Compostability of Cellulose Acetate Films

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SYNOPSIS

Composting is an accelerated biological decay process viewed by many to be a potential solution to the solid-waste management crisis existing in many parts of the world. As part of a program to develop environmentally nonpersistent polymers that are compatible with a composting environment, we have developed a bench-scale compost methodology that emulates a high efficiency municipal windrow composting operation. A series of cellulose acetate films, differing in degree of substitution, were evaluated in this bench-scale system. In addition, commercially available biodegradable polymers such as poly(hydroxybutyrate-*co*-valerate) (PHBV) and polycaprolactone (PCL) were included as points of reference. Based on film disintegration and on film weight loss, cellulose acetates, having degrees of substitution less than approximately 2.20, compost at rates comparable to that of PHBV. NMR and GPC analyses of composted films indicate that low molecular weight fractions are removed preferentially from the more highly substituted and slower degrading cellulose acetates. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Solid waste management systems have historically relied upon both terrestrial and marine disposal as their main disposal options. However, the emergence of new environmental pressures, often in the form of new legislation, as well as loss of available landfill space and rapidly increasing disposal fees are restricting these once common practices. These combined pressures are forcing municipalities to seek alternative waste disposal strategies. Accelerated composting is among the emerging technologies that are vying to meet the solid waste crisis.

Composting can be defined as an accelerated natural degradation (decay) process that results from putting organic matter into piles or heaps to conserve metabolic heat. Composting entails the biologically mediated aerobic decomposition of organic material to form humus, heat, biomass, CO_2, and water. Humus, one of the major organic components of soil, consists of humic acid, fulvic acid, and humin.[1] To thoroughly understand composting, it is essential to appreciate that it involves the same natural decay processes that occur in soil. When a plant or animal dies, its remains are attacked by soil microorganisms, ultimately reducing the organic matter to an earthlike substance. This natural decay mechanism that takes place in soil should be considered to be synonymous with composting, with the exception that the degradative rates in composting are higher because of the higher temperature. Microbial degradative processes play a vital role in the recycling of nutrients in nature. The magnitude of this recycling is immense; for example, microbial degradation of cellulose plays a significant role in the carbon cycle, returning to the atmosphere an estimated 85 billion metric tons of carbon each year.[2,3] In nature, the decay process normally takes place slowly, on the surface of the ground, and at ambient temperatures. This natural degradation process can be accelerated by gathering the material into heaps or piles to conserve metabolic heat. Conservation of heat allows the temperature of the mass to rise, resulting in higher degradation rates.[4] This key feature of being able to accelerate the natural biological decay mechanism is what makes com-

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posting so amendable to the needs of municipal waste treatment.

Composting is a dynamic process that involves a rapid succession of microbial populations, each being selected by conditions established by the previous microbial population. This natural progression can be conveniently divided into the following four phases that are based upon the compost's temperature profile: a mesophilic phase (initial phase), a thermophilic phase (high temperature phase), a cooling phase, and a maturation phase (Fig. 1). The exact length of each phase depends upon many factors, including the type of solid waste (e.g., mixed municipal waste vs. sludge from a wastewater treatment plant), temperature control mechanism, moisture level, availability of oxygen, pH, and the presence of any toxic or inhibitory compounds. In a well-controlled laboratory scaled compost system

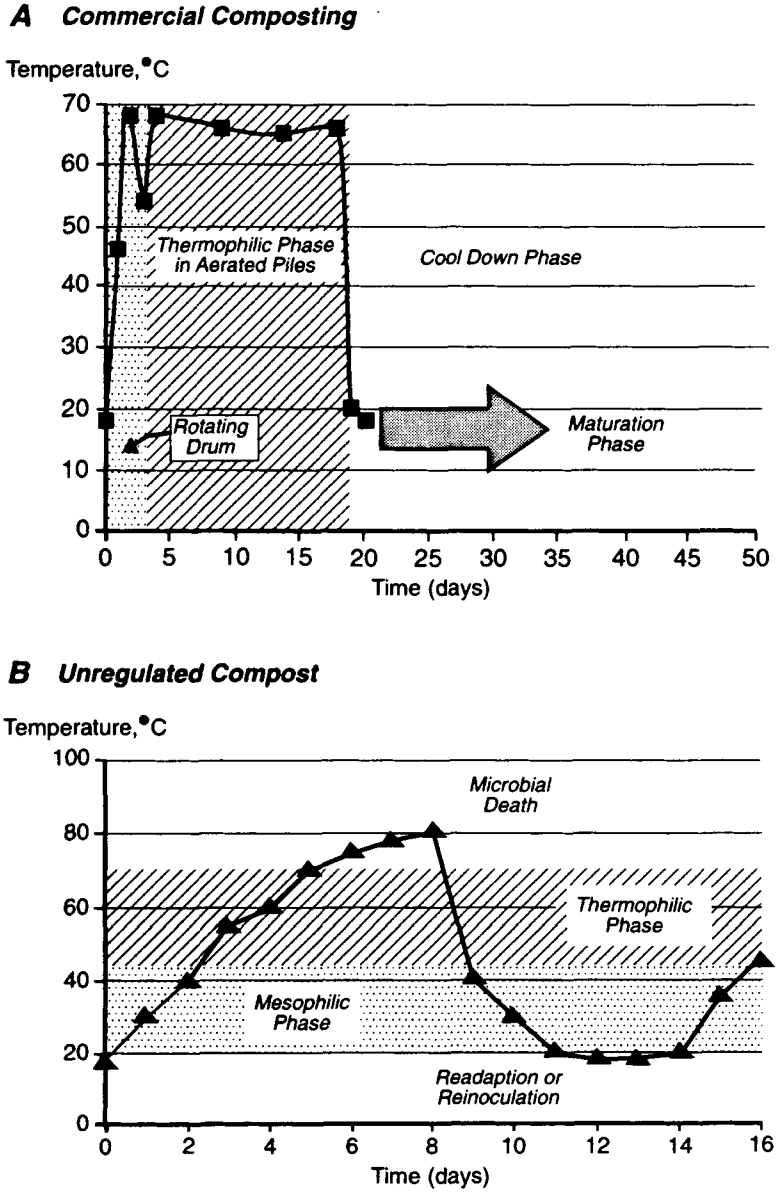

Figure 1 (A) Typical temperature profile for a commercial composting facility equipped with a 3-day rotating drum, followed by 20–30 days in aerated window piles. The length of the maturation phase may vary, as will the temperature, depending upon the desired end use of the compost. (B) Temperature profile of an unregulated compost pile. This is the temperature scenario that most backyard compost piles undergo.

(7000 to 8000 g of starting waste) that does not artificially maintain the thermophilic phase, typically, the initial mesophilic phase will last only 1 to 2 days. This is followed by a steady increase in temperature to the thermophilic phase (45°C to 70°C), which last approximately 5 days. The larger the amount of starting waste, the better the insulation properties, and the longer the thermophilic phase will be maintained. The next phase is characterized by a steady drop in temperature back to ambient conditions; typically taking 10 days or more. The final maturation phase or curing stage continues into 180 days or more, depending on the composition of starting waste and the design of the composting system.

In this account, we describe a bench-scale composting methodology developed in our laboratories and the application of this methodology to a number of commercially available polymers, e.g., poly(hydroxybutyrate) (PHB), that are widely accepted within the polymer community to be biodegradable. We also report the application of this composting methodology to cellulose acetate (CA), which has recently been demonstrated, through radiochemical labeling techniques, to be biodegradable.[5,6]

EXPERIMENTAL

Poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-*co*-valerate) (PHBV, Zeneca Bio-Products), polycaprolactone (PCL, Union Carbide), and Matter-Bi™ (Novamont, Matter-Bi™ is presumably a blend of starch or modified starch and other polymers such as polyvinyl alcohol and polyacrylics[7]) are commercially available polymers. Cellulose triacetate (CTA, DS = 2.97) and cellulose acetate CA398-30 (DS = 2.52) are commercially available and were obtained from Eastman Chemical Company. The remaining cellulose acetates were obtained by aqueous hydrolysis of the CA having a DS of 2.52.[8]

Except where noted, films were prepared by solvent casting. With the exception of CTA, the solvent for cellulose acetate (20% solids) was acetone containing 3–7% water. The solvent for CTA, PHBV, and PCL was $CHCl_3$. The solution was poured onto a metal plate and a draw blade with a 15 mil well was used to give a thin film (typically ca. 0.8–1.5 mil). Because of lack of solubility in appropriate solvents, PHB films (7.8 mil thick) were prepared by compression molding, and Matter-Bi™ film (1.8 mil thick) was prepared by a blown film process.

Each compost unit contained 15 test films and 10 Matter-Bi™ films that served as an internal positive control. Results reported herein are average values for all films in each individual unit. With the exception of PCL, the films were added to the composting unit along with the synthetic compost mixture. Because of the low melting temperature of PCL, the PCL films were not added until completion of the thermophilic phase. PHB, PHBV (90/10), PHBV (78/22), and PCL were evaluated over a 14-day composting period. Five cellulose acetates having a DS of 1.74, 1.86, 2.06, 2.21, and 2.52 were also evaluated over a 14-day composting cycle in a separate trial under the same conditions. In order to further examine the reproducibility between trials, the cellulose acetate with DS 2.52 was later examined again in a 15-day composting period. In order to explore the effect of a longer composting period on cellulose acetates, four cellulose acetates ranging in DS from 2.97 to 1.70 were examined in a 30-day composting cycle.

Compost Mixture

A uniform, reproducible compost was prepared with the following formula: 3500 g of dehydrated alfalfa meal, 1300 g of cottonseed meal, 1400 g of Poplar sawdust, 1000 g of fresh cow manure, 1500 g of black garden soil, 2500 g of finely shredded newspaper, 480 g of $CaCO_3$, 40 g of $NaHCO_3$, and 13 liters of water. This was added to a Hobart Mixer and blended until an average particle size of 3–4 mm was obtained. The carbon-to-nitrogen ratio of this starting mixture was 30 : 1 and the starting pH was 7.2.

Compost Unit Design and Control System

Bench-scale compost units were constructed from 10-$\frac{7}{8}$″ diameter (O.D.) stainless steel piping (Fig. 2). The cylinders were 17″ in height with approximately 2″ of headspace at the top and bottom. A fine mesh stainless steel screen was inserted at the interface between the compost and the headspace to facilitate air diffusion. In addition, the screens also prevented the compost from obstructing the air inlet and outlet ports. The units were sealed with gas tight lids, permitting total gas collection via the vent port, if required. The internal surfaces of the compost unit were fitted with 4 baffles (13″ × 1″), which enhanced the efficiency of mixing. Each cylinder had a thermocouple probe inserted in the bottom third; this was connected to a Yokogawa temperature monitor which recorded the continuous temperature output of each individual compost unit

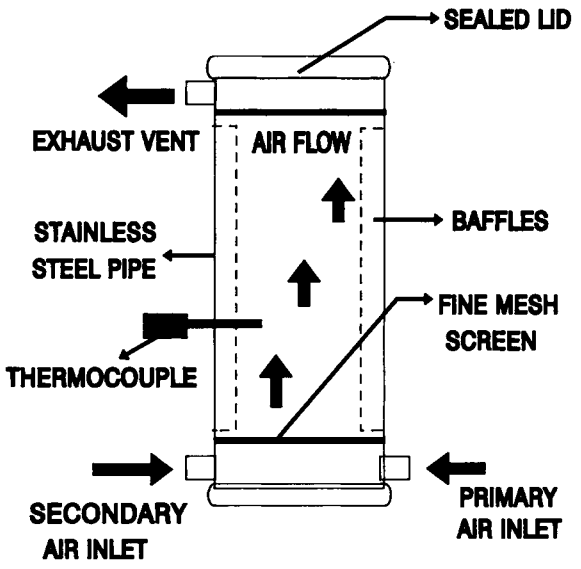

Figure 2 Individual compost unit design.

(Fig. 3). Forced air entered the unit through the primary inlet port, located at the bottom of the cylinder, and was shunted into the headspace. During the entire composting cycle, the primary air supply was fed continuously, delivering approximately 2000 mL/min. When the metabolic heat caused the compost temperature to reach 50°C or higher, a secondary air inlet added an additional 2000 mL/min of air flow into the unit. All compost units were controlled independently. When the temperature fell below 50°C, the secondary air supply was automatically shut off. Due to the high air flows that were required, it was necessary to have both the primary and secondary air streams flow through a water trap to humidify the air prior to its entry into the cylinder. The compost cylinders were kept in an insulated room (35°C) designed to minimize heat loss. To insure uniformity of moisture and temperature profile during the composting cycle, the compost was mixed daily either by rolling the cylinder or by hand.

Characterization of Compost

In order to determine the percent moisture in the compost, samples of compost were taken daily, added to pretared pans, and then dried at 105°C until a constant weight was obtained. The average sample

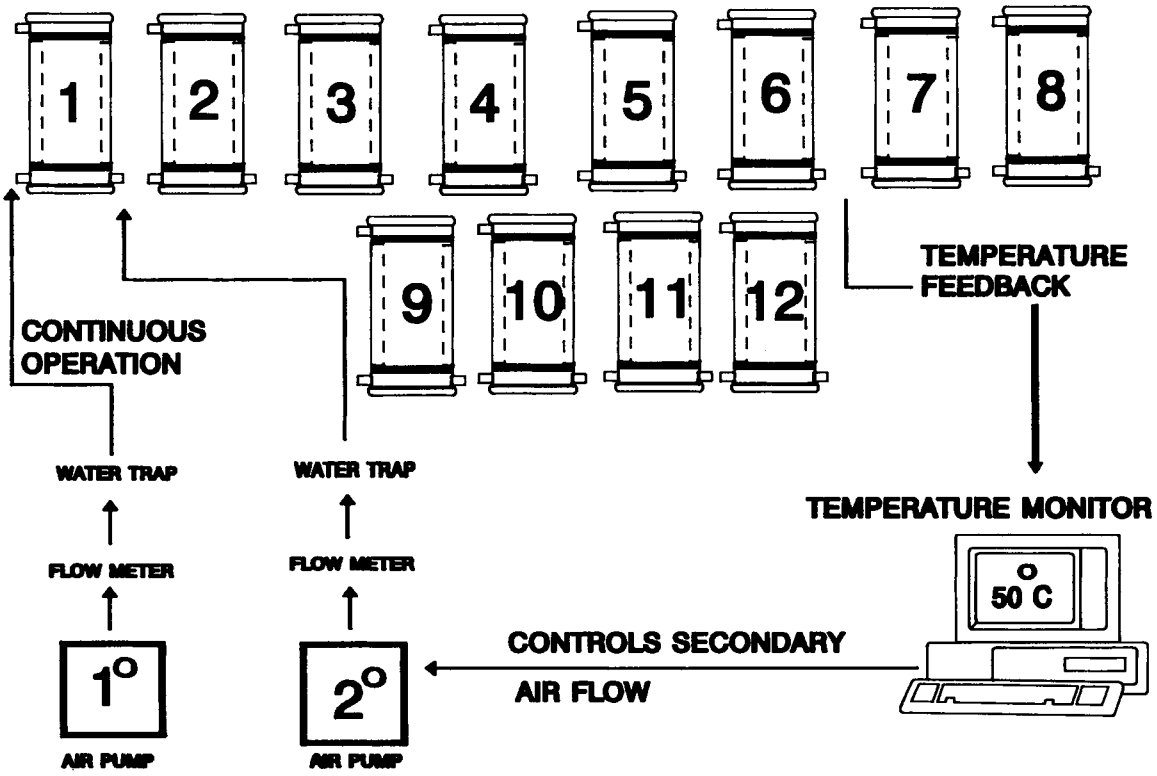

Figure 3 Control system for compost units. Control System is able to handle up to 12 units independently. The temperature set point for additional air flow was 50°C.

of approximately 10 g required drying for at least 14 h.

For compost dry weight loss determinations, at the beginning of each experiment, a tare weight was determined for each individual compost unit. During an experiment, each compost unit was weighed daily on a Mettler PM3000 top loading balance; the total weight minus the tare weight being equal to the amount of compost on a wet weight basis. To insure accuracy, all samples that were removed for moisture analysis or pH determination were weighed; these values were added back to the previous day's total weight. The percentage dry weight multiplied by the net wet weight yielded total dry weight.

The pH of the compost was determined by collecting 10 g of compost daily. To each sample, 40–50 mL of distilled water were added. Samples were allowed to sit for 30 min with periodic stirring to facilitate mixing. After 30 min, the entire contents of the container were poured through four layers of cheese cloth to remove all large particles. The precaution of filtering was necessary to insure that no interference with the pH probe occurred. The pH of the extract was then taken with an Orion model 611 pH meter.

Sample Preparation and Characterization

Following the compost cycle, recovered films were washed for 60 min in a neutral detergent solution at 50°C as previously described.[5] A screening and sorting process allowed the recovery of pieces larger than approximately 2 × 2 mm. The detergent was removed by extensive (4–6) distilled water rinses. Films were air dried and then placed in a vacuum oven held at 30°C with a low stream of N_2.

The weight of each sample film was determined after a constant weight was obtained. Due to the low temperature limits imposed by certain films (PCL), a desiccant was added to facilitate drying. Typically, 3 to 4 days of drying were required before a constant weight could be obtained.

Gel Permeation Chromatography was performed on a Waters Model 150C High performance Liquid Chromatograph (HPLC). The mobile phase was *N*-methyl pyrrolidinone and the sample size was 20–25 mg/10 mL. The molecular weights are reported in polystyrene equivalents.

^{13}C NMR and proton NMR spectra were collected on JEOL model GX-400 MHz spectrometer operating at 100 and 400 MHz, respectively. All NMR spectra were processed by using an 8 Mbyte Mac II Macintosh Computer, with VersaTerm Pro as the emulation package and MacDraw II as the graphics package, interacting with Hare's FTNMR software running on a VAX 8800 computer. Sample preparation, collection conditions, and the details of spectral assignments are contained in reference 8.

RESULTS AND DISCUSSION

In developing our composting methodology, a principal goal was to develop a laboratory scale composting methodology that reasonably modeled the microbiology that was common to commercial composting facilities. We found that one of the keys to successful laboratory scale composting was a homogeneous compost mixture (average particle size 3–4 mm). A homogeneous mixture yielded faster self-heating tendencies and better maintenance of thermophilic phase, with minimal production of offensive odor (Fig. 4). Self-heating and maintenance of the thermophilic phase are features common to municipal composting (Fig. 1) and, in fact, often serve as internal diagnostic tools.

As noted, the starting pH of the mixture was 7.2. During the mesophilic phase we found that often the pH would drop to 4–5. This lower pH significantly reduced the activity of the bacterial population, resulting in much slower composting rates, and often, the need to reinoculate the unit. To prevent this initial pH drop, we have found it convenient to add $CaCO_3$. Consequentially, the pH of the compost rises to 8.8 during a typical 24-day compost cycle (Fig. 5). The resulting pH profile is typical of that observed in commercial composting facilities. The $CaCO_3$ serves only to eliminate the initial pH drop, resulting in a more reproducible laboratory procedure.

As Figure 6 illustrates, the compost lost an average of 67% of its original starting weight after 24 days. During the same time period, the compost underwent macroscopic changes as well. The final product was much darker than the starting material, and it had an odor that was very characteristic of fresh soil.

Figure 7 shows the samples studied in this account along with the length of the composting cycle and the percent weight loss for these materials. With the exception of PHB, Matter-Bi™, and the cellulose acetates with DSs of 2.5 and 2.97, all of the films showed very extensive film breakage in 3–5 days. With Matter-Bi™, an intact, very flexible film remained after composting, which weighed approximately one-half that of the original film. Iodine staining demonstrated little of the starch component

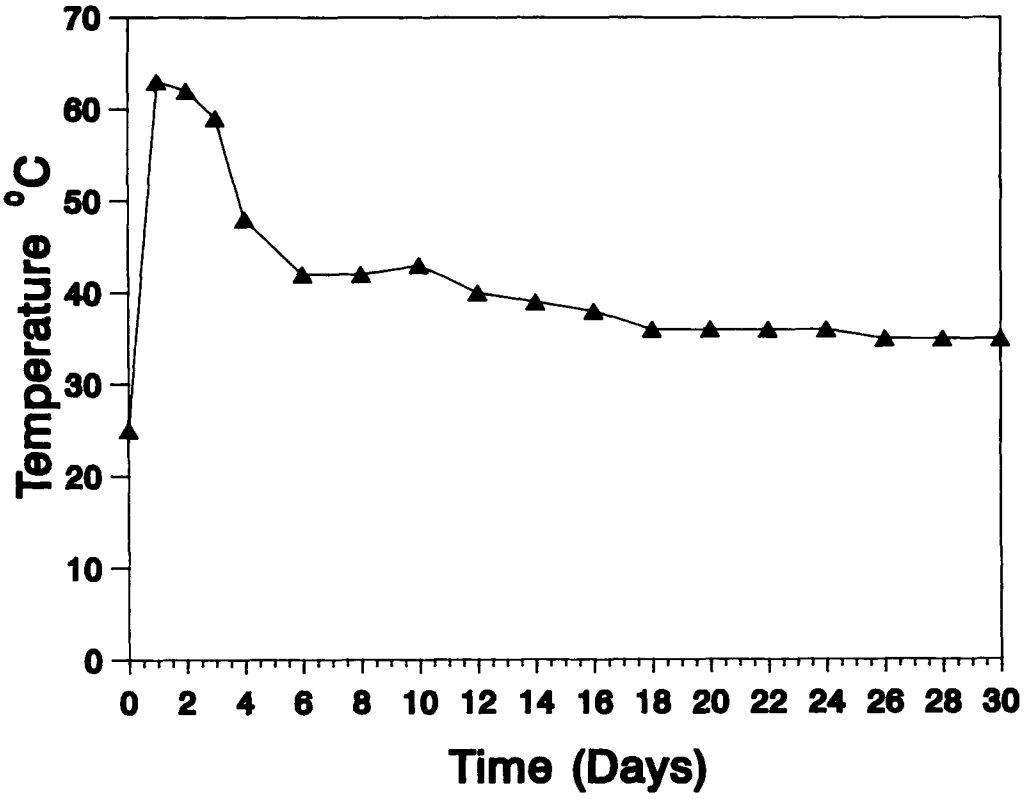

Figure 4 The typical temperature profile of the laboratory scale compost units over a 30-day compost cycle. Note all that heat produced above 35°C is due to microbial metabolism.

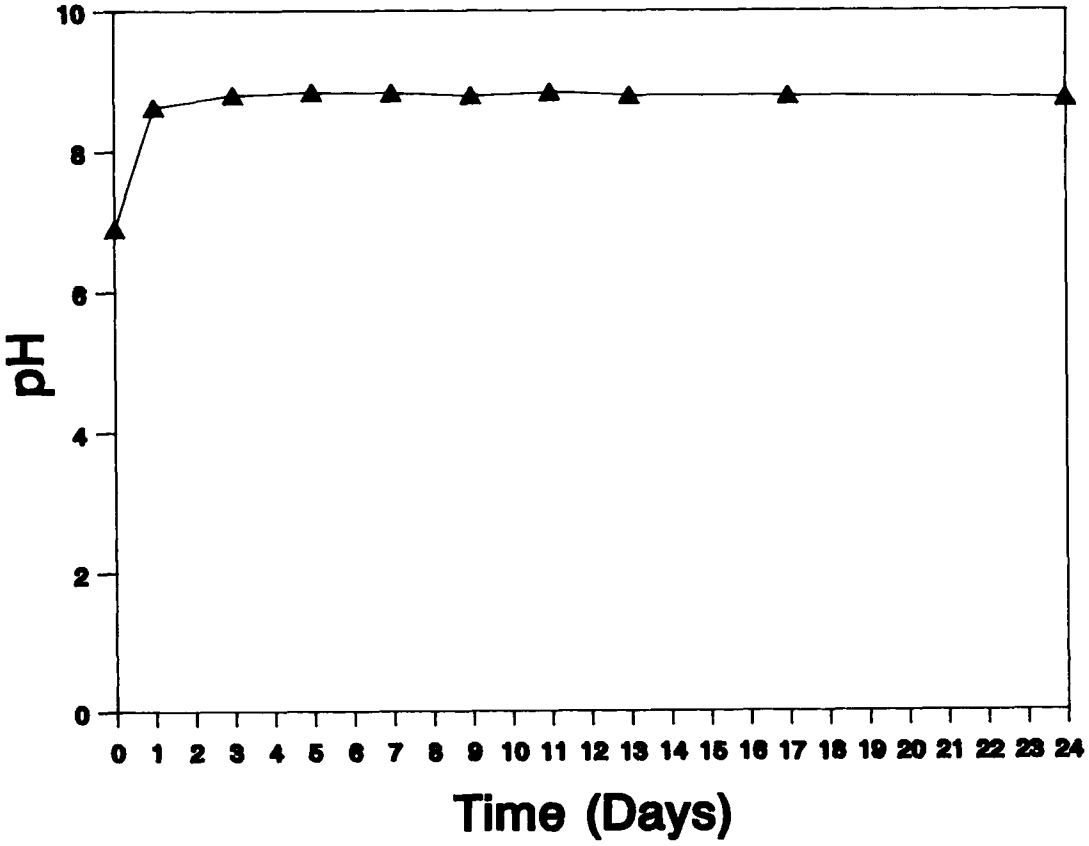

Figure 5 The typical pH profile of the laboratory scale compost unit over a 30-day compost cycle.

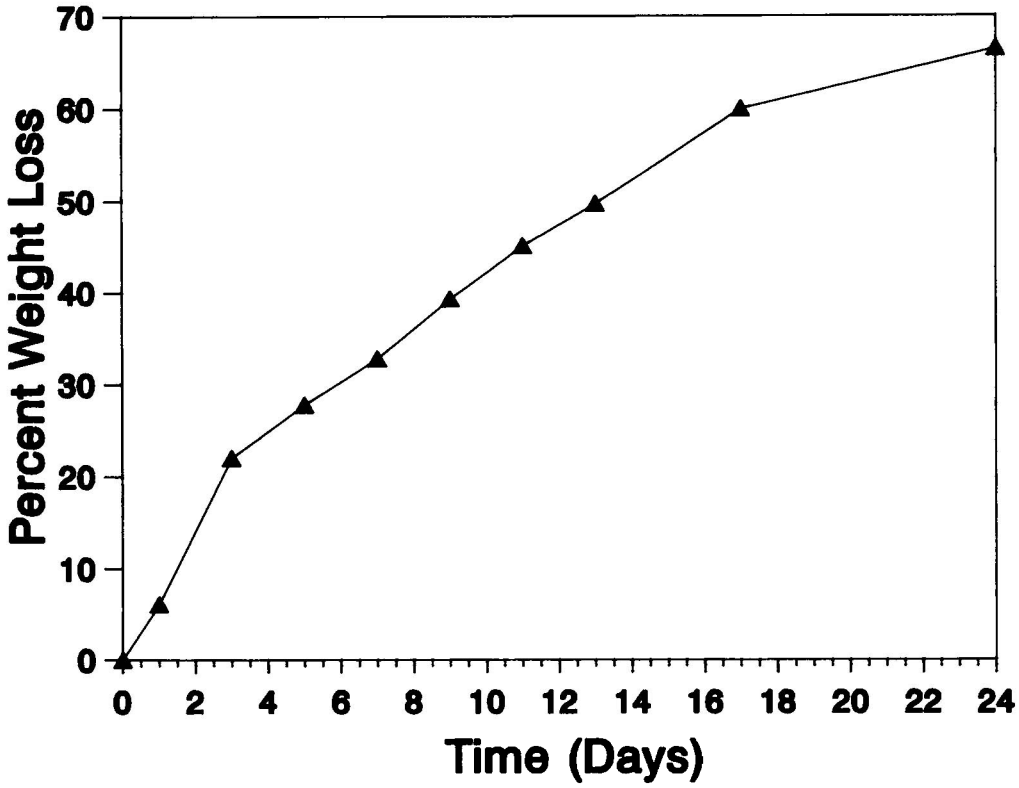

Figure 6 Compost weight loss profile for the laboratory scale compost units over a 30-day compost cycle. This highlights the excellent degradative efficiency of these units.

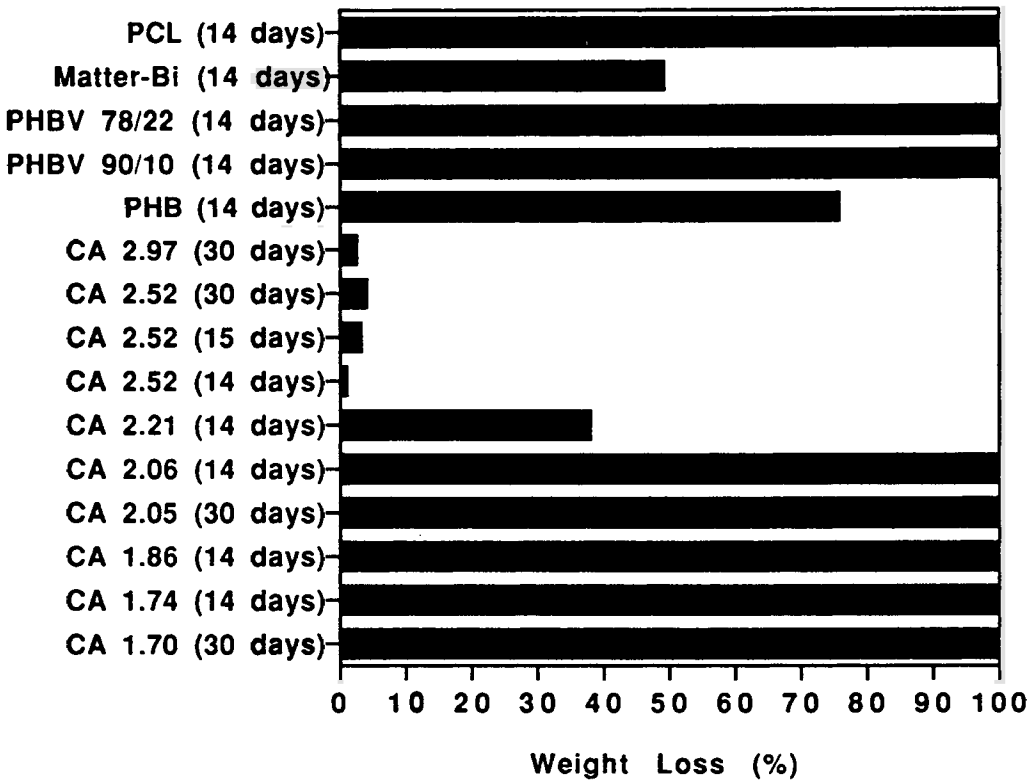

Figure 7 The relative percent weight loss of commonly excepted biodegradable films and cellulose acetate with differing degrees of substitution.

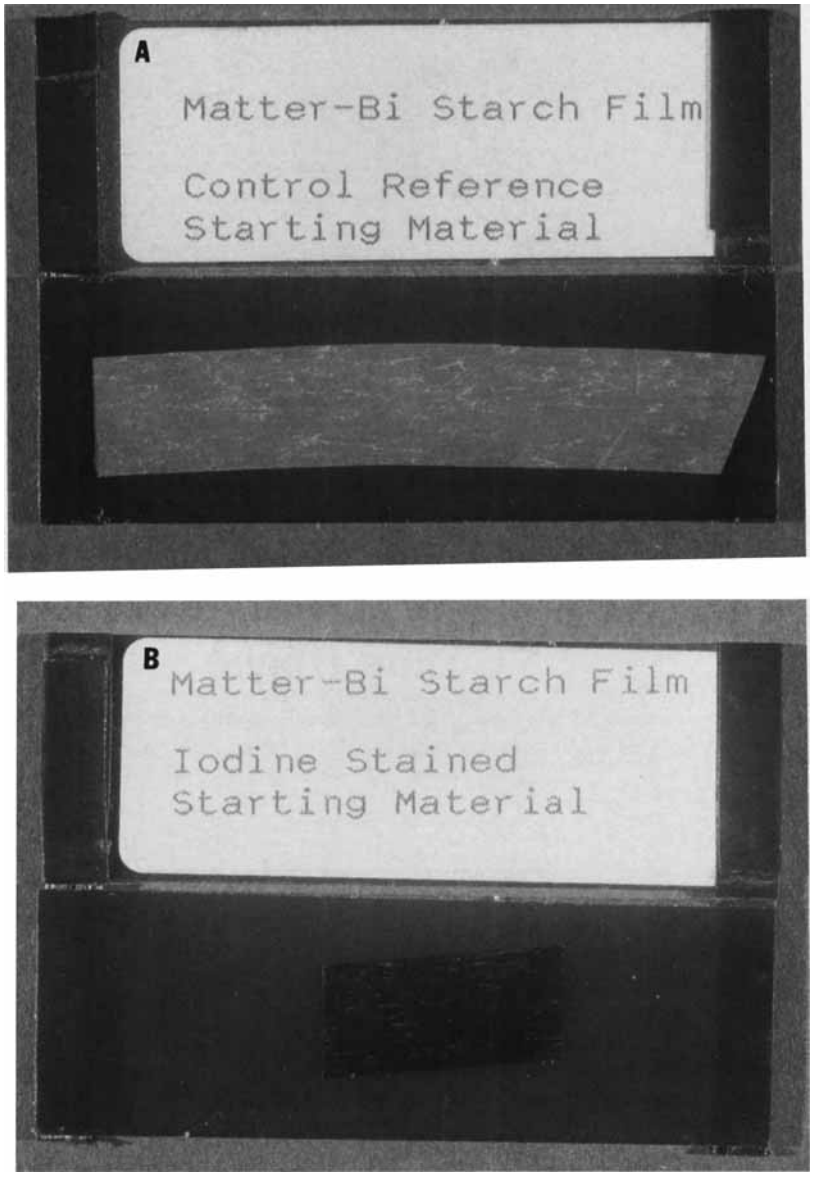

Figure 8 (A) Native Starch Matter-Bi™ film. (B) Native Starch Matter-Bi™ film stained with iodine. (C) Starch Matter-Bi™ film after 10 days in the laboratory scale compost unit. (D) Starch Matter-Bi™ film after 160 days of composting.

remained after composting (Fig. 8). The failure of the PHB films to disintegrate can be at least partially attributed to the thickness of the films (7.8 mil). As can be seen from Figure 7, the high DS cellulose acetates compost slowly and, hence, maintain their film integrity. The PHBV films and the films prepared from 1.7–2.06 DS cellulose acetate completely disintegrated, and no pieces could be recovered after 14 days. The films prepared from the CA with a DS of 2.21 showed extensive breakage, discoloring after 14 days of composting, and signs of extensive microbial attachment. The 2.5 DS CA showed a 1% weight loss after 14 days. In a separate experiment lasting 15 days, a 3.2% weight loss was observed. Extending the composting time for the 2.5 DS CA to 30 days only increased the weight loss to 4.1%. In this same 30-day experiment, the CTA showed a weight loss of 2.5% after 30 days.

As we have shown before,[5] and as the weight loss data in Figure 7 illustrates, degradation rates are highly dependent upon DS. Hence, of particular interest was the impact of composting on the molec-

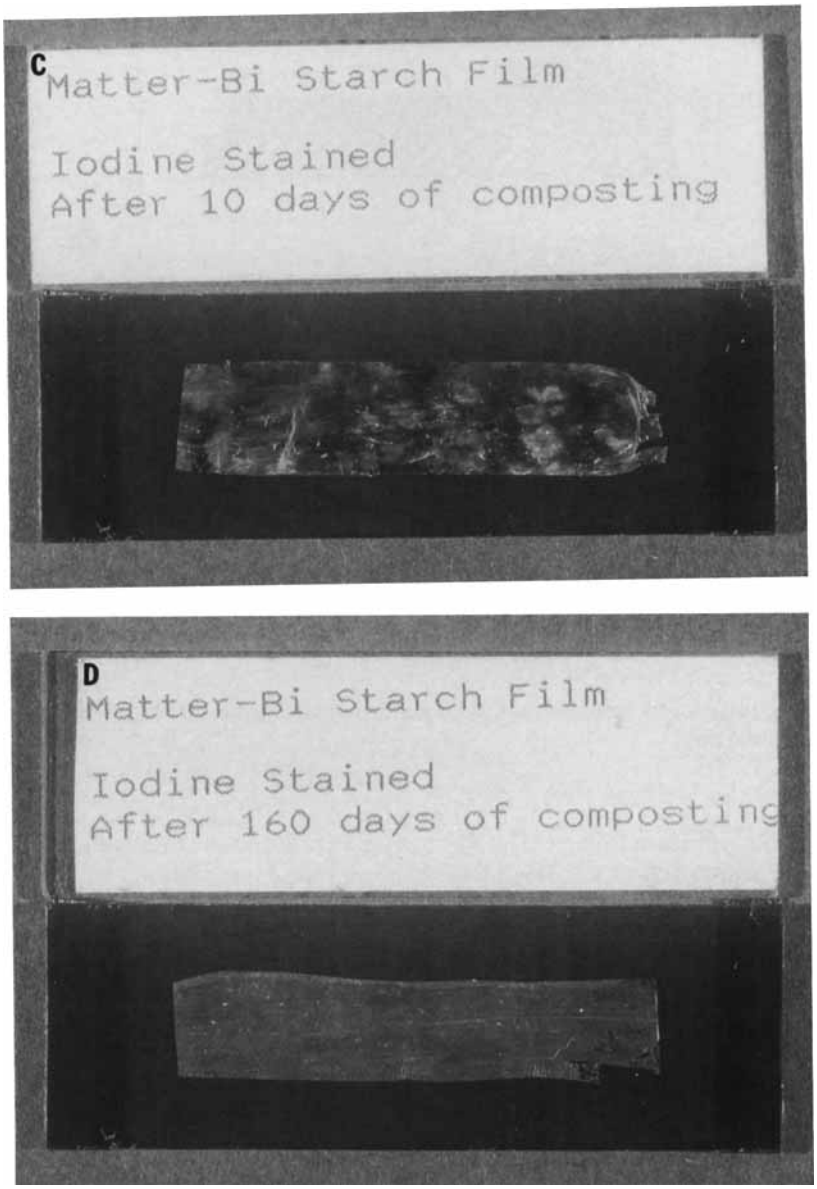

Figure 8 (*Continued from the previous page*)

ular weights and degrees of substitution of the highly substituted cellulose acetates. Figure 9 provides the initial and final molecular weights for DS 2.52 CA after 15 and 30 days of composting and for DS 2.21 CA after 14 days of composting. For DS 2.21 CA, the number-average and weight-average molecular weights dropped significantly ($p < 0.05$). However, for the more highly substituted DS 2.52 CA, we observed a small but statistically significant increase in both number-average and weight-average molecular weights ($p < 0.05$). The CTA (DS = 2.97) sample showed identical behavior ($p < 0.05$). Proton NMR showed that after 14, 15, and 30 days of composting, the DS of the 2.52 DS CA dropped to 2.39, 2.35, and 2.30 ($p < 0.05$), respectively (Fig. 10). The DS of the cellulose triacetate dropped from 2.97 to 2.90 after 30 days of composting ($p < 0.05$). Figure 11 gives the resolution enhanced ^{1}H-NMR spectra for the ring protons of a 2.5 DS CA film before and after composting for 30 days. The resonances appearing above 3.2 ppm are due to hydrogens attached to a C2 carbon which does not bear an acetyl substituent. In particular, the resonance at 3.1 ppm is part of the coupling network consisting of 3,6-disubstituted monomer, while the resonance at 2.95 ppm is part of the 6-monosubstituted coupling net-

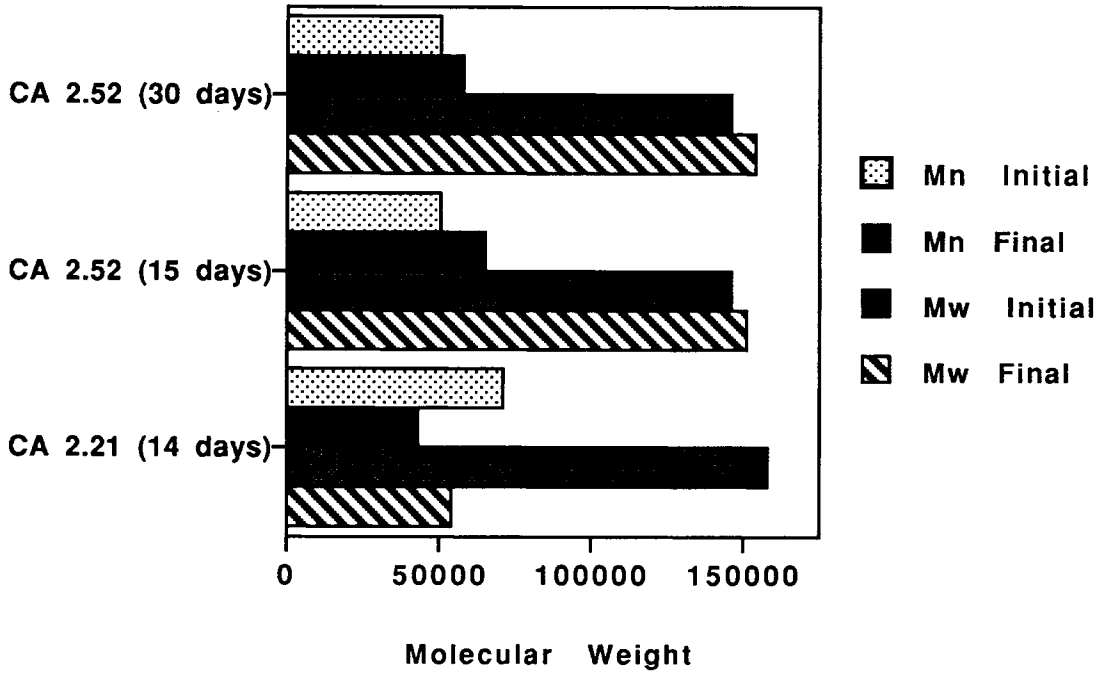

Figure 9 Initial and final film weight's for cellulose acetate films (DS 2.52 and 2.21) after 15 and 30 days.

work.[8] These NMR results indicate preferential deacetylation at the C2 positions of the 2.5 DS cellulose acetate.

As we have discussed before, the mechanism(s) involved in the biodegradation of cellulose acetate is apparently quite complex, and analysis of the material remaining after a particular test can become quite confusing or even misleading.[5] With that in mind, the loss in molecular weight for the 2.21 DS CA can be viewed to be typical of a relatively rapidly degrading polymer. In contrast, the increase in M_n and M_w while observing a decrease in DS is consistent with the preferential removal of low molecular weight fractions, a process known to occur for other slowly degrading polymers.[10]

Our approach can be contrasted with other simulated composting procedures, such as the one recently described by Gu et al., where the temperature of the compost is artificially maintained at 55°C for extended periods.[9] While the method described by Gu et al. clearly establishes inherent biodegradability, it is less clear whether artificially controlling the compost's temperature imparts selective pressures that cause the microbial population to shift from what would be normally associated with municipal compost. There is a risk that maintaining the thermophilic phase beyond the point at which it would naturally cease may select for a different type of microbial population.

In developing biodegradable polymers for composting environments, one of the criteria we use is initial breakup of films within the first few days. Unless the film fractures into pieces sufficiently small to permit their passage through a screening operation commonly used in most municipal composting facilities, the films will likely be removed from the composting operation. This criterium will not be relevant for composting operations that begin with a hammer mill or similar front end. Film breakage must be followed by complete mineralization of the fragments. The time frame for complete mineralization of compostable materials is still subject to much debate. The length of time required for complete mineralization of natural materials seems to us to be a useful guideline. The work described in this account demonstrates that PCL, PHBV, and cellulose acetates having a DS of less than approximately 2.2 meet this criterion of film disintegration. Many studies have shown that PHBV and PCL ultimately mineralize under appropriate conditions.[11] Furthermore, we have recently demonstrated, using carbon-14 labeling techniques, that cellulose acetates having a DS less than approximately 2.5 are degraded to CO_2 and other by-products under aero-

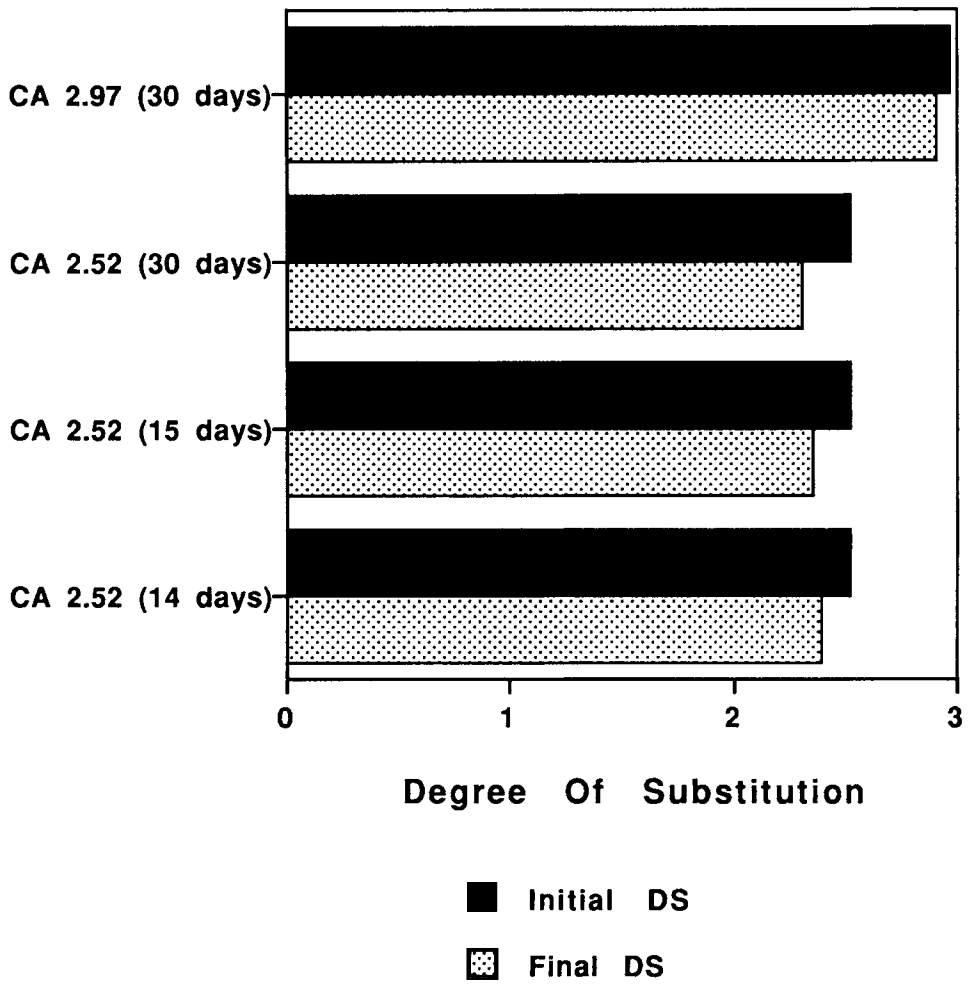

Figure 10 Changes in degree of substitution for cellulose acetate with and DS of 2.52 and 2.97, after 14, 15, and 30 days of composting.

bic conditions. Hence, we believe that it is appropriate to conclude that these polymers are completely mineralized in the composting environment described in this paper.

In the case of the cellulose acetates, we recognize that this study does not distinguish between chemical and enzymatic hydrolysis of the acetyl functionality, nor does it supply direct conclusive proof for complete mineralization in composting. Conclusive proof for complete mineralization will require respirometry and ^{14}C-radiolabeled substrate studies during composting of cellulose acetate. This work is in progress and will be reported in due course. However, we have shown that films prepared from cellulose acetates with a DS below a threshold value do rapidly disintegrate in a manner accepted for many other biodegradable polymers. This finding, when coupled with our previous work with carbon-14 labeled cellulose acetates in enrichment cultures[5] and the report of Gu,[9] strongly indicate that cellulose acetates with a DS below 2.2 will completely mineralize under composting conditions.

CONCLUSIONS

The bench-scale compost methodology that we developed emulates a high technology municipal windrow composting operation. A series of cellulose acetate films, differing in degree of substitution, were evaluated in this bench-scale system. In addition, commercially available biodegradable polymers such as poly(hydroxybutyrate-*co*-valerate) (PHBV) and polycaprolactone (PCL) were included as points of

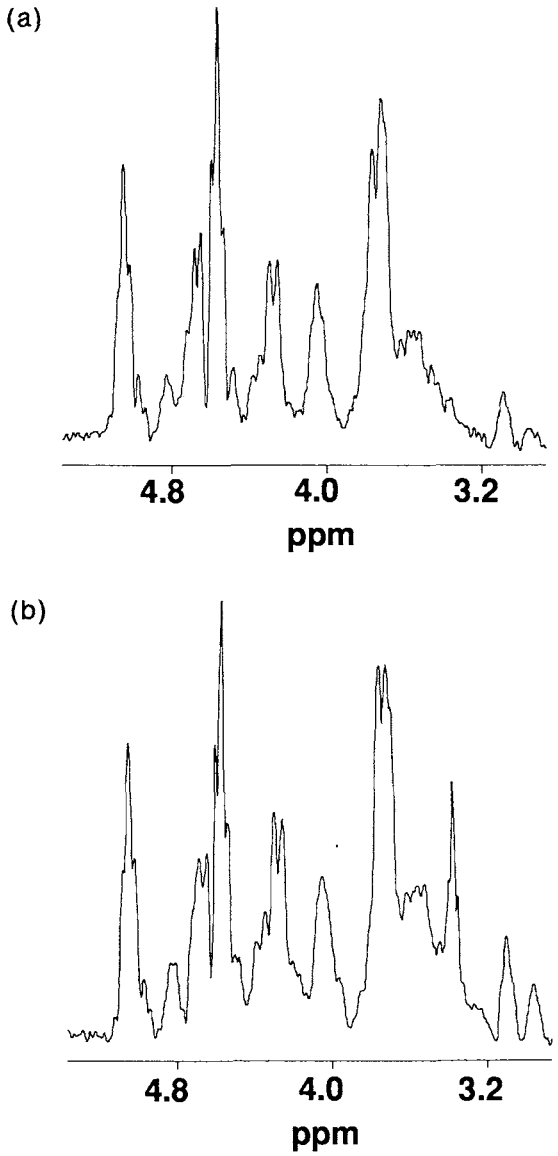

Figure 11 Enhanced H-NMR spectra for the ring protons of a 2.52 cellulose acetate (a) before and (b) after composting for 30 days.

reference. Based on film disintegration and on film weight loss, cellulose acetates having degrees of substitution less than approximately 2.20 compost at rates comparable to that of PHBV. NMR and GPC analyses of composted films indicate that low molecular weight fractions are removed preferentially from the more highly substituted and slower degrading cellulose acetates.

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