

Biodegradability...

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Biodegradability is an end-of-life option that allows one to harness the power of microorganisms present in the selected disposal environment to completely remove plastic products designed for biodegradability from the environmental compartment via the microbial food chain in a timely, safe, and efficacious manner.

Because it is an end-of-life option, and harnesses microorganisms present in the selected disposal environment, one must clearly identify the 'disposal environment' when discussing or reporting on the biodegradability of a product – like biodegradability under composting conditions (compostable plastic), under soil conditions, under anaerobic conditions (anaerobic digestors, landfills), or under marine conditions.

Specifying time to complete biodegradation or put in a better way time to complete microbial assimilation of the test plastic in the selected disposal environment is an essential requirement – so stating that it will eventually biodegrade or it is partially biodegradable or it is degradable is not acceptable.

High school or college biology/biochemistry teaches that microorganisms utilize/consume carbon substrates by transporting the material inside its cell, oxidizing the carbon to CO₂, which releases energy that it harnesses for its life processes (discussed in more detail later in the paper). So a measure of the evolved CO₂ is a direct measure of the ability of the microorganisms present in that disposal environment to utilize the carbon plastic product.

Unfortunately, there is a growing number of misleading, deceptive, and scientifically unsubstantiated biodegradability claims proliferating in the marketplace. This is causing confusion and skepticism among consumers, end-users, and other concerned stakeholders – in turn this is bound to hurt not only the fledgling bioplastics industry, but the plastics industry as a whole. Some examples of manufacturer's product claims are shown below – the direct quotes from the manufacturer's web site or product brochure are shown in italics.

Biodegradable PVC product claim

"Biodegradation process begins only when the bio PVC film is introduced into an environment (compost, both commercial and home, trash dump, the ground, lakes, rivers and the ocean) that allows microorganisms, which break down matter, to come into constant contact with the bio PVC film. Once that happens the 'special ingredients' attract the microorganisms that begin to break the hydrogen carbon chain that exists in the PVC. Once the chain is broken, this allows oxygen to enter which will attach itself to the hydrogen and carbon creating H₂O and CO₂. The lone chlorine atom bonds to a hydrogen atom creating a very weak salt that does not have any adverse effect on the ecosystem. The biodegradation process works in both aerobic and anaerobic conditions. So the absence of oxygen or water will not keep the bio PVC film from biodegrading. All that is needed are the microorganisms"

There is no scientific data provided to substantiate the complete breakdown and utilization of the PVC by the microorganisms present in the disposal system resulting in CO₂ and water as claimed. Furthermore, the proposed mechanistic chemistry describing the process would not pass muster in a high school honors chemistry classroom. However, a major corporation has adopted the biodegradable PVC card as an environmentally responsible 'green' solution because it is claimed to be 'biodegradable'.

Biodegradable PET product claim

"By having a more earth friendly PET biodegradable container and becoming a partner in helping to develop effective recycling programs, we can stem the rising tide of plastic pollution and leave our world a better place for future generations. Our bottles are 100% biodegradable in anaerobic (no oxygen, no light), aerobic and compostable environments and can be intermingled with standard PET during recycling. Our patented pending process allows our bottles to be metabolized and neutralized in the environment, turning them into inert humus (biomass), biogas (anaerobic) or CO₂ (aerobic)"

Again, no scientific data showing the 100% carbon conversion to biogas in an anaerobic environment or CO₂ in an aerobic environment using well established standard test methods in literature whether from the OECD, ISO, ASTM, or EN was presented.

Sorting through Facts and Claims



Oxo-biodegradable polyethylene (PE) film claims

"The technology is based on a very small amount of prodegradant additive being introduced into the manufacturing process, thereby changing the behavior of the plastic and the rate at which it degrades. The plastic does not just fragment, but is then consumed by bacteria and fungi and therefore continues to degrade to nothing more than carbon dioxide, water and biomass with no toxic or harmful residues to soil, plants or macro-organisms".

"Designed to interact with the microorganisms present in landfills, composters, and almost everywhere in nature including oceans, lakes, and forests. These microorganism metabolize the molecular structure of the plastic breaking it down into soil".

"Combined with an oxo-biodegradable proprietary application method to produce films for bags. This product, when discarded in soil in the presence of microorganisms, moisture, and oxygen, biodegrades, decomposing into simple materials found in nature. Completely breakdown in a landfill environment in 12-24 months leaving no residue or harmful toxins and have a shelf life of 2 years".

In each of the above cases no scientific data showing carbon conversion to CO₂ using established standard test methods is documented.

Another company claims a biodegradable plastic based on an additive technology different from the oxo-degradable additive class. Their claims reads *"Plastic products with our additives at 1% levels will fully biodegrade in 9 months to 5 years wherever they are disposed like composting, or landfills under both aerobic and anaerobic conditions".*

However, the graph of percent biodegradation against time in days shows the biodegradation curve reaching a plateau around 20% using a 50% additive master batch. In the final film samples, the recommended level of additive is only 1%. So the observed 20% would be even lower. However, the claim is made that *"the results of the aerobic biodegradation tests, indicate, that in time, plastics produced using the 1% additive will fully biodegrade."*

There are many more such examples of misleading claims. Several offer weight loss and other chemical evidence for the break down of the polymer into fragments. However, little or no evidence is offered that these fragments are completely consumed by the microorganisms present in the disposal environment in a reasonable defined time period. In a few cases evidence presented shows partial biodegradation, after which the

biodegradation curve plateaus. However, if one obtains only 5% or 30% or even 40% biodegradation, there is serious health and environmental consequences caused by the non-degraded fragments as it moves through eco compartments as discussed later.

Fundamental Principles in Biodegradable Plastics

Microorganisms (billions of them per gram of soil) are present in the environment. Figure 1 shows a low temperature electron micrograph of a cluster of E. Coli bacteria. Designing plastics and products to be completely consumed (as food) by such microorganisms present in the disposal environment in a short time frame is a safe and environmentally responsible approach for the end-of-life of these single use, short-life disposable packaging and consumer articles. The key phrase is 'complete' – if they are not completely utilized, then these degraded fragments, which may even be invisible to the naked eye, pose serious environmental consequences.

Microorganisms utilize the carbon product to extract chemical energy for their life processes. They do so by:

1. breaking the material (carbohydrates, carbon product) into small molecules by secreting enzymes or the environment (temperature, humidity, sunlight) does it.
2. Transporting the small molecules inside the microorganisms cell.
3. Oxidizing the small molecules (again inside the cell) to CO₂ and water, and releasing energy that is utilized by the microorganisms for its life processes in a complex biochemical process involving participation of three metabolically interrelated processes (tricarboxylic acid cycle, electron transport, and oxidative phosphorylation).

Figure 1 (Source: <http://emu.arsusda.gov/>)

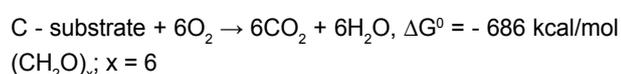


Unfortunately, all the focus is on demonstrating the break down or degradation of the carbon product (like weight loss, or oxidation levels) but no data on how much and in what time frame did the microorganisms present in the disposal environment consume the carbon food. This is how it gets misused and abused – by focusing only on the degradation but no data showing the utilization of the fragments by the microorganisms present in the disposal environment. Break down (decomposition) by non-biological processes or even biological processes, generates fragments that is utilized by the microorganisms, but also leaves behind fragments (and in some cases 50-80% of the original weight) which in many cases has been shown to be detrimental and toxic to the ecosystem.

This constitutes only degradation/fragmentation, and not biodegradation. As will be shown later, hydrophobic polymer fragments pose great risk to the environment, unless the degraded fragments are completely consumed as food and energy source by the microorganisms present in the disposal system in a very short period (one year) that is the degraded fragments must be completely removed from the environment by safely entering into the food chain of the microorganisms.

Measurement of Biodegradability

Microorganisms use the carbon substrates to extract chemical energy that drives their life processes by aerobic oxidation of glucose and other readily utilizable C-substrates:



Thus, a measure of the rate and amount of CO₂ evolved in the process is a direct measure of the amount and rate of microbial utilization (biodegradation) of the C-polymer. This forms the basis for various international standards for measuring biodegradability or microbial utilization of the test polymer/plastics. Thus, one can measure the rate and extent of biodegradation or microbial utilization of the test plastic material by using it as the sole added carbon source in a test system containing a microbially rich matrix like compost in the presence of air and under optimal temperature conditions (preferably at 58°C – representing the thermophilic phase). Figure 2 shows a typical graphical output that would be obtained if one were to plot the percent carbon from the plastic that is converted to CO₂ as a function of time in days. First, a lag phase during which the microbial population adapts to the available test C-substrate. Then, the biodegradation phase during which the adapted microbial population begins to utilize the carbon substrate for its cellular life processes, as measured by the conversion of the carbon in the test material to CO₂. Finally, the output reaches a plateau when utilization of the substrate is largely complete. Standards such as ASTM D 6400 (see also D 6868), EN 13432, ISO 17088 etc. are based on this principle.

The fundamental requirements of these world-wide standards discussed above for complete biodegradation under composting conditions are:

1. Conversion to CO₂, water & biomass via microbial assimilation of the test polymer material in powder, film, or granule form.
2. 90% conversion of the carbon in the test polymer to CO₂. The 90% level set for biodegradation in the test accounts for a +/- 10% statistical variability of the experimental measurement; in other words, there is an expectation for demonstration of virtually complete biodegradation in the composting environment of the test.
3. Same rate of biodegradation as natural materials – leaves, paper, grass & food scraps
4. Time – 180 days or less; (ASTM D6400 also has the requirement that if radiolabeled polymer is used and the radiolabeled evolved CO₂ is measured then the time can be extended to 365 days).

Two further requirements are also of importance :

Disintegration - <10% of test material on 2mm sieve using the test polymer material in the shape and thickness identical to the product's final intended use – see ISO 16929 and ISO 20200.

Safety – The resultant compost should have no impacts on plants, using OECD Guide 208, Terrestrial Plants, Growth Test or similar such as PAS 100(BSI, 2002). Furthermore, regulated (heavy) metals content in the polymer material should be less than defined thresholds e.g. 50% of EPA (USA, Canada) prescribed threshold.

Need for complete biodegradability

A number of polymers in the market place are designed to be degradable, i.e. they fragment into smaller pieces and may even degrade to residues invisible to the naked eye. While it is assumed that the breakdown products will eventually biodegrade there is no data to document complete biodegradability within a reasonably short time period (e.g. a single growing season/one year). Hence hydrophobic, high surface area plastic residues may migrate into water and other compartments of the ecosystem. In a recent Science article Thompson et al. (2004) reported that plastic debris around the globe can erode (degrade) away and end up as microscopic granular or fiber-like fragments, and that these fragments have been steadily accumulating in the oceans. Their experiments show that marine animals consume microscopic bits of plastic, as seen in the digestive tract of an amphipod. The Algalita Marine Research Foundation (see www.algalita.org/pelagic_plastic.html) report that degraded plastic residues can attract and hold hydrophobic elements like PCB and DDT up to one million times background levels. The PCB's and DDT's are at background levels in soil, and diluted out so as to not pose significant risk. However, degradable plastic residues with these high surface areas

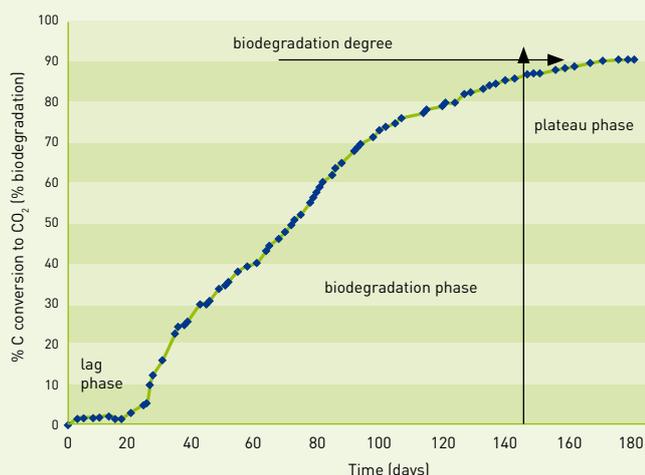


Figure 2: Test method to measure the rate and extent of microbial utilization (biodegradation) of biodegradable plastics

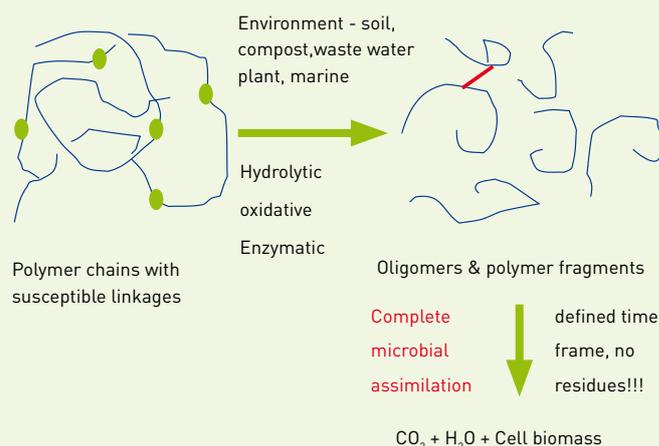


Figure 3: Complete biodegradation

concentrate these chemicals, resulting in a toxic legacy in a form that may pose risks in the environment. Japanese researchers (Mato et al., 2001) have similarly reported that PCBs, DDE, and nonylphenols (NP) can be detected in high concentrations in degraded polypropylene (PP) resin pellets collected from four Japanese coasts. This work indicates that plastic residues may act as a transport medium for toxic chemicals in the marine environment.

Therefore, designing hydrophobic polyolefin plastics, like polyethylene (PE) to be degradable, without ensuring that the degraded fragments are completely assimilated by the microbial populations in the disposal infrastructure in a short time period, has the potential to harm the environment more than if it was not made degradable. These concepts are illustrated in Figure 3 which shows that heat, moisture, sunlight and/or enzymes shorten and weaken polymer chains, resulting in fragmentation of the plastic and some cross-linking creating more intractable persistent residues. It is even possible to accelerate the breakdown of the plastics in a controlled fashion to generate these fragments, some of which could be microscopic and invisible to the naked eye. However, this degradation/fragmentation is not biodegradation per se and these degraded, hydrophobic polymer fragments pose potential risks in the environment unless they are completely assimilated by the microbial populations present in the disposal system in a relatively short period.

Summary

The take home message is very simple --

Biodegradability is an end-of-life option for single use disposable, packaging, and consumer plastics that harnesses microbes to completely utilize the carbon substrate and remove it from the environmental compartment -- entering into the microbial food chain. However, biodegradability must be defined and constrained by the following elements:

- The disposal system – composting, anaerobic digester, soil, marine.
- Time required for complete microbial utilization in the selected disposal environment – short defined time frame, and in the case of composting the time frame is defined as 180 days or less.
- Complete utilization of the substrate carbon by the microorganisms as measured by the evolved CO₂ (aerobic) and CO₂ + CH₄ (anaerobic) leaving no residues.
- Degradability, partial biodegradability, or will eventually biodegrade is not an option! – Serious health and environmental consequences can occur as documented in literature.
- Measured quantitatively by established International, and National Standard Specifications -- ASTM D6400 for composting environment, ASTM D6868 for coatings on paper substrates in composting environment, ASTM D7081 marine environment, European specification, EN13432 for compostable packaging, and International ISO 17088 for composting environment.
- If other disposal environments like landfills, anaerobic digester, soil, and marine are specified, then data must be provided showing time required for complete biodegradation using established standardized ASTM, ISO, EN, OECD methods.
- All stakeholders should review biodegradability claims against 'data' and if necessary use a third party independent laboratory to verify and validate the data using established standardized test methods and specifications, and based on the fundamental principles and concepts outlined in this paper.

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Bag Manufacturer to Stop Advertising Environmental Claims for Oxo-Products

The US National Advertising Division of the Council of Better Business Bureaus has recommended that GP Plastics Corp. modify or discontinue certain advertising claims for its PolyGreen plastic bags.

Among the criticized claims are for example:

- PolyGreen plastic bags are '100% oxo-biodegradable'
- PolyGreen plastic bags are 'disposable through ordinary channels' and go 'From front lawn, to waste bins to the landfill'
- 'Eco-Friendly Plastic Newspaper Bags'
- PolyGreen plastic bags are "environmentally friendly."

According to GP Plastics the plastic bags are manufactured using 'oxo-biodegradable' technology.

NAD noted that the advertiser's claim that PolyGreen bags 'are disposable through ordinary channels' should similarly be supported by competent and reliable scientific evidence that the entire plastic bag 'will completely break down and return to nature ... within a reasonably short period of time after customary disposal.' However, NAD determined that the evidence in the record did not support that claim.

NAD recommended that the advertiser discontinue the claim that PolyGreen bags are '100% oxobiodegradable' and otherwise modify its advertising to avoid conveying the message that PolyGreen bags will quickly or completely biodegrade when disposed of through 'ordinary channels,' e.g., when placed in a landfill.

NAD further recommended that the advertiser discontinue claims such as 'eco-friendly' and 'environmentally friendly' etc. because the claims overstate the evidence with respect to the degradation of the plastic bags.

GP Plastics Corp. has said it will appeal NAD's findings to the National Advertising Review Board.

NAD's inquiry was conducted under NAD/CARU/NARB Procedures for the Voluntary Self-Regulation of National Advertising.

For more information about advertising self regulation, please visit www.narcpartners.org.

f Source: www.nadreview.org/content/pressdoc/4944PR.pdf

Two New Laws in California

Independent testing of several so called 'oxo biodegradable' plastic bags in the marketplace have shown little or no biodegradation using accelerated aerobic test methods, such as ASTM D5338 and ISO 14855. Moreover, the reports clearly state that these materials do not meet the requirements of ASTM (6400), European (EN 13432) or international (ISO 17088) specification standards. An independent study commissioned by the State of California's Waste Management Board with a California public university and under their supervision showed that the 'oxo-biodegradable' bags on the market showed no biodegradation ('Performance Evaluation of Environmentally Degradable Plastic Packaging and Disposable Service Ware,' California Integrated Waste Management Board (CIWMB) Publications, (June 2007).

This study, and the proliferation of unsubstantiated claims on biodegradability forced the State of California to put in place laws

AB1972: ... prohibit the sale of a plastic bag that is labeled as "compostable" or "marine degradable," unless that bag meets the ASTM Standard Specification for Compostable Plastics D6400, the ASTM Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment D7081, or a standard adopted by the California Integrated Waste Management Board, as specified. The bill also would prohibit the sale of a plastic bag that is labeled as "biodegradable," "degradable," "decomposable," or as otherwise specified.

A companion bill AB 2071: ...would authorize a city, a county, or the state to impose civil liability, in specified amounts, for violations of the above provisions and would require any civil penalties collected to be paid to the office of the city attorney, city prosecutor, district attorney, or Attorney General, whichever office brought the action.

f Weblinks to the mentioned documents can be found at www.bioplasticsmagazine.de/200901a

Mark your calendar



bioplastics MAGAZINE is planning the **2nd PLA Bottle Conference** to be held during drinktec 2009 (mid September 2009) in Munich, Germany. A 'Call for Papers' is now open. Send your proposals to the editorial office.

f mtf@bioplasticsmagazine.com
www.pla-bottle-conference.com
www.drinktec.com

Use of Oxo-Additives implicates loss of Warranty

Braskem, Brazilian Petrochemical Company, developer of biobased polyolefins (Polyethylene and Polypropylene) made from renewable raw materials, mainly sugarcane-bioethanol and with a project under construction to produce 200 Kt/y of Green PE, starting end 2010, does not warrant the performance of its resins with additives for the so-called 'oxo-degradation'. The use of such additives with Braskem's polyolefins, implicates the loss of warranted qualities of the materials.

In a data sheet accompanying their 'High Density Polyethylene HF 0147' for instance it is stated:

Braskem's resins do not contain additives produced from metals or other substances which have the objective to promote oxo degradation. Such additives and the decomposition and fragmentation of resins caused by the oxo degradation compromise the approval of the resin regarding requirements of the Resolution 105/99 of ANVISA (Brazilian National Agency of Sanitary Monitoring). The use of these additives implicates the loss of the performance warranties described in this document.

www.braskem.com.br

Frost & Sullivan Award for DuPont

DuPont recently received the '2008 European Bioplastics Product Line Strategy Award' from Frost & Sullivan -- a leading market consulting company -- for its accomplishments in rapidly developing an extremely diverse range of high-performance materials based on renewable sources.

Several DuPont renewably sourced products already are in the market and can be found in textile, automotive, cosmetics, personal care and industrial applications. Adriano Bassanini, DuPont BioMaterials leader, Europe, Middle East & Africa, received the award on behalf of DuPont. "This is an achievement we should be proud of. Bioplastics lie at the heart of our growing business platform," Adriano said.

"This diverse approach makes DuPont rather unique in the industry, as most other companies are focusing on a narrow range of bio-based chemistry for their biomaterials portfolio. Frost & Sullivan is therefore proud to confer this award to DuPont," said Dr. Brian Balmer of Frost & Sullivan.

www.renewable.dupont.com

Dr.-Ing. Christian Bonten,
FKuR-Director Technology
& Marketing

News



FKuR and Ritter Pen got award for innovation

Biograde® from German FKUR Kunststoff GmbH, in the form of the new Bio-Pen from the writing utensils manufacturer Ritter-Pen GmbH has been granted the award for innovation 'Biomaterial of the year 2008'.

Biograde is a transparent, injection mouldable bioplastic based on cellulose. This co-developed product from FKUR and Fraunhofer UMSICHT combines renewable and biodegradable cellulose acetate with special additives and coupler by means of an adapted biocompounding process from FKUR. Biograde is transparent (depending on grade), dyeable, scratch and heat resistant. The cellulose acetate used is gained from European soft wood. Bio-Pen is a new series of writing utensils from Ritter-Pen for the ecologically aware consumer. 80 % of the ball pen is made from the renewable and compostable Biograde.

"With the help of Biograde Ritter-Pen is able to develop aesthetically appealing writing utensils that meet the consumers' wish for eco-friendly products. Biograde is injection mouldable, and what is more even dyeable and printable", says Fredy Büchler, managing director from Ritter-Pen. "Together with Ritter-Pen we are very pleased about the award, since it confirms that with the development of injection mouldable bioplastics we are in the pulse of time.", explains Dr. Edmund Dolfen, managing director of FKUR. Bioplastics are a class of polymer which have properties comparable to conventional polymers, but are made from renewable resources or enable the biodegradability of the products made from this material.

The innovation award 'Biomaterial of the year 2008' has been granted by the company Reifenhäuser GmbH & Co. KG within the framework of the international congress 'Raw Material Shift & Biomaterials' of the nova-institute on in Cologne the 3rd /4th December.

www.fkur.com
www.ritter-pen.de
www.umsicht.fraunhofer.de

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