The conclusion of this book relates to a topic about which the entire plastics industry and all end users of plastic resins and products are being challenged to confront and address: the sustainability of plastic materials.

With the polyolefins, polyethylene (PE) and polypropylene (PP), being by far the most visible polymers in everyday life, and especially because they are used so often for “single use” packaging, readers who use polyolefins cannot avoid questions about the “green” nature of the materials—whether the arguments emphasize the materials’ recyclability (as opposed to their being often littered) or their efficient production and uses (when compared with alternative materials such as paper, metal, or glass).

Considering their property changing roles, additives are important factors in arguments about what makes a polyolefin material or application sustainable. The arguments have to do with their effects on the materials’ production, use, recycling, and disposal phases—with these last two phases now becoming more complicated to address by the introduction of additives for promoting polyolefin biodegradability. Thus this chapter will address a few key questions in broad ways, while using real-world examples as illustrations:

- What factors make a polyolefin (PE- or PP-based) material sustainable? (Section 20.1)
- What are the characteristics of a sustainable polyolefin additive? (Section 20.2)
- What are some innovative examples of “green” uses of additives in PE and PP materials? (Section 20.3)
- And what about additives that are said to make polyolefins biodegradable? (Section 20.4)
- Finally, what are some things to keep in mind when choosing additives in terms of sustainability? (Section 20.5)

### 20.1 Factors That Make Polyolefins Sustainable

In a broad view of sustainability, polyolefins could be credited with sustainable characteristics of various kinds, in comparison to those of alternative materials that might be used for similar products. Although associated with waste and littering in the public discourse, their production, use, and end of life do have some positive “green” aspects:

1. PE and PP are based on relatively simple molecules, and the energy used in their production is relatively low compared to other polymers. And when considering a common application like shopping bags, their production energy is low in comparison with alternatives like paper bags.

2. Polyolefins, especially when compounded to be durable using additives, offer energy and material savings in use. The low-density materials are good for many automotive parts, making cars lighter and more fuel efficient. They provide inexpensive ways of packaging food, maintaining its shelf life a long time and helping to minimize food waste. And more and more in building and construction, polyolefins are used to seal up buildings, reducing heating and cooling loads. Polyolefin film wraps and thermoplastic olefin (TPO) roof membranes block air leaks and keep out water, while PP solar shingles produce energy.

3. Polyolefin polymers are nontoxic and relatively inert and durable. This makes them safe choices for applications that require a shelf life or that contact food or drugs or the human body. Their engineering durability is evident in applications like TPO automotive bumper fascia and in wood-plastic composite decking—which, now used for at least one-third of all decking, does not need to be replaced as
often as wood, and is a potential end use for recycled plastic and waste wood. (However, polyolefins’ durability makes them persistent in the environment when littered.)

4. Polyolefins’ durability and thermoplastic nature also mean that they are among the most-recycled plastics. Rigid polyolefin containers are regularly collected and recycled, and bags and wraps (usually made from polyolefins) have been growing in prevalence in the recycling stream over the last 20+ years—more so than most other commonly recycled materials. If anything, their recyclability is now being endangered by their success and versatility. New polyolefin grades, structures, and additives are making it harder for recyclers to differentiate and separate plastics in the recycling stream by resin type—with products like clarified PP packaging resembling PET or other clear plastics [20-12].

20.2 Characteristics of Sustainable Polyolefin Additives

Again, taking a broad view of the concept of “sustainability,” we might describe a “sustainable additive” simply as an additive that helps a polyolefin meet one or more of the above goals more effectively and efficiently. But it is a worthwhile exercise to look for a deeper conceptual framework with which to talk about additives specifically.

One framework to consider is the “Principles of Green Chemistry,” developed in the 1990s by P.T. Anastas and J.C. Warner for their book Green Chemistry: Theory and Practice. Although their 12 principles were formulated mainly for the chemical industry, some of them are helpful when discussing additives and sustainability [20-10].

These principles should be read keeping ideas in mind about the additive’s production, its use in the plastic product, and its end-of-life influence on the polyolefin plastic. Here are a few principles that can be made relevant to polyolefin additives:

**Atom Economy:** Under this principle, the material used for the production of an additive should be maximized in the additive itself. Thus an additive like a mineral filler could be seen as relatively efficient to produce (nearly all of its raw material’s “atoms” are used in the final product), while a complicated chemical additive may require multiple synthesis steps, each creating atoms that are not present in the final additive.

**Less Hazardous Chemical Syntheses** and **Designing Safer Chemicals:** These two principles are about minimizing toxicity in the synthesis method of the additive (which ideally should use or create nontoxic or low toxicity substances) and in the final additive/plastic product (which should be nontoxic). A plant-based fiber would seem to fulfill both of these principles well, for example, unlike some chemically complex additives like halogenated flame retardants.

**Use of Renewable Feedstocks:** A relatively straightforward goal, this principle emphasizes the use of raw feedstock materials that are based on renewable resources, when possible. With additives, an interesting conundrum involves whether mined mineral fillers that are abundant and relatively inert have a natural character that makes them somewhat “green,” even though they are not technically biologically renewable.

**Design for Degradation:** This principle will be covered at the end of this chapter. It concerns not just the biodegradability of additives at the end of a product’s lifecycle but also the effects of degradability-promoting additives used in polyolefins that allow them to disintegrate to some degree after disposal. This principle also concerns other end-of-life options like recycling, and how additives can help or hinder that.

Incorporating the above principles into a visual aid is one way to prioritize additive selection in term of sustainability. Here an “inverted pyramid” (technically a triangle) is offered in Figure 20.1 to show which additives in the future should be sought more than others in terms of sustainability; those at the top tend to satisfy all or most of the above principles; those at the bottom, the opposite. The area differences in the different sections emphasize the relative prevalence of use that should be pursued for each category.

Arguing for the placement of an additive on this graphic can be tricky, however. For example, glass fiber (at the middle of the chart) can increase strength-to-weight of parts ratios efficiently and is chemically nontoxic, but glass fiber can be unpleasant/hazardous to handle in production, and glass-filled compounds do not fit easily into conventional recycling streams. Admittedly, the “toxic additives” at the bottom of the chart do raise their own contradictions; for example, halogen-based flame retardants (FRs) are less favored.
for their chemistry, but they are more effective than other FRs (saving more human lives in fires, potentially) and require lower loadings, and thus less material usage and thus less mass, than other FRs.

One could argue that basic mineral fillers are relatively sustainable—when they are abundant, efficiently and safely mined, inert and nontoxic, and not rare or easily depleted. There can even be questions about some mineral fillers’ “renewable” nature. For example, as discussed in Section 7.2.1, one company is sourcing the common filler calcium carbonate from the ocean floor—an oolitic aragonite mineral form of CaCO₃, marketed under the name Oshenite. This form of CC is continuously precipitated in the waters off the Bahamas Islands, where “warm and cool water combine.” So it is, in a sense, renewable. In such a case the main concern would be whether we will start depleting this type of material faster than nature can create it [7-59].

So perhaps mineral fillers deserve to be even higher up on Figure 20.1. Or perhaps not—their production does usually require the use of some chemicals, especially those for coating them for resin compatibility. And most mining and extraction techniques are rarely considered “green.”

Neither are the materials at the top of the chart perfectly green. For example, despite their benefits, some useful plant fibers are grown using much water and fertilizer, burdening the environment; they require chemical coupling agents to be used in a compound; and they are difficult to recycle because of their sensitivity to heat and moisture and incompatibility with conventional recycling. So trade-offs must be considered when evaluating any additive in terms of sustainability. Figure 20.1 is not meant to oversimplify the process, but rather to serve as starting point.

20.3 Examples of “Green” Uses of Additives in Polyolefin Materials

So even though a truly sustainable additive may not exist, what are some examples of the most sustainable additives? Given the relatively low loadings of most additives in a plastics compound, perhaps it is just as important to judge their sustainability by the degree to which they make the entire compound sustainable—as in the cases of:

- **foaming**, where a small amount of foaming agent can create large reductions in resin use, part density, and processing energy;
- **reinforcement**, where fibers or fillers can create higher strength-to-weight ratio materials, carrying more load with less mass;
- **thin film and sheet**, where impact modifiers and process aids and other additives allow the economical production of tougher but leaner films.
These are just few basic examples. A more complex consideration is how additives can assist in recycling. In the simplest example here, heat-stabilizing additives can be added to a stream of recycled polyolefins, allowing them to be reprocessed without degrading. And as discussed in Chapter 14, compatibilizers can allow different grades or types of polyolefins to be recycled together or with small amounts of foreign polymers. Or, as discussed in Section 10.1.1, nucleators can level out the diverse crystallization and shrinkage characteristics of various recycled polyolefin streams like variously pigmented PPs [10-35].

And additives themselves can be based on recycled waste materials from various industries. Waste wood sawdust, for example, can be used in wood-plastic composites. Or agricultural byproducts like rice husks are being investigated as ingredients in PE and PP composites. Coupling agents bond the rice husk powder to the resin, though there is the threat of husk decomposition from heat [20-14].

Other common additives can be created from waste materials, as shown in Case 20.1.

Fillers and reinforcements can also come from managed renewable sources, like sustainably managed forests, and they can offer engineering properties too—such as the wood-based cellulose in Case 20.2.


**Problem:** New additives are sought having significant recycled content.

**Objective:** Fillers, fibers, and reinforcements based on postindustrial wastes.

**Solution:** Carbon fiber, carbon black, and milled glass fiber, each based on postindustrial discards.

Perhaps the ultimate achievement in recycling is to reappropriate material that otherwise would be discarded. The three example products below show what kinds of plastic additives can be made from postindustrial waste.

- ELG Carbon Fibre Ltd. is developing recycled carbon fiber products in compacted pellet form for use in thermoplastic processing. The milled fiber MF100 grade has an average fiber length of 100 microns; the chopped fiber CFRAN grade has random fiber lengths from 6 to 60 mm long.
- Aemerge Carbon LLC offers a grade of carbon black made from old pallet wood, in a 3-micron particle size masterbatch. Mixed with traditional carbon black in an 80/20 ratio, this “Organic Black” is said to produce no major differences in mechanical properties or coloration, compared with 100% traditional N762 black.
- 3B-the fiberglass company offers a milled fiber powder grade of plastics reinforcement made from byproducts from its glass manufacturing process. The MF 01 ER grade is intended to “close the gap” in cost–performance ratio between standard mineral fillers and standard glass reinforcement, the company says, offering a high modulus and dimensional stability.

### 20.4  Additives for Promoting Polyolefin Biodegradability: Questions and Concerns

#### 20.4.1  Background and Examples

Besides lightweighting parts and improving recyclability, another “green” attribute related to additives is biodegradability. It is a desirable quality in single use plastic packaging, at least, which is often littered and does not break down in the surface environment. Stepping aside the more philosophical question about why it is important to people that a plastic product should degrade in a landfill, we will look at this issue from various angles.

Perhaps ironic here when talking about biodegradability is the fact that polyolefins are useful specifically because they are not biodegradable. They are mostly stable, inert, and not attacked by microbes commonly found. And their molecules can be reused again and again. Thus the question of whether they can or should be formulated to truly degrade in a reasonable time at the end of their use life becomes controversial.

It is controversial because of what “biodegradability” implies. It has been difficult in the industry discourse to reach common agreement about what
biodegradibility really means for plastics. Generally, it means the reversion or deconstruction of the material into simple chemical compounds compatible with natural processes such as carbon dioxide and water. And this biodegrading process should happen relatively quickly, ideally within one growing season, or 1 year in northern climates, from the time when the biodegradable article is discarded or exposed to the elements. Some see the simple fragmentation (polymer chain breaking) of disposed polymers, in landfills or otherwise, as the start of a kind of biodegradability that could take a long time to complete.

But again, polyolefins resist all kinds of biodegradation. Even when loaded with an additive that induces polymer chain degradation under certain conditions (oxygen, sunlight, etc.), a polyolefin product might require years to fully degrade in real disposal situations—especially if it still contains antioxidants that interfere with degradation or it is buried in a landfill (or otherwise lacks exposure to air and necessary conditions of temperature, etc.).

Nonetheless, there are a number of suppliers and converters who claim to supply polyolefin compounds or additives that encourage their degradation after disposal. However, any claim that a material or product can truly be called “biodegradable” may be questioned unless it is well supported with data using the framework of the industry’s biodegradation guidelines and testing standards, such as ASTM D6400 or ASTM D6954, which reportedly was placed under revision in 2014 for updating its testing specifications. Individual countries have their own standards for biodegradable products as well [20-2, 20-3, 20-6, 20-20].

Despite the difficult hurdle of complete biodegradability, a number of proprietary additives are offered as promoters of polymer degradation under various conditions—depending on the polymer’s chemistry. Most additives are described by their manufacturers as encouraging the cutting of polymer chains in some way by promoting oxidation, after the antioxidant stabilizers in the plastic formulation are consumed during the plastic product’s lifecycle. The additive may be designed to initiate a chain reaction of chemical changes that reduce the polymer into a more degradable species, by reacting with the surrounding light, air, and soil. Additives that require oxygen to break chains are labeled with the term oxodegradable. These products are said to help “oxobiodegrade” the partially degraded polymer in biologically active conditions, after oxidatively turning it into a fragmented material that is more digestible by microorganisms. The concept is that the microbes then help mineralize the fragments into simple components such as CO₂ and water. Such additives have found some use in agricultural mulch films designed to degrade each growing season, for example, though some additives for this kind of use have been discontinued for reasons related to those laid out below in Section 20.4.2 [3-3, 20-4, 20-20].

Many oxodegradability additives use cobalt as an oxidizing agent, but this element is a restricted or regulated material in many countries. Other additives based on cornstarch require high loadings of up to 25% in polyolefins, but the effectiveness and legitimacy of using these compositions has long

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**Case 20.2  Cellulose Fiber Reinforcement from Wood for Engineering Applications [7-74]**

**Problem:** Plant fiber-reinforced polyolefin composites need higher properties for high volume engineering applications.

**Objective:** A high volume plant source of cellulose fiber that can provide engineering properties and processability in PP.

**Solution:** “Thrive” cellulose fibers from trees from sustainably managed forests.

Wood-filled polyolefin composites are nothing new, but new forms of wood-based fiber are allowing new “thermoplastic biocomposites” to be created for engineering applications like automotive components. To this end, forestry products company Weyerhaeuser has developed a nearly lignin-free cellulose fiber for use in PP, at loadings of 20–30% cellulose.

The composites, called “Thrive,” reportedly offer high stiffness, faster cycle times, and 30% lower density than similar PP materials that uses glass fiber reinforcement (the conventional approach for automotive PP materials). When compared with 20% glass fiber-reinforced PP, Thrive composites with 30% cellulose result in lighter parts, slightly higher material stiffness (3.4 GPa tensile modulus), and 50% lower pack-and-hold cooling times in injection molding.
been questioned, because only the starch and not the polyolefin itself fully degrades. There are many additives marketed as promoting biodegradability and/or "oxobiodegradability"; a few examples of formulations below reportedly cause the biodegradation of polyolefins:

- Phoenix Plastics' Gaia Element Oxo 480 concentrate is said to use sunlight, air, and heat to encourage the biodegradation of low-density polyethylene blown film, for instance, when loaded at 1% (depending on degradation requirements).
- The "d2w" additive of Symphony Environmental Technologies reportedly is based on a metal salt that, after a designed time interval, catalyzes the cleavage of C–C bonds in polyolefins, lowering molecular weight and encouraging biodegradation. As molecular weight is decreased to below 40,000, water, oxygen, and microorganisms can more efficiently attack the material (1–3% is needed in film extrusion, the company adds).
- Evive’s “P-Life” reportedly has been tested for biodegradability to the end of the samples’ lifetime, rather than tested for a short period after which the degradation data is extrapolated to show when a sample should be fully degraded. The additive lowers the molecular weight of the polymer under the influence of sunlight, heat, and oxygen, after which the smaller molecules are said to be reduced aerobically by microorganisms. It is said to be “FDA-sanctioned and compliant with the RoHS directive.”

But again, claims about such products are susceptible to industry scrutiny and independent test verification using accepted test protocols that determine the degree of degradability [3-3, 17-27, 20-3, 20-5, 20-7, 20-8, 20-9, 20-19].

20.4.2 Arguments Related to Biodegradability Additives

There are arguments in favor of and against using oxobiodegradability-promoting additives in common plastics products. “Pro” arguments, usually made by the oxodegradable additives manufacturers, point to the additives’ effectiveness in degrading littered plastics—an ever-present outcome of plastics use and a threat to the environment. They also argue that testing shows that such additives do not diminish the recyclability of the products. And they point to emerging standards that will regulate and legitimize plastics with the additives for greater use [20-20].

Completely opposite arguments are held up by detractors of oxodegradable additives for plastics. Some of them call such formulations “oxofragmen
table,” denying their true biodegradability because current test methods do not look at all long-term outcomes of their use. Along with opposing the use of metals in the additives, they point to the degraded fragments as potentially harming the environment. They also point to claims that the additives are contaminants that do indeed affect recyclability and the quality of the reused plastic that still contains the prodegradant additive. Some report that the additives can cause premature mechanical property losses in a stored plastic products (like in PE film that is exposed to sunlight, for example). And some say that biodegradability claims distract consumers from recycling plastics and instead indicate to them that improper disposal is no longer a bad thing because the plastics will biodegrade [20-20].

Putting the debate into deeper context may help. A position statement by the Biodegradable Products Institute, which supports biodegradable polymeric materials via composting, serves as one roadmap for understanding key points related to the science of the debate. The statement “BPI Position on Degradable Additives” emphasizes the testing that shows how to decide if or how fast a material has been degraded biologically, rather than simply fragmented. Favoring compostability, the BPI’s main position is that all truly biodegradable materials should be diverted away from landfills, given the powerful greenhouse gas methane that landfill wastes emit over their slow degradation periods in anaerobic conditions [20-19].

The statement notes that although polymers the biodegradability additives will fragment in a few months in many (mainly dry) environments, “fragmentation is not a sign of ‘biodegradation’,” and that there is data lacking to show how long the fragments will remain unbiodegraded in various environments. Subsequent biodegradation requires microorganisms to use the material as food, thus the rate of their production of CO₂ in aerobic conditions indicates how quickly the material is being biodegraded. This rate can be tested for in various environments, like soil, using a test like ASTM D5988. Using a recognized test method, “BPI recommends that the supplier
demonstrate that 90% of the entire plastic film or package (not just the additive) be converted to carbon dioxide under aerobic conditions (like soil burial) or carbon dioxide and methane under anaerobic conditions (as in an anaerobic digestor, or a landfill) based upon weight and carbon content relative to the positive control….” [20-19].

During this kind of test, over time, plateaus of microbial conversion are typically reached, after which no additional time will lead to more degradation. Thus proper testing should continue until the plateau is reached, and no extrapolation of test data should be made indicating that more degradation will occur [20-19].

With improved pass/fail testing methods using reasoning like this, perhaps more legitimacy can be added to (or subtracted from) biodegradability claims.

20.5 Lessons to Learn for Choosing Sustainable Additives for Polyolefins

Despite the everchanging controversies about plastics and sustainability, some basic principles and trends can be identified that could be useful when choosing additives for polyolefins in terms of sustainability.

Recyclability and sustainable/bio-based additives choices are often incompatible. As we have discussed, conventional recycling streams still have difficulty sorting and recycling polyolefins containing reinforcing additives like glass fibers. Bio-based fillers and fibers will present similar difficulties, especially when considering that plant-based materials are moisture sensitive and can be degraded by repeated heating and reprocessing. Trade-offs in decisions to use such additives—their sustainability costs and benefits—must be made.

Regulations will only increase. Experts say that plastics and their additives will be under the microscope more and more regarding their purity, their migration and leaching at the surface of the product, and their health effects. US FDA and European Union regulators will be on guard for how additives in recycled plastics, for example, might affect safety if those plastics are used in food packaging. Meanwhile, regulations related to plastics and biodegradability are expected to be refined according to where and how well and how quickly plastics deemed biodegradable actually degrade in various environments (in the open air, composting heap, landfill, ocean, etc.). [20-22].

Sustainability claims require verification and must be backed with data. In the United States, for example, the US Federal Trade Commission has established green guidelines for manufacturers who advertise claims about the sustainability of their products and materials. In one 2014 development, the FTC warned 15 makers of oxodegradable or oxobiodegradable bags not to label their products as “biodegradable” unless confirmed by testing. If “oxo” bags are sent to landfills for disposal, like most nondegradable plastics bags, the limited oxygen in landfall would limit their degrading as advertised, goes one argument. The FTC had previously fined and/or warned companies making similar claims [20-18, 20-21].

Less can be more. The potency of some new additives is increasing, in terms of the properties they supply relative to the amount of them used in a polyolefin compound. Additives products of all kinds are showing this trend, but nanocomposites, containing only a few percentage points of nanofillers, are the most obvious examples. Here a small amount of additive goes a long way toward improving properties. Nanofillers are even being considered for more mundane, everyday polyolefin products—like wood-plastic composites, where small additions of dispersed nanoclay can double the modulus of the polymer. This could make nanoclay an alternative to simply adding more wood filler, which makes processing more difficult [20-13].

Public pressure against plastic waste will persist. It is unlikely that the general public will ever start ignoring the problems associated with improperly disposed plastic waste, which for most part, consists mainly of polyolefins. Scenes of waste plastics in the ocean or on shorelines, of plastic bags in trees, of animals with plastic fragments in their stomach... all are constant reminders to the skeptical public (and to regulators looking to ban these products) of problems with littering and plastics. Littering will likely never be stopped, but users of polyolefins can still try to make the best choices for creating materials and products that are useful, efficient, and, as much as possible, reclaimable.