from your teeth. Fluoride is used to strengthen your teeth and surfactants are used to reduce foaming. The particles are dispersed in glycerol to form a dense suspension that forms a paste and this is important since it can be deposited on a toothbrush and maintain its shape until it is brushed onto your teeth. This is because the suspension was designed to have a yield stress, which must be overcome before flow can occur. There are many products that have yield stresses such as paints and body creams. Examples of emulsions are salad dressings and mayonnaise. Salad dressings are oil-in-vinegar emulsions where the formulations must be designed to arrest the coalescence of oil droplets since this would speed up phase separation. This is accomplished with the use of surfactants and the ingredients on a bottle of commercial dressing will give you this list. Mayonnaise, on the other hand, is an emulsion of olive oil and egg yolk (vinegar and mustard are added for taste). When these ingredients are whipped into an emulsion, the oil droplets are stabilized by a phospholipid called lecithin, which has the structure of a surfactant. Foams are also examples of products that require stabilization. From fire-fighting foams to ice cream, different strategies are employed. Ice cream, for example, is a foam where tiny bubbles are stabilized against coalescing and coarsening by the presence of fat globules and ice crystals.

TENTATIVE OUTLINE

July 15-19

Introduction to the concepts of stress, strain, and strain rate. The relationship between stress and strain for solid materials: definition of a modulus. The use of Hooke's law of springs to describe elastic solids. The relationship between stress and strain rate for liquids: definition of viscosity. Introduction of dimensional analysis and the concept of scaling. The use of Newton's law of viscosity and dashpots for viscous liquids.

The concept of viscoelasticity – when materials have a response that is somewhere between an elastic solid and a viscous liquid. Adding springs to dashpots – the Maxwell model of a viscoelastic material and the concept of a relaxation time.

Measurement of viscoelasticity – constant strain experiments, constant stress experiments, and constant strain rate experiments. Typical responses of viscoelastic solids and viscoelastic liquids (relaxation of moduli, compliance, shear thickening and shear thinning viscosities, yield stresses).

Simple demonstration experiments to illustrate typical viscoelastic phenomena.

July 22-26

Introduction to polymer science. Polymers are an important class of soft materials and consist of sequences of monomers that are linked together in a variety patterns. These patterns include linear and branched chains, homopolymers and copolymers, amorphous polymers and crystalline polymers, synthetic polymers and natural polymers.

Molecular weight is related to the size of a polymer. Another characteristic is the flexibility of the polymer. For rigid, rodlike polymers this relationship is straightforward. But for flexible polymers, the concept of a random walk and Brownian motion will be explained. This random coil model of a polymer also gives rise to polymer elasticity.

When polymers are in dilute solution they have as isolated random coils but as the concentration is increased, they begin to overlap and entangle. The viscosity of semi-dilute polymers is discussed and

simple theories are used to describe their behavior. Ultimately, at very high concentration, polymer melts are encountered and chains can become highly entangled. The viscosity of polymer melts is discussed.

Overlapping chains interact by physical connections. Chemical crosslinking, on the other hand, ties them together by covalent bonds. When elastic polymer chains are tied together into a network, elastomers are formed. The transition from solutions to gels of polymers is described (the sol-gel transition).

Midterm (Wed or Thurs)

July 29-Aug 2

Suspensions are an important class of soft materials. These are formed by dispersions particles within liquids at various concentrations and are the basis of products such as paints, toothpastes, skincare lotions, and foods. Indeed, even our blood can be considered a suspension (in this case the particles are red blood cells). The fluid mechanical response of suspensions will depend on particle shape and size, concentration, and the interactions between the particles.

The viscosity of dilute suspensions will be presented and the famous Einstein equation of viscosity will be discussed. However, when the concentration is increased, the particles can jam together and the viscosity can rapidly increase. Ultimately, suspensions become non-Newtonian and the viscosity can either be shear thinning or shear thickening. The reasons for either behavior will be discussed and simple experiments will be performed that describe these effects.

The interactions between particles can be controlled to produce either stabilize or aggregating systems and the methods to accomplish this are described. Particle crystallization and the formation of opals and other beautiful morphologies will be described.

Aug 5-9

The final week of the course will cover materials that are dominated by interfacial forces: emulsions and foams. Emulsions are systems of drops of one liquid that are dispersed within a second, immiscible

liquid. Foams, on the other hand, are masses of bubbles that are dispersed within a liquid (or a solid, in the case of “solid foams”). Fundamental to these systems is surface tension, which acts on the surfaces of the drops and bubbles and controls their mechanical response and stability. We will learn about capillarity and how surface tension controls the shape of interfaces and the drainage of thin films of liquids.

How are foams and emulsions stabilized? This will lead to a discussion of surfactants and the power of Marangoni flows. Both soluble and insoluble surfactants will be described and the special case of phospholipids will be discussed. The phenomenon of self-assembly and surfactant micelles will be described.

Final (Wed or Thurs)

Reference Materials

In this course, we will read and rely on the important book, “Fragile Objects” by the famous French physicist, Pierre Gilles de Gennes.

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