

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Laboratory-Scale Composting Test Methods to Determine Polymer Biodegradability: Model Studies on Cellulose Acetate

Richard A. Gross^a; Ji-dong Gu^{ab}; David Eberiel^c; Stephen P. McCarthy^d

^a Department of Chemistry, ^b Laboratory of Microbial Ecology, Division of Applied Sciences, Cambridge, Massachusetts ^c Department of Biology, ^d Department of Plastics Engineering, NSF Biodegradable Polymer Research Center University of Massachusetts Lowell One University Avenue, Lowell, Massachusetts

To cite this Article Gross, Richard A. , Gu, Ji-dong , Eberiel, David and McCarthy, Stephen P.(1995) 'Laboratory-Scale Composting Test Methods to Determine Polymer Biodegradability: Model Studies on Cellulose Acetate', *Journal of Macromolecular Science, Part A*, 32: 4, 613 – 628

To link to this Article: DOI: 10.1080/10601329508010275

URL: <http://dx.doi.org/10.1080/10601329508010275>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LABORATORY-SCALE COMPOSTING TEST METHODS TO DETERMINE POLYMER BIODEGRADABILITY: MODEL STUDIES ON CELLULOSE ACETATE

RICHARD A. GROSS* and JI-DONG GU†

Department of Chemistry

DAVID EBERIEL

Department of Biology

STEPHEN P. McCARTHY:

Department of Plastics Engineering

NSF Biodegradable Polymer Research Center
University of Massachusetts Lowell
One University Avenue, Lowell, Massachusetts 01854

ABSTRACT

Studies have been conducted to determine the time dependence of film normalized weight loss using in-laboratory simulations of a compost environment. The composting bioreactors contained a fresh synthetic waste mixture formulation which was maintained at 53°C and 60% moisture. An important result from these studies is that cellulose acetate (CA) films (approximate film thickness of between 0.025 and 0.051 mm) with degrees of substitution (DS) of 1.7 and 2.5 appeared completely disintegrated after 7 and 18 day exposure periods, respectively. Little weight loss of these films was noted under similar temperature and

†Present address: Laboratory of Microbial Ecology, Division of Applied Sciences, 40 Oxford Street, Harvard University, Cambridge, Massachusetts 02138.

moisture conditions using abiotic controls. The testing protocol which was developed provided repeatable results on normalized film weight loss measurements. The dependence of the synthetic waste formulation used on polymer film weight loss was investigated using, primarily, CA DS-1.7 as a substrate. It was found that the time dependence of CA DS-1.7 film weight loss was virtually unchanged for five of the seven formulations investigated. However, two formulations studied resulted in relatively slower CA DS-1.7 film weight loss. Decreasing moisture contents of the compost from 60 to 50 and 40% resulted in dramatic changes in polymer degradation such that CA DS-1.7 polymer films showed an increase of the time period for a complete disappearance from 6 to 16 and 30 days, respectively. Also, a respirometric test method is described which utilizes predigested compost as a matrix material to support biological activity. Using this method, conversions to greater than 70% of the theoretical recovered CO₂ for CA (1.7 and 2.5 DS) substrates were measured. Therefore, these results indicate high degrees of mineralization for CA with DS \leq 2.5 under the appropriate disposal conditions.

INTRODUCTION

There is an increased recognition that biodegradable plastics can serve an important role in the design of an intelligent, integrated, solid waste disposal scheme [1-3]. The concept is elegant, achievable in principle, and environmentally appealing. Biodegradable disposable-plastic articles can be designed such that they will be entirely converted by microbial activity in a biologically active environment to biogas (CO₂ and CH₄/CO₂ under aerobic and anaerobic conditions, respectively), biomass, and biological by-products. This process, which is also called mineralization, should be considered as a biologically mediated recycling of plastic articles.

Composting of organic wastes has been recognized as an important technology that produces organic humus materials. This compost product can be marketed and used successfully for the reclamation of mined soil, highway construction, home use, and cover for landfills [4-7]. Important work has been conducted in obtaining an understanding of the microbiological, physical, as well as chemical changes in compost environments both in the laboratory [8-16] and from outdoor studies [6, 17-23]. The composting principle has expanded into pesticides and hazardous chemicals management [24, 25]. In addition, the CO₂ evolution resulting from the microbial degradation of a chemical organic compound is used by the US Food and Drug Administration for regulatory purposes [26]. Since composting of organic solid wastes has excellent potential for future growth as a component in the solid waste solution, it then becomes desirable to obtain rates both for the loss in physical integrity (termed biodestructability herein, often measured in weight loss) and mineralization of both disposed plastic articles and water-soluble polymers.

The study of polymer degradability using in-laboratory accelerated test methods which are designed to simulate actual disposal conditions is an approach currently under development by us and others. Laboratory-scale testing methods suitably address many concerns with the use of outdoor test exposures where only limited control is possible of the environmental conditions used during testing [27-30].

The question that must be answered when in-laboratory simulation test methods are used is to what degree of certainty do they predict polymer degradability in actual disposal sites. Furthermore, some investigators who have adopted this approach for plastic degradation testing use materials to create the waste matrix supporting biodegradability that are not well defined, difficult to obtain by other laboratories, and by their very nature highly variable [31, 32]. Work described herein begins to probe the importance of environmental parameters such as the use of synthetic waste mixtures of variable nutrient content as well as the effects caused by the compost percent moisture on polymer biodegradability. It is expected that through such work and the development of appropriate mathematical models it will eventually be possible to correlate results obtained from in-laboratory testing to expected rates of degradation of plastics in variable outdoor compost sites.

In this paper, laboratory-scale composting test methods to determine the weight loss of plastic articles as well as the percent conversion of polymer carbon to CO_2 are presented. In addition, studies were carried out to determine the influence of the compost mixture composition and percent moisture on the rate of film degradation. For the purpose of this paper, the results presented are limited to those obtained using films of cellophane and cellulose acetate (CA) with degrees of substitution (DS) of 1.7 and 2.5.

MATERIALS AND METHODS

Materials Used, Film Preparation, and Characterization

CA DS-1.7 pellets and DS-2.5 powder with no additives were provided by the Eastman Kodak Company (Kingsport, Tennessee). The polymers, as received, had weight-average molecular weights (\bar{M}_w) and dispersities (\bar{M}_w /number-average molecular weight, \bar{M}_n) of 200,000 and 350,000 g/mol, respectively, and 1.7 and 1.8, respectively. As was previously described [9, 11], the molecular weight and dispersity values were determined by GPC relative to polystyrene standards, and the degree of substitution specified by the manufacturer was confirmed by $^1\text{H-NMR}$ measurements. CA films were made by solution casting onto Teflon from either acetone- H_2O (1:1 ratio, v/v; 17% CA DS-1.7, w/v) or acetone (15% CA DS-2.5, w/v). The film thickness values for CA DS-1.7 and DS-2.5 were ~ 0.013 to ~ 0.025 and ~ 0.051 mm, respectively, unless otherwise specified. These films were aged for a minimum of approximately 2 weeks prior to use. Cellophane film, noncoated, with a thickness of approximately 0.041 mm, was obtained from E. I. du Pont de Nemours & Company (Wilmington, Delaware). The films were cut into dimensions of 20×20 mm, dried in a vacuum oven at 30°C (10 mmHg) to constant weight, the weight was recorded, and the films were exposed to the test environments.

Laboratory-Scale Aerobic Composting Using Fresh Waste Mixtures to Study Plastic Degradation

General Methodology

A simulated *in-laboratory* compost procedure has been developed and used to study the degradability of shaped polymeric materials [9–11]. In this procedure, synthetic municipal solid waste formulations were used (see below and Table 1) that

TABLE 1. Contents of Synthetic MSW Formulations Used to Carry Out Laboratory-Scale Compost Degradation Testing

Name of components	Compost mix formulation ^a						
	Mix 1	Mix 2	A	B	C	D	E
Tree leaves ^b	45.0	47.0					
Shredded paper ^c	16.5	17.0	17.0	33.0	33.0	33.0	33.0
Food waste	6.7	7.0	7.0				
Meat waste	5.8	6.0	6.0				
Cow manure ^d	17.5	18.0	18.0	15.0	15.0		10.0
Saw dust	1.9	2.0	2.0				
Aluminum and steel shavings	2.4						
Glass beads	1.3						
Urea	1.9	2.0	2.0				3.0
Steam-exploded wood			47.0	33.0	33.0	33.0	33.0
Dried timothy				18.0			
Dried alfalfa					18.0		
Rabbit choice						33.0	
Starch							20.0
Compost inoculum	1.0	1.0	1.0	1.0	1.0	1.0	1.0
C/N ratio	14.0	13.9	21.2	61.4	38.2	49.9	24.7

^aAll numbers are weight percentage values.

^bShredded maple and oak leaves at 1:1 ratio.

^cShredded news and computer papers at 1:1 ratio.

^dDehydrated cow manure.

contain important components present in the municipal solid waste stream [12a]. An experimental study for a specific polymer or composting condition was carried out in triplicate in bioreactors along with a poisoned control test vessel. The control vessel was poisoned after autoclaving by the addition of KCN. Triplicate plastic samples were removed from each composting bioreactor at the desired sampling times. In some cases specified below, the results from two and three experimental runs were used to determine weight loss values and the standard deviation. All bioreactors were maintained at 53°C, 60% moisture content, and aerated at 100 mL/min. Abiotic reactors were used to assess whether chemical degradation of the polymeric materials occurs under the test conditions. A detailed description of the bioreactor configuration and the operational procedure have been published elsewhere [9, 10]. During the degradation testing, residual polymer films were recovered from the composting and abiotic test vessels at desired sampling time intervals. The recovered materials were cleaned by immersing in deionized water to remove the coarse particles on the film surface followed by gentle blotting with 70% isopropyl alcohol moistened Kimwipes EX-L (Kimberly-Clark, Fisher Scientific, Pennsylvania). The weight of residual film material was measured after the films were dried in a vacuum oven at 30°C (10 mmHg) to constant weight. Results of polymer film weight loss at a sampling time were expressed as the difference in

weight between initial and sampling, normalized to the total surface area (two exposure sides for each film, units of $\mu\text{g} \cdot \text{mm}^{-2}$).

Synthetic Compost Mixture Formulation

Synthetic MSW (municipal solid waste) composting mixtures were made from various materials available naturally or commercially, and all materials were used without any treatment unless otherwise specified [12a]. All compost formulations used in this work are presented in Table 1. Tree leaves (approximately 1:1 ratio of oak and maple) collected in the fall of 1992 were air-dried and then stored at 4°C for later use. Shredded paper was a mix of computer paper with newspaper in a ratio of 1:1 (dimensions 2 mm × 25 mm). The food waste used, which contained 3.2% protein and 13.8% carbohydrates, was a commercially available mixture of frozen vegetables including carrots, green beans, green peas, corn, and lima beans. This vegetable mixture was kept frozen and thawed prior to use. The meat waste was simulated by mixing dog and cat food in a 1:1 ratio (w/w). The major source of sawdust was from maple wood. Steam-exploded wood was generated at $\log R_0 = 3.7$, 202°C for 5.0 minutes on a mixture of maple and oak wood chips (Biobased Materials Research Center, Virginia Tech.). Dehydrated cow manure which contained a total nitrogen content of 2.0% (w/w) was from Earthgro, Inc. (Lebanon, Connecticut). Other materials used in this study included glass beads (2.0 mm in diameter, Fisher Scientific), urea (laboratory grade, Fisher Scientific), corn starch (Sigma), and Recycle compost inoculum (Ringer Compost Seeds, Minneapolis, Minnesota). The sources and nutritional content (as specified by the manufacturer) for Rabbit Choice, timothy and alfalfa, cat food, and dog food were obtained from BigRed (Syracuse, New York), Hay-Kob (L/M Animal Farms, Pleasant Plain, Ohio), Alpo (Lehigh Valley, Pennsylvania), and Cycle (The Quaker Oats Co., Chicago, Illinois), respectively.

Studies on the Percent Moisture in Composting Bioreactors [12a]

During simulation of different moisture conditions, the initial percent water content was obtained by first determining the percent water in the solid waste mixture by oven drying a sample at 105°C to constant weight (normally approximately 16 hours). Once the percent water in the solid waste mixtures were known, the mixtures were then amended with the required additional water so that 40, 50, and 60% (w/w) moisture values were obtained. Subsequently, moisture in the compost bioreactors was monitored by sampling the test solid waste mixtures at regular time intervals. Observed moisture losses were corrected by simply adding the required quantity of deionized water. In no case was it found that the percent moisture in the compost reactors increased during the composting test.

Elemental Analyses. Carbon and nitrogen elemental analyses on compost formulations were carried out by Atlantic Microlab, Inc. (Norcross, Georgia).

Respirometric Method to Measure Mineralization of Polymeric Materials in a Compost Environment [12b]

Respirometry Setup

The respirometric system used in assessing the mineralization of polymer carbon to CO₂ consisted of an air pump which served as an air source; an air pretreat-

ment system to sterilize, remove CO₂, and control the flow rate; test vessels which contained predigested compost; and posttest vessel trapping of the CO₂ produced. The predigested compost was obtained by a 42-day maturation period of a defined synthetic waste mixture described in Ref. 12b. The waste mixture used was similar in composition to that of Formulation 2 given in Table 1. The matured or predigested compost supplied the indigenous microbial population and also served as a physiological and nutritional support. For each polymer sample analyzed, a total of six vessels were set up where three vessels were amended with 1.0 g of the polymer powder (particle size was between 300 and 400 μm using mesh screens) and the other three served as background controls to measure the basal CO₂ production from the indigenous microbial population. The test vessels were maintained at 53°C and 60% moisture throughout the analysis. The difference in CO₂ production between the test vessels with and without the polymer sample was attributed to the degradation of the polymer sample. Produced CO₂ was trapped by reaction with a NaOH solution. The amount of NaOH left unreacted was quantitated by titration with HCl to pH 9.0 using a Mettler DL 12 (Mettler Instrument Co., Highstown, New Jersey). A more detailed description of the methodology has been published elsewhere [12b].

RESULTS AND DISCUSSION

Laboratory-Scale Aerobic Composting Using Fresh Waste Mixtures to Study Plastic Degradation

Normalization of Polymer Film Weight Using the Initial Film Surface Area

The weight loss values for the exposed CA and cellophane films are reported normalized to the exposed initial surface area (including both sides of a film). In other words, the film weight loss values were calculated by measuring the gravimetric weight loss and dividing this by the initial film surface area (units of $\mu\text{g}/\text{mm}^2$). For a sample density of 1 g/mL, a 12.5- $\mu\text{g}/\text{mm}^2$ normalized film weight loss value corresponds to a loss in film thickness of approximately 0.0254 mm (1 mil). In carrying out this analysis of the film weight loss, it is assumed that the degradation processes involved (such as enzyme-catalyzed chain cleavage and subsequent dissolution of degradation products) occurs exclusively at the surface of the films and that the normalized weight loss value is independent of film thickness. This method was chosen in place of percent weight loss of plastic specimens since the latter measure does not take into account the importance of available surface area of exposed samples. However, it must be noted that the assumption that the normalized film weight loss values will be independent of film thickness is an idealized model. Problems such as changes in the film surface area due to film pitting and erosion as a function of time as well as the study of plastics that contain water-soluble components that freely diffuse from the specimen into the compost are expected to result in serious deviations from the model presented above.

Cellulose Acetate (CA) Normalized Film Weight Loss Measurements

The normalized weight loss values for CA DS-1.7 and cellophane films (film thickness values of ~ 0.025 and ~ 0.041 mm, respectively) are shown in Fig. 1. Compost Formulation 2 was used for this study. About 35% of the film weight loss

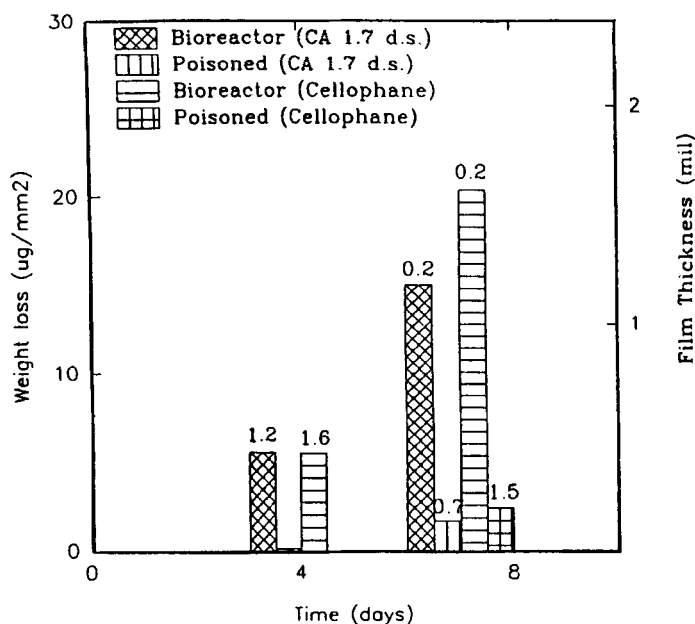


FIG. 1. Normalized weight loss of CA DS-1.7 and cellophane films in Formulation 2. The standard deviation values are given above the bars.

for the two sample types was observed on Day 4 in the biologically active bioreactors, while there was almost no change for the films in the poisoned reactor. Both samples had completely disintegrated at the end of a 7-day exposure period and were no longer recoverable. Similar film weight loss values for 7-day exposure periods were observed for biologically-active test vessels which contained Formulation A (see below and Table 1). In contrast, the samples exposed in the poisoned control vessels (see Materials and Methods Section) showed comparatively small weight loss values (see Fig. 1). Therefore, the disappearance of these materials over the 7-day exposure period was due in large part to biologically-mediated processes.

CA of relatively higher DS was exposed to the compost bioreactors containing Formulation 1 (see Table 1). The weight loss of CA DS-2.5 films (film thickness, ~ 0.05 mm) was observed periodically over an 18-day exposure period (see Fig. 2). By the end of the 18-day exposure period, the weight loss was $23.5 \pm 2 \mu\text{g}/\text{mm}^2$, which corresponded to essentially complete disappearance of the polymer films. In the poisoned reactors, CA DS-2.5 films showed negligible weight loss over an 18-day exposure period. Once again, by comparison of the biologically-active and poisoned reactor results, it is concluded that the disappearance of CA DS-2.5 is due in large part to biologically-mediated processes. In addition, as would be expected, the CA DS-1.7 films showed much more rapid degradation kinetics relative to the 2.5-DS film samples.

Changes in the dry weight and pH of the compost as a function of time have been reported by us elsewhere [9]. Furthermore, residual CA polymers after various composting exposure periods have been characterized for changes in molecular

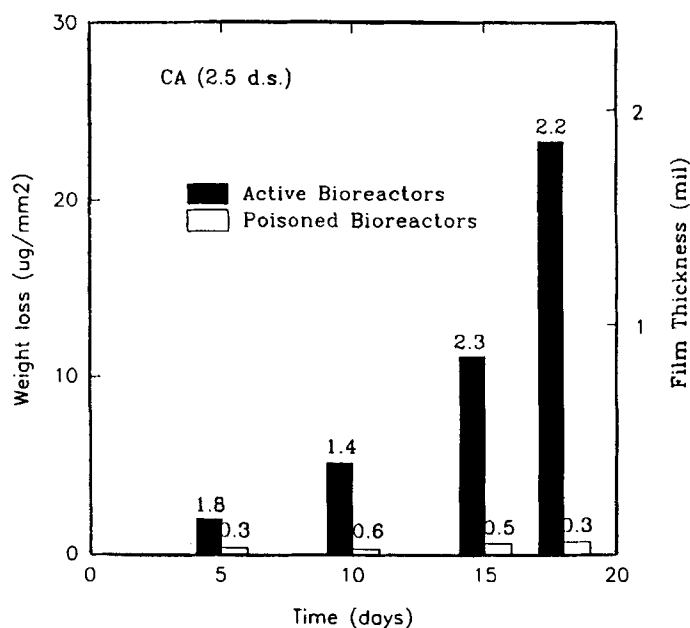


FIG. 2. Normalized weight loss of CA DS-2.5 films in Formulation 1. The standard deviation values from one experiment (triplicate in bioreactors) are given above the bars.

weight and DS [11]. Colonization and degradation at the surface of exposed CA Samples was studied by SEM [11].

Effect of Compost Mixture Composition on Polymer Film Weight Loss. Synthetic MSW mixtures were prepared using different component materials (see Table 1). Primarily CA DS-1.7 films and, in some cases, cellophane films were chosen as the polymer candidates for testing. The only difference between Formulations 1 and 2 is that the latter does not include glass beads, aluminum, and steel shavings (Table 1). Both mixes have almost identical C/N ratios (14.0 and 13.9, respectively). The extent of film weight loss as a function of the exposure time for CA DS-1.7 and cellophane films were compared for exposures to laboratory-scale reactors containing Formulations 1 and 2. Figure 3 shows that the weight loss of both film types exposed to composting reactors containing either Mixture 1 or 2 were virtually identical. Also, the time for complete film disappearance in these mixes was ~7 days for both film types.

Figure 4 shows the weight loss as a function of exposure time for CA DS-1.7 film exposed to other compost formulations. Mixture A is identical to Mixture 2 with the exception that steam-exploded wood was substituted for tree leaves in the formulation. The substitution of steam-exploded wood had no apparent effect on the time required for CA DS-1.7 film weight loss and subsequent disappearance (~7 days) although the C/N was 21.2, which is higher than Mix 2. This general

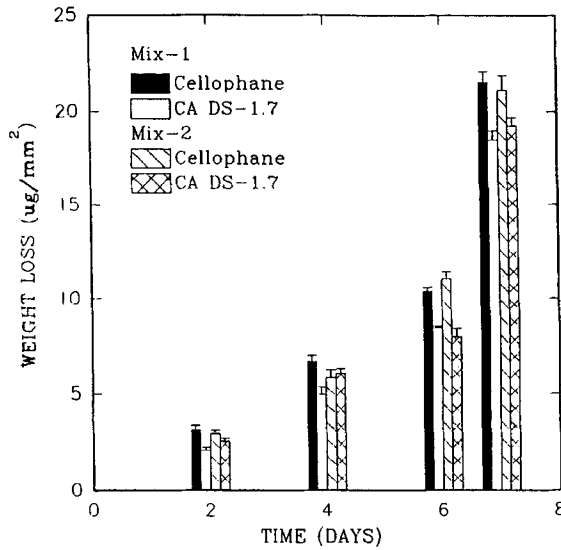


FIG. 3. Normalized weight loss of CA DS-1.7 and cellophane films in Compost Mixes 1 and 2. Vertical lines above the bars indicate the standard deviation values of three experiments.

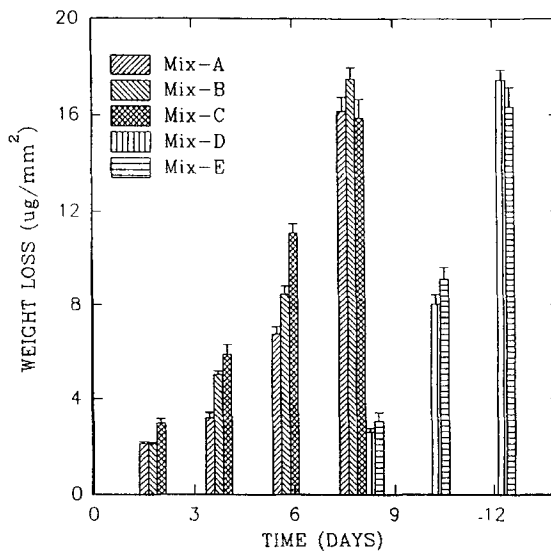


FIG. 4. Normalized weight loss of CA DS-1.7 films in bioreactors containing mixes A, B, C, D, and E. The vertical lines above the bars indicate the standard deviation values of two experiments.

lack of dependence of the mixture composition on the time required for CA DS-1.7 film weight loss and subsequent disappearance was also observed for Mixtures B and C relative to Mixtures 1, 2, and A (see Figs. 3 and 4 and Table 1). Mixtures B and C replace food and meat wastes, sawdust, and urea with the materials dried timothy and alfalfa, respectively. The nutritional contents for Mixtures B and C components timothy and alfalfa are shown elsewhere [12a]. The C/N ratio was 61.4 and 31.2 for Mixtures B and C, respectively. The artificial waste Mixtures B and C are exciting alternatives since they contain component materials that are readily available from commercial sources having consistent nutritional contents. These formulations offer the opportunity to carry out laboratory-scale compost testing with excellent run-to-run and laboratory-to-laboratory reproducibility.

Further study of the effects of mix composition on CA DS-1.7 film weight loss was carried out by investigation of Formulations D and E as synthetic waste recipes for laboratory-scale composting. Formulation D was obtained from C by the omission of cow manure and dried alfalfa and addition of rabbit choice. Formulation of mixture E was obtained from C by the omission of dried alfalfa and the addition of starch and urea (see Table 1). The C/N ratio of Formulations D and E are 49.9 and 24.7, respectively. Interestingly, the exposure time required for CA DS-1.7 film weight loss and subsequent film disappearance in the biological active reactors containing Formulations D and E was extended to 12 days relative to 7 days as was observed for Mixtures 1, 2, A, B, and C (see Figs. 3 and 4). This variation of time required for CA DS-1.7 film weight loss may be due to the differences in physical form and nutritional contents of Formulations D and E [14]. The relatively slower film weight loss in Formulations D and E cannot simply be attributed to the mixture C/N values since the values for C/N for these mixtures were within the upper (61.4, Mix B) and lower (13.9, Mix 2) C/N values of the other formulations studied. It should be pointed out that in control poisoned reactors (see Materials and Methods Section) constructed using all of the formulations described in Table 1, no significant weight loss of either CA DS-1.7 or cellophane polymer films was observed for up to 12-days exposures. Therefore, the observed film weight loss must at least in part be attributed to biomediated processes.

As expected, the results above provide evidence that the rate of film weight loss is dependent on the compost formulation. However, the similarity of film weight loss rates between Mixes 1, 2, A, B, and C was surprising. It should be noted that a biodegradable polymer film placed in a compost reactor is simply an alternative carbon source for microorganisms which are present in the composting reactor. The rate of biodegradation of the exposed polymer relative to the utilization of other nutrients in the mixture will, of course, be dependent on whether the polymer serves as a preferred carbon source. It may be speculated that exposure of another polymer type which has a significantly different nutrient value to compost microorganisms than CA DS-1.7 might show a much larger variance in film weight loss rates as a function of the compost formulation used. The fact that CA DS-1.7 showed rapid film weight loss rates in all of the mixtures studied serves as important evidence that CA DS-1.7 is in fact a readily biodegradable polymer that is utilized competitively with other compost nutrients. This is further supported by the similarity of the time dependence of film weight loss for CA DS-1.7 and cellophane films exposed to Formulations 1 and 2.

Effect of Compost Moisture Content on Polymer Film Degradation

Compost Mixture 2 (see Table 1) was chosen for analysis of the effect of compost moisture content on the rate of polymer film degradation. In this study, all other environmental parameters in the laboratory-scale composting experiment, such as the rate of aeration, C/N ratio, and the incubation temperature (see Materials and Methods Section and Refs. 9–11), were kept constant. It was determined that for moisture contents of 60, 50, and 40% the time for complete CA DS-1.7 and cellophane (data not shown) film disappearance was 6, 16, and 30 days, respectively (Fig. 5). During the same period of time, films in the control reactors showed little to no weight loss (< 5%) due to chemical or physical erosion. Therefore, the rate of film weight loss is extremely sensitive to the compost percent moisture. This is consistent with the fact that the availability of water is a critical factor dictating microbial viability and metabolic activity [13].

Mineralization of Cellulose Acetates

Mineralization of a polymeric material by microorganisms under aerobic conditions produces CO_2 , H_2O , microbial biomass, and humus. Therefore, a respirometric technique was used to quantitate the evolved CO_2 due to polymer biodegradation. The method was summarized above (see Respirometry Setup Section) and was described in detail elsewhere [12b]. The low basal level of CO_2 production in test vessels which did not contain the polymer substrate (approximately 12–15 mg $\text{CO}_2\text{-C}$ per day) was found to be linear as a function of time [11, 12b] and was

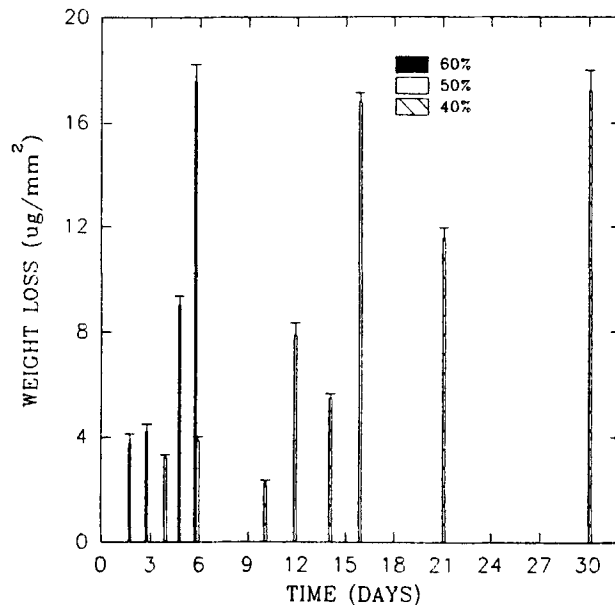


FIG. 5. Normalized weight loss of CA DS-1.7 films as a function of exposure time in laboratory-scale compost reactors at moisture contents of 60, 50, and 40%. The vertical lines above the bars indicate the standard deviation values of three experiments.

subtracted from that produced in polymer-amended vessels to obtain the total CO_2 and the corresponding percentage of the theoretical CO_2 formed as a result of substrate mineralization (see Figs. 6 and 7). Observation of Fig. 6 shows that exposure of CA DS-1.7 to the predigested compost matrix produced 72.4% of its theoretical carbon as CO_2 after a total incubation period of 24 days. In comparison, the total time required for CA DS-2.5 to reach the plateau value of 77.6% substrate carbon conversion to CO_2 was 60 days (see Fig. 7). Of additional interest, the rate of CA DS-1.7 mineralization increased rapidly after only a 10-day lag period whereas the lag period prior to rapid CA DS-2.5 mineralization was considerably longer (approximately 25 days). In agreement with these results, both the lag period prior to film weight loss and the total time for film disappearance were notably longer for CA DS-2.5 relatively to CA DS-1.7 (see Ref. 9 and above). Indeed, when one considers probable mechanisms for CA biodegradability (see below), it is not at all surprising that CA of relatively higher DS shows relatively slower rates of biodegradation. However, most importantly, the results shown in Fig. 7 suggest that CA with a degree of acetylation up to 2.5 is mineralized to a high degree under suitable environmental exposure conditions.

CA Biodegradation Mechanistic Considerations

A hypothesis has previously been presented by us [11] that deacetylase enzymes are required to provide chains or chain segments with DS values of less than approximately 0.7. Once this critical degree of deacetylation is reached, cellulase

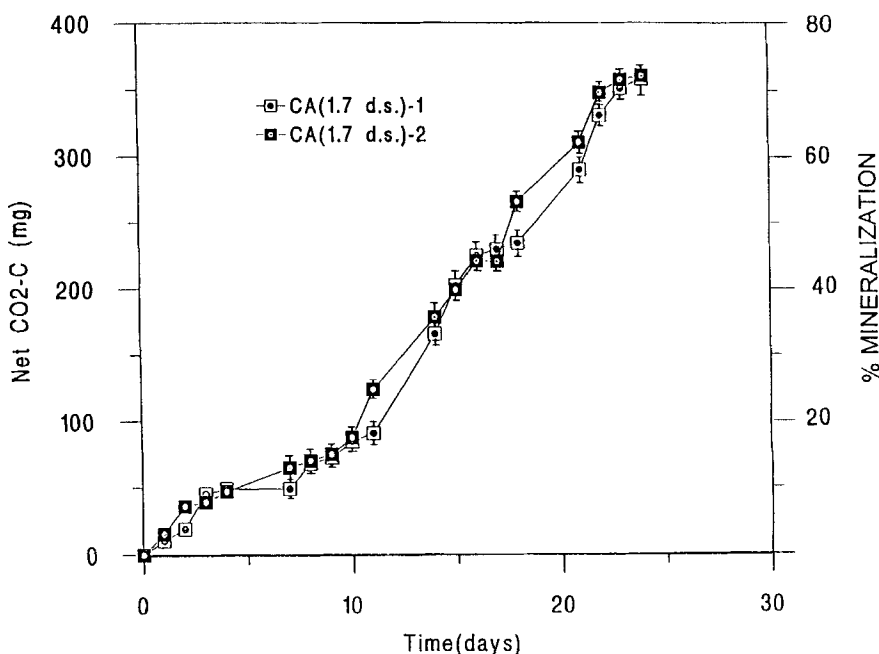


FIG. 6. Respirometric mineralization of powdered cellulose acetate (DS-1.7) in a matured synthetic MSW compost matrix under aerobic thermophilic conditions.

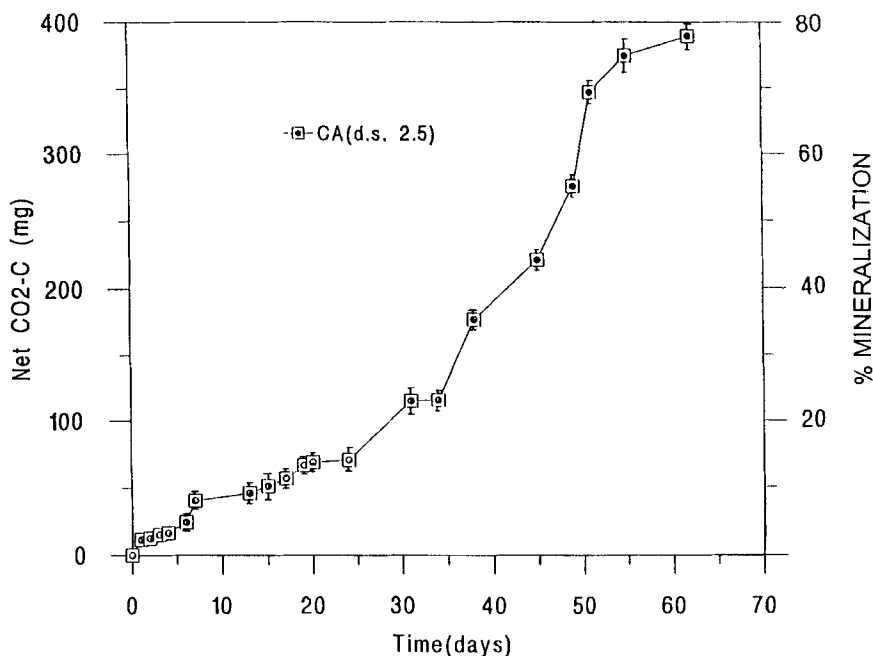


FIG. 7. Respirometric mineralization of powdered cellulose acetate (DS-2.5) in a matured synthetic MSW compost matrix under aerobic thermophilic conditions.

enzymes cause events of chain cleavage which are accelerated by further chain deacetylation. It should be noted that the critical value of deacetylation required for glycosidic bond cleavage by cellulase enzymes has not as yet been firmly established for a range of cellulase enzyme systems.

SUMMARY OF RESULTS

In-laboratory simulation of a synthetic MSW aerobic compost process using fresh synthetic waste formulations was developed and used to study the biodegradability of CA films. The exposure of CA (DS-1.7 and -2.5) and cellophane films to biologically-active and poisoned in-laboratory composting test vessels clearly demonstrated that these materials were biodegradable under controlled composting conditions. In other words, the film weight loss observed resulted, at least in part, from biologically-mediated processes.

The conversion of CA DS-1.7 and DS-2.5 to CO₂ was monitored by respirometry where powdered CA was placed in a predigested compost matrix. A lag phase of 10- and 25-day duration for CA DS-1.7 and -2.5, respectively, was observed after which the rate of degradation increased rapidly. Mineralization of exposed CA DS-1.7 and -2.5 powders reported as the percent theoretical CO₂ recovered reached 72.4 and 77.6% in 24 and 60 days, respectively. The results of this study demonstrated that microbial degradation of CA films exposed to aerobic thermophilic

simulated composting conditions not only results in film weight loss but also conversions to greater than 70% of the theoretical recovered CO₂ for CA (1.7 and 2.5 DS) substrates. Thus, it appears that CA with DS \leq 2.5 can undergo high extents of mineralization when exposed to the appropriate disposal conditions.

Alternative synthetic compost mixture formulations for laboratory-scale degradation testing were investigated. It was found that rapid CA DS-1.7 film weight loss and ultimate film disappearance was achieved with a variety of compost formulations. In two of the seven compost mixture formulations investigated, the extent of CA DS-1.7 film weight loss as a function of time was considerably slower. Thus, a dependence of film weight loss on the compost mixture composition was demonstrated. However, the fact that film weight loss occurred to a similar extent as a function of exposure time for five of the seven mixtures studied was surprising and indicates that CA DS-1.7 is a readily utilized carbon source relative to other available organic matter in the compost formulations studied. An important conclusion of this work is that laboratory-scale composting tests can be carried out using readily available commercial materials to construct synthetic MSW mixtures. It is expected that with the adoption of both standard synthetic waste mixtures as well as testing protocols, reproducibility of test results will be extended beyond run-to-run so that reproducibility between laboratories will ultimately be achieved.

Moisture conditions in composting runs was found to have a profound affect on the extent of CA DS-1.7 film weight loss as a function of the exposure time. Thus, the percent moisture is an extremely sensitive compost test parameter that must be carefully controlled to achieve rapid degradation of organic matter as well as reproducible polymer degradation testing results.

ACKNOWLEDGMENTS

We are grateful for the financial support of this research by the NSF Biodegradable Polymer Research Center (BPRC) at the University of Massachusetts Lowell and the Division of Environmental Engineering and Pollution Control, 3M Company.

REFERENCES

- [1] H. Brandl, R. A. Gross, R. W. Lenz, and R. C. Fuller, *Adv. Biochem. Eng.*, **41**, 77-93 (1990).
- [2] D. L. Kaplan, J. M. Mayer, D. Ball, J. McCassie, A. L. Allen, and P. Stenhouse, in *Biodegradable Polymers and Packaging Materials* (C. Ching, D. Kaplan, and E. Thomas, Eds.), Technomic Co., Lancaster, Pennsylvania, 1993, pp. 1-42.
- [3] A. Gibbons, *Technol. Rev.*, **92**, 69-73 (1989).
- [4] J. Glenn and N. Goldstein, *BioCycle*, **33**, 48-52 (1992).
- [5] N. Goldstein and R. Stevteville, *Ibid.*, **33**, 44-47 (1992).
- [6] M. S. Finstein, in *Environmental Microbiology* (R. Mitchell, Ed.), Wiley-Liss, New York, 1992, pp. 355-374.

- [7] R. L. Chaney, in *The BioCycle Guide to the Art and Science of Composting*, JG Press, Emmaus, Pennsylvania, 1991, pp. 240–253.
- [8] J. A. Hogan, F. C. Miller, and M. S. Finstein, *Appl. Environ. Microbiol.*, **55**, 1082–1092 (1989).
- [9] J.-D. Gu, D. Eberiel, S. P. McCarthy, and R. A. Gross, *J. Environ. Polym. Degrad.*, **1**, 143–153 (1993).
- [10] R. A. Gross, J.-D. Gu, D. T. Eberiel, M. Nelson, and S. P. McCarthy, in *Biodegradable Polymers and Packaging Materials* (C. Ching, D. Kaplan, and E. Thomas, Eds.), Technomic Co., Lancaster, Pennsylvania, 1993, pp. 257–279.
- [11] J.-D. Gu, D. Eberiel, S. P. McCarthy, and R. A. Gross, *J. Environ. Polym. Degrad.*, **1**(4), 281–291 (1993).
- [12] (a) J.-D. Gu, S. Yang, R. Welton, D. Eberiel, S. P. McCarthy, and R. A. Gross, *Ibid.*, **2**(2), 129–135 (1994). (b) J.-D. Gu, S. Coulter, D. Eberiel, S. P. McCarthy, and R. A. Gross, “A Respirometric Method to Measure Mineralization of Polymeric Materials in a Matured Compost Environment,” *Ibid.*, In Press.
- [13] F. C. Miller, *Microbiol. Ecol.*, **18**, 59–71 (1989).
- [14] K. Nakasaki, M. Sasaki, M. Shoda, and H. Kubota, *Appl. Environ. Microbiol.*, **49**, 724–726 (1985).
- [15] K. Nakasaki, M. Shoda, and H. Kubota, *J. Ferment. Technol.*, **63**, 537–543 (1985).
- [16] K. Nakasaki, M. Shoda, and H. Kubota, *Ibid.*, **64**, 539–544 (1986).
- [17] P. D. Bach, K. Nakasaki, M. Shoda, and H. Kubota, *Ibid.*, **65**, 199–209 (1987).
- [18] F. C. Miller and M. S. Finstein, *J. Water Pollut. Control Fed.*, **57**, 122–127 (1985).
- [19] M. S. Finstein, F. C. Miller, and P. F. Strom, *Ibid.*, **58**, 272–278 (1986).
- [20] F. C. Miller, S. T. MacGregor, K. M. Psarianos, J. Cirello, and M. S. Finstein, *Ibid.*, **54**, 111–113 (1982).
- [21] S. T. MacGregor, F. C. Miller, K. M. Psarianos, and M. S. Finstein, *Appl. Environ. Microbiol.*, **41**, 1321–1330 (1981).
- [22] P. M. Strom, *Ibid.*, **50**, 899–905 (1985).
- [23] D. F. Gilmore, S. Antoun, R. W. Lenz, S. Goodwin, R. Austin, and R. C. Fuller, *J. Ind. Microbiol.*, **10**, 199–206 (1992).
- [24] A. M. Fogarty and O. H. Tuovinen, *Microbiol. Rev.*, **55**, 225–233 (1991).
- [25] D. R. Reinhart and F. G. Pohland, *J. Ind. Microbiol.*, **8**, 193–200 (1991).
- [26] US Food and Drug Administration, *Environmental Assessment Technical Assistance Handbook PB87-175345*, National Technical Information Service, Washington, D.C., 1987.
- [27] J. M. Mayer, M. Greenberger, D. L. Kaplan, R. A. Gross, and S. P. McCarthy, *Polym. Mater. Sci. Eng.*, **63**, 858–861 (1990).
- [28] J. E. McCassie, J. M. Mayer, R. E. Stote, A. E. Shupe, P. J. Stenhouse, P. A. Dell, and D. L. Kaplan, *Ibid.*, **67**, 353–354 (1992).
- [29] J. M. Mayer and D. Kaplan, in *Biodegradable Polymers and Packaging Materials* (C. Ching, D. Kaplan, and E. Thomas, Eds.), Technomic Co., Lancaster, Pennsylvania, 1993, pp. 233–245.

- [30] J. E. McCassie, J. M. Mayer, R. E. Stote, A. E. Shupe, P. J. Stenhouse, P. A. Dell, and D. L. Kaplan, *Ibid.*, pp. 247–256.
- [31] R. Tillinger, B. De Wilde, and L. De Baere, *Polym. Mater. Sci. Eng.*, 67, 359–360 (1992).
- [32] L. De Baere, in *Biotechnology and Bioengineering Symposium N*, Wiley, New York, 1986, p. 321.