

1 Introduction to Plastics Engineering

1.1 Introduction to Plastics

Plastic products have become significant part of our daily life. The clothes we wear, the toothbrush we clean our teeth with, the storage containers we carry and heat our food in, the cars we drive, the electronic devices we use to communicate, the credit cards to make payments, and several such products have become essential to everyday living. These products are typically made from different types of plastic materials.

The word *plastic* or *plastics* is derived from Ancient Greek word *plastikos* meaning “fit for molding” and from Latin word *plasticus* meaning “of molding” [1]. Both words indicate forming shapes or molding by heating. Thus, shaping of plastics using heat and pressure creates the foundation of almost all plastic manufacturing processes. Typical to these manufacturing and technological processes, the plastic materials are usually made soft by applying heat [2]. The softened plastic is then given a desired shape to fit the application. Once it attains the shape, the material is then cooled to let it harden and retain the shape.

Plastic products are widely accepted primarily due to their lower cost and lighter weight. Ease of processability, resilience, recyclability, and versatility add to the benefits of adapting to plastics. During the last century, the development and acceptance to plastics have raised the comfort and standard of living. In absence of plastic products, today’s clean water, food distribution, healthcare, apparel, automobiles, aircraft, agriculture, and consumer goods would be unimaginable.

Plastics entered large-scale applications after the Second World War and quickly began to revolutionize daily life by replacing expensive and scarcely available metallic counter parts. Millions of plastic products offering unique functions and conveniences are routinely used. The end uses of plastic vary from simple economical commodity merchandize to expensive complex products for application in aerospace, automobiles, medical drug delivery devices, prosthetics, grafts, and others. To understand the growing diversity and complexity of plastic products, it becomes imperative to explore “plastics engineering” as a scientific field.

1.2 Plastics Engineering

Plastics engineering as a field focuses on designing, developing, and manufacturing of plastic parts that satisfy the requirements of the intended application. This means that each plastic product that is designed for specific application has to satisfy the three “F’s” as *form*, *fit*, and *function* for that application.

As we review examples of wearable safety, it would be clearer how form, fit, and function alter with application. In discussing “wearable safety for eye protection,” the *form* would be to produce rigid structure in the form of wearable safety glasses, *fit* would be to develop the shape and size that comfortably fit the user typically around the eyes and ears, and the *function* would be the ability of selected material to safeguard against foreign objects as a protective barrier, without interfering with user’s normal vision.

Similarly, reviewing “wearable safety for body armor,” the *form* would be to produce a flexible vest that could be worn around the chest and shoulders, the *fit* would be to develop sizes that are able to fit different body types, and *function* would be the ability of the selected material to protect against bullets and other such fast-moving objects at close range, yet remain lightweight for the user’s comfort.

The examples of “wearable safety” demonstrates how engineering a plastic product incorporates the knowledge of various interdisciplinary fields in designing of form, fit, and function for a product. Fig. 1.1 illustrates plastics engineering as an interdisciplinary field that relies on various scientific and technical disciplines. Plastics engineering not only combines the concepts of form, fit, and function, which involves design principles, but also encompasses the knowledge of various scientific and engineering fields that requires a good understanding of materials, their properties, processing methods, design principles, functional requirements, and the application.

Understanding the engineering of plastics is necessary for developing innovative, safe, economical, and convenient solutions to meet the expanding demands universally. To learn about plastics engineering, one needs to develop a basic understanding of its fundamental principles, design techniques, processing methods, material properties, and governing regulations. One of the first steps to grasp the fundamentals of polymer engineering is to understand the macromolecules and polymers that make the backbone of all plastic materials.

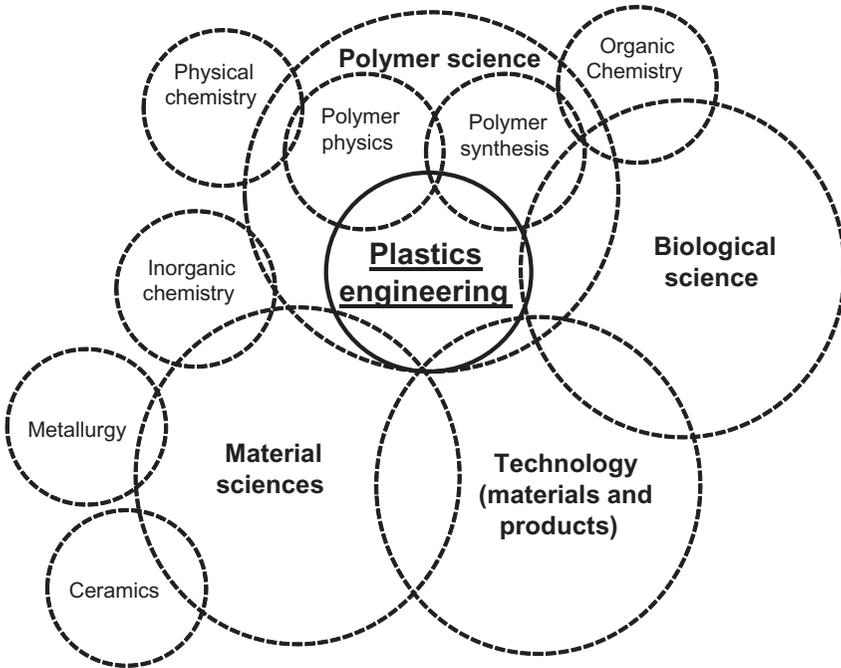


Figure 1.1 Plastics engineering as an interdisciplinary field [3].

1.3 Concept of Macromolecules and Polymers

Atoms form the building blocks of every particle in this universe. Two or more atoms combine to form a molecule. For example, two atoms of hydrogen and one atom of oxygen combine to form a molecule of water. When large number of such molecules are combined together, giant molecules are formed and these also known as macromolecules or polymers. The word *polymer*, which is derived from Greek terms *poly* meaning many and *mer* meaning parts, is defined as a chemical compound made up of small molecules (monomers) that are arranged in simple repeating structure to form a large molecule or a chain [4–6].

Hundreds and thousands of monomers are chemically bonded together by covalent bonds to form a polymer. Fig. 1.2 illustrates bonding of monomers to form a polymer. In this figure, the monomers are represented by circles and a straight line is used to represent a bond. The bonding process combines the monomers to produce a polymer [6,7]. Most polymers are organic materials consisting of carbon,

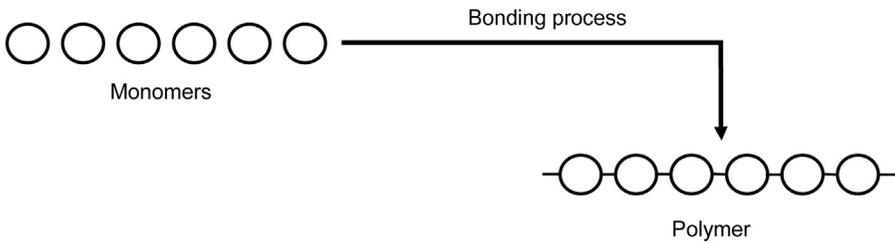


Figure 1.2 Bonding of monomers to form a polymer [7].

hydrogen, oxygen, nitrogen, and sulfur. Other elements appear in polymer structures far less frequently than the listed five constituents.

1.4 Sources of Polymers

All plastics are made of polymeric materials. These polymeric materials can occur in the plants and animals or could be artificially produced in laboratories. Plastic materials are broadly categorized as natural, semisynthetic, or synthetic based on their source of origin.

1.4.1 Natural

Natural polymers are defined as materials that widely occur in nature or are extracted from plants or animals. Natural polymers are essential to daily life as our human forms are based on them. Some of the examples of natural polymers are proteins and nucleic acid that occur in human body, cellulose, natural rubber, silk, and wool. Starch is a natural polymer that is made up of hundreds of glucose molecules, similarly natural rubber is a polymer obtained from the latex of a rubber tree. Honey is another example of naturally occurring polymers that are significantly used in everyday life. Fig. 1.3 illustrates natural polymers from plant (latex from rubber trees) and animals (honey from bees).

1.4.2 Synthetic

Synthetic polymers are defined as polymers that are artificially produced in laboratories. These are also known as man-made polymers. Some of the examples of synthetic polymers are polyethylene (PE), polystyrene (PS), polyamides (nylon), poly(vinyl chloride) (PVC), synthetic rubber, teflon, epoxy, and several others [10].

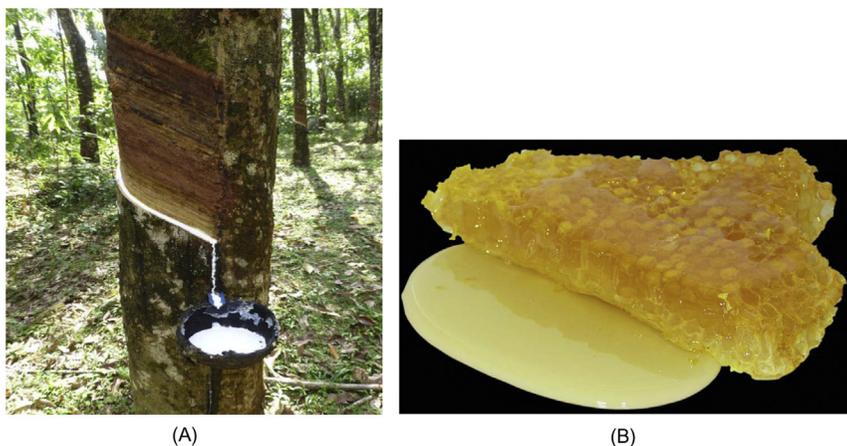


Figure 1.3 (A) Latex from the rubber tree [8] Taken from [https://commons.wikimedia.org/wiki/File:Sri_Lanka-Rubber_plantation_\(5\).JPG](https://commons.wikimedia.org/wiki/File:Sri_Lanka-Rubber_plantation_(5).JPG) and (B) Honey an natural polymer from bees [9]. Taken from <https://pixabay.com/en/honey-honeycomb-sweet-2201210>

Synthetic polymers are typically derived from petroleum oil in controlled environment and are made up of carbon–carbon bonds as their backbone. A combination of heat and pressure in the presence of a catalyst alters the chemical bonds that hold monomers together, causing them to bond with one another. Catalyst is used to begin or accelerate chemical reactions between monomers.

Millions of everyday applications are designed using synthetic polymers. These applications fall into the categories of thermoplastics, thermosets, elastomers, and synthetic fibers. This book focuses on synthetic thermoplastic polymers that are used for development of plastics materials. [Table 1.1](#) compares some of the properties and features of natural and synthetic polymers.

1.4.3 Semisynthetic or Regenerated

Semisynthetic or regenerated polymers are defined as the polymer that is derived from naturally occurring polymer by chemical modification. Some of the common examples are vulcanized rubber, cellulose acetate, and rayon. Rayon is made by chemically treating cellulose to form long fibers. Semisynthetic polymer has been experiencing growing demands in textile- and pharmaceutical-based applications. Chitosan, a linear polysaccharide that is chemically regenerated from shrimps and other crustacean shells, has observed new opportunities in biomedical application [12].

Table 1.1 Comparison of Natural and Synthetic Polymers [11]

Natural Polymers	Synthetic Polymers
Occurs naturally	Artificially produced
Have been in used since millions of years	Have been made significant since the last 125 years
Similar but nonidentical repeating	Identical repeating unit
Natural reaction controls the properties	Highly engineered properties could be determined by controlling the reaction
Usually biodegradable	Some synthetic polymers are biodegradable
Similar chain lengths of molecules	Chain lengths could be significantly varied based on the reaction conditions
Backbone could be of carbon, oxygen, and nitrogen	Backbone is mostly carbon
Environmentally friendly	Environmental friendliness is of concern
Limited recyclability	Some of the synthetic polymers could recycled multiple times

Source: [Pediaa.com](http://pediaa.com/difference-between-natural-and-synthetic-polymers/), difference between natural and synthetic polymers, <<http://pediaa.com/difference-between-natural-and-synthetic-polymers/>>, (accessed 26.3.2018).

1.5 Thermoplastics and Thermosets

The terms “plastics” and “polymers” are often used interchangeably in the industry. The materials are also referred to as “resins,” which is an old word used to refer to polymers. Plastics are a subgroup of polymeric materials and the terms plastics and polymers have more specific meanings. As described earlier, the term “plastics” represents the formability of polymers in presence of heat. Based on the response to heating, a plastic material falls in one of the two categories as thermoplastics or thermosets.

Thermoplastics are defined as material that softens (melts) reversibly when heated and hardens when cooled. Because of the reversible changes in phase, thermoplastic materials can be remolded or recycled by applying heat. This is why scrap thermoplastics can be reused. Melt processing methods such as injection molding and extrusion are benefited from the reversible behavior in reusing or recycling the scrap.

Thermosets are defined as materials that harden irreversibly during heating or processing with certain chemicals. Thermoset resin undergoes chemical change when exposed to heat and develop irreversible chemical links between the neighboring molecular chains. These links

are known as crosslinks and the structure they produce could be described as a network structure similar to molecular mesh or a three dimensional version of a web. Because of the permanent nature of crosslinks, thermoset polymer does not soften during reheating and retains their shape. This property makes these materials suitable for high-heat applications such as handles of cooking utensils and silicone baking sheets. Table 1.2 provides a general comparison between thermoplastics and thermosets materials [14,15]. It could be noted that both materials offer unique properties and applications.

Table 1.2 Comparison Between Thermoplastics and Thermosets [13]

Property	Thermoplastics	Thermosets
Flowability	Low	High
Raw material	Fully polymerized and supplied as solid pellets	Not fully polymerized often supplied as resinous liquid or semisolid
Bonding between neighboring chains	Neighboring chains are held together by physical bonds such as hydrogen bonds or van der Waals forces	Neighboring chains are held together by chemical linkages or crosslinks
Processing	Shapes are formed in molten state then cooled to retain shape	Shapes are formed in cold or warm state then heated to retain shape
Processing equipment	Standard melt processing equipment such as injection molding and extrusion could be used	Modified processing equipment is required where heat is introduced after the shapes are formed
Processing time	Short, as hardening could be performed quickly by cooling	Long, as crosslinks require longer time to develop
Recycling	Thermal recycling possible	Thermal recycling not possible
Dimensional stability	Moderate	High
Common examples	Polyolefins, polyamides, polyesters, commodity, and engineering plastics	Vulcanized rubbers, phenolic, epoxy adhesives, bakelite, sand advance composites

1.6 Morphology of Plastics

The word “morphology” represents “form” and “structure” of things. Morphology in plastics describes the way that molecular chains are arranged in a solid structure. The molecular chain arrangement in plastics could be crystalline (highly organized and regular) or amorphous (random arrangements). The arrangement of molecular chains within a solid plastics plays an important role in determining the overall properties of the product. Morphology in plastics generally refers to sizes larger than atomic arrangements and smaller than shape and size of the entire product or specimen. Often the words “structure” and “morphology” are used interchangeably, both representing the arrangement of chain [16].

1.6.1 Crystalline Materials

Crystalline materials have highly defined and repeatable arrangements of molecular chains. These materials tend to have sharp melting points. Some of the common examples are diamonds, table salt, ice, sugar, and most metals. Crystallinity refers to the degree of structural order and regularity in molecular arrangements of a plastics material. The degree of crystallinity has a significant influence on material properties such as hardness, density, melting point, transparency, and diffusion [17,18]. There are no polymers that are 100% crystalline as there is appreciable amount of amorphous content in the plastics morphology.

1.6.2 Amorphous Polymers

Amorphous materials do not have a defined geometrical shape or regularity in the arrangement of molecular chains. They appear random and jumbled up in their original state similar to a large bowl of cooked spaghetti noodles. Generally amorphous materials tend to be brittle, clear, and stiff with tangled molecular chains. These materials lack sharp melting point and soften gradually over a range of temperature. Some of the common examples of amorphous polymers are PVC, PS, poly(methyl methacrylate) (PMMA), and polycarbonate (PC). Glass transition temperature (T_g) as explained in one of the later sections of this chapter is the defining temperature for these materials.

Due to the random arrangement, the molecular chains tend to jumble up and physically stuck. This is also known as entanglement of chains

and affects certain properties such as elongation. Entanglement of the chains in amorphous materials reduces the flowability during melt processing and consequently has reduced shrinkage and warpage [19,20]. Amorphous polymers are generally transparent, have lower softening points, demonstrate higher impact resistance, and show uniform properties in all directions.

1.6.3 Semicrystalline Polymers

The morphology of several polymers is semicrystalline. As the name suggests, a semicrystalline polymer is partially crystalline (organized in definite and regular order) and partially amorphous (random). Which means that these polymers contain both crystalline and amorphous regions. The crystalline region shows a high degree of order, formed by folding and stacking of the polymer chains, whereas the amorphous or glass-like region shows no long-range order, and the chains are entangled as illustrated in Fig. 1.4. In semicrystalline portion of the plastics, the molecular chain will stack to form crystals [20]. In general, semicrystalline materials demonstrate higher resistance to chemicals. Some of the common examples are PE, polypropylene (PP), polyamide 66, and Teflon.

Properties such as hardness, strength, chemical resistance, stiffness, optical clarity, and melting point are influenced by the amount of crystallinity present in the plastic. About 30%–35% of the polymer

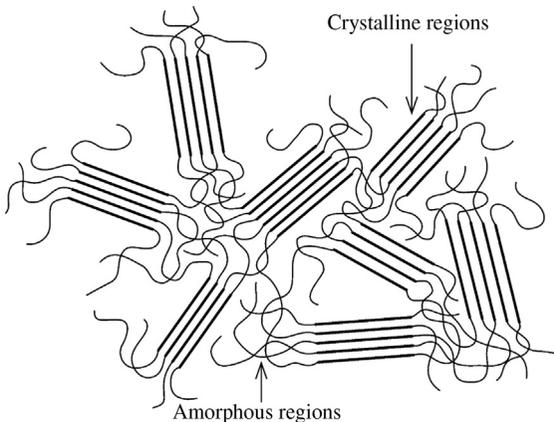


Figure 1.4 Representation of crystalline and amorphous regions in semicrystalline plastics [21].

molecular chains need to be in crystalline order for a plastic to be considered as semicrystalline material.

Often plastic specifications report the percent crystallinity. Percent crystallinity is affected by the size and shape of the molecular chains. In general, molecular chains with larger or bulky side groups have difficulty arranging themselves in defined order. This inability to organize in definite geometry creates amorphous regions instead of crystalline regions. Irregularities and bulkiness of the chains affect their ability to form stackable crystalline regions.

Amount of crystallinity in a material is also affected by processing technique. In melt processing, the plastics with higher percentage of crystalline regions require longer time to solidify to allow the molecular chains to arrange themselves in crystalline form. If they are cooled quickly (as in quenching), the molecular chains do not receive sufficient time to align themselves in proper order and are frozen-in as amorphous materials. Thus, it could be established that rate of cooling affects the degree of crystallinity during melt processing. It should be noted that all plastics in molten form are amorphous in nature [7,22].

Also, the rate at which a plastic crystallizes varies from material to material. For example, polymers such as PE crystallize fast and reach high degree of crystallinity in short durations, whereas polyester has slow rate of crystallization and requires slow cooling to crystallize [23]. Semicrystalline materials are generally stronger in the direction of molecular arrangement and weaker in the direction perpendicular (right angle) to that arrangement. A material whose properties are not uniform in all directions is called as *anisotropic* materials. Often the engineers exploit the use of cooling behavior and anisotropic nature of semicrystalline plastics to design specific properties into the product.

1.7 Temperature Dependency of Polymers

Most thermoplastics in normal room temperatures are in some sort of solid state. In the solid form, the molecular chains have limited energy available to move around. During the application of heat, the molecular chains gain energy allowing them to move farther than initially possible, and the plastic begins to expand. As the molecular chains continue to receive more energy, at some point, they gain sufficient energy to move around freely in the form of a viscous fluid also known as melt. The melt can then be shaped into various structures.

Upon cooling as the energy is extracted out from the molecular chains, the gap between the chains shrinks and the materials hardens to retain the shape. Amorphous material only indicates glass transition temperature, whereas semicrystalline temperatures indicate both glass transition and melting temperature. Melting temperature is represented by T_m [17].

1.7.1 Glass Transition and Melting Temperatures

Glass transition temperature is described as the temperature at which 30–50 carbon chains start to move. At the glass transition temperature, the amorphous regions experience transition from rigid state to more flexible state making the temperature at the border of the solid state to rubbery state. It is also said that at this temperature the free volume (gap between the molecular chains) increases by 2.5 time.

Glass transition temperature is represented by T_g and is a property of the amorphous materials or the amorphous portion of a semicrystalline materials. When the ambient temperature is below T_g , the molecular chains of amorphous materials are frozen in place and behave like solid glass. Plastic materials with flexible backbone show lower T_g , whereas plastic materials whose molecular structure is stiff, rigid, and inflexible show a higher T_g . Glass transition temperature helps determine various flexible and rigid applications for a material [17,24].

Melting point also known as melt temperature is the critical temperature above which the crystalline regions in a semicrystalline plastic are able to flow. Semicrystalline polymers begin to soften above T_g , however, they do not demonstrate fluid behavior until the T_m range is achieved. In general, T_m for a semicrystalline polymer is higher than its T_g . At temperature above T_g but below T_m , there is a “rubbery region,” where the material can exhibit large elongations under relatively low load [25].

Plastic materials are made up of uneven chain lengths and require different amount of energy to move which means that T_g or T_m for amorphous and semicrystalline polymers is not one definite temperature but a range of temperature during which all the chains start to move and experience complete flow.

Fig. 1.5 illustrates the melting and softening phenomenon of semicrystalline and amorphous materials. At temperature above melting point, semicrystalline plastics exhibit a rapid phase change from solids to viscous liquids that can be molded or given shapes. Even though, amorphous material starts transitioning into leathery region at T_g and continues to soften over a wide range of temperature. Fig. 1.5 also illustrates that as

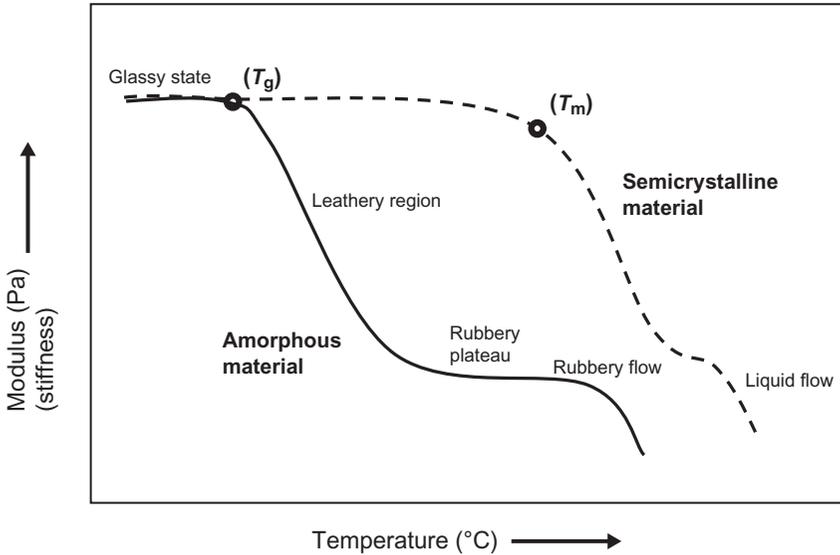


Figure 1.5 Melting and softening behavior of semicrystalline and amorphous materials.

temperature increases above T_g , amorphous materials quickly lose their strength and the semicrystalline materials continue to maintain their mechanical properties until the temperature increases to reach T_m .

1.7.2 Flexible and Rigid Behavior

Various applications require a plastic material to be flexible or rigid. Plastic materials could be designed as flexible or rigid as specified by the application and function. The factors that influence flexibility or bendability of plastic materials are plasticizers and additives, ambient temperature, speed of applying force, linear or branched chains, fillers, and part design. For example, a garden hose made of PVC requires flexibility to be able to reach the water to various areas in the garden or wash the car and once done to roll it back up for storage.

Flexibility is imparted by adding plasticizer (usually low molecular weight materials) to rigid PVC, converting it into a bendable material. Thus a plasticizer is helpful in converting rigid material into flexible materials. The ambient temperature also has its effect on the flexibility of the material. In the same example of flexible PVC, the garden hose becomes stiff during winter and is susceptible to brittle fracture, whereas during summer the pipe maintains its flexibility but does not have much strength to resist a cut.

The transitioning between flexible and rigid phenomenon can be explained by comparing ambient temperatures to glass transition temperatures. In the winter the ambient temperature falls below T_g making the material to behave as a rigid brittle plastic, and in the summer the ambient temperature is above the glass transition temperatures and the plastics remain flexible. It could be stated that glass transition temperatures are useful in predicting the brittle or ductile behavior of a material during changing ambient conditions.

Along with the ambient temperature, it is essential to understand the significance of rate of force and its effects on material behavior. A good example is silly putty, slowly pulling the material stretches it apart showing ductile behavior. However, applying sudden force such as hammering shatters the silly putty making it behave as a brittle polymer. The glass transition temperature helps explain the phenomenon as well. Hammering process significantly increases the rate of application of force, which raises the T_g . This rise in T_g above the ambient temperature makes the silly putty brittle causing it to shatter. This phenomenon illustrates that ambient temperature and rate of application of force are critical to a polymer performance. In general, flexible materials have lower T_g than rigid materials. Other factors, listed earlier, that affect the rigid and flexible behavior of plastics parts are discussed in subsequent chapters.

1.8 Commodity and Engineering Plastics

Plastic materials are frequently classified as commodity plastics or engineering plastics based on their properties and cost. Commodity plastics are cost driven and are relatively economical than engineering plastics. These plastics are considered the dominant class in terms of annual consumption that accounts to about 80%–85% of total plastics consumption annually. Commodity plastics are also known as general purpose plastics and are easy to process. These are frequently used in plastic packaging, toys, and container applications. They demonstrate low-to-moderate strengths, and show low glass transition temperatures. Due to their moderate properties, they are used in less demanding applications compared with engineering plastics [26–28].

The density of these material is generally around 1 g/cc with maximum use temperature between 54 and 149°C. Some examples of commodity plastics are PP, PE, PS, and PVC, and so on.

Engineering plastics are more performance driven than cost when compared to commodity plastics. These demonstrate higher performance characteristics and properties such as heat resistance, impact strength, chemical stability, and dimensional stability. These plastics tend to be more expensive as a large amount of engineering resources are engaged in their creation and development.

Due to their higher properties, engineering plastics are used in load-bearing structural applications. In some cases, engineering plastics exhibit potential to replace conventional materials such as metal, wood, and ceramics. Engineering plastics demonstrate high glass transition temperatures and melting temperatures, thus exhibiting higher heat resistance [27,28]. The density range of 1.06–1.42 g/cc is common to these materials. The maximum use temperature ranges between 82 and 260°C. Some examples of engineering plastics are acetals, polyoxymethylene, polyamide, polyurethanes, PC, poly(phenylene sulfide), and fluoroplastics.

1.9 Regulations

Various regulations govern the consumption of plastic materials in everyday life. Global policies as well as international standards are established to protect and conserve the user and the environment, and address potential concerns with using plastics. These doctrines also regulate the waste generated as a undesired consequence from making plastics products. Compliance to laws and regulations is necessary to ensure user safety and pollution control. Understanding the planned application, processing technique, and end-of-life cycle treatment for plastic products and compliance to the governing laws enables the scientists and engineers to develop products that are globally safe and acceptable.

Several organizations monitor the impact of using various chemicals including polymers and plastics. Some of the governing agencies for referencing in the United States and globally are: The Federal Register, United States Environmental Protection Agency (EPA), Code of Federal Regulations, the U.S. Code and the Public Law, The International Code Council (ICC), National Fire Protection Association (NFPA), Food and Drug Administration (FDA), Federal Hazardous Substance Act (FHSA), Consumer Product Safety Act (CPSA), Poison Prevention Packaging Act (PPPA), and Flammable Fabrics Act (FFA), remain the official source of regulatory information.

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