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Degradable Polymers: The Role of the Degradation Environment[1]

M. Day,[2,3] K. Shaw,[2] D. Cooney,[2] J. Watts,[2] and B. Harrigan[2]

The degradability of several degradable polymers was examined using three types of degradation environments. These include exposure in a laboratory-scale composting test system containing material representative of the organic fraction of municipal solid waste (MSW), exposure in a thermal hydrolytic environment consisting of water at 60°C, and exposure in a thermal-oxidative, dry oven environment of 60°C. The results of the investigation clearly indicate that, in addition to chemical and biological activity which can lead to polymer degradation, physical restructuring and reorganization of the macromolecular structure may also occur at temperatures typically found in a compost environment, resulting in changes in the mechanical properties of the polymer films. In the case of the polyethylene-modified polymers evaluated in this study, all behaved similarly, but differently from the other polymer types. The polyethylene-based films appeared to be susceptible to oxidative degradation and should degrade in a composting environment providing that there is sufficient air in contact with the film for a sufficient period of time. However, when exposed in a laboratory composter, it appears that although ideal temperature–time curves may be obtained, the test time period was insufficient in comparison to the induction period required to achieve the desired thermal oxidative degradation.

KEY WORDS: Biodegradation; thermal degradation; hydrolytic degradation; composting.

INTRODUCTION

Over the last few years there has been growing interest in degradable polymers. The key focus of much of the earlier research and development was on ecological applications, principally waste disposal [1–4]. Today "newer" degradable polymers are being engineered for highly specialized niche markets [5–8] such as packaging for the fast food industry, where sorting, cleaning, and recycling are not competitive with composting. Other opportunities include use as mulchable agriculture films and personal hygiene products. However, it is possible that the recent increase in the number of commercial composting operations for the management of municipal solid waste (MSW) that has spurred current renewed interest [9, 10].

It has been estimated that in North America, up to 60% of the MSW [11, 12] is organic in nature and potentially compostable. In certain states in the United States and provinces in Canada, in order to achieve mandatory landfill diversion rates of 50% or higher, composting is seen as an essential component of the solid waste management system. Consequently, the use of biodegradable polymers in the packaging of organic/biodegradable materials, such as food, enables this waste to be directly composted without the need to separate the contents from the packaging. In addition, the use of degradable plastic bags to collect yard wastes has an appeal from the compost management point of view, since it solves the problem of debagging incoming material.

This interest in degradable plastic bags has spawned numerous research projects on the compostability of a

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wide range of polymer types [13–20]. However, in many of these studies it has not been clearly established that the loss in the physical properties of the polymeric material in the composting environment was actually the result of biological processes. Other degradation processes may have been occurring which do not involve the action of naturally occurring microorganisms such as bacteria, fungi, and molds. For example, it is possible that the polymer may be degrading as a result of hydrolysis, or alternatively, it may be due to thermal oxidative cleavage of the polymer chains.

In order to assess the decomposition pathways, a series of experiments was performed in an attempt to separate the roles of thermal oxidation, hydrolysis, and biological activity. It should be pointed out that in a composting environment all the above degradable pathways are possible and all can result in the degradation of the polymer. However, irrespective of the initial degradation step, it is likely that smaller molecular fragments will be produced, which will then be more amenable to biological activity, resulting in enhanced biodegradation of the polymer [8].

EXPERIMENTAL

Materials

A wide range of degradable polymeric materials was obtained from suppliers in Canada, the United States, and Europe. These materials are listed in Table I, along with their chemical composition as provided by the supplier or obtained from other sources. The polymers selected for this evaluation included biodegradable polymers based upon polycaprolactone and polylactic acid as well as those based upon starch blends and polyethylene containing additive packages. The polyethylene samples all contained specific additive packages, which were designed so that the degradation of the polymer was initiated once specific conditions were attained. In order to facilitate the evaluation, all samples were available as either a sheet or a film.

Composting Mixture

A standard, reproducible synthetic composting mixture was used throughout the testing program. This mixture was based upon a formula developed by Procter and Gamble, which was recommended as a good simulation of MSW. This material provides a greater degree of replication of a test environment in order to ensure consistency between experimental runs [21]. The synthetic formula was made up of 27.3% rabbit chow, 23% ground corn cobs, 12.9% sand, 0.7% composted cow manure, 0.5% shredded newspaper, and 35.6% water. The resulting composition was then blended together to give a homogeneous mixture which typically had a starting carbon-to-nitrogen ratio of 30:1, a moisture content of 45.3%, a bulk density of 0.50 g/ml, 53% air voids, and an initial pH of 6.5.

The Composting System

The composting experiments were conducted in 6-L bench-scale units fabricated from 100-mm-diameter glass piping (Fig. 1). Each unit was about 600 mm tall,

Table I. Polymeric Materials Evaluated in the Study

Code	Sample name	Composition	Supplier	Application	Thickness (μm)
T1	Tone	Polycaprolactone P-787	Union Carbide (USA)	Compost bag	26
MB1	Mater-Bi ZF03U	Polycaprolactone/starch/synthetic Blend	Novamont (Italy)	Compost bag	54
MB2	Mater-Bi Z101U/T			Sheet	103
EP	Eco-Pla	Polylactic Acid	Cargill (USA)	Film	48
N1	Novon	Destructurized/gelatinized starch-based polymer	Farnell Canada	Compost bag	46
ES1	Naturegrade	77% LLDPE + 23% master batch	Ecostar (USA)	Compost bag	46
BS1	Bio-Solo Brown	Polyethylene + additive package	Indaco (Canada)	Compost bag	32
BS2	Bio-Solo Green	Polyethylene + additive package	Indaco (Canada)	Compost bag	37
EV1	Enviro White	Polyethylene + additive package	EPI (USA)	Compost bag	40
EV2	Enviro Green	Polyethylene + additive package	EPI (USA)	Film	29
EV3	Enviro Black	Polyethylene + additive package	EPI (USA)	Garbage bag	32
C1	Control	Standard black garbage bag	B&G (Canada)	Garbage bag	26

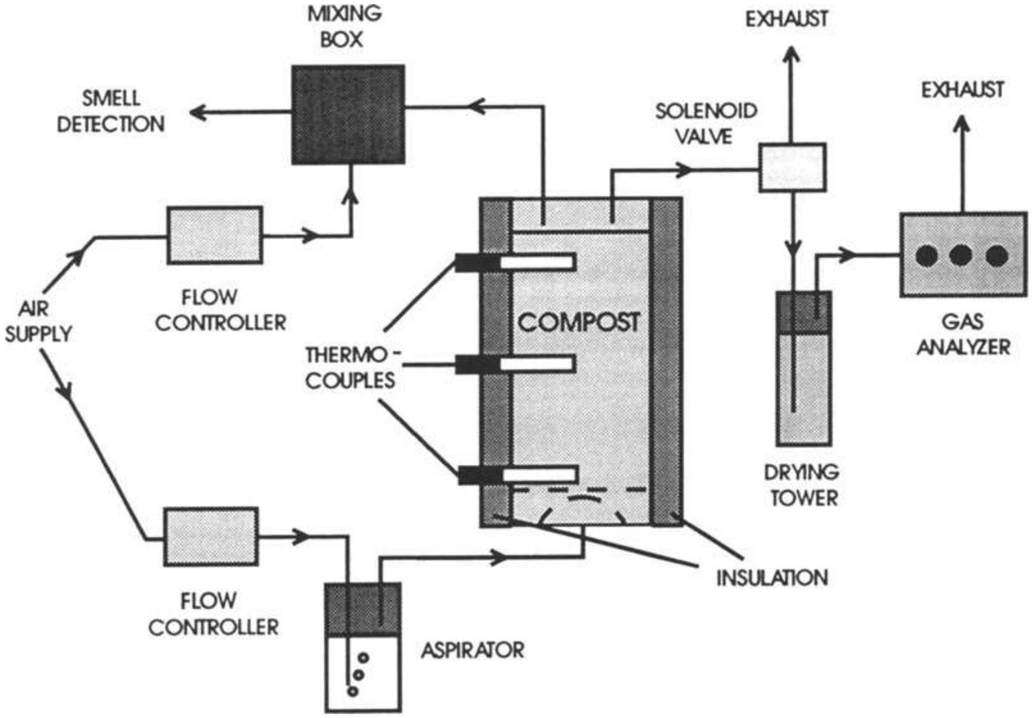

Fig. 1. Schematic of the laboratory-scale composting system.

with 50 mm of free airspace at the bottom and a 100-mm headspace at the top. Air entering the composting reactor first flowed through a water aspirator to saturate the air and prevent the mixture from drying out. The water saturated air supply was then distributed into the base of the reactor by means of a mushroom shaped air diffuser. A fine-mesh screen was used as an interface between the synthetic mixture and the air diffuser to facilitate air diffusion and prevent the compost mixture from obstructing the air inlet ports. The filling of the reactor with the test mixture was done with care to ensure that the desired bulk density was achieved and air channeling was minimized. During the filling process, three thermocouples were positioned centrally in the reactor at heights of 80, 240, and 440 mm from the base of the test mix to record temperatures during the composting process. The unit was then sealed with a gas-tight cap which allowed for the collection and analysis of the gases exiting the reactor. The exit gas from the composter was then dried and analyzed for carbon dioxide (CO_2), oxygen (O_2), and methane (CH_4) by the use of a portable Triple Landfill Gas Analyzer (ADCLFG20).

The thermocouple temperature readings and concentrations of CO_2, O_2, and CH_4 in the exit gases were all recorded automatically using a 486 DX 33 IBM-compatible computer operating under Labview Software control. The air supply to the composter was controlled at the desired flow rate of 450 ml/min by the use of a MKS flow controller. Once filled, the reactor was insulated with 4-in.-thick polyurethane foam, and all experiments were performed in a room maintained at 35 ± 1 °C in order to minimize heat loss.

The temperature–time profiles obtained using this setup were reproducible and Fig. 2 represents a typical curve as recorded by the thermocouple located in the center of the composter.

Composting Exposures

Prior to exposure, test strips 2.54 × 15.25 cm were cut from each test sample, with the long dimension parallel to the machine processing direction. These samples were then sewn into nylon, nondegrading netting bags, which allowed free contact of the composting medium with the sample, while facilitating sample recovery at the conclusion of the experiment. Samples were removed from the composter after periods of 3, 7, and 12 days, at which time most of the biological activity was complete (see Fig. 2).

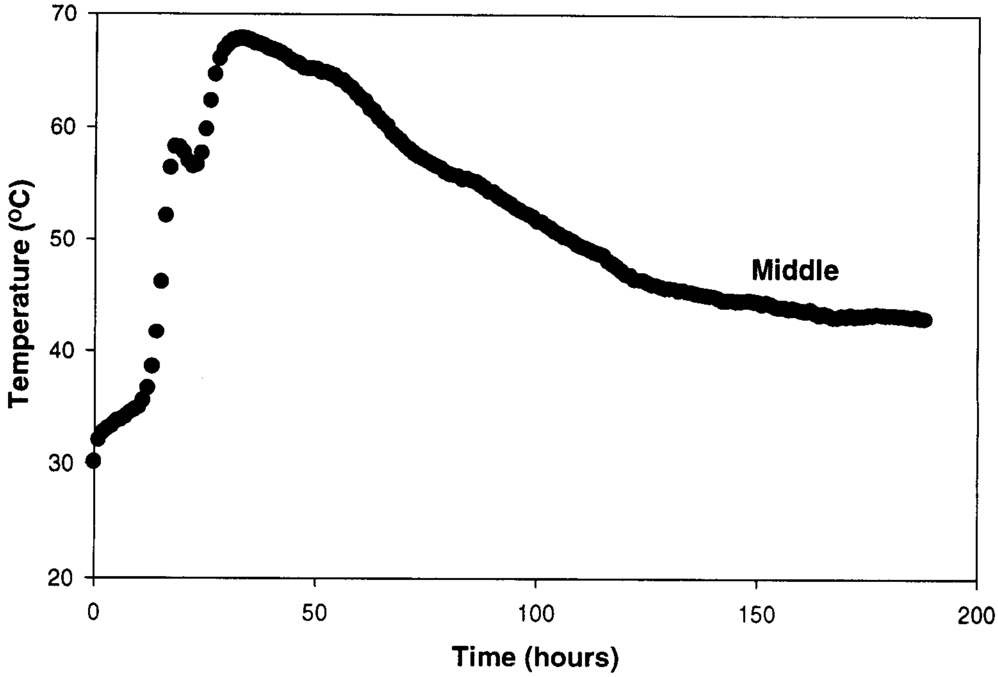

Fig. 2. Typical temperature/time curve for the synthetic composting mixture.

Hydrolytic Treatments

Once again, each sample was cut into test strips 2.54 × 15.25 cm. These samples were then placed in beakers of water, which were heated in an oven at 60°C. This temperature of 60°C was selected based upon the typical temperatures achieved in an active composting system (see Fig. 2) and the requirements for composting to be maintained at temperatures of 55–60°C for at least 3 days [22]. Samples were removed for evaluation after various exposure times up to a total of 30 days' exposure.

Thermal Oxidative Treatments

In this series of experiments the test strips were allowed to hang freely in a circulating air-drying oven maintained at 60°C, once again selected to represent the temperatures typically achieved in an active compost system. Specimens were removed, as in the other experiments, at periodic intervals up to a total of 30 days' exposure in order to assess the extent of degradation.

Material Characterization

Following the appropriate exposure, specimens were carefully removed from the test environment and dried to a constant mass on filter paper at 35°C. In the case of the composted samples, they were first rinsed well with Milli Q water before drying. The specimens were visually inspected prior to the evaluation of changes in physical characteristics such as mass loss, dimensional change, and changes in elongation and strength. The tensile properties of the films were measured using an Instron Model 1123 test machine. Test strips were cut 2 mm wide and 70 mm long and tested with a jaw separation of 25 mm. The tests were performed on an average of at least 10 specimens using "Method A—Static Weighting—Constant Rate of Grip Separation Test," outlined in ASTM D 882-83 [23]. The load at break, percentage elongation at break, and yield strength were all calculated for each specimen and the averages were calculated.

RESULTS AND DISCUSSION

In order to ensure replication of the composting methodology, the physical characteristics of the synthetic composting mixture were monitored before and after the composting process. The results of these measurements are summarized in Table II. From the data presented in this table it is clear that good repeatability was obtained from run to run, with the material achiev-

Table II. Characteristics of the Synthetic Composting Mixture

	Average	SD	Min. value	Max. value
Peak max. temp (°C)	67.7	0.7	66.6	69.0
Min. O_2 level (%)	7.6	1.2	5.7	
Max. CO_2 production (%)	14.1	1.9		16.6
pH before	6.53	0.16	6.19	6.75
pH after	7.49	0.38	6.64	7.92
Moisture before (%)	45.3	3.2	41.0	49.3
Moisture after (%)	49.6	2.5	45.0	52.0
Bulk density before (g/ml)	0.50	0.02	0.46	0.53
Bulk density after (g/ml)	0.44	0.03	0.37	0.46
Change in total mass (%)	−15.0	2.2	−12.0	−18.6
Change in dry mass (%)	−21.8	3.7	−16.6	−26.0

ing temperatures in excess of 60°C for a period of about 2 days (Fig. 2). This high biological activity was confirmed in terms of the depletion of oxygen and evolution of CO_2 noted in the exhaust gas from the composters (Fig. 3). While the initial pH of the material was just less than neutral, composting caused a slight increase in pH to a value just above 7. In 12 days, mineralization of a typical composting mix resulted in an approximately 22% mass loss. Meanwhile the use of a 450 ml/min saturated airflow rate appears to be sufficient to maintain satisfactory moisture and oxygen levels within the composting medium.

Composting Data

The changes in mass and thickness of the samples, as measured after 12 days of exposure in one of the laboratory-scale composting reactors, are summarized in Table III. These measurements represent the average of three specimens. In addition, the mechanical strengths of the samples removed from the composter are summarized in Tables IV, V, and VI, which present the data for the percentage elongation at break, the load at break, and the yield load, respectively. Because of similarities in the behavior of the tensile strength measurements,

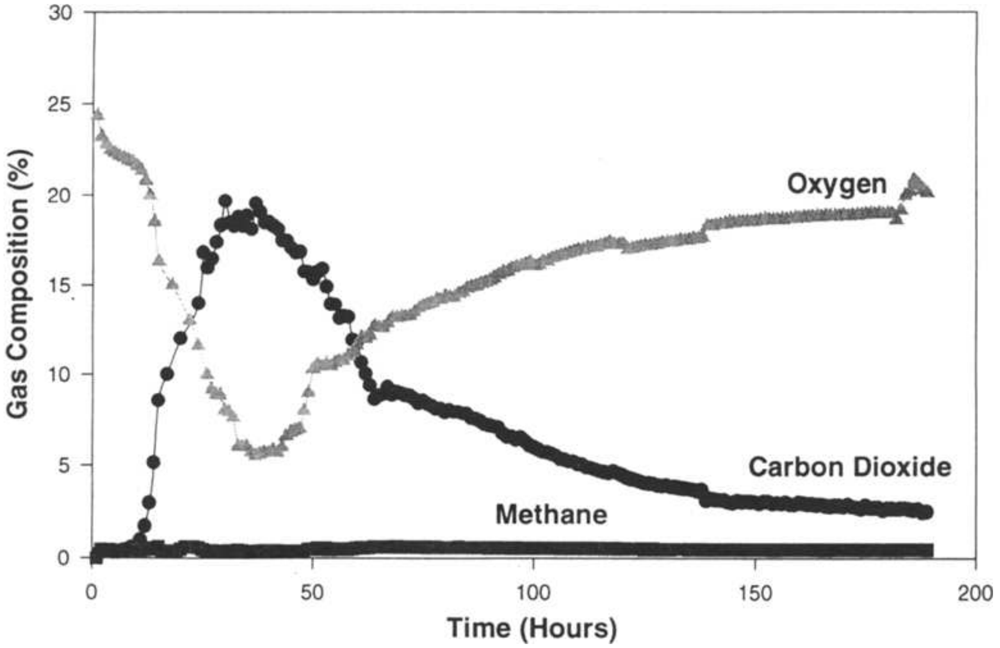

Fig. 3. Typical gas analysis curves for the synthetic composting mixtures.

Table III. Change in Mass and Thickness as a Result of Exposure in a Composting Environment

	Mass change (%)			Thickness change (%)		
Sample	3 days	7 days	12 days	3 days	7 days	12 days
T1	ND[a]	ND	ND	ND	ND	ND
MB1	−25	−59	−51	−28	ND	ND
MB2	−20	−80	−95	ND	ND	ND
EP	−50	−80	−95	ND	ND	ND
N1	−14	−12	−36	−7	ND	ND
ES1	+2	+1	+4	+8	0	0
BS1	+6	+5	+2	+6	+18	+18
BS2	+1	+1	+1	0	+8	0
EV1	0	−1	+1	+7	+5	+7
EV2	+1	0	0	+20	+27	+34
EV3	0	0	−1	+12	+18	+18
C1	+1	+1	+1	0	+3	+3

[a] Not determined.

Table IV. Percentage Elongation at Break for Polymer Samples Exposed in the Composting Environment for Different Periods of Time

	Composting duration (days)			
Sample	0	3	7	12
T1	1717 ± 647	ND[a]	ND	ND
MB1	770 ± 220	17 ± 6	11 ± 6	17 ± 6
MB2	1617 ± 283	ND	ND	ND
EP	19 ± 9	ND	ND	ND
N1	673 ± 95	5 ± 2	8 ± 3	ND
ES1	1051 ± 101	1044 ± 95	1298 ± 256	928 ± 118
BS1	960 ± 78	853 ± 89	1003 ± 77	905 ± 161
BS2	764 ± 139	1009 ± 198	1004 ± 77	836 ± 123
EV1	157 ± 23	116 ± 18	106 ± 23	110 ± 19
EV2	162 ± 27	227 ± 75	350 ± 120	251 ± 127
EV3	320 ± 100	290 ± 64	355 ± 107	322 ± 71
C1	1411 ± 340	1309 ± 130	1178 ± 251	1135 ± 167

[a] Not determined.

Table V. Load at Break (g) for Polymer Samples Exposed in the Composting Environment for Different Periods of Time

	Composting duration (days)			
Sample	0	3	7	12
T1	341 ± 125	ND[a]	ND	ND
MB1	136 ± 18	109 ± 17	78 ± 29	67 ± 11
MB2	1065 ± 70	ND	ND	ND
EP	661 ± 43	ND	ND	ND
N1	182 ± 50	136 ± 21	95 ± 27	ND
ES1	183 ± 24	161 ± 18	184 ± 23	194 ± 22
BS1	143 ± 18	198 ± 12	190 ± 16	142 ± 16
BS2	96 ± 16	168 ± 35	198 ± 27	190 ± 26
EV1	226 ± 23	238 ± 27	207 ± 14	205 ± 13
EV2	208 ± 30	186 ± 31	189 ± 15	219 ± 19
EV3	156 ± 14	164 ± 16	174 ± 18	161 ± 21
C1	115 ± 10	121 ± 10	114 ± 19	128 ± 16

[a] Not determined.

Table VI. Yield Load (g) for Polymer Samples Exposed in the Composting Environment for Different Periods of Time

Sample	Composting duration (days)			
	0	3	7	12
T1	133 ± 8	ND[a]	ND	ND
MB1	59 ± 10	55 ± 16	ND	15 ± 21
MB2	799 ± 148	ND	ND	ND
EP	248 ± 263	ND	ND	ND
N1	83 ± 13	27 ± 19	ND	ND
ES1	69 ± 7	70 ± 5	71 ± 6	75 ± 5
BS1	59 ± 6	61 ± 4	59 ± 2	61 ±
BS2	51 ± 3	55 ± 13	70 ± 3	66 ± 5
EV1	85 ± 11	71 ± 12	77 ± 10	53 ± 12
EV2	62 ± 11	68 ± 11	67 ± 6	86 ± 9
EV3	44 ± 9	61 ± 6	56 ± 6	48 ± 7
C1	54 ± 6	59 ± 4	61 ± 3	60 ± 6

[a] Not determined.

only the elongation at break has been plotted as a function of exposure time. These data are presented in Figs. 4–12 for each polymer type studied.

From these data it can be seen that some polymers do indeed rapidly degrade and disappear in the composting environment used in this study, while others show no signs of degradation.

The Tone polymer (T1) rapidly disappeared in the composting environment, with no sign of the polymer film inside the nylon net bag when the sample was removed after 3 days.

Both Mater-Bi samples (MB1 and MB2) showed substantial changes as a result of the composting exposure, with appreciable mass loss noted in both cases. In the case of MB1, after only 3 days of exposure the film showed appreciable relaxation (accounting for the observed increase in film thickness). However, the material was still in one piece after the full 12 days of ex-

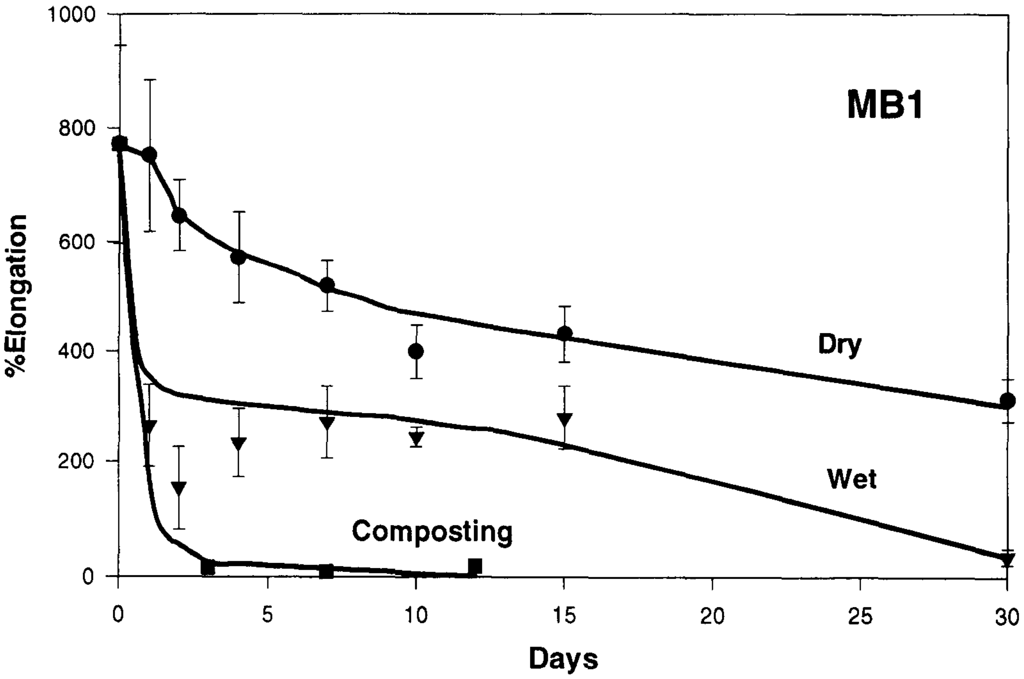

Fig. 4. Changes in the percentage elongation of the Mater-Bi sample (MB1) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

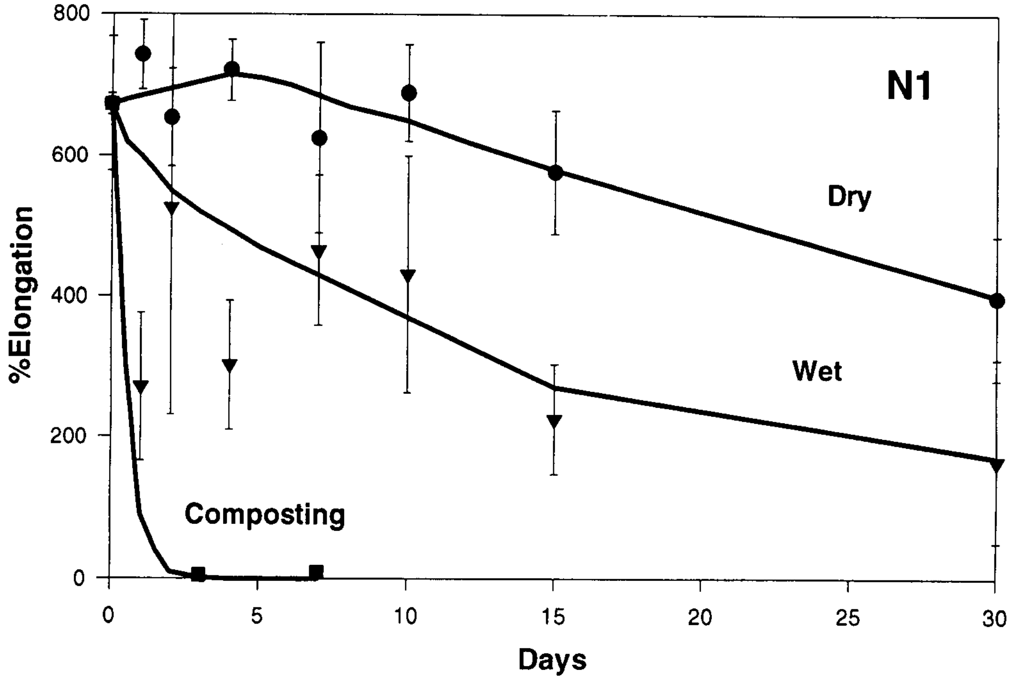

Fig. 5. Changes in the percentage elongation of the Novon sample (N1) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

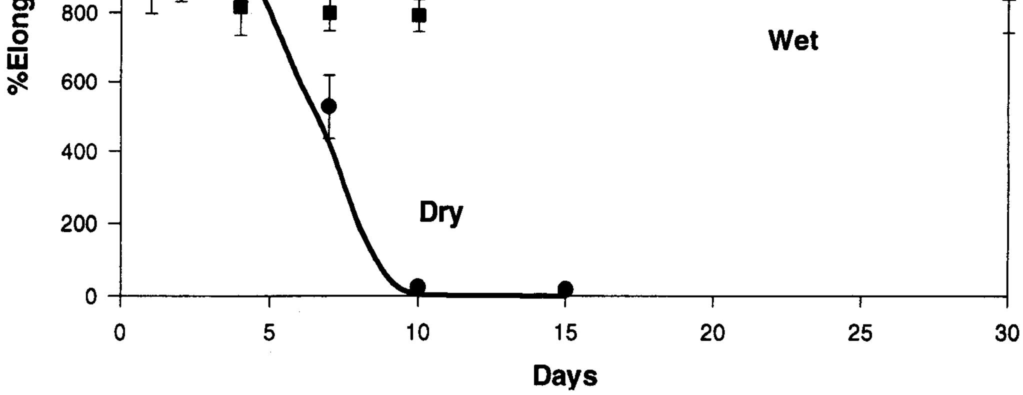

Fig. 6. Changes in the percentage elongation of the Ecostar sample (ES1) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

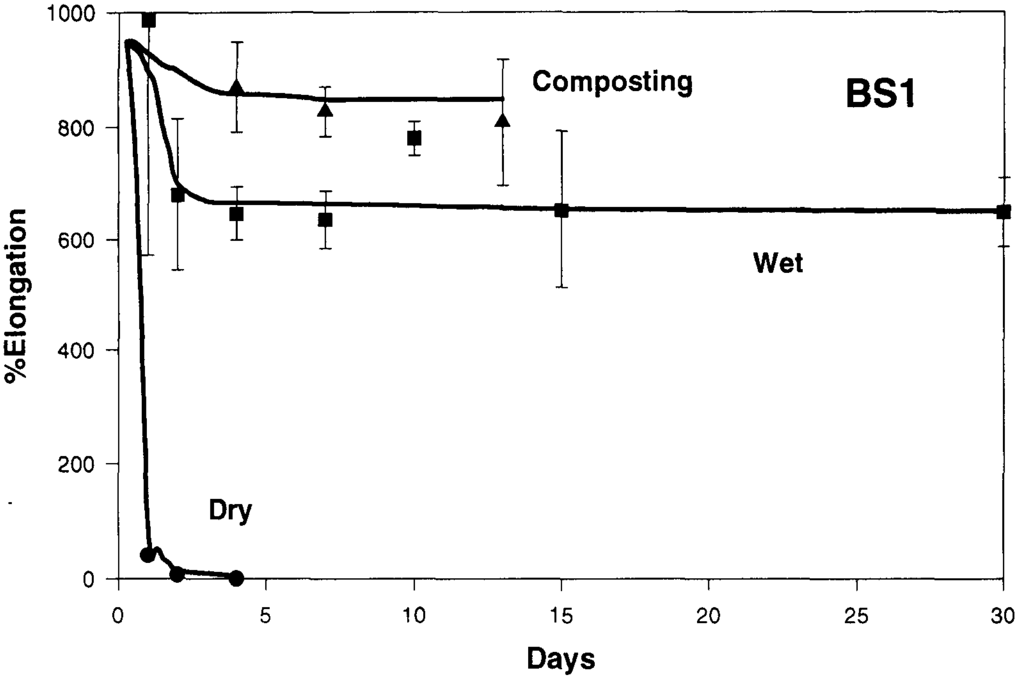

Fig. 7. Changes in the percentage elongation of the Bio-Solo Brown (BS1) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

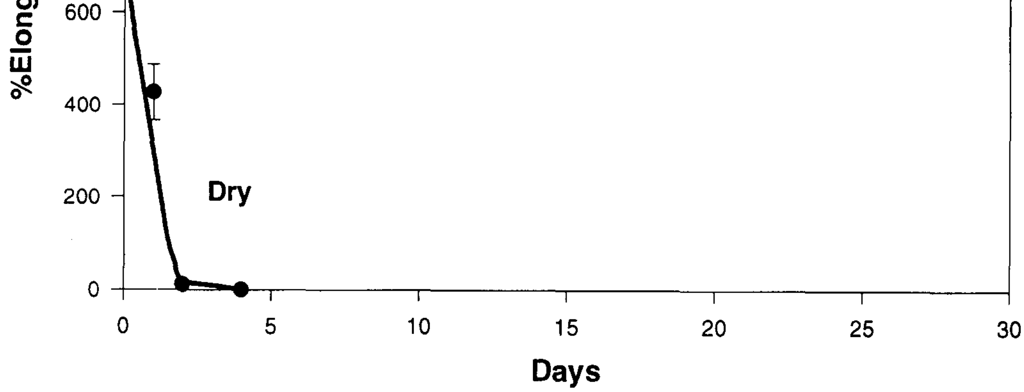

Fig. 8. Changes in the percentage elongation of the Bio-Solo Green (BS2) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

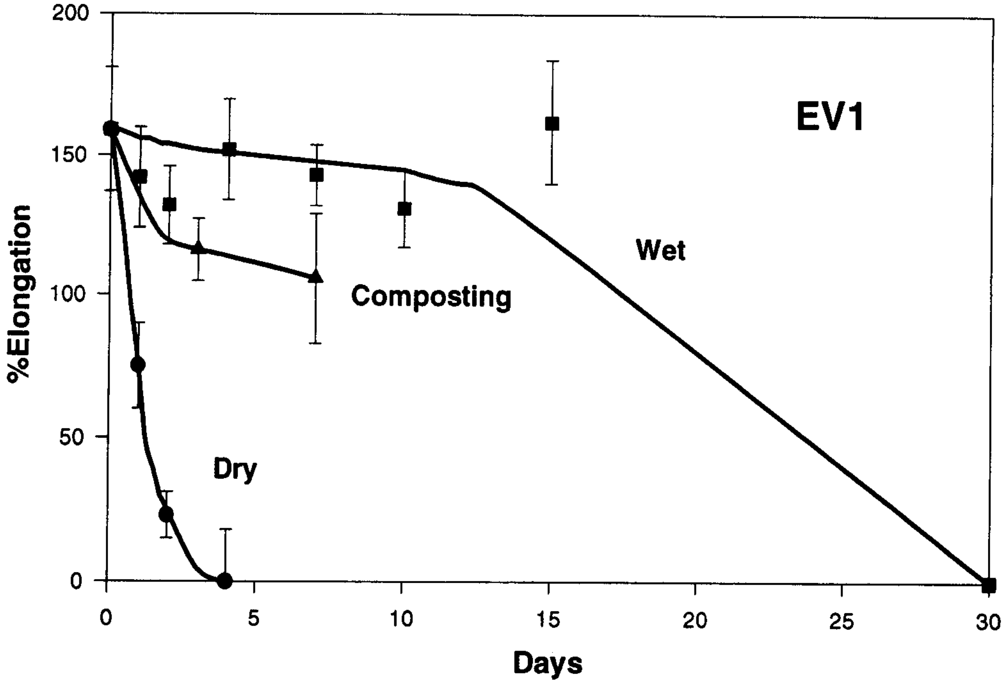

Fig. 9. Changes in the percentage elongation of the Enviro White (EV1) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

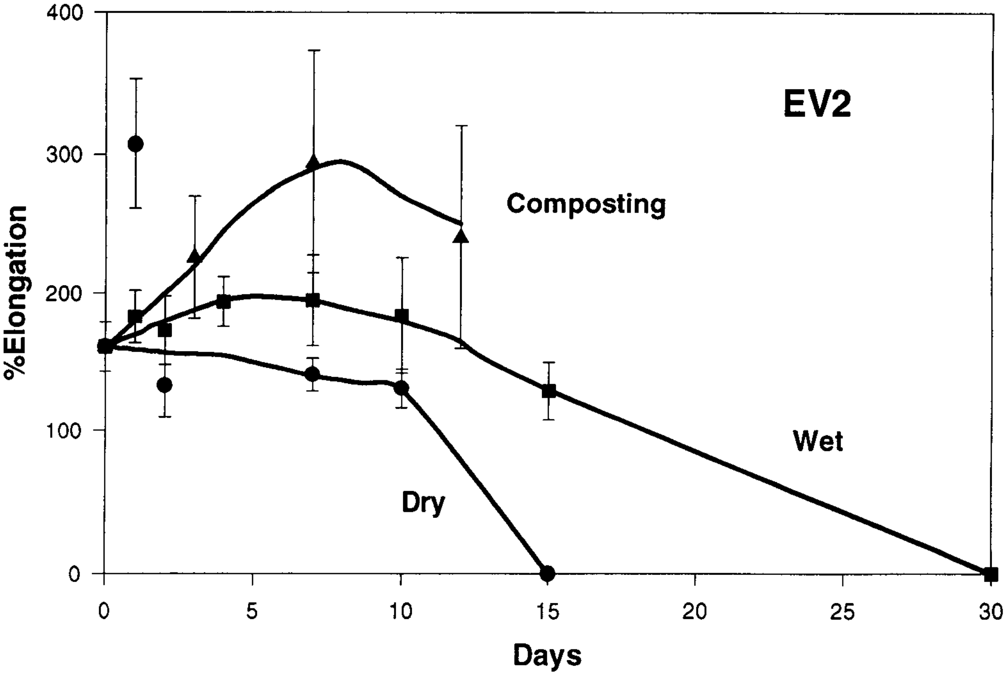

Fig. 10. Changes in the percentage elongation of the Enviro Green (EV2) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

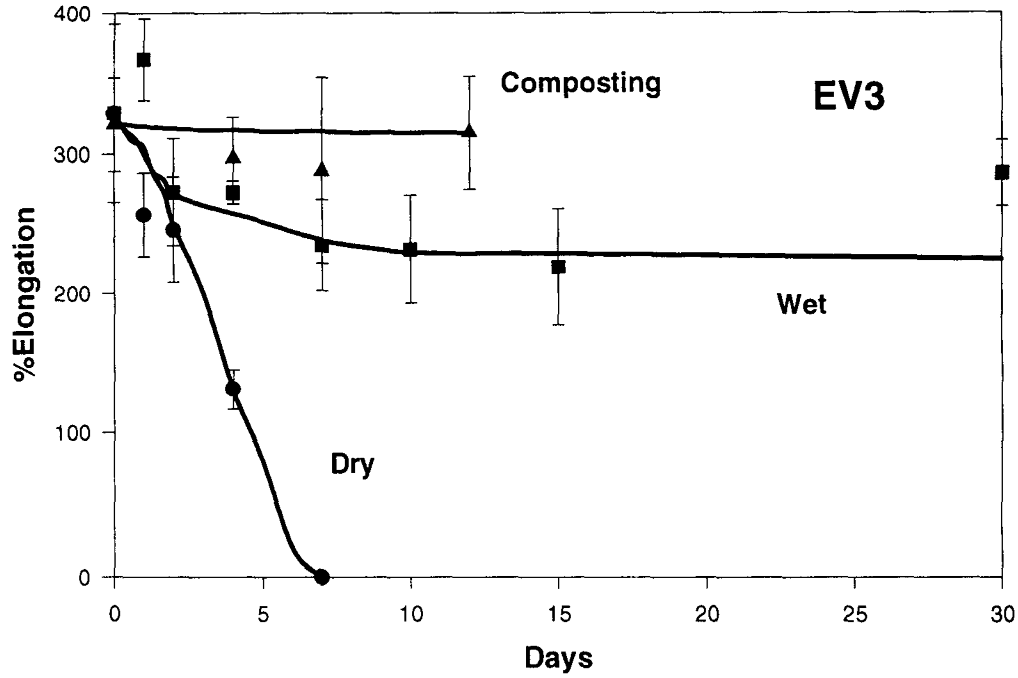

Fig. 11. Changes in the percentage elongation of the Enviro Black (EV3) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

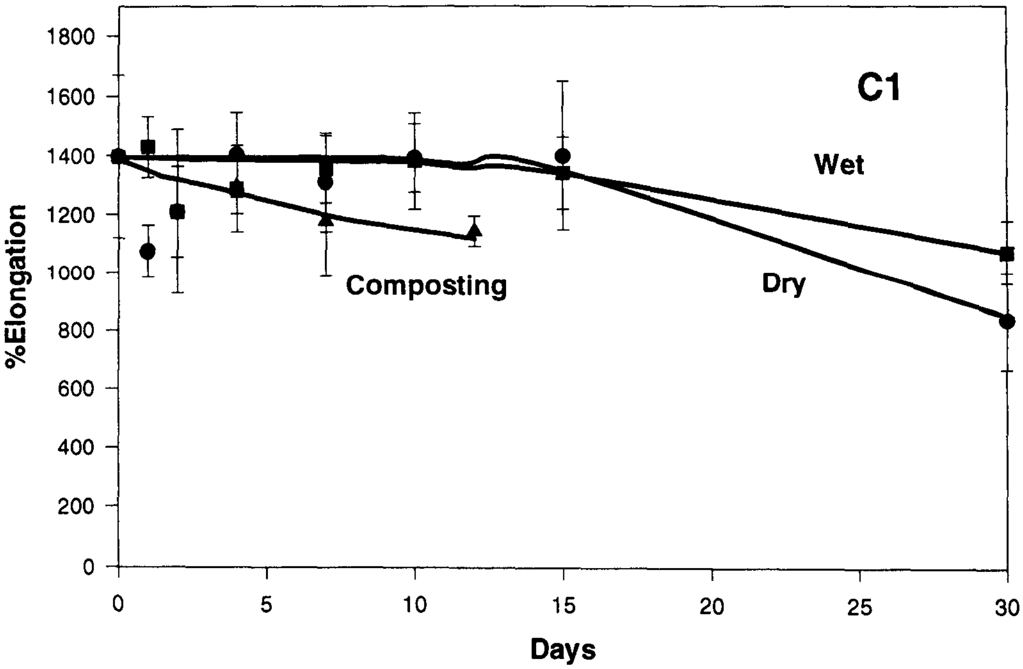

Fig. 12. Changes in the percentage elongation of the Control (C1) as a result of exposure in the composting environment, water at 60°C, and a drying oven at 60°C.

posure, and although it did show clear signs of discolouration and loss in physical strength and elongation, it was still possible to handle the film without it fragmenting. The other Mater-Bi sample, MB2, however, showed appreciable degradation after only 3 days in the composter. After this 3-day period the film became brittle and fragmented easily such that the material had insufficient strength for tensile testing. Consequently at the end of the 12-day test period not very much of the sample remained, and what was left was brown in color and adhered to the netting in small fragments. Clearly the MB2 degraded appreciably in a composting environment.

The Eco-Pla polylactic acid material (EP) also degraded very rapidly in the composting environment, such that after only 3 days of exposure the sample was exceptionally brittle and fragmented easily. On removal from the composter after 12 days of exposure, only small fragile fragments remained within the netting.

The Novon sample (N1) lost a great deal of its flexibility after only 3 days of exposure but it did retain its integrity and shape for the full 12 days of exposure, although very little strength remained after the 12 days. It should be noted, however, that the observed mass increase noted in Table II for this material was due to relatively large amounts of compost and bacterial growth which adhered to the fragile film and which could not be removed without damaging the film.

The Ecostar sample (ES1) survived the composting exposure tests with only a slight loss in mass and elongation at break. However, the physical strength of the material did show some weakening in that the break load was noticeably reduced after 6 days exposure.

Both Bio-Solo samples (BS1 and BS2) remained virtually unaffected by the 12 days of composting exposure, with both samples being in one piece and completely flexible on removal from the composting environment. The samples also showed no changes in physical properties in terms of elongation at break, break load or yield strength.

The three Enviro samples, EV1, EV2, and EV3, supplied by EPI also showed a similar behavior, i.e., complete stability during the full 12 days of composting exposure. From a control point of view, the standard garbage bag showed no measurable changes during this exposure period, as would be expected for a conventional polyethylene material.

A standard Whatman filter paper placed in a composter for the same 12 days of exposure became quite fragile, fragmented into several pieces, and was dark brown in color. This Whatman paper result clearly indicates that there was plenty of biological activity in the composting systems used for these evaluations.

Thermal Hydrolytic Data

The changes in mass of the samples heated in water at 60°C are presented in Table VII for each sample tested as a function of exposure time. The data on the elongation at break, meanwhile, are presented in Figs. 4 to 12 for each sample, from which measurements were possible. Also provided in these figures are the data for the composting and thermal oxidative degradation studies.

The Tone sample (T1), once exposed to the warm-water environment, was observed to shrivel up into a small ball, from which it was impossible to do any measurements on the changes in its physical characteristics,

Table VII. Mass Loss of Samples (%) on Exposure to Thermal Hydrolytic Conditions (60°C) for Various Time Periods[a]

	Exposure time (days)						
Sample	1	2	4	7	10	15	30
T1	0.2	0.1	0.5	0.9	(2.1)	0.3	0.1
MB1	11.0	11.3	10.2	10.6	10.8	10.7	10.7
MB2	8.6	9.1	6.5	21.1	8.4	7.5	63.0
EP	0	0	0	0.5	4.8	21.9	37.8
N1	8.6	9.4	11.0	9.0	8.1	8.7	6.9
ES1	(2)	(0.6)	0.8	(0.1)	0	0	(0.1)
BS1	0.2	(0.1)	0.5	0.5	(0.1)	0.1	0
BS2	—	—	—	—	—	—	—
EV1	(0.4)	(0.6)	(0.4)	(0.6)	(0.2)	(0.5)	0
EV2	0.5	0.8	0.9	0.8	(0.1)	0.7	47.0
EV3	0.7	0.8	(6.9)	0.7	(0.3)	5.2	0.6
C1	0	0	0	0	0	0	0

[a] Values in parentheses denote mass gains.

although the material could be recovered for mass determination. Analysis of the thermal characteristics of the material by differential scanning calorimetry (DSC), however, revealed that melting of the polymer commenced at about 49°C, with a peak transition occurring at 62°C. Clearly, in view of this low melting point it is difficult to ascertain if any degradation occurred at 60°C. This thermal behavior of the Tone sample (T1) could also explain the disappearance of the sample in the composting environment once temperatures in excess of 60°C are achieved.

Both Mater-Bi samples showed significant changes as a result of the hydrolytic exposures with MB2 exhibiting the most pronounced changes. This material became quite rubbery when exposed to the 60°C water and swelled considerably. It was difficult to handle, tearing very easily in the wet state and becoming very brittle when dried, making measurements very difficult if not impossible. Thermal analysis of the sample by DSC revealed that the material had a low endothermic transition temperature of 53°C, suggesting that this loss in physical strength could be associated with a physical restructuring of the polymer at 60°C.

The MB1 sample also showed signs of physical relaxation when placed in water at 60°C and had to be uncurled into long strips on removal from the liquid before its mechanical properties could be measured. These measurements clearly indicated that the material had become brittle and lost some of its strength as a result of hydrolytic exposure. Examination by DSC, once again, revealed a low endothermic transition temperature of about 60°C where physical relaxation and restructuring of the film were occurring. Once again, these effects appear to be responsible for the changes noted in the mechanical properties.

The Eco-Pla polylactic acid sample (EP) showed a gradual deterioration of physical properties under thermal hydrolysis exposure conditions. While it was possible to remove test specimens from the water for examination for the first 4 days, after 7 days of exposure the films had become quite brittle and opaque and difficult to handle. Finally, after 15 days of exposure the sample had fragmented into several pieces and was almost impossible to handle without breaking. DSC examination of the polymer revealed a glass transition temperature of 55°C, which suggested, once again, that molecular rearrangements are occurring within the polymer structure at 60°C which could be responsible for some of the changes being noted, rather than chemical hydrolytic action.

Although the Novon sample (N1) showed little loss in strength as a result of thermal hydrolytic exposure, the sample did show a slight loss in elongation at break indicating some change in the samples. However, with a major endothermic transition at 58°C detectable in the DSC analysis, molecular restructuring rather than thermal degradation could, once again, be the cause of these changes.

Thermal hydrolytic action appeared to have little or no effect upon the physical and mechanical properties of the Ecostar sample (ESI). Although this sample showed a slight decrease in elongation at break within the first 7 days of exposure, the load at break and yield values remained virtually unchanged for the full 30 days of exposure.

The Bio-Solo samples (BS1 and BS2) appeared to be unaffected by the thermal hydrolytic exposure, retaining most of their physical characteristics and strength throughout the whole 30-day test period. However, the BS1 sample did show a slight loss in elongation at break after 7 days of exposure, although the break load and yield values remained virtually unaltered.

The behavior of the three Enviro samples, EV1, EV2, and EV3, proved rather interesting. Sample EV3 appeared to be unaffected by the thermal hydrolytic treatment for the full 30 days of exposure. Samples EV1 and EV2, meanwhile, appeared to retain their strength for the first 10 to 15 days of exposure but then degraded rapidly, such that the samples removed after 30 days were very fragile and broke into small fragments on removal from the exposure environment.

Thermal analysis of all the polyethylene samples with additive packages (i.e., BS1, BS2, EV1, EV2, and EV3) revealed the absence of any major thermal transitions, and their DSC traces were similar to that observed for the control sample C1. Therefore, it may be concluded that the changes noted with samples EV1 and EV2 are more than likely associated with chemical degradation processes.

Thermal Oxidative Data

The results of the thermal oxidative degradation study are summarized in Table VIII and Figs. 4 to 12.

Once again, because of the temperature employed in the test, the Tone sample (T1) melted and contracted into a small ball within the first 24 h of exposure in the oven. The Mater-Bi (MB2) and the polylactic acid (EP) samples also were seriously affected as a result of heating in air at 60°C in a manner similar to that noted in the thermal hydrolytic experiments (i.e., they rapidly lost strength and became too brittle to measure any mechanical properties). For example, the Eco-Pla polylactic acid sample (EP) exhibited a deterioration in me-

Table VIII. Mass Loss of Samples (%) on Exposure to Thermal Oxidative Conditions (60°C) for Various Time Periods[a]

	Exposure time (days)						
Sample	1	2	4	7	10	15	30
T1	100	100	100	100	100	100	100
MB1	3.8	6.8	7.9	9.0	0.5		40
MB2	(1.6)	2.5	4.4	8.9	2.4	1.9	2.7
EP	0.1	0.4	0.6	0.7	7.5	2.6	14.3
N1	3.3	5.6	1.1	8.1	28.3	2.8	7.2
ES1	(0.2)	0.1	(2.5)	(0.2)	(1.1)	(1.3)	(2.3)
BS1	1.9	1.3	(0.1)	(1.2)	4.9	2.7	3.8
BS2	0	(0.4)	(0.3)	(1.6)	(0.4)	0.8	1.7
EV1	0.4	(1.8)	(3.3)	5.9	8.6	11.7	11.5
EV2	0	(0.5)	0	(0.1)	4.0	23.9	2.1
EV3	0	0	(0.3)	(3.6)	(2.9)	(1.4)	4.3
C1	0.1	(0.5)	0.1	0.1	0.1	0.1	0

[a] Values in parentheses denote mass gains.

chanical strength that appears to be consistent more with molecular rearrangement occurring at the 60°C exposure temperature than with actual chemical degradation. The Mater-Bi sample (MB1), meanwhile, did retain sufficient strength to permit the measurement of mechanical properties. However, the measured loss in elongation at break, load at break, and yield strength mirrored very closely the observations noted with the hydrolytic experiments. In a similar manner the Novon sample (N1) mirrored very closely the behavior in the wet atmosphere. These similarities in behavior of the above polymers in both the wet and the dry atmospheres, coupled with their known sensitivity to structural reorganization at temperatures below or close to 60°C, suggest that these changes in mechanical properties are more than likely physical than chemical.

In the case of the polyethylene-modified polymers, however, some very interesting and consistent changes were noted in comparing the behavior in a wet and a dry environment at 60°C. For example, while little change was noted in the mechanical strength of the Ecostar sample (ES1) in a wet environment, when the testing was conducted in a dry oxidative environment the material rapidly loss its strength and, after 12 days of exposure, had completely lost its percent elongation.

The behavior of the two Bio-Solo samples (BS1 and BS2) in the two environments were similar except that the changes were more rapid in air than in water, losing their strength within the first 4 days of exposure.

The other three samples from EPI, namely, EV1, EV2, and EV3, behaved in an almost-identical manner, in both environments, with all three samples showing a rapid loss in elongation, break load, and yield strength within the first 4–7 days.

Although not confirmed, it also appears that there are slight weight gains with many of the polyethylene-based polymers in the initial stages of exposure. This observation would be consistent with the formation of oxidative products which act as precursors to subsequent oxidative chain scission process.

CONCLUSIONS

The results of this degradation study are summarized in Table IX using a general ranking scheme. However, when examining the data presented in this table, one has to remember the thermal characteristics of the polymers as measured by DSC.

Table IX. Summary of the Degradation Study

	Change noted in environmental exposure[a]		
Sample	Compost	Thermal hydrolytic	Thermal oxidative
T1	++	++	++
MB1	++	+	+
MB2	++	++	++
EP	++	++	++
N1	++	+	+
ES1	0	0	+
BS1	0	+	++
BS2	0	0	++
EV1	0	++	++
EV2	0	++	++
EV3	0	0	++
C1	0	0	0

[a] (++) major; (+) minor; (0) none.

It appears that the tested polymer samples T1, MB1, MB2, EP, and N1 undergo physical microstructural changes when heated at temperatures between 45 and 60°C, as shown by DSC. Consequently exposure in all of the test environments used in this study, in which temperatures of 60°C were attained, is liable to cause changes in the structure of these polymers and influence the mechanical properties of the material. In the case of the samples T1, MB2, and EP, these changes were sufficiently large as to make the polymer films unsuitable for mechanical evaluations. In the case of the Novon (N1) and the Mater-Bi (MB1) samples, however, although thermally induced physical changes were noted, exposure to the biological activity of a composting environment clearly results in additional loss in the mechanical properties of these two polymers.

The polyethylene-based samples ES, BS1, BS2, EV1, EV2, and EV3, meanwhile, appear to show no signs of appreciable degradation in the laboratory composting environment. However, thermal exposure in an oxidative environment at 60°C results in a rapid loss of mechanical properties for all systems. In the case of the thermal hydrolytic conditions, however, only BS1, EV1, and EV2 show any measurable changes, and these changes are not as large as those noted under dry thermal exposure conditions. Clearly, free access of oxygen and a steady temperature of 60°C are required for the rapid degradation of these polymers. Even the protective covering of water appears to be responsible for a retardation of the degradative process. Meanwhile, the lack of changes in the composting environment are more than likely due to the limited time of exposure to temperatures in excess of 60°C (see Fig. 2).

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