Biopolymers and additived plastics : biodegradability, degradability and compostability. Basic concepts, comparisons and legislation

The case of ECM MasterBatch Pellets additive

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CONGRESSO DELLE MATERIE PLASTICHE

THE PLASTIC REVOLUTION:

How plastic materials' technological development has bettered the life quality

OCTOBER 23, 2008

Milanofiori Congress Center - Assago (MI)

1. PLASTICS BIODEGRADABILITY AND COMPOSTABILITY: GENERALITY

The search of the best possible plastic, flexible to industrial needs but also biodegradable led to develop two, large, tendencies of thought opposed apparently
An initial idea was to "imitate nature" trying to reply existing macromolecules (mainly derived from starch and sugar) verifying the possibility of their polymerization to get a plastic-like substance used for the same purposes to which is dedicated traditional "plastic" that comes largely from oil (polyethylene, polystyrene, polyvinyl).
A second tendency of thought has directed its efforts towards the use of special additives that can stimulate the transformation of traditional plastic in CO2 and water when added to a minor measure (1%) and under certain operating conditions.

Many researchers realized how difficult is to distinguish something "natural" from a product of "synthesis"; in some cases the molecules are perfectly identical, making it impossible to distinguish.
It was discovered that besides the molecular bonds, in order to a better biodegradability is of particular importance the polymer ramification and some radicals that are in the molecule.

1.1 Biodegradability, bioplastics, compostability, disintegrability and related legislation

The term "bioplastics" usually refers to two classes of materials and therefore of final products different for behavior: one is that of biodegradable and compostable materials (characterized by a particular feature), the other is that of plastics derived from renewable materials or RRM (characterized by the type of source material).
Sometimes these two classifications can be found in a single bioplastic (for example MaterBi), sometimes a bioplastic corresponds to one of these two classifications (for example some derivative from polymerization of particular sugars).
The biodegradability of a plastic material is characterized by the presence of decomposers (microorganisms like fungi and bacteria) in the environment that reduce the complex organic molecules into simpler constituents to bring to an inorganic stage (water and carbon dioxide).
The biodegradability is possibly enhanced by the presence of another feature: the compostability.
The composting biological process, which is subjected compostable material, produce carbon dioxide, biogas, water, inorganic materials and biomass.
When a plastic or any other material that is not natural (or rather not created by nature) can be defined compostable and treated as such, this is provided by a European standard:
EN 13432 (adopted in Italy as UNI EN 13432) "Requirements for packaging recoverable through composting and biodegradation Test scheme and evaluation criteria for the final acceptance of packaging" to provide presumption of conformity with the European Directive 94/62 EC.
A compostable material must have the following characteristics: biodegradability, disintegrability (that is fragmentation and loss of visibility in the final compost), low levels of heavy metals (below the predefined maximum values), other chemical -physical parameters that must not change after the degradation of the material (pH, salinity, volatile solids, N, P, Mg, K) and, of course, absence of negative effects on composting process and compost quality. The harmonized norm EN 13432 also provides that the degradation process must take place between 12 and 24 weeks, in industrial composting conditions.

In synthesis, there are natural materials that are difficult to biodegrade (for example banana peel, cooked meat, lignin or straw) and vice versa, synthesis material that are easy to degrade (citric acid esters or polyvinyl alcohol).
We must also stress that the biodegradation is a natural process that takes place when both aerobic or anaerobic conditions are favorable (for example rubbish skip, soil and landfill) , composting instead is a controlled application of the micro-organisms ability (bacteria and fungi of different species) to metabolize the substance/s mixed and kept in special environmental conditions

Plastics derived from renewable resources are exclusively those deriving from biomass, or substances of plant and animal origin. It follows that this last class materials should not necessarily be compostable and biodegradable, while biodegradable and compostable materials should not necessarily result from resources renewable.

However, in both classes it is used a high percentage of renewable raw material, from 45 to 100% of the plastic composition classified as biodegradable. While taking into account that research in the biodegradable plastics field over these last few years is leading to a significant diversification of biopolymers and raw materials from which they rise, we can distinguish mainly these basic materials: some types of polyester and amides polyester, polyvinyl alcohol-PVA-Polyvinyl (Hydrolene produced by Idroplast Srl and Gohsenol produced by The Nippon Synthetic Chemical Industry Co., Ltd.), 1,3-propanediol derived from corn sugar, polysaccharides such as starch and sugar by-products, polyhydroxyalkanoates (PHA), Polylactic acid PLA (PLA Natureworks produced by Huhtamaki Oyj), cellulose acetate. Among latest materials of renewable origin there are fructose - a sugar found in fruit, corn syrups and honey - in form of hydroxymethylfurfural (HMF). Among the origin materials of these substances we find therefore cereals, mainly maize and wheat (Mater-Bi produced by Novamont, Sorona and Hytrel-based on DuPont's PDO), vegetables (beets, tomato, potato-Solanyl produced by Rodenburg Biopolymers), the pome fruit (apples in particular) and recently even sugar cane, as well as algae and crustaceans, polyhydroxyalkanolate - PIA-(macromolecules synthesized by bacteria Gram + and Gram- Terramak produced by Unitika), cellulose and its polymers. The bioplastics derived from these natural materials in some cases may also be combined with each other, forming compound and blend or semi-finished products such as multilayer film, or can be coupled with the paper

1.1.1 Biodegradation concept

All listed biopolymers present various biodegradability characteristics especially in terms of time in which the biodegradability occur (primary and ultimate). As to this delicate issue (definition of degradation and biodegradation) the international scientific community is confronted by time providing data and results useful to a single and recognized definition

Degradation is defined as the process that for the most part through physical and chemical agent reduces a substrate in smaller pieces without a significant loss of matter. The substrate remains essentially the same but fractionated into several pieces. When chemical and / or physical action eases (increased relative area) a bacterial attack, we may have loss of matter and a partial biodegradation.

Biodegradation perhaps is a more familiar concept. When natural organic materials go into the ground, they tend to decompose progressively, to disappear. This phenomenon is very important for the environment, which has to get rid of waste to make room for new life.
Trees, plants and algae absorb carbon dioxide from the atmosphere and, with the power of the sun, the inexhaustible source of energy, use it to synthesise sugars, and a whole range of other substances present in Nature. However, this mechanism would quickly become blocked if the opposite process did not exist, that is, if it was not possible to release carbon dioxide from organic material. So, in natural equilibrium, the process of biodegradation is as important as that of photosynthesis, of which it is both the outcome and the starting point.

An important role is played in biodegradation by micro-organisms, which are present in every environment, and which are fed by organic waste occupying the last link in the food chain. Thus, organic material is transformed again into carbon dioxide, thereby completing the natural cycle. As for the plastic when it loses one or more physical-mechanical characteristics , you can say that it has begun a **primary biodegradation** or rather a chemical enzymatic reaction and / or a bacterial action that has altered the molecule so that its characteristics properties are no longer evident or when it no longer responds to analytical method (defined by Biodegradability Sub committee of WPCF-1967).
Since biological processes, in general, are long sequences of reactions in which the molecule changes little by little, we cannot wait for an answer on / off as regards, for example, the porosity or the compression strength or the method conformity because everything depends on the degradation degree and above all on its speed.

Biodegradation concept seems to be lacking in accuracy because it depends on arbitrary standard, whether analytical or functional .

Ultimate degradation is defined as the complete conversion of the molecule to carbon dioxide , water, inorganic salt, and product associated with the normal metabolic process (e.g. amino acids and fat acids more or less complex). However, the concept of "normal" is often not well defined, some natural foods such as sugars and proteins contain variable percentages between 5 and 10% of biodegradation proof catabolites.
The transformation of organic material into carbon dioxide and water is reported as mineralization and a full degradation is often considered similar to a full mineralization.
The latter term implies that all the original atoms of the organic substance can be converted into inorganic species including also synthesized products as a new organic substance.
The full mineralization practically speaking is an ideal concept that seems impossible and unnecessary to reach.
Between the two extremes (**primary biodegradation and ultimate or final biodegradation**) the WPCF (1967) offers the concept of "Environmental Acceptable Biodegradation" defined as susceptibility to biodegradation yielding end-products which are totally acceptable in the receiving environment including in that period, air soil and water.
About the meaning of the term "totally acceptable" the debate is still open.

Another distinction was made by the OECD experts group in 1981 between immediate and ingrained biodegradability or between the degradation process that begins on contact with the substance with the original microbial population and that in action after an appropriate adaptation / acclimation (hours, days or weeks).
Biodegradation concept is usually connected to aerobic and anaerobic microorganisms mix of heterotrophic kind able to grow and to auto distinguish on the considered substrate.
You must clarify that there are studies and research conducted in laboratory on pure and selected cultures that using various substrates can get very interesting results.
As to biodegradation matter the reference biomass is a natural biomass (bacteria and fungi),that is taken from sites where there are ongoing contact between the microorganisms and the substrate to degrade and is circumscribed in an artificial environment (e.g. flask) where you can follow the evolution of attacks brought to molecules in condition of oxygenation, nutrients and ideal pH.
Bacteria and fungi are relatively simple organisms and which are flexible in their metabolism contrary to other forms of life more rigidly bound to certain categories of nutritive substrates.

The great variety of bacteria and fungi existing in nature, even in a simple grail of soil, allows the use of various molecules as food. Despite their great spirit of adaptation, there are some limits to growth due to different metabolism of each species; we only remember the fundamental difference between aerobic and anaerobic bacteria (forced or otherwise) and the ability to use a few selected substrates to grow.
The available scientific literature appears then in agreement on general topics but not yet unequivocal in describing and cataloguing degrading processes ongoing in nature or in laboratory and, above all, it records difficulty to catalogue and to evaluate biodegradation concept.

2. Additives and ECM MASTERBATCH PELLETS: a revolutionary additive

2.1 Additives

It should also be noted that a possible replacement of olefins plastic with other materials (e.g. biopolymers derived from starch) would be slow and complicated; it would be impossible to convert world production plants in short or middle time. New raw materials, new process protocols, new plants require large investment and long time.
European Bioplastics Association has estimated that European potential market of biodegradable plastics amounted to 4 million tons, 10% of continental plastics consumption.
To face biodegradable plastics demand, however, would need investment in billions of Euros for the creation of an adequate production capacity, and everything should be accompanied by regulatory able to support the demand growth and the offer, so as is happening in the renewable energy field

Category association ASSOPLAST shows also that although in 2005 starch and sugar costs (raw materials for bioplastics production) were lower than those of raw materials of petrochemical origin and that over the last few years have also increased plastic natural origin producers, giving rise to more competition that will lead to further reductions in production costs, in 2008 corn and starch cost has generally tripled because of considerably demands for biofuels and bioplastics market.
In that very turbulent phase of raw materials markets seems of primary importance to bring to light and spread the additives use (probably the only effective and available remedy to solve plastic biodegradability problem without damaging important food resources).
To complicate situation regarding bioplastics use, making it negative in terms of "general environmental sustainability", is the world problem of reduction of important agronomical resources, destined to feeding (corn, rice, cereals in general); since 2006 the corn price is much increased in Latin America troubling local people accustomed to a diet based on corn for ages. The same fate could happen to rice or cereal in general causing repercussion in Europe too.

Scientific research has begun for a long time test to modify and to improve the traditional plastics intervening on key polymer of its structure by introducing additives.
In particular ECM MasterBatch Pellets additive is a copolymer of EVA with ingredients additives of grown organoleptic-organic colloids and it can then be easily added to plastic resins using existing technologies. This technology is an additive which, when combined as a one percent load to plastic resins (mainly polyvinyl and polypropylenes), renders the finished plastic products biodegradable while maintaining their other desired characteristics. The potential uses of this technology are limited only by the imagination.
The most obvious applications would include one-use, disposable products such as waste disposal bags, packaging products, disposable diapers, erosion control materials, plant containers, disposable medical apparatuses, food containers and utensils, oil spill containment systems, and many others. Due to the exceptional shelf life of products manufactured with ECM MasterBatch Pellets™, wherein biodegradation does not begin until disposal, items that are not of the "one use and then dispose" type will be very important applications for ECM's technology. Items such as toys, games, notebooks, computer and cellular telephone casings, etc., should all be considered as extremely lucrative potential markets. Considering the new uses for plastics that will be opened up or which will become more acceptable to the public because of this technology, the manufacturer will be able to compete with non-degradable plastic products.
ECM has developed the technology to the point that nearly any plastic product producer can use the additive without having to modify their existing methods of production. The resulting plastic products exhibit the same desired mechanical properties, have effectively the same shelf-lives, and yet, when disposed of, are able to be metabolized into ecologically beneficial biomass by the communities of microorganisms commonly found almost everywhere on this planet. The biodegradation process can take place aerobically and anaerobically. It can take place with or without the presence of light (i.e. landfills). The ECM technology differs significantly from other "(bio)degradable plastics" emerging in the market today because it does not attempt to replace the currently popular plastic resin formulizations but instead enhances them by rendering them biodegradable.

It is a result of decennial research and has solved biodegradation matter so that under certain operating conditions the linear structure loses its unity changing into medium-small pieces which molecules are deeply altered by a chain reaction favored by one or more catalysts (masters-additives). They can liberate carbon dioxide as demolition product and predisposing it for a bacterial / fungus attack if this material, for example is composted or placed in conditions wherein they are in contact with other organic putrescible substances both in aerobic and in anaerobic conditions.
Demolition kinetics favored by additives can be extremely changeable and they derive largely from used catalysts.
At the beginning of the process it's a chemical induced reaction, where the demolition speed is usually slow to start and then acquires ever greater speed or however a constancy in time.
The molecular structure change, caused by a mixture of physical factors (mainly by temperature, humidity, pH and carbon dioxide concentration), triggers important changes (visible also to the electron microscope) on the material surface making it open to attack by enzymes issued by bacteria and fungi if present.

Effective additives especially ECM are then able to render any derived olefinic and styrene plastic degradable and biodegradable according to the standard fixed, at the moment, by the international scientific community which stress the need to have the complete conversion to carbon dioxide and water, although there is not full agreement about times and operating way to assure this result.

Another innovative way to prevent the accumulation of non-biodegradable plastic on our planet (destined to remain almost intact for hundreds of years if not more) is looming, that will be able to intervene easily in current manufacturing processes without to alter or to upset them. At the same time they will be able to protect corn for uses to which they have always been used: human and animals food.

The additives use could allow a "soft" transition from the old to the new plastic that should use only renewable substrates rejected at the moment (e.g. straw and corn stalks) and that in the next 50 years will evolve yet, to candidate as the most versatile and ecological material never seen on the Planet.

3. Legislation and limits coming from its application

Europe and United States have attitudes and philosophies in common on this matter that may be found on this sector literature and in particular on methods and times to transform plastic from an "indestructible waste" to a substance that can be turned into carbon dioxide and water.

Biodegradation methods and times were fixed by law, so basically similar between the two sides of the Atlantic. On this matter, in U.S. reference standard are the follows ASTM D5338, D6400, D6868, D5526 in Europe instead we have UNI 13432, UNI 14855, UNI 14995, UNI 11183 but the final judgments are very similar: both in U.S. and in Europe is generally considered acceptable the biodegradation level of at least 90% reached in less than 6 months.

Knowing that "plastic" has very long degradation times (see table) any significant change compared to the time-table begins to be considered positive, some researchers have pointed out that "ordinary people" perceive biodegradation concept on the basis of information transmitted to their.
In other words there is no objective comparison to declare that a substance that completely degrades, transforming itself into carbon dioxide and water in two years, is worse than that that degrades in six months.
To be perceived as "biodegradable" it would be sufficient a reasonable time much less than the times specified in the table. In a general description of sustainability, we believe that it wouldn't be incorrect to assert that a biodegradable plastic in compost in 12-36 months should be considered fully biodegradable. In this context the use of additives that can deeply transform the polymeric molecule preparing it, under certain operating conditions, to a bacterial / fungus attack able to biodegrade all the product (> 90%) in less than three years (from 12 to 36 months) may be considered a result of great environmental value able to influence the new global production of plastic that will follow the forced road of biodegradability and, in medium long time, of renewable resources without affecting the corn production but using for example straw or corn stalks completely neglected and unused product.
The additives are an ideal transition system to achieve new plastic without market upsetting and without food removal to the people inhabiting our Planet.
Many research are going to produce cellulose (and then starch or sugar) starting from scrap wood or from plants considered by definition renewable resource, the efforts till now have not produced appreciable results by preferring to bioplastics producers starch or sugar direct use.
At present, then the use of additives is presented as the best choice to get the plastic of the future (technological and ecological), made, we hope, entirely with renewable resources currently considered of waste and of difficult use.

Table on general degradation times in soil without composting process or other controlled biomass systems (purification plants, anaerobic digestion)

PRODUCT	BIODEGRATION TIMES	ORGANIC COMPOSITION
Tissue	3 months	Cellulose
Cigarette without filter tip	3 months	Cellulose and tobacco
Filter-tipped cigarettes	2 years	Cellulose acetate
Apple-core	6 months	Water, sugar and cellulose
Wax matches	> 1 year	Stem with stearin or paraffin
Matches	<1 year	Lignin and cellulose
Newspaper	10 years	Cellulose
Beverage cans	from 10 to 100 years	Aluminum
Cigarette Lighter	100 years	Part in plastic
Plastic bottles	from 100 to 1000 years	Polyethylene and polyvinyl chloride
Plastic bag	from 100 to 1000 years	Polyethylene
Polystyrene	1000 years	Polymerized styrene
Phone card	1000 years	Plastic and polyethylene
Glass	4000 years	Siliceous sand and soda
Box of photographic film	20 -30 years	
Leather and hide	50 years	
Wool clothes	5 years	
Orange and banana peel	> 2 years	

However, this important opportunity is, in part, limited in its expansion by some European and U.S. standards that codify the criteria by which we consider biodegradable plastics and methods to render it like that and to recycle it.

4. Standard for substances / products biodegradability assessment

They were listed several standard for substances / products biodegradability assessment with different purposes and applications. Specifically we have:

- ISO 14855 determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions
- ASTM D 5338 standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions
- UNI 13432 requirements for packaging recoverable through composting and biodegradation
- UNI 1118 room-temperature biodegradable plastic materials
- UNI 14995 plastics evaluation of compostability
- ISO 14851/14853 anaerobic biodegradability of polymer films
- ISO 17556 Determination of the ultimate aerobic biodegradability in soil

Moreover, the Directive to follow at EU and national level is the European Directive 94/62 EC, of which the norm EN 13432 provides only a presumption of conformity.
The same directive specifies that other methods can be used by operators for the keeping of the rules. Therefore, the EN 13432 is not a legal obligation, but only reference Norma Technique for assessing of packaging biodegradability in high temperatures composting facilities and not biodegradable materials in general or packaging biodegradability in households facilities. To complete the picture we point out that there are also methods to determine the biodegradability in aqueous solution.

5. Composting: European approach to plastic biodegradation

Among the best processes suitable for post consumption running of biodegradable plastics, composting is certainly the best solution if some legislative changes will be made with reference to the degradation that currently are objectively too short. The additived plastics does not put any problem in composting process and in some cases there is a general improvement of final compost in its agronomic characteristics.
It is a consolidated reality for the treatment dedicated exclusively to biodegradable organic materials, composting can be achieved even with the use of plastic that show, however, to have characteristics of decomposition similar to organic matter. Together with aspects of reduction of organic waste to start in landfill (see D. lgs. 36/2003), the entry of biodegradable packaging in composting would allow to achieve a quality finished product(noticeable decrease in the fraction of unwanted inert) and in parallel to control the more amount in output from plant, whose fate remains that of landfill.
In Europe there are two marks that certify industrial compostability of a product realized only with biopolymers: "OK compost" mark of Belgian company of Vincotte certification and DIN Certco, the most popular in Europe.
Since July 2006 in Italy Consorzio Italiano Compostatori introduces its compostability Mark and since May 2007 the CIC is able to begin a certification course and the issuing of the mark to companies that are subject to the certification program of Certiquality.
Examining the content of the above-mentioned standards appears clearly how the requirements (biodegradability, disintegrability and the final quality of the compost) and the procedures to define the compostability are both common.
While for biodegradability determination and for compost quality, it refers to very specific standards (ISO, EN, UNI, ASTM etc.), regarding the disintegration there is the need to define in detail the test, providing to the reference laboratory a real test protocol.

For additived plastics don't exist a trademark of compostability yet because the currently norm to fix the requirements for biodegradation assessment foresee too short times to allow these plastics to unfold their potential biodegradability even if now is proven their complete absence of toxicity.

It opens then a comparison between the scientific and legislative community and plastic industry, that should be able to ensure the correct disposal of these interesting innovative biodegradable plastics in mean times (12-36 months) which could represent the necessary sharing step between "old" and "new" plastics.

6. Conclusion

There are enough studies and tests to say that next to biopolymers derived primarily from corn starch, rice, cereals, legumes and various sugars are coming to light new and interesting plastic products from raw materials derived from oil with the addition of additives. Degradability and biodegradability of plastic has become the most important matter to compete on world scale in the field; the unremitting increase in applications of this versatile and flexible product is expected by 2050 an average per capita consumption of 50 kg/ year of plastic. If plastic remained as now we would be invaded by this kind of waste for hundreds of years if not thousands of years; the environmental, aesthetic and ecological impact would be devastated. It is essential therefore to get to use only "biodegradable plastic" or that it is able, in acceptable times, to transform largely in carbon dioxide and water when in contact with accidental biomass (e.g. soil) or arranged in proper facilities (composting, anaerobic digestion, purification plants). Scientific research has tried to give concrete answers with the creation of biodegradable biopolymers using renewable basic products such as starches, sugars and proteins derived from plant and experimenting with the use of additives that can profoundly transform the molecule of olefinic origin when put in contact with active microorganisms (biomass).

The main difference between two kind of "plastic" is represented by "biodegradation" times:

- Most biopolymers degrade in 6-9 months
- Most additived plastics degrade in 12-36 months

In the light of the long time of degradation shown in the tab. 1 we believe that difference in time of degradation between the two kinds of products is insignificant. Research is basically succeeded in laying the basis for solving a global problem.

However, the exclusive use of plastics derived from starch and sugar begins to put serious problems of " food resources removal" to the world population.

The "perfect closing of the circle" would be with the renewable resources use discarded from production at the moment as straw, corn stalks, lignin, fresh cellulose (grass) and scraps of beet; in this way the noble part of the plant (corn or cereals starch, cane sugar and sugar beet, etc) would remain available for food without causing serious worldwide imbalances food.

Waiting for that research manages in this difficult undertaking it would be right the widespread use of additives and in special way the most effective and environmentally consistent capable of transforming the olefinic molecule in biodegradable organic matter without the use of metal catalysts or toxic substances in general.

To complete this strategy it hasn't got that to adapt existing legislation (both U.S. and Europe) to the real state of things which indicates the possibility of a complete biodegradation of plastic in a maximum of 12-36 months that is still less than one-hundredth of the time required for plastic degradation of exclusively olefinic origin (see table 1).

ECM Masterbatch Pellets, which currently represents the tip of applied research on additives with the results of optimal reliability, cost, manageability and biodegradability (see Annexes 1, 2, 3 and 4 available), would not be able to pass the test of biodegradation in composting (EN 13432) which fix strictly biodegradation level of at least 90% reached in less than 6 months.

We consider this standard anachronistic and the same is worth for all the standards that consider 6 months as the maximum time to consider biodegradable a substance; the standard, as states the paragraph 6 of the section of statute 8, must be continually updated in the light of scientific progress and, above all, the respect for nature which takes its time without to respect or to wait for standards that often, when it is applied biology, are only maxim indication.

At the moment the fundamental standard to respect is European Directive CE 94/62, of which EN 13432 is only a presumption of conformity by providing , correctly also other method that are being or will be approved. On the basis of that directive, plastics additived with ECM MasterBatch Pellets is legally in order (in full compliance) with European Union but should also work to turn a new method the plastic additive with ECM Masterbatch Pellets is in full compliance with the European Union but should also work to open a new ASTM EN method that provides biodegradation times more consonant with the times of Nature and however optimal times compared with non-biodegradability demonstrated by exclusively olefinic plastics.

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