Biodegradable Polymer Blends and Composites from Renewable Resources

Edited by

LONG YU

WILEY

BIODEGRADABLE POLYMER BLENDS AND COMPOSITES FROM RENEWABLE RESOURCES

Edited by

Long Yu

WILEY

A JOHN WILEY & SONS, INC., PUBLICATION

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

Library of Congress Cataloging-in-Publication Data:

Yu, Long.
Biodegradable polymer blends and composites from renewable resources/Long Yu.
p. cm.
Includes index.
ISBN 978-0-470-14683-5 (cloth)
1. Biodegradable plastics. 2. Polymeric composites. 3. Renewable natural resources.
I. Title.
TP1180.B55Y8 2009
620.1′92323--dc22 2008009441

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

PREFACE

The history of composites from renewable resources is far longer than that of conventional polymers. For example, in the biblical Book of Exodus, Moses' mother built a basket from rushes, pitch, and slime—a kind of fiber-reinforced composite, according to the modern classification of materials. Also, during the opium wars in the middle of the nineteenth century, the Chinese built their defenses using a kind of mineral particle-reinforced composite made from gluten rice, sugar, calcium carbonate, and sand.

There are now many well-developed techniques that are used to produce conventional polymer blends and composites, and various products have been widely commercialized. There are also numerous papers, patents, books, and handbooks that introduce and discuss the development and application of various polymeric blends and composites.

Over the past two decades, however, polymers from renewable resources (PFRR) have been attracting increasing attention, primarily for two major reasons: environmental concerns, and the realization that our petroleum resources are finite. A third reason for the growing interest in polymers from renewable resources relates to adding value to agricultural products, which is economically important for many countries.

Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein, and cellulose; (2) synthetic polymers from natural monomers, such as poly(lactic acid); and (3) polymers from microbial fermentation, such as poly(hydroxybutyrate). A major advantage of all these materials is that they are biodegradable, and that their final products of degradation are environmentally friendly.

As with numerous petroleum-based polymers, many properties of PFRR can be improved through appropriate blending and composite formulation. These new blends and composites are extending the utilization of PFRR into new value-added products.

The book comprises six sections that highlight recent developments in biodegradable polymer blends and composites from renewable resources, and discusses their potential markets. Following an overview of polymers from renewable resources (Chapter 1), the rest of Part I (Chapters 2–6) emphasizes blends from natural polymers, involving both melting and aqueous blending, as well as reactive blending. Part II (Chapters 7 and 8) focuses on aliphatic polymer blends, in particular improving the thermal properties of these systems. Part III (Chapters 9 and 10) discusses various hydrophobic and hydrophilic blends, in particular polyesters and natural polymers. Part IV (Chapters 11–14) discusses composites reinforced with natural fibers, while Part V (Chapters 15–17) introduces the development of nanoclay-reinforced composites, including novel techniques of delaminating clay for use in natural polymers. Part VI (Chapter 18) introduces multilayered systems from renewable resources.

Throughout the book, attention is given to the relationship between microstructure and properties, in particular interfacial compatibility, and mechanical and thermal characteristics. Written primarily for materials and polymer scientists and technologists, this book will also be of value to those in the commercial market concerned about the environmental impact of plastics.

I wish to take this opportunity to thank each of the authors, and their many collaborators, for their splendid contributions to the development of biodegradable polymers. I also wish to thank my postgraduate students both in CSIRO Materials Science and Engineering and the Centre for Polymers from Renewable Resources at SCUT for their hard work in this area. Lastly, I thank Cathy Bowditch for editing my publications over the years.

LONG YU

CSIRO Materials Science and Engineering
Melbourne, Victoria, Australia

Centre for Polymers from Renewable Resources
SCUT, Guangzhou, China
June 2008

CONTRIBUTORS (CORRESPONDING AUTHORS*)

Vera Alejandra Alvarez, Research Institute of Material Science and Technology, Engineering Faculty, Mar del Plata University, Juan B. Justo 4302 (7600), Mar del Plata, Argentina

Ioannis S. Arvanitoyannis*, Department of Agriculture, Animal Production and Aquatic Environment, School of Agricultural Sciences, University of Thessaly, Fytokou Str., 38446 Nea. Ionia Magnesias, Volos, Greece, Tel: +30-4210-93104; Fax: +30-4210-93144; Email: parmenion@uth.gr

Luc Avérous*, ECPM-LIPHT (UMR CNRS 7165), University Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France, Tel: +33-3-90-24-27-07; Fax: +33-3-90-24-27-16; Email: AvérousL@ecpm.u-strasbg.fr

Cheng Chen, State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, P. R. China

Guo-Qiang Chen*, Multidisciplinary Research Center, Shantou University, Shantou, Guangdong 515063, P. R. China, Tel: +86-754-2901186; Fax: +86-754-2901175; Email: chengq@stu.edu.cn

Ling Chen, Centre for Polymers from Renewable Resources, ERSPSP, South China University of Technology, Guangzhou, China

J. J. de Vlieger, TNO Science and Technology, Materials Performance, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands

Lisong Dong*, State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, P. R. China, Tel: +86-431-5262076; Fax: +86-431-5685653; Email: dongls@ciac.jl.cn

Hartmut Fischer*, TNO Science and Technology, Materials Performance, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands, Tel: +31-40-2650151; Fax: +31-40-2650850; Email: hartmut.fischer@tno.nl

Baochun Guo, School of Materials Science and Engineering, South China University of Technology, Wushan, Guangzhou, 510641, P. R. China

Milford A. Hanna*, Department of Biological System Engineering, University of Nebraska, 208 L.W. Chase Hall, Lincoln, NE 68583-0730, USA, Tel: +1-402-472-1634; Fax: +1-402-472-6338; Email: mhanna@unl.edu

Yoshito Ikada*, Department of Environmental Medicine, Faculty of Medicine, Nara Medical University, Shijo-cho, Kashihara, Nara 634-8521, Japan, Email: ikada@naramed-u.ac.jp

Demin Jia*, School of Materials Science and Engineering, South China University of Technology, Wushan, Guangzhou, 510641, P. R. China, Tel: +86-020-87113374; Fax: +86-020-87110273; Email: psdmjia@scut.edu.cn

A. Kassaveti, Department of Agriculture, Crop Production and Agricultural Environment, School of Agricultural Sciences, University of Thessaly, 384 46 N. Ionia Magnesias, Volos, Greece

Lan Liu, School of Materials Science and Engineering, South China University of Technology, Wushan, Guangzhou, 510641, P. R. China

Yongshang Lu, Department of Chemistry, Iowa State University, Ames IA 50011, USA

Rong-Cong Luo, Department of Biological Sciences and Biotechnology, Tsinghua University, Beijing 100084, P. R. China

Yuanfang Luo, School of Materials Science and Engineering, South China University of Technology, Wushan, Guangzhou, 510641, P. R. China

James Ramontja, National Centre for Nano-Structured Materials, CSIR Materials Science and Manufacturing, P.O. Box 395, Pretoria 0001, Republic of South Africa

Robert A. Shanks*, Co-operative Research Centre for Polymers, School of Applied Sciences, Science, Engineering and Technology, RMIT University, GPO Box 2476V, Melbourne, Victoria, 3001 Australia, Tel: +61-3-9925-2122; Fax: +61-3-9639-1321; Email: robert.shanks@rmit.edu.au

Mitsuhiro Shibata*, Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan, Tel: +81-47-478-0423; Fax: +81-47-478-0423; Email: shibata@sky.it-chiba.ac.jp

Randal L. Shogren*, Plant Polymer Research Unit, National Centre for Agriculture Utilization Research, USDA/ARS, 1815 N. University St., Peoria, IL 61604, USA, Tel: +1-309-681-6354; Fax: +1-309-681-6691; Email: Randy.Shogren@ars.usda.gov

Suprakas Sinha Ray*, National Centre for Nano-Structured Materials, CSIR Materials Science and Manufacturing, P.O. Box 395, Pretoria 0001, Republic of South Africa, Tel: +27-12-841-2388; Fax: +27-12-841-2135; Email: rsuprakas@csir.co.za

Nilda Soares*, Departamento de Tecnologia de Alimentos, Universidade Federal de Viçosa, 36570-000 Viçosa-MG, Brazil 36570-000, Brazil, Tel: +55-31-3899-2208; Fax: +55-31-3899-1624; Email: nfsoares@ufv.br

Lan Tighzert*, Laboratoire d'Etudes des Matériaux Polymères d'Emballage (LEMPE), Ecole Supérieure d'Ingénieurs en Emballage et Conditionnement (ESIEC), Université de Reims Champagne-Ardenne (URCA), Esplanade Roland Garros—Pôle Henri Farman, BP 1029, 51686 Reims Cedex 2, France, Tel: +33-(0)3-26913764; Fax: +33-(0)3-26913764; Email: lan.tighzert@univ-reims.fr

Persefoni Tserkezou, Department of Agriculture, Icthyology and Aquatic Environment, School of Agricultural Sciences, University of Thessaly, Fytokou Str., 38446 Nea Ionia Magnesias, Volos, Greece

Hideto Tsuji*, Department of Ecological Engineering, Faculty of Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan, Email: tsuji@eco.tut.ac.jp

Analía Vázquez*, Research Institute of Material Science and Technology, Engineering Faculty, Mar del Plata University, Juan B. Justo 4302 (7600), Mar del Plata, Argentina, Email: anvazque@fi.mdp.edu.ar

Xiaoping Wang, School of Materials Science and Engineering, South China University of Technology, Wushan, Guangzhou, 510641, P. R. China

Yixiang Wang, Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China

Susan Wong, Co-operative Research Centre for Polymers, School of Applied Sciences, Science, Engineering and Technology, RMIT University, GPO Box 2476V, Melbourne, Victoria, 3001 Australia

Yixiang Xu, Industrial Agricultural Products Center, 15A L.W. Chase Hall, University of Nebraska, Lincoln, NE 68583–0730, USA

Long Yu*, Commonwealth Scientific and Industrial Research Organization, Materials Science and Engineering, Clayton South, Melbourne, Vic. 3168, Australia, Tel: +61-3-9545-2797; Fax: +61-3-9544-1128; Email: long.yu@csiro.au

Lina Zhang*, Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China, Tel: +86-27-87219274; Fax: +86-27-68754067; Email: lnzhang@public.wh.hb.cn

CONTENTS

CHAPTER 1

Polymeric Materials from Renewable Resources

LONG YU

CSIRO, Materials Science and Engineering, Melbourne, Australia

LING CHEN

Centre for Polymer from Renewable Resources, ERSPSP, SCUT, Guangzhou, China

1.1 INTRODUCTION

Polymers from renewable resources have been attracting ever-increasing attention over the past two decades, predominantly for two reasons: the first being environmental concerns and the second being the realization that our petroleum resources are finite. In addition, this kind of material will provide additional income to those

Biodegradable Polymer Blends and Composites from Renewable Resources. Edited by Long Yu

involved in agriculture. Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers such as starch, protein, and cellulose; (2) synthetic polymers from bioderived monomers such as poly(lactic acid) (PLA); and (3) polymers from microbial fermentation such as polyhydroxybutyrate.

In this short chapter, various polymers from renewable resources, in particular those that have been used as or have been shown to have potential for use as polymeric materials, are briefly reviewed. The review focuses on the microstructure, general properties and some of the applications for these materials. Some comparisons are also made between natural and conventional synthetic polymers.

1.2 NATURAL POLYMERS

The study and utilization of natural polymers is an ancient science. Typical examples, such as paper, silk, skin and bone artifacts can be found in museums around the world. These natural polymers perform a diverse set of functions in their native setting. For example, polysaccharides function in membranes and intracellular communication; proteins function as structural materials and catalysts; and lipids function as energy stores and so on. Nature can provide an impressive array of polymers that can be used in fibers, adhesives, coatings, gels, foams, films, thermoplastics, and thermoset resins. However, the availability of petroleum at a lower cost and the biochemical inertness of petroleum-based products proved disastrous for the natural polymers market. It is only after a lapse of almost 50 years that the significance of eco-friendly materials has once again been realized. These ancient materials have evolved rapidly over the past decade, primarily due to environmental issues and the increasing shortage of oil. Modern technologies provide powerful tools to elucidate microstructures at different levels and to understand the relationships between structures and properties. These new levels of understanding bring opportunities to develop materials for new applications.

Wide ranges of naturally occurring polymers that are derived from renewable resources are available for various materials applications (Charles et al., 1983; Fuller et al., 1996; Kaplan, 1998; Scholz and Gross, 2000; Gross & Scholz, 2001). Some of them (e.g., starch, cellulose and rubber), are actively used in products today whereas many others remain underutilized. Natural polymers can sometimes be classified according to their physical character. For example, starch granules and cellulose fibers are classified into different groups, but they both belong to polysaccharides according to chemical classification. Table 1-1 lists some natural polymers (Kaplan 1998).

1.2.1 Natural Rubber

One of the best known mature materials is natural rubber, which has been and is widely used in modern life. Although rubber's usefulness was known about in the early seventeenth century, it was not until the early nineteenth century that the rubber manufacturing industry became established. Rubber biosynthesis can occur

TABLE 1-1 List of Natural Polymers (Kaplan, 1998)

Polysaccharides
• from plant/algal: starch, cellulose, pectin, konjac, alginate, caragreenan, gums
• from animal: hyluronic acid,
• from fungal: pulluan, elsinan, scleroglucan
• from bacterial: chitin, chitosan, levan, xanthan, polygalactosamine, curdlan, gellan, dextran
Protein
soy, zein, wheat gluten, casein, serum, albumin, collagen/gelatine
silks, resilin, polylysine, adhesives, polyamino acids, poly(γ-glutamic acid), elastin, polyarginyl-polyaspartic acid
Lipids/Surfactants
acetoglycerides, waxes, surfactants, emulsan
Speciality Polymers
lignin, shellac, natural rubber

in either of two different types of plant cells: specialized latex vessels or parenchyma cells. Latex vessels are the more common route. A number of research groups have investigated ways of transferring the genes responsible for rubber biosynthesis into other species (Backhaus, 1998).

Natural rubber is a *cis*-polyisoprene that occurs as natural latex or a submicroscopic dispersion of the rubber in saplike materials. All such latexes appear milk white and the polyisoprene has the chemical structure shown in Fig. 1-1. Natural rubber can be recovered by coagulation processes. It has a glass transition temperature of about $-70^{\circ}C$ and a molecular weight of 3×10^6 g/mole (Tanaka, 1991). The central portion of the rubber molecules is marked by extensive *cis*-polymerizations, which denote the structural hallmark of rubber. Rubber from different sources varies most with respect to the number of these condensations, which results in different molecular weight and molecular weight distribution.

Natural rubber is a very reactive polymer because of the presence of olefinic double bonds at every fifth carbon atom. The extensive degree of unsaturation and the close spacing of these double bonds provide a highly vulnerable target for free-radical attack and oxidation. The molecule can also undergo numerous chemical reactions such as hydrogenation, addition, and substitution. Rubber can be made inert by fully chlorinating the double bonds to afford up to 65 wt% chlorine. Natural rubber is soluble in most aromatic, aliphatic, and chlorinated solvents, but its high molecular weight makes it difficult to dissolve.

In practice, natural rubber has limited utility and must be compounded with other ingredients such as carbon black fillers, antioxidants, plasticizers, pigments, and vulcanizing agents to improve its chemical and physical properties. It should be

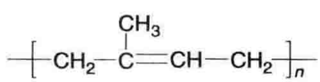

Fig. 1-1 The chemical structure of natural rubber.

realized that since vulcanized rubber is not biodegradable, natural rubber-based products are not frequently mentioned in the literature on biodegradables even though natural rubber is one of the earliest natural materials to have been used.

1.2.2 Starch

Starch is a polysaccharide produced by most higher plants as a means of storing energy. It is stored intracellularly in the form of spherical granules that are 2–100 μm in diameter (Whistler et al., 1984). Most commercially available starches are isolated from grains such as corn, rice, wheat, and from tubers such as potato and tapioca. The starch granule is a heterogeneous material: chemically, it contains both linear (amylose) and branched (amylopectin) structures; physically, it has both amorphous and crystalline regions (French, 1984). The ratio of amylose to amylopectin in starch varies as a function of the source, age, etc.

1.2.2.1 Chemical Structures Starch is the principal carbohydrate reserve of plants. It is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through α-D-(1 → 4) glucosidic bonds. Although the detailed microstructures of starch are still being elucidated, it has been generally established that starch is a heterogeneous material containing at the extremes two microstructures according to their chain structure: amylose and amylopectin. Amylose is essentially a linear structure of α-1,4-linked glucose units and amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds. Figure 1-2 shows the structure of amylose and amylopectin.

The linear structure of amylose makes its behavior closer to that of conventional synthetic polymers. The molecular weight of amylose is about 10^6 (200–2000 anhydroglucose units) depending on the source and processing conditions employed in extracting the starch, which is 10 times larger than conventional synthetic polymers. Amylopectin, on the other hand, is a branched polymer. The molecular weight of amylopectin is much larger than that of amylose. Light-scattering measurements indicate a molecular weight in millions. The large size and branched structure of amylopectin reduce the mobility of the polymer chains and interfere with any tendency for them to become oriented closely enough to permit significant levels of hydrogen

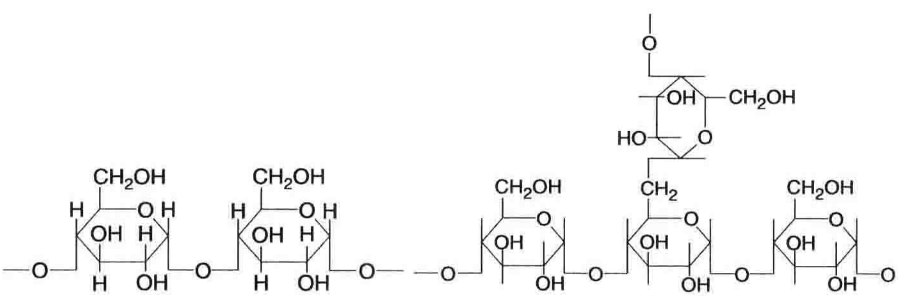

Fig. 1-2 The structures of amylose (left) and amylopectin (right).

bonding. Except the linear amylose and the short-branched amylopectin, starch of a long-branched structure has been detected (e.g., tapioca starch).

1.2.2.2 Physical Structures Most native starches are semicrystalline with a crystallinity of ~20–45%. Amylose and the branching points of amylopectin form the amorphous regions. The short branching chains in the amylopectin are the main crystalline component in granular starch. The crystalline regions are present in the form of double helices with a length of approximately 5 nm. The amylopectin segments in the crystalline regions are all parallel to the axis of the large helix. The amylose/amylopectin ratio depends upon the source of the starch but can also be controlled by extraction processing. Starch granules also contain small amounts of lipids and proteins.

Figure 1-3 shows the wide angle x-ray scattering (WAXS) patterns of cornstarch with different amylose/amylopectin content. The amylose/amylopectin ratios in waxy, maize, G50 and G80 starches are 0/100, 23/77, 50/50 and 80/20, respectively (Chen et al., 2006). It is seen that waxy and maize starches show a typical A-type pattern with strong reflections at 2θ of about 13° and 21° and an unresolved large doublet between them. G50 and G80 give the strongest diffraction peak at around $2\theta = 16^\circ$ and a few small peaks at 2θ values of 18°, 20° and 22°. An additional peak appears at about $2\theta = 4^\circ$. These latter spectra are basically the same as the characteristic B-type. From Fig. 1-3, it is also seen that the crystalline area of amylopectin-rich starches is higher than that of amylose-rich starches, which is to be expected since it is well known that amylopectin in starch granules is considered to be responsible for the crystalline structure.

1.2.2.3 Morphologies and Phase Transition During Processing Starch granules are a mixture of rounded granules from the floury endosperm, and angular granules from the horny endosperm (French, 1984; Chen et al., 2006). In their native state, starch granules do not have membranes; their surfaces consist simply of tightly

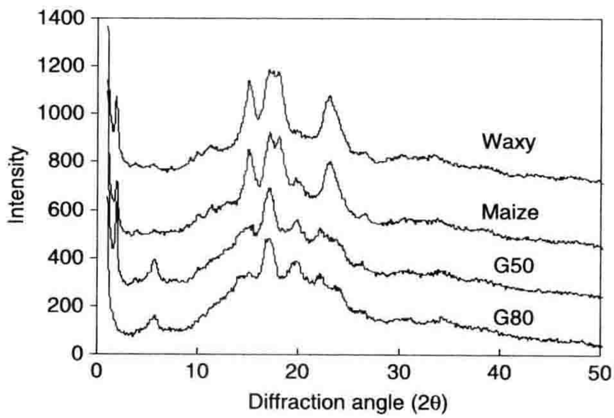

Fig. 1-3 WAXS patterns of cornstarch with different amylose/amylopectin content.

packed chain ends resembling the bottom of a broom with the straws pressed tightly together. Undamaged starch granules are not soluble in cold water but can reversibly imbibe water and swell slightly.

One of the unique characteristics of starch-based materials is their phase transition during processing, which encompasses various chemical and physical reactions including starch swelling, gelatinization, melting, crystallization, decomposition and so on (Lelievre, 1974, 1976; Whistler et al., 1984; Yu and Christie, 2001). It is well known that an order–disorder phase transition occurs when starch granules are heated in the presence of water. When sufficient water is present, this transition—referred to as "gelatinization"—results in near-solubilization of the starch (Lelievre, 1974; Donovan, 1979; Whistler, 1984). The well-accepted concept of gelatinization means destroying the crystalline structure in starch granules. Starch gelatinization is an irreversible process and includes granular swelling, native crystalline melting, loss of birefringence and starch solubilization. The concomitant changes of measurable properties such as viscosity, heat uptake, crystallinity, and size variation of starch granules have been used to detect the extent of starch gelatinization (Yu and Christie, 2001; Liu et al., 2006; Chen et al., 2007; Xie et al., 2008; Xue et al., 2008).

It has been shown that under shearless conditions, full gelatinization of starch requires about 70% water content (Wang et al. 1989; Liu 2006), while gelatinization under shear conditions requires less water since shear stress enhances processing. Extrusion cooking or processing of starch-based materials relies on the proper conversion of starch within the raw materials. In an extrusion environment, gelatinization is typically achieved with low amounts of water under high-shear and high-pressure conditions.

1.2.2.4 Starch Modification In practice, the raw materials of starch are not straightforwardly suitable for any specific nonfood application. Various modified starches have been developed for nonfood applications (e.g., starch graft copolymers, glycosides, cationic starch, or oxidized starch), to meet different specific requirements (Wurzburg, 2000). For example, sodium hypochlorite-oxidized starch which has the advantages of bright white color, easy gelatinization, and high solubility, is more suitable than native starches for applications in the papermaking and textile industries. Cationic starch, which has positive charges, can more easily be attracted by negative charges on fibers and hence is also more effective than native starches in applications in the papermaking and textile industries. Superabsorbent polymers, prepared by grafting acrylonitrile onto starch, can be used in various fields such as hygiene, cosmetics, and agriculture.

Recently, the technology of reactive extrusion has been used for starch modification (Xie et al., 2006). It has been shown that reactive extrusion is a feasible and efficient way to modify starches and to produce more applicable products. The use of an extruder as a chemical reactor allows high-viscosity polymers to be handled in the absence of solvents. It also affords large operational flexibility as a result of the broad range of processing conditions in pressure (0–500 atm [0–50 MPa]) and temperature (70–500°C), the possibility of multiple injections, the controlled residence time (distribution) and degree of mixing.

1.2.3 Protein

Proteins are one of three essential macromolecules in biological systems and can easily be isolated from natural resources. Proteins have been studied for decades for their ability to spontaneously form primary, secondary, and higher-order structures that can exhibit biological function and supramolecular protein organization in tissues and organs.

1.2.3.1 Microstructures and Properties of Proteins Proteins are constructed mainly of α-amino acids. These amino acids can be neutral such as glycine, basic (containing one or more additional amines) such as lysine, or acidic (containing one or more additional acid groups) such as aspartic acid. Also, they may contain alcohol or thio functional groups, each representing a chemical "handle" with which chemists (synthetic, inorganic and organic) are able to play their trade on either proteins containing these "available" functional groups or on the amino acids themselves. Figure 1-4 shows the structure of the amide bond linking amino acids.

Proteins have four levels of structural organization: *Primary* structure refers to the sequence of amino acids in the polypeptide chain. Proteins or polypeptides are polymers of amino acids linked by amide linkages (peptide bonds); *Secondary* structure refers to the extended or helically coiled conformation of the polypeptide chains; *Tertiary* structure refers to the manner in which polypeptide chains are folded to form a tightly compact structure of globular protein; *Quaternary* structure refers to how subunit polypeptides are spatially organized. Several interactions and linkages are known to contribute to the formation of secondary, tertiary, and quaternary structures, such as steric strain, van der Waals interactions, electrostatic interactions, hydrogen bonding, hydrophobic interactions, and disulfide cross-links (Cheftel and Cuq, 1985).

Proteins interact with water through their peptide bonds or through their amino acid side-chains. The water solubility of proteins is a function of numerous parameters such as thermodynamic standpoint. Solubilization corresponds to separating the molecules of a solvent/protein molecules and dispersing the latter in the solvent for maximum interaction between the protein and solvent. The solubility of a protein depends mainly on pH value, ionic strength, the type of solvent, and temperature (Cheftel and Cuq, 1985). Protein denaturation is any modification in conformation (secondary, tertiary, or quaternary) not accompanied by the rupture of peptide bonds involved in primary structure. Denaturation is an elaborate phenomenon during which new conformations appear, although often intermediate and short-lived. The sensitivity of a protein to denaturation is related to the readiness with which a denaturing agent breaks the interactions or linkages that stabilize the protein's secondary, tertiary, or quaternary structure. Denaturation agents can be classified as physical

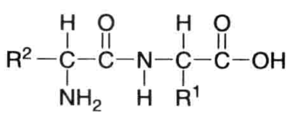

Fig. 1-4 Structure of the amide bond linking amino acids.