

Methods for Assessment of Biodegradability of Plastic Films in Soil†

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Traditional and novel techniques were tested and compared for their usefulness in evaluating biodegradability claims made for newly formulated “degradable” plastic film products. Photosensitized polyethylene (PE), starch-PE, extensively plasticized polyvinyl chloride (PVC), and polypropylene (PP) films were incorporated into aerobic soil. Biodegradation was measured for 3 months under generally favorable conditions. Carbon dioxide evolution, residual weight recovery, and loss of tensile strength measurements were supplemented, for some films, by gas chromatographic measurements of plasticizer loss and gel permeation chromatographic (GPC) measurement of polymer molecular size distribution. Six- and 12-week sunlight exposures of photosensitized PE films resulted in extensive photochemical damage that failed to promote subsequent mineralization in soil. An 8% starch-PE film and the plasticized PVC film evolved significant amounts of CO₂ in biodegradation tests and lost residual weight and tensile strength, but GPC measurements demonstrated that all these changes were confined to the additives and the PE and PVC polymers were not degraded. Carbon dioxide evolution was found to be a useful screening tool for plastic film biodegradation, but for films with additives, polymer biodegradation needs to be confirmed by GPC. Photochemical cross-linking of polymer strands reduces solubility and may interfere with GPC measurements of polymer degradation.

The production of plastics in the United States exceeds 50 million metric tons per year (21). About one-third of this material is used in the manufacture of disposable items, such as wraps, bags, and other packaging materials, cups, and trays for fast food items, and films for agricultural use (film mulch and temporary greenhouses). Disposable plastics create additional demand for scarce landfill space, representing about 18% of the solid waste by volume (12). Some items endanger wildlife and many cause considerable aesthetic nuisance. Responding to consumer attitudes, legislative initiatives, and pressure from environmental groups, some manufacturers have formulated various “environmentally friendly” and “degradable” plastic films for shopping and garbage bags. A lack of clear, standardized definitions of degradability combined with poorly documented promotional claims left both legislators and the public confused about the merits of these products (10, 21). Some of the confusion also stems from a lack of generally accepted measurement techniques concerning the environmental fate of plastics (11). The focus of early work in this field was deterioration that assessed usually undesirable changes in appearance and physical properties of plastics. A well-known example is the American Society for Testing Materials (ASTM) test for loss of tensile strength of plastic films (2). This and similar tests become less useful when the question shifts to the ultimate degradation (mineralization) of the plastic material. Recent publications directed at this problem (8, 13–16, 22) employed some innovative and some traditional techniques but made no attempt to compare the performance and accuracy of the various measurements in a statistically controlled manner. Against this background, we tested the fate of six plastic films during incubation in aerobic soil, measuring CO₂ evolution, residual weight, tensile strength, plasticizer content, and poly-

mer molecular weight distribution in a comparative manner. Five of the six films were specially formulated to render them degradable by one of the currently used approaches (3), and one was a traditional film without degradability claims. This study independently evaluated the degradability claims made by manufacturers but, more importantly, it developed data on the usefulness and reliability of various measurement approaches for future environmental evaluations of plastic films.

MATERIALS AND METHODS

Test materials and conditions. The polymers most commonly used in disposable plastic films are polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). The polymer resins may contain various additives. Although the focus of this study was biodegradation, materials claimed to be “photodegradable” were included, since it is implied that the photochemical damage primes the material for additional decay in soil. Photodegradable films were exposed to sunlight for 6 and 12 weeks prior to their burial in soil but, for comparison, were also tested in soil without prior photoexposure. For easy reference, the test materials were coded as to their polymer resin and with an additional letter referring to their appearance. The length of photoexposure, if any, is indicated by a subscript number referring to weeks, following the letter code. As an example, PE-B₆ designates a polyethylene film, black, which was exposed to sunlight for 6 weeks. The test samples were purchased in local supermarkets, except for PP-C and PVC-C, which were supplied by Borden Resinite Inc. (Andover, Mass.). These two films were used also in a previous study (22) and served in this study as negative and positive controls, respectively.

Total organic carbon of the plastic films was determined by combustion and sequential absorptive removal of the combustion products such as CO₂, while measuring changes in thermoconductivity. These analyses were carried out by the Midwest Microlab, Indianapolis, Ind. Film thickness was de-

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TABLE 1. Plastic film test materials

Code ^a	Product and brand	Additives	Thickness (mm)	Claim
PE-C	Garbage bag, Good Sense, Webster	Proprietary	0.036	Degradable (photo)
PE-B	Garbage bag, Good Sense, Webster	Proprietary	0.036	Degradable (photo)
PE-R	Garbage bag, Bioguard (Guardian Poly)	Starch, 7.7%, plus proprietary	0.036	Degradable (bio)
PE-W	Shopping bag, AMCO Plastics	Starch, 1.5%, plus proprietary	0.033	Degradable (bio)
PP-C	Food wrap, manufacturer unknown	None	0.025	None
PVC-C	Food wrap, Borden Resinite	DOA, 19.2%; ESO, 10.8%	0.043	Degradable (bio)

^a C, clear; B, black; R, red; W, white. PP-C and PVC-C were negative and positive controls, respectively (22). For cross-reference, PP-C was labeled PP-1 and PVC-C was labeled PVC-3 in the previous study (22).

terminated with a Brown and Sharpe (Starret Co., Akhol, Mass.) film micrometer. Three measurements were performed on each film, and the results were averaged. The initial starch contents of films PE-R and PE-W were determined by thermogravimetry, courtesy of A. Andrady, Research Triangle Institute, Research Triangle Park, N.C. Thermogravimetry measures weight losses of a composite material in an inert atmosphere at rising temperatures (4). Test film characteristics are summarized in Table 1.

This study was performed under generally favorable conditions for biodegradation (18). Photoexposure took place under local, outdoor, summer season conditions. It is recognized that frequently, plastic films will be disposed of under less favorable conditions. However, a study on degradation under adverse conditions was considered premature when even the inherent degradability of the materials was in doubt and when the appropriate measurement techniques had yet to be developed.

Method selection and development. On the basis of previous success (19, 22), we used the Biometer technique to measure the conversion of the plastic material to CO₂. We also measured changes in residual weight of the plastic films. For this purpose, whenever feasible, solvent extraction procedures were developed. When these were not effective, the traditional but less accurate and more tedious manual retrieval was used, with a subsequent weighing. The traditional tensile strength test was retained to connect our study to the previous literature. These three primary measurements were supplemented, as needed, by gas chromatographic analysis of plasticizer degradation and by gel permeation chromatography (GPC) analysis of plastic polymer molecular weight distribution. Difficulties encountered with solubility of irradiated and starch-containing plastics eventually forced us to restrict solvent extraction to the control samples PP-C and PVC-C. In the definitive time course experiments, the films PE-C, PE-B, PE-R, and PE-W were retrieved from soil manually rather than by solvent extraction.

Financial and work load limitations prevented the replication and statistical analysis of each time point determination, but general confidence limits for each type of analysis were established by the standard deviation of triplicate samples, at least for one time point. Details of the test procedures and analyses follow.

Photoexposure of films PE-C and PE-B. These films were used in biodegradability tests either without pretreatment or after photoexposure on the roof of Lipman Hall, Cook Campus, Rutgers University, New Brunswick, N.J., during the months of 21 September to 14 December 1989 for 6 and 12 weeks. Exposure was performed according to ASTM standards (1), using 45°-angle wooden racks, facing south. The edges of the film were reinforced by duct tape and were stapled to wooden frames. No portion of the film in contact with wood or tape was utilized in tests. Atmospheric irradiation was calculated from pyranometer measurements taken by R. Avissar

(Meteorology Department, Rutgers University), at a nearby field. The samples exposed for 6 weeks and 12 weeks received 342,428 and 639,204 kJ, respectively. Sample PE-B₁₂ disintegrated before the end of the 12-week exposure period. This photoexposure was repeated, with the same result. Consequently, no tensile strength test could be performed. Scraps were collected for CO₂ evolution measurements.

Soil incubations for CO₂ evolution, residual weight, and tensile strength measurements. Freshly collected Nixon sandy loam (College Farm, New Brunswick, N.J.) was used in all biodegradation studies. In terms of texture, this soil is composed of 50% sand, 21% silt, and 29% clay. The organic matter content of the soil was 5% and the pH was between 5.5 and 6.5 (5). The moisture content and water-holding capacity were determined and used to adjust the water content of the soil to 50% of holding capacity. This moisture level is considered ideal for aerobic biodegradation processes in soil (18). The pH of the soil was adjusted by the addition of CaCO₃ (liming) to 7.5. This pH was found to be near-optimal for hydrocarbon biodegradation (9), and it was assumed that it would also favor the biodegradation of plastic materials. The liming of soils used in Biometer flasks (6) was performed 5 days prior to the start of the experiment to avoid measuring any CO₂ released by neutralization as part of the biodegradation process. Per g of plastic material, 0.38 mg of (NH₄)₂ HPO₄ was added as fertilizer (approximate C/N ratio between plastic carbon and fertilizer nitrogen, 100:1) at time zero in order to provide sufficient nitrogen and phosphorus for the enrichment of a plastic-degrading microbial population. Incubation (burial) in soil for CO₂ evolution, residual weight, and tensile strength measurements were performed under identical conditions. For tensile strength tests, the film was cut into standard size test strips (2.5 by 20 cm) prior to burial in a covered bin containing 25 kg of soil. For easier distribution and incorporation into soil, all film samples for CO₂ evolution and residual weight measurements for the biodegradation studies were shredded, using scissors or a blender. The resulting pieces were typically 3 to 5 mm long and 1 to 2 mm in diameter. From all materials, 250-mg portions were mixed with 25 g (dry weight) of soil (1% [wt/wt]). Water and dissolved fertilizer were added, and the samples were incubated in Biometer flasks (CO₂ evolution), in covered 250-ml beakers (residual weight), or in the previously described bin (tensile strength), with periodic aeration at 27°C. Any moisture loss from soil, indicated by weight loss, was compensated for by the addition of distilled water. Poisoned controls (1% [wt/wt] HgCl₂) were included in residual weight experiments. The HgCl₂ did not interfere with the recovery process.

CO₂ evolution measurements. CO₂ evolution was measured in Biometer flasks (6). Soil controls and soil samples with test materials were prepared in triplicate. For clearer presentation, the cumulative CO₂ evolution of the soil controls was subtracted from the CO₂ evolution of the soil with test samples.

Residual weight analysis and plasticizer loss. For residual weight, samples were retrieved at time zero and after 4, 8, and 12 weeks. At the end of the incubation, the soil was air dried at room temperature and subsequently extracted by solvent, or the plastic pieces were removed manually. The film PVC-C was Soxhlet extracted with methyl-ethyl ketone (MEK), and film PP-E was extracted by boiling 1,2,4-trichlorobenzene and measured as described previously (22). We applied these procedures and numerous variations thereof to the other test materials, but unsatisfactory results eventually forced us to recover the rest of the test materials manually. In this procedure, plastic pieces were picked out of the dry soil with tweezers. This was followed by washing the plastic pieces in acetone, air drying at room temperature, and weighing. Plasticizers dioctyl adipate (DOA) and epoxidized soybean oil (ESO), present in film PVC-C only, were measured as described earlier (22). In brief, the PVC polymer was precipitated from the methyl-ethyl ketone extract and weighed. DOA in the supernatant was determined by gas chromatography. ESO was determined indirectly, by subtracting PVC and DOA from the total weight recovered.

Tensile strength measurements. For tensile strength measurements, test strips were retrieved after 3 months, washed with water and mild detergent, air dried at room temperature, and subjected to tensile strength tests as specified in ASTM standard D882-83. Force and work needed to break 10 exposed strips were compared with those needed to break 5 unexposed control strips of each material, using an Instron (Canton, Mass.) model 4200 instrument. Tensile strength measurements could not be performed on sample PE-B₁₂, as this material disintegrated during the 12-week photoexposure.

GPC. For GPC measurements, the samples were sent to L. J. Broutman and Associates (Chicago, Ill.) for analysis. The tests were performed on a Waters model 150C GPC instrument fitted with a refractive index detector. Sample PVC-C was dissolved in tetrahydrofuran and chromatographed at 35°C on a phenogel column (2 by 30 cm; particle size, 10 μ m). The films PE-C, PE-B, and PE-R were analyzed at a high temperature (135°C) on a PL gel (2 by 30 cm) in 1,2,4-trichlorobenzene. These conditions were dictated by the solubility characteristics of the analyzed polymers and are standard procedures (15). Injection volume for all samples was 150 μ l, and a flow rate of 1.0 ml/min was maintained. All measurements were performed in triplicate, and weight average molecular weight, number average molecular weight, and polydispersity were determined. The number average molecular weight (M_n) is defined as the total weight of all the molecules in a polymer sample divided by the total number of moles present. Weight average molecular weight (M_w) is the mean of the weight distribution of molecular weights. Polydispersity (Pd) is the breadth of the distribution of molecular weights in a polymer (M_w/M_n). A monodisperse polymer (uniform molecular size) would have a Pd of 1.0. In a typical polymer, Pd has values of 2 to 5.

In a polydisperse polymer, M_w is biased towards the larger and M_n is biased towards smaller molecules. Since the properties of the polymer usually depend disproportionately on the large molecules, M_w is generally more useful than M_n . Determination of both parameters allows the calculation of polydispersity ($Pd = M_w/M_n$), an important parameter for the character of the polymer.

RESULTS AND DISCUSSION

Starch content of films PE-R and PE-W. In thermogravimetric measurements between 200 and 360°C (the volatiliza-

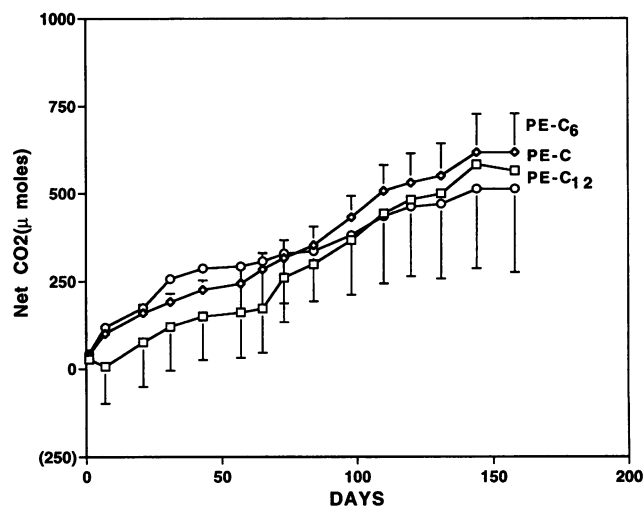


FIG. 1. Cumulative net CO₂ evolution from plastic films (250 mg) incubated in 25 g of soil at 27°C. Film PE-C received no pretreatment, while PE-C₆ and PE-C₁₂ were photoexposed for 6 and 12 weeks, respectively. The error bars mark 1 standard deviation of triplicate samples and are omitted when interfering with clarity. Within experimental error, CO₂ evolution by the three samples is identical.

tion range for modified starch), the weight of sample PE-R decreased 8% and the weight of PE-W decreased 1.5%, indicating corresponding starch contents for these samples. The starch content of film PE-R was also tested by Krupp and Jewell (14), who reported a slightly higher value (10 to 12%) than found by Andrady (4). The starch content of film batches may vary, and in our calculations we used the 8 and 1.5% values.

CO₂ evolution. CO₂ evolution from plastic film samples incubated in soil is shown in Fig. 1 to 3. Typical cumulative background CO₂ evolution from soil alone during the 160-day test period was 4,000 μ mol. The curves in the figures represent net CO₂ evolution from the respective test materials.

Samples PE-C, PE-C₆, and PE-C₁₂ evolved between 500 and 600 μ mol of net CO₂ (Fig. 1), and there was a lack of correlation between photoexposure and CO₂ evolution. Films PE-B and PE-B₆ evolved only slightly more net CO₂ (860 and 865 μ mol, respectively), while net CO₂ evolution from PE-B₁₂ was marginal, and this measurement was terminated after 100 days (Fig. 2). Measurements in Biometer flasks indicated that readings in excess of 5% of the soil background are indicative of test material biodegradation (20). In these measurements, all PE-C films exceeded soil background CO₂ evolution by 11 to 12%, and the PE-B and PE-B₆ samples exceeded soil background by 21%. Therefore, these measurements indicate the biodegradation of some component of these films, but calculations (see summary, Table 7) also show that only 3.5 to 4.9% of the total carbon available in these materials was converted to CO₂. The amounts of net CO₂ produced from the low-starch PE-W film (Fig. 3) exceeded the negative control PP-C only slightly. In a previous study (22), the latter material failed to produce any net CO₂. In contrast, the high-starch PE-R film produced substantial amounts of CO₂ (12% of total carbon). In good agreement with earlier results (22), PVC-C evolved 28% of its carbon. In this regard, the question of whether this CO₂ could have been produced from the additives alone arises. Calculations show that the DOA and ESO components of PVC-C can account for all the CO₂ evolved,

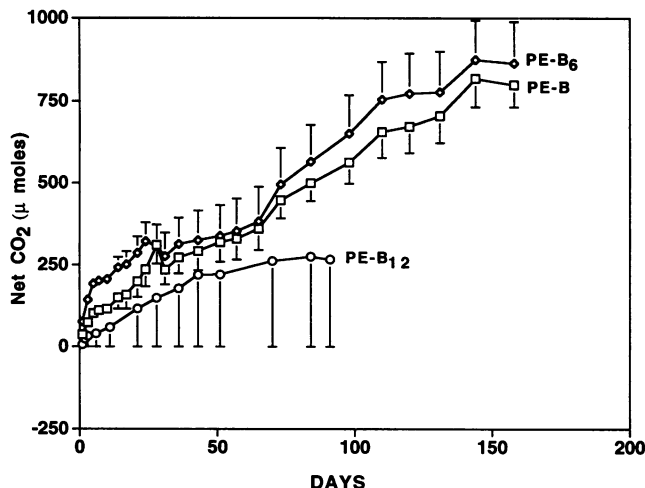


FIG. 2. Cumulative net CO_2 evolution from plastic films (250 mg) incubated in 25 g of soil at 27°C . Film PE-B received no pretreatment, while PE-B₆ and PE-B₁₂ were photoexposed for 6 and 12 weeks, respectively. The error bars mark 1 standard deviation of triplicate samples and are omitted when interfering with clarity. Within experimental error, CO_2 evolution of PE-B and PE-B₆ is identical; that of PE-B₁₂ is lower.

but an 8% starch content would only account for 900 μmol of CO_2 instead of the 2,536 μmol measured. Since the GPC results, to be presented later, make it unlikely that the excess CO_2 was derived from the PE resin, the excess CO_2 evolution was probably due to the red colorant or other minor additives.

In summary, CO_2 evolution measurements indicated substantial mineralization of positive control PVC-C and sample PE-R and very modest mineralization of samples PE-C, PE-B, PE-W, and the negative control PP-C. Sunlight exposure of samples PE-C and PE-B prior to soil incubation had either no effect or a negative effect on CO_2 evolution.

Residual weight analysis. Solvent extraction procedures, as practiced in pesticide and hydrocarbon analyses, are poten-

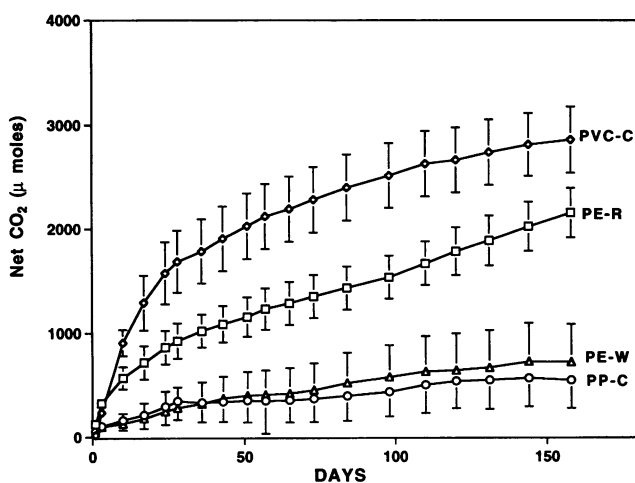


FIG. 3. Cumulative net CO_2 evolution from plastic films (250 mg) incubated in 25 g of soil at 27°C . Film PVC-C is the positive control, and film PP-C is the negative control. The error bars mark 1 standard deviation of triplicate samples. Note that the CO_2 scale is compressed compared with those of Fig. 1 and 2.

TABLE 2. Time zero recoveries of 250-mg amounts of plastic film from triplicate 25-g soil samples

Film code	Procedure ^a	Avg (mg)	SD (%)	Recovery (%)
PE-C	Manual recovery	253	2.4	101.2
PE-C ₆	Manual recovery	260	5.0	104.0
PE-C ₁₂	Manual recovery	250	1.7	100.0
PE-B	Manual recovery	259	2.4	103.6
PE-B ₆	Manual recovery	256	1.2	102.5
PE-B ₁₂	Manual recovery	251	1.7	100.4
PE-R	Manual recovery	217	1.2	86.8
PE-W	Manual recovery	228	1.0	91.2
PP-C	Boiling TCB extraction, methanol precipitation	244	2.9	97.6
PVC-C	Soxhlet extraction with MEK, Rotavap to dryness	236	1.4	94.4

^a TCB, 1,2,4-trichlorobenzene; MEK, methyl-ethyl ketone.

tially more precise and less laborious than manual retrieval. Such procedures were applied with success to films PP-C and PVC-C in an earlier study (22). Similar procedures, with many variations, were attempted for the rest of the test films in this study, but with unsatisfactory results. Hot 1,2,4-trichlorobenzene extraction was quantitative for PE-C and PE-B, but recoveries declined drastically after sun irradiation (data not shown). The decreased solubility probably reflected the photooxidative cross-linking of the PE strands.

The modified starch in PE-W and PE-R interfered with solvent extraction and filtration processes, resulting in poor recoveries (data not shown) and restricting us to the manual recovery of these four films. Table 2 summarizes the time zero recoveries for each test film. Average recoveries for the various films ranged between 87 and 104%; standard deviations ranged from 1 to 5%. Similar confidence limits were assumed for the time course recoveries in Table 3. Residual weight decreases occurred beyond error limits in case of films PE-R and PVC-C, the positive control. The poisoned controls indicated that the residual weight losses were due to biodegradation. No satisfactory solvent extraction process could be developed for the irradiated and starch-containing films.

Tensile strength determinations. Changes in tensile strength are summarized in Table 4. A significant decrease in tensile strength occurred in positive control PVC-C during incubation in soil. Somewhat surprisingly, but consistent with the CO_2 and residual weight results, a substantial decrease in tensile strength occurred also in the case of the negative control PP-C.

TABLE 3. Decline of residual weight with incubation time in soil

Code	Residual wt after incubation for:				
	Zero	4 wk	8 wk	12 wk	12 wk (PC ^a)
PE-C	253	264	246	250	256
PE-C ₆	260	265	248	242	242
PE-C ₁₂	250	252	247	251	254
PE-B	259	270	248	255	251
PE-B ₆	256	259	251	256	246
PE-B ₁₂	251	252	250	259	246
PE-R	217	182	193		240
PE-W	228	248	252	256	258
PP-C	244	237	231	223	232
PVC-C	236	210	206	205	254

^a PC, poisoned control. Plastic films were exposed for 3 months in soil containing 1% HgCl_2 .

TABLE 4. Tensile strength measurements on plastic film strips

Film sample	% Elongation ^a						% Change
	Prior to soil exposure			After 3 months in soil			
	n	Avg	SD	n	Avg	SD	
PE-C	10	269.1	62.4	5	289.9	71.2	+7.7
PE-C ₆	5	183.7	65.9	5	318.9	24.1	+73.6
PE-C ₁₂	5	111.7	43.4	5	114.8	95.5	+2.8
PE-B	9	370.5	28.9	5	354.6	69.2	-4.3
PE-B ₆	5	14.8	1.5	5	8.0	2.9	-45.9
PE-R	8	51.5	112.5	10	170.9	177.5	+231.8
PE-W	10	118.7	164.7	10	106.6	149.9	-10.2
PP-C	10	29.9	19.1	9	9.9	3.2	-66.9
PVC-C	10	85.1	29.7	10	3.6	0.3	-95.8

^a n, number of strips successfully tested. Because of instrument malfunctions, in some cases these were fewer than originally intended. PE-B₁₂ disintegrated prior to the end of the light exposure period and could not be tested.

The tensile strength of PE-W declined very moderately, but in the case of PE-R the elongation percent more than doubled during soil incubations. A possible explanation for this unexpected behavior is that the removal of starch granules promotes a slippage of PE strands past each other, thus promoting elongation (12a). The PE starch films PE-R and PE-W were subject to very high variability (high standard deviation) in tensile strength tests. We speculate that the heterogeneity in starch distribution may be responsible for this phenomenon.

Marked decreases in tensile strength of materials PE-C and PE-B occurred with photoexposure, and PE-B disintegrated between 6 and 12 weeks of exposure. The partially photodegraded PE-B₆ lost further strength during incubation in soil. This was not the case for samples PE-C₆ and PE-C₁₂. By nature, tensile strength determinations have high standard deviations. Because of instrument malfunctions, for some materials fewer than the intended number of test strips gave valid data. In future studies of this nature, especially in the case of starch plastics, the number of test strips should be increased for more accurate results.

Plasticizer loss. The time course of plasticizer degradation is shown in Table 5. Initially, plasticizer loss was rapid, with only little change past 4 weeks. This pattern was very similar to our findings in an earlier study (22). The physical occlusion of the plasticizer molecules between the undegraded polymer strands is the likely reason for the partial persistence of the plasticizers.

GPC. The weight average molecular weight, number average molecular weight, and polydispersity results obtained from GPC analysis are listed in Table 6. Consistent with the tensile strength results, photoexposure had a strong effect on the molecular weight of sample PE-B, decreasing M_w and M_n for PE-B₆ to 58.6 and 48.6%, respectively. The photoexposure had

TABLE 5. Decline of DOA and ESO plasticizers with time in 250 mg of PVC-C film incubated in 25 g of soil

Time (wk)	Amt (mg)	
	DOA	ESO ^a
0	48	27
4	23	15
8	19	12
12	17	12

^a The weight of ESO was calculated as follows: total weight - (PVC + DOA weight).

TABLE 6. Effects of photoexposure, incubation in soil, or both on plastic film samples

Code ^a	M_w^b	M_n^b	Pd
PE-C	103,800	23,260	4.46
PE-C ₆	100,700	19,790	5.09
PE-C ₆ , soil exposure	90,580	15,820	5.72
PE-B	85,640	24,330	3.52
PE-B ₆	50,210	11,820	4.25
PE-B ₆ , soil exposure	31,860	7,233	4.40
PE-R	81,930	23,180	3.53
PE-R, soil exposure	82,270	22,400	3.67
PVC-C	105,600	63,160	1.67
PVC-C, soil exposure	114,800	77,530	1.48

^a Comparing PE-C with PE-C₆ and PE-B with PE-B₆, respectively, shows the effects of photoexposure (342,428 kJ) on these films. Soil exposure, designates of a subsequent 3-month soil exposure of the previously light-exposed materials. Because of the high cost of this analysis, it was not performed on PE-C₁₂, PE-B₁₂, or any test film that showed only marginal degradation in the CO₂ evolution and residual weight tests.

^b Standard deviations for these analyses (triplicate injections) ranged between 0.15 and 2.0%.

very little effect on the molecular weight of sample PE-C. Soil incubation (3 months) in the case of PE-B₆ led to an additional decrease of M_w and M_n to 37.2 and 29.7% of the intact material (PE-B), respectively. As a consequence of the combined photodegradation and soil incubation treatments, sample PE-C₆ showed more moderate decreases to 87.2 and 68.0% of the original M_w and M_n values, respectively. No decrease in the molecular weights of sample PE-R and sample PVC-C occurred during soil incubation. This result indicates that the CO₂ evolution and weight loss of the latter samples reflected only the degradation of the additives and not of the polymer resin itself.

Comparison of the measurement approaches. The endpoint results (after 3 months of soil incubation) of this study are summarized in Table 7. Substantial CO₂ evolution and residual weight reduction occurred during soil incubation of films PVC-C and PE-R. In the case of PVC-C, these positive results correlated also with a significant reduction in elongation, but not with molecular weight decline. The latter actually appeared to increase slightly, though the mechanism for this increase is obscure. In the case of PE-R, elongation increased strongly while molecular weight did not change significantly. Molecular

TABLE 7. Summary of test results on the plastic film materials incubated in soil for 12 weeks

Film code	% Carbon converted to CO ₂	% Change in residual (wt) ^a	% Change in elongation ^b	% M_w change
PE-C	3.2	-1.2	+7.7	ND ^c
PE-C ₆	3.5	-6.9	+73.6	-10.1
PE-C ₁₂	2.9	+0.4	+2.8	ND
PE-B	4.5	-1.5	-4.3	ND
PE-B ₆	4.9	0.0	-45.9	-36.6
PE-B ₁₂	1.5	+3.2	ND	ND
PE-R	12.7	-11.1	+231.8	+0.4
PE-W	4.1	+12.3	-10.2	ND
PP-C	3.1	-8.6	-66.9	ND
PVC-C	28.8	-13.1	-95.8	+8.7

^a Negative values indicate weight decrease, positive values weight increase.

^b Negative values indicate a break at a lower elongation than in the case of the unexposed material; positive values indicate a break at a greater elongation. Normally, degradation results in a decrease of elongation at break.

^c ND, not determined.

weights declined significantly during soil incubation in the case of samples PE-C₆ and PE-B₆. In the case of PE-B₆, this correlated with a decline in elongation, but the residual weight did not change and carbon conversion to CO₂ was modest (4.9%). In the case of PE-C₆, conversion to CO₂ during incubation in soil was also modest, the decline in residual weight was small, and elongation actually increased. Overall, there was less correlation than expected among the measured parameters. In some cases, the changes were small, and it may be argued that they were within experimental error, but results on PE-C₆, PE-B₆, PE-R, and PVC-C clearly show that the four analytical techniques measure different parameters that do not necessarily correlate with each other.

Definition of plastic film degradability. The uncertainty in definitions and the variety in test approaches has prompted the ASTM to formulate definitions and standardized testing procedures. This work is not as yet complete, but decrease in the size of polymer resin molecules, as measured by GPC, is likely to be crucial for definition of degradation, while changes in additives will be defined as deterioration. In the restricted sense of these evolving ASTM definitions, our tests would fail to confirm the biodegradability of films PE-R, PE-W, and PVC-C. Films PE-R and PVC-C were strongly affected by a partial biodegradation of their additives, but the molecular sizes of their PVC and PE polymers were not decreased. The partial biodegradation of additives resulted in decreased elongation in the case of PVC-C but in increased elongation in the case of PE-R. Film PE-W, which had a very low starch content, was less affected during soil exposure than our negative control PP-C.

Some photodegradation in the sense of the emerging ASTM definitions, which again stress a demonstrable decrease in the molecular weight of the polymers, was evident in the case of test materials PE-C and PE-B, but only after photoexposures far above the expected ones. For some photodegradable films the claim is made that after initial photoexposure, degradation continues in the absence of light by free radical reaction (7), but this claim is not sufficiently documented. In the films tested, some additional decreases in M_w occurred during subsequent burial in soil for 12 weeks. These decreases were minimal in the case of PE-C (10%) but substantial in the case of PE-B (36%). The fact that these irradiated samples evolved very little CO₂ (Fig. 1 and 2) hints that the M_w reduction occurred by free radical reaction rather than biodegradation. Although the extent of biodegradation of the materials tested in this study was somewhat disappointing, these were first-generation products, and materials with improved biodegradability continue to be developed (17).

Conclusions and recommendations. This study shows a limited correlation among the techniques currently used for measuring plastic film degradation. The GPC measurement of molecular weight decrease is an expensive analysis and requires a nonselective retrieval of the plastic residue from soil. GPC measurements are complicated by photooxidative cross-linking which decreases solubility and may, in part, reverse molecular weight decline. In plastic films with additives, tensile strength decline and CO₂ evolution do not necessarily correlate with molecular weight decline as measured by GPC.

Carbon dioxide evolution in Biometer flasks was found to be useful for biodegradability screening. For photodegradation screening, the traditional photoexposure followed by tensile strength tests continues to be the most useful. In the case of composite materials, positive tests need to be verified by GPC measurement of reduction in polymer molecule size, but this costly analysis is better suited for verification than for routine

screening. We cannot recommend residual weight determinations for PE- and PP-type films that contain starch granules or other solvent-insoluble particulates.

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