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Biodegradation and hydrolysis rate of aliphatic aromatic polyester

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ABSTRACT

The biodegradation and hydrolysis rates of an aliphatic aromatic copolyester were measured in manure, food, and yard compost environments and in phosphate buffer solution (pH = 8.0) and vermiculite at 58 °C. Mineralization, molecular weight reduction, and structural changes determined by DSC, FTIR, and ^{1}H NMR were used as indicators of the biodegradation and hydrolysis rates. Poly(butylene adipate-*co*-terephthalate), PBAT, film biodegraded at distinctive rates in manure, food, and yard compost environments having different microbial activities. The highest biodegradation rate was found in manure compost, which had the highest CO_2 emissions and lowest C/N ratio. The possible presence of extracellular enzymes in manure and food composts may facilitate the hydrolytic reaction since greater molecular weight reduction rates were observed in these composts. ^{1}H NMR and thermal analysis revealed that, while PBAT is a semi-crystalline copolyester with cocrystallization of BT and BA dimers, the soft aliphatic domain (BA) and the amorphous region are more susceptible to hydrolysis and biodegradation than the rigid aromatic domain (BT) and the crystalline region.

1. Introduction

Biodegradable and compostable polymers have gained attention from industries, consumers, and governments as a potential way to reduce municipal solid waste since they can be recycled or energy recovered through composting into soil amendment products [1]. Therefore, much attention has been given to their production, implementation, and end of life scenario.

One of the biodegradable and compostable polymers that has potential in commercial use is poly(butylene adipate-*co*-terephthalate) or PBAT, due to its ease of processing and similar mechanical properties to polyethylene [2]. PBAT is an aliphatic aromatic copolyester produced from petroleum based resources and certified as compostable by the Biodegradable Products Institute (BPI) according to the ASTM D6400 specification [3]. PBAT is a linear random copolyester consisting of two types of dimer. The rigid section BT is an ester repeat unit consisting of 1,4 butanediol and terephthalic acid monomers, while the flexible section BA consists of 1,4 butanediol and adipic acid monomers (Fig. 1).

As determined by a life cycle inventory [4], PBAT, as well as other biodegradable polyesters, has the greatest environmental benefits when it is recovered through recycling or composting. Composting is a process where biodegradable materials, such as manure and leaves, are decomposed and transformed by microorganisms into a humus-like substance called compost, CO_2, water, and minerals, through a controlled biological process [5]. According to ASTM D6400, in order to be compostable, a material must possess three essential qualities: ability to easily disintegrate in a composting environment, inherent biodegradability, which is tested using the ASTM D5338 method, and absence of ecotoxicity or any adverse effects of the final compost after decomposition [5].

According to ASTM D5338, sources of inocula used in biodegradation tests for biodegradable polymers are composts [6]. In general, there are three types of wastes used as compost feedstocks: yard, food and manure wastes [7]. Any of these can be used if during the first 10 days of the test the compost inoculum produces 50–150 mg of CO_2 per g volatile solids and the C/N ratio is between 10 and 40 [4]. Yard waste is a vegetative waste, such as leaves, grass clippings, tree trunks, and pruning wastes from the maintenance of landscaped areas. Food waste is uneaten food or waste from a food preparation process from residences, commercial, or institutional sources, such as restaurants or cafeterias. Manure waste is fecal and urinal excretion of livestock and is usually rich in nitrogen [5].

The authors have previously studied the biodegradation of biodegradable polyesters, such as poly(lactic acid) and PBAT, in

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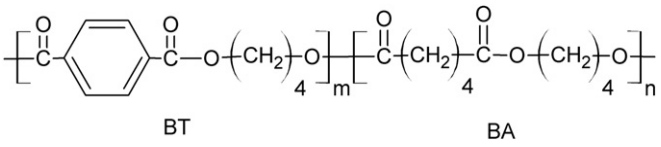

Fig. 1. Chemical structure of poly(butylene adipate-*co*-terephthalate) or PBAT.

various composting [2,8,9] and other environments such as soil burial [10]. Biodegradability of these biodegradable polymers in composting conditions and soil burial conditions is affected by both biotic and abiotic factors of the environment, such as temperature, moisture, pH, bio-surfactant and enzymes; and by polymer characteristics, such as chain flexibility, crystallinity, regularity and heterogeneity, functional groups, and molecular weight [7,11,12].

Among biotic factors, extracellular enzymes produced by different microorganisms may have active sites with different specificity, such as complementary shape, charge, and hydrophilicity/hydrophobicity [13], and hence have more capability to biodegrade certain polymers. For example, the fungi *Aspergillus niger* and *Aspergillus flavus*, present in soil and crops, residue respectively, produce enzymes that more easily digest aliphatic polyesters derived from 6–12 carbon di-acid monomers than those produced from other monomers [14]. This enzymatic specificity may contribute to different degradation rates of biodegradable polyesters in differing compost environments.

Therefore, the objective of this study was to determine the effect of the environment on the biodegradation/hydrolysis of aliphatic aromatic polyester (in this case PBAT). The biodegradation rates of aliphatic aromatic polyester under different compost environments was measured and compared with hydrolysis in buffer solution and in vermiculite as an example of an abiotic compost-like material.

2. Materials and methods

2.1. Film production

Poly(butylene adipate-*co*-terephthalate) or PBAT resin was purchased from BASF (Florham Park, N.J., USA). PBAT film was produced using a Killion KLB 100 blown film single screw extruder manufactured by Davis-Standard, LLC, (Pawcatuck, Conn., USA) with a temperature profile of 177-177-177-170-165-165-165 °C for zone 1, 2, 3, clamp ring, adaptor, die 1 and 2, respectively. The extruder screw diameter was 25.4 mm (1 in) with L/D ratio of 24:1 and a diameter of the blown die of 50.8 mm (2 in). Screw speed and take up speed were 18.6 rpm and 0.033 m/s. The final thickness of the PBAT film was 38.1 ± 5.1 μm (1.5 ± 0.2 mil).

2.2. Biodegradation

Three types of commercial representative compost were used: manure compost from the Michigan State University commercial composting facility, East Lansing, Mich., USA; yard compost purchased from Hammond Farm, East Lansing, Mich., USA; and food waste compost from a local provider (Woodcreek Elementary School, Lansing, Mich., USA). First, film samples were analyzed for carbon content and composts for carbon to nitrogen ratio using a PerkinElmer CHN analyzer (Waltham, Mass., USA). Film carbon content was used for calculation of % mineralization, which is defined as the percentage of carbon in the polymer that is converted into CO_2. The carbon to nitrogen ratio (C/N ratio) was measured to determine suitability of composts for the testing. As previously mentioned, good quality compost should have a C/N ratio between 10 and 40 [6,15].

An in-house built direct measurement respirometric system (DMR) connected to a CO_2 infrared gas analyzer was used to determine the biodegradation of the PBAT films in compost. Each bioreactor contained 250 g compost (wet basis) as control; a mixture of 250 g compost (wet basis) with 6 g cellulose powder (20 μm grade, Sigma Aldrich, St. Louis, Mo., USA) as positive control; or compost with 6 g of PBAT film cut into 1 cm × 1 cm pieces. Each test was run in triplicate. Details of the apparatus and testing conditions can be found elsewhere [8,16]. The test was conducted according to ASTM D5338 specifications [6]. The bioreactors were incubated in an environmental chamber at 58 °C for 45 days. At 7, 15, 30, and 45 days, film samples were retrieved from the bioreactors and were analyzed for changes in thermal properties, FTIR spectra, and molecular weight reduction. The percent mineralization was calculated using equation (1).

$$\%\text{Mineralization} = \frac{sCO_2 - bCO_2}{W \times \frac{\%C}{100} \times \frac{44}{12}} \times 100 \quad (1)$$

where sCO_2 is the amount of CO_2 from the sample or the cellulose reactor, bCO_2 is the amount of CO_2 from the compost reactor, W is the weight of sample or cellulose, and $\%C$ is the % carbon in the sample or cellulose obtained from the CHN analyzer.

2.3. Hydrolysis

The hydrolysis test was performed using an FDA migration cell consisting of a 40 ml glass amber, a screw cap with a hole, and a sealing PTFE/silicon septum [17]. For each cell, fourteen circular PBAT disks of 38.1 ± 5.1 μm thickness with a diameter of 0.0254 m were placed in the cells separated in between by glass beads. The cells were filled with 35 ml of phosphate buffer with a pH of 8.0 (measured using an Oakton pH meter, Vernon Hills, Ill., USA) as a control for hydrolysis, and 35 ml of vermiculite with 50% moisture content (mixed with phosphate buffer) in order to simulate only hydrolysis under composting conditions. Vermiculite was used since it has texture similar to compost and excellent water holding capacity [18]. Three replicate test cells for each medium were stored in a water bath at 58 °C for 45 days. The temperature was monitored using an HOBO® datalogger (Onset Computer, Bourne, Mass., USA). Samples were retrieved at 7, 15, 25, and 45 days for FTIR, molecular weight measurement, and ^{1}H NMR.

2.4. Molecular weight measurement

The retrieved samples were cleaned with laboratory wipe without using water in order to prevent any further degradation. The weight average molecular weight reduction of the samples was determined by dissolving the PBAT sample in tetrahydrofuran (THF), Pharmco-Aaper (Brookfield, Conn., USA), at a concentration of 2 mg/mL. Once the sample was filtered through 0.45 μm polytetrafluoroethylene (PTFE) filter, one hundred μL of each sample solution was injected into a Waters® Gel Permeation Chromatograph (GPC) equipped with three-column bank and a refractive index detector (Milford, Mass., USA.). The column bank consisted of three 7.8 mm × 300 mm single pore columns, Waters Styragel® HR4, HR3, and HR2, packed with 5 μm styrene divinylbenzene particles. A flow rate of 1 mL/min, a runtime of 45 min, and a temperature of 35 °C were used. A calibration curve of a third-order polynomial equation was conducted using 10 different molecular weight polystyrene standards (range from 1.20×10^3 to 3.64×10^6 Da).

2.5. FTIR spectra

Film samples were scanned using a Shimadzu IR-Prestige 21 (Columbia, Md., USA) with an Attenuated Total Reflectance (ATR) attachment (PIKE Technologies, Madison, Wis., USA) from 4000 to 650 cm^{-1} to measure any changes in the spectral intensities, which correlate to the formation and destruction of functional groups within the films.

2.6. Thermal behavior

A differential scanning calorimeter (DSC) from Thermal Analysis Inc., (model Q100, New Castle, Del., USA) was used to determine changes in crystallinity of PBAT due to biodegradation in different compost media via changes in the heat of fusion. The sample size used was approximately 5–10 mg. The testing temperature was from −60 to 160 °C with a ramping rate of 10 °C/min, in accordance with ASTM D 3418 [19].

2.7. ^1H NMR spectroscopy

The ^1H spectra of the films in phosphate buffer or vermiculite were collected on a Varian 300 MHz NMR-Spectrometer (Varian Inc., Palo Alto, Calif., USA). Fifty milligrams of PBAT disks were dissolved in 5 mL of deuterated chloroform ($\delta = 7.24$ ppm) from Cambridge Isotope Laboratories Inc. (Andover, Mass., USA). Chemical displacement was corrected as tetramethylsilane ($\delta = 0$ ppm) was used as an internal standard, included in the deuterated chloroform solution.

3. Results and discussion

3.1. Biodegradation in three different composts

Total biodegradation of PBAT film at 45 days in manure compost was the highest (67.3 ± 2.8%), followed by those in food compost (44.9 ± 2.6%) and yard compost (33.9 ± 1.5%), respectively (Fig. 2). The biodegradation of cellulose also shows a similar pattern,

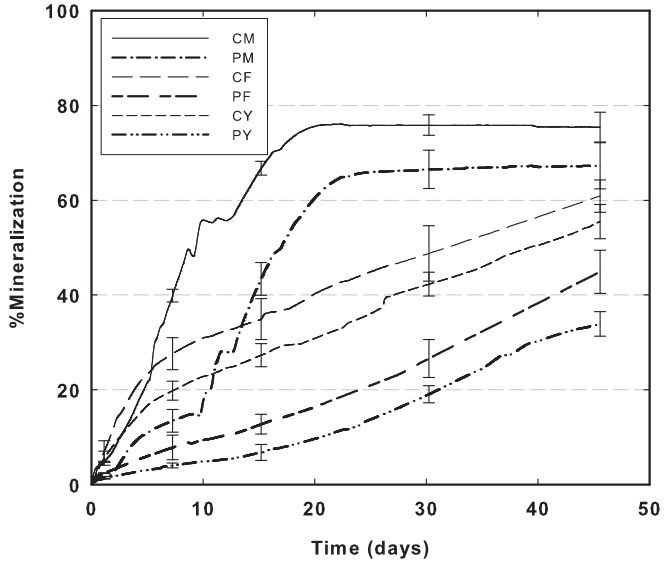

Fig. 2. Mineralization of PBAT and cellulose positive control in three different composts, where CM is mineralization of cellulose in manure compost, PM is PBAT in manure compost, CF is cellulose in food compost, PF is PBAT in food compost CY is cellulose in yard compost, and PY is PBAT in yard compost. Error bars represent standard deviation at 1, 7, 15, 30, and 45 days.

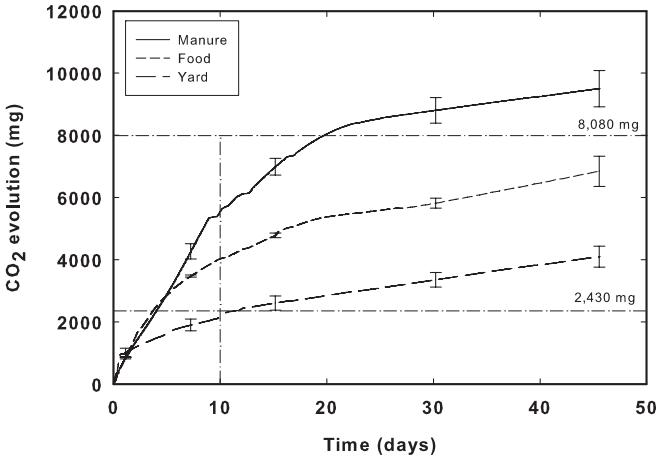

Fig. 3. Evolution of CO_2 gas from respiration of manure, food, or yard composts as function of time; values of 2,430 and 8,080 mg indicate the window of recommended compost according to ASTM D5338 standard, which was calculated from 50 mg/g and 150 mg/g volatile solid of composts. Error bars represent standard deviation at 1, 7, 15, 30, and 45 days. Each bioreactor contained 250 g of each compost type.

highest biodegradation in manure compost, followed by food and yard compost. The higher degradation in manure compost than food and yard compost can be attributed to greater microbial activity in the manure compost. Evidence of the greater activity of the manure compost includes the greater amount of evolved CO_2 gas from compost respiration (Fig. 3). In this case, the recommended compost activity was 2430–8080 mg CO_2, calculated from 50–150 mg/g volatile solid of the composts [5]. CO_2 production from yard compost during the first 10 days was just 4.3% below the recommended value, while those from manure and food compost were within the recommended range. Furthermore, the C/N ratio of yard compost (47.1 ± 5.2) was slightly outside the range of suitable compost, which possibly indicates an inactive compost [15], while those of manure (22.9 ± 1.3) and food (36.0 ± 1.7) composts were well within the recommended C/N range of 10 to 40. Therefore, this confirms that microbial activity of the compost and the C/N ratio play a significant role in the total biodegradation of biodegradable plastics as inferred by Ishii and Takii [20], Ishii et al. [21], and Nakajima-Kambe et al. [22].

3.2. Biodegradation rate and hydrolysis

While the previous biodegradation results indicated that samples in the manure compost environment degraded faster than in the other two composts, it did not determine whether there were differences in the biodegradation and/or hydrolysis rates in these different compost environments. In addition to microbial activity, hydrolysis has a substantial influence on biodegradation and biodegradation rates of biodegradable polyesters such as PBAT, since hydrolysis is one of the initial processes of biodegradation [7,23–25]. Hydrolytic random chain scission at ester linkages reduces the size of polyester chains into the size range that microorganisms can bio-assimilate. Therefore, it is critical to understand and determine if hydrolysis and/or microbial activity are the main determinants of degradation of PBAT in different compost environments. The same pattern of molecular weight reduction for the PBAT samples in the phosphate buffer solution and vermiculite media are observed in Fig. 4a and b, indicating the same hydrolysis process for these two environments. The fact that during the first 15 days only slight change in molecular weight distributions (MWD) was observed indicates that, initially, the

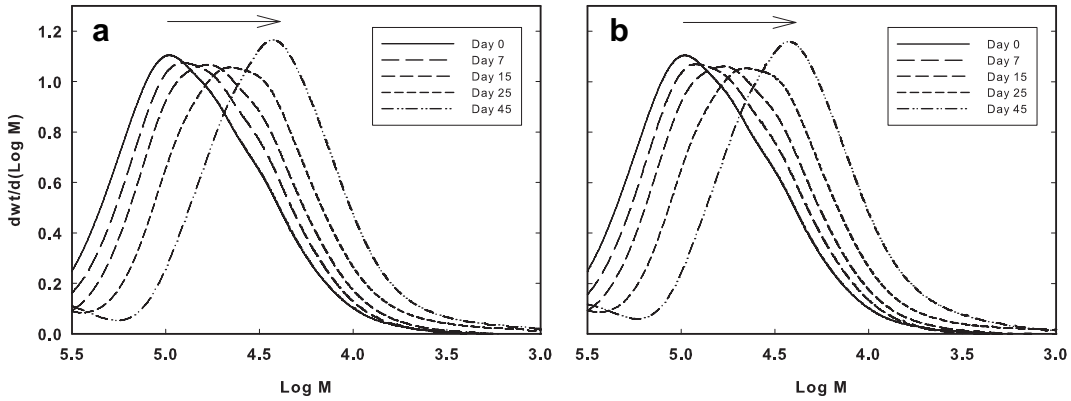

Fig. 4. Molecular weight distribution of hydrolyzed samples in (a) phosphate buffer solution of pH 8.0 and (b) vermiculite for 0, 7, 15, 25, and 45 days at 58 °C.

hydrolytic main chain scission favored the chain ends because of the increased free volume associated with them. As the hydrolysis proceeds, while the MWD of the hydrolyzed samples becomes narrower, main chain scission starts to occur at the middle of the chains, indicated by the significant shift of MWD towards lower molecular weight. Fig. 5 shows changes in number average molecular weight (M_n) of PBAT films from biodegradation in the three different compost environments, as well as from hydrolysis in pH 8.0 buffer solution or in vermiculite as a function of time.

The reduction of M_n from biodegradation in compost and hydrolysis in both media follows a first order reaction, where the rate constants (k) can be obtained from the slopes as shown in Table 1. The k value from PBAT biodegradation in manure compost was the highest ($0.0593 \pm 0.0025\ d^{-1}$) and those from biodegradation in yard compost ($0.0237 \pm 0.0017\ d^{-1}$), hydrolysis in buffer solution ($0.0192 \pm 0.0011\ d^{-1}$) and in vermiculite ($0.0216 \pm 0.0021\ d^{-1}$) are among the lowest. The reduction of M_n of PBAT from biodegradation in yard compost was not different from those from hydrolysis due to the low microbial activity of yard compost, as indicated by poor CO_2 emissions and a too high C/N ratio. Although the composts used for testing have all or most of the recommended parameters according to the ASTM and the ISO standards, e.g. C/N ratio and CO_2 production, specification of compost type and the current recommended parameters may not be sufficient as a guideline for testing because of the lack of consistency of microbial composition among different composts and within the same compost [20]. Furthermore, enzymatic preferences of microorganisms for different isomers and number of carbon atoms for polymers are diverse [22,26,27]. Therefore, relating the biodegradation rate to general compost composition and/or other factors may overlook the specific families of microorganisms present in the compost that may be more or less successful than others at biodegrading the aliphatic aromatic polyester. Microorganisms in composts and their enzymes responsible for the hydrolytic degradation can be identified in order to solve this issue. This is subject of our current and future research, and it will be further communicated.

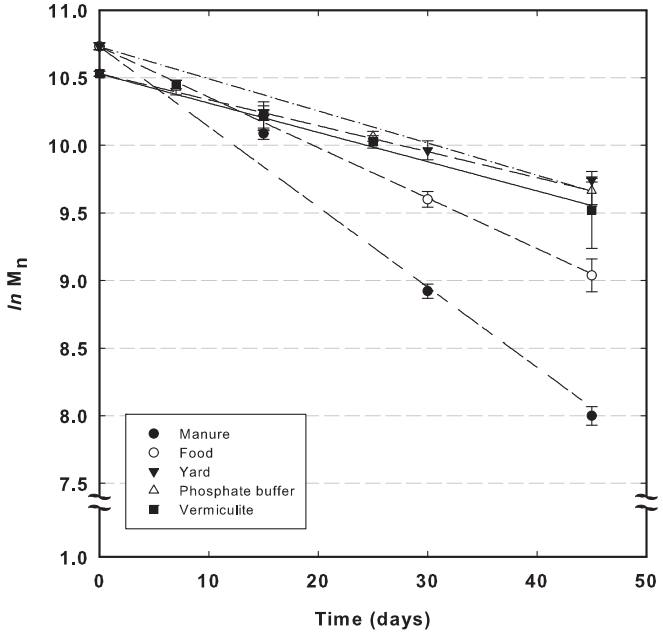

Fig. 5. Logarithmic reduction of molecular number (M_n) in of PBAT films from hydrolysis in phosphate buffer solution (pH = 8.0) or in vermiculite, or from biodegradation in manure, yard, or food composts as a function of time; the regression are performed using 1st order reaction. Values are represented as mean ± standard error.

The preference of biodegradation and hydrolysis of amorphous polymeric regions in semi-crystalline biodegradable polymers is well established [28]. DSC thermograms should indicate an increase of the crystalline region of the polymer as a function of time as samples are subjected to hydrolysis and/or biodegradation. Despite the fact that PBAT is a statistical random copolymer with a degree of randomness (r) of 0.97 to 1.02 and average block length of 1.6 to 2.6 [29], which theoretically cannot crystallize [30–32], the lower melting temperature of PBAT (130 °C) than polybutylene terephthalate (PBT) (230 °C) is evidence that cocrystallization in PBAT can occur since the soft BA sections can adjust their chain conformation to that of the rigid BT units. Furthermore, in order to undergo cocrystallization, the cohesive energies of the two comonomers should be relatively comparable so that the comonomer

Table 1
Rate constants (k) calculated from reduced molecular number of biodegradation of PBAT films in manure, yard, or food composts or hydrolysis in phosphate buffer solution or in vermiculite.

Media	k from M_n (d^{-1})
Manure	0.0593 ± 0.0025^a
Food	0.0376 ± 0.0012^b
Yard	0.0237 ± 0.0017^c
Phosphate buffer	0.0192 ± 0.0011^c
Vermiculite	0.0216 ± 0.0021^c

Note: values are represented as average ± standard error. 'k' values with a different superscript letter are statistically different at $\alpha = 0.05$ (Tukey – HSD test).

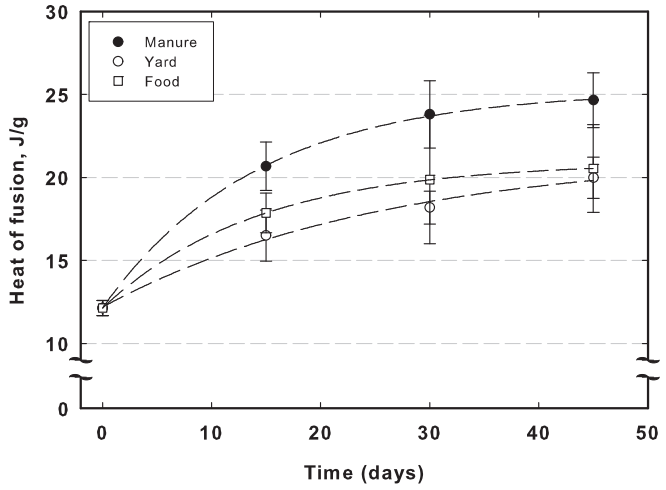

Fig. 6. Increased heat of fusion (areas under melting peak in DSC thermogram) of PBAT films incubated in manure, yard, or food composts as a function of time. Error bars represent standard deviation. Dashed lines are the fitted curves to represent the increasing trend of heat of fusion.

with greater cohesive energy does not get separated and form crystal lattices of only one copolymer. In this case, the ratio of cohesive energy of BA to BT (E_{BA}/E_{BT}) of PBAT film with f_{BA}/f_{BT} of 0.59/0.41 calculated using the functional group contribution method is 1.15 (cohesive energies of $-CH_2-$, $-(C{=}O)-O-$, and aromatic $-C_6H_4-$ are 4.19, 13.41, and 31.00 kJ/mol, respectively), which indicates that PBAT can cocrystallize [32]. In the case of PBAT, the soft aliphatic BA unit is infused into the BT crystal lattice [30].

In biodegradation of PBAT in manure, yard, and food composts, increased heat of fusion (ΔH_f) from DSC thermograms was observed in all three composts as biodegradation proceeded (Fig 6), indicating increased crystallinity as a result of the amorphous regions being degraded first. The increased crystallinity also confirmed that the amorphous regions are more susceptible to biodegradation than the crystalline regions as reported by Mochizuki and Hirami [33], Hakkarainen et al. [34], Hayase et al. [35], Gan et al. [36], Tserki et al. [37], Barone and Arikan [38], and Kijchavengkul et al. [9] in various biodegradable polymers.

Based on the structure of PBAT (Fig. 1), several functional groups, such as hydroxyl (OH) and carbonyl (C=O) groups can be used as tools to study degradation. As a result of main chain scission from hydrolysis at ester linkages, terminal alcohol and carboxylic acid groups are produced, so as hydrolysis progresses, an increase in OH groups should be observed in the FTIR absorbance spectra. An increase in OH groups (3350 cm^{-1}) in all the samples was observed, and was more prominent in the compost samples than in phosphate buffer and vermiculite (Fig. 7a–e). However, in the PBAT samples hydrolyzed in phosphate buffer, an increase in the OH group was only observed during the first week, since compounds with OH terminal groups may dissolve in the phosphate buffer due to the greater polarity of this solution compared to the PBAT matrix.

Hydrolytic main chain scission at multiple locations in the polymer chain produces smaller molecules or oligomers, which can easily permeate out of the polymer matrix. Therefore, reduction of the carbonyl absorbance (1710 cm^{-1}) also results from hydrolysis. Only slight reductions in carbonyl groups were observed in the PBAT samples hydrolyzed in phosphate buffer (Fig. 7f) and in vermiculite (Fig. 7g). However, PBAT samples in manure (Fig. 7h), food (Fig. 7i), and yard composts (Fig. 7j) manure showed greater reduction in carbonyl groups possibly due to synergistic effects of enzymatic degradation.

3.3. Comonomers, microstructures, and degradation

PBAT is a statistical random copolymer consisting of soft butylene adipate (BA) sections and hard butylene terephthalate (BT) sections (Fig. 1). Equations (2) and (3), as suggested by Herrera et al. [29], were used to determine the composition of the adipate fraction (f_{BA}) and the terephthalate fraction (f_{BT}) using the area of signals at 2.29 ppm ($-OCOCH_2-$) and 8.06 ppm (aromatic) from ^1H NMR spectroscopy (Fig. 8). Changes in f_{BA} and f_{BT} were used to determine the effects of hydrolysis on each comonomer.

$$f_{BA} = \frac{A_{2.29}}{A_{2.29} + A_{8.06}} \tag{2}$$

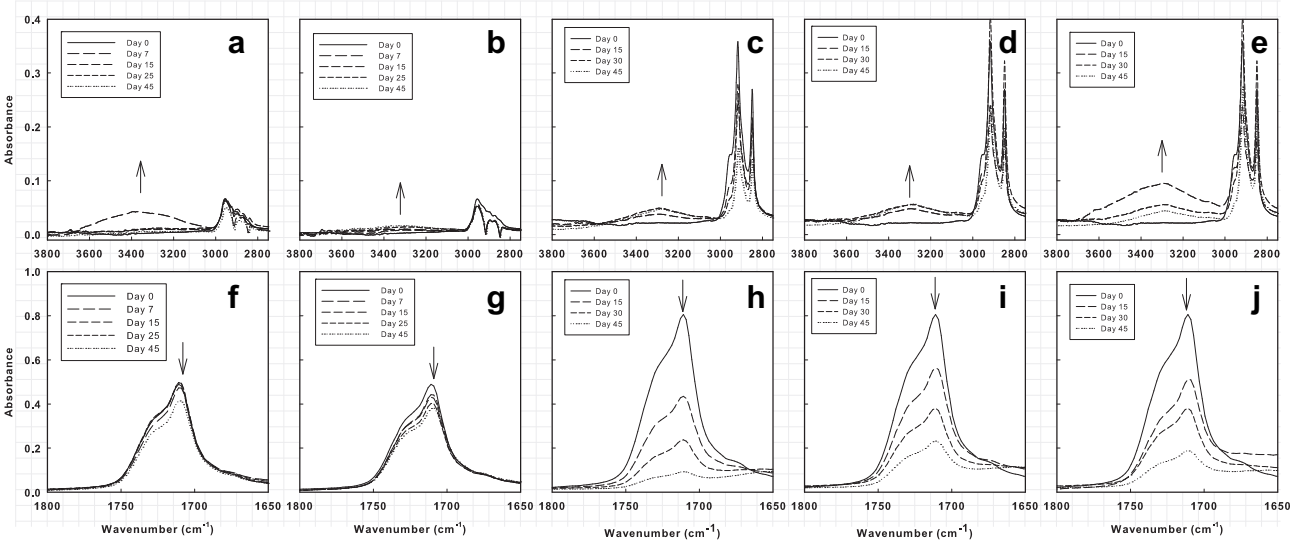

Fig. 7. FTIR absorbance spectra in the wavenumber range of 3800–2750 cm^{-1} of PBAT film in (a) phosphate buffer solution, (b) vermiculite, (c) manure compost, (d) food compost, and (e) yard compost; absorbance spectra in the wavenumber range of 1800–1650 cm^{-1} of PBAT film in (f) phosphate buffer solution, (g) vermiculite, (h) manure compost, (i) food compost, and (i) yard compost.

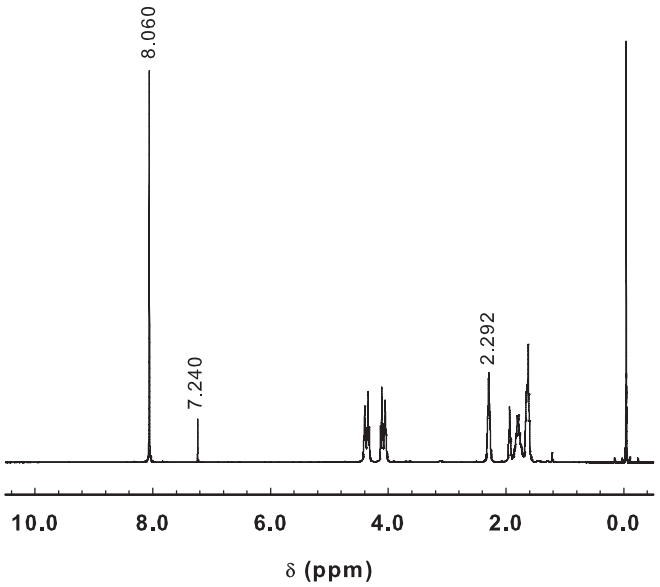

Fig. 8. ^{1}H NMR spectrum of PBAT with aromatic peak at $\delta = 8.06$ ppm, deuterated chloroform at $\delta = 7.24$ ppm, and −OCO**CH$_2$**− (adipate fraction) at $\delta = 2.29$ ppm.

$$f_{BT} = \frac{A_{8.06}}{A_{2.29} + A_{8.06}} \quad (3)$$

Initially, the PBAT film had a f_{BA}/f_{BT} ratio of 0.59/0.41, but as the hydrolysis proceeded and reduction of M_n was observed, the pattern of decreased f_{BA} and increased f_{BT} was observed in both buffer solution and vermiculite, with the change being more gradual in vermiculite than in the buffer solution (Fig. 9). In the phosphate buffer solution, the pattern of decreased f_{BA} and increased f_{BT} continued until the reverse pattern occurred (increased f_{BA} and decreased f_{BT}), which suggested that at this point the BT domains started undergoing hydrolysis. Therefore, this indicates that the ester groups in the soft aliphatic BA section are more susceptible to hydrolysis, consequently making the BA sections more susceptible to biodegradation than the hard aromatic BT sections, as previously suggested by Kasuya et al. [23], Abou-Zeid et al. [39], and Muller et al. [40]. Esterase (hydrolase) enzymes

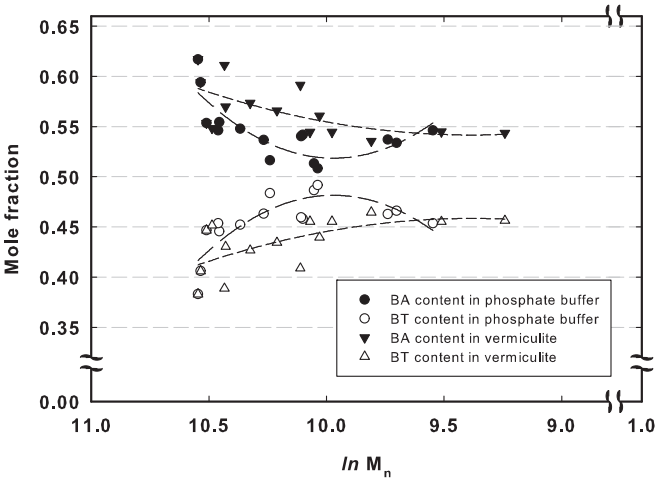

Fig. 9. Mole fraction of BA and BT content of hydrolyzed PBAT films in phosphate buffer or in vermiculite at 58 °C as a function of logarithmic reduction of molecular number (M_n).

are lipase type and enzymatic degradation rates can be dictated mainly by the mobility of the chain, i.e. the length of aromatic domains not the length of aliphatic counterparts [24,33,41–44].

Thus, there is a critical need to understand the effect of microbial population, family of microorganisms, and their enzymatic specificity in different microbial environments on the total biodegradation of biodegradable polyesters and their biodegradation rates. Compost with appropriate C/N ratio and CO_2 emission may not directly be a suitable testing media, due to lower total biodegradation of cellulose positive controls and different enzymatic specificity of microorganisms in composts. These results have implications for deployment of biodegradable polymers in commercial composting environments. There is a future need to include guidelines in current testing methodologies to determine the family and the quantity of microbial populations in the compost environment.

4. Conclusions

Biodegradation of biodegradable polyesters such as PBAT was strongly influenced by the total microbial activity of the exposure environments, which was monitored by CO_2 emissions or C/N ratio. PBAT degraded more and faster in manure compost than in yard or food waste composts. The ester group in the aliphatic BA unit was more susceptible to hydrolysis than that in the aromatic BT unit. Consequently, the BA unit was more vulnerable to hydrolysis and biodegradation. During biodegradation, increases in PBAT crystallinity were observed, which indicated that the amorphous regions biodegraded faster than the crystalline regions.

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