1 Introduction and Overview

Chapter Outline

1.1 Introduction

Polymers are a broad class of materials that include traditional engineering materials such as elastomers (rubbers), thermoplastics, and most types of adhesives. In addition to these man-made materials, many natural and biological substances are also polymers, for example, DNA, protein, skin tissue, hair, and many more. Although these materials clearly behave differently from each other—based on our every-day experience—they have many important features in common with respect to their mechanical response. The goal of this text is to outline these characteristic features, and specify different ways that the mechanical response can be predicted using analytical or computational tools.

Before embarking on a detailed discussion of these topics it is useful to have a basic understanding of the history of polymeric materials, and knowledge about the fundamentals of polymer processing and polymer mechanics. This chapter lays the foundation for the analysis that will follow and presents definitions and terminology that are needed for the following discussions.

1.2   What Is a Polymer?

To answer this question it is enlightening to first ask the complimentary question: what is not a polymer? It turns out that all solid materials can be classified into one of three basic types: metals, ceramics, or polymers. In addition to these basic material types, there are also two groups that can be considered subsets or combinations of these types: composite materials and semi-conductors.

Let us start by considering metals: a metal is a material in which the atoms are held together by metallic bonds (Figure 1.1). It is the delocalized electrons and the strong interaction forces between the positive atom nuclei that give the characteristic response of metals, such as good thermal and electrical conduction. The metallic bonds allow for relative sliding of large groups of atoms, enabling plastic deformation and ductility [1].

Similarly, a ceramic material can be defined as a material in which the atoms are held together by ionic bonds created by positive and negatively charged ions (Figure 1.2). Many ceramic
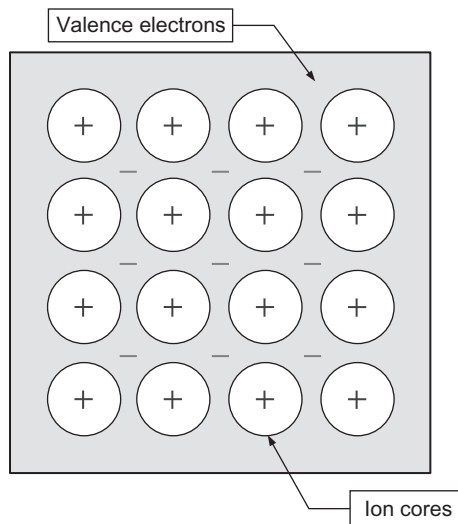
Figure 1.1 The atoms in a metal are held together by metallic bonds. The valence electrons are released from the atom nuclei and form an electron cloud.
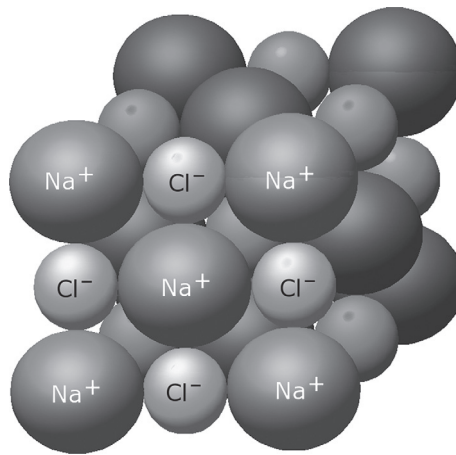
Figure 1.2 In a ceramic material, the atoms are held together by ionic bonds created by charged ions.

materials have excellent stiffness and compressive strength properties, particularly at high temperatures [2]. In ceramic materials, the electrons are tightly held giving poor conduction of heat and electricity.

The third major material type is polymers. As an informal definition, a polymer is a material with many different length scales (Figure 1.3).

On the most local scale, the atoms are arranged into monomer units and bonded together using covalent bonds. The monomer units are then connected into long chain-like structures. The different macromolecules (sometimes called chain molecules) can be arranged into a network structure by crosslinks or entanglements, and they interact by weak van der Waals forces. The atoms of the polymer backbone are held together by covalent bonds that share electrons between atoms resulting in very strong bonds with very little electron mobility (Figure 1.4). Polymers are therefore typically poor conductors of heat and electricity. The weak bonds between the molecules create very interesting mechanical properties characterized by low stiffness and high ductility. The details of these characteristic behaviors and how they can be modeled are given in the following chapters of this book.
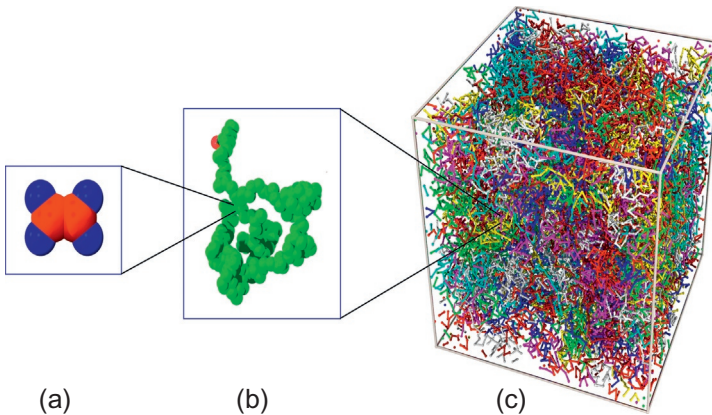
Figure 1.3 The microstructure of a polymer contains many different length scales. On the most local level, the atoms are arranged into monomer units (a). The monomers are linked into chain molecules (b), which form a macromolecular network (c).
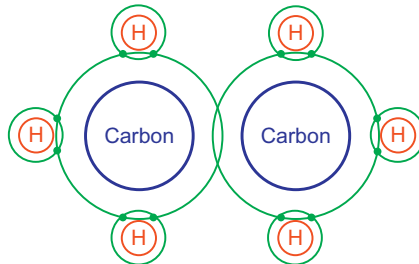

Figure 1.4 The atoms in a polymer molecule are held together by covalent bonds.

1.3 Types of Polymers

Due to the wide variety of polymers and polymer behaviors it is often useful to categorize polymers into different groups. One approach is to distinguish between natural polymers and synthetic polymers (Figure 1.5). Natural polymers, also called biopolymers, include a vast selection of materials. For example, all plants and animals are largely made from biopolymers. Plants are typically made from cellulose (e.g., cotton and wood) or starch (e.g., potatoes and carrots) both of which are polysaccharides. Another common natural polymer is protein, which is formed
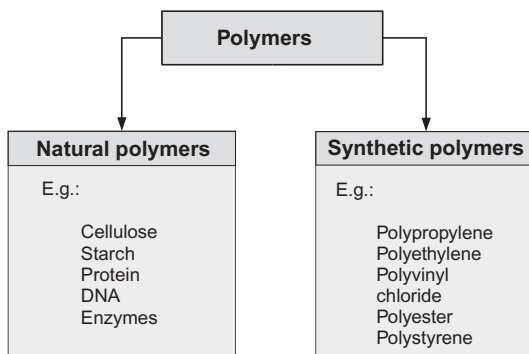
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                    ┌──────────────────────┐
                    │       Polymers       │
                    └──────────────────────┘
              ┌──────────────┴──────────────┐
              ▼                             ▼
┌──────────────────────┐      ┌──────────────────────┐
│   Natural polymers   │      │  Synthetic polymers  │
├──────────────────────┤      ├──────────────────────┤
│ E.g.:                │      │ E.g.:                │
│                      │      │                      │
│     Cellulose        │      │     Polypropylene    │
│     Starch           │      │     Polyethylene     │
│     Protein          │      │     Polyvinyl        │
│     DNA              │      │     chloride         │
│     Enzymes          │      │     Polyester        │
│                      │      │     Polystyrene      │
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Figure 1.5 Examples of natural and synthetic polymers.

from amino acids. Other examples of biopolymers are: DNA, RNA, peptides, enzymes, skin, hair, silk, and chitin. Man-made polymers, also called synthetic polymers, include most traditional engineering polymers such as polypropylene (PP), polyethylene (PE), and nitrile rubber.

Another useful approach to categorize polymers is to distinguish between thermoplastics and thermosets (Figure 1.6). A thermoplastic is a polymer that is not permanently crosslinked and that softens and can be reshaped when heated. Thermoplastics can generally be exposed to repeated temperature cycles without undergoing significant degradation, making them suitable for recycling. A thermoset is a polymer that is crosslinked (cured) through the addition of energy, typically in the form of heat or irradiation. During the curing process the macromolecules are crosslinked and permanently included in a molecular network structure. Thermosets are generally stiffer and stronger than thermoplastics, but cannot be reshaped or melted.

A third way to distinguish polymers is to separate amorphous and semicrystalline polymers (Figure 1.7). The polymer molecules in an amorphous polymer form an entangled network that is characterized by randomness and lack of long-range structure. In a semicrystalline polymer, parts of the molecular structure are crystalline and other parts are amorphous. The crystalline structure is typically considered to consist of layered lamellar crystals (Figure 1.8). One a larger scale, the amorphous and crystalline phases often aggregate to form supramolecular
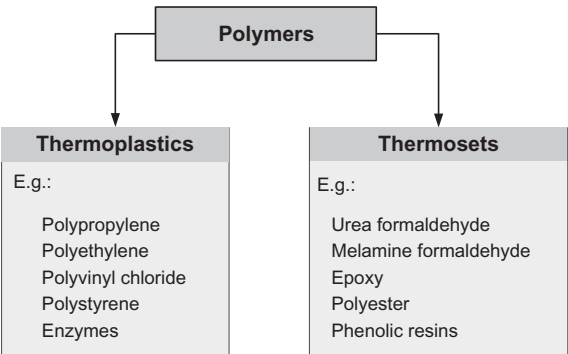
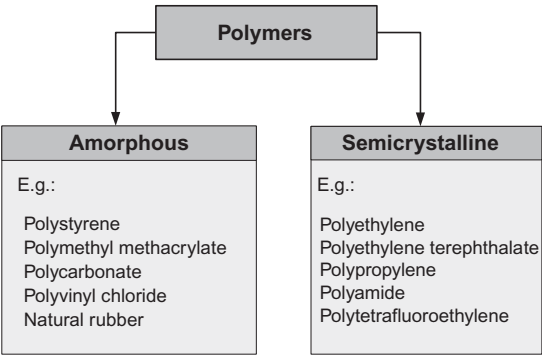**Figure 1.6** Examples of thermoplastics and thermosets.

Figure 1.7 Examples of amorphous and semicrystalline polymers.

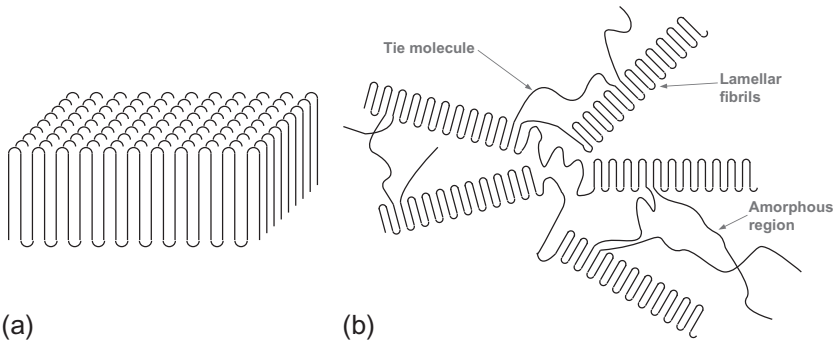(a)   (b)

Figure 1.8 (a) Crystallizing polymers from layered structures called lamellae; (b) spherulines are supramolecular structures containing both lamellae and amorphous tie regions.

spherulites. When the crystallization occurs in the absence of flow or mechanical deformation, spherulites is the most common form of the crystal structure. The kinetics of polymer crystallization if very complex and still an active area of research. Amorphous and semicrystalline polymers often exhibit different mechanical behavior. Semicrystalline polymers have a true melting temperature (T_m) at which the crystalline domains break up and become disordered. Amorphous polymers do not have a melting temperature but softens significantly above their glass transition temperature (T_g). At temperatures above T_g, large segmental motions are activated and the polymer starts to behave liquid-like.

During the last few years it has started to become more important for the polymer industry to provide products that are sustainable and bio-friendly [3]. This trend is driven by a global drive and emphasis on sustainable technology. There are currently many different polymer products available that are based on renewable resources and that are easily recyclable and renewable. Polylactic acid, PLA, is one example. This polymer is synthesized from corn, and it biodegrades after use if composted. In many applications, PLA is an alternative to PET and PVC, and it is currently used, for example, in candy wrap, optical films, and shrink labels. The main disadvantages of PLA include slightly higher density and a higher price than some traditional engineering polymers.

1.4 History of Polymers

Since all biological tissues are polymers (e.g., skin tissue, cartilage, tendons, etc.), the history of polymers is as old as the history of these materials. Estimates indicate that the age of these materials are millions of years old [4]. Natural evolution for this time period has led to very specialized biopolymers with truly amazing mechanical properties that often even today are difficult to match or replace by synthetic polymers (Table 1.1).

Natural polymers are not only occurring as biological tissue, but also as cotton, starch, and cellulose. For example, it has been know for about 500 years that Hevea brasiliensis produces a

Table 1.1 **Brief Summary of the History of Polymers [5–7]**

Date	Polymer Development
1500s	British explorers find Mayan civilizations that use natural rubber from rubber trees
1839	Charles Goodyear discovers vulcanization of natural rubber by adding sulfur and heating to 130 °C (270 °F)
1862	Alexander Parks invents the first man-made polymer, named Parkesine
1907	Leo Bakelite invents bakelite, the first completely synthetic plastic. This material is a stiff thermoset polymer with good heat resistance, useful for electrical insulation
1925	X-ray crystallography shows, for the first time, that polymers are made of long macromolecules
1927	Large-scale production of PVC begins
1930	Polystyrene (PS) is invented
1933	Polyethylene (PE) is invented
1938	Polyamide and fluoropolymers are invented at DuPont
1971	Kevlar is invented
1976	Polymers surpass steel as the most used engineering material by volume
Late 1970s	Conductive polymers are invented
Early 2000s	Use of synthetic polymers in biomedical applications

substance with quite useful properties. This material, also known as natural rubber, was known by the Mayan civilization to be a useful material for making tools and games.

It was not until 1839, when Charles Goodyear discovered vulcanization, that natural rubber became an important engineering

material. Vulcanized natural rubber has very good elastic and resilient properties, and it still remains one of the most useful and important rubbers for industrial applications. For example, car tires typically contain a large volume fraction of natural rubber. The first man-made polymer was developed by Alexander Parks in 1862. He developed an organic material, referred to as Parkesine, which could be reshaped when heated and remained stiff when cooled. The material, however, was not a big hit due to its high cost. The first completely synthetic polymer was Bakelite, developed by Leo Bakelite in 1907. This material provided significant advantages over many other contemporary materials due to its good electrical insulating properties and ability to be molded into complicated shapes. It is interesting to note that the macromolecular microstructure of polymers was not understood until 1925. Before that time, different theories had been presented related to what caused the interesting behavior of Bakelite, but the microstructure was not known. After this discovery, and the realization that it is the macromolecular structure that creates the unique behavior of polymers, a large number of common traditional engineering polymers were developed during the following 10 years. For example, PVC, PS, PE, Nylon, and PTFE were discovered during the late 1920s and during the 1930s. Since that time the use of polymers has continued to grow, and the number of different engineering polymers has continued to increase. Some of the new materials have focused on improved performance. For example, polyethyleneimine, PEI, and polyether ether ketone (PEEK) are polymers with high thermal stability, strength, and stiffness.

One interesting milestone was passed in 1976 when the produced volume of polymers for the first time exceeded the produced volume of steel. Since then, the polymer use and technology has continued to grow. For example, the first conductive polymer was discovered in the late 1970s. Conductive polymers are important because they can potentially be used to create lightweight batteries, solar cells, etc. During the last few years synthetic polymers have started to be used in biomedical applications. Artificial skin and bone, drug delivery devices, and scaffolds for growing transplant implants are just a few examples.

Also, recently a significant effort has been directed toward improving the sustainability of polymer materials to make them bio-friendly. For example, there are thermoplastic elastomers that do not require aggressive chemistry during crosslinking. Another recent development of high importance is the discovery of conducting polymers. By combining the traditional strengths of polymers: low cost and easy manufacturing; with conductive properties it is possible to create organic light-emitting diodes (LEDs), lasers, and many other unique products.

The bulk of the produced polymers today are traditional engineering polymers (Table 1.2). The polymer with the highest production volume is polypropylene (PP). The polymer with the second highest production volume is HDPE. However, if the different types of PE (i.e., HDPE, LLDPE, and LDPE) are combined, then they constitute about half of the total production volume. Today polymers are ubiquitous, and one of the most important materials in our everyday life.

Table 1.2 **Production Volume of Different Polymers in North America During 2003 [5, 6]**

Resin	Production Volume (kg)
Polypropylene (PP)	8.0×10^9
High density PE (HDPE)	7.1×10^9
Polyvinyl chloride (PVC)	6.7×10^9
Linear low density PE (LLDPE)	5.0×10^9
Natural rubber (NR)	4.9×10^9
Styrene-butadiene rubber (SBR)	3.8×10^9
Thermosets	3.7×10^9
Low density PE (LDPE)	3.5×10^9
Thermoplastic polyester	3.4×10^9
Polystyrene (PS)	2.9×10^9
Acrylonitrile butadiene styrene (ABS)	0.5×10^9
Polyamide (Nylon)	0.5×10^9

1.5   Polymer Manufacturing and Processing

Many different manufacturing procedures can be used to create man-made polymer materials and products. The macromolecular structure of the raw material is created by chemically joining together monomers either by addition polymerization or condensation polymerization.

In *addition polymerization* molecules with double or triple chemical bonds are linked together into macromolecules. The unsaturated monomers are linked up with other monomers to create the molecular chains. This type of polymerization is typically used to create polyethylene, propylene, and polyvinylchloride. The reactions are carried out in the presence of a catalyst that also can influence the structure and organization of the material.

Condensation polymerization is based on a different mechanism in which monomers bond together by condensation reactions. The chemical reactions are typically achieved through alcohol, amine, or carboxylic acid functional groups. In each step of this process a simple compound, often water, is formed. This process is used when amino acids link up to form proteins. It is also the way in which Kevlar is formed.

The required processing to create final products of the polymeric raw materials is an important field that has been extensively studied [8–15]. Some of the more common processing operations are: blow molding, extrusion, fiber spinning, filament winding, film blowing, injection molding, pultrusion, reaction injection molding, spin coating, and transfer molding. Further information on these processing operations can be found in numerous textbooks geared toward the specific subject matter.

1.6   Polymer Mechanics

The previous few sections have presented different aspects of polymer history, chemistry, and manufacturing. This section gives an overview to the main topic of this book: polymer mechanics. By definition, polymer mechanics involve the mechanical behavior of solid polymers. This field of study can be divided into

many different subtopics. The following are examples of common questions that a polymer mechanist is often interested in:

- What are the different ways a particular polymer can behave in a certain load environment?
- What is the best way to experimentally characterize the mechanical response of a polymer?
- How well will a certain polymer product behave? How can the performance be improved?
- Which polymer is most appropriate for a given application?

In order to address these questions, it is important to understand the connection between polymer material, processing conditions, material microstructure, and load environment; and how all of these factors influence the performance of the polymer product (Figure 1.9).

One topic of polymer mechanics involves the tools and techniques that are used for experimental characterization of polymeric materials. Another and complimentary topic is related to theoretical predictions, either by traditional analysis or computer
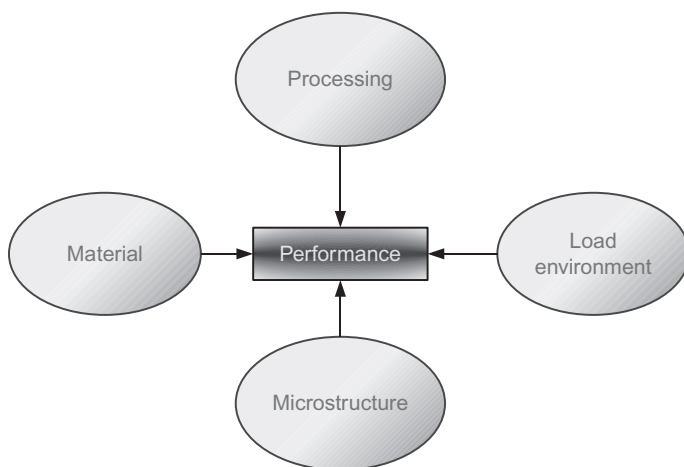

Figure 1.9 The performance of a polymer product is governed by the material type, the processing conditions, the material microstructure, and the applied load environment.

simulations. Due to the complexity of the polymer microstructure, the use of computer simulations is becoming increasingly important when studying the behavior of solid polymers. This approach to study the material response is often called *computer experiments* due to the possibility to replace time-consuming and costly physical experiments with computer simulations.

The goal of polymer mechanics is to develop an understanding of the mechanical behavior of polymers and to develop tools for predicting the observed mechanical response of polymers in different load environments. In this context, polymer mechanics is not directly involved with the chemistry behind how polymers are created, or the processing steps that are needed to create a polymer component. The main reasons for this distinction are that the chemistry and rheology involved in the manufacturing process are significantly different topics than the study of the mechanics of solid polymers. Polymer production, manufacturing, and processing are discussed in depth in many textbooks [8–16].

Polymers, due to their molecular structure, exhibit many different types of phenomena when exposed to normal loading environments. Some of the more common behaviors are listed in Figure 1.10.
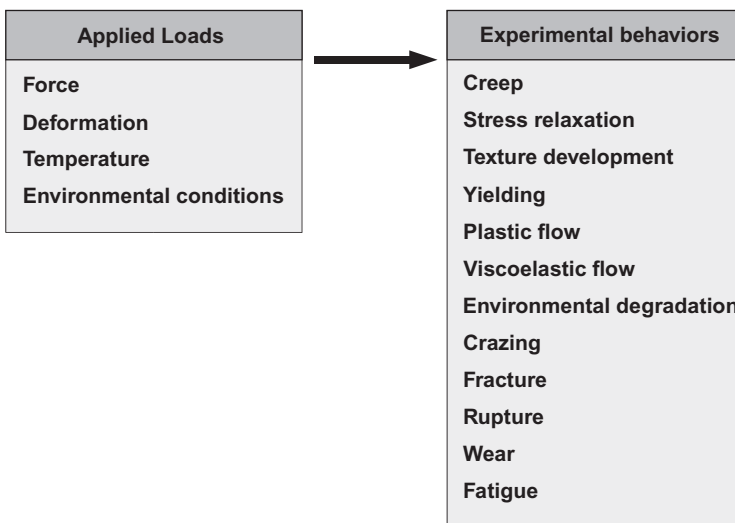
Applied Loads		Experimental behaviors
Force	→	Creep
Deformation		Stress relaxation
Temperature		Texture development
Environmental conditions		Yielding
		Plastic flow
		Viscoelastic flow
		Environmental degradation
		Crazing
		Fracture
		Rupture
		Wear
		Fatigue

Figure 1.10 The response of polymers when subjected to external loads can be of many different characteristic types.

As illustrated in this figure, the response of polymers can take many different forms when exposed to an external load environment. Some of the more common and important behaviors are: creep, stress relaxation, anisotropy, texture development, yielding, plastic flow, viscoelastic flow, environmental degradation, crazing, fracture, rupture, wear, and fatigue. The goal of this book is to address these issues. Specific emphasis will be placed on why these phenomena occur, and how they can be predicted and computationally modeled.

There are two types of modeling approaches that aim at capturing these phenomena. The first approach, and the classical approach, is to use a phenomenological experience-based model. As an example consider an attempt to predict the tensile failure of polycarbonate under monotonic uniaxial loading. By performing a sufficient number of experimental tests it might be possible to prove a significant correlation between the Mises stress and the observed onset of failure. A polymer mechanist might then take this as in indication that Mises stress is a good failure predictor for polycarbonate, using the hypothesis that failure occurs when the Mises stress in a specimen (obtained either by Finite Element Modeling (FEM) or direct closed-form calculations) exceeds the critical Mises stress, where the critical Mises stress is a material parameter. The astute reader may realize that this may not be a good model. For example, can this failure criterion be used if the polymer component was deformed 100 times faster? What if the temperature is different? What if the component is deformed in simple shear to failure? Is the Mises stress criterion still valid under these conditions? All of these questions are serious and need to be carefully addressed before the proposed failure criterion can be considered a general failure criterion. This highlights the main limitation of phenomenological models:

> *A phenomenological model is strictly only applicable for the exact loading conditions for which it was validated.*

This limitation is often somewhat neglected in industrial settings where the need to reach an answer in a short amount of time and with a limited budged is often driving the analysis.

The second modeling approach for capturing polymer mechanics phenomena is to use a micromechanical model. Micromechanical models, by definition, are models that use information and knowledge about the microstructure of the material as the basis for the model. Imaging for a moment that we have a model that relates the applied deformation to the average molecular chain stretch on a molecular level. That model would then be more reliable for predicting the response in general loading modes and temperatures. Micromechanical models are almost always preferred over phenomenological models, but due to the complexity of the deformation characteristics of the molecular microstructure it is often very difficult to develop models that are purely micromechanical. The idea of the micromechanical models is to bridge different length scales: if we understand the mechanisms driving the deformation behavior on a micro (or nano) scale, then how can we use that information to predict the behavior on a macro or continuum scale? Due to the challenge of translating information from different length scales, a number of models have been developed that combine elements from the micromechanics of deformation and phenomenological approaches. These models are often called *micromechanism inspired models* and are currently for some of the phenomena presented in Figure 1.10 the most accurate approach that is currently available.

The remaining chapters of this book address these different aspects of polymer mechanics, demonstrating when the different phenomena occur and how they can be predicted.

1.7 Exercises

1. What are the three major classes of solid materials?
2. How do you define a polymer and what makes a polymer unique?
3. Give a few examples of different polymers.
4. When was the first man-made polymer created?
5. What are the two major ways in which polymer materials can be created?

6. If a polymer product is exposed to an external load environment, what are the different ways in which the polymer might behave?
7. What are the differences between a phenomenological and micromechanical model?

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