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Dr. G. M. Chapman shares about the properties of biodegradable plastics available for industrial use today.

From the time of their discovery and commercialization, plastics were designed to be long lasting and persistent, as the industry developed techniques and additives to support this trait.

Apart from certain early cellulose derivatives, which were not necessarily thermoplastic, the first work on "biodegradable" plastics started in the 1970s with researchers studying granular starch in polyethylene, developing gelatinized starch and evaluating of the biodegradability of polycaprolactone.

Regulations

While there was commercial development of these findings, the technologies only came under public scrutiny in the late 1980s. From 1985, several plastic products were introduced to the market with claims of biodegradability, as a few were marketed to help save diminishing landfill space. However, the US Federal Trade Commission, certain states attorneys general, state legislators and the U.S. Congress became concerned over several of the claims.

In the US, 48 legal actions were initiated for misleading environmental advertising, including those against Archer Daniels Midland (ADM) and Mobil, which resulted in fines about $1 million each. The latter was making claims for the biodegradability of Hefty bags in landfill when they included a photo degradation additive. The resulting negative publicity set the biodegradable plastics industry back by several years.

In addition, the Committee D 20.96 by the American Society of Testing and Materials (ASTM) was created to standardize test methods and standards, as there was an overreaction against degradable plastics based on polyethylene and a focus on rapid mineralization (conversion of polymers by microorganisms to carbon dioxide, water and biomass).

The committee developed the test method ASTM D 5338, which is a laboratory procedure to determine carbon dioxide evolution under simulated compost conditions. This became the basis for similar test methods in Europe and Japan. However, it has several drawbacks, the most significant being that the test does not take account of the amount of the plastic polymer that is biodegraded and assimilated into the biomass.

[A cup containing 2% of Addiflex additive after exposure to ultra violet light for 25 days.]

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A Standard Guide, D 6954-04, was later created for exposing and testing plastics that degrade in the environment using a combination of oxidation and biodegradation. While this is a significant step forward to the acceptance of the oxo-biodegradable technologies, it has yet to be a standard.

Biodegradable plastics technologies

As oxo-biodegradable plastics require oxidation before the polymer or polymer fragments can be metabolized by microorganisms, "biodegradable" polyesters need hydrolysis before they can be mineralized, particularly polylactic acid, which is hydrolyzed during composting and later mineralized. The polylactic acid is also not directly attacked by the microorganisms. Here are more details about bioplastics.

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1. Naturally derived polymers

Many naturally derived polymers have been tried in plastic applications and some of these have been deemed as thermoplastic. While the polymers derive from nature and there is an availability of enzymes to metabolize them, the polymer properties are however not necessarily compatible with typical plastic processes; nor are their properties comparable to synthetic polymers.

Cellulose and its derivatives have been used for many years. Cellulose can be made into thermoplastic by chemical treatment. The main derivatives, cellulose acetates, unfortunately become less biodegradable due to the higher degree of substitution by acetate that improves processing.

Starch, derived from corn, wheat or other cereal sources, is readily and widely available and has been the target of many attempts at commercialization in the plastics industry. However, starch decomposes at a lower temperature than it melts and therefore, for conventional processing, it needs to be plasticized, for example with water, glycerol or urea.

Because of the properties of starch, particularly its sensitivity to humidity, it needs to be blended with other processible polymers, such as polycaprolactone, in many applications. It is widely used in the loose fill sector, where starch is often blended with small amounts of polyvinyl alcohol, and can be used to replace expanded polystyrene.

Granular starch has been used as an additive to enhance the biodegradability of materials such as polyethylene. However, it does not render the synthetic polymer biodegradable.

While the biodegradability of natural starch has not been questioned by industry players, it has been shown to mineralize rapidly in aerobic or anaerobic conditions. However, like cellulose, with increasing substitution by acetyl groups, the biodegradation rate of starch falls.

Several other natural polymers have been proposed for biodegradable plastics, such as chitin/chitosan, proteins, particularly those derived from soy or wheat. However, their performance has not yet been satisfactory enough for commercialization. But with the spiraling cost of fossil fuel derived polymers, they could have a future.

2. Polyesters

Many varieties of polyesters have been proposed for biodegradable plastic applications, as several of them are produced microbiologically, particularly polyhydroxy butyrate/valerate. Until now this has not been a cost-effective process and Monsanto with Biopol (the technology belonged to ICI formerly) withdrew from the business. Metabolix and ADM, Procter and Gamble and Nodax are however proposing to commercialize these polymers.

Biodegradable aliphatic polyesters have been produced in Japan by companies such as Dhowa Highpolymer with Bionolle and in Korea by Ire Chemical. The materials are however costly to use.

Biodegradable aliphatic/aromatic polyesters have been developed by Eastman and Eastar (the technical know-how is currently owned by Novamont), as well as BASF and Ecoflex. These developments also face cost issues. Another version of aromatic polyester is Biomax from Dupont. The material biodegradables slowly and does not mineralize in less than 180 days in many tests.

Polylactic acid has been produced for many years mainly for medical applications and only in the last 10 years has it been proposed for commodity type applications. Much of this thrust

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has come from Cargill, whose production includes fermentation followed by formation of the dimmer and then polymerization, which means a high cost of production. There are several other polylactic acid producers, mainly in Japan. Other polyesters include materials such as polyglycolic acid, but these are not used in thermoplastic applications.

3. Vinyl polymers

The two main biodegradable vinyl polymers are polyvinyl alcohol (PVAL) and ethylene vinyl alcohol (EVOH). The degradation of these polymers requires oxygen and they do not biodegrade anaerobically. The speed of biodegradation of these polymers depends on several factors – for polyvinyl alcohol the degree of hydrolysis, whether it is pre-dissolved in water and whether the microbial population has been acclimatized to the material. For EVOH, its speed of biodegradation depends on the ethylene content (the higher the ethylene content the slower the rate of degradation).

There has been considerable commercial activity with polyvinyl alcohol in the past few years, particularly in Europe with companies such as Idroplast, Polyval, Aquafilm (now part of Monosol) and the Environmental Polymer Group (now part of Stanelco) promoting mainly PVAL film.

Because of the strength of PVAL it can be cost competitive on the basis of simple strength. However, it requires plasticization (like starch), is difficult to work with and is susceptible to moisture and changes in humidity. Its biodegradability can be slow and depends critically on the conditions.

Polyvinyl chloride has been suggested as a biodegradable material but the degradation is usually due to loss of plasticizer resulting in embrittlement, although it can be made oxidatively degradable.

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4. Oxidatively degradable, biodegradable systems

Instead of designing special biodegradable polymers, researchers have developed a technology to provide suitable additives for commodity polyolefines, such as polyethylene and polypropylene. These polymers generally have to be stabilized in order to be susceptible to oxidative degradation. Polymers such as linear low density polyethylene and polypropylene need antioxidants for processibility and stability in use.

By selecting a suitable commodity polymer and designing an appropriate additive, the necessary stability in use and degradation in the designated environment can be tailor-made with a "programmable life". As the additive, generally used at low levels, is added to a standard polymer, processing is straightforward as changes are not necessary in the manufacturing procedure. The physical properties of the product remain the same or are insignificantly different from the standard. Furthermore, the cost of the finished product is very close to the standard.

5. Others

Other biodegradable polymers include Polyox, poly(ethylene oxide), which is water soluble and environmentally degradable due to oxidation and aerobic biodegradation. Polyox has been used to make films.

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Performance in Oxo-Biodegrading

Eugen Karl Mössner details an experiment using an oxo-biodegradable additive system.

Oxo-biodegradable plastic additives provide viable, practical and easy to use solutions to littering of plastic products. These additives have been developed in Europe and the US for over the last 15 years.

In a life test of Addiflex system, oxidative degradation of a high-density polyethylene (HDPE) polymer carrier bag was observed within six weeks in outdoor weather conditions – between 18°C and 40°C with sunlight and rain.

A parallel test in Germany was also carried out under weather conditions between 5°C and 28°C with sunlight and rain. The results exceeded the performance seen in controlled laboratory tests. Here are the details of the typical degradation process initiated by oxo-biodegradable systems.

• The first stage of the degradation process leads to macromolecular chain breakdown due to the decomposition of peroxides, which drives the auto-accelerating oxidation of the polymer. The decomposition is accelerated by the transition metal catalysts.

The molecular weight (Mw) of the HDPE film was reduced from the original 180,000 daltons to Mw of 1,253 daltons within six weeks, resulting in polymer fractions that are small enough to be metabolized by environmentally ubiquitous microorganisms. The threshold value of Mw for transformation is less than 40,000 daltons.

• The second stage, known as the biodegradation stage, metabolizes the material from stage one with microorganisms resulting in biomass, water and carbon dioxide.

From extensive testing and research, it is observed that oxidative degradation is a normal precursor to biodegradation in the same way nature disposes off lignin fractions of wood and other plant matter. The term oxo-biodegradation is therefore used to emphasize the biodegradation of plastics in the two stages.

Using additive

From research, the AddiFlex additive provided results related to compostable plastic characteristics in addition to its oxo-biodegradable properties. Under composting conditions of 60°C and 5% oxygen, the Mw value dropped to less than 5,000 in six weeks and at 70°C and 5% oxygen in less than two weeks. The mineralization of the plastic reached was more than 60% within 180 days, which meets the specification of the ASTM D 6400, under composting conditions.

Oxo-biodegradable plastic additives have been developed in Europe and the US for over the last 15 years.

A parallel test in industrial compost showed that AddiFlex modified polyethylene-film in its unfilled as well as wood-fiber filled version disintegrated during the maturation of industrial compost. Only 19.3% of the original film material was found after 12 weeks.

There was a negligible weight (ratio) in the residue after 12 weeks had, with the plastic averaging 0.003% of dry weight after screening with a 20mm mesh. This was below the maximum allowable volume of 0.1% set by the Swiss Compost Regulations.

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