

# Biodegradable green composites from bioethanol co-product and poly(butylene adipate-co-terephthalate)

Sudhakar Muniyasamy<sup>a</sup>, Murali M. Reddy<sup>a</sup>, Manjusri Misra<sup>a,b</sup>, Amar Mohanty<sup>a,b,\*</sup>

<sup>a</sup> Bioproducts Discovery & Development Centre (BDDC), Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, N1G 2W1, ON, Canada

<sup>b</sup> School of Engineering, Thornbrough Building, University of Guelph, Guelph, N1G 2W1, ON, Canada

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## ABSTRACT

This work summarizes the development of green composites from distillers dried grains with solubles (DDGS), a major co-product of the corn ethanol industry, and poly (butylene adipate-co-terephthalate), PBAT. The composites were fabricated using a twin-screw micro extruder with micro injection molding. The DDGS was pretreated, yielding a noticeable improvement in the degradation onset temperature of DDGS from 140 to 240 °C, which was shown by thermogravimetric analysis (TGA). The composite fabricated with pretreated DDGS showed better mechanical and thermal properties compared to the composite with non-treated DDGS. TGA analysis showed that the maximum degradation rate shifted slightly to lower values with the increase of filler content. Differential scanning calorimetry (DSC) analysis showed that the glass transition temperature ( $T_g$ ) of the matrix increased slightly with an increase in filler content, indicating that filler did not lead to significant change in crystalline structure. The biodegradability study showed that, PBAT/treated DDGS composite was found to be the most bio-susceptible material, being totally biodegraded. This suggests that DDGS domains were preferentially attacked by microorganisms, and increased the percentage of biodegradation. All composite materials showed a degree of biodegradation similar to the biodegradation rate of DDGS and cellulose. This study showed that the incorporation of DDGS into a PBAT matrix can produce green composites with enhanced biodegradability.

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## 1. Introduction

Distillers dried grains with solubles (DDGS) is the major co-product of the ethanol fuel industry. The production of DDGS is increasing dramatically in the United States, where production was 12 million tons in 2006, and 32.5 million tons by 2010 ([www.ethanolrfa.org](http://www.ethanolrfa.org), 2012). DDGS is a rich source of protein (26.8–33.7% dry weight basis), carbohydrates (39.2–61.9% including fibers), oils (3.5–12.8%), and ash (2.0–9.8%). As such, the primary use of DDGS to date has been in animal feed applications. However, there are limits to its dietary intake by livestock based on nutritional requirements (Hanson et al., 2012; Kim et al., 2008; Li et al., 2010; Robinson et al., 2008; Xu et al., 2009). Simultaneously, the ethanol industry has experienced record growth, with annual production volumes increasing by an average of greater than 20% over the past four years, and greater than 10% over the past 20 years (Robinson et al., 2008). There is a need, therefore to find alternate uses and new market channels for ethanol-derived DDGS. Currently,

most research focuses on the value of using protein and cellulose for developing bio-based materials and composites. The use of biodegradable plastics instead of traditional non-biodegradable materials may offer a solution to environmental problems caused by biostable plastic waste (Iovino et al., 2008). Several potential alternatives have been proposed for using biodegradable polymer blended with low-cost organic fillers, with the prospect of extracting higher value protein and cellulose from DDGS and other fillers for biocomposites and bioadhesives (Tatara et al., 2009; Wu and Mohanty, 2007; Li and Susan Sun, 2011).

In recent years, materials called biocomposites, which are composed of agricultural residues and biodegradable polymers, have become very attractive materials (Chen et al., 2011; Chivrac et al., 2009; Liu et al., 2004; Reddy and Yang, 2011; Rosa et al., 2009a,b; Song et al., 2008; Li and Susan Sun, 2011; Zhao et al., 2010) in terms of their properties and biodegradability after their uses. 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 have energy recovered through composting into soil amendment products. Therefore, much attention has been given to environmentally degradable polymeric materials and plastics. For such novel materials to make claims to be “environmentally friendly”, it must be proven, using scientifically based and accepted methods, that they

\* Corresponding author at: Bioproducts Discovery & Development Centre (BDDC), Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, N1G 2W1, ON, Canada. Tel.: +1 519 824 4120x56664; fax: +1 519 763 8933.  
E-mail address: [mohanty@uoguelph.ca](mailto:mohanty@uoguelph.ca) (A. Mohanty).

undergo biodegradation under natural environmental conditions, such as in landfills and compost. According to ISO and ASTM (Ohtaki et al., 1998; Pagga et al., 1995), composting is a process where biodegradable materials undergo biological degradation to yield carbon dioxide, water, inorganic compounds and biomass, at a rate consistent with other known compostable materials, and leaving no visually distinguishable or toxic residues.

In this study, we explore the feasibility of using DDGS with poly (butylene adipate-co-terephthalate), PBAT. PBAT is an aliphatic–aromatic polyester with properties comparable to many fossil–oil-based plastics, and it is biodegradable (compostable). This material can be used for packaging, agriculture and disposable bags, but its utilization is rather limited due to its high production cost. A possible problem solving strategy is the preparation of blends of PBAT with inexpensive, readily available and biodegradable materials, such as starch and polysaccharides, which are derived from agricultural plants and therefore susceptible to biological attack (Alvarez et al., 2006; Kasuya et al., 2009; Rosa et al., 2009b). The biodegradation of biodegradable polyesters such as PLA and PBAT in compost or soil is affected by both biotic and abiotic factors of the environment, including temperature, moisture, pH, bio-surfactants and enzymes. Their biodegradation is also affected by polymer characteristics, such as chain flexibility, crystallinity, regularity and heterogeneity, functional groups and molecular weight (Witt, 2001).

The aim of this work was to investigate the aerobic biodegradation of biocomposites prepared using DDGS and PBAT. The biodegradability of these composites was correlated with the biodegradability of its individual constituents in the presence of compost, using standard test methods designed for biodegradable plastics (ASTM D5338). To the best of our knowledge, very few studies have been made on the biodegradability of such novel composites. Biodegradation studies were based on the estimation of the percentage of mineralization (i.e. measuring the evolved carbon dioxide) of the material's carbon content versus time. To monitor and describe the materials degradation, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform spectroscopy (FT-IR) were also employed.

## 2. Experimental

### 2.1. Materials

The PBAT, poly(butylene adipate-co-terephthalate) pellets – Biocose 2003 were obtained from Zhejiang Hangzhou Xinfu Pharmaceutical Co., Ltd., China. The DDGS was obtained from GreenField Ethanol Inc., Chatham, Canada.

### 2.2. Methods

#### 2.2.1. Pretreatment of DDGS

The pretreatment of DDGS was carried out by stirring 100 g of as-received DDGS with 1.5 L of deionized water for 30 min at room temperature as reported earlier (Zarrinbakhsh et al., 2011). After stirring, the DDGS was filtered through a 0.1 mm-thickness sieve and dried overnight at room temperature. This pretreated DDGS (wwDDGS) was used for the preparation of composites.

#### 2.2.2. Processing of composite materials

The composites were prepared with PBAT pellets and DDGS filler (untreated and pretreated DDGS) using a twin-screw micro extruder. Approximately 12 g of PBAT and DDGS mixture was fed into a twin-screw micro extruder (DSM Research, The Netherlands), and processed at a temperature of 160 °C for a residence time of 3 min, with a screw speed of 100 rpm. The molten mixture was collected and injection molded to make various test specimens using

a micro 12-cc injection molding machine (DSM, The Netherlands). PBAT and DDGS (untreated and pretreated) were dried for 24 h prior to processing, at 80 °C in a ventilated oven to eliminate moisture from the material. After processing, all test samples were stored at room temperature, and characterized after 48 h.

### 2.3. Characterization

#### 2.3.1. Mechanical properties

Tensile and flexural properties of the composites were measured using a Universal Testing Machine, Instron 3382, according to ASTM D638 and ASTM D790 standards, respectively. System control and data analysis were performed using Blue Hill software. The notched Izod impact strength was measured with a TMI Monitor Impact Tester (model no. 43-02-01) according to ASTM D256, using a pendulum of 5 ft lb.

#### 2.3.2. Dynamic mechanical analysis (DMA)

A DMA Q800 from TA Instruments was used to evaluate the storage modulus of rectangular samples, with dimensions of 3.2 mm × 12.5 mm × 65 mm. The experiments were performed from –50 to 100 °C, with a temperature ramp rate of 3 °C/min. A dual cantilever clamp was used, at a frequency of 1 Hz and an oscillating amplitude of 15 μm.

#### 2.3.3. Thermal analysis

**2.3.3.1. Differential scanning calorimetry (DSC).** Heat flow as a function of temperature was studied using a differential scanning calorimeter (DSC Q 200, TA Instruments, Inc.) using the heat–cool–heat setting. Nitrogen was used as purge gas during the experiment. The data was collected by heating the specimen from –50 to 150 °C at a constant heating and cooling rate of 10 °C/min. The data were analyzed using Universal Analysis software (TA Instruments).

**2.3.3.2. Thermogravimetric analysis (TGA).** Thermogravimetric analysis was carried out using a thermogravimetric analyzer (TGA Q500, TA Instruments, Inc.). The samples were scanned from room temperature to 600 °C, at heating rate of 20 °C/min, in a nitrogen atmosphere.

#### 2.3.4. Fourier transform infrared spectroscopy (FT-IR)

A Thermo Scientific Nicolet™ 6700 FTIR spectrometer in attenuated total reflection infrared (ATR-IR) mode, with a resolution of 4 cm<sup>–1</sup> and a number of 32 scans per sample, was used to obtain the spectra.

#### 2.3.5. Density

The densities of the polymer and the composites were measured using an electronic densimeter MD-300S (Alfa Mirage, Japan). The density is measured according to the Archimedes principle.

#### 2.3.6. Carbon and nitrogen analysis

Total carbon and nitrogen content of the samples was evaluated through elemental analysis at Laboratory Services, University of Guelph.

### 2.4. Biodegradation studies

#### 2.4.1. Simulated aerobic composting set-up

Biodegradability was tested using a simulated laboratory composting set-up, designed to satisfy the performance requirements of standard ASTM D5338-98 (ASTM, 2004). Samples were milled to fine particles with an average size of ≥ 100 μm, using manual grinding in a liquid nitrogen environment. Three-month-old organic

**Table 1**  
Chemical properties of the compost.

| Analysis                          | Compost |
|-----------------------------------|---------|
| Total dry solids (%) <sup>a</sup> | 48      |
| Volatile solids (%) <sup>b</sup>  | 53      |
| pH of compost solution            | 7.5     |
| Total organic carbon amount (%)   | 30.6    |
| Total nitrogen amount (%)         | 3.6     |
| C/N ratio                         | 8.5     |

<sup>a</sup> The amount of solids obtained by taking known volume of compost and drying at about 105 °C for 10 h.

<sup>b</sup> The amount of solids obtained by subtracting the residue of a known volume of compost after incineration at about 550 °C.

manure compost was kindly supplied by Sunshine Environmental (Orangeville, Canada) and used as the compost medium. The compost was sieved to a consistent size of <0.8 cm. Its physical and chemical characteristics were determined according to the ASTM D6400 standards before use in the biodegradation experiments, and are shown in Table 1. Activity of the compost was measured as required by the standard method, and the compost produced 65 mg of carbon dioxide per gram of volatile solids over the first 10 d of the test.

#### 2.4.2. Biodegradation tests: apparatus and procedure

Biodegradation tests on polymeric composites and their base materials were carried out in a laboratory-scale composting experiment, according to ASTM D5338-98 (ASTM, 2004). Glass flasks of approximately 2 L internal volume were used as the bioreactors. The compost and test materials in each flask were mixed in the ratio of 6:1 (w:w dry mass). In each test, a series of vessels (in triplicate) containing compost, the polymeric material and/or their constituents were prepared, along with a control (compost without the polymeric materials). Carbon dioxide produced during the biodegradation process was trapped in 500 mL of 0.5 M KOH. The CO<sub>2</sub> traps were changed every 2–3 d, depending on the degradation rate of the sample material. A 10 mL aliquot of KOH from each trapping solution was titrated with 0.5 M HCl, using phenolphthalein indicator. The total amount of CO<sub>2</sub> produced by the sample was calculated with reference amount of CO<sub>2</sub> produced by the control flask. To provide aerobic conditions during the test, a continuous air-supply system was used for each composting vessel. Air was bubbled through distilled water to maintain relative moisture content of at least 50% in the compost inoculum. This set-up was incubated at a constant temperature of 58 ± 2 °C, and maintained throughout the 200 d of the experiment. The glass flasks were shaken and weighed weekly to ensure proper aeration and mixing of the bio-waste.

According to ASTM standard (ASTM, 2004), the theoretical amount of carbon dioxide produced in each flask (ThCO<sub>2</sub> in g per vessel) which can be produced by total oxidation of incubated materials can be calculated by the following expression:

$$\text{ThCO}_2 = M_{\text{tot}} \times C_{\text{tot}} \times \frac{44}{12} \quad (1)$$

where  $M_{\text{tot}}$  is the total dry amount of constituent or plastic materials (g) added to the compost,  $C_{\text{tot}}$  is the relative amount of total organic carbon (g) in the total dry solids, 44 is the molar mass of carbon dioxide and 12 is the atomic mass of carbon.

A biodegradation curve was obtained by plotting released CO<sub>2</sub> (%) versus exposure time. Biodegradation was calculated as the percentage of carbon in the polymer mineralized as CO<sub>2</sub> according to the expression:

$$\text{Biodegradation (\%)} = \frac{(\text{CO}_2)_s - (\text{CO}_2)_c}{\text{ThCO}_2} \times 100 \quad (2)$$

where (CO<sub>2</sub>)<sub>s</sub> and (CO<sub>2</sub>)<sub>c</sub> are the amount of CO<sub>2</sub> produced in the sample and in the control, respectively.

### 3. Results and discussion

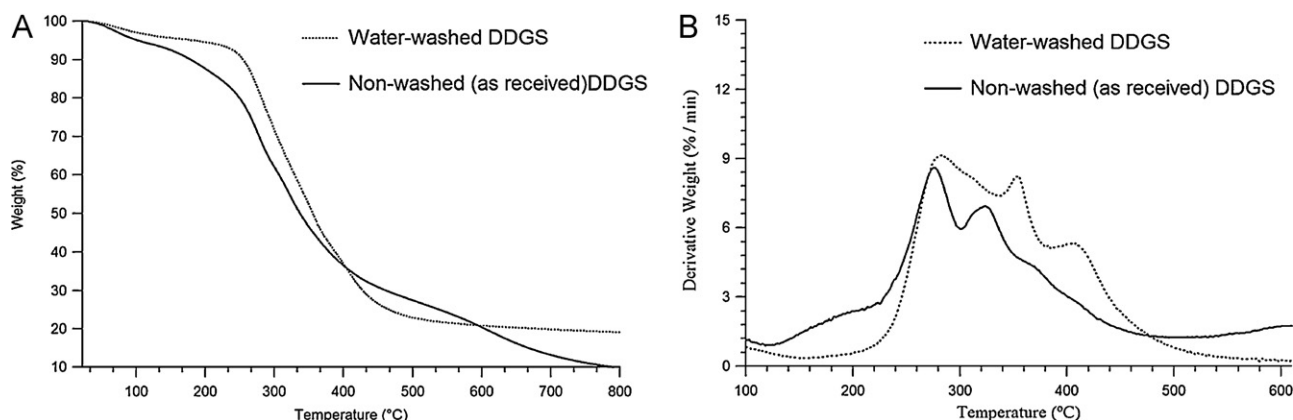
#### 3.1. Surface pretreatment of DDGS

DDGS without any pretreatment has a very low thermal stability, which limits its application as a filler for polymer biocomposite processing. Since dried samples were used for the experiments, no significant weight loss was observed below 100 °C in all the materials analyzed (Fig. 1). DDGS has two decomposition mechanisms: the initial step, between 150 and 230 °C, corresponding to the thermal degradation of hemicelluloses, and the second step, between 230 °C and 360 °C, which corresponds to the thermal degradation of cellulose (Morey et al., 2009). However, with the water washing, the decomposition pattern for DDGS was changed. This could be due to the elimination of many water soluble components, thereby shifting the weight loss curve toward higher temperatures. The weight loss curves with the increase in temperature in water washed DDGS compared to untreated DDGS are shown in Fig. 1. It can be seen that there significant difference in the thermal stability of the fillers due to their compositional differences.

#### 3.2. Characterization of composite materials

##### 3.2.1. Mechanical properties

Untreated and treated DDGS (bio-based filler) and PBAT based composites were investigated in detail. Fig. 2 shows the stress–strain plot of neat PBAT and PBAT–DDGS composites. These



**Fig. 1.** TGA (a) and DTGA (b) curves obtained for untreated and water-washed DDGS.

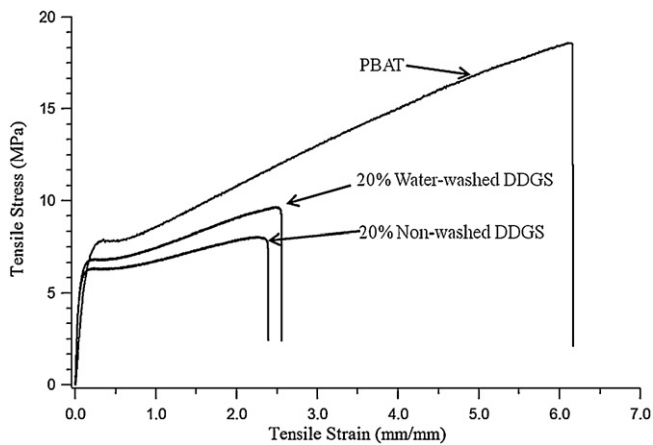


Fig. 2. Stress–strain curve of PBAT and its composites with DDGS.

results suggested there was ductile behavior with the strain hardening phenomenon. However, the maximum stress values of the composites differed by an order of three compared to the neat PBAT polymer. These differences could be due to the a low compatibility between the polymer and fillers. It can be observed that the water-washed DDGS displayed a better resistance to applied stress in comparison to the unwashed DDGS. These results suggested that water-washing treatment helps in removing the water soluble fractions from DDGS that are not compatible with polymer matrix, or low molecular weight fractions. Fig. 3 and Table 2 show the mechanical properties of the PBAT and PBAT–DDGS composites. A similar trend has been previously observed by the incorporation of DDGS into PHBV based bioplastic (Zarrinbakhsh et al., 2011). It can be seen from Fig. 3 that with the addition of DDGS, tensile strength decreased, whereas modulus values improved, due to non-interacting filled polymer systems without any compatibilization (Rosa et al., 2009a). It is well known that the tensile properties

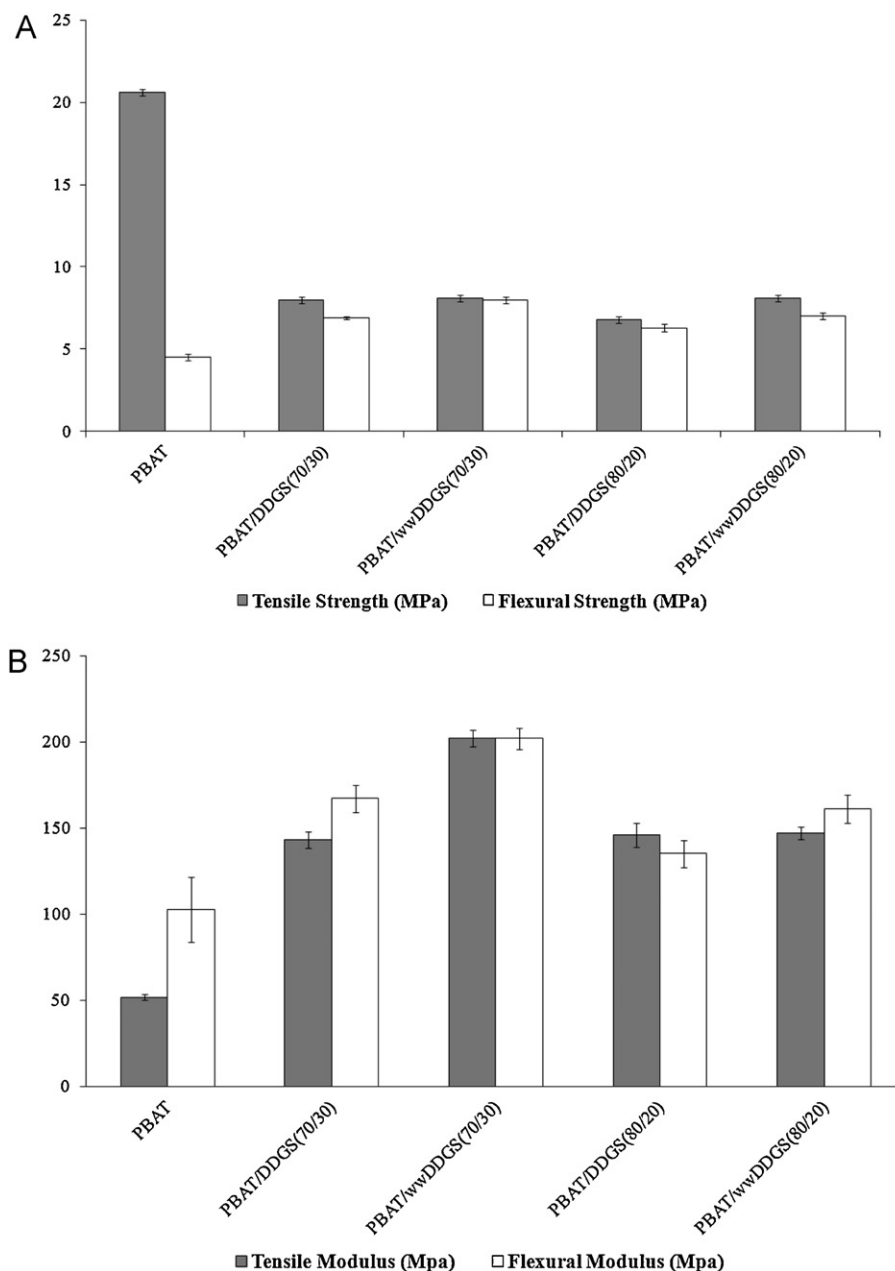


Fig. 3. Mechanical properties: (a) tensile strength and flexural strength; (b) tensile modulus and flexural modulus of the composites containing untreated and treated DDGS.



**Table 2**  
Mechanical properties of the composites containing untreated and treated DDGS.

| Composite                        | Elongation (%) | Impact (J/m) |
|----------------------------------|----------------|--------------|
| PBAT                             | 631 ± 26.0     | Not breaking |
| 80/20 (PBAT/DDGS) <sup>a</sup>   | 254 ± 11.8     | 188.4 ± 30.5 |
| 80/20 (PBAT/wwDDGS) <sup>b</sup> | 284 ± 17.4     | 217.6 ± 11.3 |
| 70/30 (PBAT/DDGS) <sup>a</sup>   | 182 ± 6.4      | 180.1 ± 17.0 |
| 70/30 (PBAT/wwDDGS) <sup>b</sup> | 184 ± 7.9      | 142.9 ± 11.7 |

<sup>a</sup> Untreated DDGS as received as such from green field ethanol (Canada).

<sup>b</sup> Pretreated (water-washed) DDGS from the experimental procedure.

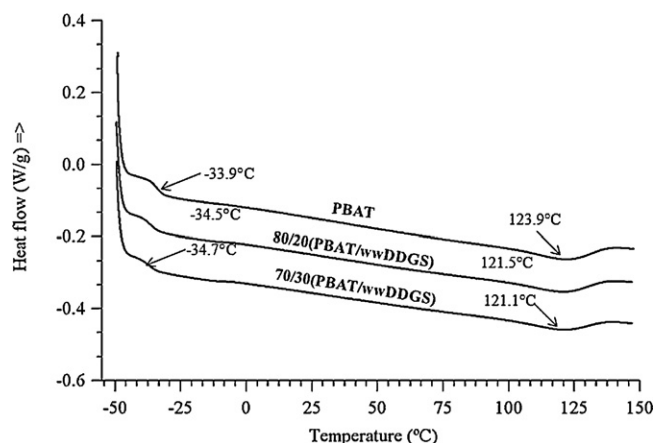
**Table 3**  
Dynamic mechanical analysis (DMA) of the composites containing untreated and treated DDGS.

| Sample                           | Storage modulus (GPa) |       |       |
|----------------------------------|-----------------------|-------|-------|
|                                  | 25 °C                 | 50 °C | 75 °C |
| PBAT                             | 117.9                 | 70.6  | 32.8  |
| 80/20 (PBAT/DDGS) <sup>a</sup>   | 190.5                 | 112.4 | 58.8  |
| 80/20 (PBAT/wwDDGS) <sup>b</sup> | 185.8                 | 116.4 | 67.1  |
| 70/30 (PBAT/DDGS) <sup>a</sup>   | 237.3                 | 152.2 | 75.9  |
| 70/30 (PBAT/wwDDGS) <sup>b</sup> | 243.1                 | 156.2 | 90.6  |

<sup>a</sup> Untreated DDGS as received as such from green field ethanol (Canada).

<sup>b</sup> Pretreated (water-washed) DDGS from the experimental procedure.

of polymer biocomposites depend on the strength and modulus of the filler. However, in our study, only modulus values have increased with an increase in DDGS loading. The decrease in the tensile properties can be attributed to the poor adhesion of DDGS to the polymer matrix, leading to the absence of involuntary anchoring in the system. In other words, there was no effective stress transfer mechanism in the composites between the matrix and the fillers (Zarrinbakhsh et al., 2011). Also, the improvement in modulus values is an indication of good dispersion of the DDGS particles in the PBAT matrix, which offers better resistance to the applied stress. It can be seen that the standard deviation of the moduli is very negligible, indicating the optimization of the processing conditions. Table 3 shows the impact and percent elongation of the PBAT and its biocomposites, which measures the energy required to break specimen completely. This impact energy value is a combination of crack initiation followed by crack propagation phenomenon. In our work, we have found that the impact strength and percent elongation values have decreased as the DDGS content increased (Table 2). It is well known that the impact strength of composites depends on various factors, such as filler-to-matrix adhesion, toughness of the matrix, the filler alone, crystalline morphology, and even distribution of fillers (Cheesbrough et al., 2008; Rosa et al., 2009a). The composites prepared in this study revealed that the



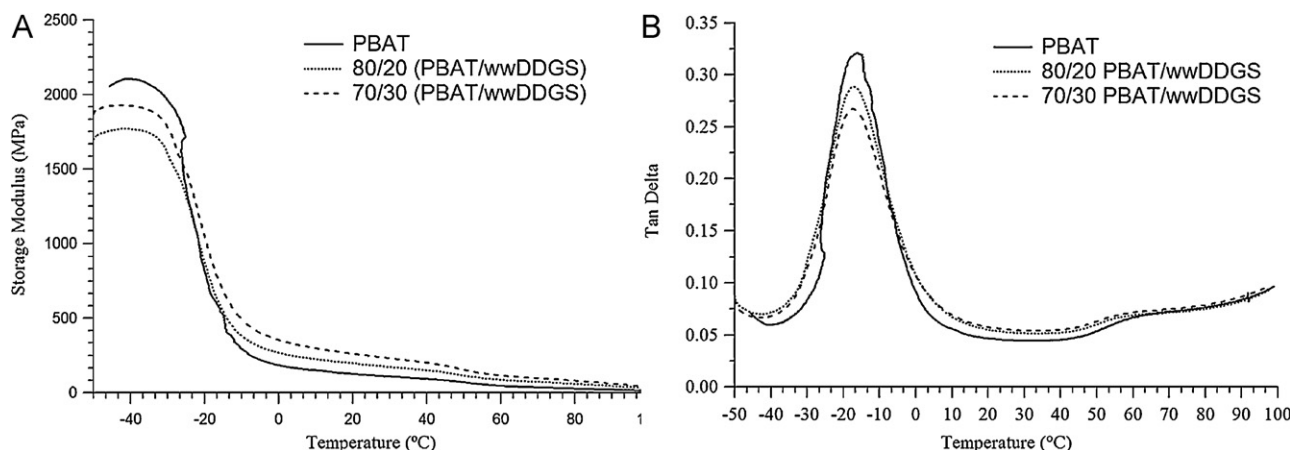
**Fig. 5.** DSC second-heating curves of the PBAT-DDGS biocomposites.

fillers were impeding the mechanism of energy absorption, rather than improving the energy absorption.

The storage modulus and tan delta of the PBAT-DDGS composites, as a function of the temperature, is shown in Fig. 4. It can be seen that storage modulus values decreased with increasing temperature for both the polymer matrix and its composites. This could be due to the fact that the PBAT chain mobility has increased at higher temperatures, leading to softening behavior and thus decreasing the modulus values. Also, it was noticed that the modulus values are higher for the DDGS composites than for neat PBAT. This may be due to the fact that DDGS particles are stiffer than PBAT itself. The increase in storage modulus with an increasing quantity of DDGS in the biocomposite could be due to physicochemical interaction, intramolecular bonds, and a crystalline structure in the biocomposite, which improves the reinforcement imparted by the DDGS filler that allowed stress transfer from the matrix to the DDGS. Fig. 4b shows that the height of the tan delta peak decreased with the presence of DDGS particles. This is due to the fact that there is no restriction to the chain motion in the case of pure PBAT matrix, while the presence of DDGS particles hinders the chain mobility of the composites. This restriction of chain mobility results in a reduction of the sharpness and height of the tan delta peak.

### 3.2.2. Thermal properties

The DSC analysis of the PBAT-DDGS composites showed slightly increased glass transition temperatures ( $T_g$ ) of the matrix with the increase of filler content, indicating that the filler did not lead to significant changes in crystalline structure (Fig. 5). Fig. 6 shows TGA



**Fig. 4.** Storage modulus (a) and tan delta (b) of the PBAT-DDGS biocomposites as a function of temperature.

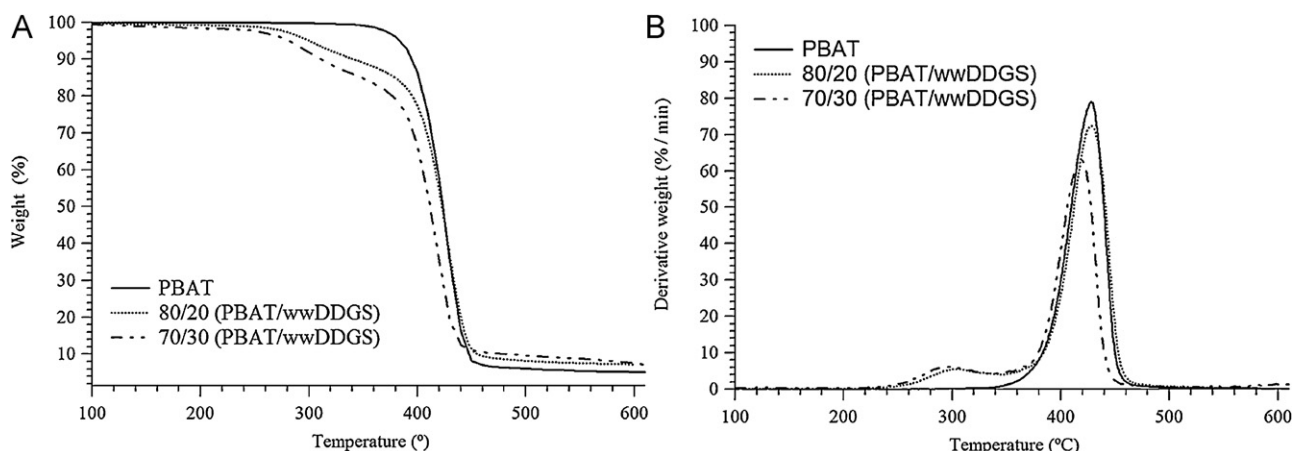


Fig. 6. TGA (a) and DTGA (b) curves obtained for DDGS/PBAT composites with 0%, 20% and 30% pretreated DDGS.

and DTGA curves obtained for different biocomposites (0, 20% and 30% pretreated DDGS). The temperature at the maximum degradation rate was shifted to lower values as the filler content increased because of the decrease in PBAT, which is much more thermally stable than pretreated DDGS. In addition, the presence of DDGS filler decreased the thermal stability in comparison to that of the raw matrix, because of the lower degradation temperature of pretreated DDGS fillers. The same behavior was observed for composite materials in the work of Rosa et al. (2009a) and Li and Susan Sun (2011). In our work, we have adopted water washing techniques to remove the components that are water soluble, and this has helped in improving the thermal stability of the DDGS. Fig. 1 shows clearly that the initial degradation of DDGS has improved from 140 °C to 240 °C after water washing. This has helped us to obtain better composites, with improved ductility and bonding, as observed in the mechanical properties discussed in the earlier sections.

### 3.2.3. FT-IR characterizations

The structural characterizations of neat PBAT, composite materials and DDGS were done using FT-IR spectroscopy (Fig. 7). The DDGS broad-centered peak at  $3364\text{ cm}^{-1}$  was attributed to the stretching vibration of  $\text{—OH}$  and  $\text{—NH}$  from carbohydrates and protein, the peak at  $2930\text{ cm}^{-1}$  to the stretching of  $\text{—CH}$  from lipids, the peak at  $1654\text{ cm}^{-1}$  to the amide absorption of corn protein, and the peaks at the regions of  $1250\text{--}1000\text{ cm}^{-1}$  to carbohydrates (Giuntoli et al., 2009). These results confirm that DDGS is composed of carbohydrates, protein, and lipids. After thermal compounding of PBAT and pretreated DDGS, the peak of  $\text{—N=C=O}$  in the biocomposite was slightly influenced (Fig. 7). Moreover, the strong absorption peak of  $\text{—OH}$  and  $\text{—NH}$  group becomes very weak during thermal compounding. It is not influenced by the filler content of pretreated DDGS (20 and 30%), which is particularly overlapped with amide and  $\text{—C=O}$  absorption (ester and keto-carbonyl).

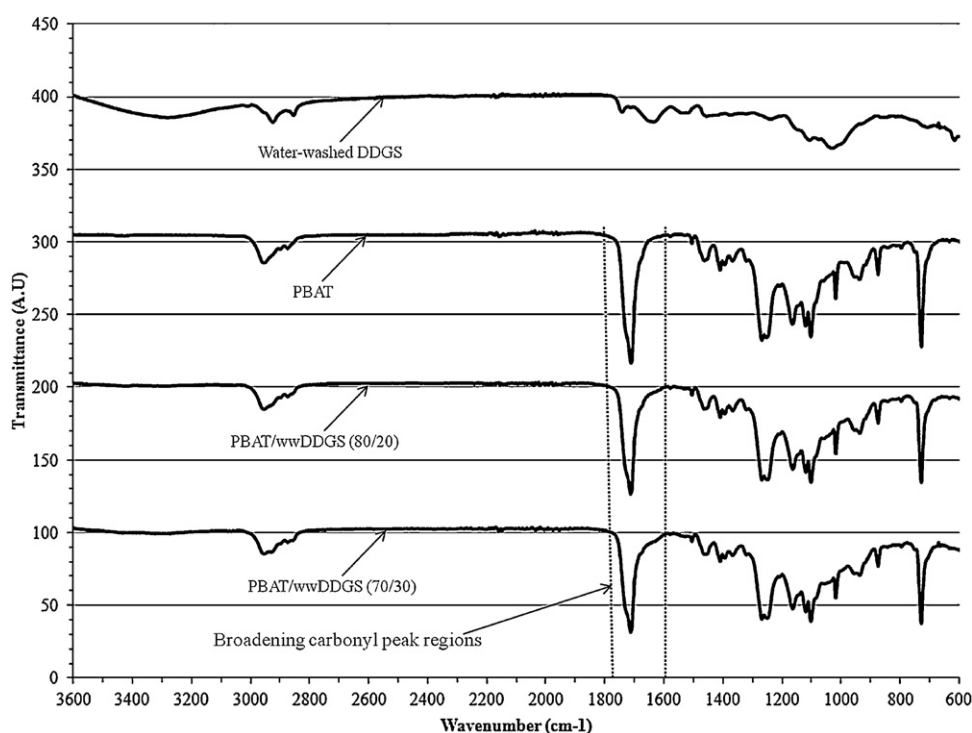
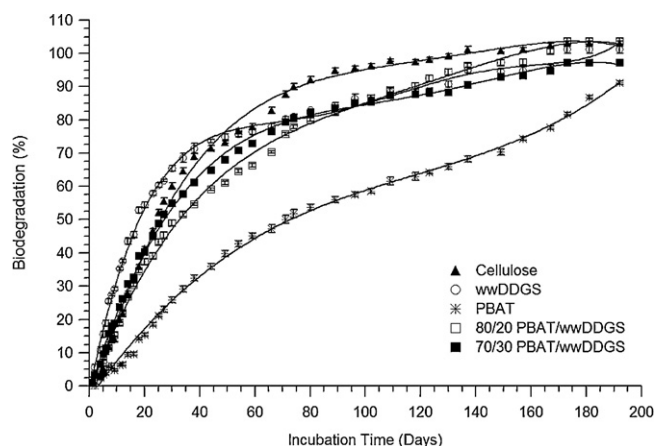


Fig. 7. FT-IR spectra obtained for DDGS/PBAT composites with 0%, 20% and 30% pretreated DDGS.

**Table 4**  
Biodegradability of composites and its constituents.

| Sample              | Carbon (%) | Carbon (g) | ThCO <sub>2</sub> (g) | Biodegradation (%) <sup>a</sup> |
|---------------------|------------|------------|-----------------------|---------------------------------|
| Cellulose           | 42.30      | 21.2       | 77.7                  | 103.3                           |
| wwDDGS              | 39.4       | 19.7       | 72.2                  | 101.2                           |
| PBAT                | 63.90      | 32.0       | 117.2                 | 92.0                            |
| 80/20 (PBAT/wwDDGS) | 62.40      | 31.3       | 114.6                 | 103.8                           |
| 70/30 (PBAT/wwDDGS) | 61.00      | 30.5       | 111.8                 | 97.3                            |

<sup>a</sup> Biodegradation refers to the percentage after incubation period of 200 d.



**Fig. 8.** Biodegradation of microcrystalline cellulose (positive reference), wwDDGS, 80/20 (PBAT/wwDDGS), 70/30 (PBAT/wwDDGS) and PBAT under simulated aerobic compost (ASTM D5338).

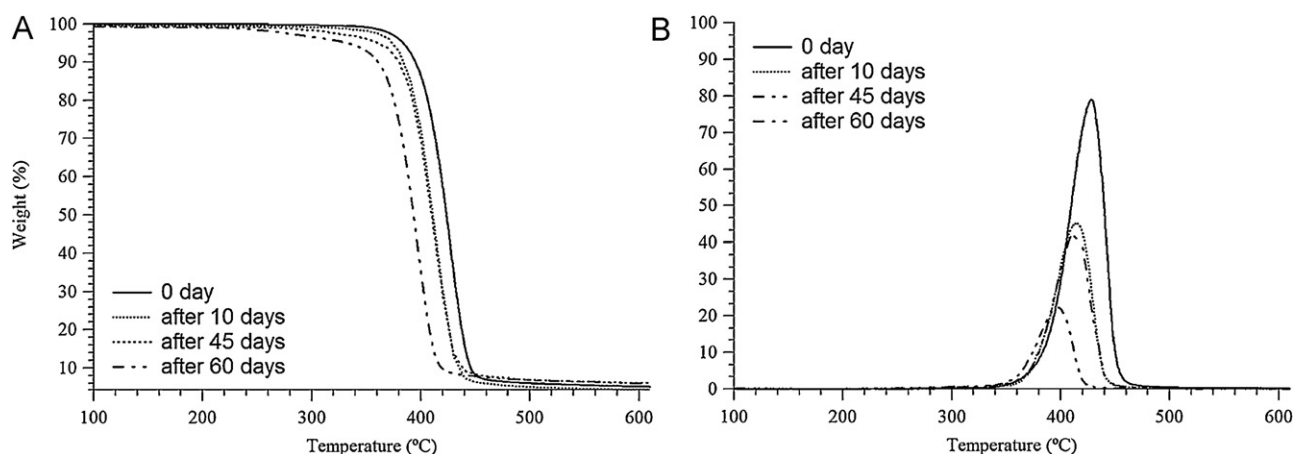
### 3.3. Biodegradation of composite materials

The total carbon dioxide evolved during the 200 d period of incubation was measured by manual titration, and its values are reported as percentages of the theoretical CO<sub>2</sub> in Table 4. The curves reported in Fig. 8 clearly indicate a different response of the investigated materials to compost biodegradation. After 200 d of incubation, standard cellulose powder and DDGS were quite completely transformed into CO<sub>2</sub> and cell biomass, and an extreme deterioration of the initial pieces was visually evident. An important criterion regarding the quality of the inocula is the biodegradation of the positive reference of cellulose. The standard cellulose powder (microcrystalline cellulose) used as reference material and was degraded 70% within 45 d of incubation as shown in Fig. 8 as prescribed in the ASTM D5338. The other natural origin material, DDGS, degraded readily. In particular, the lag phase

was higher compared to that of cellulose. The initial lag phase biodegradation of DDGS was influenced by the material composition; DDGS contains about 26.8–33.7% protein (dry weight basis). Moreover, high-moisture conditions (50–60%) apparently provide a more suitable environment for microbial growth and proliferation by causing cells to secrete enzymes (Imam and Gordon, 2002). In this regard, environmental factors such as water, oxygen, redox potential, nutrients, pH and temperature could influence the enzyme catalysis of plant-based polymers (Imam and Gordon, 2002).

A completely different behavior was observed for biodegradation of the neat PBAT polymer. A microbial lag phase, starting at approximately 18 d was observed, and followed by an exponential phase after 60 d of incubation (Fig. 8). As previously studied (Mohanty and Nayak, 2012), PBAT material undergoes biodegradation under composting conditions, and reached 80% biodegradation in 180 d. In our studies, similar degradation behavior was observed, and the rate of biodegradation about 90% within 180 d. It is noteworthy that biodegradation behaviors of the biocomposite materials containing pretreated DDGS 20 and 30%, were very close to that of natural materials such as cellulose and DDGS. The data pertaining to the biodegradability of biocomposites clearly indicate that DDGS filler had a significant influence on the biodegradability of the PBAT matrix.

During composting tests, the neat PBAT particles were observed after 10, 45 and 60 d of incubation in the test flask and it was carefully recovered in order to evaluate the effect of mineralization on the thermal properties and structural characterization of the material. The recovered PBAT material particles were easily distinguishable, and further washed with deionized water and dried in an oven at 40 °C for 4 h. In the case of the biocomposite material, recoverable particles were not distinguishable after 10 d of incubation. The TGA analyses of neat PBAT showed that after 10, 45 and 60 d of composting tests, the degradation onset temperature reduced from 368 to 353, 311 and 253 °C, respectively (Fig. 9). The derivative peak of TGA clearly indicated that 80% weight reduction of PBAT was observed after 60 d incubation. These results indicate



**Fig. 9.** TGA (a) and DTGA (b) curves of PBAT before and after composting for 10, 45 and 60 d.

that composting microbial systems and conditions appeared to provide a very suitable environment for the biodegradation of PBAT material. Moreover, due to the mechanism of microbial activity, hydrolysis has a substantial influence on biodegradation and the rate of degradation of biodegradable polyester such as PBAT, since hydrolysis is one of the initial processes of biodegradation (Kale et al., 2007; Kasuya et al., 2009; Lucas et al., 2008). It is generally accepted that there is different enzymatic specificity in microorganisms for the degradation of cellulose and the biodegradable polymer PBAT in composting environments.

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. This correlates with the reduction of the carbonyl absorbance ( $1710\text{ cm}^{-1}$ ) of the material due to enzymatic hydrolysis (data not shown). There is a critical need to understand the effect of microorganism population, family of microorganisms and their enzyme specificity in different microbial environments on the ultimate biodegradation of neat PBAT and biocomposite materials based on DDGS. The biodegradation of PBAT biocomposite materials based on treated DDGS was strongly influenced by the addition of DDGS, in comparison to the neat PBAT polymer. Thermal analysis and structural characterization of PBAT matrix show that it is susceptible to enzymatic hydrolysis and biodegradation under composting conditions.

#### 4. Conclusion

In this study, the influence of untreated and pretreated DDGS on the mechanical, thermal, structural, and biodegradability properties of PBAT biocomposites were evaluated. The data indicated that an increase in DDGS filler content resulted in a decrease in tensile strength and elongation, but a significant improvement in modulus. It was found that the biocomposites with pretreated DDGS had a better improvement in their mechanical and thermal properties than biocomposites with non-treated DDGS. During composting tests, the presence of DDGS had a strong influence on the biodegradation of PBAT matrix, which was monitored by  $\text{CO}_2$  emissions. The degree of biodegradability of all composite materials was similar to that of natural materials, such as cellulose and DDGS. TGA and FT-IR analysis indicated the biodegradation of PBAT through enzymatic hydrolysis, followed by microbial assimilation. All of the results reported in this study indicated that the materials have a short survival time in biotic environments such as compost, and are therefore suitable for disposal in landfills after their use.

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