

Degradable polyethylene film—the facts

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What role do starch additives play in producing a degradable polyethylene?

In the 1990s, environmental responsibility is going to be a focal point in the political and public arenas. Solutions are being suggested faster than the problems are being defined. Confusion, misperception, miscommunication, and inaccurate information abound in regard to solid waste and environmental concerns.

Recycling and reducing wastes at the source, known as "source reduction," are generally accepted practices that will help with the solid-waste problems. The value of degradable plastic materials is being debated in an effort to understand their role in the solution to our environmental problems.

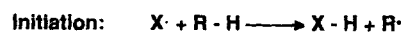
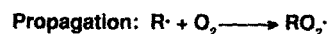
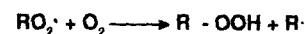
The purpose here is to examine the technology of degradable polyethylene film, focusing on definitions, mechanisms, and testing procedures. Three technological areas will be reviewed: (a) photodegradation, (b) biodegradation, and (c) oxidative or chemical degradation. In addition, we will look at the current technology and research at Consolidated Thermoplastics Co.

Photodegradation

Much of the research on photodegradable products was originally conducted in the late 1960s and early 1970s by such researchers as Guillet (1), Scott (2), and Griffin (3). As a result of this research, a variety of products are being used commercially by such companies as Ampacet, Ecolyte, and Plastigone.

This technology can be divided into two basic categories for photodegradable concentrates and compounds. One category can be defined as copolymer technology. By polymerizing ketone functional groups or carbon monoxide with a polyethylene monomer, a copolymer can be created with sections of the backbone sensitive to ultraviolet radiation at a specified wavelength. The advantage of this technology is that the oxidation potential can be engineered into the polymer through the concentration of the comonomer in the synthetic plastic. The degradation mechanism is reportedly via a Norrish I- or II-type reaction (4). The details of the reaction kinetics, dynamics, and specific mechanisms for these oxidation reactions are not well understood.

1. Metal salt photodegradation mechanism



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In the second class of photodegradable products, the chromophore functional group is based on metal salts. These metal salts are usually divalent transition-metal salts of stearates, dithiocarbonates, and acetoacetates. These compounds are produced through classical compounding technology, and degradation is facilitated through the mechanism depicted in Fig. 1 (5).

This reaction sequence is the principal mechanism by which polyethylene is oxidized through photodegradable metal salt additives currently used in commercial products. The mechanism is also important because a similar mechanism may be functional through the auto-oxidants used in combination with the starch masterbatches. The reaction kinetics and specific reaction dynamics are not well understood with this mechanism either, but the alkoxy radical ($RO^\cdot$) seems to be the species that leads to chain scission, yielding aldehydes and ketones. These aldehydes and ketones are prone to further free radical formation and subsequent oxidation.

A variety of techniques can be used to detect the intermediate species in the propagation step of this reaction scheme, including Fourier transform infrared

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(FTIR) techniques. The metal preferred for the popular photodegradable concentrates is iron, because of its relative reactivity and its compatibility with the environment.

Advantages and disadvantages can be documented for both of these photodegradable technologies. The copolymer materials will be more "programmable" in terms of their degradation endpoints. However, the metal salt compounds may produce more low-molecular-weight fractions, which might possibly be assimilated by microorganisms. The reasoning for this hypothesis has its roots in the oxidative mechanisms in Fig. 1.

In addition, the metal salt compounds utilize the oxidative mechanism, which has a chain reaction sequence. As a result, this reaction will continue in the absence of an ultraviolet radiation source after a threshold of free radical formation is reached. How long this chain reaction mechanism continues after the threshold is reached and the ultraviolet source has been removed has not been well documented.

The copolymers, on the other hand, are made degradable as a result of the specific site of copolymerization. When the ultraviolet radiation source is removed, the reaction virtually stops. This can be seen as an advantage or disadvantage, depending on the particular application.

Suppliers of photodegradable products are working to understand more about the fate of the low-molecular-weight fractions that arise from the chemical oxidation of the polyethylene substrate.

Biodegradation

The American Society for Testing and Materials (ASTM) Committee D-20 on plastics has a subcommittee that is currently contending with the definitions and issues of biodegradable plastics testing. As might be expected with an emotionally charged issue like the "solid-waste crisis," the work towards a definition and standardized testing procedures has been tedious and frustrating. It may yet be some time before a consensus is reached in this committee.

At present, the definition for a "degradable" plastic film is based on a loss in physical properties as measured by ASTM testing procedures. The definition refers to a specific period of time for a loss in tensile strength properties to take place, and it involves a classification system based on this length of time. The proposed definition for a biodegradable plastic is "a degradable plastic wherein the primary degradation mechanism is through the action and metabolism of microorganisms."

For our purposes here, we will understand that biodegradability alludes to a plastic material's susceptibility to the metabolism of microorganisms and to the utilization of its carbon backbone as a carbon source for the microbiological species. It has been suggested that a co-metabolic pathway has been functional as a biodegradation mechanism (6). The theory is that while a microorganism may not be capable of utilizing a polyethylene fragment as a carbon source in a classical way, the metabolic activity of the microorganism may be capable of chain scission oxidation, and as a result the polyethylene will be degraded systematically. The microorganism that oxidizes the polyethylene is not able to utilize this energy

derived in order to support growth. Nevertheless, the co-oxidative pathway and capability to oxidize polyethylene exists and is functional. This type of microbial oxidation would also be considered a form of biodegradation.

A number of methods for detecting microbial growth have been used to try to understand the suitability of a synthetic polymer as a carbon source. ASTM F-21-70 uses a carbon-poor nutrient media along with a synthetic polymer as a carbon source to determine the ability of a fungal population to assimilate the carbon in the synthetic polymer. Among those fungus species considered favorable are the *Penicillium* and *Aspergillus* species.

In this method, the synthetic polymer material is mechanically pulverized and mixed with the growth medium. Growth is reported subjectively at approximately three weeks of incubation. ASTM Test No. G-22-76 is a similar test, except that it uses a bacterial population that includes such organisms as *Pseudomonas aeruginosa*.

There have also been several weight loss methods attempted in conjunction with nutrient agar media as well as soil substrates. Carbon 14 labeling has been used effectively to trace the carbon source from the polymer backbone to carbon dioxide arising from microbial respiration (7). Unless pure hydrocarbon polyethylene samples are used in this testing, there is a danger of a false positive result. Many additives commonly used in polyethylene manufacturing are active microbial substrates; as a result, some growth will be indicated even though the polyethylene is not being metabolized. On the other hand, a false negative can also result from those additives that might have antimicrobial activity. It is important that pure samples of polyethylene be incorporated into these microbial studies.

Carbon dioxide and oxygen respiration rates and biological oxygen demand (BOD) have also been effective measures of microbiological activity. One complicating feature here might be a synergistic effect between the polymer and the metabolic pathways. In other words, if the polymer or the additive within the polymer acts as a metabolic stimulant to the microbial population, an increase in the metabolic rate might indicate a false positive with this testing procedure.

In the late 1960s and early 1970s as the photodegradable products were being developed, an effort was made to understand the susceptibility of straight-chain polyethylene and *n*-alkane hydrocarbons to microbial degradation. A number of factors have been reported to be important with regard to the ability of microorganisms to assimilate synthetic polymers such as polyethylene. These factors can be divided into three areas:

1. Environmental conditions
2. Polymer parameters
3. The microbial population.

Environmental conditions

The condition of the environment for microbiological activity can affect the potential for the microorganism to use the polymer as a carbon source. These environmental conditions are important not only for hydrocarbon utilization but also for most microbiological activity.

I. The effect of starch on film properties

Property	ASTM no.	LDPE	LDPE + 6% starch	LLDPE blend	LLDPE blend + 6% starch
Average gauge, μm	...	50	50	34	45
Gloss, %	D-2457	70	25.7	67	25
Elongation, %	D-882				
Machine direction		400	160	615	585
Cross direction		650	615	705	660
Stress, kPa	D-882				
Machine direction		24,115	16,363	30,660	17,225
Cross direction		22,392	11,747	26,660	16,536
Coef. of friction	...	0.60	0.39	1.0	0.53
Tear strength, g/mm	D-1992				
Machine direction		3,740	2,559	6,693	5,315
Cross direction		10,236	9449	13,779	13,385
Impact, g/mm	D-1709	3,740	1,260	7,480	5,905

II. Comparison of physical properties using the conventional and modified processes

Property	Typical values	
	Conv. process	Modified process
Average gauge, μm	32	32
Gloss, %	19	12
Elongation, %		
Machine direction	280	480
Cross direction	840	700
Stress, kPa		
Machine direction	22,737	21,359
Cross direction	17,225	19,292
1% secant modules, kPa		
Machine direction	289,380	234,260
Cross direction	372,060	275,600
Coef. of friction	0.53	0.52
Tear strength, g/mm		
Machine direction	1,771	4,527
Cross direction	31,496	28,346
Impact, g/mm	40	130

III. Physical properties of blown film at higher starch loadings

Property	Blown film + 12% starch	Blown film + 20% starch
Average gauge, μm	51	53
Gloss, %	11	6
Opacity, %	39	39
Elongation, %		
Machine direction	455	445
Cross direction	555	570
Stress, kPa		
Machine direction	11,506	11,472
Cross direction	8,578	8,923
1% secant modules, kPa		
Machine direction	96,563	110,481
Cross direction	92,774	119,121
Coef. of friction	0.51	0.52
Tear strength, g/mm		
Machine direction	3,858	4,843
Cross direction	12,637	11,850
Impact, g/mm	2,402	2,047

IV. Effects of starch masterbatch and prodegradant on tensile strength and elongation in the cross and machine directions

	Ultimate tensile strength, g/in.		Ultimate elongation, %	
	MD	CD	MD	CD
Mean response for factor levels				
Starch				
Low	1326	1014	126	316
High	781	570	107	258
Prodegradant				
Low	1693	1255	225	569
High	414	329	8	6
Mean effect for independent variables				
Starch masterbatch	-545	-444	-19	-58
Prodegradant	-1278	-926	-217	-562

These environmental conditions include such variables as pH, temperature, humidity, oxygen, water availability, nutrient availability, the physical environment, macroorganisms, and the chemical environment. As an example, a fungal population will prefer an acid pH in the range of pH 3-6, whereas a bacterial culture prefers a more neutral pH, in the range of pH 5-7.

The biochemical pathways for microorganisms are extremely sensitive to temperature. Certain microorganisms are conveniently classified into appropriate groups based on the temperature. For example, thermophilic microorganisms are found at temperatures common in compost piles (140-170°F). On the other hand, most modern landfill environments are fairly poor in microbial activity because they lack available moisture, oxygen, and appropriate nutrients.

Polymer parameters

Variables relating specifically to the polymer can be important to its biodegradability. These variables include chemical structure, additives used in the formulation, the polymer's crystallinity or morphology, and its average molecular weight and molecular weight distribution.

Several researchers have indicated that polyethylene and *n*-alkane hydrocarbons will become more susceptible to microbial biodegradation as the molecular weight of the carbon source is reduced (8-13). For example, Haines and Alexander indicate that microbial oxidation was apparent at a carbon chain length of approximately 44 carbons (10). This sample, which had a molecular weight of approximately 620, began to show oxygen utilization by microbes at approximately 20 days in this BOD study. In spite of all these studies, however, it remains unclear as to how long it would take for a sizable quantity of polyethylene to be biodegraded under these conditions.

Also, some work to understand the mechanism for this oxidative chemical activity has been attempted (13-16). Apparently, most of the oxidative activity occurs at the termination of the hydrocarbon chain: as more and more chain ends become available through chemical oxidative mechanisms, the rate of reaction increases proportionately. In other words, the length of the hydrocarbon chain may not be as important as the availability of chain ends for microbial oxidation.

Potts *et al.* (17) studied additives to try to understand more about their susceptibility to microbial degradation. These additives include common slips, lubricants, cling agents, and antioxidants used in polyethylene. Many of the common plastic additives are reasonably suitable food sources for microorganisms; in some cases, they are active substrates (17). Branching is a deterrent to microbial metabolism; that is, linear hydrocarbons are much more susceptible to microbial oxidation than their branched cousins (17).

A fundamental conflict between the metabolic environment of a microbial population and a synthetic polymer lies in the affinity for water. Since the surface of a polyethylene material is relatively hydrophobic and because most biochemical pathways are aqueous, there is something of an incompatibility. Polyethylene modifications through copolymerization and corona or flame treatment can increase the surface energy of the film to make it closer to that of water. Results indicate that these

V. Statistical information for tensile strength and elongation data

Source	Sum of squares	Division factor	Mean square	F stat.
MD tensile strength				
Factor 1	592960	1	592960	7.9
Factor 2	3269124	1	3269124	43.5
1 × 2	140451	1	140451	1.9
Error	300381	4	75095	
Total	4302916	7		
MD elongation				
Factor 1	722	1	722	3.9
Factor 2	94178	1	94178	506.3
1 × 2	288	1	288	1.5
Error	744	4	186	
Total	95932	7		
CD tensile strength				
Factor 1	394716	1	394716	9.4
Factor 2	1717731	1	1717731	40.8
1 × 2	75078	1	75078	1.8
Error	168260	4	42065	
Total	2355786	7		
CD elongation				
Factor 1	6670	1	6670	1.1
Factor 2	633375	1	633375	108.6
1 × 2	5460	1	5460	0.9
Error	23320	4	5830	
Total	668825	7		

Factor 1 = Ampacet 20835 let-down.
Factor 2 = Prodegradant let-down.

modifications have little, if any, effect on microbial activity (8).

The microbial population

The microbial population itself can be an important variable in the biodegradable potential of low-molecular-weight polyethylene fragments. If the appropriate microorganisms are not available, degradation simply will not occur.

Oxidative degradation

Oxidation of a polyethylene material can occur through a mechanism similar to that of photodegradable compounds of polyethylene with metal salts. The interesting feature of this technology is that an ultraviolet energy source is not needed to initiate the oxidative chain reaction.

Much of this work was introduced in a British patent by G. J. L. Griffin (18). He has worked in England and the United States to refine this technology and continue its development. The commercially available starch masterbatches contain both starch and a "prodegradant system." The prodegradant system consists of the components involved in the reactions leading to oxidation. It seems that most of the interest has focused on the starch,

VI. Effects of starch masterbatch and prodegradant on CD tear strength

	CD tear strength, g/mil
Mean response for factor levels	
Starch	
Low	172
High	218
Prodegradant	
Low	389
High	1
Mean effect for independent variables	
Starch masterbatch	45
Prodegradant	-388

VII. Statistical information on CD tear strengths

Source	Sum of squares	Division factor	Mean square	F stat.
Factor 1	4186	1	4186	21.9
Factor 2	300700	1	300700	1575.4
1 × 2	4186	1	4186	21.9
Error	763	4	190	
Total	309835	7		

Factor 1 = Ampacet 20835 let-down.
Factor 2 = Prodegradant let-down.

VIII. Effects of starch masterbatch and prodegradant on molecular weight by number average, weight average, and Z-average

	Average molecular weight		
	Number average	Weight average	Z average
Mean response for factor levels			
Starch			
Low	14	52	567
High	13	50	138
Prodegradant			
Low	20	71	156
High	7	31	548
Mean effect for independent variables			
Starch masterbatch	-1.0	-2	-429
Prodegradant	-14.0	-41	392

away from the prodegradant. Nevertheless, the patent literature refers to the prodegradant as much as it refers to the starch portion of the material.

The principal function components of the prodegradant system are a transition metal salt and a quantity of unsaturated polymer, which may include vegetable oils, fatty acids, and fats. The specific reaction kinetics and dynamics are not well understood, but apparently the transition metal salts react first with the unsaturated polymer or fatty acid at the surface of the film, creating peroxides and hydroperoxides in the initiation phase of the reaction (Fig. 1). These peroxides and hydroperoxides then participate in the classical oxidation mechanism leading to free radical chain reactions and ultimately to the oxidation of the polyethylene product.

Once again, the oxidation reaction is initiated through heat energy instead of ultraviolet radiation. As a result, exposure to sunlight is not necessary to initiate the oxidation reactions. Polypropylene is reportedly more prone to this oxidative activity (19-20), because of its tertiary carbon structure. Undoubtedly, there will be more research to understand the potential for this technology.

Starch is being used commercially as a degradable additive for polyethylene. Presently, it is unclear whether or not the starch has an effect on polyethylene degrada-

bility, but starch is a reasonable energy source and a biodegradable additive for polyethylene. As more starch is added to the film, a greater portion of the film becomes biodegradable. Griffin has reported using a number of different sources for the starch molecule, including rice, maize, arrowroot, wheat, bean, potato, and, of course, corn starch. Corn starch has been utilized in the commercially available concentrates because it is available and economical. However, rice starch may be more appropriate because its mean particle size is smaller.

The amylase enzyme, which is an enzyme in many of the metabolic pathways of microorganisms, is the biochemical responsible for the digestion of the starch molecule. Apparently, most of the starch is digested in a relatively short period of time regardless of its location in the polymer film material.

Much of the work with the starch masterbatches is being conducted under the supervision of the masterbatch suppliers. There is also an ongoing effort to understand the potential of modifying the starch material to improve the physical properties of the film. The interface between the hydrophilic starch molecule and the hydrophobic polyethylene creates a weak link that impairs the physical properties of the thermoplastic film. Research efforts continue in the direction of increasing the amount of starch in a film material. Warner-Lambert, Feruzzi Company, and others are looking at higher levels (up to 100%) of starch in a film material.

Studies at Consolidated Thermoplastics

Our efforts have been (a) to study the commercially available starch masterbatch materials in terms of their performance in a "degradable" film and (b) to develop their processability and potential in commercial products. Consequently, we are examining the processing problems and the physical properties of the starch-filled film products. Here, the discussion will be related to the development efforts and testing which are focused on producing a coextruded cast product using a starch filler in the center and a prodegradant system in the outer layers of the product.

In spite of reports that starch is a reasonably well-behaved thermoplastic material, the combination of starch and polyethylene poses a variety of problems. Polyethylene

is processed at a temperature range of approximately 280–500°F, depending on the species of polyethylene. Linear low-density and high-density polymers require a higher processing temperature, as does a cast extrusion process. Starch is a carbohydrate that is susceptible to heat oxidation . . . especially at temperatures greater than 420°F in film extrusion processes. Therefore, blown extrusion is a more appropriate processing technique for film manufacturing, and the choice of the polyethylene raw material is critical.

One of the problems inherent in the starch molecule is the hydrophilicity and resulting moisture level in the starch masterbatch. We have documented moisture levels from a low of approximately 0% to a high of 0.5–0.6% moisture in the starch masterbatches from Ampacet (20835), ADM (Archer Daniels Midland Co.), and St. Lawrence Starch. At a moisture level of 0.2–0.3% and an extrusion melt temperature of approximately 350°F, a number of moisture voids become apparent in the extruded film. As the starch concentration is raised in the film composition, moisture becomes a more important variable, and the control of the moisture level becomes more critical.

Although many processors and manufacturers are secretive about the process of extruding starch in their film materials, it is widely known that die lip buildup is a problem. Because of the relative incompatibility of the starch with the polyethylene and the difference in surface energies of the materials, the starch climbs to the surface of the melt stream and builds up on the lips of the die, where the shear rates are significant. The problem is aggravated by the higher shear rates of cast film processing. As these starch and low-molecular-weight polyethylene fractions sit on the surface of the die, the starch begins to oxidize. Intermittently, the oxidized starch will pick off into the film material, causing holes and defects in the film product. Many film processors and masterbatch producers are endeavoring to understand more about this phenomenon and to attempt a solution.

Blown film

The commercially available starch masterbatches used at a level that results in a film with a starch composition of 6% or greater have an effect on physical properties. Table I contrasts the physical properties of a "barefoot" low-density polyethylene (LDPE) resin with that of the same material with 6% starch in a conventional blown film extrusion process. The physical properties are affected in almost every category, with the major effects being reflected on impact, coefficient of friction, toughness or area under the stress-strain curve, and tear properties.

To understand the interaction of the starch with the polyethylene materials, we produced blends using a linear low-density polyethylene (LLDPE) with the starch masterbatch. Presented in the last two columns of Table I, these results show that the linear blends are less severely affected when used as a substrate for starch-filled film products, but the effect of the starch on physical and optical properties remains. In subsequent research, we found that the processing parameters can also have an effect on the film properties. With the appropriate processing conditions, the impact and physical properties can be improved.

Table II contrasts a conventional process with the

IX. Statistical information for molecular weight averages

Source	Sum of squares	Division factor	Mean square	F stat.
Number average molecular weight				
Factor 1	1	1	1	0.5
Factor 2	378	1	378	177.9
1 × 2	3	1	3	1.5
Error	8	4		
Total	390	7		
Weight average molecular weight				
Factor 1	10	1	10	0.1
Factor 2	3321	1	3321	38.1
1 × 2	0.1	1	0.1	1.4
Error	348	4		
Total	3679.1	7		
Z average molecular weight				
Factor 1	368940	1	368940	173.3
Factor 2	307328	1	307328	144.3
1 × 2	308898	1	308898	145.1
Error	8517	4	2129	
Total	993683	7		

Factor 1 = Ampacet 20835 let-down.
Factor 2 = Prodegradant let-down.

X. Molecular weight distributions of oxidized coextruded polyethylene film

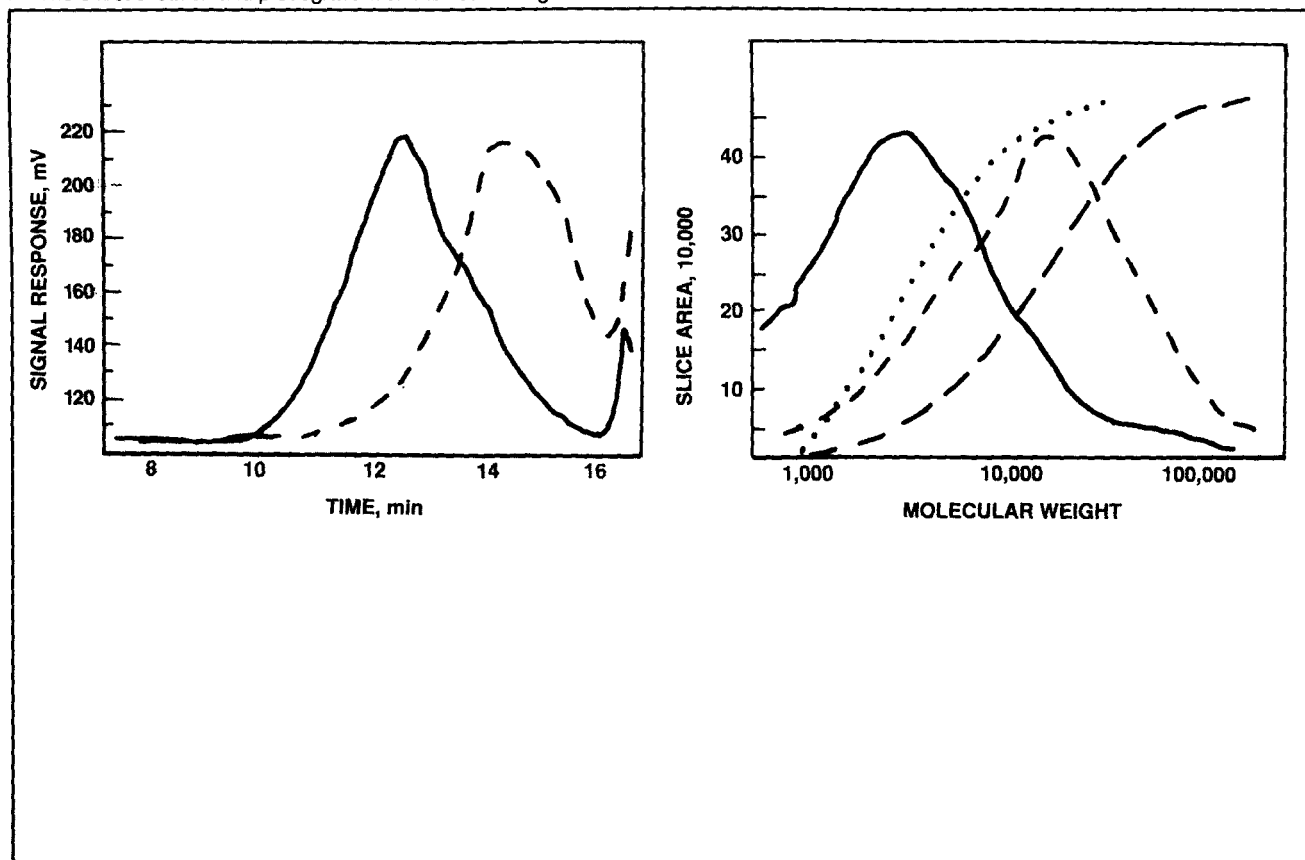
Trial	Run	Molecular weight averages			Polydispersity
		Number	Weight	Z	
1	2	22	75	175	3.6
	10	19	71	175	3.7
2	1	8	33	880	3.9
	11	8	31	940	4.1
3	5	20	70	162	3.4
	12	22	71	115	3.3
4	4	5	17	80	3.3
	13	7	43	195	5.9
5	7	10	47	200	4.9
	14	10	44	125	4.2
D	15	18	70	200	4.4
	control	18	73	195	4.1

All values × 10⁵ and calibrated vs. NBS polyethylene.

improved process in terms of the physical properties of a typical starch-filled blown product. As the data show, impact, tear, and toughness properties are improved with the new process, while gloss levels are reduced.

Table III illustrates the effect of starch on a polyethylene film blend up to approximately 20% starch. The gloss at approximately 20% starch is approaching that of a cast-embossed backsheets film, and the physical properties are reasonable in spite of the increase in starch loading. The

2. The effect of starch and prodegradant on molecular weight



variable limiting the loading of starch in these experiments was the moisture level in the starch masterbatch. When moisture voids began to appear in the blown film, we ceased trying to increase the loading of starch in the blown product.

Coextruded cast films

Monolayer cast film processing has been virtually impossible because of the high temperature requirements of the cast process and because of the processing problems caused by the buildup of oxidized starch. If the starch filler were buried in a coextrusion with thin outer layers of polyethylene, many of the processing problems would be eliminated, and a cast product might be feasible. By burying the starch in the center layer, we would preclude any biodegradable activity in the starch layer unless a prodegradant system degraded the outer layers so much that oxidation led to embrittlement and fracture, exposing the inner core.

This theory was tested through a classical two-factor, two-level, full-factorial design with a centerpoint and full replication. The design matrix is presented in the appendix. The independent variables were the starch masterbatch with standard levels of Ampacet 20835 prodegradant and the prodegradant supplied by ADM. The prodegradant system, as mentioned, is a transition metal salt and an unsaturated polymer. The low level of the starch masterbatch is represented as approximately 3% starch in the center layer, and the high level of the starch is represented as approximately 9% starch in the center layer. The prodegradant system concentration in

the outer layer was significant. The film products were extruded with outer layers at a thickness of approximately 15% each and with the inner layer composing approximately 70% of the film thickness. These film materials were aged at approximately 160°F for 24 days at a relative humidity of approximately 50%.

Tables IV-IX summarize the effects of the starch masterbatch and prodegradant system on physical properties and molecular weight. Table IV defines the effect on machine-direction (MD) and cross-direction (CD) tensile properties in terms of ultimate breaking stress and strain, while Table V provides the statistical information pertinent to the data for these experiments. Tables VI details the effects of the independent variables on CD tear properties, while Table VII gives the statistical information. Table VIII defines the effect of starch and pro-oxidant on molecular weight averages, and Table IX presents the pertinent statistical information.

On examining these tables, we see that the prodegradant system in the outer layer has the most significant effect on physical properties and average molecular weight. The high level of pro-oxidant in the outer layers seems to be functional in the core. As an example, in the trials with the high level of pro-oxidant used in the outer layers, the result is a product that virtually crumbles into tiny pieces with normal handling.

Ultimate elongation appears to be a more sensitive test for the effect of the pro-oxidant and loss in physical properties. Ultimate tensile stress, however, is a better test for the effect of the starch loading in the center layer, as a result of the relative low levels of pro-oxidant in this

layer. Also, the CD tear properties appear to be very sensitive to changes in molecular weight as a result of the oxidative action of the prodegradant system. Much of this sensitivity is due to the relatively high initial values.

Understanding the effects of the pro-oxidant and starch masterbatch on the molecular weight of the entire product is more difficult. GC molecular weight measurements are reported in terms of number average, weight average, Z average, and polydispersity index in Table X. Without considering the actual distribution graphics, it is difficult to make sense out of this information.

Figure 2 contrasts the molecular weight distributions of the control sample with the sample having the high levels of starch and pro-oxidant. The molecular weight distribution on the upper graph, which illustrates time on the *x*-axis and the response signal on the *y*-axis, is strongly bimodal. The reason for this is unclear without further study; however, a number of theories can be proposed. The fact that the polymeric substrate comes from a coextruded product is a logical hypothesis. Another explanation might be that the prodegradant system is acting only on the area adjacent to the prodegradant constituents. Therefore, the outer layers, as well as the inner layer materials adjacent to the metal salt and unsaturated polymer, will have lower molecular weight fractions as a result of the local oxidation mechanism.

The shift in the average molecular weight as a result of the prodegradant is rather significant. Because of the risk of obscuring the low-molecular-weight fractions with the stabilizer used in the GC analysis process, the low-molecular-weight fractions were prematurely cut off. As a result, the low-molecular-weight material is not well defined, and the number average molecular weight is less accurate. The weight average molecular weight is probably the most accurate and precise data from this analysis.

One anomaly from the experimentation seems to be rather confusing—the discrepancy between the trial replicates at the high level of prodegradant. The polydispersity index, an indirect measurement of the molecular weight distribution, reveals that something strange is occurring. Ignoring these defects in the experimentation, it appears that the number average molecular weight is affected by the prodegradant system in the outer layer. This effect is statistically significant and relatively strong. The weight average molecular weight is also affected by the prodegradant system in the outer layer. The Z average molecular weight, on the other hand, is more dependant on the high-molecular-weight fraction and is affected almost identically by the starch masterbatch loading and the prodegradant system in the outer layer. Here, the two-factor interaction is also significant, and in this experimentation it is the only interaction that has a statistically significant effect.

This response makes sense if we assume that the starch masterbatch, which is in the center layer of the material, and the prodegradant contained therein are the only materials available to oxidize the bulk of the polymer in the center layer. As these data are massaged and more analyses are conducted, the dynamics of this oxidative activity will become clear. Further studies will be conducted to determine the potential of the residue as a biodegradable substrate. Additional oxidation experimen-

tation will be conducted at various temperatures, starch loadings, and prodegradant levels.

One of the unanswered questions related to this oxidative degradation concerns the toxicity of the oxidation by-products. The film residue from this work will be analyzed to help define the toxicity and understand more about the residual components. One of the fundamental questions with regard to the potential for the oxidative masterbatches is whether or not the polyethylene "dust," or low-molecular-weight fraction of polyethylene and other by-products, poses a threat to the environment. This question remains unanswered and is the subject of current research and activity in the industry.

Conclusions

A number of conclusions can be propounded.

1. Polyethylene by itself, in the molecular weight ranges typical for extruded film products, is not biodegradable at significant rates in most naturally occurring environments.
2. Molecular weight has a significant effect on the potential for polyethylene biodegradation. We need to study the rate of degradation further to understand the potential for biodegradation of low-molecular-weight polyethylene fractions.
3. The branching and crystallinity of the polyethylene substrate have a significant effect on biodegradation. The effect depends on the level of crystallinity and branching in the polymer network.
4. Many additives currently used as slip agents, lubricants, compatibilizers, anti-oxidants, etc., in polyethylene are actively biodegradable in many environments.
5. It is possible to utilize the commercially available starch masterbatches in extruded film through the blown and cast film processes, but there are some processing problems associated with the hydrophilic nature of the starch and the incompatibility of the starch and the polyethylene substrate.

Blending the starch masterbatch with the appropriate polyethylene products can reduce the effect of the starch on the physical properties of the film product. Process conditions can also affect the film properties in blown film.
6. In our experimentation, the pro-oxidant system supplied by ADM has a strong effect on oxidation and the resulting molecular weight of the polyethylene after heat aging in the absence of ultraviolet radiation. At the high level of pro-oxidant, the film lost any measurable physical tensile properties and crumbled during normal handling procedures.
7. Higher loadings of starch fillers in polyethylene blown and cast film appear to be feasible, especially if processes can be developed or manufacturing techniques can be discovered that result in starch products with lower inherent moisture levels.

A reduction in molecular weight and a subsequent loss in film properties indicate that the pro-oxidant combinations have some potential as a degradable alternative, especially in thermophilic environments such as encoun-

tered in composting. More research is needed at lower temperatures and in other environments to understand the activity of the pro-oxidant packages. Subsequent analysis of the degradation residue is needed to understand the compatibility with the environment in terms of the toxicity and in terms of potential benefits.□

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Appendix: Experimental design using coextruded film

1. Factor 1 = prodegradant level
2. Factor 2 = starch masterbatch level in center layer

Letdowns

3. Level 1 (-) Factor 1 = 0%
4. Level 2 (+) Factor 1 = high level of metal salt and unsaturated polymer
5. Level 1 (-) Factor 2 = 7.5% starch masterbatch
6. Level 2 (+) Factor 2 = 22.5% starch masterbatch
7. Center point (0) = midpoint of pro-oxidant and starch masterbatch

A-1. Design matrix

Treatment no.	Prodegradant	Starch/ masterbatch
1	-	-
2	+	-
3	-	+
4	+	+
5	0	0

Full replication to measure experimental error and test for significance.

For more on experimental designs, see the appendix in the recent article by Parthasarathy *et al.*, *Tappi J.* 73(7): 185(1990).