



SUSTAINABLE COMPOSITES

Fibers, Resins and Applications

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Sustainable Composites

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Introduction

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AFTER the development of the first synthetic fiber, nylon, by Wallace Carothers at DuPont, in the 1930s, a significant amount of research has been done in the area of polymers. This has resulted in the development of a host of other important fibers, such as polyester, acrylic, polypropylene, aramid, carbon, ultrahigh molecular weight polyethylene (UHMWPE), etc. which have changed our lives forever. Along the way, many polymers/resins, such as epoxies, unsaturated esters, urethanes, and polyetheretherketone (PEEK), have also been developed. The inexpensive and plentiful availability of petroleum, from which these fibers and resins are synthesized, has been responsible for the significant growth of polymers in the past 7–8 decades. We use polymers in every aspect of our lives, from the nylon toothbrushes we use, to the clothing we wear, to the polyurethane foam mattresses we sleep on. The applications of polymers keep expanding as we develop newer and more sophisticated polymers with better properties and functionalities. Polymers have become so ubiquitous that it is virtually impossible to live without them.

One of the major applications of polymers and resins is composite materials, where two dissimilar materials are put together to extract synergetic effects, hence creating better properties when put together that cannot be obtained from either of these materials alone. Formally, composites are monolithic materials that are formed from two chemically and physically distinct phases. This definition covers a wide gamut of materials including steel. Typically, a composite has one continuous phase that surrounds and binds a discontinuous phase. The discontinu-

ous phase (also called the reinforcement) could be particles or short fibers of any size and shape; continuous fibers, woven fabrics, knitted fabrics, nonwovens, braids or any combination of these. From a practical point of view, the majority of composites use polymers as the continuous phase and contain fibers in some form as the reinforcement. These could be nanocomposites (a composite where the reinforcement has at least one spatial dimension smaller than 100 nanometers). Fibers such as aramids, carbon/graphite, glass, UHMWPE, etc., are commonly used to produce “advanced composites” that have excellent mechanical properties. In fact, their specific strength and stiffness, i.e., strength and stiffness per unit weight, can be several times that of commonly used metals and alloys. Because of their high specific properties, these advanced composites were first developed and used in aerospace applications. However, now they can be found in a variety of applications including sports gear, automobile parts, boats, appliances, circuit boards, etc. In recent years their use in large volume civil infrastructure applications such as bridge and building construction and rehabilitation has expanded.

Most advanced composites available in the market today are made using nondegradable polymeric resins such as epoxies, esters, polyurethane, etc., and high strength and/or high stiffness fibers such as graphite, aramids, and glass, designed with long term durability in mind. While they have desirable mechanical, thermal and chemical properties, they have two major disadvantages. First, the materials used are not sustainable. High performance fibers (except glass) and resins are almost entirely derived from petroleum, and further, use petroleum to fuel their production and transportation. At present, we are consuming oil, a fossil fuel, at the rate of 100,000 times the rate the earth can generate it [1]. While over 90% of it is used as fuel, 6–8% of oil is used to produce chemicals, polymers, fibers, etc. With the expected rise in population from just about 7 billion today to an estimated 8–10.5 billion by 2050 [2], and along with the reduction in world poverty, polymer and composite consumption are expected to rise in the next few decades. Second, almost all of these composites are nondegradable under normal environmental conditions. With increasing number of applications and mass volume applications in particular, composites have been recording double-digit growth worldwide in the past couple of decades. As a result, disposal of these composites at the end of their useful life, has already become critical as well as expensive. Composites made using two dissimilar materials cannot be easily recycled or reused. At pres-

ent, over 90% of composites end up in landfills at the end of their lives [3]. Currently, there are efforts to extract fibers from used composites as well as waste generated during fabrication and recycle them. For example, Boeing, which uses a large amount of carbon fiber, has been working to find ways to reuse fibers. As most high performance fibers are used with resins that are highly crosslinked, reconstitution is not a viable option without significant loss in properties. While it is possible to remove resin from composites to reclaim fibers, this typically results in damage to the fibers as well as much shorter fiber lengths than the original component. A small fraction of composites are incinerated after their use to reclaim some of the stored energy or ground to powder and used as fillers. However, incineration requires expensive scrubbers to capture particulates and poisonous gases generated during the process, and ground composites can only be used in limited applications. Further, incineration and landfilling are expensive and wasteful and may add to the existing ground, water, and air pollution. In addition, landfills are decreasing in number, making less space available to discard the waste. For example, between 1988 and 1998 the number of landfills in the United States dropped from 8,000 to 2,314, a more than 70% decline [1]. Similar situations exist in many other countries as well. Ireland, for example, declared a few years ago that they no longer had any space for landfills, and began imposing large taxes on the use and disposal of polymers [4]. Landfill space in the United Kingdom has also been steadily decreasing. In many countries, governments have taken steps to alleviate these problems by establishing laws to encourage the use of recycled and/or rapidly renewable sustainable and green products. Some governments have enforced strict “take back” laws requiring the manufacturers to take their packaging and products back after their intended use while other governments have banned use of plastic bags that do not degrade and block sewage pipes.

The growing global environmental awareness, societal concerns, high rate of depletion of petroleum resources, concept of sustainability, and new environmental regulations have triggered the search for new products and processes that are compatible with the environment. Sustainability, “cradle-to-cradle” design, industrial ecology, carbon footprint, life cycle assessment (LCA), eco-efficiency, and green chemistry are not just newly coined buzz words, but form the new principles that have been guiding the development of new generation of green and sustainable materials [5]. Composite materials are no exception to this new paradigm. Environmentally friendly, fully biodegradable reinforced

plastics, or green composite materials will undoubtedly play a major role in greening of the products in the future.

Most major manufacturers see the “green wave” coming; have plans to make their products sustainable, green, or recyclable to the maximum extent possible; and are working hard toward that goal. As a result, there have been many innovations. For example, Braskem, a large Brazilian chemical company, now manufactures green polyethylene (PE) from the 100% renewable resource, sugarcane. In the future, the company will also be producing green polypropylene (PP) from the same sustainable resource. Biodegradable polymers, such as polylactic acid (PLA), produced from corn by NatureWorks LLC, and starch based Mater-Bi,TM produced by Novamont, are becoming more affordable and hence more common. In some other polymers, one of the two chemicals from which they are synthesized may be produced sustainably, reducing their carbon footprint. For example, polyurethanes (PU) can now be produced using polyols from soybean oil, polyethylene terephthalate (PET) from ethylene glycol, and polybutylene succinate (PBS) from succinic acid. Use of such polymers in consumer goods has also been spreading fast. For example, Ford Motor Company uses soybean oil-based PU foam in many of their car seats, while PepsiCo and the Coca-Cola Company have begun using green polyethylene terephthalate (PET) for their beverage bottles. PBS is being promoted for biodegradable packaging including cosmetic bottles, disposable dinnerware, and medical articles. While this is just a tiny collection of examples, there are hundreds of large and small companies that are involved in producing and/or using green polymers and composites.

GREENER COMPOSITES

In the case of composite materials, many applications, such as secondary and tertiary structures as well as those used in consumer products for casing, packaging, furniture, housing panels, etc., do not require the high mechanical properties that advanced composites possess. Use of biodegradable, environment friendly, and renewable plant-based lignocellulosic fibers has been a natural choice for reinforcing (or filling) polymers to make them greener [5]. Availability of inexpensive plant-based fibers in every part of the world, in part, has fueled their use in the past couple of decades. These fibers offer several other advantages: they are nonabrasive to processing equipment, can be incinerated, are CO₂ neutral (when incinerated at the end of life), and because of their

hollow and cellular nature, perform well as acoustic and thermal insulators [6]. The hollow, tubular structure, in many cases, also reduces their bulk density making them light weight.

Plenty of examples can be found where plant-based fibers are used for reinforcing nondegradable thermoplastic polymers such as PP, high, medium, and low density polyethylene (HDPE, MDPE, LDPE), nylons, polyvinylchloride (PVC), and polyesters as well as thermoset resins such as epoxies and esters to produce what may be termed greener composites [7–16]. Many examples can be found in the chapters of this book as well. The bulk of commercial plant-based fiber composites that are used as inexpensive filler for PP and PVC are made using wood flour (sawdust like waste from saw mills) or wood fiber and are obtained from waste wood products such as packaging pallets, old furniture, and construction wood scraps [17]. These composites, also called plastic lumber, are commonly used in outdoor decking, railroad ties, window and door frames, automotive panels, and furniture. Sawdust, wood flour, and wood fibers/particles have also been commonly used with formaldehyde-based resins to produce particle boards, oriented strand boards, and various grades of medium density fiber boards (MDF) as inexpensive substitutes for wood.

Due to their good mechanical properties, longer plant-based fibers, extracted from the stems or leaves of plants such as abaca, bamboo, flax, henequen, hemp, jute, kenaf, pineapple, ramie, sisal, etc., are being evaluated as low cost alternative reinforcements to commonly used glass fibers to make composites. These fibers are annually renewable, as compared to wood, which takes 20–25 years to grow before it can be cut and used. Some plants, such as bamboo, grow so fast that they can be harvested every six months. As a result, their supply could be virtually endless, and clearly fall in the realm of rapidly renewable materials.

Since these so-called greener composites combine nondegradable resins with degradable fibers, at the end of their lives they can neither return to an industrial metabolism nor to a natural metabolism. Unfortunately, they cannot be food stock for either system. They can only be down-cycled (because of the inevitable property degradation associated with reprocessing) or incinerated to recover some of the stored energy.

FULLY GREEN COMPOSITES

Significant research efforts are currently being spent in developing a new class of fully biodegradable or compostable green composites by

combining natural fibers with biodegradable resins. Being in its infancy, most of the current technology is still in the research and development stage. These composites are environment friendly, fully biodegradable and sustainable: they are truly green in every sense. At the end of their life they can be easily disposed of or composted without harming the environment, completing the nature-intended life cycle. These green composites may be effectively used in many applications such as mass-produced consumer products with short life cycles of 1–2 years (non-durable) or products intended for one-time or short term (a few times) use before discarding. However, most green composites may also be used in indoor applications, with a long life of many years, just like wood.

Resins used in these green composites vary from modified starches (thermoplastic or thermoset); modified proteins obtained from beans (soy and others), animals, chitin, polyhydroxyalkanoates (PHAs), natural rubber, etc.; to some synthetic biodegradable resins such as polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), etc. These resins, when combined with natural fibers, can produce composites with acceptable mechanical properties. Further, there are developments in high strength green fibers as well. For example, liquid crystalline cellulose fibers developed at Groningen University in the Netherlands have shown tensile strength close to 2 GPa. These fibers have been used to produce advanced green composites [18,19]. There is also research in developing spider silk-like protein fibers that can have high strength and toughness. Micro- and nanofibrillated cellulose fibers (MFC/NFC) can have tensile strength between 2 and 6 GPa, and tensile modulus of over 130 GPa. These values are close to Kevlar[®] fibers. While MFC and NFC do not come in continuous fiber form, they can be easily used as reinforcement in a green resin.

This book should appeal to a broad range of academic and industrial scientists; those working in government agencies; and anyone involved in chemistry, physics, agriculture, materials science, or civil, mechanical, or manufacturing engineering and related disciplines. It will also appeal to those who deal with polymer processing, composite manufacturing, and their applications and who are interested in making composites sustainable or wish to reduce their carbon footprint through the use of biobased and biodegradable fibers and resins.

In this book we start with providing a strong case for green materials (Chapter 1, Fryer), which is based on many factors from population to security, greenhouse gas emissions to climate change, and innovations to government regulations.

A range of sustainable materials suitable for resins are explored in Chapters 2–5. Chapter 2 (Ghosh Dastidar and Netravali) presents a detailed review of biobased green resins that can be used for making films and composites. These include lignin, PHAs, pullulan, PLA, triglyceride based polymers, chitin, polycaprolactones (PCL), and PBS. Chapter 3 (Quirino and Kessler) discusses vegetable-oil-based thermoset resins, their various modifications and properties, and their composites using various fillers and reinforcing agents. Chapter 4 (Kim and Netravali) discusses the soy protein and starchbased resins, their preparation and application in green composites, and their properties. Chapter 5 (Lyons) explores sustainable additives that can be used in polymeric materials to enhance the performance characteristics of resins, and introduces new uses and applications.

Different sustainable fibers suitable for composite applications are explored in Chapters 6 and 7. Chapter 6 (Kozen and Netravali) presents a brief review of the natural cellulosic fibers, their origins, properties, and applications. Chapter 7 (George and Bogash) provides the history of feathers in textile applications. While feathers have been used in textile products as cushioning and warmth, most are disposed of as waste. With the successful invention of separating the fibers from quill, it has been possible to use these fibers in many other applications, particularly composites.

Combinations of sustainable fibers and resins to produce green composites are explored in Chapters 8–12, including discussion of manufacturing processes. Chapter 8 (Nyambo, Nagarajan, Mohanty and Misra) presents an overview of natural fiber composites from agricultural by-products. The chapter covers issues such as fiber supply and economics to composites produced. It also deals with the fiber surface modification needed to control the fiber/resin adhesion and compatibilization, polymer matrices for natural fiber composites, and mechanical characterization. Chapter 9 (Rane) explores polysaccharide composites formed from a combination of cellulose fiber and chitosan resin. Chapter 10 (Fujii) provides detailed discussion of bamboo fiber varieties and their processing and properties. Various applications of bamboo composites are also provided. Chapter 11 (Billington, Srubar, Michel and Miller) discusses applications of biobased composites for civil engineering applications. The manufacturing of building materials used in construction accounts for nearly 13% of the national energy demand and contributes significantly to global greenhouse gas emissions, accounting for 38% of all CO₂ emissions. The chapter discusses how biobased composites

can be designed to change this scenario. Chapter 12 (Rao, Jayaraman and Bhattacharyya) discusses in detail the current methods of fabricating composites panels with a hollow core (honeycomb), their fracture behavior, and various ways of improving the properties.

Chapter 13 (Rostami) introduces the use of a waste material—alkali activated ash materials—that can be used for structural applications and has performance-meeting (or often exceeding) concrete for building applications.

An understanding of the mechanical properties of sustainable composites and how to predict them, and an understanding of the manufacturing process of sustainable composites are presented in chapters 14 and 15. Chapter 14 (Gowayed and Shady) presents methodologies for predicting and understanding the mechanical properties of fiber composites with an emphasis on natural materials. These techniques are applicable to traditional composites as well as sustainable composites, and provide an excellent framework for more advanced study such as presented in the Chapter 15 (Phoenix and Bai), which discusses the stochastic processes in modeling of fiber reinforced composites. Even when the synthetic fibers have been produced using the same process, the flaw distribution varies from fiber to fiber. As a result of this variation, when under stress, the fibers break at different locations and at different stresses. The chapter discusses the key features of composite tensile strength behavior models that have been developed in the past 50 years. These models also apply to natural fiber based green composites. Natural fibers, however, have significantly higher variability in strength and diameters. They also tend to be fibrillar, unlike carbon or glass, making it even more difficult to predict their properties. Never the less, similar models can be used for natural fiber based composites.

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The Future of Green Materials

ROBERT FRYER

INTRODUCTION

IT is possible to observe today a pattern that has become quite common, that is, climate scientists are identifying global climate change thresholds while decision makers do not seem to be concerned. There is little discussion in the materials manufacturing domain that ties together these thresholds into a meaningful long term analysis of implications for the future of the industry. However, by using a conventional forecasting method, it is possible to highlight convergent implications that may occur in the near future, although no forecasting method is perfect. In the near future, products and materials will be better for the environment, and manufacturers will increase market share as long as their actions and decisions appropriately account for the unprecedented changes that lie ahead.

According to climate scientists, greenhouse gas (GHG) emissions are predicted to increase at a time when they should be decreasing to avoid irreversible climate change. Interestingly, British Petroleum (BP) agrees. “A wake-up call” is how Bob Dudley, Group Chief Executive of BP reacts to the company’s most recent Energy Outlook report (British Petroleum, 2011). Although this reaction could be perceived cynically as a good PR message for the company since the oil spill in the Gulf of Mexico in 2010, Mr. Dudley’s message does reasonably take into account credible sources predicting a very different future than the past 50 years. Although this message may not be what other CEOs are telling their shareholders, BP’s message more fully accounts for climate ex-

perts' warnings, which result in a more robust report for its shareholders. The projections of GHG emissions in the report are large at a growth of 27% by 2030 (British Petroleum, 2011). This is more than other experts had predicted, such as the U.S. Energy Information Administration's (EIA) 15.6% by 2035 (U.S. Energy Administration, 2011). However, another industry report also concludes that higher emissions can be expected. Exxon/Mobil's report states, "In total, global Carbon Dioxide emissions are likely to increase about 25 percent from 2005 to 2030" (Exxon/Mobil 2010).

Decision makers look to these three reports for guidance, including those in the materials manufacturing sector. Despite the disagreement between the oil companies' reports and the government's, all three reports agree that GHG emissions are only going to increase. Furthermore, this is occurring in the same time frame that climate scientists are warning of crossing irreversible thresholds if GHG emissions are not reduced.

Not Acting in Time to Avoid Climate Change Triggers

It is becoming more likely that humans will not be able to avoid triggering the climate change thresholds. The thresholds that are at risk of being crossed are the acceptable concentrations of GHG in the atmosphere (350 ppm) and the warming that such concentrations may cause (2°C). Although the 350ppm threshold is already crossed (current CO₂ concentrations are over 390 ppm), what matters is how long this violation is sustained. But this does not seem to bother many because of the common cultural inheritance among industry decision makers, scientists, and engineers that human ingenuity and technology will solve humanity's problems. This makes it more difficult to argue for immediate conservation actions. Such actions from their perspective are unwarranted and hold large downsides, such as economic contraction. Others argue that waiting for technology to solve the problem is wishful thinking and that time is running out while waiting for innovations or government action.

It's likely that the time required to innovate to avoid high-risk domains is not available. The longer the concentration of CO₂ remains above the climate trigger thresholds, the more difficult and costly it will be for industry and governments to change course away from catastrophic events and their associated destruction. This is especially true given that the impact of CO₂ and other GHGs are compounded by

slower feedback loops that are more difficult to model and thus project into the future.

Fossil Fuels and Building Materials

Most building materials are made using petroleum or contain petroleum themselves. This causes two financial challenges for the building material industry. First, the cost of materials fluctuates with the cost of oil. Second, the combustion of petroleum releases GHGs into the atmosphere contributing to global climate change, which has direct and indirect financial costs associated with it. The climate threshold triggers are being approached by the GHG emissions associated with the use of petroleum and other fossil fuels. Therefore, building material extraction, transportation, manufacturing, and installation are contributing directly to climate change.

There is a correlation between the cost of fuels (including petroleum and natural gas) and building materials, as well as supply chain disruption (Brooks 2010). The material/fuel cost correlation is a result of the embodied energy in materials. The U.S. Bureau of Labor Statistics (2011) tracks the costs of building materials, and the prices in 2011 are increasing. Edie Ousley, public affairs director for the Florida Home Builders Association said in an interview that, “In January, those measures jumped 1 percent for December and they are saying the chief contributors for that are lumber, fuel prices, plumbing fixtures and copper products” (Brooks 2010).

The Commendable, yet Insufficient, Actions Taken by the Best Material Manufacturers

For two consecutive years, the US Department of Energy (DoE) selected CertainTeed for outstanding environmental stewardship actions. The buildings materials manufacturer was selected for improving efficiency in several of its plants, which translated to less consumption of fossil fuels in its manufacturing processes (EPA 2009). It also was singled out for its efforts at reducing carbon emissions by using rail lines to transport goods (CertainTeed 2010).

Assuming that these awards are based on merit, and this paper does not argue otherwise, then it is reasonable to conclude that CertainTeed’s efforts are the best in the industry, and that the rest of the industry, although parts of it may be making efforts, simply are not achieving as much. If that is the case, the actions of the industry are simply not at

a scale to make a significant difference, and are not as urgent as other, reputable sources indicate the problem to be. Most important of these is the climate change thresholds that predict how much average global temperature change will occur from a specific concentration of GHGs in the atmosphere, the most abundant of which is CO₂.

The Unfortunate Need to Make Future Predictions

There does not seem to be much evidence that the materials manufacturing industry is connecting the dots between several driving forces, and yet it is essential because the potential impact is very significant. This chapter seeks to connect these dots to present a picture that demonstrates the large downside inaction implies. To do so, unfortunately, requires forecasting into the future. This is an endeavor that is not easy to undertake, simply because it is so difficult to do, and so easy to get wrong. However, forecasting is a common method to plan for future contingencies. It is possible to use tools to improve forecasts, even though they remain highly unstable and imperfect. As President Eisenhower said, "I have always found that plans are useless, but planning is indispensable." This paper applies scenario planning, a common forecasting method, in the pursuit of a more robust, clear, and accurate look into the future of green building materials.

CONTEXT

This chapter investigates building materials only. Although there are other sectors within material manufacturing, as well as other sectors that are affected by the dynamics and driving forces discussed, they fall beyond the boundaries of this paper. Building materials will be investigated and future projections made in order for the materials engineer to understand how green materials may be different in the future from what he/she currently expects, in the hopes that the engineer will be better prepared.

Unprecedented Conditions

It is often said that the next 20 years are going to be very different than the past 20 years. Studies seem to confirm this. Among the unprecedented conditions converging simultaneously between now and midcentury are:

1. The number of humans living in cities outnumbers those outside of cities for the first time in history and this number will increase
2. The asymmetric power of the few to impact the security of the many
3. The amount of known energy resources at or near peak production and the rate of new discoveries has already passed peak
4. GHG emissions cause the climate to change and these emissions will only increase
5. Building regulations already require resource efficient materials and these requirements will become more strict and stringent

The Population of Cities

The United Nations State of World Cities Report 2008/2009 states that for the first time in human history more people are living within urban areas than outside. The rate of this change is nonlinear, and by 2050 projected population distribution will be 70% of humans living in cities (UN-Habitat 2008). Moreover, the projected total urban population in 2050 will be 6.4 billion, roughly the *total* global population in 2011, which is approximately 6.9 billion (U.S. Census Bureau 2011).

The form that these large, dense cities will take is important to note. The UN report defines cities with a population of 10 million or greater as “megacities”—and notes that currently, Asia has the most, the United States has two, while Europe has none. Megacities will grow into “city regions” by attaching adjacent areas onto each other. In the areas with highest projected growth rates, this method of “attachment” is mostly by slum formation (UN-Habitat 2008). This is already seen in the development of Hong Kong-Shenzhen-Guangzhou region in China. Its population is 120 million, which is roughly 40% of the entire U.S. population, or 15 times the population of New York City.

There are unique consequences of this unprecedented and rapid redistribution and growth of humans. First, the location of these cities is exposed to other risks. For example, a majority of them are located along coastlines. “The projected rise in sea levels [as a result of climate change] could result in catastrophic flooding of coastal cities. Thirteen of the world’s 20 megacities are situated along coastlines. Coastal cities that serve as ports are a vital component of the global economy . . . A recent study by the Organisation for Economic Cooperation and Development (OECD) found that the populations of Mumbai, Guang-

zhou, Shanghai, Miami, Ho Chi Minh City, Kolkata, New York City, Osaka-Kobe, Alexandria, and New Orleans will be most exposed to surge induced flooding in the event of sea level rise. By 2070, urban populations in cities in river deltas, which already experience high risk of flooding, such as Dhaka, Kolkata, Rangoon, and Hai Phong, will join the group of most exposed populations” (UN-Habitat 2008).

Second, the pressures and challenges of so many people living so closely together will have their own challenges, regardless of geography. Some challenges may exacerbate known issues that can be addressed by current technology, such as noise, privacy, and thermal comfort. But it is also conceivable (and likely) that high levels of human density could also create challenges which overwhelm existing technology, such as sanitation and spread of disease. Innovative solutions, including the design of materials, can address these issues. “By identifying the particular deprivation that is prevalent in slums, governments and local authorities can focus public resources for the improvement of slums more effectively. In the case of Benin, for instance, targeted investments in sanitation facilities in slums could easily elevate a quarter of the slum households to nonslum status” (UN-Habitata 2008).

Security

Since the events of Sept. 11, 2001, the awareness of security threats from nonstate actors has reached the global mainstream population. However, it is also a concern of governments and militaries, impacting decisions both globally and in the U.S. government. In a report from 2007 prepared for the U.S. Congress by the Congressional Research Council, the possible threats are “unlimited,” but the report also points out that threat analysis often “leads to far more potential attack scenarios than likely ones” (Parformak and Frittelli 2007).

Security is a concern to material manufacturers because it depends on globally sourced raw materials, energy, and supply chains. Global operations rely on very efficient and sophisticated networks of commerce and trade. However, a side effect of the well-developed efficiency that makes global commerce and trade so successful is system fragility and infrastructure vulnerability to cascading failure that can be triggered by sabotage, open source warfare, and other forms of intentional systems disruption. It is this very quality of any global operation that makes it such a good target for those who wish to alter the status quo.

Regardless of the ability to detect the likely threats, the number of

“terrorist” attacks has increased, especially ones meant to disrupt key systems supplies, such as petroleum and natural gas. For example, a recent news report states that “Attacks have been growing exponentially since 2007 as young Somalis in small skiffs with AK-47s and rocket propelled grenades took to the water is [sic] to seek their fortunes . . . despite a growing presence from international navies, they have since pushed further into the Indian Ocean, rendering the entire region a ‘war risk zone’ in the eyes of insurers” (Saul and Maltezou 2011). Additionally, there seems to be little in the way of progress in how large militaries are able to adjust strategy or tactics to defeat such open source warfare. “ ‘The situation is only going to worsen,’ says John Drake, a senior risk consultant for London-based security firm AKE. ‘With rising ransoms, pirates are able to hire more men, bribe more officials and wait longer periods to negotiate’ ” (Saul and Maltezou 2011). The increased rate of occurrences combined with an inability to stop them, does not look good.

These disruptions are typically executed by nonstate, leaderless organizations with the intent to compromise the legitimacy of states (Robb 2010b). For example, the attacks in Nigeria by MEND are targeted at weakening the Nigerian government by attacking petroleum manufacturing facilities and assets in the Niger Delta (Robb 2010a). In fact, the frequency and effectiveness of attacks in Nigeria have grown to the point that Dutch Royal Shell is “capitulating,” according to the Wall Street Journal, and “is seeking buyers for 10 of its Nigerian onshore oil-production assets following years of militant attacks on its facilities that have squeezed the company’s profit” (Swartz 2009).

Another target for attacks of systems disruption is along busy shipping lanes. Because of the nature of the geography around the major petroleum shipping lanes, the tankers are vulnerable to attacks. This makes system disruption easier, and more likely. One such shipping lane is the Malacca Strait in south east Asia. Threats there are on the rise, too. “Singapore’s Navy warned that a terrorist group is planning attacks on oil tankers in the Malacca Strait, one of the world’s busiest shipping lanes” (CBS News 2010).

This is also occurring in Columbia with FARC, and there, the victim is the environment. “A presumed FARC attack on an oil pipeline in the southern Colombian Nariño department is causing an environmental emergency as crude oil spills into two local rivers” (Begg 2010).

The term for this type of leaderless, organized attacks is “open source warfare.” An expert in the field, and author of *Brave New War*, John

Robb reports that al Qaeda has made this its organizational goal. “Earlier this year, al Qaeda formally announced that it had adopted open source warfare (a new, extremely potent theory of 21st Century warfare that makes it possible for a large number of small autonomous groups to defeat much larger enemies) as its preferred method of conducting its insurgency against the west” (Robb 2010b).

The trend of the frequency and sophistication of attacks is increasing. This poses the real and “likely” phenomenon of inconsistent oil and natural gas supplies in the future. Combining this with the likelihood of reaching peak oil soon seems to suggest that future energy supplies will need to be sourced more locally and from more diverse sources. This will have a direct impact on the global economy, including materials manufacturers and engineers.

Energy Resources, Production, and the Rate of New Discoveries

Although the threat from open source warfare does not register very high with many manufacturers, the threat from peak oil is more of a general concern. However, even this is debated and pushed aside. But, there is mounting evidence that this is an immanent problem for the global economy and manufacturers.

Several sources are pointing to the time between 2012 and 2020 as the point at which oil production will peak. In 2009 the chief economist of the International Energy Agency (IEA), an authority that most governments rely on for information regarding energy, was interviewed by the UK newspaper *The Independent*. The interview states, “Dr. Birol said that the public and many governments appeared to be oblivious to the fact that the oil on which modern civilisation depends is running out far faster than previously predicted and that global production is likely to peak in about 10 years—at least a decade earlier than most governments had estimated” (Connor 2009). Dr. Birol is most famously quoted as saying “we have to leave oil before oil leaves us” and he adds, “The earlier we start, the better, because all of our economic and social system is based on oil, so to change from that will take a lot of time.

Additionally, new discoveries peaked several decades ago, as Figure 1.1 shows. New discoveries are still being made, but they are too small to provide any significant effect on global reserves or prices. Mainstream media reports of the discoveries are often misleading, too. In early June 2011, Exxon Mobil reported a discovery of roughly 700 million barrels of oil equivalent in the Gulf of Mexico. The Wall Street

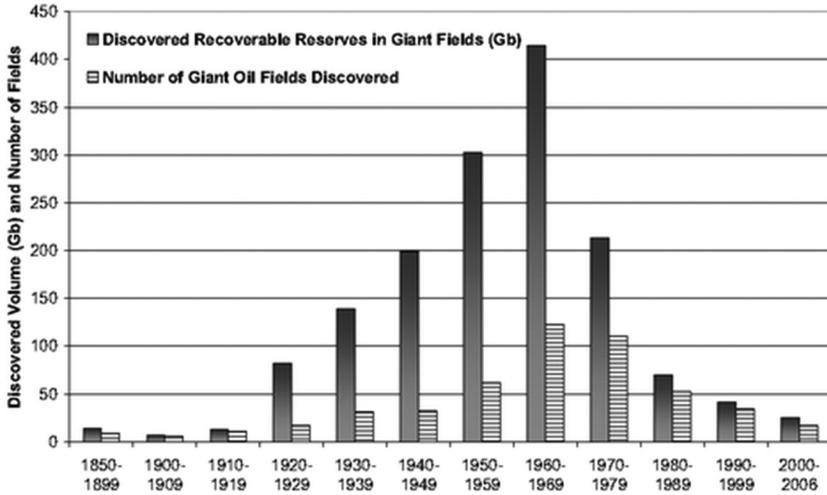


FIGURE 1.1. Rate of oil discoveries in decline (Robelius 2007).

Journal headline for this discovery read, “Exxon Unveils Big Finds in Gulf”. However, according to Dr. Joe Romm this discovery, “represents only 9 days of global oil consumption.” Despite the recent increase in domestic oil production in the United States, the EIA found that “there is no impact on U.S. gasoline prices whatsoever in 2020. Gasoline prices would be a mere three cents a gallon lower in 2030” (Romm 2011).

Another source points to 2012 as when the world would reach peak oil. The infamous Wikileaks recently released diplomatic cables which lead to the arrest of the organization’s head, Julian Assange. *The Guardian* broke the news of specific cables in which Sadad al-Husseini, a geologist and former head of exploration at the Saudi oil monopoly Aramco, states that Saudi Arabia’s oil reserves are likely overestimated by 40%. “According to the cables, which date between 2007–09, Husseini said Saudi Arabia might reach an output of 12 million barrels a day in 10 years but before then—possibly as early as 2012—global oil production would have hit its highest point” (Vidal 2011).

Although some are suggesting these cables are unreliable, others have noted that since this public disclosure of confidential communications the price of oil has not fluctuated. This is curious to many observers, since news of this nature often results in some effect on the commodity’s highly volatile price. “The story has gotten a lot of attention, but prices haven’t risen, which suggests that experts already knew this (and indeed, people have been speculating about such an overstatement for at least four years). It’s actually kind of interesting to note that early

takes on a potential reserve overstatement date to 2007, which is when oil prices began rising at a faster pace. Saudi Arabia has about a fifth of known oil reserves, so a revision in its holdings of this magnitude is significant” (The Economist 2011).

Although the White House and the U.S. Congress are slow to move on the threat posed by peak oil, the U.S. military is not. *The Guardian* reports that in the Joint Operating Environment report from the US Joint Forces Command it states “By 2012, surplus oil production capacity could entirely disappear, and as early as 2015, the shortfall in output could reach nearly 10 million barrels per day” (Macalister 2010).

Peak oil will result in less supply and higher prices for oil. Many building materials are based on oil, and rely on petrol, diesel, and gasoline to deliver the products from all over the world to the end-use construction site. One impact that peak oil will have on the building material sector is the need to ship the raw ingredients, energy, and final product shorter distances. In fact, Jeff Rubin, former head of the CIBC and who was “named Canada’s top economist on ten separate occasions” argues this very point (McMullen 2009). “Competitive advantage used to be a one equation mode: find the lowest wage rate; and now it’s a more complex equation; distance costs money. The physical separation from producer to market . . . that starts to become a bigger factor,” says Rubin (Mackenzie 2009).

The Impact of GHG Emissions

Another major threat to the building materials sector is GHG emissions. Not only could this lead to materials and energy disruption, but also to climate change, which has the potential to negatively impact much more than just the economy.

Since the Kyoto Protocol, governments have been trying to find a way to reduce carbon emissions. However, the trend in emissions is heading the other way. As already discussed in the introduction, three reports that many companies and governments look to for guidance are the energy outlook reports from the EIA, BP, and Exxon Mobil. These reports seem to “one up” each other by projecting carbon emission increases that are more than the other. However, they all agree that emissions will increase at the time scientists are warning about climate threshold triggers and the need to stabilize or decrease emissions.

Climate scientists commonly discuss the impact of GHG concentrations in the atmosphere along with the projected increase in average

global temperatures that these concentrations cause. These numbers are adjusted over time to reflect current results of simulations and improved understanding of the very complex nature of climate science. The concentrations and associated temperatures can be thought of as “triggers” that once reached are irreversible and catastrophic climate change follows.

As the values of the triggers are adjusted over time, they are converging on the current values of GHG concentrations in the atmosphere—and even exceeding those values in the case of CO₂ concentrations. This means that our evolving understanding of climate change is making it more likely that we are at, or near, the undesirable condition of triggering these irreversible thresholds.

Dr. Joe Romm, a respected environmental policy expert and former Acting Assistant Secretary of Energy for Energy Efficiency and Renewable Energy during the Clinton Administration, writes at *Climate Progress*,

Three years ago, Hansen (and others) argued in *Science* that [due to fast feedbacks], we would warm another “0.6°C without further change of atmospheric composition” [i.e. with no more CO₂ emissions]. Now he’s saying “Warming ‘in the pipeline’, most due to slow feedbacks, is now about 2°C.” So the paper concludes:

An initial 350 ppm CO₂ target may be achievable by phasing out coal use except where CO₂ is captured and adopting agricultural and forestry practices that sequester carbon. If the present overshoot of this target CO₂ is not brief, there is a possibility of seeding irreversible catastrophic effects. (2008)

Relying on one person—or a few—who make this prediction may seem short on evidence, but Dr. James Hansen heads the NASA Goddard Institute for Space Studies, has a proven track record. His testimony to congress in 1988 is seen as a major milestone in raising awareness of climate change. Since then, he has worked to refine climate models.

It is important to acknowledge that other scientists do not agree, and that part of the scientific community believes the GHG concentrations can go higher before triggering a threshold change. However, these higher levels do not account for slower feedbacks into the climate dynamics. Instead, those arguing for higher GHG concentrations are looking at only fast feedbacks (such as the lifespan of CO₂ in water vapor) (Hansen 2007).

Again, Dr. Romm writes, “Now Hansen has a draft article that looks at both current climate forcings and the paleoclimate record to conclude

Cellulosic Fibers: A Brief Review

FRANCES H. KOZEN and ANIL N. NETRAVALI

ABSTRACT

CELLULOSIC FIBERS suitable for textile application can be obtained not only from the seeds, stems, and leaves, but even from the roots of the plants. Usable staple fibers are obtained from a wide variety of plants globally, with some grown and traded internationally, while many others are grown and used in localized areas. Readers will find throughout this chapter that many of these fibers are now being used as sustainable reinforcing components in composites. Use of plant fibers in composites has grown rapidly in the past few years and will continue to grow as the sustainability issue grows larger. This chapter briefly discusses some of the most common cellulose fibers and their characteristics. Table 6.1 groups natural cellulosic fibers by their source, i.e., seed pod, stem (bast), leaf, fruit husk, grass, or agricultural stalks. Table 6.2 lists the primary cultivation locations and global cultivation figures for many natural cellulosic fibers.

Plant fibers are referred to as natural cellulosic or lignocellulosic fibers. They are composed largely of cellulose, the most abundant linear natural polymer made by polymerizing thousands of glucose units. Natural cellulosic fibers contain varying amounts of other compounds, including an insoluble complex polymeric material called lignin, polysaccharides such as hemicelluloses and pectin, and small amounts of

TABLE 6.1. Plant Fiber Sources.

| Seed | Bast (Stem) or Soft | Leaf or Hard | Grass | Fruit | Agricultural By-products |
|---|---|--|---|--|---|
| Cotton (Gossypium) | Jute (<i>Corchorus capsularis</i> and <i>Corchoris olitorius</i>) | Abaca or Manila Hemp (<i>Musa textilis</i>) Banana (<i>Musa acuminata</i> or <i>balbisiana</i>) | Bamboo (<i>Bambuseae</i>) | Coir or coconut husk (<i>Cocos nucifera</i>) | Sugar cane bagasse (<i>Saccharum</i>) |
| Kapok or silk cotton (<i>Ceiba pentandra</i>) | Flax (<i>Linum utatissimum</i>) | Agave <ul style="list-style-type: none"> • Sisal (<i>A. sisalana</i>) • Henequen or Mexican sisal (<i>A. fourcroydes</i>) • Istle, Ixtle, Tampico (<i>A. lecheguilla</i>) • Cantala or Maguey (<i>A. cantala</i>) • Letona, Salvador hemp (<i>A. letonae</i>) • Pita (<i>A. Americana</i>) • Haiti hemp (<i>A. foetida</i>) | Miscanthus, Chinese silver grass, elephant grass (<i>Miscanthus sinensis</i>) | | Rice straw |

(continued)

TABLE 6.1 (continued). Plant Fiber Sources.

| Seed | Bast (Stem) or Soft | Leaf or Hard | Grass | Fruit | Agricultural By-products |
|---|---|---|---|--------------|---------------------------------|
| | Kenaf (<i>Hibiscus cannabinus</i>) Roselle (<i>H.sabdariffa</i>) Meshta (<i>H.cannabinus</i>) | Pineapple, piña (<i>Ananas comosus</i>) Curaua (<i>Ananas erectifolius</i>) | Switchgrass (<i>Panicum virgatum</i>) | | Corn stalks |
| | Ramie, China grass, rhea (<i>Boehmeria nivea</i>) | Fique, Cabuya, Pitiera, Maguey, (<i>Furcraea macrophylla</i>) Mauritius Hemp (<i>F. gigantea</i>) | Alfa, Esparto, (<i>Stippa tenacissima</i>) | | Wheat straw |
| | Hemp (<i>Cannabis sativa</i>) | Phorium, New Zealand flax, Harakeke (<i>Phormium tenax</i>) | Indian Grass (<i>Sorghastrum nutans</i>) | | Soybean straw |
| Milkweed or vegetable silk (<i>Asclepias</i>) | Sunn Hemp (<i>Crotalaria juncea</i>) Aramina, Urena, Congo Jute, Cadillo, Caesaarweed (<i>Urena lobata</i>) Nettle (<i>Urticaceae</i>) Abutilon, Chinese jute, Velvet leaf, Indian mallow (<i>Abutilon theophrasti</i>) Apocynum (<i>Apocynum venetum</i>) Milkweed (<i>Asclepias</i>) | Caroa (<i>Neoglazovia variegata</i>) Sansevieria, Bowstring hemp (<i>Sansevieria</i>) | | | |

TABLE 6.2. Global Production of Selected Fiber Plants.

| Fiber | Major Cultivation Locations | Estimates of Global Cultivation (Tonnes) |
|---------------------------------------|--|---|
| Abaca and Banana | Philippines, Ecuador | 106,004 ^a |
| Albutilon | China | |
| Apocynum | China | |
| Agave (other than sisal and henequen) | Mexico, Nicaragua | 12,000 ^b |
| Bamboo | China | |
| Caroa | Brazil | |
| Coir | India, Sri Lanka, China | 1,103,000 ^a |
| Cotton | China, United States, India, Pakistan | 26,102,935 ^a |
| Curaua | Brazil, Philippines | |
| Fique (Cabuya) | Colombia | 22,200 ^b |
| Mauritius hemp (Piteira) | Mauritius, Madagascar | |
| Flax | France, China, Belarus, Russian Federation | 315,084 ^a |
| Hemp | China, Korea, Netherlands, Chile | 81,964 ^a |
| Jute | India, Bangladesh | 3,181,900 ^a |
| Kapok | Indonesia, Thailand | 99,000 ^a |
| Kenaf and Roselle | China, India, Thailand | 278,600 ^b |
| Nettle | India, Nepal, United Kingdom, Germany | |
| Phormium | New Zealand | 2,300 ^b |
| Pineapple | Philippines, Taiwan, India | 128,782 ^a |
| Ramie | China | |
| Sisal and Henequen | Brazil, Tanzania, Kenya, Mexico | 257,400 ^b |
| Sunn Hemp | India, Bangladesh, Brazil | |
| Urena (Congo Jute, Cadillo, Aramina) | Cuba, Madagascar, Nigeria | |

^aFood and Agriculture Organization of the United Nations (2013).

^bFood and Agriculture Organization of the United Nations (2012).

waxes, ash, and silica. Table 6.3 breaks down the chemical composition, i.e., the percentage of cellulose, hemicellulose, and lignin, of the more common natural cellulosic fibers.

Cellulose molecules typically display a high degree of polymerization, and being linear, can easily be oriented and crystallized. In plants, molecules are generally oriented longitudinally although they can be aligned along the fiber axis or in other patterns unique to certain plants. Very commonly, molecules are organized into very fine fiber-like struc-

tures known as nanofibrils. Many nanofibrils organize together to form microfibrils and microfibrils organize together as fibers. Because of high crystallinity, strong intermolecular hydrogen bonding, and a stiff polymeric chain, natural cellulosic fibers tend to be strong and stiff. They share certain common properties: high moisture absorbency, low resilience, high density, the ability to withstand high temperatures, flammability, electrical conductivity, susceptibility to damage by strong mineral acids, resistance to damage by alkalis, and susceptibility to

TABLE 6.3. Chemical Composition of Selected Plant Fibers.

| Fiber Type | Cellulose wt.% | Hemicellulose wt.% | Lignin wt.% | Reference |
|---------------|----------------|--------------------|-------------|------------------|
| Abaca/Banana | 55–64 | 18–23 | 5–18 | Vaughn (2011) |
| Abutilon | 67–71 | | 17 | Reddy (2008) |
| Agave | 43–78 | 10–13 | 4–12 | Mwaikambo (2006) |
| Alfa | 45 | 25 | 23 | Paiva (2007) |
| Apocynum | 55–58 | | | Wang (2009) |
| Bagasse | 32–48 | 21 | 20–24 | Mwaikambo (2006) |
| Bamboo | 74 | 12 | 10 | Yueping (2010) |
| Caroa | 35 | 18 | 30 | D'Almeida (2008) |
| Coir | 46 | 0.3 | 45 | Mwaikambo (2006) |
| Corn Stalk | 81 | | 8 | Reddy (2006) |
| Cotton | 82–96 | 2–6 | 0.05–1 | Mwaikambo (2006) |
| Curaua | 71–74 | 10 | 8–11 | Silva (2008) |
| Fique | 63 | | 15 | Gañan (2002) |
| Flax | 60–81 | 14–19 | 2–3 | Mwaikambo (2006) |
| Hemp | 70–92 | 18–22 | 3–5 | Mwaikambo (2006) |
| Jute | 51–84 | 12–20 | 5–13 | Mwaikambo (2006) |
| Kapok | 43 | 32 | 15 | Mark (1986) |
| Kenaf | 44–57 | 21 | 15–19 | Mwaikambo (2006) |
| Milkweed | 73–76 | | 3–5 | Reddy (2009) |
| Miscanthus | 39–44 | | 27–29 | Ververis (2004) |
| Nettle | 65–86 | 2–12 | 1.6–4 | Bacci (2010) |
| Phormium | 67 | 30 | 11 | Mwaikambo (2006) |
| Pineapple | 80–81 | 16–19 | 5–12 | Mwaikambo (2006) |
| Ramie | 76 | 15 | 0.7 | Mark (1986) |
| Rice straw | 64 | | 8 | Reddy (2006) |
| Soybean straw | 84 | | 12 | Reddy (2006) |
| Sunn hemp | 78 | 3.6 | 4 | Chaudhury (1978) |
| Switchgrass | 61–68 | | 9 | Reddy (2007) |
| Wheat straw | 65 | | 9 | Reddy (2006) |

damage by micro-organisms and insects. The chemical and physical properties of natural cellulosic fibers can vary considerably from year to year based on plant variety, growing conditions, and geographic regions.

Plant fibers are termed staple fibers because they occur in finite lengths. Their lengths, depending on the plant type, may vary from just a few millimeters to a couple of meters. Data on lengths of ultimate fibers, or the smallest fibrillar units, is given along with other physical and mechanical properties in Table 6.4.

SEED POD FIBERS

Seed pod fibers are attached to individual seeds within a pod which opens when the seeds mature. The fibers help the seeds disperse in the wind and provide and retain moisture needed for sprouting the seed. Each fiber is a single cell, or ultimate fiber. Cotton is the most familiar seed pod fiber, although many others have been harvested globally for local use.

Cotton

Cotton is the single most widely grown and used plant fiber in the world. It is cultivated in more than 80 countries globally, with China, Brazil, India, Pakistan, the United States, and Uzbekistan accounting for more than 80% of the approximately 23 million tons of cotton grown annually (FAO 2009). Cotton thrives in temperate to hot climates, with a minimum temperature of 21°C, and adequate rainfall or irrigation. Plant breeders work to engineer cotton to increase resistance to disease, insects, fungi, and common herbicides as well as to obtain cottons with natural colors.

Four species of the cotton genus *Gossypium* are widely cultivated for fiber. The most important commercially is *Gossypium hirsutum*, of Mexican origin, and known as upland cotton, which accounts for nearly 90% of the world's cotton. It is of medium staple (22–32 mm) length. About 5% of cultivated cotton is *Gossypium barbadense*, originally from Peru, and termed long-staple cotton (33–65 mm). This is considered premium textile cotton, and may be termed Pima, Supima, Egyptian, or Sea Island. Short-staple cottons, *Gossypium arboreum* and *Gossypium herbaceum*, grown primarily in India and Africa, make up

Polysaccharide Composites

YATINKUMAR N. RANE

INTRODUCTION

Composite Materials: A Brief Overview

A typical composite could be described as a structural material that consists of a suitable combination of at least two insoluble constituents: a reinforcing material and a matrix material. The reinforcing material could be in various forms such as fine particles, fibers, yarns, fabric, etc., while the matrix material is generally monolithic; the majority of the reinforcing materials are polymeric based, although ceramics and metals are used for high performance applications. The reinforcing material is embedded into the matrix, which supports and maintains its relative position. If a load is applied to the composite, it is carried by the reinforcing material and is distributed by the matrix material.

It is necessary that the reinforcing material should possess good physical and mechanical properties for the resulting composite to be stronger. The matrix material should be able to mold into appropriate shapes and sizes for the desired end use. If a failure begins to occur in the composite, the reinforcing material will try to oppose it by distributing stresses throughout the matrix material. In contrast, a similar failure in a monolithic material such as metal tends to be localized and difficult to repair.

Composite materials exist in nature. An example of a naturally found composite is wood, in which cellulosic fibers are reinforced in a lignin matrix. One of the more common human-made composites is concrete in which gravel and other aggregates are added to cement that increases its compressive strength for construction application. Sometimes concrete has an additional “composite” hierarchy in construction, which is accomplished by incorporating metal rods (rebar) to increase tensile response.

The synergism produced by distinct constituents allow the production of lightweight materials having high strength and stiffness that find applications in many fields including industrial and high performance uses. Composite materials have been used for thousands of years for a variety of structural and nonstructural applications such as in sinew backed bows and straw/clay (bricks) building materials. The development of modern composites was dramatically advanced by the accidental discovery of fiberglass in 1930 by an engineer while he was lettering a glass bottle. Dr. Games Slayter, also known as the Father of Fiberglass, patented this material in 1933 (heartlandscience.org).

Conventionally used reinforcing and matrix materials are petroleum-based, and recycling such materials is very difficult; the majority of products eventually end up in landfills or are incinerated (Wollerdorfer and Bader 1998). Shafiee and Topal (2009) reviewed consumption and accelerated depletion of fossil fuel reservoirs using various mathematical models. According to their calculations, depletion time for oil, gas, and coal are approximately 35, 37, and 107 years, respectively. During the manufacturing and decomposing of petroleum-based products, large amounts of carbon dioxide are released into the atmosphere resulting in an increase in the greenhouse effect (Marsh 2003). Hence, it seems prudent to explore alternative sources of energy and methods of reducing energy consumption. Industrial ecology, sustainability, and new environmental regulations (Mohanty *et al.* 2002; Marsh 2003) have induced a search for new resources, processes, and products.

Polysaccharides

Polysaccharides are environmentally friendly and are abundantly available natural, renewable resources. They have been used for many years in the basic needs of human beings such as food (starch), clothing (cotton, flax, jute), and shelter (wood) (Shen and Patel 2008).

There are various theories about the origin of life on the earth; most

TABLE 9.1. Worldwide Production of Polysaccharide Products.

| Polysaccharide Materials | Global Production | Production EU | Production U.S. |
|--------------------------|-------------------|---------------|-----------------|
| Man-made cellulose fiber | 2,700–3,300 kton | 416 kton | 46 kton |
| Starch polymers | 40 kton | 30 kton | 10 kton |
| Natural fiber composites | n/a | 51 kton | n/a |
| Wood plastic composites | 720 kton | 65 kton | 655 kton |

prominent is the Primordial Soup Theory. In this theory, polysaccharides must be present, which had enhanced the costability and reduced the separation of nucleic acids and proteins (Tolstoguzov 2003, 2004). Thus, it can be said that polysaccharides were the first biopolymers on the earth. Table 9.1 gives details about bulk polysaccharide material production (Shen and Patel 2008).

Polysaccharides are comprised of a chain of monosaccharide repeating units joined by glycosidic linkages. Various plant and animal biological systems contain polysaccharides and hence, usually their properties, like degree of polymerization and molecular weight, is in a range rather than a specific number. The polysaccharides can be classified in different ways; depending on origin or source they can be classified according to their molecular shape, molecular structure, electrostatic charge, and rheological properties (Huber *et al.* 2006).

Polysaccharides (*saccharum* in Latin means sugar) are basically one or more sugar units in linear or branched fashion. Chemical structure gives ideas about properties and possible applications. Classification of polysaccharides based on structure can be done in two types, homopolysaccharides and heteropolysaccharides. Homopolysaccharides are comprised of a single sugar unit in the form on a straight chain, *linear*, or branched structure, *branched*. Heteropolysaccharides are comprised of two or more sugar units and are also found in linear or branched structures, see Table 9.2 (Corvi Mora and Baraldi 2002).

Polysaccharides classified into two groups according to structural properties are fibrous polysaccharides and matrix polysaccharides (Denez and Young 1998). This chapter will focus on a system of such polysaccharides to prepare green composites.

Synopsis

Flax fiber and chitosan polymer are the most abundantly available natural polysaccharide polymers on the earth. Reinforcing and matrix

TABLE 9.2. Typical Polysaccharides.

| Polysaccharides | Sugar Component and Linkage |
|------------------------------|--|
| Homopolysaccharides | |
| <i>Linear</i> | |
| Cellulose | Glucose, α 1 \rightarrow 4 |
| Amylose | Glucose, β 1 \rightarrow 4 |
| Chitin | N-acetylglucosamine, β 1 \rightarrow 4 |
| Galactan (pectin) | Galactose, β 1 \rightarrow 4 |
| <i>Branched</i> | |
| Amylopectin | Glucose, α 1 \rightarrow 4, 6 \leftarrow 1 α |
| Glycogen | Glucose, α 1 \rightarrow 4, 6 \leftarrow 1 α |
| Dextran | Glucose, α 1 \rightarrow 6, 4 \leftarrow 1 α , α 1 \rightarrow 6, 3 \leftarrow 1 α |
| Galactan | Galactose, β 1 \rightarrow 6, 3 \leftarrow 1 β |
| Mannan | Mannose, α 1 \rightarrow 2 and α 1 \rightarrow 3, 6 \leftarrow 1 α |
| Heteropolysaccharides | |
| Pectin | Galacturonic acid, galacturonic acid methyl ester, α 1 \rightarrow 4 |
| Alginate | D-Mannuronic acid, 1-glucuronic acid, β 1 \rightarrow 4 |
| Hyaluronic acid | Glucuronic acid, N-acetyl glucosamine, α 1 \rightarrow 3, β 1 \rightarrow 4 |
| Chondroitin sulfate C | Glucuronic acid, N-acetyl glucosamine O-6-sulfate, β 1 \rightarrow 3, β 1 \rightarrow 4 |
| Chondroitin sulfate B | L-iduronic acid, N-acetyl glucosamine 4-O-sulfate, β 1 \rightarrow 3, β 1 β 4 |
| Keratosulfate | D-galactose, N-acetyl glucosamine 6-O-sulfate, β 1 \rightarrow 3 |
| Heparitin sulfate | D-glucuronic acid, N-acetyl glucosamine 6-O-sulfate, α 1 \rightarrow 4 |
| Heparin | D-glucuronic acid, N-sulfoglucosamine ester sulfate, α 1 \rightarrow 4 |

materials obtained from waste will further help in reducing the greenhouse effect. Flax (*Linum usitatissimum*) production dates back around 5,000 BCE (Salmon-Minotte and Franck 2005). Over the years, flaxseed oil, also known as linseed oil, has found many uses in food processing and industrial applications (agmarc.com). Canada is the largest producer of linseed in the world (gc.ca). Most of the linseed farmers in Canada burn the flax plant after taking out their seeds, although a small amount is used in the paper and pulp industry (Rana *et al.* 2006). Flax fiber has comparable properties to that of fiberglass (Joffe *et al.* 2003) and hence is a potential alternative to the reinforcing material in composites. The second most abundantly available biopolymer after cellulose is chitin, which is found in the shells of crustaceans and arthropods and is also found in fungi and yeast (Rinaudo 2006). The shells contain chitin, which can be converted into chitosan, a versatile polymer that is

useful in many fields, e.g. waste water treatment, cosmetics, medical, biotechnology, and agricultural use (Ravi Kumar *et al.* 2004; Weska *et al.* 2007; Kurita 2006). This research work focuses on the use of waste flax fibers and chitosan to prepare green composites for possible use in structural applications.

BIODEGRADABLE POLYMER

Natural biodegradable polymers have the potential be used as matrix material to prepare fully biodegradable composites. However, the cost of production of such polymers is the main hurdle (Bogoeva-Gaceva *et al.* 2007; Netravali and Chabba 2003). Figure 9.1 shows a classification of biodegradable polymers from various sources (John and Thomas 2008).

A natural polymer from the polysaccharide family, i.e., chitosan, was used to prepare composite materials. The chitosan is prepared from a

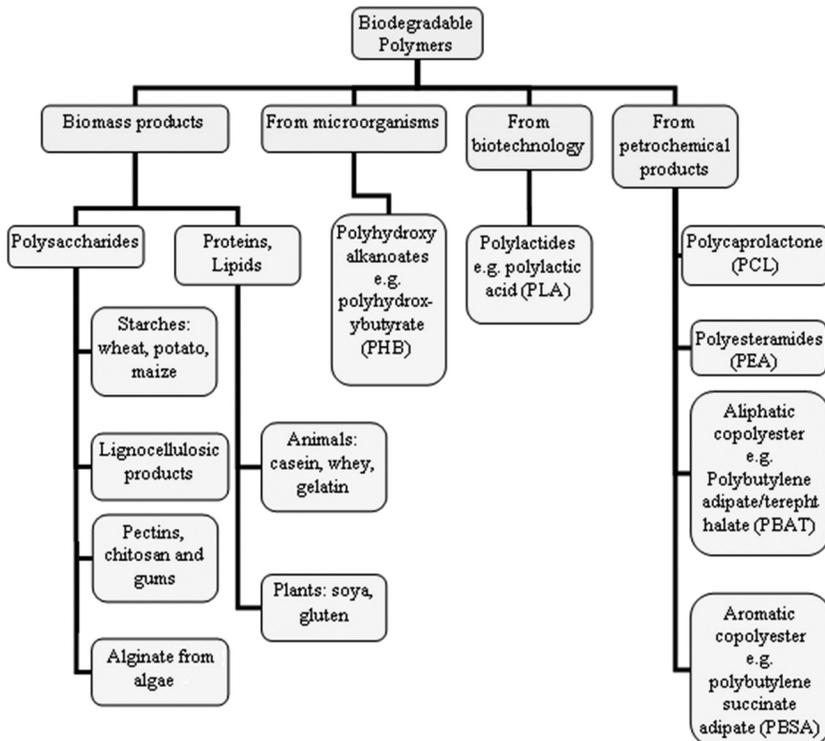


FIGURE 9.1. Biodegradable polymers and their source.

Renewable Biobased Composites for Civil Engineering Applications

S.L. BILLINGTON, W.V. SRUBAR III, A.T. MICHEL and S.A. MILLER

INTRODUCTION

The Built Environment and Natural Resource Use

WHILE today's built environment is a woven urban fabric of assembled civil engineered systems including transportation, public works, wastewater, and hydroelectric facilities, the construction and operation of buildings is one of the greatest consumers of all materials, energy, and natural resources worldwide. The manufacture of typical construction materials encompass a number of processing steps and embody the energy associated with each step along the way, from its raw material allocation, processing, manufacture, transport, assembly, and, if any, end-of-use energy recovery.

According to the United States Department of Energy (US DoE), the manufacture of building materials used in construction accounts for nearly 13% of the national energy demand and contributes significantly to global greenhouse gas emissions, accounting for 38% of all CO₂ emissions [1]. The emanation of high global warming potential greenhouse gases, such as methane, nitrous oxide, and other halogenated compounds, are second only to CO₂ in the list of greatest contributors to climate change. The manufacture of contemporary high-performance engineered structural materials such as steel, concrete, masonry, and glass relies primarily on energy and pollution-intensive processes. For example, the petroleum-based fuel combustion and chemical reactions involved in cement production alone were responsible for approximate-

ly 7% of global CO₂ emissions in 2001 [2], and the advantageously high recyclability of metals, such as steel and aluminum, is offset by the high initial production energy cost from mining ore to producing a structural grade material.

The manufacture of dimensional lumber, timbers, and glue-laminated wood products poses both environmental and toxicological concerns. The construction industry consumes 25% of all globally harvested lumber resources. Forests help sequester CO₂ from the atmosphere, and the depletion of these resources leads to soil erosion and the disturbance of wildlife habitats. For the production of oriented strand board (OSB), plywood, and glue-laminated construction materials, several million tons of adhesive resins are used every year. The most widely used adhesives are derived from amino and phenol-formaldehyde resins. Hot pressing during laminate processing emits formaldehyde. The U.S. Occupational Safety and Health Administration (OSHA) has declared formaldehyde as a carcinogen, because, if inhaled, it can cause significant respiratory problems.

While in service, maintenance issues are a concern for wood-based products due to their susceptibility to fire, moisture, biodeterioration, and decay by wood-boring insects and foreign microbial species, and the integrity of wood is compromised by the infiltration of water, termites, and fungus. Consequently, varnishes, paints, and sealants are needed to prolong the service life of structural-grade lumber, adding not only material costs, but also time and labor costs for the prescribed treatments.

For all structural and nonstructural materials used in construction, recycling is generally an option. However, material recycling, which often results in down-cycling to a product of lesser quality than the previous generation, typically beneficial in terms of environmental impacts, but only prolongs the inevitable; construction materials are often landfilled at the end of their useful lives. The U.S. Environmental Protection Agency (EPA) estimates that 160 million tons of waste is generated annually from construction and demolition (C&D) activities alone. While a significant proportion of metals and wood is diverted from the linear waste streams and either reused, recycled, or sent to waste-to-energy facilities, 96 million tons per annum of C&D waste are added to the nation's total landfill volume. Materials typically used in lower performance residential construction applications, such as wood, drywall, and polymeric composite materials comprise nearly 45% (43 million tons) of this recalcitrant landfill waste [3].

Plastics and Composites in Civil Engineering

Plastics are used in a wide variety of civil engineering applications from transportation assemblies, piping, and temporary building materials to full scale structural components, flooring, and facades. Popular for their customary low weight, low cost, high strength, and general resistance to physical and chemical degradation, polymers have become essential elements in the built environment. However, many of the advantages of polymers are also disadvantages, especially when considering their environmental impact. The low cost of many polymers is an artifact of its traditionally inexpensive petrochemical feedstock, and the strength and chemical recalcitrance of polymers make them very difficult to degrade after their useful life [4]. The result is a material that, while useful in service, persists in the environment long after the original, intended design life.

Approximately 30 million tons of plastics are estimated to be disposed of each year, accounting for 12.3% of the total municipal solid waste (MSW) stream, an increase from 1% in 1960 [5] and from 8% in 1990 [6]. The aggregate recycling rate in 2009 for these materials was only 7% [5] leaving nearly 28 million tons to be disposed of in landfills or incinerated. While landfilling constitutes responsible disposal of plastics, many plastics inevitably migrate into the environment. One of the most notable examples of plastic accumulation in the environment is the “Pacific garbage patch” which gathers waste through the circulating oceanic currents of the North Pacific Central Gyre [7]. Plastics, the primary constituent of this waste, persist just below the surface of the water due to their neutral buoyancy and are frequently ingested by seabirds, fish, and plankton, jeopardizing their health [8]. The rates of polymer accretion in the environment are increasing as plastics become more and more integral in our daily lives. Between 1994 and 1998 the amount of plastics discovered along the coasts of the United Kingdom doubled and during the 1990s plastic debris found along the Japanese coastlines increased 10-fold every 2–3 years [9].

The construction industry accounts for significant amounts of virgin plastic consumption in the United States. For example in 1998 Duchin and Lange [10] reported 20% of virgin plastic consumption was for construction, second only to packaging, which accounted for over 30% at the time. Plastic use in construction can be subdivided into two distinct categories, plastics for nonstructural components and plastics for structural components. Polyvinyl chloride (PVC), commonly used for

nonstructural piping, is the single largest consumer of plastics in construction, accounting for 58% of all plastics used. Structural plastics, such as high density polyethylene (HDPE) and epoxies for fiber reinforced polymer (FRP) composites, constitute a smaller yet substantial subset of the total plastics used (e.g., [10]).

The construction industry continues to be a particularly interesting growth market for plastics and FRP composites as a result of their light weight, high stiffness, and competitive price [11,12]. As structural components, polymers and composites are commonly manufactured as pultruded glass FRP structural shapes, FRP reinforcing bars, FRP bridge decks, and fiber wrapping retrofits for structural concrete. Due to their long service life, retrofit capabilities, and structural efficiency, synthetic fiber reinforced polymer composites are considered by some to meet many of the life cycle criteria of a sustainable construction material [13]. However, long-term durability in-service results in slow or nonexistent degradation post use. Recycling or reuse of polymers in construction is often difficult, especially in the case of composites, which typically cannot be separated back into their constituent materials. Techniques such as grinding [14] and pyrolysis [15] exist, but the industry standard is to landfill composite materials after service.

To counter the proliferation of synthetic plastics in the environment and to address environmental concerns of a globally unsustainable dependence on petroleum resources, new classes of fully biobased composites have begun to infiltrate the construction material market primarily due to the widespread utilization of partial biobased composites such as plastic lumber and wood-plastic composites (WPCs) as replacements for wood-based products in building applications [16,17]. The plastic lumber and WPC U.S. market is expected to continually grow at a rate of 9.2% annually to over \$5.3 billion in 2013 [18], owing to continued consumer acceptance and several advantages over natural wood lumber, including longer life cycles, minimal maintenance requirements, and improved resistance to decay and biodeterioration.

With at least one petroleum-based constituent, partial biobased composites represent a class of transitional sustainable materials—materials that are partly synthetic and partly biorenewable (more detail on this can be found later in this chapter). Considerable research on natural fiber composites with petroleum-derived (or partially petroleum-derived) polymer matrices has in some cases focused on building related applications [19–23]. The market success of these partial biobased composites has established an interest in the development of completely

biorenewable composites—materials that incorporate plant-based lignocellulosic fibers into fully biodegradable polymer matrices.

Fully biobased composites are now being developed and engineered for specific construction applications. Investigations of short-hemp fiber/cellulose acetate composites [24,25] suggest that this fully biobased combination of materials produces behavior appropriate for use in construction. PHAs combined with hemp [26–28], flax [29,30], jute [31,32], bamboo [33], abaca [34], rice hulls [35], chicken feathers [36], wood flour [37], and pineapple leaf fibers [38] also show promise for use in construction. Textile fabrics have been investigated and observed to provide multidimensional properties [31,32,39,40] and are often the focus of research for their potential use in building applications. The demand for natural fibers in composites is expected to grow 15–20% annually with a growth rate of 15–20% in automotive applications and even more than 50% in building and construction applications [41].

Closing the Loop: Engineering Rapidly Renewable Biobased Composites for Civil Engineering Applications

Construction materials are considered most sustainable when environmental, economic, and social impacts are weighed and considered over the entire lifespan of the product—from raw resource acquisition, material processing, application and use, to recovery and/or end-of-life. As a result, new classes of biobased composites are being engineered with the vision of having carbon neutral life cycles and with the intent to be cost-effectively manufactured in any location around the world. For example, raw plant-based fiber materials from natural, plentiful, and rapidly renewable resources can be extracted and processed locally to lower the embodied energy required for material transport. Biorenewable structural composite components and assemblies can be prefabricated using regionally manufactured biopolymeric resins to improve quality control and increase the recycling of processing waste, while reducing on-site noise and dust pollution. Furthermore, composites made from biobased constituents can be engineered to exceed any occupant-safety/indoor air quality benchmarks that mandate green materials to have low toxicities.

An example of transforming traditionally linear cradle-to-grave composite material life cycles into cradle-to-cradle methodologies is shown schematically in Figure 11.1. In this example, renewable biobased composites are manufactured with poly(hydroxyalkanoates) (PHAs), a

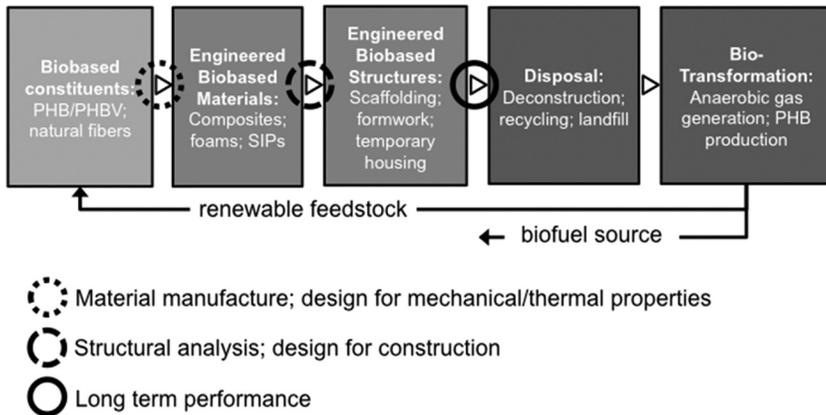


FIGURE 11.1. Envisioned life cycle for biorenewable PHA-natural fiber composites in construction.

family of aliphatic biodegradable polyesters synthesized via microbial fermentation under nutrient-limited conditions [42]. The PHAs referred to in this example are polyhydroxybutyrate (PHB) and polyhydroxybutyrate-co-valerate (PHBV). It has been shown that PHAs can be biosynthesized using methane, a gas that is generated by processes associated with landfills and wastewater treatment facilities [43] and can be combined with many natural fibers and woven natural fiber fabrics as well as reclaimed textiles to make fully biorenewable composite laminate and wood-plastic materials with comparable mechanical properties to wood and wood products. The composites can also be combined with foam materials to make lightweight, thermal resistant structural-insulated panels (SIPs). The materials can be engineered for specific target construction applications and, at the end of their useful lives, be deconstructed, and either reused or landfilled. In an anaerobic landfill environment, PHA-based composite materials have been shown to rapidly biodegrade relative to cellulose acetate- and soybean oil-based composites [44]. The degradation process produces biogas including methane, which may be captured and sold as a fuel or used as a feedstock to produce a new generation of biopolymers. As noted in Figure 11.1, the closed-loop carbon-neutral perspectives require not only consideration of processing, manufacture and achievement of target mechanical and thermal properties for structural applications (cradle-to-gate), but also knowledge of the long-term durability performance and end-of-use decomposition and biotransformation phases of the structural materials.

The degradation characteristics of rapidly renewable biobased com-

posites remain among the most advantageous qualities of the material and must not be adversely affected by synthetic fillers or detrimental processing additives. The use of natural fiber reinforcements in certain applications often demands the use of chemical coupling agents (e.g., silane, maleic anhydride) or other interfacial modifiers to impede moisture absorption and to improve the mechanical compatibility between fiber and matrix (e.g., [45]); however, the tradeoff effects of chemical coupling agents on improving in-service durability performance must be weighed and balanced with preserving the propensity for rapid out-of-service biodegradation of the composites. Considerations of both in-service and out-of-service phases are essential in order to make adequate material design decisions.

The primary advantage of the rapidly renewable biobased composites depicted in Figure 11.1 is the potential for a reduced environmental footprint over the entire life cycle of the material. To consider the environmental impact of biorenewable composite manufacture, life cycle analysis (LCA), a tool used to assess all environmental, social, and economic impacts associated with a product or process, can be employed to determine environmental impacts and to aid in composite constituent selection [46]. When designing biorenewable composites, it is necessary not only to consider mechanical properties, but also to take into account environmental impacts associated with the material in order to engineer an environmentally favorable composite. Recent efforts have been made to include LCA in the design of products and materials to influence decisions with the ultimate goal of reducing the total embodied energy and environmental impact of biorenewable composites designed for use in construction applications [47] drawing on similar approaches used in the automotive and construction industries [48–50].

While it is commonly assumed that natural fiber reinforced composites have favorable environmental impacts, in fact the impact is highly dependent on the production techniques employed. The level of processing will vary depending on the form of the natural fiber reinforcement and this processing can result in a high life-cycle energy demand [51]. As an example, the manufacturing of woven hemp fabrics involves harvesting the hemp, retting and scutching fiber from non-fiber components by hand or with the aid of machines or chemical additives, spinning and softening the yarns, and finally weaving resulting fabrics. The production of burlaps (typically from woven jute fibers) requires many of the same manufacturing procedures, but the fiber is not refined to the same extent as fabrics and therefore requires less energy during manu-

facture. Additionally, different cultivation techniques and crop yields may result in varying environmental impacts between fiber types.

The effects on environmental impact for several PHBV/natural fiber composites can be seen in Figure 11.2, which displays a life-cycle impact comparison of three biobased composites and a glass-fiber reinforced polyamide with all results weighted based on the amount of composite required to achieve the same deflection when loaded equivalently. These life cycle impacts are based on inventories developed in [52] and [53]. Shown in Figure 11.2 are greenhouse gas emissions in g-CO₂ equivalents and energy consumption in MJ equivalents based on the Building for Environmental and Economic Sustainability (BEES) 4.01 weighting scheme [54].

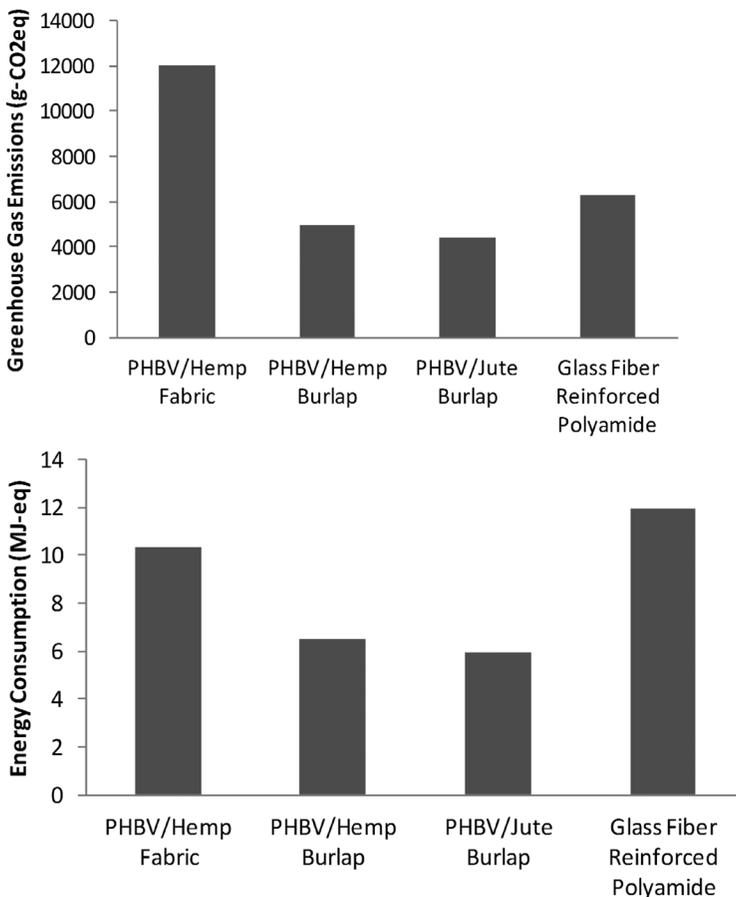


FIGURE 11.2. LCA comparison of different composite materials.

Physical and Chemical Properties of Alkali-Activated Fly Ash Materials

HOSSEIN ROSTAMI

ABSTRACT

Alkali Ash Material (AAM) concrete is a unique material that is cost effective because it utilizes waste fly ash and has properties superior to other concrete products. The AAM concrete described here is produced from the addition of inexpensive chemicals to fly ash. Fly ash is by far the largest by-product of the consumption of coal for the generation of electricity. Only 40% of the 71 million tons of fly ash generated each year are recycled for use in structural fill, waste stabilization, and additives to concrete.

AAM can be used to create a wide range of materials including high performance concrete (AAM-HPC) and lightweight (AAM-LW). AAM-HPC provides rapid strength gain along with high ultimate strengths of more than 110 MPa. LW-AAM can produce materials with densities ranging from 1,200–2,200 kg/m³ and compressive strength from 2–65 MPa.

Both AAM-HPC and AAM-LW has far better environmental resistance than Portland cement concrete, resisting attack from sulfuric acid (H₂SO₄), hydrochloric acid (HCl), and organic acids. AAMs resist freeze-thaw attack and high abrasion, possesses low chloride permeability, and does not exhibit alkali silica reactivity.

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AAM concrete is mixed and molded like ordinary Portland cement using conventional technology adapted from existing facilities in manufacture of pipe, block, and wet cast concrete products. AAM hardens with dry curing, whereas Portland cement is hydrated and requires moist curing.

The activating chemicals in the production of AAM are sodium silicate and sodium hydroxide. However potassium silicate and potassium hydroxide can be replaced for sodium based chemicals. In the second part of this chapter, the properties of sodium-based and potassium-based AAM are compared. Overall, physical and chemical properties of both sodium- and potassium-based AAM were almost the same, and potassium-based chemicals are more costly than the sodium based chemicals.

Potential immediate applications of AAM material are blocks, pipe, burial vaults, median barriers, sound barriers, and overlaying materials. Eventual markets are high strength construction products, bridge beams, prestressed members, concrete tanks, highway appurtenances, and other concrete products.

INTRODUCTION

In the United States, approximately 1,050 million tons of coal is consumed yearly for electrical and industrial use. This produces 121 million tons of ash consisting of bottom ash, boiler slag, and 71 million tons of fly ash (Bauer 2003). Currently, 40% of the fly ash is reused. The rest is landfilled or surface impounded. This is not a preferable method because it creates a huge financial burden for the foundries and keeps them responsible for environmental effects far into the future (Bauer 2003; Khale and Chaudhary 2007). Scientists have therefore been looking for a way to reuse or recycle this waste into a productive, environmentally friendly alternative. Alkali activation or geopolymerization is a field developed for the purpose of utilizing this solid waste into cost-effective solutions (Bauer 2003; Khale and Chaudhary 2007).

Geopolymers are of the family of inorganic polymers, but their microstructure is much more porous than that of natural materials. The chemical reaction is extremely fast and creates 3-D polymeric chains and ring structures (Alonso 2001; Duxson *et al.* 2007; Criado *et al.* 2007). These cause any products to be unusually durable and resistant to environmental factors. Alkali activation has two main necessities to be created: source materials high in silicon and aluminum, and alkaline

liquids. Good source materials include by-product materials such as fly ash, blast furnace slags, and silica fume (Alonso 2001; Duxson *et al.* 2007; Criado *et al.* 2007). Alkali activation involving blast furnace slag has already been used for over 65 years in concrete production (Alonso 2001; Duxson *et al.* 2007). Alkali activated fly ash is now thought to have a better effect. Geopolymers gain strength very quickly as well, obtaining 70% strength within the first 3–4 hr. of production (Bauer 2003; Khale and Chaudhary 2007).

Disposal of waste products such as fly ash has been difficult. They must be stored so they do not seep into the ground water and they must have structural stability with respect to adverse environmental conditions (Khale and Chaudhary 2007). Alkali activation became the most cost effective solution to this problem and can be utilized in precast structures and concrete products that are resistant to heat and environmental decay (Khale and Chaudhary 2007). It can obtain a variety of characteristics depending on the mix design, including high compressive strength, light weight, and resistance to acid decay (Bauer 2003; Khale and Chaudhary 2007). It also has a significantly reduced energy requirement for the manufacture of materials involving geopolymers (Alonso 2001; Duxson *et al.* 2007; Criado *et al.* 2007). Geopolymers are also known as alkali-activated alumino-silicate binders and need an alkali material to act as a catalyst to start the chemical process (Alonso 2001; Duxson *et al.* 2007; Criado *et al.* 2007; Huntzinger *et al.* 2009). Because of this, fly ash is a suitable material to use and can be recycled in these products to create durable and long lasting cement products. Fly ash has been researched for the past three decades with different methods of alkali activation. The AAM uses a blend of chemicals, fly ash, and aggregates to produce unexpected results (Jahanian and Rostami 2001; Rostami 2004; Rostami 2004a; Rostami *et al.* 2009). This chapter discusses the high performance and light weight characteristics of AAM.

Composition of Fly Ash

There are two primary types of fly ash according to ASTM C-618: class F, low calcium fly ash, and class C, high calcium fly ash. Table 13.1 (Bauer 2003) gives the chemical composition of class F and class C fly ash, Portland cement, and the fly ash used in this work.

The same oxides appear in fly ash and Portland cement concrete, but in very different amounts. Fly ash has a higher SiO_2 content while

TABLE 13.1. Composition of Class F and Class C fly Ash and Portland Cement.

| Oxides | Class F Fly Ash | Class C Fly Ash | Portland Cement | Fly Ash (this work) |
|--------------------------------|-----------------|-----------------|-----------------|---------------------|
| SiO ₂ | 45–65 | 48–68 | 20 | 61.3 |
| Al ₂ O ₃ | 20–45 | 18–34 | 6 | 22.7 |
| Fe ₂ O ₃ | 3–12 | 2–8 | 3 | 4.8 |
| CaO | 3–10 | 15–39 | 63 | 4.1 |
| MgO | 1–3 | 3–6 | 1.5 | 1.3 |
| Alkali | <1.5 | <2 | 0.9 | 1.1 |
| SO ₃ | 1–5 | 1–5 | 2 | 1.2 |
| LOI* (% unburned C) | 0.1–12 | 0.1–12 | 2 | 0.2 |
| Heavy Metals | trace | trace | none | trace |

*Loss on ignition.

Portland cement contains more CaO. Typically, class F fly ash has less than 15% CaO content and class C fly ash has greater than 20% CaO. More than 70% of the class F fly ash consists of the oxides of silicon, aluminum, and iron. Its particles are classified as an aluminosilicate glass that exhibit pozzolanic reactivity in the presence of alkali, but do not themselves exhibit cementitious properties when mixed with water. Class C fly ash has a combined silicon oxide, aluminum oxide, and iron oxide content greater than 50%. The material is a calcium aluminosilicate and exhibits cementitious properties when exposed to water along with pozzolanic reactivity (Alonso 2001).

FLY ASH AND ALKALI ACTIVATION IN CONCRETE

Fly ash is commonly used as an additive to Portland cement mixtures due to its pozzolanic activity and high specific surface area. Over 9 million tons of fly ash was utilized in concrete in 2002 (Bauer 2003), a process that has been thoroughly studied (Huntzinger *et al.* 2009; Jahanian *et al.* 2001; Rostami 2009; Pacheco-Torgal *et al.* 2007; Pacheco-Torgal *et al.* 2008; Pacheco-Torgal *et al.* 2008a; Park and Kang 2006; Phair 2006). Significant benefits of the use of fly ash in concrete include better economics, increased ultimate strength, better chemical resistance, and reduced alkali-silica reactivity.

Fly ash can also be converted into cementitious material, without Portland cement. A new reactive fly ash cement was produced via hydrothermal transformation of class F fly ash in the presence of lime

(Prigiobee *et al.* 2009; Provis *et al.* 2009). The alkali activation of latent hydraulic materials to create ceramic-based composites is also described (Sindhunata *et al.* 2008; Majing *et al.* 1999). Recent patents by Lone Star Industries and Louisiana State University describe methods of alkali activation of class C fly ash (Roy *et al.* 1995; Gravitt *et al.* 1991). Alkali activated lime fly ash pastes with high levels of fly ash in an alkali activated systems have been described by Shi (Shi 1996; Shi 1996a). The alkali activation catalysis of hydration reaction in slags (which contain about 50% calcium) is reported with and without fly ash (Soong *et al.* 2006). The reaction of fly ash with an alkali silicate aqueous solution at moderate temperature (60–98°C) to yield a rapidly setting, solid mass of strength up to 60 MPa has been reported (Park and Kang 2006; Phair 2006; Prigiobee *et al.* 2009; Provis *et al.* 2009; Sindhunata *et al.* 2008). Of all the studies above, the two involving the use of class F and class C fly ash are most closely related to the work here in which AAM technology produces high performance concrete and light weight concrete from class F fly ash and class C fly ash, respectively.

To be a viable material, AAM must be both economically and technically competitive. The activating chemicals for AAM-HPC are relatively inexpensive type N sodium silicate (3.22 Na₂O/SiO₂) and 50% sodium hydroxide. The cost of AAM is less than that of comparable strength Portland cement, as shown in Table 13.2 (Jahanian and Rostami 2001; Rostami 2004; Rostami 2004a; Rostami *et al.* 2009).

AAM exhibits the chemical resistance of silicate cements along with the excellent mechanical properties of high performance concrete. In addition, LW-AAM-LW does not require autoclaving, in contrast to the production of conventional Autoclave Cellular Concrete (ACC). AAM-LW can produce materials with densities ranging from 1,200 kg/m³ to 2,200 kg/m³ and compressive strength from 2 MPa to 65 MPa. These are highly resistant to the corrosive action of sulfuric, nitric, hydrochloric, and acetic acids that are known to readily deteriorate Portland

TABLE 13.2. Cost of Portland Cement vs. AAM.

| Material | Strength MPa | US \$/m ³ |
|-----------------|--------------|----------------------|
| Portland cement | 35 | 90 |
| AAM | 35 | 60 |
| Portland cement | 90 | 350 |
| AAM | 90 | 110 |

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