材料科学与工程专业系列教材

材

料概论

袁晓燕 李志宏 万怡灶 万小山 郭新权 摘编

Introduction to Materials



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内容提要

本书以各种材料的概述性基础知识及其重要品种的结构与应用为主要内容,涵盖金属材料、无机非金属材料、高分子材料及生物材料和复合材料。是继专业外语之后发展的一门材料类综合性双语教学课程教材。本书内容选自外文书籍、期刊和相关网站。全书共设5章,每章后附有关键词和简答题。

本书为高等理工科院校材料科学与工程专业本科公共基础理论课教材,同时也适用于本专业研究生的教学与科研,还可供从事材料方向研究和应用的科研技术人员参考。

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前 言

材料概论不仅包括高分子、无机非金属和金属三大材料,还涉及生物材料和复合材料的内容,是一门基于材料科学与工程一级学科的材料类概述性课程。

随着新的专业体制的调整,以往的三大材料专业——高分子材料专业、无机非金属材料专业和金属材料专业已合并为材料科学与工程专业。作为材料科学与工程专业下设的外文基础课程,专业外语已不能满足当前教学的需要。同时,随着材料科学的迅速发展,出现了许多新的材料品种,如纳米材料、生物降解材料等。为了适应新形势下材料专业的教学要求,培养学生灵活使用专业技术英语的能力,使之具备综合基本素质,我们结合以往的教学经验和科研背景,选取通俗易懂且知识新颖的内容,整理完成了这部《材料概论》双语课程教材。

本书是在天津大学"十五"规划重点课程建设项目的支持下完成的,是天津大学材料科学与工程专业平台课程《材料科学基础》、《材料物理性能》、《材料力学性能》、《材料分析方法》、《材料科学与工程实验》和《概料概论》系列教材的组成部分。不同于其他教材,本书以全英文的形式讲述高分子材料、陶瓷材料、金属材料以及复合材料的基础知识、各类材料的重要种类及其典型的应用实例。自2003年以来,本教材讲义已在本科生教学中使用过两次,并进行了多次修改。

全书共分5章,第1章介绍金属、陶瓷、高分子三大材料的结构特征,第2章至第5章分别介绍了金属、陶瓷、高分子和复合材料的重要类型及其应用。其中第1章由袁晓燕、李志宏、万小山、郭新权和万怡灶合作完成,第2章由万怡灶和万小山共同完成,第3章由李志宏完成,第4章由袁晓燕完成,第5章由万怡灶和郭新权共同完成。

在本书的整理过程中,李志崇教授审阅了全文,提出了有益的建议,同时也得到了原续波老师的指点,在此表示感谢!

由于本书的整理者水平有限,所选题材和内容可能存在片面性和不足,欢迎读者批评指正。

编者 2006年8月

Contents

1 Introduc		(1)
1.1 His	torical perspective	(1)
1.2 Clas		(1)
1.3 Stn		(2)
1.3.1		(2)
1.3.2		(6)
1.4 Pol	ymer structures ·····	
1.4.1	Macromolecules	(7)
1.4.2	U Company of the comp	(8)
1.4.3	Molecular structures ····	(9)
ricy words		(10)
* TODICETED		(10)
	n ······	(11)
	faterials ·····	(12)
2.1 Str	acture and properties of steel	(12)
2.1.1		(13)
2.1.2	Strength versus carbon content in steels	(14)
2.1.3	Formation of pearlite ·····	(16)
2.1.4	Effect of cooling rate ·····	(20)
2.1.5		(21)
2.1.6	Selecting carbon steels	(22)
2.2 He	at treatment of steels	(24)
2.2.1	Response of steels to heat treatment	(24)
2.2.2	Hardenability	(26)
2.2.3	Surface hardening ·····	(27)
2.2.4	Tempering ·····	(28)
2.2.5	Choice of heat treatment	(29)
2.3 Sta	inless steels ·····	(30)
2.3.1		(30)
2.3.2	Common stainless steel alloy systems	(33)
2.3.3		(34)
2.4 No	nferrous alloys ·····	(39)
2.4.1	Copper and its alloys	(39)
2.4.2	Aluminum and its alloys	(41)

2.4.3	Magnesium and its alloys ·····	(43)
2.4.4	Titanium and its alloys ·····	(44)
2.4.5	Refractory metals ·····	(45)
2.4.6	Superalloys ····	(46)
2.4.7	Noble metals ·····	(46)
2.4.8	Miscellaneous nonferrous alloys	(46)
Keywords ·		(47)
LIODICIES		(47)
	1	(48)
3 Ceramic	Materials ·····	(49)
3.1 Intr	oduction to ceramics	(49)
3.1.1	Definition of ceramics	(49)
3.1.2	Classification of ceramics	(49)
3.1.3	Overview of ceramic and glass manufacturing	(50)
3.1.4	Structure and properties of ceramics	(51)
3.1.5	History of ceramics	(52)
3.1.6	Impact on society	(52)
3.2 Wh	at are advanced ceramics	(55)
3.3 Str	actural ceramics and its development	(57)
3.3.1	Introduction and current status	(57)
3.3.2	Trends	(57)
3.3.3	Future work strategies	(59)
3.4 Ele	ctroceramics and its developing directions	(60)
3.4.1	What are electroceramics	(60)
3.4.2	Common applications for electroceramics	(60)
3.4.3	Fundamental research needs and developing trends for electroceramics	(61)
3.5 Bio	ceramics	(65)
3.5.1	Introduction	(65)
3.5.2	Bioinert and bioactive materials	(66)
3.5.3	Compatibility between bioceramics and the human environment	(67)
3.5.4	Most common bioceramics ·····	
3.5.5	Uses for bioceramics ·····	(69)
3.6 Adv	vanced ceramic materials: Summary of possible applications	(71)
3.6.1	Introduction	
3.6.2	State of the art	(71)
3.6.3	Trends for the future ·····	(73)
3.7 Ad	vanced ceramic materials: Basic research viewpoint	(78)
3.7.1	Introduction	
3.7.2	State of the art	(79)
3.7.3	Trends in technology ·····	(80)

3.7.4	Needs for future basic research ·····	(81)
LLCy Words		(85)
		(86)
Selected from	1	(86)
4 Polymer	Materials	(87)
4.1 Intr	oduction ·····	(87)
4.1.1	Formation ·····	(87)
4.1.2	Classification	(89)
4.1.3	Nomenclature	(90)
4.1.4	History ·····	(91)
4.2 Nat	ural polymers ·····	(93)
4.2.1	Polysaccharides ·····	(93)
4.2.2	Proteins	(96)
4.3 The	ermoplastics ······	(97)
4.3.1	Polyethylene ·····	
4.3.2		(105)
4.3.3		(107)
4.3.4		(108)
4.4 Eng	miodring processo with the contract of	(110)
4.4.1		(111)
4.4.2	1 01/001010	(113)
4.4.3		(114)
4.4.4		(115)
4.4.5		(116)
4.5 Ap		(117)
4.5.1		(118)
4.5.2	Didnious approximation and the second	(123)
4.5.3	Applications in electronics	(126)
Keywords ·		(129)
Problems ·		(129)
Selected fro		(130)
5 Compo	site Materials	(132)
5.1 Int	roduction ·····	(132)
5.2 Dis	spersion-strengthened composites ·····	(132)
5.3 Tr	ue particulate composites ·····	(134)
5.4 Fil	ber-reinforced composites ·····	(137)
5.5 Ch	naracteristics of fiber-reinforced composites	(139)
5.6 Ma	anufacturing fibers and composites	(144)
5.7 Fi	ber-reinforced systems and applications	
5.8 Ia	minar composite materials	(153)

5.9 Examples and applications of laminar composites	(154)
5.10 Sandwich structures	(156)
Keywords ·····	
Problems	(157)
Selected from ······	(157)

1 Introduction

1.1 Historical perspective

Materials are probably more deep-seated in our culture than most of us realize. Transportation, housing, clothing, communication, recreation, and food production — virtually every segment of our everyday lives is influenced to one degree or another by materials. Historically, the development and advancement of societies have been intimately tied to the members' ability to produce and manipulate materials to fill their needs. In fact, early civilizations have been designated by the level of their materials development (i.e., Stone Age, Bronze Age).

The earliest humans had access to only a very limited number of materials, those that occur naturally; stone, wood, clay, skins, and so on. With time they discovered techniques for producing materials that had properties superior to those of the natural ones; these new materials included pottery and various metals. Furthermore, it was discovered that the properties of a material could be altered by heat treatments and by the addition of other substances. At this point, materials utilization was totally a selection process, that is, deciding from a given, rather limited set of materials the one that was best suited for an application by virtue of its characteristics. It was not until relatively recent times that scientists came to understand the relationships between the structural elements of materials and their properties. This knowledge, acquired in the past 60 years or so, has empowered them to fashion, to a large degree, the characteristics of materials. Thus, tens of thousands of different materials have evolved with rather specialized characteristics that meet the needs of our modern and complex society; these include metals, plastics, glasses, and fibers.

The development of many technologies that make our existence so comfortable has been intimately associated with the accessibility of suitable materials. An advancement in the understanding of a material type is often the forerunner to the stepwise progression of a technology. For example, automobiles would not have been possible without the availability of inexpensive steel or some other comparable substitute. In our contemporary era, sophisticated electronic devices rely on components that are made from what are called semiconducting materials.

1.2 Classification of materials

Solid materials have been conveniently grouped into three basic classifications: metals, ceramics, and polymers. This scheme is based primarily on chemical makeup and atomic structure, and most ma-

terials fall into one distinct grouping or another, although there are some intermediates. In addition, there are three other groups of important engineering materials — composites, semiconductors, and biomaterials. Composites consist of combinations of two or more different materials, where as semiconductors are utilized because of their unusual electrical characteristics; biomaterials are implanted into the human body. A brief explanation of the material types and representative characteristics is offered next.

Metallic materials are normally combinations of metallic elements. They have large numbers of nonlocalized electrons; that is, these electrons are not bound to particular atoms. Many properties of metals are directly attributable to these electrons. Metals are extremely good conductors of electricity and heat and are not transparent to visible light; a polished metal surface has a lustrous appearance. Furthermore, metals are quite strong, yet deformable, which accounts for their extensive use in structural applications.

Ceramics are compounds between metallic and nonmetallic elements: they are most frequently oxides, nitrides, and carbides. The wide range of materials that falls within this classification includes ceramics that are composed of clay minerals, cement, and glass. These materials are typically insulative to the passage of electricity and heat, and are more resistant to high temperatures and harsh environments than metals and polymers. With regard to mechanical behavior, ceramics are hard but very brittle.

Polymers include the familiar plastic and rubber materials and so on. Many of them are organic compounds that are chemically based on carbon, hydrogen, and other nonmetallic elements; furthermore, they have very large molecular structures. These materials typically have low densities and may be extremely flexible.

A number of composite materials have been engineered that consist of more than one material type. Fiberglass reinforced plastics is a familiar example, in which glass fibers are embedded within a polymeric material. A composite is designed to display a combination of the best characteristics of each of the component materials. Fiberglass acquires strength from the glass and flexibility from the polymer. Many of the recent material developments have involved composite materials.

Semiconductors have electrical properties that are intermediate between the electrical conductors and insulators. Furthermore, the electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of impurity atoms, which concentrations may be controlled over very small spatial regions. The semiconductors have made possible the advent of integrated circuitry that has totally revolutionized the electronics and computer industries (not to mention our lives) over the past two decades.

1.3 Structures of metals and ceramics

1.3.1 Structure of metals

One important feature which distinguishes a metal from most other materials is that in the solid state it is crystalline. This is another way of saying that its atoms are arranged in a regular three-dimensional pattern which has long-range order. Why should this be significant? Most of the properties which interest us in the use of metals in engineering are in some way related to the atomic arrangement. The properties obtained when metals are mixed together (i.e. in alloying) are dictated by the atomic structure. This also controls the way in which metals can be processed. Heat treatment and forming by plastic deformation are two examples of common metal-processing operations. How they can be used and the results achieved depend on the structure of the metal. If we are to understand how metals behave, we must be able to recognize the different arrangements of atoms which exist in commonly used metals.

Types of lattice structure

When discussing lattice structures, it is very convenient to think of atoms as solid spheres. We know this is not correct, of course; but, as we are interested only in the space occupied in the lattice by each atom, we do not need to consider its internal structure. This means that we can use spheres of, say, polystyrene or cotton wool to produce models which illustrate the various possible geometrical arrangements.

If we place a large number of spheres on a tray and line them up in rows, it can be seen that there are two basic arrangements. In the first (Figure 1.1(a)), the spheres are located at the corners of imaginary squares. Each sphere is in touch with four other spheres, and the tangents at points of contact are at right angles to each other. This is, therefore, a square arrangement. Alternatively, the rows can be displaced so that the spheres nestle between each other (Figure 1.1(b)). Each sphere is now in contact with six others which forms a hexagon around it. It will be noticed that there is less space between the spheres with this arrangement, and for this reason it is often referred to as close-packed.

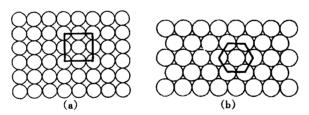


Figure 1.1 Two basic arrangements for spheres
(a) Square arrangement (b) Hexagonal arrangement

The next step in our investigation is to stack further layers of spheres on top of the first layer. With the square arrangement, we could position the spheres in the second layer immediately over those in the first, and so on with the third, fourth, and subsequent layers (Figure 1.2(a)). The result would be that the spheres would be sited at the intersections of a cubic space lattice (Figure 1.2(b)). It would also be possible to visualize the same arrangement being made up of a number of cubes stacked together. It follows that the unit cell, or basic "building block", for a lattice made up from a square arrangement is a simple cube. With a closed-packed arrangement, the unit cell is a hexagonal prism.

These two unit cells — cubic and hexagonal — feature in most of the lattice structures found in metals, although we must remember that the atoms, unlike our spheres, do not actually touch each

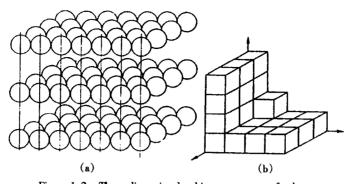


Figure 1.2 Three-dimensional cubic arrangement of spheres

(a) Layers of spheres placed above each other to form a cubic structure (b) Cubic space lattice

other, the dimensions of the cells in metals are, of course, vastly different from those of our models. The spheres we use for these give cubes with sides measuring from 20 mm to 50 mm. In the iron lattice, the lattice parameter of the cubic unit cell (i.e. the length of one of its sides) is about 2.86×10^{-10} m. How, then, do we know that our model lattices are reproduced at an atomic level? The main evidence has some from X-ray diffraction studies.

X-rays are electromagnetic waves which have very short wavelengths. They are able to penetrate metals and are frequently used to show the presence of internal flaws such as blow-holes in castings. If X-rays with wavelengths of the same magnitude as the interatomic spacings in a metal are directed at an angle to the planes of atoms, the rays are reflected. The planes thus act like a mirror reflecting light. By recording the reflected rays, it is possible to calculate the distances between the planes and to plot the positions of the atoms. This technique is known as X-ray diffraction and by its use it has been possible to show that in the majority of common metals there are only three basic lattice arrangements (Figure 1.3):

- (a) body-centered cubic (b.c.c.)
- (b) face-centered cubic (f.c.c.)
- (c) close-packed hexagonal (c.p.h.)

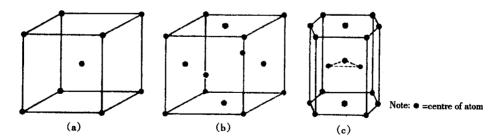


Figure 1.3 Space lattices for a metal (a) b.c.c. (b) f.c.c. (c) c.p.h.

Body-centered cubic lattices have a cubic unit cell in which there is an atom at each corner and one in the center of the body of the cube. Although a b.c.c. lattice appears to be simple, it is not very often found in commercially available metals. Iron is the best-known metal which has a b.c.c.

lattice.

Face-centered cubic lattices also have an atom at the corner of each cube, but these are further apart than in the b.c.c. type. This leaves room for an additional atom at the center of each face of the cube. Many metals have f.c.c. lattices; examples are aluminum, copper, and nickel. In general, the most ductile metals have a f.c.c. structure.

Close-packed hexagonal lattices are significantly different from the cubic structures. The unit cell is not symmetrical. There are three layers in each cell. The top and bottom layers consist of six atoms in a hexagon with one atom at the center. The middle layer has three atoms in the form of a triangle. The vertical faces of the cell are rectangular. This is the least common of the lattice structures. Examples of metals with a c.p.h. lattice are zinc and magnesium — it is worth nothing that these are among the least ductile metals.

Imperfections in crystal lattices

At first sight, there is no reason to suppose that the lattice structure should not be uniform throughout its length, breadth, and depth. The positions which atoms occupy are determined by the forces acting on them. Since all the atoms in a metal are essentially uniform, it is reasonable to expect that interatomic forces are the same at all points in the lattice. In practice, however, imperfections do occur. This may be because there was some interruption in the growth of the crystal from molten metal. Imperfections can also be created by the inclusion of an atom of another metal, whether added intentionally or present as an impurity. They are worthy of note because they can have a significant effect on the behavior of a metal.

An important type of imperfection is a dislocation (Figure 1.4). As its name implies, this is a break in the continuity of the lattice. Very often a plane of atoms will come to a stop. At this point the two neighboring planes move closer until they are at the correct interatomic spacing. It looks almost as if one plane has been squeezed out. The change from three to two planes causes a disruption of the lattice and leaves a small gap; this is called an edge dislocation. Dislocations are an essential element in the forming of metals since they allow plastic deformation to take place at achievable stress levels.

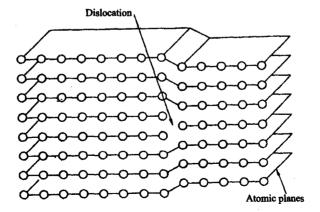


Figure 1.4 Dislocation in a crystal lattice

Another form of imperfection is a vacancy. This is literally a hole in the lattice which is there because an atom did not take up the prescribed site. Vacancies play an important role in the diffusion or

movement of atoms through the lattice.

Grain structure

It is possible to produce rods of metal in which the orientation or direction of the lattice planes remains the same throughout the body of the specimen. Each plane goes from one side of the rod to the other without change in direction. Similarly along the length, continuity is maintained from one end to the other. These are identified as single crystals. They are very useful in studying the basic properties of a metal, but they are very difficult to produce and are not found in general manufacture. The metals which we use are polycrystalline, i.e. they are made up of a number of small crystals or grains bonded together by interatomic forces. Within each grain, the lattice structure is uniform.

Grains do not have the regular surface appearance we normally associate with crystals. Their shape is determined by interaction with neighboring grains and can be quite irregular. If we took a slice through a piece of metal — say copper — the boundaries of the grains would appear as a network of lines. The grain boundary represents a change in the direction of the lattice planes. As the planes of one grain meet those of a neighbor at an angle, there is considerable mismatch with the result that along the boundary there may be gaps. The width of the boundary area is usually equivalent to several atomic diameters, but forces can still act across it to provide cohesion between the grains.

1.3.2 Structure of ceramics

Ceramics are composed of at least two elements, thus the crystal structures are generally more complex than those of metals. One of the key ideas behind ceramics is that ceramics exhibit atomic bonding through either covalent or ionic bonding. Ceramics that exhibit predominantly ionic bonding can be thought of as being electrically charged ions instead of atoms. In ionic bonding of ceramic structure, the metallic ions, or cations (+ charge) give up their valence electrons to the nonmetallic ions, or anions (- charge). This causes the crystal structure to become electrically neutral. One common example of this type of structure is that of table salt (NaCl), in this case there are equal number of cations and anions.

The bonding mechanisms for ceramics produce the primary bonds: ionic and covalent. The crystal structure of bulk ceramic compounds is determined by the amount and type of bonds. The percentage of ionic bonds can be estimated by using electronegativity determinations. Being compounds, ceramics have different types of atoms. Hence, their resistance to shear and high-energy slip is extremely high.

Because the atoms are held (bonded) so strongly compared to metals, there are fewer ways for atoms to move or slip in relation to each other. Thus, the ductility of ceramic compounds is very low and these materials act in a brittle fashion. Fracture stresses that initiate a crack build up before there is any plastic deformation and, once started, a crack will grow spontaneously. The combination of high shear stresses and reduced ductility produces high compressive strength but low tensile strength. At room temperature, metals and ceramics are often competitive, but at temperatures above 1,500 °F, metals weaken while ceramics retain much of their strength. Ceramics are noted for their heat resistance. The maximum service temperature for alumina is 3,450 °F and for silicon carbide, it is 3,000 °F. Heat-resistant nickel alloys are considered unserviceable above 1,500 °F.

The porosity of ceramics plays a major role in the strength. Ceramics are generally very porous,

enhancing its ability to insulate but limiting its tensile strength.

1.4 Polymer structures

Naturally occurring polymers, those derived from plants and animals, have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers such as proteins, enzymes, starches, and cellulose are important in biological and physiological processes in plants and animal. Modern scientific research tools have made possible the determination of the molecular structures of this group of materials, and the development of numerous polymers, which are synthesized from small organic molecules. Many of our useful plastics, rubbers, and fiber materials are synthetic polymers. In fact, since the conclusion of World War II, the field of materials has been virtually revolutionized by the advent of synthetic polymers. The synthetics can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts. In some applications metal and wood parts have been replaced by plastics, which have satisfactory properties and may be produced at a lower cost.

1.4.1 Macromolecules

The molecules in polymers are gigantic in comparison to the hydrocarbon molecules; because of their size they are often referred to as macromolecules. Within each molecule, the atoms are bound together by covalent interatomic bonds. For most polymers, these molecules are in the form of long and flexible chains, the backbone of which is a string of carbon atoms; many times each carbon atom singly bonds to two adjacent carbon atoms on either side, represented schematically in two dimensions as follows. Each of the two remaining valence electrons for every carbon atom may be involved in side-bonding with atoms or radicals that are positioned adjacent to the chain. Of course, both chain and side double bonds are also possible.

These long molecules are composed of structural entities called mer units, which are successively repeated along the chain. "Mer" originates from the Greek word meros, which means part; the term polymer was coined to mean many mers. Generally, we use the term monomer, which refers to a stable molecule from which a polymer is synthesized. The polymer molecule contains a structural identity, repeating itself several times. These repeating entities are called repeat units or monomeric units of the polymer molecule.

When all the repeating units along a chain are of the same type, the resulting polymer is called a homopolymer. There is no restriction in polymer synthesis that prevents the formation of compounds other than homopolymers; and, in fact, chains may be composed of two or more different monomeric units, in what are termed copolymers.

Polymer chemists and scientists are continually searching for new materials that can be easily and economically synthesized and fabricated, with improved properties or better property combinations than

those offered by the homopolymers. One group of these materials is the copolymer. Consider a copolymer that is composed of two monomeric units as represented by O and • in Figure 1.5. Depending on the polymerization process and the relative fractions of these monomer types, different sequencing arrangements along the polymer chains are possible. For one, as depicted in Figure 1.5(a), the two different units are randomly dispersed along the chain in what is termed a random copolymer. For an alternating copolymer, as the name suggests, the two monomeric units alternate chain positions, as illustrated in Figure 1.5(b). A block copolymer is one in which identical monomers are clustered in blocks along the chain (Figure 1.5(c)). And, finally, homopolymer side branches of one type may be grafted to homopolymer main chains that are composed of a different monomer; such a material is termed a graft copolymer (Figure 1.5(d)).

1.4.2 Molecular weight

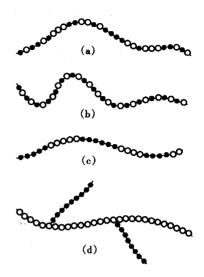


Figure 1.5 Schematic representations of (a) random, (b) alternating, (c) block, and (d) graft copolymers. The two different monomer types are designated by open and solid circles

Extremely large molecular weights * are to be found in polymers with very long chains. During the polymerization process in which these large macromolecules are synthesized from smaller molecules, not all polymer chains will grow to the same length. This results in a distribution of chain lengths or molecular weights.

Ordinarily, an average molecular weight is specified, which may be determined by the measurement of various physical properties such as viscosity and osmotic pressure. There are several ways of defining average molecular weight. The number-average molecular weight \overline{M}_n is obtained by dividing the chains into a series of size ranges and then determining the number fraction of chains within each size range. The weight-average molecular weight \overline{M}_w is based on the weight fraction of molecules within the various size ranges. A typical molecular weight distribution along with these molecular weight averages are shown in Figure 1.6.

An alternate way of expressing average chain size of a polymer is as the degree of polymerization, which represents the average number of monomeric units in a chain.

Various polymer characteristics are affected by the magnitude of the molecular weight. One of these is the melting or softening temperature; melting temperature is raised with increasing molecular weight (for \overline{M} up to about 100,000 g/mol). At room temperature, polymers with very short chains (having molecular weights on the order of 100 g/mol) exist as liquids or gases. Those with molecular

^{* &}quot;Molecular mass", "molar mass", and "relative molecular mass" are sometimes used and are really more appropriate terms than "molecular weight" in the context of the present discussion — in actual fact, we are dealing with masses and not weights. However, molecular weight is most commonly found in the polymer literature, and thus will be used throughout this book.

weights of approximately 1,000 g/mol are waxy solids (such as paraffin wax) and soft resins. Solid polymers (sometimes termed high polymers), which are of prime interest here, commonly have molecular weights ranging between 10,000 and several million g/mol.

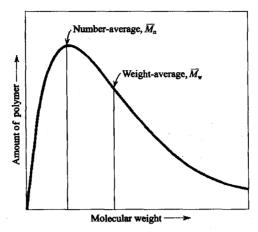


Figure 1.6 Distribution of molecular weight for a typical polymer

1.4.3 Molecular structures

The physical characteristics of a polymer depend not only on its molecular weight and shape, but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network.

Linear polymers are those in which the monomeric units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in Figure 1.7(a), where each circle represents a monomeric unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly (methyl methacrylate), nylon, and the fluorocarbons.

Polymers may be synthesized in which side-branch chains are connected to the main ones, as indicated schematically in Figure 1.7(b); these are fittingly called branched polymers. The branches, considered to be part of the main-chain molecule, result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density. Those polymers that form linear structures may also be branched.

In crosslinked polymers, adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure 1.7(c). The process of crosslinking is achieved either during synthesis or by a nonreversible chemical reaction that is usually carried out at an elevated temperature. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization.