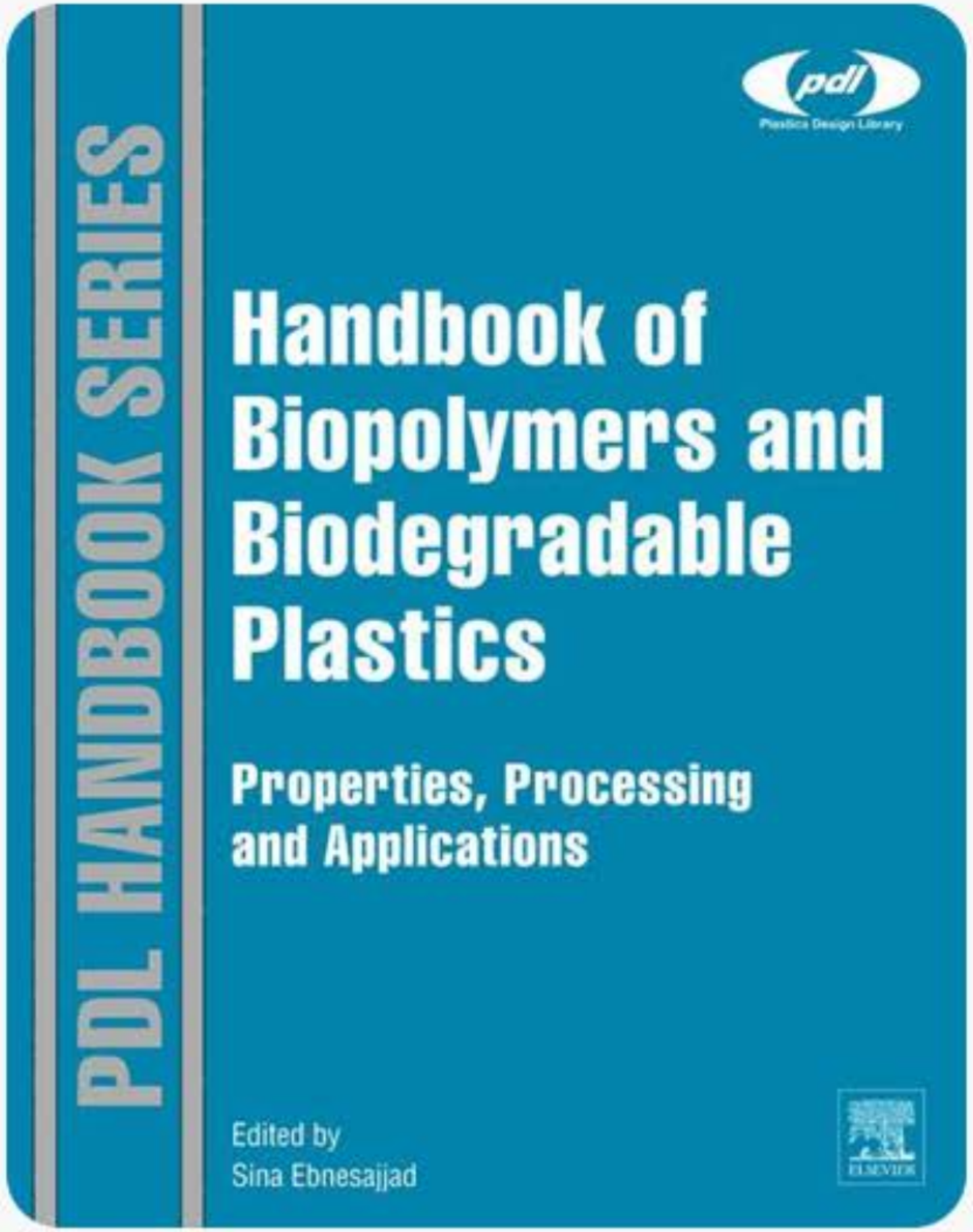

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Handbook of Biopolymers and Biodegradable Plastics

Properties, Processing and Applications

Edited by
Sina Ebnesajjad

ELSEVIER

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Preface

This book is about biobased and biodegradable polymers and plastics. It covers a fairly broad range of biopolymers with a strong focus on plastics, simply because of the large global consumption and impact of the latter on the environment and different life forms on the Earth. No matter where in the world plastics objects are thrown out, eventually they find their ways to the oceans and continents around the globe.

There are many sustainability issues which have been driving the development of monomers and biodegradable polymers from renewable plant resources. Some of those issues better known by the public include the cost of the traditional raw material source petroleum, global warming and environmental damage. A less understood problem is the extent of post-use pollution caused by plastic objects. Of all the plastics, metals and papers collected for recycling only an estimated 25% actually makes its way to reuse. The rest are disposed of because contamination renders them unusable.

A poorly addressed issue is the containers, bags, bottles, toys and other plastic objects that litter the roadsides and have been finding their way into the oceans. There are now five massive "Garbage Patches" in the Pacific, Atlantic and Indian Oceans in which immense quantities of plastic objects have gathered in the swirling vortex of these oceans' currents. Typically, plastic objects appear submerged just under the water surface. The Great Pacific Garbage Patch is one of the largest trash gyres, which takes up a large area of the Pacific Ocean estimated twice the size of the continental United States. The marine animals and birds ingest the plastics, mistaken for food, resulting in a build up of toxins, starvation and premature death. The ocean currents have been depositing massive quantities of intact and ground plastics on beaches of Pacific Islands such as Hawaii.

The estimated weight of the plastics in the Pacific

on reduction in the disposal of plastics and the development of commercial biodegradable plastics with relatively short lives. Ideally, a wholly plant-driven biodegradable plastic would decompose to carbon dioxide and water after a *short* exposure to the weather elements. It would be carbon dioxide neutral by being plant derived.

There are numerous books about biopolymers, covering the scientific research that is enabling the new generation of plastics. The goal in this handbook is to bring together some of the core knowledge in the field to provide a practical and wide-ranging guide for engineers, product designers and scientists involved in the commercial development of biopolymers and bioplastics, and their use in applications as varied as drinks bottles, medical devices and automotive manufacturing. The handbook includes a broad selection of material previously published in a number of Elsevier books; some of this material has been updated specially for this book. In addition, a section on polylactic acid (PLA), its synthesis, properties and applications, appears in print for the first time—material that will be included in a forthcoming book on PLA.

This book provides information about polymeric biomaterials: plant-derived polymers, methods of manufacture, applications and disposal. Whole chapters describe biodegradable and biobased polymers and plant polymer resources, demands, and sustainability. Separate chapters cover PLA, starch, cellulose and polymers based on plant oils, and their applications. The use of natural polymers in medicinal chemistry and tissue engineering has been covered in some detail.

Disposal methods covered here include composting, direct biodegradation and measurement tools for the biodegradability of polymers and plastics. One chapter has been devoted to compostable polymer materials experts in their fields and provide valuable information and insights into the polymers of the future. The contributors include: X. S. Sun, A. R. Rahmat, L. T. Sin, W. A. W. A. Rahman, A. Gandini, M. N. Belgacem, W. He, R. Benson, L. Jiang, J. Zhang, A. J. F. Carvalho, A. Dufresne, L. Avérous, E. Rudnik, R. P. Wool, A. Nussinovitch, K. Pal, A. T. Paulson, D. Rousseau, L. M. Grover, A. M. Smith, M. Gomes, H. Azevedo, P. Malafaya, S. Silva, J. Oliveira, G. Silva, R. Sousa, J. Mano, R. Reis, A. Kramschuster and L. S. Turng.

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Contents

1 Overview of Plant Polymers: Resources, Demands, and Sustainability

Xiuzhi Susan Sun

OUTLINE

Advances in petroleum-based fuels and polymers have benefited mankind in numerous ways. Petroleum-based plastics can be disposable and highly durable, depending on their composition and specific application. However, petroleum resources are finite, and prices are likely to continue to rise in the future. In addition, global climate change, caused in part by carbon dioxide released by the process of fossil fuel combustion, has become an increasingly important problem, and the disposal of items made of petroleum-based plastics, such as fast-food utensils, packaging containers, and trash bags, also creates an environmental problem. Petroleum-based or synthetic solvents and chemicals are also contributing to poor air quality. It is necessary to find new ways to secure sustainable world development. Renewable biomaterials that can be used for both bioenergy and bioproducts are possible alternatives to petroleum-based and synthetic products.

Agriculture offers a broad range of commodities, including forest, plant/crop, farm, and marine animals, that have many uses. Plant-based materials have been used traditionally for food and feed and are increas-

durability of petrochemicals. This chapter focuses on bio-based polymers derived from plant-based renewable resources, their market potential, and the sustainability of the agriculture industry of the future.

The three major plant-based polymers are protein, oil, and carbohydrates. Starch and cellulose, also called polysaccharides, are the main naturally occurring polymers in the large carbohydrate family. Agricultural fiber is also a member of the carbohydrate family. Natural fiber such as flax, hemp, straw, kenaf, jute, and cellulose consists mainly of cellulose, hemicellulose, and lignin, but is usually listed as a material when used as a fiber in composites.

Corn, soybean, wheat, and sorghum are the four major crops grown in the United States (Table 1.1), with total annual production of about 400 million metric tons (800 billion pounds) in the year 2000. Annually, 10–15% of these grains are used for food, 40–50% for feeds, and the rest could be for various industrial uses. Based on U.S. Department of Agriculture statistics, the total land used for crops is about 455 million acres, which is about 20% of the total usable land (Fig. 1.1) [1]. Including other crops, such

Table 1.1 Production of Selected Grains and Legumes (Million Metric Tons)

	Wheat	**Soybean**	**Corn**	**Sorghum**
World production	578	172	585	55
United States	60 (2nd)	75 (1st)	253 (1st)	12 (1st)
Other countries	99.6 (1st)	37 (2nd)	106 (2nd)	9 (2nd)
	China	Brazil	China	India
	37 (3rd)	15.4 (4th)	40 (3rd)	2.8 (6th)
	France	China	India	China

Sources: From Ref. [31] *and USDA World Agriculture Production, July 27, 2001.*

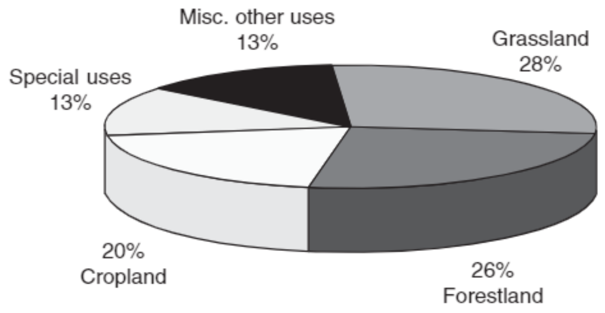

Figure 1.1 Land use and distribution. Total useful land in the United States is about 2.3 billion acres.

about 45–52% of the dry mass of a plant. This means that there is the potential to produce about 400 million metric dry tons of cellulosic sugar-based biomass (agriculture fiber residues) annually in the United States alone based on the total production of corn, soybean, wheat, and sorghum. Including other crops, plants, and forest products, the total annual US production of cellulosic sugar-based biomass could be about 800 million dry tons.

1.1 Plant Proteins

Plant proteins are amino acid polymers derived mainly from oilseeds (i.e., soybeans) and grains (i.e., wheat and corn), and are usually produced as by-

pharmaceuticals, nutraceuticals, paper coating, textile sizing, and, increasingly, adhesives. Plant proteins are complex macromolecules that contain a number of chemically linked amino acid monomers, which together form polypeptide chains, constituting the primary structure. The helix and sheet patterns of the polypeptide chains are called secondary structures. A number of side chains are connected to the amino acid monomers. These side chains and attached groups interact with each other, mainly through hydrogen and disulfide bonds, to form tertiary or quaternary structures. These proteins often have large molecular weights, in the range of 100,000–600,000 Dalton (Da) (Dalton = grams per mole), which makes them suitable for polymers and adhesives.

Proteins can be modified by physical, chemical, and enzymatic methods. Modification results in structural or conformational changes from the native structure without alteration of the amino acid sequence. Modifications that change the secondary, tertiary, or quaternary structure of a protein molecule are referred to as *denaturation* modifications [3]. The compact protein structure becomes unfolded during denaturation, which is accompanied by the breaking and reforming of the intermolecular and intramolecular interactions [4].

Physical modification methods mainly involve heat [5] and pressure [6] treatments. Heat provides

Table 1.2 Average Composition of Cereal Grains and Oilseeds (% Dry Weight Basis)

Cereal Grains	Protein	Fat	Starch	Fiber	Ash	Source
Wheat	12.2	1.9	71.9	1.9	1.7	[45]
Rye	11.6	1.7	71.9	1.9	2.0	[45]
Barley	10.9	2.3	73.5	4.3	2.4	[45]
Oats	11.3	5.8	55.5	10.9	3.2	[45]
Maize	10.2	4.6	79.5	2.3	1.3	[45]
Millet	10.3	4.5	58.9	8.7	4.7	[45]
Sorghum	11.0	3.5	65.0	4.9	2.6	[45]
Rice	8.1	1.2	75.8	0.5	1.4	[45]
Oilseeds						
Soybean	51–70[1]	18–26	—	6.5	3.7–7.4	[47]
Rapseed	36–44[1]	38–50	—	12–18	7.4–8.8	[47]
Sunflower	20.8	54.8	18.4	2.1	3.4	[47]
Peanut	30	50	14	2.9	3.1	[47]
Canola	22.0	41.0	22	10.0	5.0	[46]
Caster bean	12–16	45–50	3–7	23–27	2	[47]
Cottonseed	22	19.5	35	19.0	4.5	[46]
Copra	4.6–8.0	68–79	17.4–21	4.6–7.7	2.4–3.7	[47]
Safflower	21	41.0	14.5	19.0	4.5	[46]
Linseed	22–26	41.5–45.5	27–31	5.5–9.7	4.3–2.7	[47]
Sesame	20	52	23	—	5.6	[47]

[1] *Oil-free basis.*
Sources: From Refs. [45], [46], and [47].

Chemical modification methods may cause alteration of the functional properties, which are related closely to protein size, structure conformation, and the level and distribution of ionic charges. Furthermore, chemical treatments could cause reactions between functional groups, resulting in either adding a new functional group or removing a component from the protein. Chemical modification methods include acetylation, succinylation, phosphorylation, limited hydrolysis, and specific amide bond hydro-

[9]. Phosphorylation is another effective method to increase negative charges, thereby affecting gel-forming ability and cross-linking [10]. Gel-forming ability can also be increased by alkylation treatment [8]. Chemical hydrolysis is one of the most popular methods for protein modifications by acid-based agents. For example, peptide bonds on either side of aspartic acid can be cleaved at a higher rate than other peptide bonds during mild acid hydrolysis [11]. The hydrophobicity of a protein greatly

lysis. Acetylation is the reaction between a protein amino, or a hydroxyl group, and the carboxyl group of an acetylating agent. The acetylation reaction can modify the surface hydrophobicity of a protein [7]. Succinylation converts the cationic amino groups in the protein to an anionic residue, which increases the net negative charge, resulting in an increase in hydrophobicity under specific succinylating conditions [8]. This treatment also increases the viscosity

increases under specific conditions of mild acid hydrolysis [12, 13].

1.2 Plant Oils

Plant oils, such as soy oil, corn oil, and flax oil, can be derived from many crops (Table 1.2). The United States has the potential to produce about 30 billion