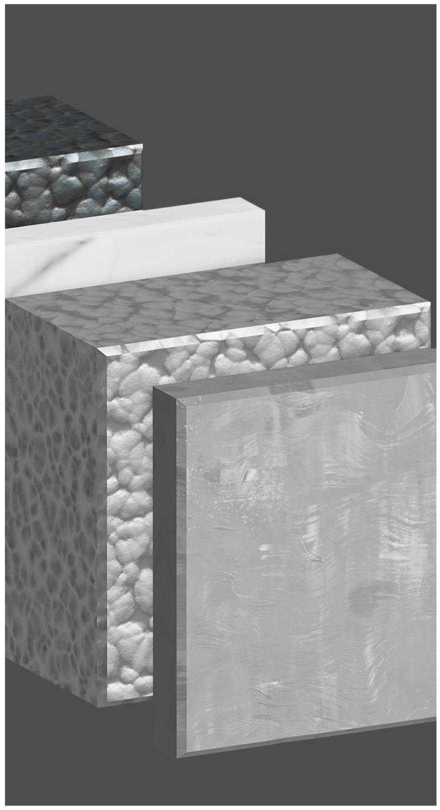
BIOCARBON POLYMER COMPOSITES



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Bentham Books

Biocarbon Polymer Composites

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ISBN (Online): 978-981-5196-68-9

ISBN (Print): 978-981-5196-69-6

ISBN (Paperback): 978-981-5196-70-2

First published in 2023.

CONTENTS

PREFACE

The editors are pleased and excited to present the book titled ***Biocarbon Polymer Composites***. The title of the book reflects the authors' awareness of the significance of biocarbon-based composites in the modern industrial and manufacturing fields, as well as their desire to introduce readers to one of the most unique classes of materials.

The 21st century has seen an increasing global demand for materials that are sustainable, ecofriendly, and biodegradable. The growing concerns about the environmental impact of plastic waste have spurred research and development of alternative materials, such as biocarbon polymer composites. Dr. Jane Goodall, the internationally acclaimed environmentalist said that *Biocarbon polymer composites have the potential to revolutionize the way we manufacture products, by providing an environmentally friendly alternative to traditional plastics*. As said, one of the remarkable features of biocarbon polymer composites is that they have the potential to reduce our dependence on non-renewable resources, mitigate the environmental impact of plastic waste, and create new economic opportunities for rural communities. Biocarbon polymer composites are an exciting new option as we seek out greener alternatives to petroleum-based plastics.

The book is organized into three sections and has nine chapters in total. The three sections Section I - State of the Art, Section II is the Sources of biocarbon and preparation of polymer composites, and Section III is the Properties and Applications of biocarbon polymer composites. Section I includes Chapters 1 and 2, Section II contains Chapter 3, and Section III contains Chapters 4 through 9. Chapter 1 introduces the use of bio nanocarbon to enhance fiber-reinforced nano biocomposites, addressing challenges in composite properties. It covers biocarbon nanoparticle synthesis and their integration into polymeric composites, with a focus on bio-inspired structures. Chapter 2 explores the circular economy and biochar production from waste, emphasizing its potential as a filler for polymer matrices. Section II, Chapter 3, discusses the use of animal waste-derived biochar in polymer nanocomposites, highlighting improved mechanical and thermal properties. Chapter 4 in Section III delves into biochar's application in thermal energy storage materials. Chapter 5 explores biocarbon extraction from various natural waste sources for 3D printing. Chapter 6 investigates rice husk ash as a sustainable filler for biocomposites, analyzing its impact on tensile properties. Chapter 7 discusses biochar-based nanocomposites and their enhanced electrochemical properties, particularly in agriculture. Chapter 8 focuses on synthesizing high-quality graphitic carbon from coconut shell powder for LDPE composite films with improved properties. Lastly, Chapter 9 emphasizes the environmental importance of polymer nanocomposites and biocarbon-reinforced composites in pollution remediation and sustainability efforts.

The main aim of this book is to offer a thorough introduction to biocarbon polymer composites, including the most recent research and practical applications of this material. This book brings together contributions from prominent researchers, engineers, and industry professionals in the field of biocarbon polymer composites. The chapters are structured to provide a clear and concise understanding of biocarbon-based composites' fundamental concepts and practical applications. This book is a must-read for anyone interested in the science of these materials and their prospective uses.

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ACKNOWLEDGEMENT

First and foremost, we would like to express our sincere gratitude to God, the almighty, with whose grace that we are able to complete this book. His blessings have given us the strength and perseverance to pursue our passion and bring this project to fruition. We are also deeply grateful to our parents and families for their unwavering support and encouragement throughout this journey. Their patience, understanding, and love have been constant source of inspiration and motivation. Their belief in us and our work kept us motivated and helped us overcome any obstacles that came our way. We are deeply indebted to our friends for their insightful feedback, constructive criticism, and stimulating discussions. Their contributions have helped shape the ideas and refine the writing, and we are truly grateful for their friendship and camaraderie. We would also like to extend our thanks to all the contributing authors who helped make this book possible. Their expertise and knowledge have greatly enriched this work, and we are grateful for their contribution.

We extend our heartfelt gratitude to the contributing authors, reviewers, editors, advisory board members and the team of Bentham Books for their invaluable guidance and support throughout the writing process. We are immensely grateful for their contributions and for believing in our vision for this project. We would like to express our sincere appreciation to everyone who has played a role in making this book a reality, from those who provided encouragement and support throughout the writing process to those who provided technical assistance in formatting and publishing. Your help has been essential, and we are truly grateful for your contributions.

Finally, our heartfelt thanks to all the students, researchers, and professionals who will read this book. We hope that this book will be an invaluable resource and inspire and inform the next generation of scientists and engineers who will shape the future of materials science. We believe that these materials represent a crucial step forward in the development of sustainable and eco-friendly alternatives to standard plastics, and we are delighted to contribute to this important and timely topic with this book.

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CHAPTER 1

Synergistic Effect of Bio-Nanocarbon Embedded Polymer Nanocomposite and its Applications

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Abstract: For applications involving sustainable materials, bio-nanocarbon was examined as a material to improve the properties of fiber-reinforced nano-biocomposite. A thorough investigation has been conducted using nano biocarbon as a filler and reinforcing material. However, the composite's inferior mechanical, physical, and thermal properties are a result of a poor fiber-matrix interface. As a result, in this study, biocarbon nanoparticles were created and used as functional components to enhance the properties of polymeric composite materials. To emphasize the scientific and technological issues that need to be resolved in order to create artificial composites with bio-inspired structures, recent studies of bio-inspired nano-carbon composites are discussed in this study. These include the production techniques for resolving the nano-carbon dispersion problem and creating bio-inspired structures, as well as the microstructure and composite characteristics characterization. In order to reveal natural design principles and serve as a resource for future research, bio-inspired composites and their applications are thoroughly examined and explained.

Keywords: Biocarbon, biochar, nano-biocomposite, nano-carbon, microstructure.

1. INTRODUCTION

Carbon is one of the periodic table's most versatile elements, having unrivaled qualities [1]. The atomic organization and hybridization of carbon determine its properties as an insulator (diamond) or a semiconductor (stacked graphite) or, amorphous carbon in a high-floor location. The ability of carbon to catenate opens the door for expanding the various fields of science such as chemistry, physics,

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Deepa Kodali & Vijaya Rangari (Eds.)

and biology to facilitate people's lives. Carbon nanostructures, including activated carbon (AC), carbon nanotubes (CNT), graphite, fullerene, carbon quantum dots, *etc*., are low dimensional allotropes of carbon emerging as bright spots in the domains of science and technology. Carbon allotropes are the primary building blocks of biological life. Carbon is used by nature together with other elements to generate a variety of species and offers sustainable ways to change matter and energy. These carbon-based resources, or biomass, have been used as renewable starting materials for the controlled manufacture of carbon compounds, which might minimize the usage of fossil-based fuels and hasten the sustainable growth of human society. Carbon is found in all living organisms, including plants, animals, and humans. So, nature is the best source for deriving carbon from agricultural waste, forest, and household waste. Synthesizing carbon nanomaterials from biomass is cost-effective and environmentally friendly. Many studies have been conducted to transform carbon from bio-resources to nanomaterials for diverse uses. Sugarcane bagasse, bamboo, paper pulp sludge, fruit and vegetable peels, rice husk, oil seeds, coconut shells, and other bioresources have been used as carbon precursors. Lignocellulose in biomass is the primary precursor for synthesizing biocarbon nanomaterials [2]. Biomass can be either lignocellulosic or non-lignocellulosic depending on the composition. Most biomass is lignocellulosic. Cellulose, hemicellulose, and lignin are the three distinct constituents of non-edible biomass generated from agriculture and forest wastes. Carbonaceous materials can also be made from non-lignocellulosic biomass including fruit, animal, and food waste, which is high in carbohydrates, polysaccharides, and protein. It is important to note that the heterogeneous chemical components and structure of biomass make the production of homogenous and controlled carbonaceous materials challenging [3]. The BCMs (Biocarbon materials) made from plant- and animal-derived biomass often had some noticeable variations, particularly in their structural and chemical make-ups. For instance, doping-free wood-based BCMs mostly include C and O and may readily maintain the original biomass structures. The crucial step in synthesizing BCMs with the necessary shapes and morphologies is selecting the appropriate biomass precursors. The majority of biomass resources are made up of complex compounds, and these molecules often have various pyrolysis pathways [4]. BCM topologies and architectures are important factors in determining applications. It depends on whether the BCMs have inherited the original macro- or micro-structures of the biomass. Numerous compounds found in biomass vary in kind and amount from one species to another, and as a result, have unique breakdown pathways. In general, when plant biomass is transformed into BCMs *via* an hydrothermal carbonization method, the original structure may be preserved since it comprises more crystalline cellulose and less hemicellulose. The majority of chitin biomass may be immediately pyrolyzed into BCMs. Proteins have been routinely employed to create BCMs that include nitrogen since they are necessary for all living things. The ultimate architectures and characteristics of the BCMs can be influenced by a variety of circumstances [5].

Thermochemical conversion of biomass resulted in the production of biochar and carbon fibers initially. Later on, the possibility of synthesizing carbon nanomaterials from biomass expanded the world of biomass as nanocarbon precursors. CNT, fullerene, quantum dots, graphite and graphene, and carbon nanosphere are also prepared from biomass precursors [5]. Biomass feedstocks go through a sequence of simultaneous events during pyrolysis, including dehydration, decarboxylation, aromatization, and recondensation.

The surface morphology and porous nature of carbon materials were investigated using FE-SEM images (Fig. **1**). The formation of thick and large-sized carbon particles with a smooth surface could be seen in the images. This clearly confirms that the carbonization process at different temperatures from 600 to 800 ^{o}C in an Ar or N_2 atmosphere could convert the dried biowaste into a valuable carbon product. However, all raw samples were characterized by a dense structure. After the pyrolysis processes, the pores were created. In case of bio-chars from wheat straw, a small amount of pores was observed on the surface. Their amount was increased with increasing the process temperature, but the pores were very small. The SEM images of the all obtained activated carbons show more porous structures. For all samples, the structure was crashed, but the micropores are visible.

Usually, to make porous carbon nanomaterials, templated-assisted synthesis is used. Anuj *et al*. reported that carbon nanosphere derived from oil palm biomass precursors has silica content which helps the material to become porous during pyrolysis. Plants absorb silicon from the soil as $Si(OH)_4$ or $Si(OH)_3O$-, which is then used to produce silica to incorporate into their epidermis and cell walls [7]. Biomass with higher lignin concentrations (grape seeds, cherry stones) produces carbon nanomaterial (CM) with a macroporous structure. In contrast, raw materials with a higher cellulose content (apricot stones, almond shells) produce CMs with a primarily microporous structure [8]. These pores serve different functions [9], with macropores acting as ion reservoirs for micro and mesopores, mesopores providing appropriate channels for the transport of ions during the diffusion process, and micropores acting as molecular sieves that regulate ion diffusion to control the material's capacitance and charge status. Different applications can benefit from these behaviors of porous materials. Physical and chemical treatments are used to decrease particle size and eliminate pollutants from biomass precursors. Powerful acid hydrolysis using HNO_3, H_2SO_4, and HCl is used for chemical treatment, although these strong acids must be neutralized.

CHAPTER 2

Biochar-thermoplastic Polymer Composites: Recent Advances and Perspectives

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Abstract: To fulfill the current circular economy concept, several attempts to reuse and valorize wastes and by-products coming from different sectors (such as the agri-food, textile, and packaging industries, among others) are being carried out at least at a lab scale by academics, despite the increasing interest that also involves the industrial world. One of the up-to-date strategies to transform wastes and by-products into new added-value systems refers to the production of biochar (BC), a carbonaceous solid residue derived from the thermo-chemical conversion, under controlled conditions, of wastes or, more generally, biomasses. Apart from its conventional uses (such as for soil remediation, heat and power production, low-cost carbon sequestration, and as a natural adsorbent, among others), BC is gaining a continuously increasing interest as a multifunctional micro-filler for different thermoplastic and thermosetting polymer matrices. Undoubtedly, the wide possibility of producing BC from different biomass sources, wastes, and by-products offers an attractive prospect toward a circular bio-economy with "zero waste". When incorporated into a polymer at different loadings, BC can provide thermal and electrical conductivity, EMI shielding features, enhanced mechanical properties, and flame retardance as well. This chapter aims to summarize the current achievements in the design, preparation, and characterization of thermoplastic polymer/biochar composites, discussing the current limitations/ drawbacks, and providing the reader with some perspectives for the future.

Keywords: Biochar, Degree of Graphitization, Electrical Conductivity, EMI Shielding, Flame Retardance, Mechanical Behavior, Thermoplastic-biochar Composites, Thermal Conductivity.

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1. INTRODUCTION

Nowadays, both environmental protection and the increasing depletion of fossil resources (crude oil, carbon, and natural gas) are stimulating not only academic research but also the industrial world toward the design and development of sustainable manufacturing strategies [1, 2]. In particular, the current research trends indicate a huge interest in the valorization of low environmental impact products derived from renewable wastes and biomasses for different uses [3] For an effective exploitation, these products should satisfy different requirements: in particular, they should exhibit acceptable performances for the envisaged applications, highlighting their suitability, as sustainable materials, for replacing fossil-derived counterparts. In addition, they should exhibit a certain “flexibility” of use, *i.e.*, providing either multifunctional features or being exploitable for diverse application sectors [4].

In this perspective, particular attention is currently being paid to biochar (BC), a renewable carbonaceous product that can be obtained through the thermo-chemical conversion, under controlled conditions, of different wastes, by-products, and biomasses. Generally speaking, BC is a micron-sized filler that shows a porous structure with an extended surface area and high thermal stability, notwithstanding acceptable thermal and electrical conductivities [5 - 8]. Thanks to its high porosity, biochar has been extensively exploited for filtration purposes, remediation of pollutants [9], and even as an antimicrobial product, taking advantage of the possibility of tuning its final properties based on the feedstock and the conditions adopted for its production [10 - 14]. More specifically, the graphitization degree achieved during BC production is strictly related to the composition of the pristine wastes, by-products, and biomasses, as well as to the adopted pyrolysis temperatures and residence times. Usually, increasing these two parameters accounts for an increased graphitization degree, determining, at the same time, a lowering of the hydrogen and oxygen content [15]. Conversely, when pyrolysis is performed at low temperatures, some volatile residues can be entrapped in the pores, hence decreasing the porosity of the final material [16]. Although its conventional uses in the agriculture sector (namely as a nutrient source, for soil conditioning and for remediation and absorption of contaminants, among others [17, 18]), in the last decade, biochar started to be employed as an electrode material in the design of supercapacitors [19, 20], as a catalyst in the processing of syngas [21], and as an anode for fuel cells [22]. Because of its peculiar features, the ease of tailoring its structure and morphology, and the wide functionality that can be provided, biochar is also currently being exploited for replacing conventional carbon-based materials in the design and manufacturing of polymer composites exhibiting improved thermal, mechanical, and electrical features [23 - 25]. The scientific interest in BC is remarkably rising, as witnessed by the increasing number of articles that appeared in scientific journals (Fig. **1**).

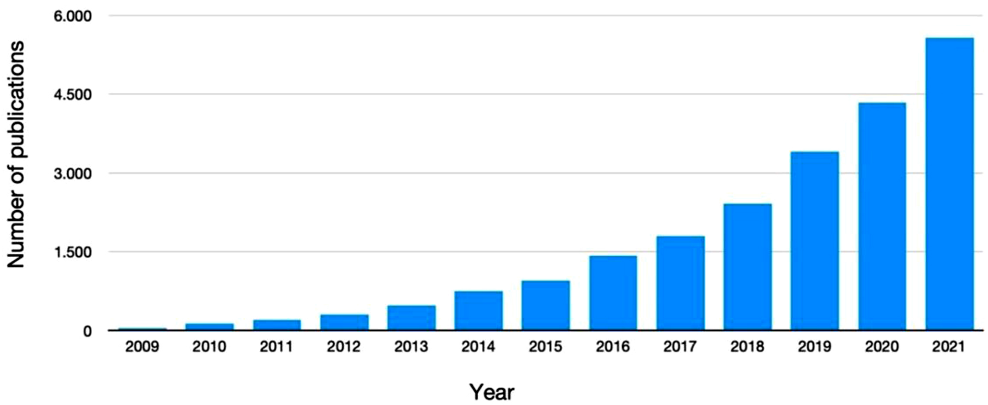

Fig. (1). Number of publications dealing with biochar from 2009 to 2021. (Source: Web of ScienceTM, accessed on 2 December 2022).

In this view, the present chapter reviews the latest progress in the design, preparation, and characterization of thermoplastic polymer composites containing biochar, highlighting the structure-property-production relationships established based on biochar structure, morphology, composition, loading, and possible functionalization. The current limitations are also discussed, providing the reader with some perspectives for the future development of these composite materials.

2. SYNTHESIS OF BIOCHAR (BC)

As mentioned in the previous paragraph, biochar is obtained by thermally treating (*i.e.*, pyrolyzing) biomasses in an O_2-free (or O_2-limited) environment; usually, the thermal treatment is carried out above 350°C for different times. It is possible to process different biomasses/wastes/by-products, such as wood, food wastes, plant residues, industrial biowastes, and animal carcasses, among others [26]. The chemical treatment generally preserves a significant part of the carbon of the biomass (*i.e.*, about one-third), leading to the formation of non-condensable gases and biofuel (*i.e.*, combustible bio-oil) as well [27, 28]. Besides, thanks to the pyrolysis process and the related structural changes, the porosity and surface area of BC significantly increase compared with that of the pristine biomass [29].

The pyrolysis takes place according to three step-wise reactions [30]: first, moisture is removed, then lignocellulosic components of the biomass undergo depolymerization and fragmentation processes, during which bonded water and

CHAPTER 3

Animal-Based Biochar Reinforced Polymer Composites

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Abstract: Biomass-derived waste management has become an increasingly pressing concern due to rising levels of environmental issues. As a result, interest has risen in finding ways to turn biomass wastes into useful products. The conversion of biowaste into biochar is one of the efficient and environmentally friendly methods of disposing of biowaste. Developing polymer composites by reinforcing biochar as the filler material is gaining popularity due to their affordability and exceptional thermal and mechanical properties. Animal waste is one of the biomass wastes that can be converted into biochar and can be used in various applications. This review work aimed at synthesizing biochar from animal wastes, preparing polymer composites, and analyzing the thermo-mechanical properties. This review also focuses on various animal feedstocks for the synthesis of biocarbon and methods to fabricate polymer composites. The biocarbon-induced polymer composites showed an improvement in mechanical and thermal properties with varying percentages of loading.

Keywords: Animal Waste, Biochar, Polymer Nanocomposite, Pyrolysis.

1. INTRODUCTION

With the world's population expanding, the demand for goods, energy, and food is always increasing. Humans need a lot of resources for their survival, producing millions of tons of waste, which has a negative influence on our ecosystem [1]. It is predicted that by 2050, worldwide production of municipal solid garbage will increase to 3.4 billion metric tonnes, representing an increase of almost 70%. There are no signs that the tremendous rise in waste production that has occurred

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Deepa Kodali & Vijaya Rangari (Eds.)

in recent decades will abate. Dealing with this expanding volume of biowaste poses one of the greatest challenges to the sustainability of human civilization. Consequently, it is essential that biowaste should be disposed of efficiently and sustainably [2]. The conversion of biowaste into biocarbon is one of the efficient and environmentally friendly methods of disposing of biowaste that fascinates researchers and enterprises. Biocarbon, also known as biochar is a porous solid, with high carbon content, formed by biomass thermal decomposition in a reactor with little or no availability of air. In view of the rapid depletion of non-renewable resources and the increase of greenhouse effects, biochar became an undeniable resource to substitute fossil fuels and thus tailor the needs by serving as a filler in the polymer matrix. Owing to its affordability, extensive availability, and eco-friendliness, biocarbon prepared from inexpensive, abundant, and eco-friendly resources is gaining popularity in a wide variety of emerging industries including agriculture, environment, energy storage, biomedical, drug delivery, structural, materials and filtration [3]. Any affordable substance that contains a high carbon content and minimal inorganic matter can be utilized as a feedstock for producing biochar [4]. The biocarbon synthesized from biowaste makes it viable for the reinforcement of bio-based fillers with synthetic as well as natural polymers.

The polymer composite consists of a polymer as the matrix phase and the fibre or particles as the reinforcement phase. The particles can be macro/micro/nano size. Polymer composites are popular due to their low density, high specific strength, high specific stiffness, effortless fabrication, and cost-effectiveness. Reinforced polymers, which offer better properties than pure polymers, have attracted a lot more attention in recent years. A polymer nanocomposite is a composite material consisting of polymers of thermoplastics, thermosets, or elastomers reinforced with nanoparticles of sizes less than 100nm diameter with aspect ratios greater than 300 [5]. It is a multiphase solid material in which one of the phases has one, two or three-dimensions nanofillers. Nanoparticles have a remarkably high surface-to-volume ratio which significantly alters the inherent properties of a polymer when compared with their bulk-sized reinforcement [6]. Nowadays, nano-sized carbonaceous fillers including carbon nanotubes (CNTs), graphene, carbon nanospheres (CNSs), *etc.* are being used to fortify a wide range of polymer composites, with the goal of enhancing their mechanical and functional qualities [7]. However, these carbon nano fillers' extensive application has been severely hampered by their high manufacturing costs, limited production volumes, the need for modern instruments for synthesis, and environmentally hazardous preparation techniques [8]. As a result, there is a growing demand for nanostructured carbons made from inexpensive, plentiful, and environmentally friendly materials including vegetable biomass and agricultural waste, animal waste, and by-products. Nano-structured carbons are synthesized by thermal decomposition of biowaste. A lot of research is going on polymer nanocomposites reinforcing biocarbon derived from vegetable biomass and agriculture waste. Relatively limited research has been done on polymer nanocomposite reinforcing biocarbon derived from animal waste. Hence, this review focuses on the polymer composites reinforced with animal-based biochar of micro/macro/nano size.

2. OVERVIEW OF CARBON

Carbon is one of the exciting elements, with the ability to form a vast array of configurations that often exhibit a wide variety of properties [9]. The varieties of configurations are possible due to the covalent bonds with other carbon atoms and also with metallic or non-metallic elements in different hybridization states (sp, sp2, or sp3). Carbon materials are categorized based on carbon-carbon bonds of the hybrid orbitals of sp3, planar sp2 $+\pi$, curved sp2 $+\pi$ p, and sp $+2\pi$ [10]. Diamond, graphite, fullerenes, and carbynes are allotropes of carbon that primarily include either of these hybrid orbitals. Diamond is important for its carbon-containing sp3 hybridization. Graphite with its sp2 hybridization and layered graphene sheets has been identified as having the softest interior nature of all known materials. Also, graphite is an excellent conductor of heat, an opaque material, a good lubricant, and a good conductor of energy. In addition to diamond and graphite, other carbon allotropes include Buck balls (fullerenes), amorphous carbon, glassy carbon, carbon nanofoam, and carbon nanotubes. Carbonaceous materials are favoured and are one of the most sought-after materials due to their versatile nanostructure, outstanding mechanical, electrochemical, thermal, chemical stability, and electrical characteristics. Due to its diverse dimensionality (0 to 3D), it is a functional material that meets a variety of requirements for various applications. It can be obtained in various forms including powders, fibres, composites, tubes, felts, mats, monoliths, and foils [11]. Because of its exceptional characteristics, it is an appealing candidate for use in a wide range of applications, some of which are found in the fields of electronics, electrochemistry and sensing, energy, biomedicine, aerospace, automobiles, and the environment [12]. The high cost of manufacture and the material's reliance on fossil fuels pose the greatest barrier to the widespread use of carbon-based materials. Due to these reasons, researchers have recently become interested in eco-friendly carbon materials made from renewable resources that can be mass-produced. Biocarbon, also known as biochar, has gained widespread attention as a new sustainable material for a variety of commercial applications [13]. Biocarbon made from renewable resources is becoming increasingly popular because it avoids the environmental consequences associated with unreplenishable sources of carbon, like fossil fuels, coal, oil, and gas, in addition to being extremely cost-effective [1].

CHAPTER 4

Harnessing Agro-based Biomass for Sustainable Thermal Energy Storage with Biochar Polymer Nanocomposites

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Abstract: Food loss due to wastage is a severe issue for the entire world. Wastage accounts for up to one-third of lost food output globally. Although there are various ways to turn food waste into useful functional materials, landfilling is still a frequent practice. This results in greenhouse gas emissions, which increase the already significant greenhouse gas emissions linked to the agriculture sector. In this review, we start by identifying multiple biomass sources and synthesis methods for biochar made from biomass. This contains methods for the characterization of phase change polymer nanocomposite materials impregnated with biochar. In order to compare the thermal properties of phase change materials and gain an understanding of the various biowastes, a comprehensive methodology was used.

Keywords: Biomass, Biochar, Composite Phase Change Materials, Energy Storage, Sustainability.

1. INTRODUCTION

Agricultural waste disposal continues to be a major socio-economic problem. As rapid urbanization and population growth continue to mount pressure on the manufacturing and agricultural industries to meet the demand, waste generation will accelerate. Agricultural waste, such as biomass residues, is an underutilized feedstock for synthesizing valuable products. More than 140 gigatons of biomass waste are produced globally every year [1], providing a considerable stream of feedstock material. Biomass disposal has a devastating effect on our environment.

Although the repercussions led by biomass disposal are alarming, this issue presents an opportunity to utilize this ample material as a potential feedstock.

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Deepa Kodali & Vijaya Rangari (Eds.)

Biomass is an abundant renewable resource, as the supply can be replenished over a short amount of time and is virtually limitless [2]. In the United States, roughly 386 million tons of biomass waste is generated annually. The agriculture industry remains a vital part of the US economy, providing 10.3% of the nation's employment and 5.2% of the country's overall GDP [1]. Biomass refers to any organic material that comes from living or recently living organisms. This can include plants, crops, trees, and agricultural and forestry residues, as well as waste from the food, paper, and biofuel industries. A good example of this is almond biomass, wherein, over the past several years, the demand for almond-based products has skyrocketed, resulting in over three billion pounds of almond biomass waste being produced annually. The global production of almonds has significantly grown from ≈0.7 million tons in 2007 to ≈1.5 million tons in 2019 [1], enabling the simultaneous accumulation of almond woody biomass, which can negatively impact the environment and economics of almond production. More importantly, when producing almond kernel for human consumption, the remaining almond hulls, shells, and woody biomass (*e.g.*, twigs and wood clippings) from the production process do not have much commercial value.

According to the International Nuts and Dried Fruits Statistical Yearbook, the USA is the largest producer of almonds, with over 700,000 hectares of land dedicated to almond production [2]. For instance, California alone produces 80% of the almonds used worldwide, and production is rising. Almonds are grown and processed by roughly 7600 people annually, yielding about 746,000 tons of shells. More specifically, the average production in California in 2019 included 1.03 million tons of kernels, 0.72 million tons of shells, and 2.06 million tons of hulls [3, 4]. On the other hand, walnut shells are useful for producing biochar due to their easily modifiable pore structure and volatile nature. Walnuts are a commonly produced nut, with China producing 1.06 million tons out of the 3.7 million tons produced globally in 2019. Moreover, the shells of walnuts account for 60% of the fruit's mass [5].

Historically, biomass waste has mostly been either burnt or disposed of due to mobility issues and, thus, the lack of adequate applications. While some biomass is repurposed into sources of energy or heat, the majority is disposed of in incinerators and landfills, accounting for 18% of total global emissions of CO_2 every year and resulting in deteriorated surface and groundwater quality [1]. These are often used as bedding for poultry. This leads to an increase in greenhouse gas emissions and other environmental pollution. Furthermore, almond woody biomass left in the field as mulch has been shown to cause reduced nitrogen availability, which could affect crop yields and productivity.

Thus, new, more environmentally friendly solutions are needed to minimize environmental hazards. One of the promising pathways of waste management is utilizing them in developing bio-based polymer composites, which are eco-friendly materials. Especially, biomass-derived biochar and their subsequent fabrication of phase change composite materials are interesting for thermal energy storage applications.

Hence, this book chapter reviews synthesizing biochar from different biomass feedstock, including almond and walnut shells. This includes techniques for biochar impregnation of phase change materials, and characterization. Finally, a holistic approach is undertaken to compare the thermal properties of phase change materials to gain insight into the diverse biowastes.

2. COMPOSITION

2.1. Almonds

The almond tree, one of the most popular nut-based trees for snack foods and ingredients in many processed foods, yields almonds. The International Nut and Dried Fruit Council (INC) reports that in 2017 and 2018, almost 1.2 million tons of almonds were produced. The United States leads the world in production with 81% of the total. With 7% and 4%, Australia and Spain are close behind, respectively.

The hull and shell enclosing the edible kernel are mechanically isolated to produce the almond biomass (Fig. **1**) during the hulling and shelling process [6]. Almond hulls, which make up 52% of the fresh fruit, have erratic ripening cycles that change depending on several growing conditions [7]. The intermediate shell, which accounts for around 33% of the total fresh weight, can house a variety of shapes and sizes with varying mechanical properties that are greatly influenced by environmental factors [6].

Fig. (1). Photograph of three different as-received almond woody biomass including hulls, shells and twigs.

CHAPTER 5

The Application of Biocarbon Polymer Nanocomposites as Filaments in the FDM Process – A Short Review

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Abstract: Fused Deposition Modeling (FDM) is a solid-based 3D printing process. It is one of the additive manufacturing technologies that is used to create a three-dimensional (3D) object using a CAD model. In the FDM process, raw material also known as filament, is initially in the solid state. Nowadays, biocarbon-incorporated polymer-based nanocomposite is used as a filament in the FDM process, due to the enhanced strength of the base polymer. In this paper, a review of carbon extracted from natural waste, such as tea powder, coffee grounds, egg shells, ocean plastic, coconut shells, *etc*., is presented The extraction procedure of biocarbon is given in detail. The results indicate that the strength enhancement of polymers can be achieved by incorporation of derived carbon from industry as well as agriculture waste. In addition, biocarbon-based polymer nanocomposite filaments in the FDM process can be developed by reinforcing the polymer matrix with carbon nanoparticles. Future work of this review process will explore the biobased carbon from various waste resources. The application of biocarbon-based polymer nanocomposites for the 3D printing process is highlighted.

Keywords: 3D Printing Process, Biocarbon Polymer Nanocomposite, FDM, Filament.

1. INTRODUCTION

The 3D printing process is one of the additive manufacturing technologies. It uses a CAD model and introduces it layer by layer to form a three-dimensional object. A CAD model is sliced into layers, generally called Standard Triangular Language (STL). It is classified into the liquid form, solid form, and powder form.

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Deepa Kodali & Vijaya Rangari (Eds.)

FDM is one of the solid-based 3D printing processes. FDM uses a filament, which is in a solid form. In FDM, the filament is heated in the nozzle, converted into a semi-liquid form, and finally squeezed out. This semi-liquid is deposited onto the platform of the machine and solidified. FDM utilizes a nozzle and moves in different directions, such as x, y, and z, and can be controlled numerically [1, 2].

The filament used in the FDM process is a thermoplastic feedstock. FDM filament involves feeding a spool of filament to the nozzle, in which filament gets heated, melted and forms a required shape on a platform through a controlled direction. Filaments are available in different sizes and colors. Each filament has significant advantages, properties, and limitations. Tensile strength, impact strength, and hardness are the important properties to be considered. Printing speed, adhesion, melting temperature, and ease of printing are some of the important process parameters in the 3D printing process. The selection of appropriate filament plays a significant role in the functional activities of printed specimens [3 - 5].

The use of polymer-based nanocomposites in 3D printing has recently garnered a great deal of interest. In polymer-based nanocomposites, synthetic and bio-based fillers are reinforced to enhance the strength of the base polymer [6, 7]. Bio-based fillers are obtained from various industrial as well as agricultural wastes. Some researchers have attempted to produce carbon from agricultural waste (spent coffee grounds, PET composite, waste coconut shells, ocean plastic, chicken feathers, and starch-based biochar) and industrial waste (from the packaging industry).

2. LITERATURE REVIEW

Mohammed *et al*. [8] derived carbon from chicken feathers and used it for 3D printing. In their work, synthetization was carried out to derive carbon from waste chicken feathers with the help of the pyrolysis process. Potassium hydroxide was used to activate the synthesized carbon. The results of the experimentation revealed that the derived carbon was successfully used in the 3D printing application of electrode preparation of a supercapacitor device. Idrees, *et al*. [9] developed a supercapacitor using the 3D printing process. In their investigation, an electrode was 3D printed with incorporated activated carbon which was synthesized from packaging waste. The results demonstrated that the 3D-printed electrode, with the inclusion of activated carbon, exhibited the ability to withstand high loads. Synthesized carbon from packaging industry waste was used to develop 3D-printed electrodes, thereby leading to enhanced sustainability. Mohammed *et al*. [10] investigated effective reinforcement fillers in polymer nanocomposites. They used carbon derived from starch-based packaging waste as a filler in polymer composites. High-quality biochar was synthesized from packaging waste using the pyrolysis process. The results revealed an improvement in surface area with fewer defects compared to the biochar obtained from natural biomass. 3D printed samples were subjected to mechanical tests and the experimental results showed enhanced strength. Shao *et al*. [11] developed a conductive structure using the 3D printing process. Pyrolysis was performed using lignocellulosic materials. The results indicated that carbon was characterized effectively and thus contributed to improved mechanical and electrical properties of the nanocomposites. Mohammed *et al*. [12] suggested that achieving uniform dispersion and better adhesion were crucial factors in the fabrication of polymer nanocomposites. In their study, surface property modification using low-temperature plasma treatment was performed on biocarbon, which was derived from starch-based packaging waste. The results showed that plasma-based surface treatment has effectively influenced the carbon surface and improved its mechanical strength. Idrees *et al*. [13] developed a polymer composite using consumer-grade Polyethylene terephthalate (PET) and packaging waste derived biocarbon for 3D printing applications. Pyrolysis was used to derive biocarbon from packaging waste. An experimental investigation of surface morphology, textural analysis, and thermal stability of 3D printed specimens was conducted. The results showed improved mechanical properties with the incorporated biocarbon-based polymer nanocomposite. A sustainability approach was attempted utilizing consumer waste for the 3D printing process. Alhelal *et al*. [14] used pyrolysis to derive semi-crystalline biochar from spent coffee grounds. This derived carbon was used as reinforcement in epoxy resin with a ratio of 1 wt. % to 3 wt. % for the direct wire 3D printing process. A mechanical performance analysis was carried out on the 3D printed samples, and the results indicated increased strength with 1 wt %. Also, the strength of 3 wt% reinforced specimen was less at higher loading due to agglomerations. Guptha *et al*. [15] investigated biocomposites developed from recycled consumer PET bottles and biocarbon derived from spent coffee grounds. The pyrolysis process was performed to extract the biocarbon from the spent coffee grounds. The results revealed the enhanced performance of developed biocarbon-based polymer nanocomposites due to better interfacial bonding and improved flexural strength. Thus the developed composite was successfully used in the filament preparation of the 3D printing process. García *et al*. [16] used a 3D printing process to develop a prototype using recycled ocean plastic material-based polymer composite. In their work, the issue of warpage related to the printing of recycled plastic material was discussed. One solution to mitigate this problem was to incorporate fillers into a reinforced blend. Pyrolyzed biocarbon was blended with ocean waste plastic, and filaments were made for 3D printing. Taguchi analyses were performed to execute the experiments. The results of the experiments showed improvement in the mechanical properties. Also, it was noticed that the products developed for 3D

CHAPTER 6

Tensile Characteristics of FDM 3D Printed PBAT/PLA/Carbonaceous Biocomposites

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Abstract: The use of carbonaceous fillers in polymeric biocomposite materials has been widely studied due to their potential to add better engineering properties to biocomposites and expand their field of applications. Currently, due to the growing global concerns over environmental pollution and climate change, carbonaceous fillers derived from biomass are the preferred choice for production of the sustainable biocomposite materials. Rice husk ash (RHA), an abundant and sustainable carbonaceous filler obtained from the burn of rice husk in kilns of the processing rice was incorporated into the PBAT/PLA blend. The influence of RHA loading on the tensile properties of FDM-3D printed samples was investigated. Neat PBAT/PLA filament and its biocomposite filaments with 2.5, 5.0 and 7.5 wt. % RHA were prepared by the extrusion process. The filaments were characterized by FTIR, TG, and SEM. FDM-3D printed specimens were subjected to tensile tests.

Keywords: 3D printing, Biocomposites, Carbonaceous Fillers, RHA, SEM, Tensile Properties.

1. INTRODUCTION

The use of carbonaceous fillers in polymeric biocomposite materials has garnered attention due to potential for enhanced engineering properties and their field of

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Deepa Kodali & Vijaya Rangari (Eds.)

applications. Besides simple processing, lightweight character, cost-effective, and superior mechanical reinforcement, carbonaceous fillers are also important fillers to impart heat dissipation properties, electrical and thermal conductivities [1,2]. Currently, the interest in the conversion of agricultural and forest waste biomass to carbonaceous fillers and their use in polymeric biocomposites has increased notably. The growing global concerns over environmental pollution aspects, climate change, and the necessity to conserve material resources, make these carbonaceous fillers a preferred choice for the production of advanced sustainable biocomposites with enhanced properties. They are considered eco-friendly carbon precursors, which are readily available, economically feasible, green, and renewable in nature. Furthermore, the conversion of biomass into carbonaceous fillers and its use in the production of advanced sustainable biocomposites can also contribute to solid waste management [3, 4].

The FDM 3D printing process, an additive manufacturing (AM) technique, finds applications in various industrial fields. This process enables the production of complex parts by depositing successive layers of thermoplastic material filament. FDM 3D printing processing has been used in many industrial sectors, such as aerospace, automotive, food, and medical. In the medical industry, this technology has been adopted to manufacture orthopedic devices as prostheses as well as other devices, bone tissue engineering, and the development of scaffolds with different porosity. Other segments like home appliances and creative gifts have also benefited from the 3D printing process. The increased interest in this technology is because of its easy use, simple operation, low cost, and facile production of complex geometries [5, 7].

The parameters for fused filament 3D printing are fundamental characteristics for deposition of materials. Some configurations allow for greater physical and mechanical resistance, beyond impacting the visual quality of prints while some parameters are notable for the efficient fluid functioning of 3D printing. The process of slicing 3D parts depends on the technical settings of the equipment [8]. 3D Printers have an extrusion assembly, located at its end, consisting of a temperature-controlled metal nozzle, allowing the material to be continuously melted for layer-by-layer deposition [6]. The nozzle has an orifice from which the polymer is expelled followed by the deposition on the bed. 3D printing machines were generally equipped with 0.4 mm thick nozzles, which is the most common configuration for 3D printing by FDM. Therefore, the printing wall thickness was set according to the original 3D printer nozzle configuration. Other alterations to the slicing process that are unrelated to the machine's physical architecture allow for a greater degree of control to be exercised over the prints that are produced [5]. Some of them are discussed below:

• **Layer height** is the relative measurement of the extrusion between layers. It is the height of each layer that is deposited to form the part. This measure directly influences speed, appearance physique, and endurance. Smaller measures include lower speed, better visual finish, and greater resistance.

• **The Walls** of a 3D object is represented by the part's outer fill. This is responsible for forming the physical and visual identity of the exterior of the piece. The walls influences the strength and quality of the object. Greater number of walls: better resistance and print quality.

• **Flow** is the parameter that defines the percentage of the amount of extrusion to be performed during printing. That is, according to the percentage, the printer deposits a greater or lesser amount of melted filament.

• **The infilling** is responsible for setting in a percentage of the amount of material deposited inside the part, *i.e.*, with 100% fill, parts are completely solid. In the slicing software, it is also possible to modify the filling angles. Commonly, for resistance tests, impressions are made with filling angles of 0°, 45° and 90°.

• **Printing temperatures** always vary as specified by the filament manufacturer. Poor temperature calibration can cause warping, filling, and printing problems. For some polymers, there is a need to use the table heating system, to ensure the adhesion of the material on its surface.

• **Speed** is an important parameter to have a close expectation regarding the time it takes to print any part. Therefore, the speed variation allows for reduction or increasing the printing time. The increase in speed can lead to reduced visual quality and increase the probability of errors during printing. This parameter is given in relation to distance (mm) per time (s).

Conventional thermoplastic materials like polycarbonate (PC), polyamide (PA), acrylonitrile butadiene styrene (ABS), ethylene vinyl acetate (EVA), and the biodegradable polylactic acid (PLA) are usually used to produce FDM 3D printing filaments. However, with the increasing attention to environmental issues, biopolymers such as PLA, and their biocomposites and blends became the preferred choice for FDM 3D printing filaments instead of petroleum-based ones due to their biodegradability and environmental friendliness [8 - 11].

Rice husk (RH) is removed during the industrial process of rice milling and polishing. A large part of this material is used as fuel in rice processing kilns, generating a significant amount of rice husk ash (RHA) as waste. Unfortunately, not all the amount of available rice husk is used as fuel, part of it is still discarded in landfills as waste, contributing to the increase in environmental pollution. RH

CHAPTER 7

Biochar-Based Polymer Composites: A Pathway to Enhanced Electrical Conductivity

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Abstract: In the past 20-25 years, biochar has been promoted as a valuable resource of a carbon filler in polymer composites, sustainable agriculture, and environmental quality protection given its improved porous structure and electrochemical properties in comparison to other carbon-based materials. Recent works focusing on biochar and biochar-based nanocomposites are highlighting such properties and are even enhanced with nanotechnology. The higher porosity attributed to biochar is highlighted along with its great electrochemical properties able to retain nutrients for longer and favors their slow release. The use of biochar as a filler material to improve the electrical conductivity properties of polymers and the emphasis on various parameters, such as pyrolysis temperature, the type of feedstock, and compaction pressures on the electrical conductivity of the resultant composites are discussed.

Keywords: Biochar, Electrical Conductivity, Polymer Composites, Percolation, Organic Conductors.

1. INTRODUCTION

Biochar (BC) is a charcoal-based material made from biomass, such as wood, crop residues, or other organic materials. It is produced by pyrolyzing (heating in the absence of oxygen) those materials [1, 2]. The pyrolysis process can be carried out in a variety of methods, including using a kiln, retort, or gasifier [3 - 5]. The pyrolysis temperature and duration, as well as the type of biomass used, can affect the properties of the resulting BC. Additionally, the production of BC has positive effects on the environment. It sequesters carbon from the atmosphere and stores it in the soil, reducing greenhouse gas emissions and improving soil health [6, 7].

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Deepa Kodali & Vijaya Rangari (Eds.)

Furthermore, it can also help with waste management [3, 8], as it can be produced from agricultural waste and other organic materials that would otherwise be discarded. Historically, BC has been recognized as a valuable product in agriculture since it contributes to crop yield enhancement, serves as an organic fertilizer, neutralizes soil pH, and supports media for microbial growth [9, 10]. In the soil, biochar was also found to reduce lime application because of its potential to neutralize the pH of acidic soils [11 - 13] and minimize the application of commercial fertilizers [14]. In addition to increasing the available levels of macronutrients such as nitrogen (N), phosphorus (P) and potassium (K), biochar addition also reduces the need for nitrogen (N) application, which in turn reduces N leaching to groundwater [15]. The role of biochar in increasing soil pH and soil organic carbon (SOC) storage, as well as improving cation exchange capacity (CEC) was also highlighted in the past literature [16].

Due to sustainable production methods and ease of production, researchers consider BC an alternative material filler material in polymers and ceramics [17 - 19]. Carbon-based filler materials such as Carbon nanotubes (CNTs), Graphene, and Carbon black are already established as filler materials in various materials to produce selectively engineered products. Products engineered for specific applications include conductive polymers, high conductive alloys, and reinforced alloys for special applications such as high corrosion resistance, high strength and temperature resistance in polymers, and others [20 - 23]. The carbon structure of biochar can be characterized by several parameters such as pore size, the intensity of pores, ash content, pH value, and others.

Among many special applications, materials with low electrical resistance have special attention among researchers in the fields of electronics and material science. The growing need for special sensors and flexible electronics created an opportunity to exploit suitable materials for organic conductors. Organic conductors are conductive polymers developed by embedding carbon fillers [24 - 27]. Carbon fillers such as CNTs and Graphene showed promising results, however, the cost of these fillers is relatively high compared to BC. The carbon structure of BC makes it an attractive candidate for use in polymer composites owing to its high electrical conductivity and thermal stability. BC can be added to polymers such as polyaniline (PANI), Polypropylene (PP), and Polyvinyl Alcohol (PVA) to enhance their electrical conductivity, which promotes the potential to be used in areas such as energy storage and electronic devices. However, additional research is necessary to fully clarify the potential of BC in this area and to develop practical and cost-effective methods for incorporating it into polymers. In addition, not all BCs are the same, different types of BCs will have different properties, and the specific application will determine which type of BC is the most appropriate. There are a multitude of factors that affect the properties of resulting BC, the type of production method, the type and condition of feedstock (biomass), the temperature of pyrolysis, and others [28, 29].

The electrical conductivity presented in biochar-filled polymers is significantly affected by the temperature of pyrolysis used during the biochar production. High-pyrolysis temperatures usually yield biochar with higher carbon content, which can result in higher electrical conductivity when used as a filler in polymers. This is because the carbon structure of biochar is highly porous, and the pores can act as pathways for electrical current to flow. Higher carbon content in the biochar will result in more pores and therefore more pathways for electrical current to flow, increasing conductivity. Additionally, at higher temperatures, the biochar structure will be more graphitized, meaning that the carbon atoms are more ordered and the electrical conductivity will be higher. On the other hand, low-pyrolysis temperatures tend to produce biochar with lower carbon content, which can result in lower electrical conductivity when used as a filler in polymers. It is worth noting that the electrical conductivity of biochar-filled polymers is also affected by the polymer type and the biochar loading in the polymer matrix. This paper discusses the mechanisms of electrical conductivity in polymers followed by experimental studies on the factors that affect electrical conductivity in biochar-filled polymer composites.

2. MECHANISMS OF ELECTRICAL CONDUCTIVITY IN POLYMER COMPOSITES

The theory of electrical conductivity in polymers is based on the idea that polymers are made up of long chains of repeating units called monomers, which are held together by covalent bonds. Monomer chains have various levels of structures and can be made up of complete amorphous to varied ranges of crystalline.

In general, electrical conductivity in polymers arises from the movement of charged particles such as electrons, holes, or ions within their matrix. The movement of these particles can be caused by several mechanisms [30 - 33], such as hopping, tunneling, and percolation as shown in Fig. (**1**).

CHAPTER 8

Coconut Shell Derived Carbon Reinforced Polymer Composite Films for Packaging Applications

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Abstract: With the advancement toward global sustainability, there is a widespread demand for sustainable materials that can be used for various applications. Carbon has gained much attention in the past few decades due to its scope of utilization in energy and environment related applications. Biomass resources are considered a prominent precursor for the synthesis of carbon-based materials due to their availability and economic viability. In this study, high-quality graphitic carbon is synthesized from Coconut Shell Powder (CSP) by pyrolysis and reinforced into a low-density polyethylene (LDPE) matrix for fabricating films for packaging applications. A custom-built high-temperature autogenic pressure reactor was used for conducting the pyrolysis to synthesize carbon from the coconut shell powder and a blown film extruder was used for fabricating composite films. For preparing the films, coconut shell powder-derived carbon was added to the LDPE matrix at various weight percent loadings of 0.25, 0.5, and 1 wt.%, respectively. Various analytical techniques such as scanning electron microscopy, X-ray diffraction, Raman spectroscopy, thermogravimetric analysis, tensile test, and differential scanning calorimetry were used for studying the properties of carbon and LDPE/carbon composite films. Upon adding carbon as fillers, there were significant improvements in the tensile and thermal degradation properties of the polymer carbon composite films. Upon the incorporation of carbon into the LDPE matrix, the crystallinity and tensile strength were found to improve by a maximum of 29% and 13%, respectively.

Keywords: Biochar, Blow Films, Coconut Shell Powder, Film Extrusion, Food Packaging, LDPE, Low-density polyethylene, Raman, SEM, XRD.

1. INTRODUCTION

The global demand for materials that are more sustainable, efficient, and economical is rising exponentially along with the population. Due to this, the

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Deepa Kodali & Vijaya Rangari (Eds.)

development of sustainable materials has become one of the most prominent needs of society. Carbon-based materials (CBM) are the most versatile materials used for energy and environmental applications [1, 2]. In earlier days, CBM with properties such as optimum surface area and porosity were widely synthesized from fossil-derived precursors using complex techniques such as the electric discharge method and chemical vapor deposition. The most popular synthetic route to prepare CBM with high-surface-area and porosity is the nano-casting approach but this also involves several limitations of being high cost and complicated. Therefore, the development of novel and improvised approaches that are easily scalable, economical, and efficient for the synthesis of CBM from renewable natural precursors is highly desired. Among the CBM synthesized from biomass, different forms of carbon such as carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, activated carbon, *etc*. have gained popularity [3 - 5].

There are widespread carbon-based natural resources created by nature, coupling carbon with other elements. Nowadays, these biomass renewable resources are being widely used as precursors for the synthesis of CBM and they aid in the sustainable development of human society. Some of the common precursors for obtaining CBM are plants [6 - 8], aquatic organisms [9, 10], and animals [11]. Several thermal methods are being used for the synthesis of CBM from biomass such as pyrolysis, hydrothermal carbonization, microwave irradiation, and laser processing. The properties of the CBM highly depend on the composition of the precursor [5].

1.1. Overview of Plant-derived Carbon-based Materials

Plant-based CBMs are commonly derived from plants and their byproducts which are lignocellulose rich materials. Plant-based biomass resources can be commonly classified into two categories which are woody and non-woody resources. Woody resources include materials composed mainly of lignin, cellulose, and hemicellulose whereas non-woody resources consist of materials that are composed of additional components such as lipids, proteins, sugar, starch, *etc* [12]. The carbon derived from bio-based resources is often known as biochar. Some of the common lignocellulose precursors for CBM are palm shells, wood birch, olive waste, wheat straw, hemp, coir, jute, abaca, flax and coconut shell. The composition of precursors has an important role in the properties of the CBM derived from them. In former studies, precursors having a high lignin content have been found to be ideal for getting CBM with high porosity and surface area [13]. Coconut shells are widely used precursors for synthesizing CBM. The composition of lignin, cellulose, and hemicellulose is 46%, 14%, and 32%, respectively [14]. Due to the high content of lignin, coconut shell-derived carbon is desired to have high porosity [13]. Coconut shell-derived CBMs are often used for applications such as reinforcement fillers [15], dye removal [16], supercapacitor [17], and water filtration [18].

1.2. Biochar Carbon-reinforced Polymer Composites

Biochar, a renewable carbonaceous material synthesized through thermochemical processes conducted in an oxygen-restricted environment is an alternate environment-friendly option to reduce the dependency on fossil fuel-derived carbon materials. Since biochar is obtained from sustainable bio-based resources and possesses supreme properties such as high surface area, high thermal stability, and electrical conductivity, it has gained great attention recently among both academic and industrial researchers [19]. The process of carbonization of raw material in an oxygen-free environment is called pyrolysis. It is one of the most common methods preferred for the synthesis of biochar among numerous methods like combustion, liquefication, gasification, *etc*. The properties of biochar obtained from pyrolysis depend on various process parameters such as heating rate, temperature, the type of raw material, and residence time. Lignocellulose rich precursors are often considered as ideal raw materials for synthesizing high-quality biochar. Along with biochar, pyrolysis of biomass can also give some valuable byproducts such as bio-oil and other useful chemicals [20]. Reinforcement of biochar in a polymer matrix is found to be very efficient as it helps in the enhancement of the properties of the polymer. In a work done by Poulose *et al.*, reinforcement of biochar synthesized from pyrolysis of date palm waste into a polypropylene matrix was found to improve the electrical and mechanical properties of the polypropylene matrix considerably [21]. In another study, biochar obtained from the pyrolysis of starch-based packaging waste was modified using ultrasonication and was added to a polypropylene matrix for effective reinforcement and it was found that the modified biochar helped considerably improving the mechanical and thermal properties [22]. Coconut shell, a bio-based waste present abundantly in Asian and South American countries is considered a suitable precursor for pyrolysis to synthesize biochar because of its high lignin content. Researchers have used coconut shell-derived biochar as fillers in various polymers. When coconut shell-derived biochar was added to a polylactic acid/ polybutylene adipate-co-terephthalate matrix, the mechanical and electrical properties were found to improve as a result of superior interfacial interaction between the polymer blend matrix and biochar [23]. Similarly, there are numerous studies portraying the improvement of polymer matrix properties upon the incorporation of coconut shell-derived carbon fillers [7, 24].

CHAPTER 9

Carbon Based Polymer Composites in Water Treatment and Filtration

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Abstract: The world at large has acknowledged the importance of environmental issues. The depletion of natural resources, such as drinking water, and the emission of greenhouse gases that result in climatic change and the deterioration of human health, are the primary concerns. As urban areas expand rapidly, they exert enormous strain on nearby water supplies, leading to a global freshwater demand surge that is outpacing population expansion. The development of polymer nanocomposites has contributed significantly to the search for viable answers to pressing ecological concerns. Their ability to eradicate pollutants, including gas emissions, heavy metals, and dyes in wastewater has garnered researchers' attention. In this overview, polymer nanocomposites, as well as the composites reinforced with biocarbon that are used in environmentally friendly ways, are discussed in detail. The adsorption mechanism and applications of polymer nanocomposites for the removal of hazardous metal ions and dyes were also studied.

Keywords: Adsorption, Biochar, Biocarbon, Inorganic Pollutants, Metal Ions, Organic Pollutants, Polymer Membranes, Polymer Composites, Sorption, Water Treatment, Water Filtration, Wastewater Treatment.

1. INTRODUCTION

Polymer nanocomposites reinforced with nanofillers grew rapidly and formed novel materials with enhanced properties. They have versatile applications in aerospace, mechanical, electrical [1], catalyst [2], food packaging [3], medicinal [4], and environmental [5, 6] industries. The chemical compatibility of polymer nanocomposites depends on the shape and size of the nanoparticles [7]. If nanomaterials are properly functionalized, they can improve polymer-filler compatibility and prevent agglomeration effects. Different nanoparticles can

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Deepa Kodali & Vijaya Rangari (Eds.)

change the stability and degradation of a polymer matrix [8, 9]. Polymer nanoparticles can also help in the crystallization of the polymer matrix [10].

Different inorganic and organic materials are used for the synthesis of membranes that are used for wastewater treatment [11]. In comparison to typical membranes, nanocomposite membranes display improved performance [12]. Ceramics, metals, and glass were categorized as inorganic materials, while mixed nanocomposites and polymeric materials were categorized as organic materials [13]. Inorganic membrane synthesis is an expensive synthesis process due to excessive chemical resistance, making it suitable for wastewater treatment [14]. Polymeric membranes were a better choice than inorganic membranes in industrial applications. Owing to their versatile applications and simple preparation methods, polymeric membranes were chosen over inorganic membranes [15]. For water decontamination, excellent permeability, retention, and outstanding antifouling properties of membranes were quintessential [16].

Out of all separation technologies available, adsorption is the most efficient, cost-effective, and easy-to-use wastewater treatment technology for contaminant separation [17]. In recent years, biocarbon has emerged as a new sorbent due to its excellent properties, such as being eco-friendly, containing substantial functional groups, porous structures, and having outstanding adsorption capability. These properties have led to biocarbon's widespread use in the process of removing contaminants from wastewater [18].

Waste biomass is used to produce biochar. This is economical and simultaneously beneficial. Biochar that originates from animals or plants has great potential for waste management and can help decrease the pollution. Different variations in waste biomass can be found in nature. It includes crop residues, forestry waste, animal manure, food processing waste, paper mill waste, municipal solid waste and sewage sludge [19]. Animal manure and sewage sludge-based biochar from pyrolysis can kill bacterial populations [20]. Toxic heavy metals are collected from sewage sludge and can have long-term applications. In this book chapter, we discuss the preparation and application of different polymer nanocomposites, along with their antimicrobial properties and their use in water filtration.

2. BIOCHAR IN WATER TREATMENT

The expansion of industry has led to an increase in the amount of waste material disposed of in bodies of water, which in turn has led to contamination of the water. Cd^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Ni^{2+}, and Cr^{6+} are the heavy metals that cause environmental pollution. Heavy metals and organic compounds are removed from industrial wastewater by using biochar. Biochar, also known as pyrogenic black carbon, is created when organic matter like wood or grass is heated in the absence of nitrogen or oxygen. Biochar has been proposed as a cost-effective adsorbent for use in water treatment because of its unique surface qualities. If chitosan is added on the surface of biochar, it can remove three heavy metals like Cd^{2+}, $Pb^{2+}$and Cu^{2+} [21]. Zhou *et al.* demonstrated that applying a chitosan coating to biochar surfaces improved its adsorption and soil amendment properties. Chitosan-modified biochars were more effective in removing Pb, Cu, and Cd from the solution. Lead sorption on chitosan-modified biochar lowered metal toxicity as well [22]. The biochar that is obtained from the pyrolysis of wheat straw is used to remove Cd^{2+}, $Pb^{2+}$and Cu^{2+} from aqueous solutions [23]. Pyrolysis of malt wasted rootlets at 850 °C yielded biochar with 63% micropore volume. Malt-based biochar removed Hg(II) from pure aqueous solutions and has shown good sorption and kinetics. It may adsorb 103 mg/g at pH 5. The sorption kinetics were represented by a pseudo second-order model, and the Langmuir isotherm model was shown to be a good fit for the experimental data [24]. $ZnCl_2$-modified biochar from glue residue was created for the sorption of Cr(VI), which showed a maximum capacity of 325.5 mg/g compared to other sorbents. The results demonstrated that the modified biochar has the largest specific surface area and the most functional groups on the surface, making it an effective and reusable adsorbent for Cr(VI) [25].

Wastage from textile industry also causes water pollution. Bamboo powder chemically activated with phosphoric acid at 400–600°C yields nanoporous carbon with high surface area (NCMs), which can absorb Lanosyn orange and Lanosyn gray effectively [26]. This research showed that high surface area NCMs made from agricultural byproducts have the potential to serve as efficient and inexpensive adsorbent materials for the treatment of dye-contaminated industrial effluent.

The presence of new organic pollutants in industrial effluent, like phenols and polycyclic aromatic hydrocarbons (PAHs), has raised significant alarm. The biochar from sewage sludge was pyrolyzed at 500 ºC in the presence of strong HCl. Activated carbons (ACs) made from sludge were made using both traditional heating methods and microwave pyrolysis. The ACs were employed to remove six phenolic compounds from aqueous solutions, and their performance was assessed using a number of analytical and functional methods. All of the adsorbents shared the same characteristics and were hydrophobic on the outside. The mesoporous materials used for the ACs have specific surface areas of up to 641 m2 g1 for the CAC-500 and 540 m2 g1 for the MAC-980. This study proposes that π–π interactions are key to adsorption [27]. At 800ºC, biochar from malt spent rootlets can adsorb phenanthrene (PHE). It is higher in magnitude in comparison to other raw materials [28]. Biochar from orange peels was derived from pyrolysis at temperatures ranging from 150 to 700 ºC (OP 150-OP 700).

SUBJECT INDEX

A

B

Deepa Kodali & Vijaya Rangari (Eds.)

C

D

E

M

N

O

P