Biodegradable Pellets Based on Poly (3hydroxybutyrate-co-3-hydroxyvalerate)/Poly (vinyl alcohol)/Sugarcane Bagasse: Thermal and Biodegradable Properties

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Abstract-Bagasse is considered to be a by-product after milling process of sugarcane stalk. In the study, sugarcane bagasse was used as filler in the composite which based on the poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and the polyvinyl alcohol (PVOH). A three-variable and three-level experimental design, including the levels of sugarcane bagasse content, the levels of maleic anhydride contents, and screw speed, was chosen for finding out the relationship between variables and the responses. Test samples were to investigate of their thermal properties by using Differential Scanning Calorimetry (DSC). thermogravimetric analysis and biodegradation test. The results demonstrated that the melting point (Tm) of extruded pellets ranged from 157.61 °C-168.40 °C as well as the decomposition temperatures (Td) which ranged from 242.02 °C-249.73 °C. The melting point and decomposition temperatures of the composite have been influenced by maleic anhydride contents. In biodegradability analysis according to Chinese National Standards (CNS) 14432 regulations, the biodegradability of the extruded pellets reached 72.8% after 32 days and 83.3% after 45 days, respectively.

Index Terms—extrusion technology, biodegradable plastic pellets, thermal properties

I. INTRODUCTION

The production and the use of Petrochemical-based polymers increase the problem of waste disposal since they are extremely stable. The growing interest in environmental impact has directed research to the development of degrade plastics [1], [2]. Biodegradable Plastics (BPs), which are renewable and can be degraded naturally by microorganisms of living organisms such as bacteria, yeast, and fungi, are gaining public commendation as a possible alternative to petroleumderived plastics. The research and development of environment-friendly polymer materials can be classified into two different categories based on the raw material used: degradable synthetic polymers and renewable natural polymers [3]. These materials offer a possible alternative to the traditional non-biodegradable polymers, especially in tough recycling.

Bio-based polymers are produced by bacterial fermentation processes by synthesizing monomers from renewable resources, including starch, cellulose, fatty acids, and organic waste. Poly (vinyl alcohol) (PVOH) is a hydrophilic biodegradable polymer, which is mainly composed of C-C bonds [4]. PVOH is also well known as a synthetic biodegradable polymer and performs excellent mechanical properties. Its biodegradability in various microbial environments has been reported [3], [5]. Poly (hydroxyalkanoates), or PHAs, have gained considerable attention in recent years as biodegradable alternatives to synthetic thermoplastics. The copolymers of 3hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV), named poly (3-hydroxybutyrate-co-3-hydroxyvalerate) or PHBV has been developed in an effort to improve its properties for industrial application [6]. Sugarcane bagasse fiber is the by-product of the sugar industry. Biodegradable composites reinforced with bagasse fiber, which used as filler have been studied for the improvement of the characteristics of material with a suitable design and processing techniques, to obtain materials with commercially useful properties [7].

There have been many studies on the use of biodegradable polymers for polymer blending, such as starch [1], PHAs [8], and Polycaprolactone (PCL) [9]. Also, in another approach various natural fibers such as wood fiber, bamboo fiber, wheat straw and coir fiber have used to broaden its applicability in various industries [10]-[13].

Up to now, there have been few reports on the degradation of PHBV/PVOH/ bagasse blends by extrusion technology. Therefore, the aim of this work was to investigate the thermal properties of PHBV/PVOH/ bagasse blended composite analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) as well as the effects of process parameters on thermal properties. Additionally, the biodegradability of the composite in controlled compost was investigated.

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II. MATERIALS AND METHOD

A. Materials

Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [Y1000, [5% Hydroxyvalerate (HV), purity of 98.8%] was supplied by Chinese Tianan Biologic Material Co., Ltd. Poly (vinyl alcohol) (PVOH) was obtained from the Chang Chun Petroleum Chemistry Co. Ltd. Sugarcane bagasse was obtained from Hong Chi Co., Ltd. Triethyl citrate (TEC) was used as biodegradable plasticizer for PHBV from Sigma-Aldrich Co. Glycerol (AR grade) and Maleic Anhydride (MA) was obtained from Sigma-Aldrich Co.

B. Experimental Design and Processing Condition

Three independent variables and three-level Box-Behnken Design (BBD) [14], including the levels of sugarcane bagasse content (X1), the levels of maleic anhydride contents (X2), and screw speed (X3) was adopted. The total weight of one treatment was was set at one kilogram including the major and auxiliary formulations 75% and the chemical agent 25%, respectively. The bagasse content of composite formulations (10%, 20%, 30%), as well as the maleic anhydride content (2%, 5%, 8%) of the chemical agent and the screw speed of extruder (35, 40, 45 RPM), were chosen for the extrusion process. The three levels of process variables were coded as -1, 0, and 1, thus making the total number of experiments equal to 15 instead of 27 for full factorial design. Table I lists the coded and encoded levels of the RSM design with different raw composition. A single-screw extruder made by Yea Jing Machinery Co., Ltd. The experiments were run at barrel temperature of 155, 155, 155, and 158 °C. The generation of contour and response surface plot was performed using the experimental design software (Design-Expert version 7, Stat-Ease Inc., Minneapolis, USA).

TABLE I. THE ARRANGEMENT AND RESPONSES OF BOX-BEHNKEN DESIGN

Treatments	Coded			Encoded		
	X1	X2	X3	X1	X2	X3
1	-1	-1	0	10	2	40
2	1	-1	0	30	2	40
3	-1	1	0	10	8	40
4	1	1	0	30	8	40
5	-1	0	-1	10	5	35
6	1	0	-1	30	5	35
7	-1	0	1	10	5	45
8	1	0	1	30	5	45
9	0	-1	-1	20	2	35
10	0	1	-1	20	8	35
11	0	-1	1	20	2	45
12	0	1	1	20	8	45
13	0	0	0	20	5	40
14	0	0	0	20	5	40
15	0	0	0	20	5	40

X1: Sugarcane bagasse content (%), X2: Maleic anhydride content (%), X3: Screw speed (RPM).

Experiments were randomized to minimize the effects of unexplained variability in the observed responses due

to external factors, and the melting temperature (Tm), degradation temperature (Td) are hypothesis that are functionally related to specific composition [15].

C. Measurement

Thermogravimetric analysis of the samples and its components was carried out in inert atmosphere (nitrogen) of 50ml/min with a heating rate of 10 $^{\circ}$ C/min. The sample with the each weight around 5mg was heated to 600 $^{\circ}$ C using a thermal analysis instrument Dynamic Q500.

Differential Scanning Calorimetry Analysis was carried out on a DSC 2920 (TA Instruments, USA) under nitrogen atmosphere of 50ml/min. The temperature and heat flow were calibrated with indium. The samples with the each weight of 3mg and DSC traces of specimens were recorded upon heating from 25 °C to 190 °C at a rate of 10 °C/min and held at 190 °C for 5 minutes. The data were collected based on three runs.

Biodegradation test was used to investigate the degradability potential of degradable and biodegradable plastics under simulated aerobic degradation conditions. The aerobic degradation testing conditions were in accordance to CNS 14432. This standard is a general method to evaluate the ultimate aerobic biodegradability of plastics under controlled composting conditions by measurement of the amount of carbon dioxide evolution and the degree of biodegradation of the plastic at the end of the test. The plastic sample is mixed with the inoculums which are derived from compost. The compost was placed in a water bath maintained at of $58.0 \,^{\circ}{\rm C}$ (± 2.0 °C). The total amount of CO₂ evolution was calculated by referencing to the blank control reactor. The percentage of biodegradation (Dt) of the plastic sample was calculated as in (1):

$$Dt(\%) = \frac{((CO_2)_T - (CO_2)_B)}{ThCO_2} \times 100\%$$
(1)

where $(CO_2)_T$ is the cumulative amount of carbon dioxide evolved in each composting reactor containing extruded plastic sample, in grams per reactor; $(CO_2)_B$ is the mean cumulative amount of carbon dioxide evolved in the blank reactor, in grams per reactor, and ThCO₂ is the theoretical amount of carbon dioxide of extruded plastic sample.

III. RESULTS AND DISCUSSION

A. Thermogravimetric Analysis and Model Description

Thermogravimetric Analysis (TGA) has been used widely in the study of polymeric biomaterial [16], [17]. The samples were measured in the temperature range from 25 °C to 600 °C with a constant rate of 10 °C/min under nitrogen atmosphere. The result of the decomposition temperature of each treatment group ranged from 242.02 °C to 249.73 °C. Fig. 1a shows that the weight loss of the sample decreases as the temperature increases. Fig. 1b shows the Derivative Thermogravimetric (DTG) curve, i.e., the first derivative of the sample mass change as a function of temperature; shows the rate of the mass change. The TGA data analysis also provided thermal degradation temperatures of the composites listed in Table II. These show that the degradation of the sample occurred in the system. PHBV degrades in single stage; PVA degrades in two stages; sugarcane bagasse degrades in three stages and their blends with additive in five stages. Ref. [18] found the same pattern in their study on PHBV/PVA mixtures as biodegradable polymeric materials. In each treatment, the first stage, mass loss around 4% up to $100 \,^{\circ}{\rm C}$ due to moisture escape during the melting and the vaporization of water absorbed by hydroxyl groups of sugarcane bagasse and PVOH while the second stage displays the decomposition of maleic anhydride and plasticizers [19]. The third stage reaching 70% or less for mass losses around 250 °C shows the decomposition of PHBV due to the burning of organic matter. The fourth stage indicates the decomposition of hemicellulose and cellulose content of sugarcane bagasse [20] and side chain of PVOH [21]. The fifth smaller stage indicates the decomposition of main chain of PVOH [21] and lignin content of sugarcane bagasse [22], [23]. There were different amounts of carbonaceous residue after all volatile products have evolved; the amount was higher in composites having a higher content of fibers. The pure PVOH has a higher thermal stability than that of PHBV/PVOH/ sugarcane bagasse crosslinked blending composite.



Figure 1. TGA (a) and DTG (b) curves obtained for thermogravimetry analysis of different treatments and raw materials.

Fig. 2 shows the contour and response surface plot of the extrudate's Td. The levels of maleic anhydride content have a positive effect on extrudate's Td. The levels of sugarcane bagasse content have a positive parabolic effect on extrudate's Td. The addition of sugarcane bagasse could improve the thermal stability of PHBV/PVOH component. Ref. [12] reported that bagasse was proposed as an effective filler for PHBV.

TABLE II. TOTAL WEIGHT LOSSES OF EACH TREATMENT IN TGA PRESENTED IN WEIGHT PERCENTAGES

	Weight losses (%)							
Treatment	100 °C	200 °C	300 °C	400 ℃	500 °C			
1	3.4	19.5	74.6	93.2	96.7			
2	3.4	19.3	70.5	90.2	93.1			
3	3.4	19.7	79.9	90.5	94.2			
4	3.6	19.7	81.5	92.0	93.5			
5	3.6	19.1	81.6	91.6	95.4			
6	3.8	19.9	71.9	88.3	91.4			
7	3.7	20.4	81.2	91.8	94.9			
8	3.8	20.2	72.0	88.6	91.8			
9	4.0	19.4	76.1	92.3	95.3			
10	3.8	19.9	76.2	89.1	92.5			
11	3.8	19.8	73.8	91.3	94.2			
12	3.7	19.3	72.8	87.6	91.8			
13	4.2	19.9	73.2	91.7	95.2			
14	4.2	19.9	73.2	91.7	95.2			
15	4.2	19.9	73.2	91.7	95.2			
PHBV	0.37	0.64	99.8	99.9	99.9			
PVOH	3.2	3.8	42	88.7	96.9			
sugarcane bagasse	4.3	10.1	45.1	81.6	84.6			



Figure 2. The response surface and contour plots of extrudate's Td.









B. Differential Scanning Calorimetry Analysis and Model Description

An endothermic peak in a DSC heating curve calls melting temperature (Tm). The result of the Tm of each treatment group ranged from $157.61 \,^{\circ}$ C to $168.40 \,^{\circ}$ C as shown in Fig. 3. Pure PHBV is a thermoplastic material with a melting temperature around $172.5 \,^{\circ}$ C, crystallizes to form large spherulites when cooled slowly after melting [24]. Fig. 4 shows the contour and response surface plot of the extrudate's Tm. In moving along the horizontal axis, it can be seen that with the increase of screw speed has a negative effect on extrudate's Tm. The levels of sugarcane bagasse content have a negative parabolic effect on extrudate's Tm as well as maleic anhydride content. The addition of sugarcane bagasse could improve the thermal stability of PHBV/PVOH matrix. The polymeric chain may break down during extrusion such as shearing force when dealing with large scale/industrial applications of PHB [25].

C. Biodegradability

Most of biodegradation tests are based on the determination of CO₂ produced by microbial respiration [26], [27]. The biodegradation curve of the optimum extrudate was detected in a controlled composting condition at 58 °C according to the CNS14432 standard in biodegradability analysis as shown in Fig. 5. It can be observed that composite started to degrade after 5 days. The degree of biodegradation of composite after 31 days was 70.9%, exceeding the standard, which is 70%, and the biodegradation curves of the sample tended to level off. The ultimate degree of biodegradation of composite was 85.3% after 45 days. Ref. [28] reported that biodegradability of PHB product can reach more than 70% in composting environment in 6 weeks. The biodegradation of polymers is affected by their chemical structure, their hydrophobic-hydrophilic balance and other properties [11].



Figure 5. The percentage of biodegradation.

IV. CONCLUSIONS

This study investigated the thermal property and biodegradability of PHBV/PVOH/sugarcane bagasse extruded composite by DSC. The results of thermal analysis showed that thermal stability was increased by addition of the sugarcane bagasse. Thermal stability for the blending was more stable than pure PHBV. In the case of biodegradation tests according to CNS 14432 shows the ultimate degree of biodegradation of composite was 85.3% after 45 days. The present work contributes to information about the use of sugarcane bagasse to engineer polymeric composites for industrial applications.

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REFERENCES

- Y. H. Yun, Y. W. Wee, H. S. Byun, and S. D. Yoon, "Biodegradability of chemically modified starch (RS4)/PVA blend films: Part 2," *Journal of Polymers and the Environment*, vol. 16, pp. 12-18, Jan. 2008.
- [2] G. F. Moore and S. M. Saunders, Advances in Biodegradable Polymers, Shawbury, UK: Rapra Technology Ltd, 1998, p. 126.
- [3] J. H. Yang, J. Park, D. Kim, and D. H. Lee, "Effects of calcium carbonate as the expanding inhibitor on the structural and mechanical properties of expanded starch/polyvinyl alcohol blends," *Journal of Applied Polymer Science*, vol. 93, pp. 1762-1768, Jun. 2004.
- [4] T. Nakashima, C. Xu, Y. Bin, and M. Matsuo, "Morphology and mechanical properties of poly (vinyl alcohol) and starch blends prepared by gelation/crystallization from solutions," *Colloid and Polymer Science*, vol. 279, pp. 646-654, Jul. 2001.
- [5] R. Fukae, T. Fujii, M. Takeo, T. Yamamoto, T. Sato, Y. Maeda, and O. Sangen, "Biodegradation of poly (vinyl alcohol) with high isotacticity," *Polymer Journal*, vol. 26, pp. 1381-1386, 1994.
- [6] N. M. Barkoula, S. K. Garkhail, and T. Peijs, "Biodegradable composites based on flax/polyhydroxybutyrate and its copolymer with hydroxyvalerate," *Industrial Crops and Products*, vol. 31, pp. 34-42, Jan. 2010.
- [7] D. H. Mueller and A. Krobjilowski, "Processing, applications and new delelopments of natural fiber," presented at 6th Beltwide Cotton Conference, Nashville, TN, Jan. 6-10, 2003.
- [8] T. M. Don, C. Y. Chung, S. M. Lai, and H. J. Chiu, "Preparation and properties of blends from poly (3-hydroxybutyrate) with poly (vinyl acetate)-modified starch," *Polymer Engineering and Science*, vol. 50, pp. 709-718, Apr. 2010.
- [9] D. Lovera, L. Márquez, V. Balsamo, A. Taddei, C. Castelli, and A. J. Müller, "Crystallization, morphology, and enzymatic degradation of polyhydroxybutyrate/ polycaprolactone (PHB/PCL) blends," *Macromolecular Chemistry and Physics*, vol. 208, pp. 924-937, May 2007.
- [10] M. Shibata, S. Oyamada, S. I. Kobayashi, and D. Yaginuma, "Mechanical properties and biodegradability of green composites based on biodegradable polyesters and lyocell fabric," *Journal of Applied Polymer Science*, vol. 92, pp. 3857-3863, Jun. 2004.
- [11] D. Oldak, H. Kaczmarek, T. Buffeteau, and C. Sourisseau, "Photoand bio-degradation processes in polyethylene, cellulose and their blends studied by ATR-FTIR and Raman spectroscopies," *Journal* of Materials Science, vol. 40, pp. 4189-4198, Aug. 2005.
- [12] A. Hodzic, R. Coakley, R. Curro, C. C. Berndt, and R. A. Shanks, "Design and optimization of biopolyester bagasse fiber composites," *Journal of Biobased Materials and Bioenergy*, vol. 1, pp. 46-55, Apr. 2007.
- [13] P. Persico, D. Acierno, C. Carfagna, and F. Cimino, "Mechanical and thermal behaviour of ecofriendly composites reinforced by *Kenaf* and *Caroà* fibers," *International Journal of Polymer Science*, vol. 2011, pp. 1-7, 2011.
- [14] G. E. P. Box and D. W. Behnken, "Some new three level designs for the study of quantitative variables," *Technometrics*, vol. 4, pp. 455-463, Nov. 1960.
- [15] S. Chatterjee and B. Price, "Selection of variables in a regression equation," in *Regression Analysis by Example*, R. A. Bradley, D. G. Kendall, and G. S. Watson, Eds., New York: John Wiley and Sons, 1977, pp. 201-203.
- [16] T. Ohkita and S. H. Lee, "Thermal degradation and biodegradability of poly (lactic acid)/corn starch biocomposites," *Journal of Applied Polymer Science*, vol. 100, pp. 3009-3017, May 2006.
- [17] M. Run, X. Li, and C. Yao, "Thermal degradation behavior and kinetic analysis of poly (L-lactide) in nitrogen and air atmosphere," *Frontiers of Materials Science in China*, vol. 4, pp. 78-83, Mar. 2010.

- [18] O. Sharhan, A. H. Yahaya, and M. M. Nasef, "Preparation and characterization of poly (3-hydroxybutyric acid)/poly (vinyl acetate) blend films," *Asian Journal of Chemistry*, vol. 27, pp. 979-983, 2015.
- [19] C. N. Cascaval, G. Chitanu, and A. Carpov, "On the thermal decomposition of copolymers of maleic anhydride with styrene," *Thermochimica Acta*, vol. 275, pp. 225-233, 1996.
- [20] D. L. Klass, *Biomass for Renewable Energy, Fuels, and Chemicals*, San Diego: Academic Press, 1998.
- [21] W. B. Lui and J. Peng, "Thermal properties and cellular structure of cornstarch-based foams formed by extrusion technology," *Journal of Food Processing and Preservation*, vol. 39, 2014.
- [22] A. Quensanga and C. Picard, "Thermal degradation of sugar cane bagasse," *Thermochimica Acta*, vol. 125, pp. 89-97, Apr. 1996.
- [23] J. I. Guimar ães, E. Frollini, C. G. Silva, F. Wypych, and K. G. Satyanarayana, "Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil," *Industrial Crops and Products*, vol. 30, pp. 407-415, Nov. 2009.
- [24] A. Javadi, A. J. Kramschuster, S. Pilla, J. Lee, S. Gong, and L. S. Turng, "Processing and characterization of microcellular PHBV/PBAT blends," *Polymer Engineering and Science*, vol. 50, pp. 1440-1448, Jul. 2010.
- [25] W. M. Pachekoski, C. Dalmolin, and J. A. M. Agnelli, "The influence of the industrial processing on the degradation of poly (hidroxybutyrate) - PHB," *Materials Research*, vol. 16, pp. 237-332, Apr. 2013.
- [26] A. Calmon, L. D. Bresson, V. B. Maurel, P. Feuilloley, and F. Silvestre, "An automated test for measuring polymer biodegradation," *Chemosphere*, vol. 41, pp. 645-651, 2000.
- [27] A. Krzan, S. Hemjinda, S. Miertus, A. Corti, and E. Chiellini, "Standardization and certification in the area of environmentally degradable plastics," *Polymer Degradation and Stability*, vol. 91, pp. 2819-2833, Dec. 2006.
- [28] S. Lee and J. Yu, "Production of biodegradable thermoplastics from municipal sludge by a two-stage bioprocess," *Resources, Conservation and Recycling*, vol. 19, pp. 151-164, Mar. 1977.



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