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Edited by Raju Francis

Recycling of Polymers

Methods, Characterization and Applications

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WILEY-VCH
Verlag GmbH & Co. KGaA

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Cover
Blue bottles: choness@gettyimages (No 475893605)
Background: PhotoAlto/James Hardy@gettyimages (No 107906856)

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-33848-1
ePDF ISBN: 978-3-527-68903-3
ePub ISBN: 978-3-527-68909-5
Mobi ISBN: 978-3-527-68902-6
oBook ISBN: 978-3-527-68900-2

Typesetting SPi Global, Chennai, India
Printing and Binding

Printed on acid-free paper

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Preface

Polymer products are indispensible to humans because of their several advantages, such as easy processability into various shapes, low cost, lightweight, and durability, over conventional products. But the irony is that some of these advantages make polymeric materials a threat to life on Earth through widespread and irreparable damage to environment. This comes mainly because some of us still believe that polymer products are of the “use and throw” type. Because of this, our soil, water, and air are catastrophically affected. Therefore, it is high time to think and work on alleviating the serious ill effects of polymers and attempt to regenerate our environment for future generations. One of the possible remedies that is being considered and debated by the general public, scientists, and academicians is polymer recycling. This is because all other alternatives are either extremely dangerous or economically unviable. One can see that the two common substitutes for polymer recycling are (i) the simple burning of used polymers in open air, which is more dangerous to the environment, and (ii) the use of biodegradable polymers, which is uneconomical. Therefore, “recycle and reuse” is considered the best option for a sustainable environment.

Secondly, recycling minimizes the need for raw materials so that the rainforests can be preserved. Great amounts of energy are used when making products from raw materials. Recycling requires much less energy and therefore helps us preserve natural resources.

This book *Recycling of Polymers* is a collection of recent research and academic studies on the methods of recycling, followed by applications and, finally, the merits and demerits of recycled polymer products. It is noteworthy that this book encompasses almost all categories of polymers, namely plastics, elastomers, and fibers, and, in addition, also blends, composites, and resins.

This book consists of nine chapters. The first chapter mainly presents the overall idea that recycling is one of the best options for making a positive impact on the world in which we live. It gives a general idea about its importance, why we should do recycling, what are the sources of recycling, various stages of recycling, and so on.

Chapter 2 (Parts 2.1 and 2.2) provides the different types of additives that are commonly used for recycling. Additives play a leading role in the success of commercial plastics, elastomers, rubbers, coatings, and adhesives. It also describes the common additives used in the recycling of polymers. This includes a study of the different classes of additives that are employed alone or in combination with other additives in the polymer recycling or manufacturing process. After describing the different additives that are not included in the first part of this chapter, a quick look into the recent trends, advancements, and the future of additives is included in the second part.

The third chapter includes the method of recycling of polymers. Part 3.1 of the chapter comprises a significant review of the chemical recycling of the generally used addition polymers such as polypropylene (PP), polystyrene (PS), low-density polyethylene (LDPE), high-density polyethylene (HDPE), poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA), and Part 3.2 includes chemical recycling of condensation polymers such as poly(ethylene terephthalate) (PET), polycarbonate (PC), nylon, and so on.

Fourth chapter reviews the recycling of thermoplastic waste from some traditional polymers such as polyethylene (PE), PP, PS, PVC, PS, PET, and so on.

Chapter 5 includes the production and world consumption of rubber products and applications of recycled rubber. The recycling of rubber products is not a trivial process because their crosslinked structure restricts reprocessing. Efficient methods of devulcanization include chemical, mechanical, biological, thermal, microwave, and ultrasonic techniques.

Chapter 6 mainly focuses on the recycling of fibers. The most commonly recycled natural and synthetic fibers are included in this chapter. Natural polymers are biodegradable. They can be blended with plastics to produce materials that are more biodegradable while retaining the more desirable features of conventional plastics. Synthetic polymers are non-biodegradable. So this chapter mainly gives an idea about the recycling and use of recycled products of synthetic fibers.

Chapter 7 deals with the recycling of polymer blends and composites. Epoxies are thermoset polymers and are very difficult to degrade. Therefore, the different types of recycling techniques used for the epoxy thermosets are presented in this chapter. Examples of recycled epoxy thermosets that are converted into useful products are highlighted.

Chapter 8 deals with the recycling of polyurethanes. Mainly polyurethanes are used to obtain rigid and flexible foams. Nowadays, recycling of polyurethanes is drawing more and more attention worldwide because of the variety of products developed with them for various applications.

Chapter 9 gives an idea on the benefits of recycling and the impact of some significant recycled polymers on the environment. First part of this chapter discusses the advantages of recycling with the help of six major recycled polymers. Recycled polymers leads to the following positive impacts: (i) they save the Earth, (ii) they conserve energy, (iii) they help in mitigating global warming and in reducing pollution, (iv) they minimize waste products placed in landfills, (v) they help save money, (vi) they reduce the need for allied activities such as transportation and mining, and (vii) they spread awareness for the environment. The second part of this chapter evaluates the effects of recycled polymers from three angles – environmental, human health, and economic.

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August 11, 2016

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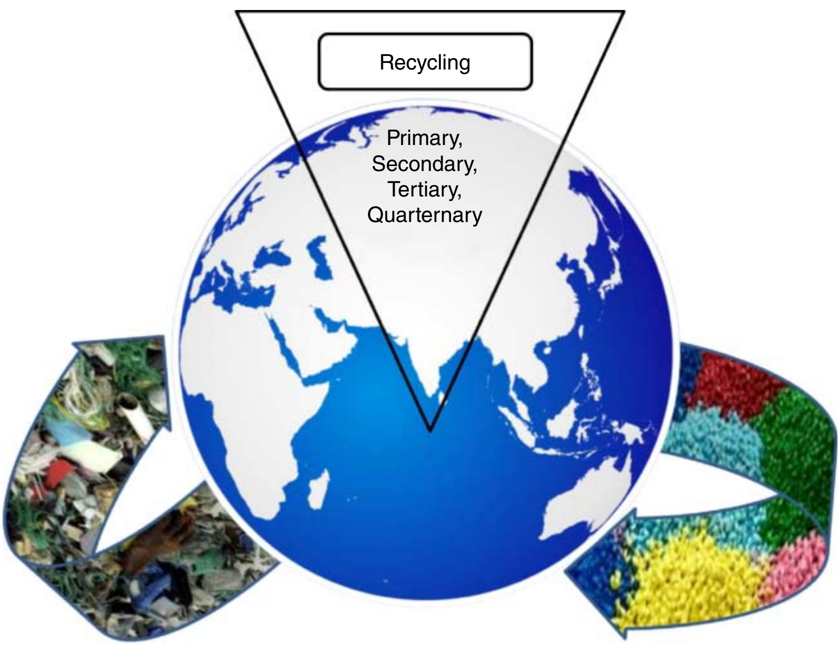
Abbreviations

ABS	Acrylonitrile/butadiene/styrene
AC	Acidification
AIBN	Azobisisobutyronitrile
ADN	Adiponitrile
BLL	Blood lead level
BPA	Bisphenol A
CD	Circular disk
CPE	Chlorinated polyethylene
CSBR	Conical spouted bed reactor
DCP	Dicumylperoxide
DFE	Design for environment
DMC	Dimethyl carbonate
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
DTST	Dynamic thermal stability time
EPDM	Ethylene – propylene – diene monomer rubber
EPR	Ethylene – propylene rubber
EPS	Expanded polystyrene
FCC	Fluid catalytic cracking
FRP	Fiber-reinforced plastic
FTIR	Fourier transform infrared
GC	Gas chromatography
GF	Glass fiber
GHG	Greenhouse gas
GOP	Vaccum gas oil product
GW	Global warming
HALS	Hindered amine light stabilizers
HCl	Hydrogen chloride
HDPE	High-density polyethylene
HDT	Heat distortion temperature
HIPS	High-impact polystyrene
HMDA	Hexamethylenediamine
HT	Human toxicity

IPP	Isopropenyl phenol
IR	Infrared
LCA	Life-cycle analysis
LDPE	Low-density polyethylene
LHV	Lower heating value
LLDPE	Linear low-density polyethylene
LPG	Liquefied petroleum gas
MBS	Methacrylate/butadiene/styrene
MFI	Melt flow index
MMA	Methyl methacrylate
MSW	Municipal solid waste
MW	Microwave
MWD	Molecular weight distribution
NE	Nutrient enrichment
OPS	Oriented polystyrene
PAH	Polyaromatic hydrocarbons
PAHs	Polycyclic aromatic hydrocarbons
PBCDDs	Polybrominated–chlorinated dibenzo-*p*-dioxins
PC	Polycarbonate
PCDFs	Polychlorinated dibenzofurans
PE	Polyethylene
PEHD	Polyethylene high density
PET	Poly(ethylene terephthalate)
PHAs	Polyhydroxyalkanoates
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
POF	Photochemical ozone formation
POP	Persistent organic pollutant
PP	Polypropylene
PS	Polystyrene
PSBD	Poly(styrene–butadiene)
PSW	Plastic solid waste
PT	Persistent toxicity
PVC	Poly(vinyl chloride)
R-PVC	Rigid poly(vinyl chloride)
SAPO	Silicoaluminophosphate
SEP	Styrene–ethylene–propylene block copolymer
TBE	Tetrabromoethane
TDF	Tire-derived fuel
TG	Thermogravimetry
TGA	Thermogravimetric analysis
TPH	1,3,5-Triphenylhexane
VCC	Veba Combi cracking
VOC	Volatile organic compound
WEEE	Waste electrical and electronic equipment

1
Introduction

Raju Francis, Geethy P. Gopalan, and Anjaly Sivadas



"Recycling saves energy, preserves natural resources, reduces greenhouse-gas emissions, and keeps toxins from leaking out of landfills."
–*Marc Gunther*

Recycling of Polymers: Methods, Characterization and Applications, First Edition. Edited by Raju Francis.

1.1
Introduction

1.1.1
Why Recycling?

During the past decades, the enormous population increase worldwide, together with the need for people to adopt improved conditions of living, has led to a dramatic increase of the consumption of polymers (mainly plastics). Materials appear interwoven with our consumer society, where it would be hard to imagine living without plastics, which have found a myriad of uses in fields as diverse as household appliances, packaging, construction, medicine, electronics, and automotive and aerospace components. The unabated increase in the use of plastics has led to an increase in the quantity of plastics ending up in the waste stream, which has stimulated intense interest in the recycling and reuse of plastics [1]. Worldwide, the production of plastics was 168 million tons in the year 1999 and approximately 210 million tons in 2010 .

Since the treatment of plastic wastes has become a serious problem, the development of effective recycling processes is urgently needed [2].

1.1.2
Sources of Waste

Plastics play an important role in almost every aspect of our lives. Plastics are used to manufacture products of daily use such as beverage containers, toys, and furniture. The widespread use of plastics demands proper end-life management [3]. A large number of items can be easily recycled in most curbside programs, including all kinds of paper and cardboard, glass of all colors and types, plastic bottles, aluminum cans, and yard trimmings. In addition, a number of localities offer drop-off programs for recycling other items, such as household hazardous wastes (paints, cleaners, oils, batteries, and pesticides), automobile items (tires, used engine oil, car batteries, antifreeze), wood construction materials, certain metals, appliances, and consumer electronics [4].

The largest amount of plastics is found in containers and packaging (e.g., soft drink bottles, lids, shampoo bottles), but they also are found in durables (e.g., appliances, furniture) and nondurables (e.g., diapers, trash bags, cups, utensils, and medical devices). Commercial waste is often produced by workshops, craftsmen, shops, supermarkets, and wholesalers. Agricultural waste can be obtained from farm and nursery gardens outside the urban areas. This is usually in the form of packaging (plastic containers or sheets) or construction materials (irrigation or hosepipes). Municipal waste can be collected from residential areas (domestic or household waste), streets, parks, collection depots, and waste dumps [5].

Around 50% of plastics are used for single-use disposable applications, such as packaging, agricultural films, and disposable consumer items; between 20% and 25% for long-term infrastructure such as pipes, cable coatings, and structural materials; and the remainder for durable consumer applications with intermediate lifespan, such as in electronic goods, furniture, and vehicles [6].

1.1.3 Plastics

Plastics are made up of polymers and other materials that are added to give the polymer increased functionality. The polymer content in a plastic can vary widely from less than 20% to nearly 100%. Those plastics consisting virtually entirely of polymers are termed *prime grades*. The level and type of the other additives used depend on the application for which the plastic is intended. Plastics are inexpensive, lightweight, and durable materials, which can readily be molded into a variety of products that find use in a wide range of applications. As a consequence, the production of plastics has increased markedly over the last 60 years [6]. Thermosets and thermoplastics are the two major classifications of plastics. This distinction is based on both the molecular structure and the processing routes that can be applied. It also relates to recycling routes, as each category needs a different approach to utilize its recovery potential. Thermoplastics and thermosets will now be discussed.

- **Thermoplastics**
  These materials melt and flow when heated and solidify when cooled. On subsequent reheating, they melt and regain the ability to flow. This means that they can be used again and hence recycled by remelting them. Thermoplastics are used to make consumer items such as drinks containers, carrier bags, and buckets.
- **Thermosets**
  These materials are processed by melting, often in a similar manner to thermoplastics. However, once formed and cooled, they cannot be reprocessed; they decompose before they can melt. This is because they are chemically crosslinked by a process termed *curing*. The material becomes stiff and brittle with a highly dense molecular network [7].

1.1.4 Recycling of Plastics

Recycling of plastics is one method for reducing environmental impact and resource depletion. Recycling can therefore decrease energy and material usage per unit of output, leading to improved eco-efficiency. The only way to decrease the environmental problems caused by polymeric waste accumulation produced from day-to-day applications of polymer materials such those used in packaging and construction is by recycling. This helps to conserve natural resources because most polymer materials are made from oil and gas [8].

Recycling is the final result of the intermediate stages of collection, sorting by type, and processing of polymers. It reduces the quantity of residues in landfills and those indiscriminately discarded in the environment. Thus, it also leads to a reduction of problems such as the spread of diseases as well as contamination of soil, air, and water bodies [9]. It is one of the most important options currently available to reduce these impacts and represents one of the most dynamic areas in the plastics industry today. It provides opportunities to reduce oil usage, carbon dioxide emission, and the quantities of waste requiring disposal.

Recycling plastics encompasses four phases of activity, namely collection, separation, processing, and manufacturing and marketing. Because only the use of clean, homogeneous resins can produce the highest quality recycled plastic products in the existing secondary process (material recycling) and high-value chemical products in the existing tertiary process (feedstock recycling) [10], an effective separation of mixed plastics waste is necessary.

1.1.5
Municipal Solid Waste

The growth of plastics waste has a great impact on the management of municipal solid waste (MSW) by landfilling and incineration, because the available capacity for landfill of MSW is declining and plastics incineration may cause emission and toxic fly and bottom ash containing lead and cadmium [10]. Plastics waste recycling is a method of reducing the quantity of net discards of MSW. Although the benefits have not been quantified, plastics recycling also offer the potential to generate demonstrable savings in fossil fuel consumption, both because the recycled plastics can supplement and even compete with “virgin” resins produced from refined fossil fuel and because the energy required to yield recycled plastics may be less than that consumed in the production of the same resins from virgin feedstock. Therefore, plastics waste recycling conserves both material and energy and provides a comparatively simple way to make a substantial reduction in the overall volume of MSW [11].

The major plastics recycled are polyolefins (high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP)) and poly(ethylene terephthalate) (PET), poly(vinyl chloride) (PVC), polystyrene (PS), and polycarbonate (PC). The recyclable polymers and the recycling codes are shown in Table 1.1.

There are several options for how this can be done: primary recycling, mechanical or secondary recycling, tertiary or chemical recycling, and energy recovery or quaternary recycling (Figure 1.1).

- Primary recycling involves the use of the same product without essential changes in a new use cycle (e.g., refillable packaging after cleaning).
- Mechanical recycling implies the application of the material used, without changing the chemical structure, for a new application.
- Chemical recycling implies the chemical structure of the material is changed, which means that the resulting chemicals can be used to produce the original material again [12].

Table 1.1 Various polymers with their characteristic recycling codes for particular applications.

Symbol	Acronym	Full name and uses
1	PET	Polyethylene terephthalate - Fizzy drink bottles and frozen ready meal packages.
2	HDPE	High-density polyethylene - Milk and washing-up liquid bottles
3	PVC	Polyvinyl chloride - Food trays, cling film, bottles for squash, mineral water and shampoo.
4	LDPE	Low density polyethylene - Carrier bags and bin liners.
5	PP	Polypropylene - Margarine tubs, microwave-able meal trays.
6	PS	Polystyrene - Yoghurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
7	Other	Any other plastics that do not fall into any of the above categories. For example melamine, often used in plastic plates and cups.

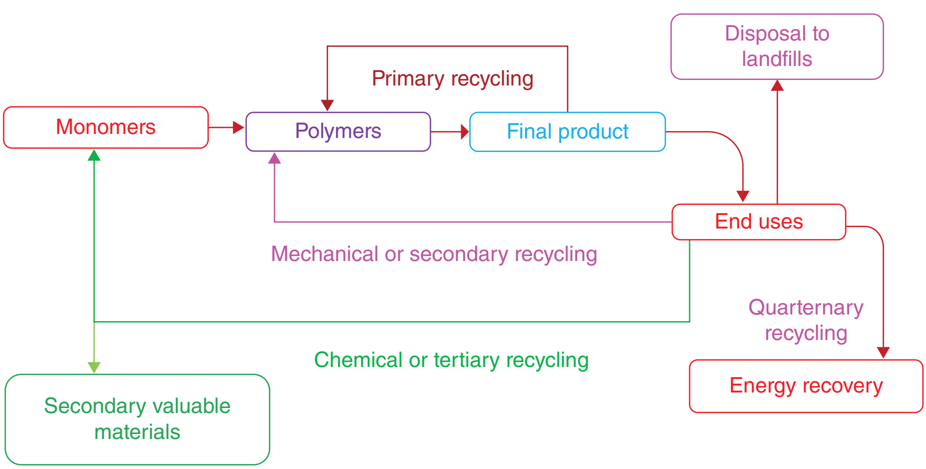


Figure 1.1 Four methods of recycling.

- Energy recovery refers to the recovery of plastic's energy content. Incineration aiming at the recovery of energy is currently the most effective way to reduce the volume of organic materials. Although polymers are actually high-yielding energy sources, this method has been widely accused as ecologically unacceptable owing to the health risk from airborne toxic substances, for example, dioxins (in the case of chlorine containing polymers).

1.1.6
Various Stages of Recycling Plastic Wastes

There are various stages of recycling:

- *Collection*: Plastic waste is collected from different locations. This can be achieved by keeping special containers at home, public places, farms, and so on. These wastes are then collected by professional waste collectors and transported to the recycling sites.
- *Cleaning*: The cleaning stage consists of washing and drying the plastic items. Cleaning is important since clean waste materials fetch better prices and they improve the quality of end products. Plastics can be washed at various stages of recycling process: before, after, or even during sorting.
- *Sorting*: This involves not only the separation of the polymers from recoverable foreign bodies but also the separation of these polymers themselves.
- *Size reduction*: It aims to reduce the size of the waste, which in turn facilitates not only in the separation of different polymers but also recovery of the micronized powder which is used to feed processing machines. The end products of shredding can be irregularly shaped pieces of plastics, which can be sold to reprocessing industries and workshops.

After processing, these materials are further subjected to various techniques such as extrusion, injection molding, blow molding, and film molding. Finally, the processed materials are converted into various products such as pipes, tubes, bags, sheets, and miscellaneous items.

1.1.7
Additives

Polymer industry cannot survive without additives. Additives in plastics provide the means whereby processing problems, property performance limitations, and restricted environmental stability are overcome. In order to get a technical effect additives used to incorporate into the plastics. So additives are expected to be the key part of the finished particle. A few examples of additives are antistatic agents, antioxidants, emulsifiers, antifogging agents, impact modifiers, fillers, plasticizers, lubricants, solvents stabilizers, UV absorbers, release agents and thickeners. It might be either inorganic (e.g., oxides, salts, fillers), organic (e.g., alkyl phenols, hydroxybenzophenones), or organometallic (e.g., Ni complexes, Zn accelerators, metallocarboxylates) [13].

Benefits of adding additives in plastics significantly shows varying properties with one or more directions such as stiffness, and strength, general durability, thermal resistance, impact resistance, resistance to flexure and wear, acoustic isolation and so on. In the broadest sense, these are essential ingredients of a manufactured polymeric material. An additive can be a primary ingredient that forms an integral part of the end product's basic characteristics or a secondary ingredient that functions to improve performance and/or durability.

The other recyclable materials are fibers, rubbers, mixed plastics, blends and composites, and so on. The recycling techniques, use of additives, and reusing applications are discussed in the following chapters.

Rubber recycling is growing in importance worldwide because of increasing raw material costs, diminishing resources, and the growing awareness of environmental issues and sustainability [14]. The rubber industry faces a major challenge in finding a satisfactory way to deal with the increasing quantities of rubber goods that reach the end of their useful life and are rejected from factories as scrap. The main source of waste rubber is discarded rubber products, such as tires, rubber hoses, belts, shoes, flash, and so on [15].

Reclaimed rubber is the product resulting when waste vulcanized scrap rubber is treated to produce a plastic material that can be easily processed, compounded, and vulcanized with or without the addition of either natural or synthetic rubbers. Regeneration can occur either by breaking the existing crosslinks in the vulcanized polymer, or by promoting scission of the main chain of the polymer, or a combination of both processes. Reclaiming of scrap rubber is, therefore, the most desirable approach to solve the disposal problem. Reclamation is done from vulcanized rubber granules by breaking down the vulcanized structure using heat, chemicals, and mechanical techniques. Reclaimed rubber has the plasticity of new unvulcanized rubber compound, but the molecular weight is reduced so reclaimed compounds have poorer physical properties when compared to new rubber [16].

Natural fibers are obtained from plants and animals whereas synthetic fibers are obtained by chemical processing of petrochemicals. Natural fibers have recently attracted the attention of scientists and technologists because of the advantages that these fibers provide over conventional reinforcement materials; the development of natural fiber composites has been a subject of interest during the past few years [17–19]. These natural fibers are of low cost, low density, and high specific properties. These are biodegradable and nonabrasive unlike other reinforcing fibers. Also, they are readily available and their specific properties are comparable to those of other fibers used.

Fiber-reinforced plastics (FRPs) are inherently difficult to separate into the base materials, that is, fiber and matrix, and the FRP matrix into separate usable plastic, polymers, and monomers. These are all concerns for environmentally informed design today, but plastics often offer savings in energy and cost in comparison to other materials. Also, with the advent of new and more environmentally friendly matrices such as bioplastics and UV-degradable plastics, FRP will similarly gain environmental sensitivity [20].

One of the biggest challenges posed by FRPs is their recycling. Many different recycling techniques have been studied during the last two decades, such as mechanical processes (mainly grinding) [21 – 24], pyrolysis and other thermal processes [25, 26], and solvolysis [27 – 29].

1.1.8 Mixed Plastics

Another type of plastics used for recycling is mixed plastics. Mixed plastics contain different types of plastics with different processing behavior and stability. Usually, these plastics are not compatible (or thermodynamically miscible) with each other, and the resulting properties are very often inferior to those of the parent polymers. In its broadest sense, mixed plastics constitute a a mixture of plastic resins or a mixture of package/product types which may or may not be the same plastic type or color category, and may not have been fabricated using the same manufacturing techniques.

1.1.9 Composites

Composites are generally considered high-value, high-performance materials that are employed in producing end products of high net worth. The term *composite* can be used to describe a large number of multiphase materials, consisting of a wide variety of matrix materials along with a correspondingly large array of different fillers and reinforcements. Composites can be easily recycled. Additionally, composites have been demonstrated to often have a better ecological track than traditional materials such as steel, aluminum, and concrete [30].

1.2 Conclusion

Recycling or reuse is one approach for end-of-life waste management of plastic products. It makes increasing sense economically as well as environmentally, and recent trends demonstrate a substantial increase in the rate of recovery and recycling of plastic wastes. This process has advantages and disadvantages. The foremost advantage of recycling is that it helps in protecting the environment in the most balanced manner. It helps in conserving important raw materials and protecting natural habitats for the future. Protecting natural resources such as wood, water, and minerals ensure their optimum use. Governments and various environmental organizations regularly emphasize the many benefits of recycling. First and foremost, recycling reduces the amount of waste that must be placed into landfills or incinerated. The recycling of metals, glass, and other materials reduces the pollution that would be caused by the manufacturing of products from virgin materials. Using recycled materials also saves energy because it takes less energy to use recyclables than to make a product from raw materials.