Handbook of
Plastics
Technologies

The Complete Guide to Properties and Performance

- Design and manufacture of polymers

- Resins, adhesives, and plastic additives

- Industry specifications and standards

- Thermoplastic and thermosetting processing strategies

Charles A. Harper

Handbook of Plastics Technologies

Technologies

The Complete Guide to Properties and Performance

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PREFACE

It is a pleasure to present to my reading audience this new book in my series, entitled *Handbook of Plastics Technologies.* This new book, an extension of my Materials Science and Engineering Series, is a thorough, comprehensive, and completely up-to-date treatment of the ever more important and critical field of plastics. Prepared by a leading team of professional experts in this field, it will be a useful and practical addition to the bookshelves of both my established and new readers. Like the other books in my series, this *Handbook of Plastics Technologies* provides the broad array of practical information, data, and guidelines necessary to easily understand and use plastics to best advantage in all types of products and applications. This book will be useful to the wide spectrum of readers ranging from product designers to researchers to plastics application and marketing people.

Like the other books in my series, this book has been organized for easy reader convenience. First, a chapter is presented covering the fundamental and introductory aspects of plastics—a basic understanding of plastics types, categories, and forms. Next, a set of chapters is offered on the individual plastics categories, namely, thermoplastics, thermosets, and elastomers. Following that is a chapter covering plastics additives—the myriad ways in which plastics can be modified for specific end-use or application requirements. Then, a chapter is included on nanotechnology, the increasingly vital and exciting area in modern plastics technology. Finally, a set of chapters is included to cover three other areas of great importance in the successful application of plastics, namely the myriad techniques for joining of plastic parts, the increasingly critical area of plastics recycling by conventional means and by use of biodegradable plastics, and lastly, the successful use of plastics in the large and very critical area of automotive applications.

Needless to say, a book of this caliber could only have been achieved with a group of outstanding contributing authors, such as I have been extremely fortunate to have in preparing this book. I would like to take this opportunity to express my thanks to them. They have not only been great from the technology viewpoint, but they have been great people with whom to work. My thanks to all of them and the organizations that they represent. And my special thanks to Dr. Anne-Marie Baker for her work with the University of Massachusetts-Lowell team.

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CHAPTER 1
INTRODUCTION TO POLYMERS AND PLASTICS

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1.1 INTRODUCTION

Plastics are an important part of everyday life; products made from plastics range from sophisticated products, such as prosthetic hip and knee joints, to disposable food utensils. One of the reasons for the great popularity of plastics in a wide variety of industrial applications is the tremendous range of properties exhibited by plastics and their ease of processing. Plastic properties can be tailored to meet specific needs by varying the atomic composition of the repeat structure, by varying molecular weight and molecular weight distribution. The flexibility can also be varied through the presence of side chain branching, via the lengths and polarities of the side chains. The degree of crystallinity can be controlled through the amount of orientation imparted to the plastic during processing, through copolymerization, blending with other plastics, and through the incorporation of an enormous range of additives (fillers, fibers, plasticizers, stabilizers). Given all of the avenues available for tailoring any given polymer, it is not surprising that the variety of choices available to us today exist.

Polymeric materials have been used since early times even though their exact nature was unknown. In the 1400s, Christopher Columbus found natives of Haiti playing with balls made from material obtained from a tree. This was natural rubber, which became an important product after Charles Goodyear discovered that the addition of sulfur dramatically improved the properties; however, the use of polymeric materials was still limited to natural-based materials. The first true synthetic polymers were prepared in the early 1900s using phenol and formaldehyde to form resins—Baekeland's Bakelite. Even with the development of synthetic polymers, scientists were still unaware of the true nature of the materials they had prepared. For many years, scientists believed they were colloids—a substance that is an aggregate of molecules. It was not until the 1920s that Herman Staudinger showed that polymers were giant molecules or macromolecules. In 1928, Carothers developed linear polyesters and then polyamides, now known as nylon. In the 1950s, Ziegler and Natta's work on anionic coordination catalysts led to the development of polypropylene, high-density, linear polyethylene, and other stereospecific polymers. More recent developments include Metallocene catalysts for preparation of stereospecific polymers and the use of polymers in nanotechnology applications.

Materials are often classified as either metals, ceramics, or polymers. Polymers differ from the other materials in a variety of ways but generally exhibit lower densities, thermal conductivities, and moduli. Table 1.1 compares the properties of polymers to some representative ceramic and metallic materials. The lower densities of polymeric materials offer an advantage in applications where lighter weight is desired. The use of additives allows the compounder to develop a host of materials for specific application. For example, the addition of conducting fillers generates materials from insulating to conducting. As a result, polymers may find application in EMI shielding and antistatic protection.

Polymeric materials are used in a vast array of products. In the automotive area, they are used for interior parts and in under-the-hood applications. Packaging applications are a large area for thermoplastics, from carbonated beverage bottles to plastic wrap. Application requirements vary widely but, luckily, plastic materials can be synthesized to meet these varied service conditions. It remains the job of the part designer to select from the array of thermoplastic materials available to meet the required demands.

1.2 POLYMER STRUCTURE AND SYNTHESIS

A polymer is prepared by stringing together a low molecular weight species (monomer; e.g., ethylene) into an extremely long chain (polymer; in the case of ethylene, the polymer is polyethylene) much as one would string together a series of bead to make a necklace (see Fig. 1.1). The chemical characteristics of the starting low molecular weight species will determine the properties of the final polymer. When two low different molecular

TABLE 1.1 Properties of Selected Materials[48]

Material	Specific gravity	Thermal conductivity, Joule cm/(°C cm^2 s)	Electrical resistivity, $\mu\Omega$ cm	Modulus, MPa
Aluminum	2.7	2.2	2.9	70,000
Brass	8.5	1.2	6.2	110,000
Copper	8.9	4.0	1.7	110,000
Steel (1040)	7.85	0.48	17.1	205,000
Al_2O_3	3.8	0.29	$>10^{14}$	350,000
Concrete	2.4	0.01	–	14,000
Borosilicate glass	2.4	0.01	$>10^{17}$	70,000
MgO	3.6	–	10^5 (2000° F)	205,000
Polyethylene (H.D.)	0.96	0.0052	10^{14}–10^{18}	350–1,250
Polystyrene	1.05	0.0008	10^{18}	2,800
Polymethyl methacrylate	1.2	0.002	10^{16}	3,500
Nylon	1.15	0.0025	10^{14}	2,800

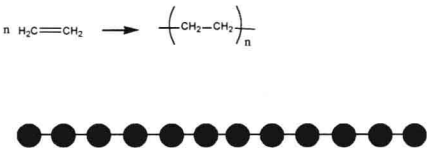$$n \; H_2C = CH_2 \longrightarrow \left(CH_2 - CH_2 \right)_n$$

FIGURE 1.1 Polymerization.

weight species are polymerized, the resulting polymer is termed a *copolymer*—for example, ethylene vinylacetate. This is depicted in Fig. 1.2. Plastics can also be classified as either *thermoplastics* or *thermosets*. A thermoplastic material is a high molecular weight polymer that is not crosslinked. It can exist in either a linear or branched structure. Upon heating, thermoplastics soften and melt, allowing them to be shaped using plastics processing equipment. A thermoset has all of the chains tied together with covalent bonds in a three-dimensional network (crosslinked). Thermoset materials will not flow once crosslinked, but a thermoplastic material can be reprocessed simply by heating it to the appropriate temperature. The different types of structures are shown in Fig. 1.3. The properties of different polymers can vary widely; for example, the modulus can vary from 1 MN/ m^2 to 50 GN/m^2. For a given polymer, it is also possible to vary the properties simply by varying the microstructure of the material.

FIGURE 1.2 Copolymer structure.

| Linear | Branched | Cross-linked |
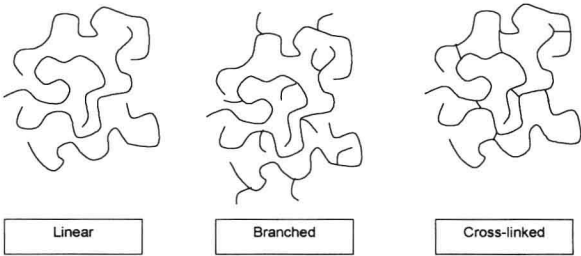
FIGURE 1.3 Linear, branched, and cross-linked polymer structures.

There are two primary polymerization approaches: *step-reaction polymerization* and *chain-reaction polymerization.*[1] In step-reaction (also referred to as *condensation polymerization*), reaction occurs between two polyfunctional monomers, often liberating a small molecule such as water. As the reaction proceeds higher molecular weight species are produced as longer and longer groups react together. For example, two monomers can react to form a dimer then react with another monomer to form a trimer. The reaction can be described as n-mer + m-mer → (n + m)mer, where n and m refer to the number of monomer units for each reactant. Molecular weight of the polymer builds up gradually with time, and high conversions are usually required to produce high molecular weight

polymers. Polymers synthesized by this method typically have atoms other than carbon in the backbone. Examples include polyesters and polyamides.

Chain-reaction polymerizations (also referred to as *addition polymerizations*) require an initiator for polymerization to occur. Initiation can occur by a free radical, an anionic, or a cationic species. These initiators open the double bond of a vinyl monomer, and the reaction proceeds as shown above in Fig. 1.1. Chain-reaction polymers typically contain only carbon in their backbone and include such polymers as polystyrene and polyvinyl chloride.

Unlike low molecular weight species, polymeric materials do not possess one unique molecular weight but rather a distribution of weights as depicted in Fig. 1.4. Molecular weights for polymers are usually described by two different average molecular weights, the number average molecular weight, $\overline{M}_n$, and the weight average molecular weight, $\overline{M}_w$. These averages are calculated using the equations below:

$$\overline{M}_n = \sum_{i=1}^{\infty} \frac{n_i M_i}{n_i} \tag{1.1}$$

$$\overline{M}_w = \sum_{i=1}^{\infty} \frac{n_i M_i^2}{n_i M_i} \tag{1.2}$$

where ni is the number of moles of species i, and Mi is the molecular weight of species i. The processing and properties of polymeric materials are dependent on the molecular weights of the polymer as well as the molecular weight distribution. The molecular weight of a polymer can be determined by a number of techniques including light scattering, solution viscosity, osmotic pressure, and gel permeation chromatography.

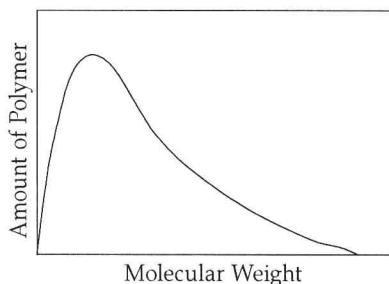**FIGURE 1.4**   Molecular weight distribution.

1.3 SOLID PROPERTIES OF POLYMERS

1.3.1 Glass Transition Temperature (T_g)

Polymers come in many forms, including plastics, rubber, and fibers. Plastics are stiffer than rubber yet have reduced low-temperature properties. Generally, a plastic differs from a rubbery material due to the location of its glass transition temperature (T_g). A plastic has

a T_g above room temperature, while a rubber has a T_g below room temperature. T_g is most clearly defined by evaluating the classic relationship of elastic modulus to temperature for polymers as presented in Fig. 1.5.
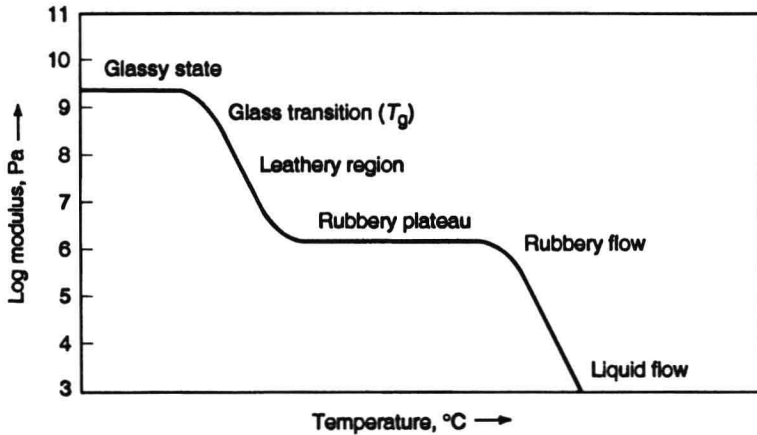

FIGURE 1.5 Relationship between elastic modulus and temperature.

At low temperatures, the material can best be described as a glassy solid. It has a high modulus, and behavior in this state is characterized ideally as a purely elastic solid. In this temperature regime, materials most closely obey Hooke's law:

$$\sigma = E\varepsilon \tag{1.3}$$

where σ is the stress being applied, and ε is the strain. Young's modulus, E, is the proportionality constant relating stress and strain.

In the leathery region, the modulus is reduced by up to three orders of magnitude from the glassy modulus for amorphous polymers. The temperature at which the polymer behavior changes from glassy to leathery is known as the glass transition temperature, T_g. The rubbery plateau has a relatively stable modulus until further temperature increases induce rubbery flow. Motion at this point does not involve entire molecules but, in this region, deformations begin to become nonrecoverable as permanent set takes place. As temperature is further increased, the onset of liquid flow eventually takes place. There is little elastic recovery in this region, and the flow involves entire molecules slipping past each other. This region models ideal viscous materials, which obey Newton's law:

$$\sigma = \eta\dot{\varepsilon} \tag{1.4}$$

In the case of a thermosetting material, the rubbery plateau is extended until degradation and no liquid flow will occur.

1.3.2   Crystallization and Melting Behavior (T_m)

In its solid form, a polymer can exhibit different morphologies, depending on the structure of the polymer chain as well as the processing conditions. The polymer may exist in a ran-

dom unordered structure termed *amorphous*. An example of an amorphous polymer is polystyrene. If the structure of the polymer backbone is a regular, ordered structure, then the polymer can tightly pack into an ordered crystalline structure, although the material will generally be only semicrystalline. Examples are polyethylene and polypropylene. The exact makeup and architecture of the polymer backbone will determine whether the polymer is capable of crystallizing. This microstructure can be controlled by different synthetic methods. As mentioned above, the Ziegler-Natta catalysts are capable of controlling the microstructure to produce stereospecific polymers. The types of microstructure that can be obtained for a vinyl polymer are shown in Fig. 1.6. The isotactic and syndiotactic structures are capable of crystallizing because of their highly regular backbone, while the atactic form would produce an amorphous material. The amount of crystallinity actually present in the polymer depends on a number of factors, including the rate of cooling, crystallization kinetics, and the crystallization temperature. Thus, the extent of crystallization can vary greatly for a given polymer and can be controlled through processing conditions.

| Isotactic | Syndiotactic | Atactic |
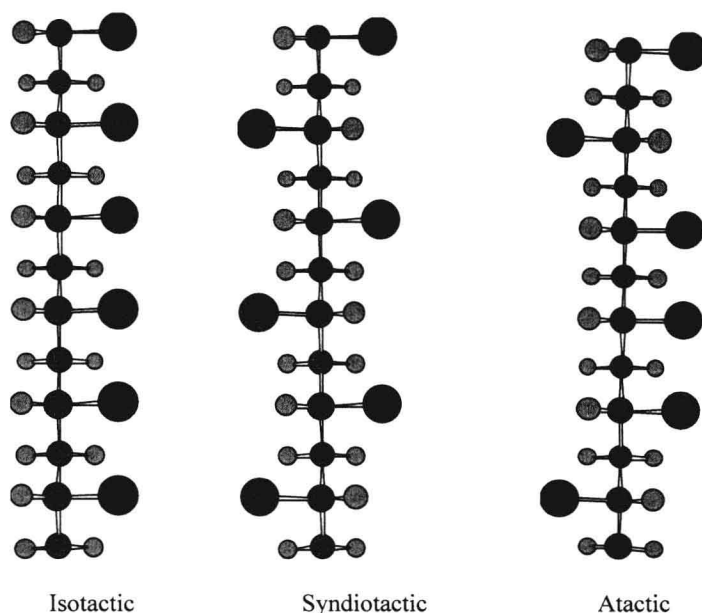
FIGURE 1.6   Isotactic, syndiotactic, and atactic polymer chains.

1.4 MECHANICAL PROPERTIES

The mechanical behavior of polymers is dependent on many factors, including polymer type, molecular weight, and test procedure. Modulus values are obtained from a standard tensile test with a given rate of crosshead separation. In the linear region, the slope of a stress-strain curve will give the elastic or Young's modulus, E. Typical values for Young's modulus are given in Table 1.2. Polymeric material behavior may be affected by other fac-

TABLE 1.2 Comparative Properties of Thermoplastics [49,50]

Material	Heat deflection temperature @ 1.82 MPa (°C)	Tensile strength, MPa	Tensile modulus, GPa	Impact strength, J/m	Density. g/cm^3	Dielectric strength, MV/m	Dielectric constant @ 60 Hz
ABS	99	41	2.3	347	1.18	15.7	3.0
CA	68	37.6	1.26	210	1.30	16.7	5.5
CAB	69	34	.88	346	1.19	12.8	4.8
PTFE		17.1	.36	173	2.2	17.7	2.1
PCTFE		50.9	1.3	187	2.12	22.2	2.6
PVDF	90	49.2	2.5	202	1.77	10.2	10.0
PB	102	25.9	0.18	NB	0.91		2.25
LDPE	43	11.6	0.17	NB	0.92	18.9	2.3
HDPE	74	38.2		373	0.95	18.9	2.3
PMP		23.6	1.10	128	0.83	27.6	
PI		42.7	3.7	320	1.43	12.2	4.1
PP	102	35.8	1.6	43	0.90	25.6	2.2
PUR	68	59.4	1.24	346	1.18	18.1	6.5
PS	93	45.1	3.1	59	1.05	19.7	2.5
PVC—rigid	68	44.4	2.75	181	1.4	34.0	3.4
PVC—flexible		9.6		293	1.4	25.6	5.5

1.7

TABLE 1.2 Comparative Properties of Thermoplastics (*Continued*)[49,50]

Material	Heat deflection temperature @ 1.82 MPa (°C)	Tensile strength, MPa	Tensile modulus, GPa	Impact strength, J/m	Density, g/cm³	Dielectric strength, MV/m	Dielectric constant @ 60 Hz
POM	136	69	3.2	133	1.42	19.7	3.7
PMMA	92	72.4	3	21	1.19	19.7	3.7
Polyarylate	155	68	2.1	288	1.19	15.2	3.1
LCP	311	110	11	101	1.70	20.1	4.6
Nylon 6	65	81.4	2.76	59	1.13	16.5	3.8
Nylon 6.6	90	82.7	2.83	53	1.14	23.6	4.0
PBT	54	52	2.3	53	1.31	15.7	3.3
PC	129	69	2.3	694	1.20	15	3.2
PEEK	160	93.8	3.5	59	1.32		
PEI	210	105	3	53	1.27	28	3.2
PES	203	84.1	2.6	75	1.37	16.1	3.5
PET	224	159	8.96	101	1.56	21.3	3.6
PPO (modified)	100	54	2.5	267	1.09	15.7	3.9
PPS	260	138	11.7	69	1.67	17.7	3.1
PSU	174	73.8	2.5	64	1.24	16.7	3.5

tors such as test temperature and rates. This can be especially important to the designer when the product is used or tested at temperatures near the glass transition temperature, where dramatic changes in properties occur as depicted in Fig. 1.5. The time-dependent behavior of these materials is discussed below.

1.4.1 Viscoelasticity

Polymer properties exhibit time-dependent behavior, meaning that the measured properties are dependent on the test conditions and polymer type. Figure 1.7 shows a typical viscoelastic response of a polymer to changes in testing rate or temperature. Increases in testing rate or decreases in temperature cause the material to appear more rigid, while an increase in temperature or decrease in rate will cause the material to appear softer. This time-dependent behavior can also result in long-term effects such as stress-relaxation or creep.[2] These two time-dependent behaviors are shown in Fig. 1.8. Under a fixed displacement, the stress on the material will decrease over time, termed *stress relaxation*. This behavior can be modeled using a spring and dashpot in series as depicted in Fig. 1.9. The equation for the time dependent stress using this model is

$$\sigma(t) = \sigma_o e^{-t/\tau} \qquad (1.5)$$
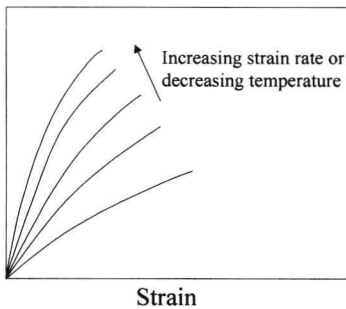
FIGURE 1.7 Effect of strain rate or temperature on mechanical behavior.
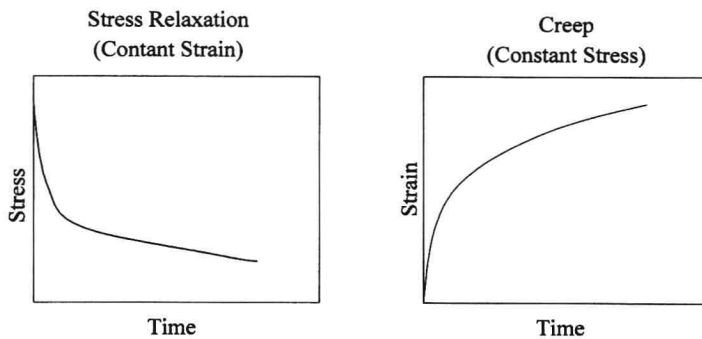
FIGURE 1.8 Creep and stress relaxation behavior.
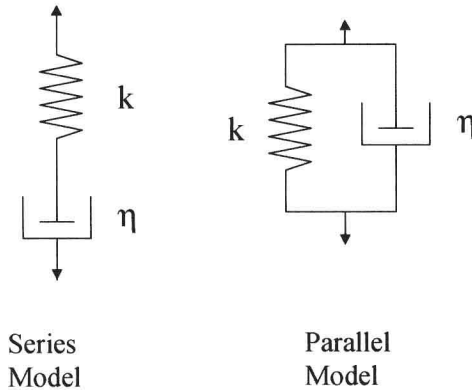
Series
Model

Parallel
Model

FIGURE 1.9   Spring and dashpot models.

where τ is the characteristic relaxation time (η/k). Under a fixed load, the specimen will continue to elongate with time, a phenomenon termed *creep*, which can be modeling using a spring and dashpot in parallel as seen in Fig. 1.9. This model predicts the time-dependent strain as

$$\varepsilon(t) = \varepsilon_o e^{-t/\tau} \tag{1.6}$$

For more accurate prediction of the time-dependent behavior, other models with more elements are often employed. In the design of polymeric products for long-term applications, the designer must consider the time-dependent behavior of the material.

If a series of stress relaxation curves is obtained at varying temperatures, it is found that these curves can be superimposed by horizontal shifts to produce a master curve.[3] This demonstrates an important feature in polymer behavior: the concept of time-temperature equivalence. In essence, a polymer at temperatures below room temperature will behave as if it were tested at a higher rate at room temperature. This principle can be applied to predict material behavior under testing rates or times that are not experimentally accessible through the use of shift factors (aT) and the equation below:

$$\ln a_T = \ln\left(\frac{t}{t_o}\right) = -\frac{17.44(T - T_g)}{51.6 + T - T_g} \tag{1.7}$$

where T_g is the glass transition temperature of the polymer.

1.4.2   Failure Behavior

The design of plastic parts requires the avoidance of failure without overdesign of the part, leading to increased part weight. The type of failure can depend on temperatures, rates, and materials. Some information on material strength can be obtained from simple tensile stress-strain behavior. Materials that fail at rather low elongations (1 percent strain or less) can be considered to have undergone brittle failure.[4] Polymers that produce this type of