SUSTAINABILITY, THE PATHS FORWARD

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Abstract

Sustainability can be achieved by many methods. Methods of sustainability include recycling, product and package downsizing, product life extension, and the use of bio-based monomers and polymers. The following areas will be examples for the purpose of this presentation. The effect of product life extension in the olefin pipe market will be discussed to show the effect of expected product improvements on the size and growth of the mining pipe market. What are the bio-based materials and are they making inroads into traditional applications? Is the switch by brand owners to bio-based polymers versus petroleum based polymers the beginning of a market trend or is it a "Brand" limited inroad by the bio-based materials? How can the different "end of life" options for biodegradable materials affect certain applications such as agricultural films and food packaging films?

What is Sustainability?

Sustainable

"relating to, or being a method of, harvesting or using a resource so that the resource is not depleted or permanently damaged". Merriam Webster

EPA

"Sustainability is based on a simple principle: Everything that we need for our survival and well-being depends, either directly or indirectly, on our natural environment. To pursue sustainability is to create and maintain the conditions under which humans and nature can exist in productive harmony to support present and future generations."

Sustainability

Is now a major environmental, political and economic issue impacting markets and investment decisions. There is growing concern by NGO's, governments, and companies about whether food, feed, and fuel feedstock materials are being supplied sustainably. Supply chains are often thousands of miles long, and data has been lacking to assess whether claims being made about sustainability are factual. Sustainability, in a general sense, is the capacity to support, maintain, or endure. The results of a recent survey by Asia Pulp and Paper that were published in the September 2015 edition of Packaging Strategies magazine claimed that "46% 0f Americans say they actively seek out packaging that can be recycled or reused". It also states that "62% of consumers want more environmentally- friendly packaging". According to the 2015 March Packaging Digest online poll, when asked "How do you expect your beverage portfolio will increase?" 73% of the respondents chose "Develop new packaging formats/sizes".

The National Environmental Policy Act of 1969

Committed the United States to sustainability, declaring it a national policy "to create and maintain conditions under which humans and nature can exist in productive harmony, that permit fulfilling the social, economic and other requirements of present and future generations."

Presidential (Executive) Orders 13101, 13123, 13134, Public Laws (106-224), AG ACT 2003

And other Legislative Actions all require Federal Agencies to develop procedures to identify, encourage and produce products derived from biobased, renewable, sustainable and low environmental impact resources so as to promote the Market Development Infrastructure necessary to induce greater use of such resources in commercial, non-food, products. Section 1501 of the Energy Policy Act of 2005 (Public Law 109–58) and EPA 40 CFR Part 80 (Regulation of Fuels and Fuel Additives: Renewable Fuel

Standard Requirements for 2006) require petroleum distributors to add renewable ethanol to domestically sold gasoline to promote the nation's growing renewable economy, with requirements to identify and trace origin.

The Sustainable Materials Mandate Program (SMM) of the EPA

The EPA focuses on three main strategic priorities. The Built Environment- This focuses on the conservation of materials and developing community resiliency to climate change. Sustainable Food Management- This focuses on reducing food loss and lowering food waste. Sustainable Packaging- This focuses on increasing the quantity and quality of recovered food waste.

What are Methods of Sustainability

The usual methods used to achieve sustainability are recycling, product redesign, and/or the use of bio-based materials. When discussing recycling we should not forget the "end of life" for the product discussed. The term "life cycle" refers to the major activities in the course of the product's life-span from its manufacture, use, and maintenance, to its final disposal, including the raw material acquisition required to manufacture the product. Life cycle assessment is a "cradle-to-grave" approach for assessing industrial systems. "Cradle-to-grave" begins with the gathering of raw materials from the earth to create the product and ends at the point when all materials are returned to the earth. LCA evaluates all stages of a product's life from the perspective that they are interdependent, meaning that one operation leads to the next.

Typical examples of sustainable processes include recycling, product and package downsizing, product life extension, and using materials based on bio-monomers.

Recycling

of plastics is only a partially sustainable activity. Let me explain that statement by comparing the recycling of plastics to other recycled materials. Consider the following facts about glass recycling. Glass bottles and jars are 100% recyclable and can be recycled endlessly without any loss in purity or quality. The container and fiberglass industries collectively purchase 3 million tons of recycled glass annually, which is remelted and repurposed for use in the production of new containers and fiberglass products. Recycled glass is substituted for up to 95% of raw materials. An estimated 80% of all glass containers recovered for recycling are remelted in furnaces, and used in the manufacture of new glass containers. Source, Strategic Materials, Inc.

Metals have similar statistics, but the most significant issue is the 100% reusable nature of glass and metals versus the inevitable end of life scenario of landfill for the petroleum based plastics. Unless the plastic is converted back into its' monomers and is repolymerized, recycling only delays the inevitable. Glass and metals, however, are truly sustainable because they can be endlessly recycled without any loss in purity or quality. The exception to this statement is the recycling of bio-based polymers such as Bio-PE.

Redesigning the package

Downsizing a product or product package is another optional path towards sustainability. A large and growing number of manufacturers, distributors, and retailers are realizing substantial brand, financial and environmental benefits from sustainable business practices. Sustainable manufacturing is the design and creation of products through economically-sound processes that minimize negative environmental impacts while conserving energy and natural resources. Walmart and many of the other large" box stores" lead in this effort because of the huge cost savings not just in materials used but also in transportation costs. The effect on the "brand image" is also a positive issue.

Product life extension

is another approach to improving sustainability. An example of this is the development of improved abrasion resistant pipes for use with mining slurries. Rio Tinto is in the process of field testing pipes designed to give longer field life when used to handle mining slurries. Pipes transporting abrasive mining slurries tend to selectively wear on the inside bottom of the pipe. In many cases the pipes are rotated so that a new surface on the bottom of the pipe comes into contact with the slurry. This allows for a longer life of the pipe in the field. With very abrasive slurries, however, the rotations can be as frequent, as much as every three months, resulting in a product life of as short as one year. More typical are usage lifespans of 18 to 30 months.

The new abrasion resistant pipes that are being field tested are designed as a coextrusion with an inner layer, which contacts the slurry, utilizing a highly abrasion resistant material that can double the life span of the pipe. One of the two companies supplying this type of pipe is considering a 4 year life guarantee on its' products.

Bio-based polymers

Bio-based polymers or biopolymers are a type of plastic which include living microorganisms, such as plants or bacteria, in their production process. They offer important contributions by reducing the dependence on fossil feedstocks and the related positive environmental impacts such as reduced carbon dioxide emissions. The legislative landscape is also changing where bio-based products are being favored through initiatives such as the *Lead Market Initiative* (European Union) and *BioPreferred* (USA). As a result, there is a worldwide demand for replacing petroleum-derived raw materials with renewable resource-based raw materials for the production of polymers.

Among these examples is the commercialization by Coca-Cola of a plant based PET bottle and the production of a biobased PE by Braskem. Coca-Cola is calling it the "plant bottle". They have partnered with a number of companies including H.J.Heinz, and Procter and Gamble to form the "Plant PET Technology Collaboration. Coca-Cola is also a member of the Bioplastic feedstock alliance, which was formed to help companies responsibly select feedstocks for biobased plastics. Coca-Cola intends to be producing 100% of their bottles from plant based feedstocks in four years.

Braskem is producing a drop-in polyethylene made from sugar cane. The companies already using the Bio-PE includes Accredo, Aveno, Este Lauder, General Mills, Nestle, Printpack, Small Planet Foods, Tetra Pak, Whole Foods, and many others. This is truly a sustainable product because it is made from 100% bio-derived carbon. It is essentially a method of carbon capturing.

Now we have the technology to create chemicals and intermediates that take advantage of biological pathways and sugars to create C4 carbon intermediates and drop-in chemicals from new feedstock sources. Targets include MEG (mono-ethylene glycol) and PTA (purified terephthalic acid) for PET, and adipic acid and HMD for Nylon-6,6.

There are a number of factors to consider regarding this aggressive move towards bio-based technology. These companies are all large "name brand" companies. The drive to change is a marketing decision based on their brand recognition and their brand image. Although they are moving towards a new raw material technology, the manufacturing technology, the packaging design, and the end of life for the polymer remains the same. In this case the preferred "end of life" is recycling. In fact, Coca-Cola estimates that over 35 billion bottles of the present version of the PlantBottle have been distributed in 40 countries. The present version is 30% bio-based resulting in a reduction of 315,000 metric tons of carbon dioxide emissions.

Biopolymers have the biochemical advantage of being totally or partially produced from renewable materials, such as sugar cane or cornstarch, and can be biodegradable into carbon dioxide, methane, water and inorganic compounds. Production of biopolymers can be classified according to their type of production method; such as the synthesis of renewable resources, such as starch or sugar, to produce polylactic acid (PLA) or bio-polyethylene. Bacteria using the fermentation process can also produce products such as such as polyhydroxyalkanoates (PHAs) and polyhydrobutyrate (PHB).

The production of bioplastics is not a new idea. The use of biopolymers goes back to the 1920's when soybean based polymers were used in the manufacture of automobile parts such as interior trims and dashboard panels. In 1941 American industrialist Henry Ford produced car components by using soybean based biopolymers and he introduced bio-composites which were made from hemp and cellulose based plastics to reinforce the automobile parts. However, with the expanded use of petrochemical polymers, which provided low cost polymers with superior properties for specific applications, biopolymers were quickly over shadowed. Today with the focus on sustainability the bioplastics are getting a fresh look.

The ASTM D6866 method has been developed to certify the biologically derived content of bioplastics. Cosmic rays colliding with the atmosphere change some of the carbon to the radioactive isotope carbon-14. CO_2 from the atmosphere is used by plants in photosynthesis, so new plant material will contain both carbon-14 and carbon-12. Under the right conditions, and over geological timescales, the remains of living organisms can be transformed into fossil fuels. After ~100,000 years almost all the carbon-14 present in the original organic material will have undergone radioactive decay leaving only carbon-12. A product made from biomass will have a relatively high level of carbon-14, while a product made from petrochemicals will have no carbon-14. Thus the percentage of renewable carbon in a material (solid or liquid) can be measured with an accelerator mass spectrometer.

There is an important difference between biodegradability and biobased content. A bioplastic such as high density polyethylene (HDPE)[43] can be 100% biobased (i.e. contain 100% renewable carbon), yet be non-biodegradable. These bioplastics such as HDPE nonetheless play an important role in greenhouse gas abatement, particularly when they are combusted for energy production at the end of their useful life span. The biobased component of these bioplastics is considered carbon-neutral since their origin is from biomass. Some of most common biopolymers today are thermoplastic starches, polylactic acid (PLA), poly-hydroxyalkanoates (PHA), and biopolyethylene.

Thermoplastic starch (TPS) is one of the most widely used bioplastics, constituting about 45 percent of the bioplastics market. Flexibilizers and plasticizers such as sorbitol and glycerine are added so that the starch can also be processed thermoplastically. The characteristics of the resulting bioplastic can be tailored to specific needs by adjusting the amounts of these additives. TPS holds the major market share in the compostable bag market. TPS bioplastics are also blended with biodegradable polyesters to produce blends. These blends are used for industrial and agricultural applications and can also be compostable.

Polylactic acid (PLA) is a common biopolymer mostly used as a raw material for packaging and food handling applications. PLA is a thermoplastic polyester whose starting material is lactic acid which can be made via the fermentation of sugar.

PLA can offer good thermal and mechanical properties similar to conventional plastics. However the properties of PLA highly depend on the molecular weight of polymer chain, the level of crystallinity, and the ratio between two enantiomers, L-PLA and D-PLA. Increasing the purity or concentration of L-PLA in the polymer chain increases the melting temperature while decreasing the elasticity of the PLA. Decomposition of PLA requires a hydrolysis step which makes it slower decomposing than most other biopolymers.

Polyhydroxyalkanoates (PHA) are biodegradable linear polyesters that can be obtained from several microorganisms such as bacteria. The microorganisms can accumulate the PHA in their cells as a reserve energy source. Extraction of the polymers from microorganism is done by breaking the cell walls or by enzymatic digestion followed by washing in centrifuge. The size of the PHA particles are about 0.5 µm and in a suitable environment for the microorganism, they can produce PHA up to 90% of their dry cell weight. Common types of PHA's are Polyhydroxy-butyrates (PHB), poly-hydroxybutyrate-hydroxyhexanoate (PHBH), and polyhydroxy-butyratevalerate (PHBV). PHA materials tend to have a maximum crystallization rate in the 40°C to 60°C range which means cause slower crystallization rates at lower temperatures.

Biodegradable polymers will degrade in bioactive environments by the enzymatic reactions of microorganisms such as bacteria or fungi. Chemical hydrolysis also helps break down biopolymer chains into their monomers. A biopolymer's life cycle in the environment starts with the photosynthesis reaction to produce sugars as a product which will be stored in plant cells. Starch can used as source of nutrients for bacterial anaerobic fermentation to produce bioplastics or to make lactic acid. With composting or anaerobic digestion of biopolymer waste, such as used films, trays, or plastic bottles the degradation of the bio-waste releases CO_2, H_2O, and biomass. Then the CO_2 and H_2O released from the degradation process is again used by plants with sunlight to perform photosynthesis. This is a very different life cycle and a much more balanced life cycle than the life cycle of petroleum based plastics which begin their life cycle with the extraction of petroleum from the earth and typically ends in a landfill.

Testing of materials to determine their use in Industrial composting is done per ASTM D 6400. "This specification covers plastics and products made from plastics that are designed to be composted in municipal and industrial aerobic composting facilities. The properties in this specification are those required to determine if plastics and products made from plastics will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials. The purpose of this specification is to establish standards for identifying products and materials that will compost satisfactorily in commercial and municipal composting facilities." (ASTM)

Agricultural Films and Sustainability

Agricultural films are protective films that are placed over soil, wrapped around fodder or covered over greenhouses. Agricultural films offer several advantages such as reducing soil compaction and erosion, increasing soil temperature, providing nutrients, suppressing the growth of weeds, supporting seed germination, and protecting against UV rays. Agricultural films can be classified based on their applications as: greenhouse film, mulch film, and silage film. They are generally manufactured using polyethylene (PE), polyvinyl chloride (PVC), and ethylene vinyl alcohol polymer (EVOH) and nylon among other materials. Linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) dominate the overall agricultural films market. Approximately 80% of the agricultural films are produced from LLDPE and LDPE.

Greenhouse cover films and mulch film products together accounted for more than 85% of the overall market in 2012. The consumption of agricultural film in North America was over 150,000 tons in 2015. Greenhouse covers are typically polyethylene and could be replaced by Bio-PE or a non PE bioplastic. However, because greenhouse cover materials are easily recycled Bio-PE is the best alternative. Mulch film is about 40% of the total PE film used in agriculture. Mulch film raises soil temperature, conserves moisture, and in some cases provides a protective fumigant barrier. With mulch films, crops are able to grow in a modified environment, allowing the plants to grow earlier and to a better size and quality. The barrier properties of the films also prevent the dispersal of the toxic fumigant into the environment. A biodegradable version of this film could eliminate the need to remove the film at the end of the growing season. Or, if removal is desired, these films could be recycled, composted, or used to produce biogas.

Soil fumigants are pesticides that, when applied to soil, form a gas to control pests that live in the soil and can disrupt plant growth and crop production. Soil fumigants are used on many high value crops and provide benefits to growers in controlling a wide range of pests, including nematodes, fungi, bacteria, insects and weeds. As gases, however, fumigants can move from the soil to the air at the application site and may move off site at concentrations that can produce adverse health effects in people from hours to days after application. These health effects range from mild and reversible eye irritation to more severe and irreversible effects, depending on the fumigant and the level of exposure. Because of these health risks, buffer zones are required around areas being fumigated. Using barrier films may result in a reduction in the size of a required buffer zone.

Broadcast fumigation requires a buffer zone to protect the surrounding neighborhood. The size of the buffer zone is determined by a calculation that includes the fumigant permeation characteristics of the film being applied to the field. In general, the better the barrier properties of the film the smaller the buffer zone and the larger the allowed growing area. Therefore high barrier films allow more growing acreage and greater safety. EVOH or nylon polymers are used in fumigation films together with PE to prevent contamination of the surrounding area. Films that utilize EVOH can be considered a totally impermeable film (TIF) material. A TIF film is multilayer film comprising typically, outer layers of PE, adhesive layers and a middle EVOH layer. Nylon can also be used as the barrier layer, but it is not as effective. It is considered a very impermeable film (VIF film). VIF nylon films also are multilayered with PE, as the EVOH is. TIF and VIF films produced using PE and/or nylon and EVOH are not compostable so they must be removed from the field at a cost to the grower.

Also, these TIF and VIF films are multi layered and require tie layers, so they can be difficult to recycle after being removed from the field. In a perfect condition they should be able to be recycled. However, the film sheets are glued together and the glue may not be compatible with the film materials and, after removal from the field, the films are very dirty from contact with the soil and require washing, drying and the use of more compatibilizers to make them useful. They are far from being clean recyclable materials and much of film removed from the fields ends its' life in a landfill. Their best option at this point may be incineration to produce power but that exacerbates the environmental issues further. These films are useful products that protect our environment from fumigant contamination, but they do not have a good end of life strategy.

There is also some use of biopolymers as mulch film, as they have physical properties similar to the polyethylenes, see Table 1. But they are not used for mulch films requiring fumigant barrier properties. The reason for this is because biopolymers do not typically have the barrier properties to resist the permeation of the fumigant chemicals.

Table 1. Typical Material and Application Properties

	LDPE	PLA	PBAT	PHA
Physical Properties				
Specific Gravity ASTM D792	0.92	1.26	1.23	1.21
Crystalline Melt Temp. (°C) ASTM D3418	110	162	126	125-160
Glass Transition Temp. (°C) ASTM D792	-70	60	-30	0
Mechanical Properties				
Tensile Yield Strength, (MPa) ASTM D638	26	52	38	20-30
Tensile Elongation, (%) ASTM D638	700	5	500	300
Notched Izod Impact, (J/m) ASTM D256	414	25	-----	20-48
Heat Distortion Temp. (°C) ASTM D648	106	60	-----	103

Among the compostable biopolymers, our research has shown that some could be modified for possible use as a barrier material for fumigants. Using oxygen permeation testing, which had previously been correlated with fumigant barrier characteristics, some of the biopolymers exhibited permeation values that were better than the nylon values and approached the permeation values of EVOH. Monolayer films of the biopolymers were then extruded and then tested for their resistance to fumigant permeation (see Table 2 below).

Table 2. Permeation Characteristics

	Oxygen (ccmm/m2 d atm)	Methyl Bromide (cm/hr)	Chloropicrin (cm/hr)
Material			
Compound A	5.0	0.003	0.005
Compound B	20.9	0.021	0.026
VIF film	65.0	0.06	0.06
TIF film	0.5	0.0005	0.0005
LDPE	198	0.6	1.2

These results show that a VIF film with very low permeation values could be produced using Compound A or Compound B. Fillers and additives are now being evaluated to determine if the TIF permeation levels can be reached. Even if TIF permeation levels cannot be reached, VIF films can be produced which would have different life cycle and end of life options.

Conclusion

Sustainability is now a part of our life style. Biopolymers can be used to improve the sustainability of many of our products. They can be carbon neutral and can have different end of life options than petro-based polymers. Agricultural mulch films used for fumigation can be made from biodegradable biopolymers that then can be composted or used for the production of biogas at the end of their life as a film. Non-biodegradable biopolymers can act as carbon traps, sequestering carbon dioxide from the atmosphere.