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ANAEROBIC BIODEGRADATION OF CONVENTIONAL THERMOPLASTICS AS INDUCED BY ORGANIC ADDITIVES

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Summary

The types of additives under discussion here promote the biochemical degradation of synthetic polymers primarily in an anaerobic landfill environment. The resins so treated are not, nor are they related to, so-called oxo-degradable polymers. The additives themselves do not modify the host polymer resin in any manner. Thus, shelf life, use conditions, performance levels and recyclability of the original resins is unaffected. Nothing happens to these resins until they encounter the microbial environment present in a landfill.

There, after microorganism acclimatization, an enzyme-catalyzed sequence of oxidations and polymer chain breakage occurs, where biodegradation leads ultimately to methane, CO_2 and inert humus. Though the environment is anaerobic, the oxidations occur via any of several known routes where oxygen atoms are transferred from simpler molecules present in the landfill to the polymer backbone. The generation of methane and CO_2 from these synthetic polymers as well as the size reduction of the polymer chains have been thoroughly studied and documented. Some of these results are presented here.

Description of Additive Systems

The subject additives compounded into a conventional thermoplastic clearly differ vastly from biochemically synthesized polymers like PLA or the PHA (eg: Mirel™) series where part performance, especially toughness, is not always at desired levels and despite claims, repeated microwavability is tenuous at best. Bioplastics such as PLA must be recycled in a separate stream and new recycle numbers for them are presently under discussion at ASTM. They are more expensive and heavier (density >1.2 *vs.* PP at 0.905 and HDPE at 0.95-0.96).

These new additives do not promote oxobiodegradation or uv degradation that is then reportedly followed by biological attack on the residues. Thus, there is no issue with premature kick-off, limited part shelf life and in-use performance, and recyclability of parts when they enter the recycle stream remains intact. There are no transition metals incorporated in the additives. They are not based on starch or similar blends, and they do not modify the conventional base resin to which they are added.

These additives typically are a proprietary blend of selected organic compounds that are melt-compounded into a masterbatch carrier resin, which is then pelletized. The masterbatch is subsequently melt-blended into the final base resin (PE; PP; PS; PET) by the enduser in manufacturing the biodegradable product. Final additive loading levels of **0.5-2.0%** are typical.

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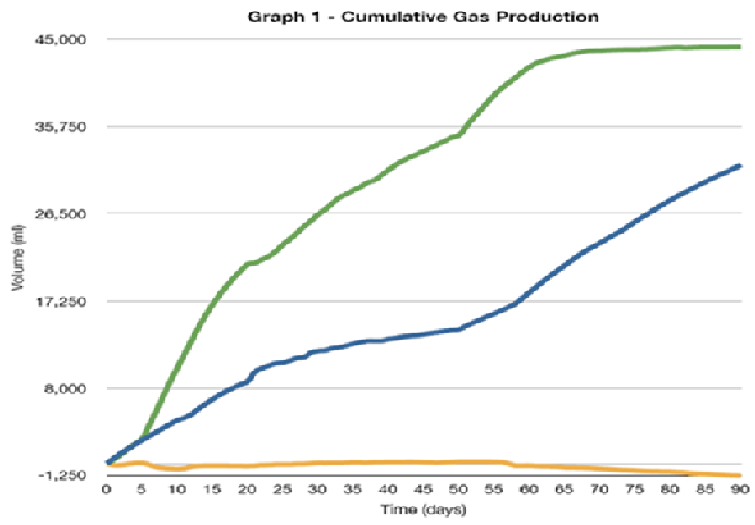
The most important feature is that an additive of the subject type initiates and promotes solely a biodegradation process, and does so only in the presence of microorganisms. Polymer alteration only commences when the material is exposed to an active biomass primarily in a moist anaerobic environment, such as in an active landfill. The entire subject of landfill biodegradation and energy generation therefrom is the subject of a separate follow-up document.

In a landfill, the additive blend renders the hydrophobic (water-repellent) base resin much more hydrophyllic, facilitating the formation and intimate adhesion of a moisture-borne biofilm. It then attracts and initiates the growth of microorganisms within the biofilm that can acclimatize to the base polymer as the primary nutrient source, and promotes the active and vigorous growth of the adapted microorganisms. This is seen in the following discussions.

Laboratory Biodegradability Testing: the ASTM D5511-02 Anaerobic Digestion Test

This method determines the degree of anaerobic biodegradation of plastic materials in a high-solids anaerobic environment. High solids conditions are usually considered to be greater than 20% solids, and the test usually is run under solids levels in the 40-55% range. We have had very extensive conversations with numerous researchers and landfill operations personnel over the past year and have secured unequivocal confirmation of this test as representative of biologically active landfill conditions in most of the US. This also will be summarized in a separate follow-up document. An attempt by BPI-led factions within ASTM to disconnect the ASTM D5511-02 test from biologically active landfills was recently defeated.

In the D5511 test, the test sample is exposed to a methanogenic inoculum cultivated from a wastewater treatment facility's anaerobic digesters operating on household waste. The digester test conditions remain static. This test method involves measuring the volume of carbon dioxide (CO_2) and methane (CH_4) evolved over time from the biodegradable test sample relative to a positive control (typically cellulose), a negative control (typically the same resin lacking the additive), and the inoculum alone. At the conclusion of the test, the remaining solid test sample mass and control sample masses are determined by weight.



The graph at the right shows the cumulative gas production from a sample of polypropylene film that had been compounded with 1% of one of the additives of the subject type (blue) against the gas production from cellulose (green) and a blank PP film sample that was untreated (yellow). The chart below shows cumulative gas evolution of 37% from the treated PP, which when adjusted for the 82% gas production from the cellulose control translates to 45% based on 82% maximum gas rate production.

Similarly, many D5511 tests on polystyrene and polyethylene systems including molded parts, foams and sheets/films have shown cumulative gas evolutions into the 20-40% ranges in the periods of 30-200 days that the tests have been run. **Note: these gas evolutions far exceed the 0.5-2.0% additive levels. Simple degradation only of the additive as claimed by competitive bioplastics producers is thus totally false and misleading.** Longer times are being investigat-

PP at 90 Days	Sample Wt (g)	CH_4 Wt (g)[1]	CO_2 Wt (g)	Total Carbon (C); g			Biodegradation[3]	
				Total	Net[2]	Theo.	%	Adj. %[4]
PP + Additive	50.0	31.58	0.64	23.86	15.68	42.55	**36.85%**	**45.1%**
Positive Control	40.0	29.95	0.81	22.68	14.50	17.76	**81.63%**	100.0%
PP w/o Additive	100.0	9.55	0.26	7.23	-0.95	86.00	**-1.11%**	-1.4%
Inoculum	1000.0	10.81	0.29	8.18				

ted in terms of maintenance of viable biomasses, etc, with a view towards eventually establishing a realistic elapsed-time standard for projected landfill biodegradation along the lines of the ASTM D6400 standard for commercial compostablity (90% disappearance in 180 days or less).

The challenge here is that the variation in landfills, primarily in moisture content by US region as well in terms of other variables, is much greater and degradation times much longer than in commercial composters. Thus, attempts to define longer-term anaerobic landfill biodegradation limits in terms of manufacturing-style commercial composting standards such as ASTM 6400 does not address these realities of landfill biodegradation, for **all** degradable materials deposited there. In addition, the public perception of total "biodegradation" in one year or less clearly does not take into account the reality of much longer actual landfill biodegradation time periods.

Evidence of Polymer Chain Degradation (Chain Length Reduction)

Plastic materials are composed of an array of long-chain polymer molecules of varying length. In general, the longer the chains, the tougher the plastic, and cutting the chain lengths will degrade the plastic. This can happen by the action of excessive heat during product manufacture or use, by the action of air or sunlight unless properly stabilized, and - under the influence of suitable enzymatic catalysis - by the action of microorganisms.

There are several analytical techniques used to look for cleavage of the long chains. These are frequently used in forensic analysis of product failure, competitive material or product analysis, etc. One method, **Gel Permeation Chromatography (GPC)** actually separates the chains by length in solution and gives measures of these lengths and the distribution of the various lengths.

GPC depends on the selective entrapment of polymer molecules in the micropores present in the gel particles in a column. As the polymer solution passes down the column, the individual molecular chains get "stuck" more or less deeply in the micropores depending on their size, the smaller the deeper penetration. The longer chains pass by and are eluted first, and so on to the shortest chains which "get out last". The result is a bell-shaped curve showing the distribution of chain lengths, which is mathematically analyzed and the molecular weight (MW) ranges reported. In particular, one looks for number average MW (Mn; from the low-MW end), the weight average MW (Mw; from the curve peak), and the MW distribution (MWD; Mw/Mn), which measures the breadth of the bell curve.

We have looked at a number of polypropylene (PP), linear low density polyethylene (LLDPE), and polystyrene (PS) systems via GPC. For the PP systems, reductions of up to 40% in Mn and Mw were seen with an increase in MWD of 10% or more in 45 days, clearly suggesting an increase in shorter chain lengths with consequent MW broadening. In PE film systems, decreases in Mn of 55-60% were seen with associated Mw drops of 10-15% and a near-doubling of the MWD after 160 days, suggesting even greater generation of shorter chains and MWD broadening. PS systems show very interesting behavior in the work done to date: Mw reductions of 3-5% were seen after 160 days while gas evolution and plastic residue mass loss showed more like 30% biodegradation. However, 75% of the mass of polystyrene is not a part of the chain but is present as the pendant aromatic rings. It is evident that the overall PS residual

polymer size as "seen" by the gel pores hasn't changed much, but significant mass loss has occurred most likely from aromatic ring degradation.

There is ample evidence in the literature for enzymatically-catalyzed ring opening in aromatic systems, and indeed in our own work we have seen evidence in infrared (FTIR) spectra for the presence of phenolic and aliphatic hydroxyl groups (-OH) in residues taken from the D5511 test media. We also see FTIR evidence of carbonyl-containing (C=O) groups in the residues, which confirm our hypothesis as to the enzymatically catalyzed degradation mechanisms at play here. This is discussed below

How these Additives Promote Anaerobic Biodegradation of Conventional Thermoplastics

First, the additive renders the hydrophobic (water-repellent) base resin much more hydrophyllic, facilitating the formation and intimate adhesion of a moisture-borne biofilm.

Close adhesion of a biofilm to the substrate in many cases is a pre-requisite to microorganism acclimatization; mobility throughout the polymer is also a factor. However, virtually all plastic resin surfaces are by their nature hydrophobic; this is particularly true of polyolefins, to which very little of anything adheres without some form of pre-treatment (corona; flame; etc.)

The additive functions in some respects as a surface-active agent in rendering the resin more hydrophyllic in nature, and being also hygroscopic in nature, retains moisture, promoting the approach and adhesion of a moisture-borne biofilm composed of the microorganisms present in biologically active landfills, composters, etc.

The additive attracts and initiates the growth and colonization of microorganisms within the biofilm that can acclimatize to the base polymer as the primary nutrient source.

The landfill environment is largely aerobic near the surface and largely anaerobic down deeper. Moisture is essential of course, and according to our dialogs with landfill experts, is perhaps the single most important variable in determining relative landfill biological activity.

Resins such as PP and PE are in a fully saturated (reduced) state. The literature strongly suggests that an enzymatically-catalyzed polymer oxidation process is occurring via oxygen transfer from an oxygen source such as alcohols, acids, sugars, carbohydrates, etc, most or all of which are present at one point or another in a biologically active landfill. They are present by design in the ASTM D5511-02 test. This introduces olefinic, aldehyde, ketone, carboxylate or similar functionality into the polymer, and can happen anaerobically as well as aerobically.

A most likely mechanistic pathway involves enzymatically catalyzed oxidation of a chain carbon to a ketone (C=O) function, followed by cleavage of the bond between that carbon and its nearest neighbor on the chain. This will typically generate a carboxylic acid at the original ketone carbon. All of these functions are readily seen in the FTIR spectra of our D5511 test residue samples. Similarly, our FTIR spectra confirm the presence of the same types of functionalities in our PS residues, but here, with 75% of the polymer weight carried in big, bulky pendant aromatic rings that also very effectively shield the chain itself from attack, the likeliest locations of the oxidized groups are where the aromatic rings were opened up.

We are in process of further evaluating the D5511 test residues to gain further knowledge of the structure of these various intermediate residues.

In heteropolymers such as polyesters and polyamides, enzymatically catalyzed hydrolysis will most likely occur first at the ester or amide linkages to start a more general process such as those described above. We have not yet begun a similarly exhaustive assessment of the anaerobic degradation of polyesters such as PET or of polyamides.