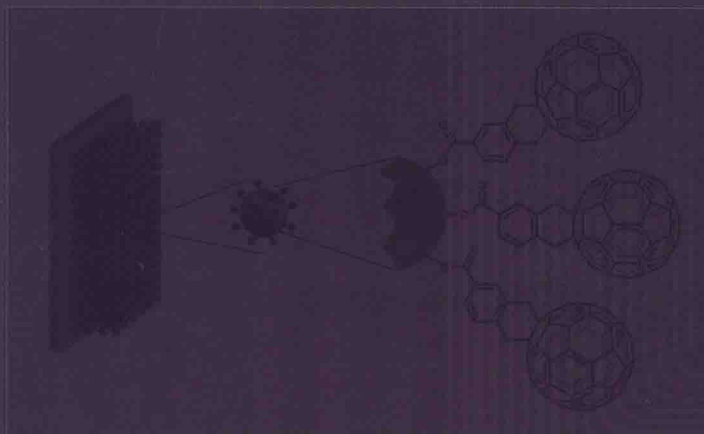
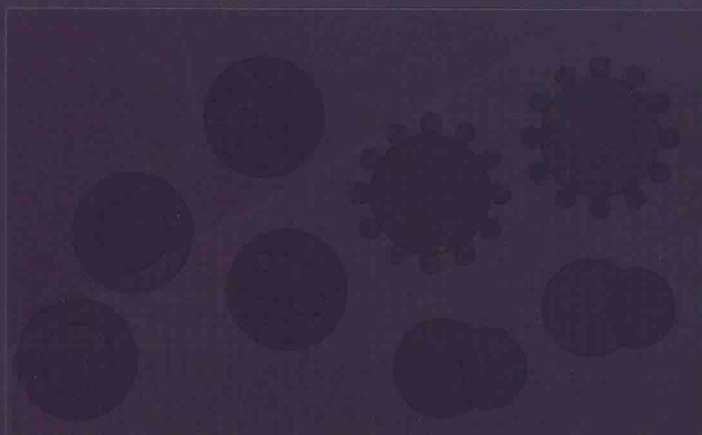


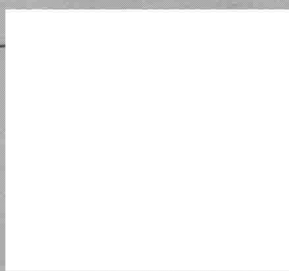

Applied Polymer Materials

应用高分子材料

王者辉 著



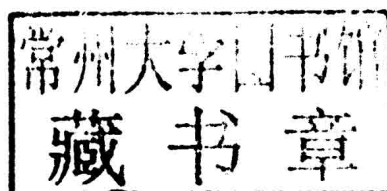
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Applied Polymer Materials

应用高分子材料

王者辉 著



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· 北京 ·

本书以高分子材料的结构·性能·应用为主线,联系其他材料科学,理论结合实际,介绍了各类高分子材料的基础知识和相关的加工成型方法。全书共分6章,高分子材料科学概述、塑料与增塑剂、高分子材料在汽车工业中的应用、医用高分子材料、高分子材料加工技术、纳米材料与高分子材料的新发展,此外,书末附有高分子材料专业词汇注释。本书阐述了高分子材料的基本理论,同时注重高分子材料科学技术知识的实用性。

《Applied Polymer Materials (应用高分子材料)》可供从事高分子材料专业及其他材料科学的科研和生产技术人员使用。

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前言

材料是人类用来制造各种产品的物质，是人类生活和生产的物质基础，它先于人类存在，人类社会一开始就与材料结下了不解之缘。材料的进步和发展直接影响到人类生活的改善和科学技术的进步。目前，材料已和能源、信息并列成为现代科学的三大支柱。其中材料是工业发展的基础，一个国家材料的品种和产量是直接衡量其科学技术、经济发展和人民生活水平的重要标志，也是一个时代的标志。

高分子材料也叫聚合物材料，按照其来源可以分为天然高分子材料和合成高分子材料。天然高分子材料有天然橡胶、纤维素、淀粉、甲壳素、蚕丝等。合成高分子材料的种类繁多，如合成塑料、合成橡胶、合成纤维等。按照高分子材料的物理形态和用途分类，可分为塑料、橡胶、纤维、黏合剂、涂料、聚合物基复合材料、聚合物合金、功能高分子材料、生物高分子材料等。

研究高分子材料，掌握高分子材料科学的基本内容，了解高分子材料的基本结构、性能、用途、合成制造和加工方法，是本书的主要目的。由于篇幅所限，本书只简要介绍了高分子科学——高分子化学和高分子物理的基础知识，介绍了高分子材料的成型加工，及其在汽车工业、医药卫生、建筑材料、包装材料等领域的应用，最后还讲述了纳米技术在高分子材料中的应用。

本书共分六章，其中第一、六章由王者辉撰写，第二章由中材科技集团泰山玻纤有限公司的李庆杰撰写，第三章由孙红撰写，第四章由张宏志撰写，第五章由卫振华撰写，巩学勇和常海涛对全书进行了校阅，最后由王者辉进行统一校订。

由于时间仓促，水平有限，本书不足之处在所难免，敬请读者指正。

作者
2016年3月

Preface

The field of materials science and engineering is important both from a scientific perspective, as well as from an engineering one. When discovering new materials, one encounters new phenomena that may not have been observed before. Hence, there is a lot of science to be discovered when working with materials. Materials science also provides test for theories in condensed matter physics. Material for an engineer is of the utmost importance. The usage of the appropriate materials is crucial when designing systems, and hence, engineers are always involved in materials. Thus, materials science is becoming increasingly important in an engineer's education.

Polymer is also an important part of materials science. Polymers are the raw materials (the resins) used to make what we commonly call plastics. Plastics are really the final product, created after one or more polymers or additives have been added to a resin during processing, which is then shaped into a final form. Polymers which have been around, and which are in current widespread use, include polyethylene, polypropylene, PVC, polystyrene, nylons, polyesters, acrylics, polyurethanes, and polycarbonates. Plastics are generally classified as “commodity”, “specialty” and “engineering” plastics.

Specialty plastics are materials with unique characteristics, such as ultra-high strength, electrical conductivity, electro-fluorescence, high thermal stability, etc.

The dividing lines between the various types of plastics are not based on materials but rather on their properties and applications. For instance, polyethylene (PE) is a cheap, low friction polymer commonly used to make disposable shopping bags and trash bags, and is considered a commodity plastic, whereas medium-density polyethylene (MDPE) is used for underground gas and water pipes, and another variety called Ultra-high Molecular Weight Polyethylene (UHMWPE) is an engineering plastic which is used extensively as the glide rails for industrial equipment and the low-friction socket in implanted hip joints.

Nanotechnology topics have been included at the end of this book. These topics include the study of materials with nano scale features (for instance, nano grain size), instruments that are needed to study nano scale features, processing techniques, and properties of materials with nano scale features.

The author would like to acknowledge the efforts of the collaborating authors Qingjie Li, Hong Sun, Hongzhi Zhang, Zhenhua Wei, and, Xueyong Gong and Haitao Chang for writing the sections on medical polymer materials and assembling the chapter. The author would like to acknowledge with appreciation the numerous and valuable comments, suggestions, constructive criticisms and praise from evaluators and reviewers.

Zhehui Wang
2016.03

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Chapter

1

Fundamentals of Polymer Science

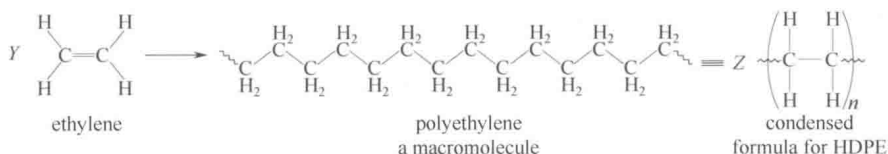
1.1 Introduction

Prior to the early 1920s, chemists doubted the existence of molecules having molecular masses greater than a few thousand. This limiting view was challenged by Hermann Staudinger, a German chemist with experience in studying natural compounds such as rubber and cellulose. In contrast to the prevailing rationalization of these substances as aggregates of small molecules, Staudinger proposed they were made up of **macromolecules** composed of 10000 or more atoms. He formulated a **polymeric** structure for rubber, based on a repeating isoprene unit (referred to as a monomer). For his contributions to chemistry, Staudinger received the 1953 Nobel Prize. The terms **polymer** and **monomer** were derived from the Greek roots poly (many), mono (one) and meros (part).

Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Some important examples of these substances are discussed in section 1.1.1.

1.1.1 Writing Formulas for Polymeric Macromolecules

The repeating structural unit of most simple polymers not only reflects the monomer(s) from which the polymers are constructed, but also provides a concise means for drawing structures to represent these macromolecules. For polyethylene, arguably the simplest polymer, this is demonstrated by the following equation. Here ethylene (ethene) is the monomer, and the corresponding linear polymer is called high-density polyethylene (HDPE). HDPE is composed of macromolecules in which n ranges from 10000 to 100000 (molecular mass 2×10^5 to 3×10^6).



If Y and Z represent moles of monomer and polymer respectively, Z is approximately $10^{-5} Y$. This polymer is called polyethylene rather than polymethylene, $(\text{---CH}_2\text{---})_n$, because ethylene is a stable

compound (methylene is not), and it also serves as the synthetic precursor of the polymer. The two open bonds remaining at the ends of the long chain of carbons are normally not specified, because the atoms or groups found there depend on the chemical process used for polymerization. The synthetic methods used to prepare this and other polymers will be described in section 1.2~1.4.

Unlike simpler pure compounds, most polymers are not composed of identical molecules. The HDPE molecules, for example, are all long carbon chains, but the lengths may vary by thousands of monomer units. Because of this, polymer molecular masses are usually given as averages. Two experimentally determined values are common (Fig.1.1): M_n , the number average molecular mass, is calculated from the mole fraction distribution of different sized molecules in a sample; and M_w , the mass average molecular mass, is calculated from the mass fraction distribution of different sized molecules. Since larger molecules in a sample weigh more than smaller molecules, the mass average M_w is necessarily skewed to higher values, and is always greater than M_n . As the mass dispersion of molecules in a sample narrows, M_w approaches M_n , and in the unlikely case that all the polymer molecules have identical weights (a pure mono-disperse sample), the ratio M_w/M_n becomes unity.

$$M_n = \sum n_i M_i \quad \text{where} \quad n_i = \text{mole fraction of chains with molecular mass } M_i$$
$$M_w = \sum w_i M_i \quad \text{where} \quad w_i = \text{mass fraction of chains with molecular mass } M_i$$

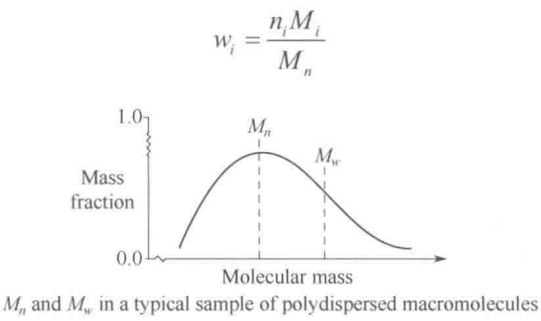


Fig.1.1 Polymer molecular mass and mass distribution

The influence of different mass distributions on M_n and M_w may be examined with the aid of a simple mass calculator.

Many polymeric materials having chain-like structures similar to polyethylene are known. Polymers formed by a straightforward linking together of monomer units, with no loss or gain of material, are called **addition polymers** or **chain-growth polymers**. A listing of some important addition polymers and their monomer precursors is presented in Table 1.1.

Table 1.1 Some common addition polymers

Name(s)	Formula	Monomer	Properties	Uses
Low-density polyethylene (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
High-density polyethylene(HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation, bottles, toys
Polypropylene (PP) different grades	$[-CH_2-CH(CH_3)]_n-$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE, carpet, upholstery
Poly (vinyl chloride) (PVC)	$-(CH_2-CHCl)_n-$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly (vinylidene chloride) (Saran A)	$-(CH_2-CCl_2)_n-$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films

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Name(s)	Formula	Monomer	Properties	Uses
Polystyrene (PS)	$\text{--[CH}_2\text{--CH(C}_6\text{H}_5\text{)]}_n\text{--}$	styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets, packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$\text{--[CH}_2\text{--CHCN)]}_n\text{--}$	acrylonitrile $\text{CH}_2=\text{CHCN}$	high-melting solid, soluble in organic solvents	rugs, blankets, clothing
Polytetrafluoroethylene (PTFE, Teflon)	$\text{--[CF}_2\text{--CF}_2\text{)]}_n\text{--}$	tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	resistant, smooth solid	non-stick surfaces, electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$\text{--[CH}_2\text{--C(CH}_3\text{)CO}_2\text{CH}_3\text{)]}_n\text{--}$	methyl methacrylate $\text{CH}_2=\text{C(CH}_3\text{)CO}_2\text{CH}_3$	hard, transparent solid	lighting covers, signs, skylights
Poly(vinyl acetate) (PVAc)	$\text{--[CH}_2\text{--CHOCOCH}_3\text{)]}_n\text{--}$	vinyl acetate $\text{CH}_2=\text{CHOCOCH}_3$	soft, sticky solid	latex paints, adhesives
<i>cis</i> -Polyisoprene natural rubber	$\text{--[CH}_2\text{--CH=C(CH}_3\text{)--CH}_2\text{)]}_n\text{--}$	isoprene $\text{CH}_2=\text{CH--C(CH}_3\text{)=CH}_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (<i>cis</i> + <i>trans</i>) (Neoprene)	$\text{--[CH}_2\text{--CH=CCl--CH}_2\text{)]}_n\text{--}$	chloroprene $\text{CH}_2=\text{CH--CCl=CH}_2$	tough, rubbery solid	oil resistant synthetic rubber

1.1.2 Properties of Macromolecules

A comparison of the properties of polyethylene (both LDPE & HDPE) with the natural polymers rubber and cellulose is instructive. As noted above, synthetic HDPE macromolecules have masses ranging from 10^5 to 10^6 amu (LDPE molecules are more than a hundred times smaller). Rubber and cellulose molecules have similar mass ranges, but fewer monomer units because of the monomer's larger size. The physical properties of these polymeric substances differ from each other, and of course from their monomers.

HDPE is a rigid translucent solid which softens on heating above 100°C , and can be fashioned into various forms including films. It is not as easily stretched and deformed as LDPE. HDPE is insoluble in water and most organic solvents, although some swelling may occur on immersion in the latter. HDPE is an excellent electrical insulator.

LDPE is a soft translucent solid which deforms badly above 75°C . Films made from LDPE stretch easily and are commonly used for wrapping. LDPE is insoluble in water, but softens and swells on exposure to hydrocarbon solvents. Both LDPE and HDPE become brittle at very low temperatures (below -80°C). Ethylene, the common monomer for these polymers, is a low boiling (-104°C) gas.

Natural (latex) rubber is an opaque, soft, easily deformable solid. It becomes sticky when heated (above 60°C), and brittle when cooled below -50°C . It swells to more than double its size in nonpolar organic solvents like toluene, eventually dissolving, but is impermeable to water. The C_5H_8 monomer isoprene is a volatile liquid (b.p. 34°C).

Pure cellulose, in the form of cotton, is a soft flexible fiber, essentially unchanged by variations in temperature ranging from -70°C to 80°C . Cotton absorbs water readily, but is unaffected by immersion in toluene or most other organic solvents. Cellulose fibers may be bent and twisted, but do not stretch much before breaking. The monomer of cellulose is the $\text{C}_6\text{H}_{12}\text{O}_6$ (aldohexose, D-glucose). Glucose is a water soluble solid melting below 150°C .

To account for the differences noted here we need to consider the nature of the aggregate macromolecular structure, or **morphology**, of each substance. Because polymer molecules are so large, they generally pack together in a non-uniform fashion, with ordered or crystalline-like regions mixed together with disordered or amorphous domains. In some cases the entire solid may be amorphous, composed entirely of coiled and tangled macromolecular chains. Crystallinity occurs when linear polymer chains are structurally oriented in a uniform three-dimensional matrix. In Fig 1.2, crystalline domains are black line.

Increased crystallinity is associated with an increase in rigidity, tensile strength and opacity (due to light scattering). Amorphous polymers are usually less rigid, weaker and more easily deformed. They are often transparent.

1.1.3 Three Factors that Influence the Degree of Crystallinity

There are three factors that influence the degree of crystallinity.

- (i) Chain length
- (ii) Chain branching
- (iii) Interchain bonding

The importance of the first two factors is nicely illustrated by the differences between LDPE and HDPE. As noted earlier, HDPE is composed of very long unbranched hydrocarbon chains. They pack together easily in crystalline domains that alternate with amorphous segments, and the resulting material, while relatively strong and stiff, retains a degree of flexibility. In contrast, LDPE is composed of smaller and more highly branched chains which do not easily adopt crystalline structures. This material is therefore softer, weaker, less dense and more easily deformed than HDPE. As a rule, mechanical properties such as ductility, tensile strength, and hardness rise and eventually level off with increasing chain length.

The nature of cellulose supports the above analysis and demonstrates the importance of the third factor (iii). To begin with, cellulose chains easily adopt a stable rod-like conformation. These molecules align themselves side by side into fibers that are stabilized by inter-chain hydrogen bonding between the three hydroxyl groups on each monomer unit. Consequently, crystallinity is high and the cellulose molecules do not move or slip relative to each other. The high concentration of hydroxyl groups also accounts for the facile absorption of water, which also is characteristic of cotton.

Natural rubber is a completely amorphous polymer. Unfortunately, the potentially useful properties of raw latex rubber are limited by temperature dependence; however, these properties can be modified by chemical change. The *cis*-double bonds in the hydrocarbon chain provide planar segments that stiffen, but do not straighten the chain. If these rigid segments are completely removed by hydrogenation (H_2 & Pt catalyst), the chains lose all constraints, and the product is a low melting paraffin-like semisolid of little value. If instead, the chains of rubber molecules are slightly cross-linked by sulfur atoms, a process called **vulcanization** which was discovered by Charles Goodyear in 1839, the desirable elastomeric properties of rubber are substantially improved. At 2% to 3% crosslinking, a useful soft rubber, that no longer suffers stickiness and brittleness problems on heating and cooling, is obtained. At 25% to 35% crosslinking, a rigid hard rubber product is formed. Fig.1.2 shows a cross-linked section of amorphous rubber (a), and a display of the corresponding stretched section (b). The more highly-ordered chains in the stretched conformation are entropically unstable and return to their original coiled state when allowed to relax.