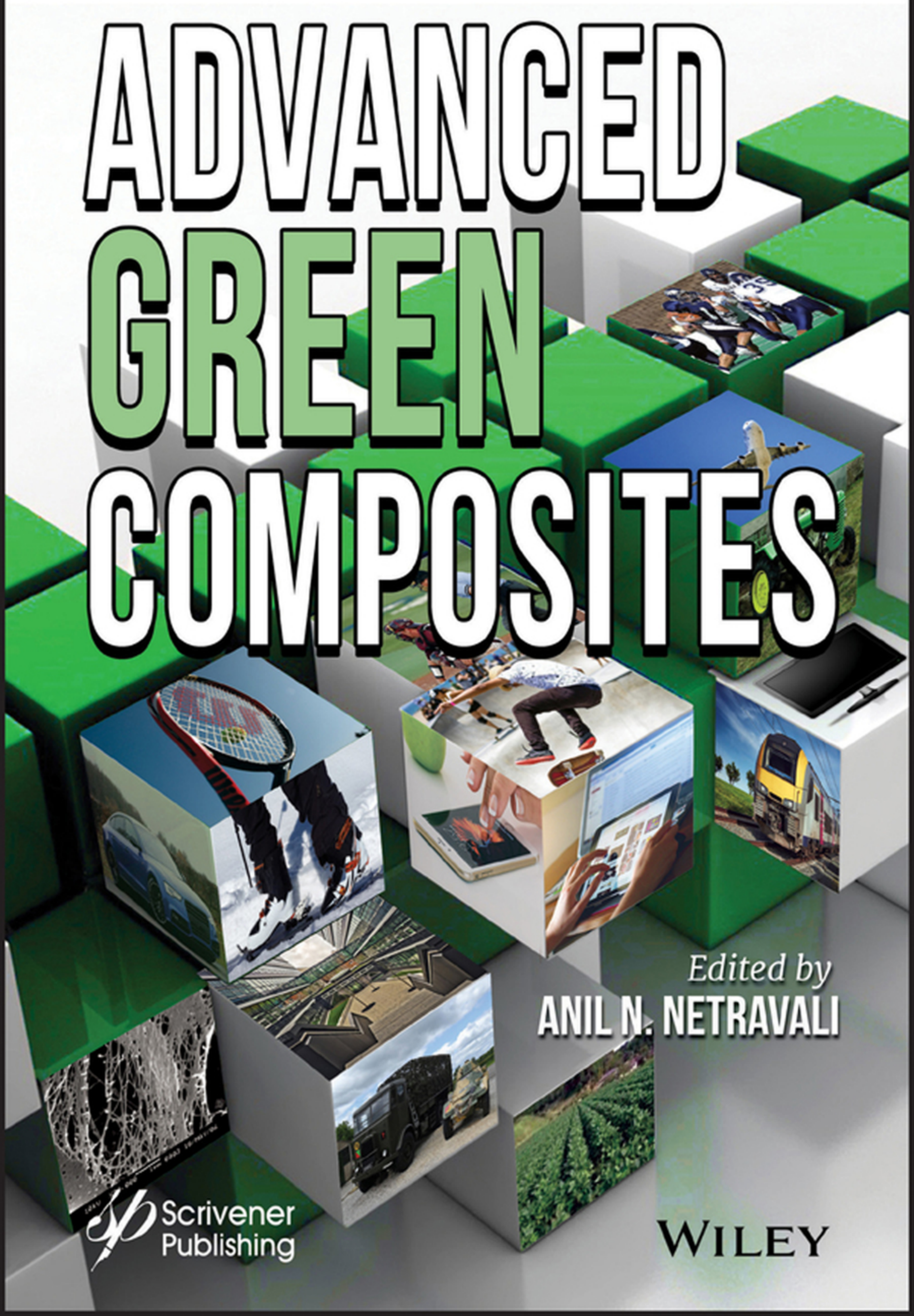

ADVANCED GREEN COMPOSITES

Edited by

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Scrivener Publishing

WILEY

Advanced Green Composites

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Scrivener
Publishing

WILEY

This edition first published 2018 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
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Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-32326-6

Cover image: Pixabay.Com
Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Exeter Premedia Services Private Ltd., Chennai, India

Printed in the USA

10 9 8 7 6 5 4 3 2 1

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Preface

Polymer composites are made of two distinct components: matrix or resin (continuous phase) and filler or reinforcement (discontinuous phase) and have properties that cannot be achieved by a single component alone. Conventionally, advanced composites have been defined as those that have excellent tensile properties. Three factors contribute to their high tensile properties: (1) high strength fibers such as carbon, aramid, or glass used as reinforcement, (2) good resins such as epoxies, and (3) excellent bonding between the fiber and the resin. Specific tensile properties of advanced composites are significantly higher than most metals because of their low density. As a result, advanced composites have replaced metals in many applications from aerospace to sports gears and from automobiles to wind turbines. It is being envisioned that future civil structures such as bridges and buildings will use advanced composites in place of steel, which will require significantly larger volumes. As we know, every material has a life span, and advanced composites are no exception. Unfortunately, we have not found an environmentally friendly way to dispose these composites at the end of their useful life nor have we found any sustainable raw material source to make them. Composites, at present, use unsustainable petroleum as the raw material to synthesize fibers and resins and end up in landfills at the end of their life, making that land useless for any other use for several decades or even centuries. Fortunately, this is slowly beginning to change with the advent of green polymers that are derived from fully sustainable plant based sources. Green composites are also being fabricated using these polymers with plant based fibers as reinforcement. At the end of their life, they can be easily composted, rather than being dumped into landfills. Thus, they can not only save the petroleum but also the land used for landfills.

Significant research is going on around the world to develop green composites that use both fibers and resins that are derived from plants. However, composites using common fibers such as jute, kenaf, sisal, ramie, hemp, banana, and many others have only moderate tensile properties, comparable to wood and wood-based products such as particle board and medium density fiber (MDF) boards. They are not suitable for structural applications where much higher strength and stiffness are required. Their durability, fire performance, and other functionalities are also not par with conventional composites. As a result, their applications have been very limited.

In the last decade or so, however, many new developments in the area of green composites have come about that are changing the landscape drastically. For example, high strength cellulose fibers have been developed using liquid crystalline cellulose solutions and air-gap wet spinning technique used for spinning Kevlar® fibers. Being 100% cellulose, they are fully degradable. Although this technology is still not mature, fibers with strength in the range of 1.5–1.7 GPa have been obtained. Furthermore, researchers have found ways to improve their properties further to around 2.0 GPa using chemical and heat treatments under tension. There is great promise that once the technology matures, these fibers could have tensile properties close to Kevlar®. Advanced green composites with high strength and stiffness have already been fabricated using these fibers and soy protein and maize starch based resins that would be suitable for structural applications.

Other than high strength and stiffness, composites are also being developed with a wide range of functional properties for a variety of applications. This has changed the conventional definition of Advanced Composites based on mechanical properties and now includes all composites that have special functional properties such as high transparency, fire resistance, ultra-light weight, autonomously repairing, and resin-less composites. Researchers have been able to obtain many of these properties in green composites as well, making them Advanced Green Composites.

This book provides the current state of advanced green composites that have been developed or are at the research stage of being developed with a variety of functional properties. Chapter 1 presents a broad introduction to green composites and their development to date. In Chapter 2, Rahman and Netravali discuss green resins that have been derived from plant-based sources and seem to be promising to fabricate structural composites. The chapter also discusses some of the most promising bio-based and inorganic nano-fillers that are considered as potential candidates for enhancing the properties of these green resins. Improving resin tensile properties should automatically reflect on composite properties made using them. The third chapter by Huang and Chen discusses the development of high strength cellulosic fibers, the primary load-bearing component in current green composites. Viscose rayon process used for spinning cellulose fibers is more than a century old and is incapable of producing high strength cellulose fibers. This chapter provides an overview of high strength cellulosic fibers that can be obtained from liquid crystalline solutions of cellulose derivatives and nonderivatized cellulose as well as new methods to reinforce the liquid crystalline solutions of cellulose. It is to be noted that all high strength advanced green composites, until today, have been made using liquid crystalline cellulose (LCC) fibers. In the fourth chapter, Hsieh highlights top-down and bottom-up approaches to generate ultra-fine cellulose fibers of nano-scale dimensions, micro- and meso-porous and sheath-core hybrid structures as well as surface-functionalized fibrous materials. Micro- and nano-fibrillated cellulose (MFC/NFC) and other forms of nanocelluloses have high strength as well as aspect ratio and can be efficiently extracted from a variety of waste products such as apple, carrot, and orange pulps that remain after extracting juice, grape, and tomato skins, various straws, etc. They have been used as reinforcement in resins among many other applications. Chapter 5 discusses up to date efforts in developing high strength composites that use LCC fibers and are termed as advanced green composites. There are other opportunities for obtaining high strength composites as well. For example, researchers are trying to develop high strength fibers from spider-silk like protein. Once such fibers are commercially produced, they can be used to make green composites. Bacterial nanocellulose is another fiber with high strength. If these fibers can be oriented, they would be excellent as reinforcement as well. Chapter 6, by Fujisawa and colleagues, summarizes the latest in a new class of composites that do not require resin at all. These composites are made using only one component, cellulose, which acts as the reinforcing fibers as well as the resin that bonds the fibers. These all cellulose composites (ACC) are considered a green alternative to glass- and carbon-fiber-reinforced polymer composites. The authors also provide a future perspective on ACC development for applications in various fields, including optical devices, food, and medicine. Chapter 7 presents composites that have the ability to autonomously self-heal the damages such as microcracks, punctures, cuts, and scratches that result from the constant stress and strain they are subjected to during use. The damages continue to accumulate, ultimately failing the composites. Self-healing is designed to heal the damages as they occur and, hence, can increase the service life of the composites significantly. The chapter discusses different ways developed by researchers to achieve self-healing in conventional composites and how some methods have been extended to self-heal green resins and green composites. Self-healing green resins and composites, with increased service life, should be more acceptable in mainstream applications in the future. In Chapter 8, Nakagaito and colleagues discuss optically transparent composites that have been developed of late for use in place of glass as substrates in electronic devices. Flexible electronics represents a common technology employed in gadgets that are ever-present in our daily lives. Among them, electronic displays are about to become flexible and foldable in the near future. Nanofibers that are invisible to our eyes can not only strengthen amorphous polymers but retain their transparency and also reduce their coefficient of thermal expansion, a critical requirement for electronic displays. Making transparent green composites is an active area of research at present and this chapter presents a thorough review of the current efforts. One of the deficiencies of the thermoset green resins such as plant-based proteins and starches as well as poly(lactic acid) is their brittle nature. That also translates into brittle composites. This is the topic of Chapter 9 in which Goda discusses ways of toughening composites with an emphasis on their impact properties. Chemical treatments of natural cellulosic fibers can make them stronger or tougher. Another key strategy to obtaining higher toughness is to control fiber/resin interfacial shear strength.

Chapter 10 by Obradovic and colleagues introduces the science, technologies, and applications of ultralight porous green composites in the form of biofoams. The chapter presents a thorough review of the biofoam compositions, process methods, properties as well as their performance and applications. In Chapter 11, Xia and colleagues discuss fire retardants developed from renewable resources. Most fibers and composites used in construction, transportation, electronics, and protective textile applications must have fire retardant functionality. Commercially available halogenated flame retardants tend to be toxic and persist in the environment for a long time. The authors, based on the current state of research, conclude that exploring the use of renewable materials as feedstock for FR alternatives is quite promising. In addition to sustainability aspects, the research has unlocked exciting new possibilities in fundamental understanding of fire retardants and their mechanisms of action. Chapter 12 by Gupta *et al.* discusses the recent technological advancements and innovations in the development of novel biodegradable polymers and nanofillers derived from renewable feedstock with a strategy to convert "waste into wealth" with special focus on green composite films for stringent food packaging that require excellent barrier properties. Finally, in Chapter 13, Osorio and colleagues discuss nanocellulose-based composites in biomedical applications. Although cotton has been used in gauzes for treatment of wounds since ancient times, nanocellulose-based composites have become of great interest in biomedical applications, given their inherent biocompatibility. Nanocellulose from microorganism assembly is similar to that of collagen, the major component of extracellular matrices, and its applications are diverse, ranging from scaffolds for tissue engineering, implants for cell regeneration or biosensors. Although the chapter discusses some relevant biomedical applications of nanocellulose based composites, authors predict that in medium to long term, nanocellulose-based composites will play an important role for developing *in vitro* tissues and organs, accelerating healing processes and improving life quality of mankind without impacting the environment.

The book covering a broad range of green technologies should be of interest to researchers in academia, in government research labs, and R&D personnel in a host of industries (e.g., aerospace, automotive, biomedical, composites, fibers, medical, microelectronics, packaging, plastics, textiles, and others) who are interested in designing with green fibers, polymers, and composites or advancing the sustainable materials technology. Industries such as aerospace and automotive that are increasingly turning to composites for lightweighting each component but use conventional composites should be able to find greener alternatives in their applications. Anyone working in sustainable plastics/polymers and composites industries should find this book of great interest and very useful as well.

It is my great pleasure to thank all those who made this book possible. First and foremost, I would like to profusely thank the outstanding authors who spent enormous amount of their valuable time in writing the chapters. Sharing their deep knowledge in the field and cutting edge research they are involved in, with the interested community, is greatly appreciated. This book would have been impossible to complete without their hard work, sustained interest, great enthusiasm, and cooperation. Thanks are also due to Martin Scrivener (Scrivener Publishing) for his unwavering support, interest, and encouragement, as well as patience in getting this book completed.

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Introduction

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Abstract

Advanced composites using high strength fibers such as graphite and Kevlar® have been replacing metals in load bearing structures for several decades. Initially introduced in aerospace applications where lighter structures are critical, the technology has become common and now being used in mundane applications such as automobiles and, in future, will be used in civil structures such as buildings and bridges. Obviously, there are several advantages of using these composites. However, disposal of these composites, at the end of their life, is already a problem and with large volume applications, e.g., automobiles and civil structures, it will be a significant issue. Also, the fibers and resins used in these composites are made from petroleum which itself is not sustainable. These issues along with government regulations all around the world on restricting the use of petroleum-based materials have created a great interest among the scientists to develop polymers, chemicals and composites using sustainable raw materials. Plants, grown every year, are perhaps the most sustainable resource for developing monomers and polymers. Also, cellulose, derived from plants and microbial sources, seems to be an excellent linear polymer for developing fibers. Composites using plant derived polymers (resins) and fibers, known as Green Composites, can already be found in the market. The next generation of green composites called *advanced green composites* are being developed that will have special functionalities such as high strength, stiffness or toughness, fully transparent, autonomously self-healing, fire retardant, nano-composites for biomedical applications, resin-less composites, light-weight foam composites, composites with gas barrier properties, etc. These will be able to compete with the petroleum based conventional composites in many applications. However, they will enjoy significant advantages such as composting at the end of their life rather than putting in landfills and never-ending raw material supply, i.e., fully sustainable. Rather than harming the environment, they will help it by

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Anil Netravali (ed.) Advanced Green Composites, (1–10) © 2018 Scrivener Publishing LLC

completing the nature's intended carbon cycle. This book details the state-of-the-art in advanced green composites.

1.1 Introduction

Fiber reinforced composites based on fibers such as graphite, Kevlar®, glass, etc., and resins such as epoxies, poly (etheretherketone) (PEEK), polyurethanes, etc., have been used in many structural applications from airplanes to windmill blades and from space stations to automobiles. These high performance composites possess extremely high strength and stiffness and when combined with their low density they exhibit high specific properties compared to all metals and alloys. As a result, they are commonly referred to as *advanced composites*. They also have other distinct advantages. They can be engineered to obtain desired properties by varying fiber forms, fiber placement and amount in different laminates. They can also be molded into desired shapes. In addition, they do not rust and can last for many decades when properly used. Their long-lasting nature, rather the 'not-degrading' characteristic, however, has created a real problem. Most plastics discarded on land or in sea, stay in 'as is' condition, i.e., without degrading, for many decades. This has not only created a severe litter problem but has also affected both wildlife and sea life in many ways.

In case of composites, there is an additional issue that needs to be addressed. Because they contain two constituents, resin and fibers, that are bonded together, sometimes even covalently, at the end of their life they are impossible to be separated and reused. In case of thermoset resins such as epoxies, once cross-linked or cured, they cannot be re-formed or re-used. At present, there is no acceptable environment friendly solution to dispose them off at the end of their life. And unfortunately, there is a life span for every composite, beyond which they cannot be used safely and, hence, have to be discarded. There are some efforts in reclaiming carbon fibers by burning off the resin. Some composites are incinerated to recover energy value. However, burning composites or resins creates toxic gases, which, if released into the environment, can lower the air quality. In addition, the burning process, along with additional handling involved, reduces the fiber strength significantly. Also, the fibers cannot be obtained in their original continuous form. For both these reasons, they can only be down cycled and may not be cost effective. Another way of recycling composites is to grind them into fine powder for use as filler in some applications. This also consumes a large amount of energy. At present, reclaiming fibers, recovering energy and grinding composites to powder are all carried out on a very small scale and can consume only a tiny fraction of the composites being discarded. As a result, most composites get discarded in landfills. Unfortunately, they stay in the landfills not just for several decades, but even centuries, without degrading. In fact, several studies have suggested that even the most biodegradable materials such as corn on the cob or even banana peel will not degrade in the anaerobic conditions of the landfills for decades. This can leave the land being used for landfills to be unavailable for any other productive use for centuries. Over the last three decades, the number of landfills in the US has gone down. As per the 1997 US census, the US had only 3091 active landfills. In addition, according to Leak Location Services, Inc., in 2000, 82% of the surveyed landfills had leaks which could pose threat to the water table. The tipping fees for landfills have also increased over the years. According to the Waste Business Journal, the average tipping fee in the US increased to $50.6 as of May, 2017, up by 3.5% from December 2016, in just 6 months! Since landfills are located far from the cities where most waste is generated, there is also a significant cost of transporting the waste to the landfills.

While disposal is one critical problem associated with polymeric composites, their origin or the raw material used to derive them is the second big problem. Most commercial fibers, with the exception of glass fibers, and resins used in composites are produced using petroleum as the raw material. It is estimated that 5–7% of the total petroleum produced is used for making chemicals and materials such as polymers and composites. It is commonly accepted that petroleum will not last forever. We have been consuming petroleum at an unsustainable rate over the past 4–5 decades. By some estimates the consumption rate at present is 100,000 times faster than the earth can generate it. With countries such as China and India growing faster, petroleum consumption can only accelerate in the near future. At present to find new petroleum sources, we have to go deeper and farther into the sea. Many studies have suggested that at the current rate of consumption, we will have petroleum left for only 5–6 decades. That means in just over 100 years we will have consumed most petroleum earth took several million years create.

As mentioned in the previous paragraph, at present, the only source to obtain plastics (polymers), fibers, and composites, is petroleum. So the questions we should be asking now are; what would happen when we run out of petroleum? From where will we get polymers/plastics that have become part of our daily life? How and which sustainable sources do we have to develop polymers, fibers and composites? While sustainable sources such as wind and sun (photovoltaic) exist for energy and are increasingly being used, the only sustainable source for obtaining materials is *Plants*.

The growing global environmental consciousness about the persisting litter problem, concerns regarding air, water and land pollution, high rate of depletion of petroleum resources have resulted in new environmental regulations all over the world. Many governments have put in place laws to curtail the use of petroleum based materials and moved to sustainable plant-based materials that are also biodegradable and, hence, can be easily composted. The laws are also in place to collect and recycle polymers/plastics. All these factors have together triggered the search for new products and processes that are environment friendly. Companies have realized that their existence will be in jeopardy in just 3–4 decades if they do not find a suitable substitute for petroleum that is sustainable. 'Green' chemistry, 'green' materials, recycling, sustainability, cradle-to-cradle design, life cycle analysis, industrial ecology, are no more 'feel good' buzz words but have begun guiding the developments of many new products. Researchers from academia, industry and governments world over have seriously taken the challenge in exploring plants and agricultural/food processing wastes as sources for chemicals and polymers/plastics and to design new products. This realization alone is significant and progress is being made in this direction. For example, plant-based polylactic acid (PLA) has already been a commercial success. Ethylene glycol developed from plant source is now being used for making poly (ethylene terephthalate) (PET) used in soda bottles and apparel. Polyethylene (PE) and polypropylene (PP) can also be made from sugar obtained from sugarcane. Poly (butylene succinate) (PBS) is increasingly made from plant source. Research has even indicated that resins such as epoxies can also be made from sugars. Many more examples of other polymers can be found at research stage and will be commercialized in the coming years.

The above discussion should convince anyone that the materials world is experiencing a true *Green Revolution*, perhaps because of the realization that there is no other alternative. Fiber reinforced composites are no exception to this new paradigm. Past 2–3 decades have seen exponential rise in research in the field of Green Composites. This is clear if the number of papers and books published and research presented at conferences is any indication. Since plant based cellulosic fibers have been available and used universally for centuries, it has been easy to combine them with various resins as reinforcing constituents to fabricate composites. They are also available in a variety of forms, from fibers to yarns and from fabrics to nonwoven mats. This makes it easy to combine various forms to engineer the properties of composite as desired for the applications. Many examples can be found where plant fibers have been combined with resins such as epoxies, PE, PP, PET, PVC, etc., forming what are termed as 'Greener

Composites'. These greener composites have properties comparable to or even better than wood and wood based products such as plywood, particle boards, medium density fiber (MDF) boards, etc. They have been successfully used in applications such as automobile dashboards and door panels, ceiling tiles, wall panels, furniture, shelving, z-truss structures for flooring in recreation vehicles, etc. Since these greener composites combine degradable fibers and non-degradable resins, they cannot return to industrial metabolism or natural metabolism. They can only be down cycled to make low value products, incinerated to recover energy value or put in the landfills.

The current trend is to fabricate composites that are fully 'Green' by using both resins and fibers that are plant based, sustainable, biodegradable and using processes that are water based, where possible, in effect, reducing their carbon footprint to zero. In some cases, it may be even possible to obtain a negative carbon footprint by preserving the carbon sequestered by nature. Many resins such as those based on plant proteins, starches, other gums, as well as synthesized biodegradable polymers such as PLA, have been used to fabricate green composites. While still in its infancy, research in this area has been on the rise in the past 2 decades. At the end of their life green composites can be composted without harming the environment. In fact, composting can create organic soil that can be used in growing more plants, thus, helping the environment…a truly win-win situation! Green composites can be used in many applications such as mass-produced consumer items that are used only once or just a few times before discarding. As many of these green composites are made using resins based on plant proteins or starches, they tend to be hydrophilic and absorb moisture when exposed to humid conditions or water (rain) and swell. This swelling is reduced when the composites are placed in dry environment and desorb the moisture. Cyclic absorption/desorption of moisture invariably degrades the fiber/resin bond that is accompanied by loss in mechanical properties. While one way to solve this issue is to limit these hydrophilic composites to indoor applications, another way would be to use paints, varnishes or hydrophobic coatings, as is commonly done to wooden articles. The latter method can allow using green composites in outdoor applications.

Many examples can be found of green composites made using natural cellulosic fibers. However, since the natural cellulosic fibers have average strength of around 400 MPa, these composites cannot be strong. Most of these composites have strength in the range of 150 MPa to 250 MPa and can be used as replacement for wood, particle boards, MDF boards in applications such as cabinetry, door panels, etc., that do not require high strength. These composites, as mentioned earlier, are suitable for indoor applications. For outdoor applications, they need to be protected by hydrophobic paints, varnishes, or coatings.

By conventional definition, composites with high strength and/or high modulus such as those made using glass, graphite or Kevlar® fibers are called as *Advanced Composites*. They are commonly used in load bearing structural applications in place of metals to reduce weight. In the same spirit green composites that possess high strength, modulus and/or toughness have been called *Advanced Green Composites*. Such composites, up until now, have been successfully made using liquid crystalline cellulose (LCC) fibers that have been recently developed at Groningen University in The Netherlands. LCC fibers have higher crystallinity and molecular orientation than any other continuous cellulose fibers, natural or regenerated. In addition, their original strength of about 1.5 GPa has been successfully increased to about 2.0 GPa by combined chemical and mechanical treatments carried out at temperatures of 50 to 80 °C. The same combination of treatments has also increased their modulus from about 45 GPa (original) to close to 70 GPa making them a prime reinforcing constituent to fabricate advanced green composites by combining them with green resins. Such composites, made with hand layup, resulted in strengths of around 800 MPa and modulus of over 30 GPa with just 55% LCC fiber volume. With fiber volume between 65 and 70%, normal for any fiber reinforced composites, and eliminating some of the defects created by hand layup, the strength of these advanced green composites could be increased to over 1 GPa and modulus to over 40 GPa. Since these fibers have higher fracture strain compared to conventional fibers such as graphite, glass or Kevlar®, they can absorb significant amount of energy during fracture. Such advanced green composites could be suitable not only for load bearing structures but also in ballistic applications.

Another significant advantage of the plant based cellulosic fibers lies in their fibrillar nature. While the fibrils themselves may not be oriented along the fiber axis, the molecular orientation and crystallinity within the fibrils is very high. As a result, cellulose nanofibrils (CNFs), microfibrillated cellulose (MFC) or nanocrystals (CNCs) obtained from plant fibers have excellent tensile properties and have been used to strengthen and stiffen protein and starch based resins. CNFs have also been shown to improve resin toughness by crack-bridging mechanism. The modulus and strength of CNFs has been estimated at 140 GPa, and between 2 and 6 GPa, respectively. It should be noted that these values are close to or better than those of Kevlar®. In addition to being biodegradable and sustainable, CNFs and CNCs can be obtained from waste products such as used newspaper, and apple, orange or carrot pulps that remain after extracting juice and are often discarded as waste. It has also been found that adding CNFs or MFC, with high aspect ratio, to green resins can improve the fiber/resin mechanical bonding in composites by providing possibilities for entanglement between the two, thus, further improving the composite properties.

There are also abundant opportunities to use bacterial nanocellulose (BC) to obtain advanced green composites with high mechanical properties. BC nanofibers are 50–70 nm in diameter or width. BC is produced by aerobic bacteria such as *acetobacter xylinum* and has cellulose-I crystal structure with extended chain conformation. However, compared to plant based cellulose, BC has a higher degree of polymerization. It is also extremely pure form of cellulose and does not contain hemicellulose, lignin, pectin or wax that plant based cellulose fibers contain. As a result, BC nanofibers have high strength and stiffness and can be useful for fabricating advanced green composites. However, since bacteria move in a random fashion in the culture medium, most BC pellicles obtained from conventional process contain nanofibers that are randomly oriented and highly entangled. It is well known that in a composite, randomly oriented fibers cannot contribute to the strength and stiffness fully. Most advanced composites contain fibers that are highly oriented within individual laminates. As a result, there have been some efforts in orienting the BC and to take advantage of their high strength. Efforts using poly (dimethylsiloxane) (PDMS) substrates with micro-channels and restricting the bacterial movement inside those channels to form BC arrays and drawing them further to improve the orientation have been successful. This process has resulted in significant improvement in BC orientation which, in turn, resulted in enhanced strength and stiffness of the starch based green composites reinforced with them. Never the less, the results have also indicated that significant scope exists to improve the BC orientation further by optimizing the channel design and substrate geometry. Other methods to obtain highly oriented BC may be developed that are easier than using PDMS substrates with channels and may result in higher productivity.

Besides obtaining higher mechanical properties, in the past couple of decades, researchers have achieved significant progress in enhancing various functional properties of green composites, making them ‘advanced’ in many ways. Functionalization of composites has clearly broadened the definition of Advanced Green Composites to encompass all green composites that have special functional capabilities. This book presents advanced green composites that have been developed with many functional properties. For example, all-cellulose composites that do not have any resin. The cellulose fibers used in these composites are bonded not by any resin but by cellulose itself. This is achieved by dissolving a very thin outer layer of cellulose fibers by a suitable solvent. The dissolved cellulose, in amorphous state, allows bonding of neighboring fibers. Once the fibers are bonded, the solvent is removed. All-cellulose composites can be made in the form of membranes that are strong and, hence, suitable for many applications.

Another functional property is transparency. Fully transparent green composites have been made using cellulose CNFs, CNTs, or BC that have diameters less than 100 nm, much lower than the wavelength of visible light, and transparent green resin such as amorphous PLA. The CNFs, CNTs, and BC not only strengthen the composites but toughen them as well because of their crack bridging action. Transparent green composites can have many applications in light-weighting products by replacing glass which tends to be not just heavier but brittle as well.

Green composites with brittle resins such as soy protein and starch are known to develop microcracks when subjected to stress. These microcracks slowly grow with time and all that is needed is for one of them to reach catastrophic level and fracture the composite. The catastrophic growth of the microcracks can be prevented if the microcracks can be healed as and when they are formed. This is commonly accomplished by releasing a healant which stays encapsulated in either microcapsules or a network of vascular system. Self-healing green resins, protein and starch based, and composites have now been developed that can autonomously heal in a similar fashion compared to conventional composites. However, all materials used in the case of green composites are green and sustainable. The healing mechanism in this case is obtained by fracture of the microcapsules that come in the path of the microcracks, releasing the healant and healing them. This is a new development and can keep the green composites operating for a much longer time, thus, extending their life significantly and making them economical than the current ones.

Light weight reinforced green composite foams have also been made with the help of reinforcing CNFs and CNTs. These reinforced foams can be used for insulation or packaging. Much research has been conducted on synthesizing green fire retardant chemicals and fabricating fire resistant green composites. Proteins, used as resin in green composites, do not burn easily because of their inherent chemical composition that contains large amount of nitrogen. In addition, they also contain polar groups such as hydroxyl, carboxyl and amine groups. In normal environment, these polar groups absorb water which can help retard or extinguish the fire. In addition, when heated, there are possibilities that hydroxyl and amine groups could react with adjacent carboxyl groups to form ester and amide groups, respectively. These reactions not only cross-link the protein and tighten the structure but every time these condensation reactions occur, they eliminate a water molecule which can help retard the fire. In addition, the intumescent char produced by the fire on the composite surface can also significantly reduce the fire effects. Protein based green composites tend to be inherently fire retardant.

Green composite films and membranes with excellent barrier properties have also been developed for stringent food packaging. These have high gas barrier properties and can preserve foods equally well compared to conventional petroleum based polymers. They are made using an existing wide pool of bionanofillers derived from biomass. And like all green composites, these films can be easily composted.

Nanocellulose, as stated earlier, is also biocompatible. Nanocellulose can be used to mimic many tissues such as cartilage, skin, blood vessels, etc. Nanocellulose based biomedical green composites are predicted to play an important role in developing *in vitro* tissues and organs, accelerating healing and improving overall quality of life.

In summary, great progress has been made in the field of green composites in just the past 2–3 decades. Many special functional characteristics, apart from high strength and stiffness, have been achieved in these composites making all of them advanced green composites. The field of advanced green composites is still in its infancy but with significant research going on all over the world, it won't be much longer before these composites are commercialized and give conventional advanced composites a run for their money.