

Plastics Fundamentals, Properties, and Testing

Plastics Engineering Series

Manas Chanda
Salil K. Roy



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Preface

Plastics today represent one of the fastest changing fields with new polymers being synthesized, new uses being found, and existing processes and products being modified and improved for ecological needs, better economics, and better values. Plastics touch every one of us in our daily lives as many of the things we use—our clothing, our food, and our bodies—are made of polymers. In one form or other, plastics also have some role to play in every realm of human activity, endeavor, and experience. Today the use of plastics ranges from being minor to major and from being an alternative to indispensable in such diverse areas of applications as packaging and transportation, building and construction, domestic appliances and business machines, agriculture and horticulture, electrical and electronic, medical and biomedical, automotive and aerospace, as well as sports, marine, and corrosion prevention. The remarkable versatility of the nonmetallic class of materials called *polymers* (often loosely referred to as *plastics*) poses many questions, even to a lay user — What makes plastics so distinctly different from metals? How and why different types of plastics differ from each other? What gives rise to the characteristic properties of plastics that we are familiar with? Which plastics melt on heating and which ones harden on heating? Which plastics should be used for any given application? What are the limitations of plastics? How stable and resistant are plastics to different use conditions, such as high or low temperature, sunlight, humidity, microorganisms, solvents, acid, alkali, radiation, high voltage, load, and impact? How can the properties of plastics be modified to meet specific needs? Answers to these questions can be found in this book, written in a lucid style so as to be comprehensible even to a non-technical layperson.

Chapter 1, which is the largest chapter in the book, looks at polymers at the molecular level to explain their inherent properties and how through changes in their molecular architecture or incorporation of various fillers and additives their end-use properties can be influenced. The chapter covers a wide spectrum of topics, coherently presented with focus on macromolecular basis of polymer behavior. Starting with basic definitions commonly used in polymer science, the reader is introduced, in a graded and sequential manner, to various aspects of polymers with the emphasis gradually shifting from structural aspects to properties and onto applications. Thus the main topics on polymers comprising this chapter are molecular weights, polymerization processes, structural shapes, configuration and conformation, amorphous and crystalline states, thermal transitions, cross-linking, thermal stability, deterioration and stabilization, diffusion and permeability, toxicity, and biodegradability. Also discussed are the functions of compounding agents, metal deactivators, light stabilizers, plasticizers, antistatic agents, flame retardants, smoke suppressants, colorants, and antimicrobials in the use of plastics.

While a qualitative concept regarding the genesis of polymer behavior and properties is gained from reading Chapter 1, the reader gets a more focused and quantitative picture of polymer behavior, evaluation, and characterization in Chapter 2. What gives polymers the dominant place among all materials is the wide range of properties inherent in them or imparted by various means. Chapter 2 discusses polymer properties under four main headings—mechanical, electrical, optical,

and thermal—giving theoretical derivations where necessary and providing explanations on a molecular and structural basis. A major focus is given on mechanical properties of polymers as these often constitute the most important consideration and dictate the use of specific polymers in diverse industrial applications and myriad other uses. A wide range of topics have been covered under mechanical properties including stress-strain behavior, stress-strain-time behavior, mechanical models, effect of temperature, time-temperature superposition, dynamic mechanical properties, rheological behavior, impact behavior, fatigue, and hardness.

Reinforced plastics form an important area of structural application of plastics since the modulus and strength of plastics can be increased significantly through reinforcement. In reinforced plastics, the polymer (popularly called the *resin*) forms the matrix and a filler (mostly used in the form of fibers, but particles, for example glass spheres, are also used) provides the reinforcing effect. In view of their distinctive nature and extensive use as materials of construction in load-bearing applications, a special focus has been on analysis of properties of reinforced plastics, especially those reinforced by continuous or discontinuous fibers, as well as their deformation, fracture, fatigue, and impact behaviors.

Electrical and thermal insulation properties of plastics make these materials indispensable in many applications. These properties are discussed in detail and with a constant focus on the molecular origin of these properties. The discussion on electrical properties covers, specifically, dielectric strength, insulation resistance, arc resistance, dielectric constant in relation to use conditions, and dielectric losses. Optical properties of plastics, including optical clarity, index of refraction, piped lighting effects, and stress-optical characteristics, are discussed highlighting application aspects and relation of these properties to polymer composition and structure. The useful thermal properties of plastics, which include specific heat, thermal expansion, thermal conductivity, and thermal softening, are discussed in a lucid manner and their significance with regard to various applications, some of which are as commonplace as the teapot handle or the insulating connection to an electric iron, is explained.

Standard test methods have been developed for measuring the aforesaid properties. Since the property values are highly dependent on the specimen preparation, equipment, and testing techniques used, it is essential to refer to the appropriate official standard test methods when executing the work. Chapter 2 presents schematically (in simplified form) the bases of many of these standard test methods, according to ASTM and BS 2782 specifications, to indicate broadly the principles involved.

As plastics have become an inalienable part of our daily lives, it is important to be able to identify them and to know their characteristic properties so as to put them to better use. Various test methods are available to identify plastics some of which are very simple, such as observing behavior on heating and holding in a gas flame to take note of one or more of the following effects: (1) if the plastic burns and if so, how readily; (2) the nature and color of the flame as the material burns; (3) whether the material is self-extinguishing or continues to burn after removal of the flame; and (4) the nature of the residue. A section is therefore provided toward the end of the book dealing with identification of common plastics. For example, polyethylene burns with a luminous flame producing vapor-like paraffin wax (extinguished candles) and melts forming droplets that continue to burn, whereas PVC produces yellow-orange, green-bordered flame, producing strongly acidic fumes and black residue. Such observations on heating and ignition of common polymers are listed in a tabular form for easy reference. Tests for characteristic elements, such as nitrogen, sulfur, and halogens, may also serve to roughly indicate the nature of the base material and additives, if present. The different polymers have been classified into several groups according to the elements present, and the focus of identification has been further narrowed on the basis of other preliminary observations, e.g., fusibility or otherwise, melting point, heat distortion temperature, flame tests, thermal degradation, and solubility or extractability in water or different organic solvents. The solubility behaviors of common polymers have been compared in a tabular form for ready reference and use. When the observations and results of preliminary tests have been considered and most of the possible structures for the polymer base eliminated, an exact identification can then be made by carrying out specific tests. Some such tests for ready identification of specific polymers are described in Section 2.7. These will be useful to those who are interested in analysis and identification of unknown plastic samples.

The stimulus to bring out this book as a spin-off of our *Plastics Technology Handbook* has come from the constantly excellent response and acceptance shown by readers to the handbook ever since the publication of its first edition in 1982. Being much smaller in size and more convenient to use, the present book with its lucidity of approach and wealth of valuable information and specific data storage should find a wider reach and satisfy the knowledge thirst of a wide spectrum of people in diverse walks of life, ranging from a layman to a college student, an industry worker, and a scientist engaged in R&D activities. This book is an outcome of the initiative taken by Allison Shatkin, Materials Science and Chemical Engineering Editor at CRC Press/Taylor & Francis, who was the first to come up with the idea of producing this book for the convenience of readers. We thank her for the initiative and interest she has shown in the project.

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Salil K. Roy

Authors

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Characteristics of Polymers

1.1 What Is a Polymer?

A molecule has a group of atoms which have strong bonds among themselves but relatively weak bonds to adjacent molecules. Examples of small molecules are water (H_2O), methanol (CH_3OH), carbon dioxide, and so on. Polymers contain thousands to millions of atoms in a molecule which is large; they are also called macromolecules. Polymers are prepared by joining a large number of small molecules called monomers. Polymers can be thought of as big buildings, and monomers as the bricks that go into them.

Monomers are generally simple organic molecules containing a double bond or a minimum of two active functional groups. The presence of the double bond or active functional groups act as the driving force to add one monomer molecule upon the other repeatedly to make a polymer molecule. This process of transformation of monomer molecules to a polymer molecule is known as polymerization. For example, ethylene, the prototype monomer molecule, is very reactive because it has a double bond. Under the influence of heat, light, or chemical agents this bond becomes so activated that a chain reaction of self-addition of ethylene molecules is generated, resulting in the production of a high-molecular-weight material, almost identical in chemical composition to ethylene, known as polyethylene, the polymer of ethylene (Figure 1.1).

The difference in behavior between ordinary organic compounds and polymeric materials is due mainly to the large size and shape of polymer molecules. Common organic materials such as alcohol, ether, chloroform, sugar, and so on, consist of small molecules having molecular weights usually less than 1,000. The molecular weights of polymers, on the other hand, vary from 20,000 to hundreds of thousands.

The name polymer is derived from the Greek *poly* for many and *meros* for parts. A polymer molecule consists of a repetition of the unit called a *mer*. Mers are derived from monomers, which, as we have seen for ethylene, can link up or polymerize under certain conditions to form the polymer molecule. The number of mers, or more precisely the number of repetitions of the mer, in a polymer chain is called the degree of polymerization (DP). Since the minimum length or size of the molecule is not specified, a relatively small molecule composed of only, say, 3 mers might also be called a polymer. However, the term polymer is generally accepted to imply a molecule of large size (macromolecule). Accordingly, the lower-molecular-weight products with low DP should preferably be called oligomers (*oligo*=few) to distinguish them from polymers. Often the term high polymer is also used to emphasize that the polymer under consideration is of very high molecular weight.

Because of their large molecular size, polymers possess unique chemical and physical properties. These properties begin to appear when the polymer chain is of sufficient length—i.e., when the molecular weight exceeds a threshold value—and becomes more prominent as the size of the molecule increases. The dependence of the softening temperature of polyethylene on the degree of polymerization is shown

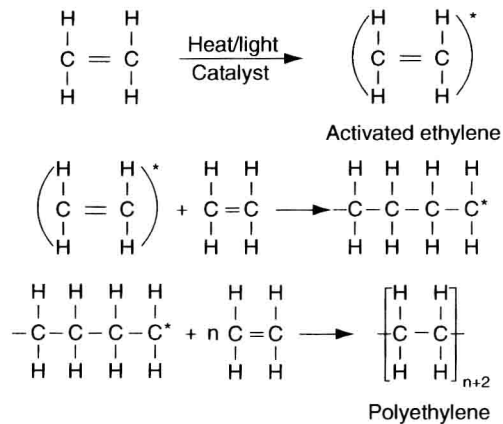


FIGURE 1.1 Intermediate steps during formation of polyethylene.

in Figure 1.2a. The dimer of ethylene is a gas, but oligomers with a DP of 3 or more (that is, C_6 — or higher paraffins) are liquids, with the liquid viscosity increasing with the chain length. Polyethylenes with DP's of about 30 are greaselike, and those with DP's around 50 are waxes. As the DP value exceeds 400 or the molecular weight exceeds about 10,000, polyethylenes become hard resins with softening points about 100°C . The increase in softening point with chain length in the higher-molecular-weight range is small. The relationship of such polymer properties as tensile strength, impact strength, and melt viscosity with molecular weight is indicated in Figure 1.2b. Note that the strength properties increase rapidly first as the chain length increases and then level off, but the melt viscosity continues to increase rapidly. Polymers with very high molecular weights have superior mechanical properties but are difficult to process and fabricate due to their high melt viscosities. The range of molecular weights chosen for commercial polymers represents a compromise between maximum properties and processability.

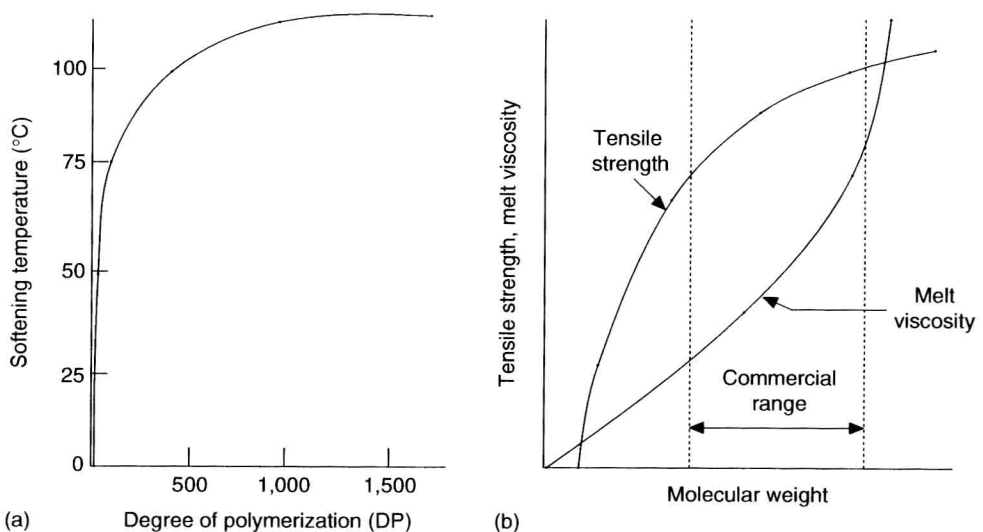


FIGURE 1.2 Polymer properties versus polymer size. (a) Softening temperature of polyethylene. (b) Tensile strength, and melt viscosity. (Adapted from Seymour, R. B. and Carraher, C. E. Jr., 1992. *Polymer Chemistry. An Introduction*. Marcel Dekker, New York.)

1.2 Molecular Weight of Polymers

In ordinary chemical compounds such as sucrose, all molecules are of the same size and therefore have identical molecular weights (M). Such compounds are said to be monodisperse. In contrast, most polymers are polydisperse. Thus a polymer does not contain molecules of the same size and, therefore, does not have a single molecular weight. In fact, a polymer contains a large number of molecules—some big, some small. Thus there exists a variation in molecular size and weight, known as *molecular-weight distribution* (MWD), in every polymeric system, and this MWD determines to a certain extent the general behavior of polymers. Since a polymer consists of molecules of different sizes and weights, it is necessary to calculate an average molecular weight (\bar{M}) or an *average degree of polymerization* (\overline{DP}).

The molecular weights commonly used in the characterization of a polydisperse polymer are the number average, weight average, and viscosity average.

Consider a sample of a polydisperse polymer of total weight W in which N =total number of moles; N_i =number of moles of species i (comprising molecules of the same size); n_i =mole fraction of species i ; W_i =weight of species i ; w_i =weight fraction of species i ; M_i =molecular weight of species i ; x_i =degree of polymerization of species i .

1.2.1 Number-Average Molecular Weight (\bar{M}_n)

From the definition of molecular weight as the weight of sample per mole, we obtain

$$\bar{M}_n = \frac{W}{N} = \frac{\sum N_i M_i}{N} = \sum n_i M_i \quad (1.1)$$

$$= \frac{\sum W_i}{\sum W_i / M_i} = \frac{\sum w_i}{\sum w_i / M_i} = \frac{1}{\sum w_i / M_i} \quad (1.2)$$

Dividing \bar{M}_n by the mer weight M_0 , we obtain a number-average degree of polymerization, \overline{DP}_n , where

$$\overline{DP}_n = \frac{\bar{M}_n}{M_0} = \frac{\sum N_i x_i}{\sum N_i} \quad (1.3)$$

The quantity \bar{M}_n is obtained by end-group analysis or by measuring a colligative property such as elevation of boiling point, depression of freezing point, or osmotic pressure [1,2].

1.2.2 Weight-Average Molecular Weight (\bar{M}_w)

Equation 1.1 indicates that in the computation of \bar{M}_n , the molecular weight of each species is weighted by the mole fraction of that species. Similarly, in the computation of weight-average molecular weight the molecular weight of each species is weighted by the weight fraction of that species:

$$\bar{M}_w = \sum w_i M_i = \frac{\sum W_i M_i}{\sum W_i} \quad (1.4)$$

$$= \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (1.5)$$

The weight-average degree of polymerization, \overline{DP}_w , is obtained by dividing \bar{M}_w , by the mer weight:

$$\overline{DP}_w = \frac{\bar{M}_w}{M_0} = \frac{\sum W_i x_i}{\sum W_i} \quad (1.6)$$

\bar{M}_w can be determined by measuring light scattering of dilute polymer solution [3,4]. \bar{M}_w is always higher than \bar{M}_n . Thus for a polymer sample containing 50 mol% of a species of molecular weight 10,000 and 50 mol% of species of molecular weight 20,000, Equation 1.1 and Equation 1.5 give $\bar{M}_n = 0.5(10,000 + 20,000) = 15,000$ and $\bar{M}_w = [(10,000)^2 + (20,000)^2]/[10,000 + 20,000] = 17,000$.

1.2.3 Viscosity-Average Molecular Weight (\bar{M}_v)

The viscosity-average molecular weight is defined by the equation

$$\bar{M}_v = \left[\sum w_i M_i^a \right]^{1/a} = \left[\sum N_i M_i^{1+a} / \sum N_i M_i \right]^{1/a} \quad (1.7)$$

For $a=1$, $\bar{M}_v = \bar{M}_w$ and for $a=-1$, $\bar{M}_v = \bar{M}_n$. Thus, \bar{M}_v falls between \bar{M}_w and \bar{M}_n , and for many polymers it is 10%–20% below \bar{M}_w . \bar{M}_v is calculated from the intrinsic viscosity $[\eta]$ by the empirical relation

$$[\eta] = K \bar{M}_v^\alpha \quad (1.8)$$

where K and α are constants. $[\eta]$ is derived from viscosity measurements by extrapolation to “zero” concentration [5,6].

In correlating polymer properties (such as reactivity) which depend more on the number of molecules in the sample than on the sizes of the molecules, \bar{M}_n is a more useful parameter than \bar{M}_w or \bar{M}_v . Conversely, for correlating polymer properties (such as viscosity) which are more sensitive to the size of the polymer molecules, \bar{M}_w or \bar{M}_v is more useful.

Because it is easy to determine, *melt index* often is used instead of molecular weight in routing characterization of polymers. It is defined as the mass rate of polymer flow through a specified capillary under controlled conditions of temperature and pressure. The index can often be related empirically to some average molecular weight, depending on the specific polymer. A lower melt index indicates a higher molecular weight, and vice versa.

1.2.4 Polydispersity Index

The ratio of weight-average molecular weight to number-average molecular weight is called the dispersion or polydispersity index (I). It is a measure of the width of the molecular-weight distribution curve (Figure 1.3) and is used as such for characterization purposes. Normally I is between 1.5 and 2.5, but it may range to 15 or greater. The higher the value of I is, the Greater is the spread of the molecular-weight distribution of the polymer. For a monodisperse system (e.g., pure chemicals), $I=1$.

There is usually a molecular size for which a given polymer property will be optimum for a particular application. So a polymer sample containing the greatest number of molecules of that size will have the optimum property. Since samples with the same average molecular weight may possess different molecular-weight distributions, information regarding molecular-weight distribution is necessary for a proper choice of polymer for optimum performance. A variety of fractionation techniques, such as fractional precipitation, precipitation chromatography, and gel permeation chromatography (GPC), based on properties such as solubility and permeability, which vary with molecular weight, may be used for separating polymers of narrow size ranges.

Example 1

A sample of poly(vinyl chloride) is composed according to the following fractional distribution (Figure 1.3).

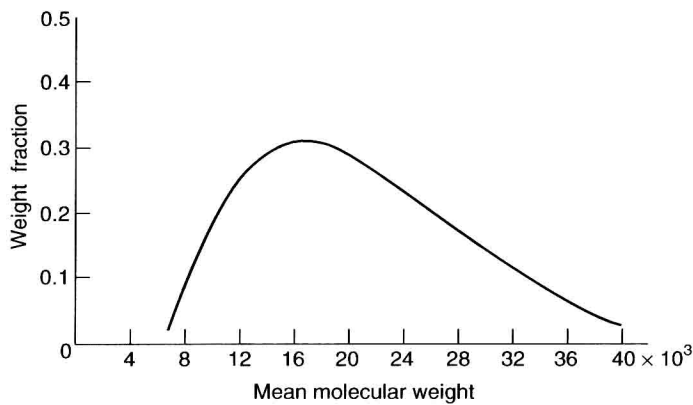


FIGURE 1.3 Molecular-weight distribution of a polymer.

Wt fraction	0.04	0.23	0.31	0.25	0.13	0.04
Mean mol. wt×10 ⁻³	7	11	16	23	31	39

- (a) Compute \bar{M}_n , \bar{M}_w , \overline{DP}_n , and \overline{DP}_w .
- (b) How many molecules per gram are there in the polymer?

Answer. (a)

Wt fraction (w_i)	Mean mol. wt (M_i)	$w_i \times M_i$	w_i/M_i
0.04	7,000	280	0.57×10^{-5}
0.23	11,000	2,530	2.09×10^{-5}
0.31	16,000	4,960	1.94×10^{-5}
0.25	23,000	5,750	1.90×10^{-5}
0.13	31,000	4,030	0.42×10^{-5}
0.04	39,000	1,560	0.10×10^{-5}
Σ		19,110	6.21×10^{-5}

From Equation 1.2

$$\bar{M}_n = \frac{1}{6.21 \times 10^{-5}} = 16,100 \text{ g/mole}$$

From Equation 1.4

$$\bar{M}_w = 19,110 \text{ g/mole}$$

1 mer weight of vinyl chloride (C_2H_3Cl) = (2)(12) + (3)(1) + 35.5 = 62.5 g/mer

$$\overline{DP}_n = \frac{16,000 \text{ g/mole}}{62.5 \text{ g/mer}} = 258 \text{ mers/mole}$$