Handbook of Composites from Renewable Materials
Handbook of Composites from Renewable Materials
Edited by Vijay Kumar Thakur, Manju Kumari Thakur and Michael R. Kessler

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Handbook of Composites from Renewable Materials

Volume 6
Polymeric Composites

Edited by
Vijay Kumar Thakur, Manju Kumari Thakur and Michael R. Kessler
To my parents and teachers who helped me become what I am today.

Vijay Kumar Thakur
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The concept of green chemistry and sustainable development policy impose on industry and technology to switch raw material base from the petroleum to renewable resources. Remarkable attention has been paid to the environmental friendly, green and sustainable materials for a number of applications during the last few years. Indeed the rapidly diminishing global petroleum resources, along with awareness of global environmental problems, have promoted the way to switch towards renewable resources based materials. In this regards, bio-based renewable materials can form the basis for variety of eco-efficient, sustainable products that can capture and compete markets presently dominated by products based solely on petroleum based raw materials. The nature provides a wide range of the raw materials that can be converted into a polymeric matrix/ adhesive/ reinforcement applicable in composites formulation. Different kinds of polymers (renewable/nonrenewable) and polymer composite materials have been emerging rapidly as the prospective substitute to the ceramic or metal materials, due to their advantages over conventional materials. In brief, polymers are macromolecular groups collectively recognized as polymers due to the presence of repeating blocks of covalently linked atomic arrangement in the formation of these molecules. The repetitive atomic arrangements forming the macromolecules by forming covalent links are the building block or constituent monomers. As the covalent bond formation between monomer units is the essence of polymer formation, polymers are organic or carbon compounds of either biological or synthetic origin. The phenomenon or process of polymerization enables to create diverse forms of macromolecules with varied structural and functional properties and applications. On the other hand, composite materials, or composites, are one of the main improvements in material technology in recent years. In the materials science field, a composite is a multi-phase material consisting of two or more physically distinct components, a matrix (or a continuous phase) and at least one dispersed (filler or reinforcement) phase. The dispersed phase, responsible for enhancing one or more properties of matrix, can be categorized according to particle dimensions that comprise platelet, ellipsoids, spheres and fibers. These particles can be inorganic or organic origin and possess rigid or flexible properties.

The most important resources for renewable raw materials originate from nature such as wood, starch, proteins and oils from plants. Therefore, renewable raw materials lead to the benefit of processing in industries owing to the short period of replenishment cycle resulting in the continuous flow production. Moreover, the production cost can be reduced by using natural raw materials instead of chemical raw materials. The waste and residues from agriculture and industry have been also used as an alternative renewable resources for producing energy and raw materials such as chemicals, cellulose, carbon and silica. For polymer composites applications, an intensifying focus
has been directed toward the use of renewable materials. Bio-based polymers are one of the most attractive candidates in renewable raw materials for use as organic reinforcing fillers such as flex, hemp, pine needles, coir, jute, kenaf, sisal, rice husk, ramie, palm and banana fibres which exhibited excellent enhancement in mechanical and thermal properties. For green polymer composites composed of inorganic reinforcing fillers, renewable resources based polymers have been used as matrix materials.

Significant research efforts all around the globe are continuing to explore and improve the properties of renewable polymers based materials. Researchers are collectively focusing their efforts to use the inherent advantages of renewable polymers for miscellaneous applications. To ensure a sustainable future, the use of bio-based materials containing a high content of derivatives from renewable biomass is the best solution.

This volume of the book series “Handbook of Composites from Renewable Materials” is solely focused on the “Polymeric Composites”. Some of the important topics include but not limited to: Keratin as renewable material for developing polymer composites; natural and synthetic matrices; hydrogels in tissue engineering; smart hydrogels: application in bioethanol production; principle renewable biopolymers; application of hydrogel biocomposites for multiple drug delivery; nontoxic holographic materials; bioplasticizer - epoxidized vegetable oils-based poly (lactic acid) blends and nanocomposites; preparation, characterization and adsorption properties of poly (DMAEA) – cross-linked starch gel copolymer in waste water treatments; study of chitosan cross-linking hydrogels for absorption of antifungal drugs using molecular modelling; pharmaceutical delivery systems composed of chitosan; eco-friendly polymers for food packaging; influence of surface modification on the thermal stability and percentage of crystallinity of natural abaca fiber; influence of the use of natural fibers in composite materials assessed on a life cycle perspective; plant polysaccharides-blended ionotropically-gelled alginate multiple-unit systems for sustained drug release; vegetable oil based polymer composites; applications of chitosan derivatives in wastewater treatment; novel lignin-based materials as a products for various applications; biopolymers from renewable resources and thermoplastic starch matrix as polymer units of multi-component polymer systems for advanced applications; chitosan composites: preparation and applications in removing water pollutants and recent advancements in biopolymer composites for addressing environmental issues.

Several critical issues and suggestions for future work are comprehensively discussed in this volume with the hope that the book will provide a deep insight into the state-of-art of “Polymeric Composites” of the renewable materials. We would like to thank the Publisher and Martin Scrivener for the invaluable help in the organisation of the editing process. Finally, we would like to thank our parents for their continuous encouragement and support.

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Keratin as Renewable Material to Develop Polymer Composites: Natural and Synthetic Matrices

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Abstract
Keratin is a structural fibrous protein, considered as the main constituent of wool, hair, horns, feathers and other outer coverings of mammals, reptiles and birds. This protein represents an inexhaustible source of non-contaminant materials for possible diverse applications. In the last decade the use of keratin in different forms to elaborate polymer composites has opened a novel and outstanding research field. Ongoing research have been developed keratin materials from diverse sources as reinforcements. These have been in the form of fibers, particles, nanoparticles or powder, among others. Thus, this chapter reviews different studies related to the use of keratin materials obtained from feathers, wool, hair and other renewable sources in order to reinforce polymer matrices. The properties obtained in these polymer composites are discussed separately depending on the nature of the matrix, natural or synthetic. The possible applications and the future of these kinds of composites are also discussed.

Keywords: Keratin, natural fiber, polymer composites, biodegradable polymer

1.1 Introduction
Biocomposites can be obtained from plant or living beings (natural/biofiber) and crop-derived plastics (bio-plastic). Actually, these are considered novel materials, still in development during the beginning of the twenty-first century (Singha & Thakur, 2009a–c; 2010a–c). The study of these materials started as an answer to a growing environmental threat and as attempt to supply solutions for the coming problem about petroleum supply (Mohanty et al., 2002; Thakur et al., 2016). It was reported that since the 1960s the demand for non-continuous components of composites has been growing incessantly. For example, in 1967, in the United States, necessities for fillers by the plastic production were around 525,000 tons, whereas in 1998, 1,925,000 tons were

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required by the same industry (Eckert, 1999). By this century, in 2000 the US market for natural composites exceeded $150 million (Mohanty et al., 2002), but for 2010, the projected requirement for fillers for the United States plastic production was to 3.85 billion kilograms, from which 0.31 billion kilograms (8%) were expected to be bio-based fibers (Farsi, 2012).

Natural fibers are the support to develop high performing fully biodegradable eco or green composites (Thakur et al., 2013a-e). Natural fibers are considered as biodegradable and environmentally friendly, mainly due to their plant-based cellulosic or lignocellulosic fibers. Much research is being undertaken of these as natural prospects for reinforcing (or filling) polymers to make them less aggressive towards the environment (Netravali & Chabba, 2003). In agreement with Thakur et al., (2014), one of the most successful emerging areas of interest in polymer engineering and materials science is precisely related to the proper application of raw natural fibers as an essential element towards achievement of new low-cost green composites.

In reality, many scientists have found an interesting research field by using plant-based fibers due to their ready availability. However, different prospects exist if high-strength protein fibers are taken into account. For example, keratin can be obtained from chicken feathers, wool, hair and horns. Keratin, a non-food protein, is an abundant biopolymer, and because of its animal origin, it is a renewable and low-priced feedstock. It is also assessed that worldwide there are some million tons per year of material-based keratin disposed in landfills that comes from non-used residues of wools, hairs, feathers, horns and nails (Bertini et al., 2013).

This chapter reviews the latest advancements in the field of composites with synthetic and natural matrices using keratin as reinforcement. The first section begins with a brief description of the structural characteristics of keratin. Subsequently, different natural materials that contain keratin are compared. In the second section, composites with synthetic matrices and different sources of keratin as reinforcement are detailed. The methods, techniques and properties are described for these composites. The last part discusses composites with natural matrices reinforced with keratin from different natural sources.

It is worthy of mention that there are many matrix systems that have been reinforced with keratin materials; therefore these novel composites are versatile to different applications depending on the desired properties. However, important criteria in the synthesis procedures must be carefully observed, since natural characteristics of keratin represent certain processing restrictions. Examples of these criteria could be: processing methods, morphological structures of keratin reinforcements, quantity of keratin used to reinforce matrices, among others. Thus, this review aims to describe the development of different polymeric composites using natural and synthetic matrices and applying renewable keratin reinforcements obtained from different natural sources.

### 1.2 Keratin

Keratin is present in almost all animals that have a backbone; this protein is the product of the keratinization process, which occurs because the skin cells die and accumulate in the surface layer. This protein can be considered as soft or hard, according to the diverse mechanism of biosynthesis (Meyers et al., 2008). Mammals have diverse tissues
formed by hard keratin (skin, hair, wool, nail, claw, quill, horn, hoof and whale baleen),
all of which are sophisticated epidermal appendages, differentiated not only by their
external morphology and physical properties but also in their amino acid composi-
tions, especially the content of amino acids like cysteine and tyrosine (Meyers et al.,
2008; Gillespie & Frenkel, 1974). Generally, the keratin class of proteins is mechanically
strong, designed to be unreactive and resistant to most forms of stress encountered
by animals (Whitford, 2005). There are 30 different variants of keratin in mammals;
these have been identified according to cells in a tissue-specific manner. In spite of the
basic unit of keratin being an α helix, this structure is slightly distorted as a result of
interactions with a second helix that leads to the formation of a left handed coiled-coil.
Commonly, the arrangement for keratin is a coiled-coil of two α helices, although three
helical stranded arrangements are known for extracellular protein domains, whereas
those in bugs have been found as four-stranded coiled coils (Whitford, 2005).

There are two major groups of keratin that can be identified: α- and β-keratin, depend-
ing on keratin’s molecular structure (Meyers et al., 2008). Hard α-keratin is a hierarchi-
cally ordered material, with a fibrillar organization from the micrometer to the nanometer
scale. In addition, α-keratin is rich in cysteine residues that form disulfide bonds linking
adjacent polypeptide chains (Kreplak et al., 2004; Whitford, 2005). α-keratin is found
in skin, hoof, baleen and wool, whereas β-keratin is found in feather, beaks, claw and
silk fibroin structures (Meyers et al., 2008; Whitford, 2005). The term “soft” or “hard”
refers to the sulfur content of keratins, but also originates from the keratins’ biosynthesis
process, which is related to their mechanical properties. In fact sulfur presence is due to
cysteine amino acid, hard keratin has high content of this amino acid and it is resistant
to deformation. Hard keratin is found in nails and hair, whereas a low content of cysteine
residues induces keratin with less mechanical resistance to stress (Whitford, 2005).

Keratin assembles in its primary structure around 18 different amino acids; these
form polypeptide chains by condensation reactions. These biopolymer chains have
molecular weights in the range from 59,000 to 65,000 (Mercer, 1961). Amino acids per-
form as monomers to construct the biopolymer, in this sense the polypeptide chain is
assembled by 16% of serine, 12% of proline, 11% of glycine, 9% of valine, 7% of cysteine,
and other amino acids comprise smaller percentages (Huda & Yang, 2008). Figure 1.1
shows a schematic representation of the main chain of keratin with the most abundant
amino acids. The amino acid content in keratins depends on diverse factors directly
related to the animals, the primary source of this protein, among these, breed, diet and
environment. Despite of the diversity in composition, a common arrangement can be
observed, since keratin contains a two-phase structure involving nanometric filaments
embedded in diverse quantities of filamentous matrix. One of the most important
amino acids in keratin is cysteine, due to stabilize the structure through disulphide
cross-linkages. If these bonds are disrupted around 90% of the keratinous tissues can be
extracted and easily separated into three types of proteins with different composition:
a low sulphur protein, which originates in the filaments and is partly α-helical, a high
sulphur protein, which is rich in cysteine, and finally the high tyrosine protein; the last
two kinds are identifiable from matrix (Gillespie & Frenkel, 1974). The high content of
cysteine causes stability in the protein, because the α-amino group and α-carbonyl are
useful functional links capable to weave a network between the nearby structures of
polypeptides (Schmidt, 1998; Martinez-Hernandez et al., 2005a).
Keratin is a fibrillar protein, a product of the keratinization process, which generates a highly structured protein with arrangement in different levels. The primary structure is constituted by the assembly of amino acids forming the polypeptide chain; this is folded upon itself, acquiring three dimensions and forming the called secondary structure, which represents its molecular structure ($\alpha$-keratin and $\beta$-keratin). The first one could be arranged as a spiral, known as protein $\alpha$-helix. The shape of this structure is maintained by hydrogen bonding and hydrophobic forces that hold together the amino acids of protein, which gives that special characteristic hardness. The $\alpha$-keratin is also called mammalian keratin, and the $\beta$-keratin is found in avian and reptilian keratin. However, it is possible to find the two types of keratin in the same tissues, for example, the hair has $\alpha$-keratin based on fiber cortex and $\beta$-keratin based cuticle (Hill et al., 2010). The main difference between both kinds of keratins is basically the intermediate filament (IF). The $\alpha$-keratin has an IF arranged as an $\alpha$-helix folding pattern with diameter of 8 nm, while $\beta$-keratin is based on a folding pattern $\beta$-sheet and its diameter is 4 nm. Although there are fundamental differences, both molecular structures have similar mechanical behavior and are linear elastic. In fact these two structures could be rearranged according to the environment needs, for instance during mechanical stretching the $\alpha$-keratin structure changes into $\beta$-keratin (Meyers et al., 2008). Figure 1.2 represents both kinds of molecular structures of keratin. Other general features of keratin are important in materials field, since because of hierarchical and stable structure, this protein is characterized by durability, non-soluble in organic solvents, chemically non-reactive and flexible. In addition keratin is able to recover its original mechanical properties, after repeated deformations and only with minimal loss (Martinez-Hernandez et al., 2005a).

Keratin is a main protein component in many external appendages in different animal species. Thus, natural different keratinous materials can be divided according to their function (McKittrick et al., 2012), for example:

a. Protection and/or covering: skin, hair and wool, quills, spines and pangolin armor
b. Defense and/or aggression: Horns, claws, nails, beaks, teeth, hagfish slime

c. Motion: hooves and feathers

In the next sections four of these types of keratin, feathers, hair and wool, and horns will be described briefly in order to understand their structure and most important characteristics.

1.2.1 Feathers

Feathers are about 90% protein, mostly β-keratin (Stettenheim, 2000). Feathers are non-homogeneous arrangements distributed in almost all living birds’ bodies. Feathers are used in a diversity of functions and are enormously variable in structure and color (Norell & Xu, 2005). Feathers are probably one of the most complex appendages that have evolved since the dinosaur era (Martinez-Hernandez & Velasco-Santos, 2011; Bartels, 2003).

The evolution of feathers has not been resolved completely because there is no morphological history of its origin. The first recorded history structurally corresponds to modern feathers of Archaeopteryx. Xu et al., have studied in depth some important discoveries of fossilized feathers, and they argued that primitive feathers had their beginning in certain filamentous integumental appendages observed on some theropod dinosaurs. However, there is not an exact homology between these primary structures and feathers, resulting in the theory that two taxa with true feathers (Caudipteryx and Protarchaeopteryx) have been proposed to be flightless birds (Xu et al., 2001). They observed the filamentous primitive feather of the basal dromaeosaurid dinosaur Sinornithosaurus milenii, and indicated those appendages were constituted by complex structures formed by multiple filaments, which exhibit two types of branching arrangement. These are distinctive in avian feathers. The first structure is based on filaments joined in a basal tuft, and the other configuration involves filaments joined at their bases in series along a central filament. These observations are useful to conclude
that integumental appendages of *Sinornithosaurus* and avian feathers can be considered structurally homologous (Xu et al., 2001). In contrast, the question about the evolutionary cause of avian flight is tangled due to first birds (i.e., feathered vertebrates) may not necessarily have had the capability for flight, because primitive feathers were improbable to have been specialized flight appendages (Maderson & Homberger, 2000).

Research has reported a classification of feathers on living birds: contour, down, semiplumes, filoplumes, powder-down and bristles (see Figure 1.3). Contour feathers are the most familiar kind. They cover most of the bird’s body as well as the bird’s integumentary flight surfaces. Contour feathers comprise hollow tubes, called the calamus proximally and the rachis distally. Barbs are branches growing from the rachis or calamus (Norell & Xu, 2005).

Feathers from chicken (*Gallus gallus*) are complex hierarchical arrangements of a three level branched structure. A feather is structured by a central shaft, which is inserted in a follicle by an initial segment called calamus or quill. This is a short, tubular basal segment. The next part is called rachis, and this is a much longer, pith-filled section. Quill or calamus is cylindrical, transparent, and hollow. Barbs grow up from shaft or rachis, this last one is compacted on the sides in order to support the growing of barbs and is roughly rectangular in cross-section, which is the main difference with respect to quill. Internally it is packed with a succinct material containing air cells. The branches (barbs) grow up sideways the rachis; these constitute structures in the shape of sheets or vanes, although some feathers also have series of lateral barbs growing from the upper end of the quill. The barbs (so called rami) originate from flattened sides of rachis and grow in parallel ordered rows opposing one another and directing outward and toward the tip of the feather. Barbs morphology is characterized by a slight ovoid cross-section, broader near their origin in the rachis, but flattening and narrowing close the tip. In similar way to rachis, barbs are also filled with a kind of light material containing air cells. A feather may have only a couple of dozen barbs or several hundred.

![Figure 1.3](image)

*Figure 1.3* Different types of feathers and most significant parts of their hierarchical structure.