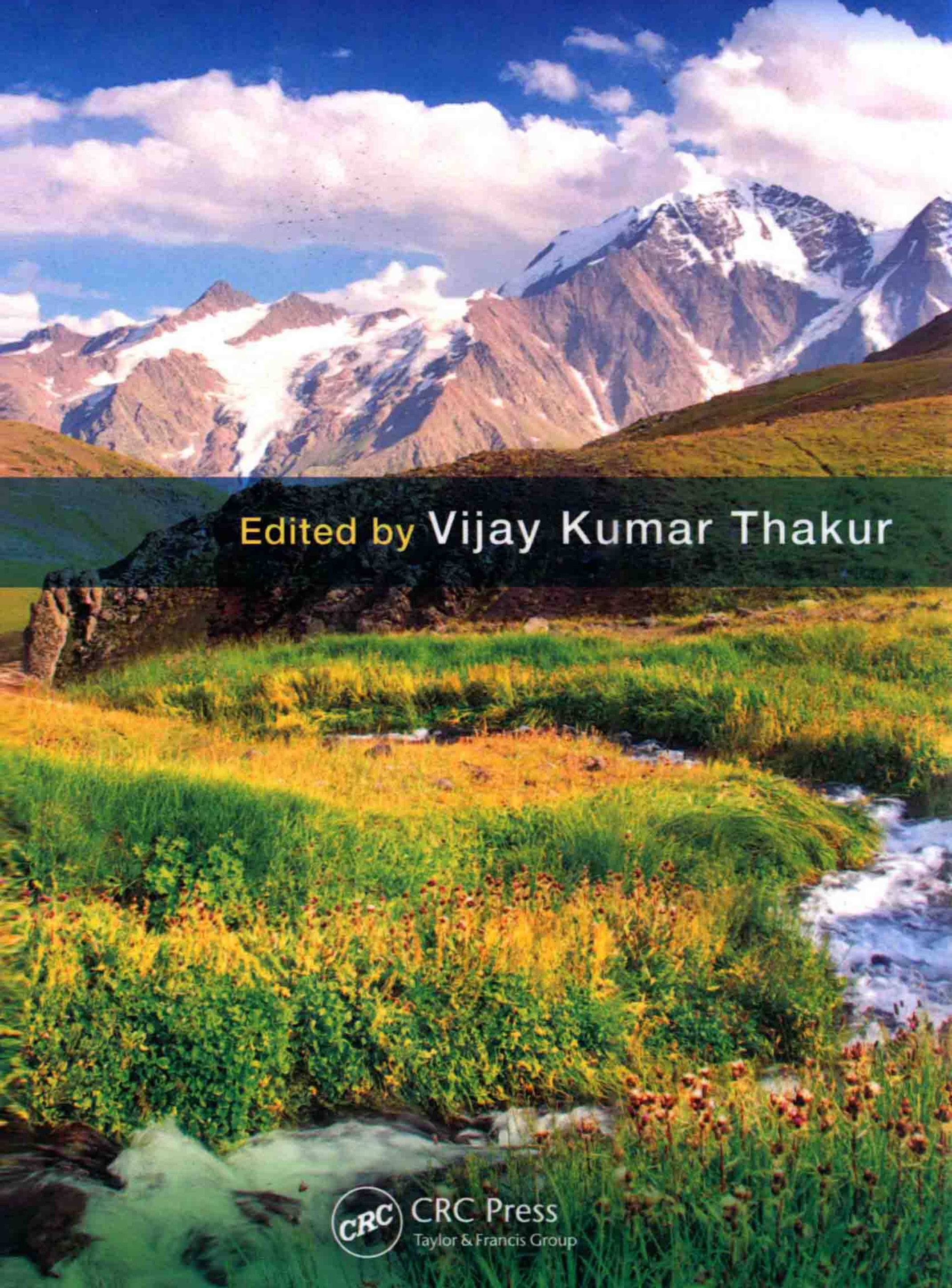
GREEN COMPOSITES *from* NATURAL RESOURCES



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Preface

Global warming, rising environmental awareness, waste management issues, dwindling fossil resources, and rising oil prices are some of the reasons why green materials obtained from renewable resources are increasingly being promoted for sustainable development. Various kinds of renewable green materials, such as starchy and cellulosic polymers including natural fibers, vegetable oils, wood bark, cotton, wool, and silk, have been used for thousands of years for food, furniture, and clothing. However, it is only in the past two decades they have experienced a renaissance as one of the most feasible alternatives to synthetic polymers for a variety of industrial applications, such as building, construction, automotive, packaging, films, and paper coating, as well as in biomedical applications. The prime disadvantages of synthetic polymers, such as release of toxic gases and vapors as a result of incineration and difficulty in their disposal, have led to intense investigations in the field of new green polymeric materials with a particular interest in the use of biopolymers obtained from renewable resources for green composite applications. This book is the outcome of contributions by world-renowned experts in the field of green polymer materials from different disciplines, and various backgrounds and expertise. The material enclosed in the book gives a true reflection of the vast area of research in green composites, which is also applicable to a number of industries.

This book contains precisely referenced chapters, emphasizing green composite materials from different natural resources with eco-friendly advantages that can be utilized as alternatives to synthetic polymers through detailed reviews of various lignocellulosic reinforcing materials and their property control using different approaches. Each chapter in this book covers a significant amount of basic concepts and their development until its current status of development. The book aims at explaining basic characteristics of green composite materials, their synthesis, and applications for these renewable materials obtained from different natural resources that present future directions in a number of industrial applications including the automotive industry. The book attempts to present emerging low-cost and eco-friendly green composite materials. I hope this book will contribute significantly to the basic knowledge of students and researchers all around the globe working in the field of green materials. I thank all the contributors for their innovative contributions and Laurie Schlags (project coordinator) along with Allison Shatkin (senior editor) for their invaluable help in the editing process.

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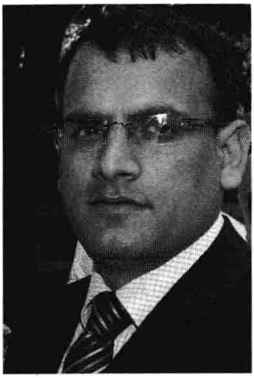

Vijay Kumar Thakur, PhD, graduated with a BSc in chemistry (nonmedical), physics (nonmedical), and mathematics (nonmedical); BEd; and MSc in organic chemistry from Himachal Pradesh University, Shimla, India, in 2006. He then moved to the National Institute of Technology, Hamirpur, India, where he obtained his doctoral degree in polymer chemistry from the Chemistry Department in 2009. After a brief stay in the Department of Chemical and Materials Engineering at Lunghwa University of Science and Technology, Taiwan, he joined Temasek Laboratories at Nanyang Technological University, Singapore, as a research scientist in October 2009 and worked there until 2012. He has a general research interest in the synthesis of polymers, nanomaterials, nanocomposites, biocomposites, graft copolymers, high-performance capacitors, and electrochromic materials. He has coauthored five books, 20 book chapters, one U.S. patent, and has published more than 60 research papers in reputed international peer-reviewed journals, including *Advanced Materials*, *Journal of Materials Chemistry*, *Polymer Chemistry*, and *RSC Advances*, along with 40 publications in proceedings of international/national conferences. He has been included in the *Marquis Who's Who in the World* in the field of science and engineering for the year 2011. He is a reviewer for more than 37 international journals and currently serves as a member on the steering committee of the WAP Conference Series: Engineering and Technology Frontier. He also serves on the editorial board of 22 international journals including *Advanced Chemistry Letters*, *Lignocelluloses*, *Drug Inventions Today* (Elsevier), *International Journal of Energy Engineering*, and *Journal of Textile Science & Engineering* (USA) being published in the fields of natural/synthetic polymers, composites, energy storage materials, and nanomaterials.

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An Introduction

Vijay K. Thakur, Manju K. Thakur, Raju K. Gupta, Raghavan Prasanth, and Michael R. Kessler

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1.1 INTRODUCTION

Global environmental concerns, such as rising sea levels, rising average global temperatures, decreasing polar ice caps, and rapidly depleting petroleum resources, have intensified pressure on humans and industries. How to respect the environment and improve living conditions for the benefit of all living organisms are key global issues. These concerns and an increased awareness of renewable "green" materials have initiated efforts in many industries to mitigate their impact on the environment. With an emphasis on reduction of greenhouse gas emissions and carbon footprint, there is a demand for sustainably produced green materials with improved performance (Luo and Netravali 1999).

Sustainable development has become a major issue in recent years, and the foreseeable depletion of oil-based resources will require the use of biopolymer materials from renewable resources (Bledzki and Gassan 1999; Singha and Thakur 2012; Thakur et al. 2011). The generally accepted definition of sustainable development is "development that meets the needs of the present without compromising the ability of future generations to meet their own need" (Brundtland Commission 1987). In a broader approach, sustainable development is defined to be comprised of three components: society, environment, and economy. Biopolymeric materials obtained from different natural resources offer the potential to aid the transition toward sustainable and green development (Zain et al. 2011). One of the most significant advantages of some biopolymeric, green materials is that they easily decompose into environmentally benign components, such as carbon dioxide, water, and humus-like matter (Klemm et al. 2005; Scott 2000; Wambua et al. 2003). Biodegradation of bio-based, biodegradable polymers can be achieved by exposing them to environmental influences (such as UV, oxygen, water, and heat) or microorganisms that will metabolize the polymer and produce an inert, humus-like material that is not harmful to the environment and can be easily mixed with natural soil.

The effective use of eco-friendly, green materials in a variety of applications, with a particular focus on energy-efficient, cost-effective materials, is one of the daunting challenges of the twenty-first century. This brings natural polymeric materials, such as cellulosic fibers, vegetable oils, wood bark, cotton, wool, and silk, into focus as feasible alternatives to traditional synthetic polymeric materials for a variety of industrial applications, such as building construction, automobiles, packaging, films, and paper coatings (Klyosov 2008). Archeological artifacts suggest that human beings used natural fibrous materials in fabrics several thousand years ago (Nikolaos 2011). Natural fibers have been used in ropes, lines, and other one-dimensional products. Some other applications of natural fibers in earlier times included suspension bridges for on-foot passage of rivers and rigging for naval ships.

Biopolymers have already made inroads in biomedical applications, such as surgical sutures, implants, and controlled drug-delivery devices (Averous 2004). However, most commercial polymers used in everyday applications are still prepared from nonbiodegradable/nonrenewable constituents (Hon 1996). These polymers are generally derived from petroleum, by definition a nonsustainable resource. We are currently consuming petroleum at an "unsustainable" rate: nearly 100,000 times faster than nature can create it.

These concerns have led to intense investigations in the field of environmentally friendly, green polymeric materials with a particular interest in the use of biopolymers for green composite applications (Bledzki et al. 2010). Humans have been using biopolymeric, natural, renewable materials, such as wood, amber, silk, natural rubber, celluloid, shellack, for many centuries (Cipriani et al. 2010; Davim 2011). Naturally occurring biopolymeric materials were used beginning in early civilizations and have been increasingly utilized since the industrial revolution in the late nineteenth century to meet specific needs. Today, the demand for the effective utilization of biopolymeric materials is increasing significantly. In particular, the idea of using biopolymer-based materials as one of the components in advanced green composite materials is gaining more and more interest both in academia and in industry (Hamad 2002; Thakur et al. 2011). This chapter covers a brief introduction of green composites/natural fibers and does not cover traditional synthetic composites/animal fibers.

1.2 OVERVIEW OF COMPOSITES

Composites are made of individual materials referred to as constituent materials. The properties of composites are typically determined by the combination of the respective properties of the constituent materials (Klyosov 2008). The term "composite" comes from the Latin word *compositus*, stemming from the root word *componere*, which means "to bring together." Different researchers have defined composite materials in different ways (Singha and Thakur 2012). In general, composites are defined as engineering materials made from two or more constituents with significantly different physical or chemical properties. Composites are typically stronger than the

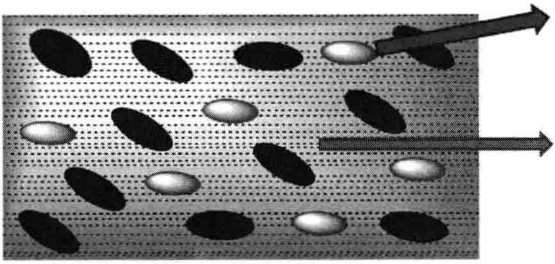

FIGURE 1.1 General schematic of a composite.

individual materials and may exhibit entirely different properties than the individual constituents (Thakur et al. 2011). According to American Society for Materials Handbook, composites can be defined as "a macroscopic combination of two or more distinct materials having a recognizable interface between them" (Hazizan and Cantwell 2003). A composite is made of at least two materials, where one material essentially acts as the binding material (the matrix), while the other acts as reinforcement (Chapter 10 provides a detailed description of composites, classification of green composites, and factors affecting composite properties). Figure 1.1 shows the general schematic of a composite.

The matrix material surrounds the reinforcement; it is also referred to as the "continuous phase." The type and level of reinforcement determines the mechanical and physical properties of the composite; it is referred to as the "discontinuous phase." The discontinuous phase is generally harder and exhibits mechanical properties superior to those of the continuous phases. In a given composite material, both the matrix and the reinforcement are distinguishable. To a considerable extent, each of the materials maintains its distinctive characteristics, which enhance the properties of the resulting composite material. In particular, mechanical and physicochemical properties of the composite are superior to those of the matrix material (Thakur and Singha 2012). Composites can be tailored to exhibit a wide range of desired properties. Many composite materials offer advantageous properties in terms of high fatigue strength, low weight, corrosion resistance, and higher specific properties such as tensile, flexural, and impact strengths (Oksman and Sain 2008).

1.2.1 Potential Merits of Composites

The advantages of composite materials have led to their widespread use in a variety of industries. Some of the important features and benefits that some composites provide are as follows:

- Light weight: composites are significantly lighter, especially in comparison to materials such as concrete and metals
- Increased design flexibility
- High strength
- Better damage tolerance

- Increased impact resistance
- Increased chemical resistances
- Increased fracture toughness
- Superior corrosion resistance
- Low coefficient of thermal expansion
- Superior fatigue resistance
- Potentially lower component costs

Composites are generally classified by the type of matrix, such as polymer, metal, or ceramic, or by the type of reinforcement, such as fibers, particulate, flake, or whiskers. Figure 1.2 shows the classification of different types of composites.

Each type of composite material is designed to meet the requirements of specific applications. In this book, the term composites will always refer to *polymer composites.*

Although we find polymers in a wide range of applications, from low-cost/high-volume consumer products to automotive engineering components under the hood to highly complex medical devices, in some applications their stiffness and strength cannot compete with metals. Polymer composites were developed to meet the need for light weight, high stiffness materials that exhibit additional functionalities, such as wear resistance, electrical properties, and thermal stability (Oksman and Sain 2008). Polymer composites consist of two or more distinct phases, including a polymer matrix (continuous phase) and fibrous or particulate reinforcing material (dispersed phase). Based on their reinforcements, polymer composites can be categorized into three main classes: particulate composites, continuous fiber composites, and discontinuous fiber composites.

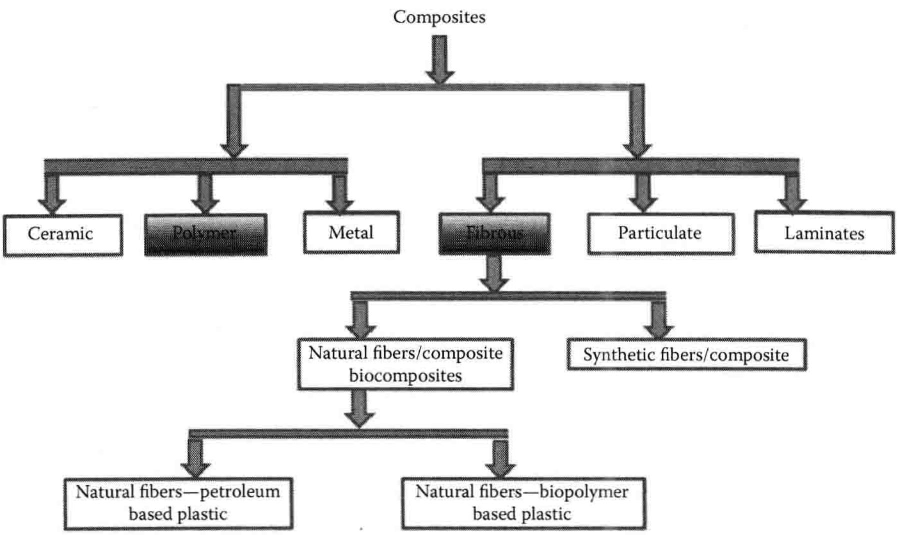

FIGURE 1.2 Classification of different types of composites.

1.3 GREEN COMPOSITES

Increasing environmental pollution, concerns over petroleum supplies, high crude oil prices, and lack of resources have resulted in increased research in materials that are friendly to our health and environment (Luo and Netravali 1999). A number of renewable biopolymer materials, including cellulose, proteins, starch, vegetable oils, and sugar, have been investigated as potential components of green polymer composites (Luo and Netravali 1999).

Green composites are a specific class of composites, where at least one of the components (such as the matrix or the reinforcement) is obtained from natural resources (Netravali and Chabba 2003). The terms green composites, biocomposites, and eco-composites all broadly refer to the same class of materials (Nikolaos 2011; Oksman and Sain 2008). Green composites, especially natural fiber–reinforced composites, have been used by humans since the beginning of human civilization (Richard 1994; Thakur et al. 2011). They were used as a source of energy, and as a material to make shelters, clothes, tools, and more. In ancient Egypt, 3000 years ago, people used straw as the reinforcing component for the mud-based wall materials in houses. These green composites were produced in simple shapes by layering the different structural elements to create the desired design. They made bricks of mud with straw as reinforcement and used these bricks to build walls.

Biopolymer-based green composites can offer green, renewable alternatives to the most widely used petroleum-based polymers with equal or better properties, enabling new applications (Azizi et al. 2005; Pandey et al. 2013; Thakur and Singha 2012). The interest in green composites that contain biopolymers as one of the essential components has increased in recent years due to the renewable and biodegradable nature of biopolymers (Markarian 2005). Biopolymeric composites, such as cellulosic fiber–reinforced polymer composites, are gaining greater acceptance in a number of applications, particularly in structural and packaging applications (Kabir et al. 2012). For a material to be effectively used in packaging applications, the basic raw materials should be renewable and the end products should be compostable to reduce the use of fossil fuels and limit the cost and environmental impact of waste treatment (Rowell 2012). The industrial-scale production processes used to prepare different kinds of packaging materials using biopolymers should be efficient, economically competitive, and environmentally friendly (Dufresne et al. 1999).

Natural fiber–reinforced polymer composites represent an emerging area in polymer science (Ouajai and Shanks 2009a). These composites are both environmentally friendly and sustainable. After decades of high-tech development of artificial fibers, such as aramid, carbon, and glass, natural fibers, such as wood fibers, sisal, pine needles, kenaf, flax, jute, hemp, and others, have attracted renewed interest (Rowell 2012; Thakur and Singha 2012). These natural cellulosic fibers have shown great potential as substitutes for synthetic fibers, in particular glass fibers in composites that are extensively used in the automotive and construction industries. The advantages of natural fibers over synthetic fibers are their low cost, eco-friendliness, low density, low abrasion, acceptable specific strength properties, ease of separation, carbon dioxide sequestration, and biodegradability, to name a few (Thakur et al. 2011; Thakur and Singha 2012).

1.3.1 Classification of Green Composites

Intense research efforts are currently focused on developing "green" composites by combining (natural/bio) fibers with suitable polymer matrices (Schneider and Karmaker 1996; Singha and Thakur 2012). A variety of natural and synthetic polymer matrix resins are available for green composites, including polythene, polypropylene, polystyrene, polyester, epoxy, phenolic resins, starch, and polylactic acid (Garlotta 2001; Ouajai and Shanks 2009b). Depending on the type of reinforcement and polymer matrix, green composites can be divided into three main types:

1. Totally renewable composites, in which both the matrix and reinforcement are from renewable resources
2. Partly renewable composites, in which the matrix is obtained from renewable resources and reinforced with a synthetic material
3. Partly renewable composites, in which a synthetic matrix is reinforced with natural biopolymers

Although the number of green composites made from renewable resources has been increasing, spurred by the growing seriousness of environmental problems (Uma Devi et al. 2010), the processing temperature remains a limiting factor in the choice of a suitable polymer matrix for green composites. Polymer matrices are generally classified into thermosetting, thermoplastic, or biodegradable (Bledzki and Gassan 1999; John and Thomas 2008).

In fiber-reinforced green composites, the fiber serves as reinforcement and provides strength and stiffness to the resulting composite structure (Rowell 2012). Natural biomass (agricultural residues, wood, plant fibers, etc.), which primarily contains cellulose, hemicelluloses, and lignin, represents an abundant source of renewable reinforcement for green composites and is considered one of the most important components of green composites. The numerous advantages of natural fiber–reinforced green composites such as low cost, light weight, eco-friendliness, nonabrasiveness, and biodegradability place them among the high-performance composites having both economic and environmental advantages (Voichita 2011). Although natural fiber reinforcement was used in various applications in the last two decades, extensive research is still required in order to fully understand and explore the potential of natural fibers (Voichita 2006). The effective utilization of natural fibers derived from renewable resources provides environmental benefits with respect to ultimate disposability and utilization of raw material (Singha and Thakur 2012). Therefore, many industrial sectors consider natural fibers as potential substitutes for synthetic reinforcement. Natural fiber–reinforced green composite materials are presently used in various applications, such as door components, furniture, deck surfaces, windows, and automotive components.

The properties of natural fibers vary to a considerable degree, depending on the processing method used to obtain the fibers (Hon 1996). At the present state of technology, wood as well as non-wood fibers such as hemp, kenaf, flax, and sisal have achieved commercial success in green composites automotive sector, employing different polymer matrices (Davim 2011). A number of studies on natural