CHAPTER 1

NATURAL POLYMERS

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1. INTRODUCTION

The scarcity of natural polymers during the world war years led to the development of synthetic polymers like nylon, acrylic, neoprene, styrene-butadiene rubber (SBR) and polyethylene. The increasing popularity of synthetic polymers is partly due to the fact that there are unlimited and economic avenues for modification of chemical structure to obtain a product with specific properties. However, this rampant use of petroleum products has created a twin dilemma; depletion of petroleum resources (Figure 1) and entrapment of plastics in the food chain and environment[1]. The exhaustive use of petroleum based resources has initiated the efforts to develop biodegradable plastics. This is based on renewable bio-based plant and agricultural products that can compete in the markets currently dominated by petroleum based products. Table 1 presents a selected list of the common synthetic polymers

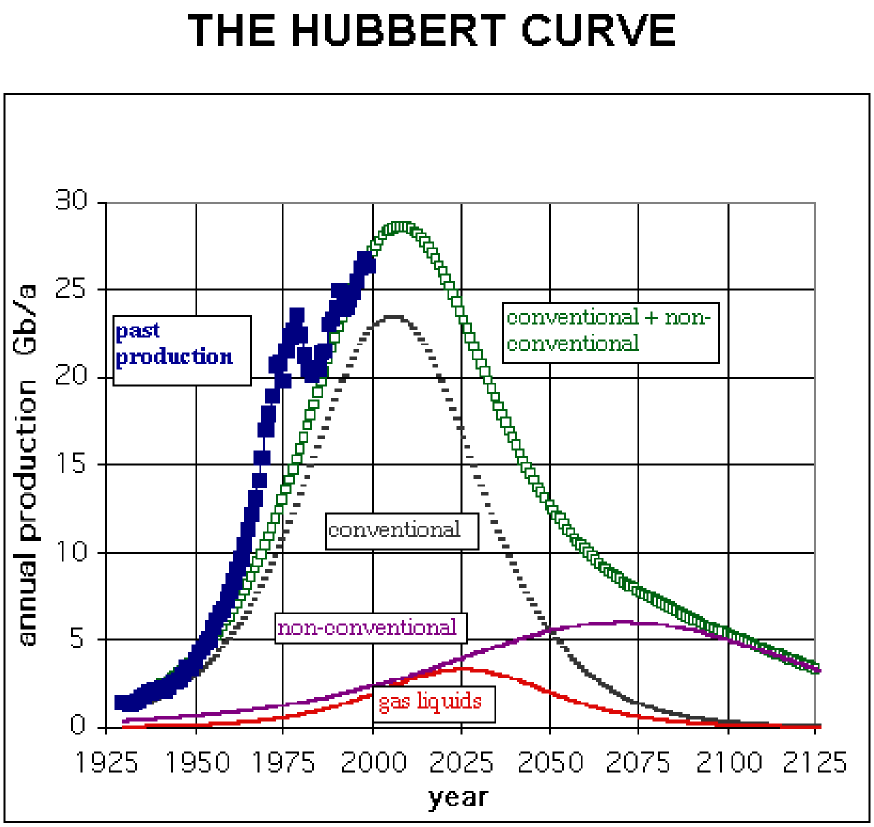

Figure 1: Chart for world oil reserves

Table 1: List of selected synthetic polymers

Synthetic Polymers
Polyethylene terephthalate
Polyethylene
Polyvinyl chloride
Polypropylene
Polystyrene

Polytetrafluroethylene
Polyurethane
Polyamide
Polyacrylamide

Another issue is that the disposal of plastics in landfills creates a serious aesthetic problem in large urbanized areas of the world. The chemical stability of plastic prevents plastic waste from decomposing into the environment at a rate comparable to the rate of waste generation. In the long run, the incentive to preserve the local environment is reduced and the costs of cleaning and recovery of contaminated sites rise. Large streams can also transport excess plastic waste to other areas creating a mobile contamination problem. Plastic waste comprises 60% to 80% of marine debris litter accumulated in ocean shores. The problem of marine waste is aggravated by the low reliability of removal mechanisms aimed at reducing marine plastic residual concentration in the oceans. Effects on marine life of plastic waste include the entanglement and ingestions of harmful plastics by marine vertebrates and the bioaccumulation of toxicants along the food chain.

Natural polymers are those which are present in, or created by, living organisms. These include polymers from renewable resources that can be polymerized to create bioplastics. There are two main types of natural polymers: those that come from living organisms (these include carbohydrates and proteins); and, those which need to be polymerized but come from renewable resources (lactic acid and triglycerides). Both types are used in the production of bio-plastics.

Among the different types of natural polymers, the best known resources capable of making biodegradable plastics are starch and cellulose. Cellulose is the most abundant carbohydrate in the world – 40% of all organic matter is cellulose. It is the main constituent of plants, serving to maintain their structure, and is also present in bacteria, fungi, algae and even in animals. Cellulose from trees and cotton plants is a substitute for petroleum feedstocks to make cellulose plastics.

Starch is a condensation polymer made up of hundreds of glucose monomers, which releases water molecules as they chemically combine. Starch is a member of the basic food group carbohydrates and is found in cereal grains and potatoes. It is also referred to as a polysaccharide, because it is a polymer of the monosaccharide glucose. Starch molecules include two types of glucose polymers, amylose and amylopectin, the latter being the major starch component in most plants, making up about three-fourths of the total starch in wheat flour. Amylose is a straight chain polymer with an average of about 200 glucose units per molecule. Starch is one of the least expensive biodegradable materials available in the world market today. It is a versatile polymer with immense potential for use in non-food industries. Annual world production of starch is well over 70 billion pounds, with much of it being used for non-food purposes, like making paper, cardboard, textile sizing, and adhesives.

Chitin, a polysaccharide similar to cellulose, is Earth's second most abundant polysaccharide (after cellulose). It is present in the cell walls of fungi and is the fundamental substance in the exoskeletons of crustaceans, insects, and spiders. The structure of chitin is identical to that of cellulose, except for the replacement of the OH group on the C-2 carbon of each of the glucose units with an $–NHCOCH_3$ group. The principal source of chitin is shellfish waste. Commercial uses of chitin waste include the making of edible plastic food wrap and cleaning up of industrial wastewater.

Chitin is the main source of production of chitosan, which is used in a number of applications, such as a flocculating agent, a wound healing agent, a sizing and strengthening agent for paper, and a delivery vehicle for pharmaceuticals and genes. Chitin deacetylation leads to the formation of chitosan. The process involves the use of strong alkali solutions for the removal of *N*-acetyl groups both at room or elevated temperatures. The amount of chitin obtained annually from harvested shellfish is estimated to be over 39,000 tonnes. At least ten billion tonnes of chitin are produced in the biosphere each year, chiefly in marine environments[2].

Collagen is one of the most plentiful proteins present in the bodies of mammals, including humans. In fact, it makes up about 25 percent of the total amount of proteins in the body. It has found increasing applications in tissue engineering and repair[3]. The ability of collagen to polymerize into a three-dimensional fibrous matrix makes it an appealing material for extensive therapeutic applications including medical implants[4].

Some of the other important natural polymers that are under scrutiny by the research community but beyond the scope of this book include lignin, shellac and natural rubber. In the category of natural polymers which need to be polymerized, is the interesting development of biodegradable plastics from edible and non-edible vegetable oils like soybean oil, peanut oil, walnut oil, sesame oil, sunflower oil, tung oil and castor oil.

Table 2 presents a selected list of the common natural polymers[5].

Natural Polymers
Polysaccharides
Starch
Cellulose
Chitin
Proteins

Collagen/ Gelatin
Casein, Albumin, Fibrogen, Silks
Polyesters
Polyhydroxyalkanoates
Other Polymers
Lignin
Lipids
Shellac
Natural rubber

The production of 100 % bio-based materials as substitute for petroleum based products is not an economical solution. Some of the possible solutions are blending biopolymers with synthetic polymers and reinforcing natural fibres with synthetic polymers (termed as bio-composites) which are a viable alternative to glass fibre composites.

2. NATURAL POLYMERS

The aim of this book was to examine the research conducted world-wide on the use of different types of natural polymers. This book looks at the different processing techniques of natural polymers as well as the application in advanced industrial sectors. The structure, mechanical and thermal characteristics of selected natural polymers has been highlighted.

2.1NATURAL FIBRES

The history of fibre reinforced plastics began in 1908 with cellulose fibre in phenolics, later extending to urea and melamine and reaching commodity status with glass fibre reinforced plastics. Natural fibres are subdivided based on their origins, coming from plants, animals or minerals. All plant fibres are composed of cellulose while animal fibres consist of proteins (hair, silk, and wool). Plant fibres include bast (or stem or soft sclerenchyma) fibres, leaf or hard fibres, seed, fruit, wood, cereal straw, and other grass fibres. Knowledge of the structure of natural fibres is crucial in understanding the structural parameters (number, size and shape of cells, chemical constituents) and fracture mechanisms in the fibres[6].

Some of the important natural fibres used as reinforcement in composites are listed in Table 3.

Table 3 List of important natural fibres

Fibre source	Species	Origin
Abaca	*Musa textilis*	Leaf
Agave	*Agave americana*	Leaf
Alfa	*Stippa tenacissima*	Grass
Bagasse	-	Grass
Bamboo	(>1250 species)	Grass
Banana	*Musa indica*	Leaf
Broom root	*Muhlenbergia macroura*	Root

Cantala	*Agave cantala*	Leaf
Caroa	*Neoglaziovia variegata*	Leaf
China jute	*Abutilon theophrasti*	Stem
Coir	*Cocos nucifera*	Fruit
Cotton	*Gossypium* sp.	Seed
Curaua	*Ananas erectifolius*	Leaf
Date palm	*Phoenix Dactylifera*	Leaf
Flax	*Linum usitatissimum*	Stem
Hemp	*Cannabis sativa*	Stem
Henequen	*Agave fourcroydes*	Leaf
Isora	*Helicteres isora*	Stem
Istle	*Samuela carnerosana*	Leaf
Jute	*Corchorus* capsularis	Stem
Kapok	*Ceiba pentranda*	Fruit
Kenaf	*Hibiscus cannabinus*	Stem
Kudzu	*Pueraria thunbergiana*	Stem
Mauritius hemp	*Furcraea gigantea*	Leaf
Nettle	*Urtica dioica*	Stem
Oil palm	*Elaeis guineensis*	Fruit
Piassava	*Attalea funifera*	Leaf
Pineapple	*Ananus comosus*	Leaf
Phormium	*Phormium tenas*	Leaf
Roselle	*Hibiscus sabdariffa*	Stem
Ramie	*Boehmeria nivea*	Stem
Sansevieria (Bowstring hemp)	*Sansevieria*	Leaf
Sisal	*Agave sisilana*	Leaf

Sponge gourd	*Luffa cylinderica*	Fruit
Straw (Cereal)	-	Stalk
Sun hemp	*Crorolaria juncea*	Stem
Cadillo/ Urena	*Urena lobata*	Stem
Wood	(>10,000 species)	Stem

Over the last few years, a number of researchers have been involved in investigating the exploitation of natural fibres as load bearing constituents in composite materials. The use of such materials in composites has increased due to their relative cheapness, their ability to recycle and for the fact that they can compete well in terms of strength per weight of material.

Volume 1 of the book focuses on different sources and applications of natural fibres. There are eight chapters under Volume 1. The first chapter deals with novel renewable sources from which natural fibres can be extracted. The second chapter looks at co-relating structural anisotropy of natural fibres with mechanical properties. One of the challenges of using natural fibres in aerospace applications is the airworthiness requirements. Currently natural fibres are being explored for use in secondary structures in aircrafts for which flame, smoke and toxicity (FST) requirements are very stringent. This has led to a lot of developmental research being undertaken in this field. One of the chapters explores the flammability properties of natural fibre reinforced composites. A crucial problem associated with the use of natural fibres in composites is its hydrophilic properties. This aspect is dealt with in a chapter on probing the water sorption characteristics of natural fibres. Chemical modification of natural fibres has been well documented in the literature. But ideally it would also be desirable that the chemicals used for modification should also be from renewable resources as it would preserve the biodegradable nature of natural fibres. One of the chapter focuses on environmentally friendly coupling agents for natural fibre reinforced composites. Other chapters include examining the characterization techniques of interfacial properties of natural fibre reinforced composites and the increasing applications of natural fibre composites in automotive sector.

2.1PROTEIN FIBRES

The book also deals with the properties of selected protein fibres. Protein fibers are formed by natural animal sources through condensation of α-amino acids to form repeating polyamide units with various substituents on the α -carbon atom. The sequence and type of amino acids making up the individual protein chains contribute to the overall properties of the resultant fiber[7]. In general, protein fibers possess moderate strength, resiliency, and elasticity. They have excellent moisture absorbency and transport characteristics and do not build up static charge. Some of the common protein fibres include wool, spider silk, cashmere etc. Among natural fibres, silk exhibits exceptional properties especially in toughness and biocompatibility properties. Chapter ? focuses on the studies and properties of silk fibre reinforced composites. Other chapters include studies on collagenous waste based composites and exploring the properties and applications of mussel byssus fibres. Important advancements in the field of zein fibres have also been discussed.

Volume 2 of the book deals with properties and characterization of selected natural polymer nanocomposites. Cellulose nanowhiskers (CNW’s) have emerged as one of the most interesting bio-based nano-reinforcements in the last decade[8,9]. Cellulose nanowhiskers can be generated, from various plant sources, with transverse dimensions as small as 3–30 nm, giving a high surface to volume ratio. It has also been shown that since the nanowhiskers are rod-like, they can be self-assembled into chiral nematic liquid crystalline structures, not only in solution, but also in the dry state. The first chapter in Volume 2 explores nanocellulose as a potential reinforcement in composites. Chitosan – a natural polymer - is a good candidate for the development of conventional and novel drug delivery systems. Chitosan has been found to be used as a support material for gene delivery, cell culture, and tissue engineering. However, practical use of chitosan has been mainly confined to the unmodified forms. For a breakthrough in utilization, especially in the field of controlled drug delivery, graft copolymerization onto chitosan will be a key point, which will introduce desired properties and enlarge the field of the potential applications of chitosan by choosing various types of side chains. The properties and applications of chitosan and soy protein based nanocomposites have been discussed in subsequent chapters. Other chapters include studies on furanic based nanocomposites, characterization of molecular interactions in amylose-starch nanocomposites and unique properties of nacre from mollusc shells[10,11]. The last two chapter touches upon the industrial and biomedical applications of natural polymer nanocomposites.

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