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Preparation and properties of biodegradable cat litter produced from cassava (*Manihot esculenta* L. Crantz) trunk

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Abstract. Organic based cat litter becomes more and more popular in many countries including Thailand because of the concern on environmental and health impacts in cats and cat owners. Most of the cat litter sold in Thailand is manufactured and imported from abroad. Cassava trunk pith, the stele of cassava trunk, is the biomass obtained from agricultural waste which presents excellent water absorption. Thus, the purpose of this article was to investigate the preparation of the biodegradable cat litter from cassava trunk pith. The composition of cassava trunk pith was analyzed by standard methods. The preparation of the cat litter was performed by mixing cassava trunk pith with the binder (glycerol, and palm oil) at the ratio 49.7:40.0 by weight. The effects of two clumping agents, guar gum and xanthan gum at 5-15%, on the properties of cat litter were determined. The cassava trunk pith consisted of cellulose (47.12%), lignin (30.18%), hemicellulose (14.07%), extractives (5.69%) and ash (2.94%) by wet weight basic. The litter from all formulations obtained a high rating scale for clump strength with the use of palm oil. The addition of guar gum, and xanthan gum as a clumping agent resulted to the products with desirable physical properties. These results demonstrated that cassava trunk pith has a high potential for product development as biodegradable cat litter.

Keyword. Cat litter, Cassava trunk pith, Lignocellulose, Absorbent, Clump strength, Clumping agents

1 Introduction

Society and lifestyle have been changed presently. Household is getting smaller while the elderly and singles are increasing. Pets are friends and members of the family, treated like celebrities in this pet trends. As a result, pet business has grown by 10-15% from 2014 to 2018 in Thailand [1].

Cats are one of the most popular pets. According to statistics of cat breeders around the world, Thailand has the 8th highest number of cat breeders in the world [2], which accounts for 33 percent of the country's population. Cat urine and feces have a naturally strong smell inside the house. Therefore, the cat litter is commonly used for cats to excrete their waste nowadays [3]. In general, cats can generate 40 grams of fecal waste per day [4], which can be estimated that 281,952 tons of fecal waste are produced per year in Thailand.

The cat litter is an absorbent material that can absorb liquid, odors and help to eliminate cat waste more easily and comfortable to clean. Inorganic based cat litter such as bentonite cat litter and pumice cat litter are the products obtained from the mining industry and volcano [5]. Both

products are able to retain odors and clump well, but still make small dust and could negatively affect to the health of cats and owner. In previous studies, it was found that using the litter for a long time, cat got sick and then died from inhalation and eating of the litter [6]. Cat's health concerns [7] and more landfill space requirement for the non-biodegradable cat litter [8] led to the needs for biodegradable cat litter. Consequently, cat owners currently tend to choose products that are safe and environmental-friendly, resulting in less sale amount for the inorganic cat litter [9]. Hence, organic based cat litter becomes more popular [10] and has been sold in a larger number nowadays [11]. Moreover, most of the cat litters sold in Thailand are manufactured and imported from abroad [12]. The products from local production still require more improvement for the quality.

Organic based cat litter could be made from starch, modified starch [13] and plant fiber such as rice straw, water hyacinth, coffee grounds, coconut husk, palm oil mesocarp, olive oil waste [14], and cassava pulp waste [15] which is lignocellulosic material. The lignocellulose can be found as the main composite of plant cell walls that consist of cellulose, hemicellulose and lignin. The

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structure of lignocellulose also contains many hydrophilic functional groups, which obtain high water holding capacity [16]. Additionally, cellulose has a structure and ion exchange with organic substance as the resin, which is a desired property of absorbent. Therefore, from these aspects, lignocellulose had been studied in cat litter as an absorbent [17].

Cassava is an important economic and energy crop in Thailand [18]. Interestingly, almost all parts of the cassava can be used. For instances, the seed extracts are applied in the pharmaceutical industry, and root and leaf are generally used to make cassava starch and animal feed, respectively. Moreover, cassava pulp can be supplied for making dietary fiber noodles [19], the superabsorbent [20] and cat litter [15]. In terms of cassava trunk, it is estimated that around 116 million tons of fresh cassava trunk are produced worldwide each year approximately 10-20% [21] of the harvested cassava roots. Cassava trunks are used for propagation, while most of them have to be removed by landfilling or openburning which leads to the air pollution. The trunk mainly consists of lignocellulose [22], glucan-rich feedstock which makes them especially suited for bioethanol production [23] or convert into biochar [24]. Moreover, the cassava trunk pith is a stele of cassava trunks that are abundant agricultural wastes and obtain an excellent water absorption [25], high porous and good adsorbent. In addition, there is no report on the use of cassava trunk pith as adsorbent in cat litter yet.

Thus, this study aimed to develop the biodegradable cat litter from the cassava trunk pith. The determination of the chemical compositions of the cassava trunk pith have been studied. The effects of binders and clumping agents on the properties of the cat litter such a water absorption, clumping percentage and clump strength were also determined.

2 Materials and methods.

2.1 Raw materials and composition

Fresh cassava trunks collected from Nakhon Nayok province were cut into 8-15 cm long (Fig. 1) with a diameter of 5-21 mm (Fig. 2). Two types of binders used in this study, glycerol was supplied from Krungthepchemi Co., Ltd. (Bangkok, Thailand) while palm oil was bought from Sime Darby Oils Morakot Public Co., Ltd. (Bangkok, Thailand). Sodium propionate, guar gum and xanthan gum were supplied by Chemipan Co., Ltd. (Bangkok, Thailand).

2.2 Preparation of cassava trunk piths and chemical analysis

Fresh cassava trunk piths (Fig. 3) were pushed out of the cassava trunk by a round stick and dried at 40 °C for 24 hours. Then, cassava trunk piths were ground into fine particles by cutting mills (Retsch cross beater mill, Germany) and screened through a 2 mm sieve. The ground samples were separated into various sizes using a sieve shaker (Minor M200 Endecotts Ltd., London,

United Kingdom) fitted with 12, 14, 35 and 80 mesh sieves (USA Std Test Sieve, Endecotts Ltd., London, United Kingdom). The samples retained on the top of the 14 mesh sieves were then used in cat litter experiments. The finer particles retained on 35 mesh sieves were used for further analysis. The chemical compositions of the samples the methods of Technical Association of the Pulp and Paper Industry [26] with the preparation of wood for chemical analysis (TAPPI-T-264 om-88), determination of ash (TAPPI-T-211 om-93), extractives (TAPPI-T-203), and lignin (TAPPI-T-222 om-98). Holocellulose (cellulose and hemicellulose) was analyzed by Browing method, while hemicellulose was measured followed TAPPI-T-203 om-88. The chemical composition was calculated by dry weight basic of raw materials. The functional groups and basic structure of the samples were analyzed using Fourier transform infrared spectroscopy (FTIR).

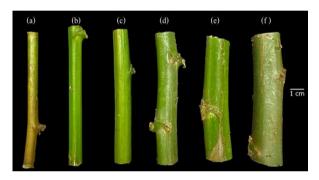


Fig. 1. Cassava trunks with a length of 8-15 cm: (a) 5.85 mm, (b) 7.88 mm, (c) 10.47 mm, (d) 13.07 mm, (e) 16.08 mm and (f) 18.47 mm.

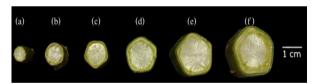


Fig. 2. Cross-section of cassava trunk with the diameter 5.00-21.00 mm: (a) 5.85 mm, (b) 7.88 mm, (c) 10.47 mm, (d) 13.07 mm, (e) 16.08 mm and (f) 18.47 mm.

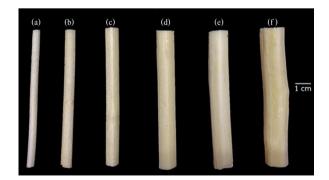


Fig. 3. Cassava trunk pith with the diameter of 5.00-21.00 mm: (a) 4.22 mm (b) 6.14 mm, (c) 7.68 mm, (d) 10.00 mm, (e) 11.50 mm and (f) 13.14 mm.

2.3 Preparation of cat litter

To investigate the effects of binder on clump strength, the cat litters were prepared from 49.7% (w/w) of the ground cassava trunk pith 14 mesh, 40% (w/w) of binder, 10% (w/w) of guar gum and 0.3% (w/w) of sodium propionate.

To observe the effects of clumping agent on bulk densities, hydration capacities and clumping activity, the cat litters were prepared with the formulation listed above with the guar gum, and xanthan gum at 0.0, 5.0, 7.5, 10.0, 12.5 and 15.0% (w/w). The palm oil was applied as binder in the range 35-50% (w/w).

The ingredients for the cat litter preparation were mixed with the ground cassava trunk pith 14 mesh and each binder by a Food Mixer (Kenwood Electronics, Kenwood Ltd., LDN, UK) for 3 min. Thereupon, the clumping agent was then added to the mixture and mixed for 5 min and packed in a plastic zip lock until further analysis.

2.4 Physical Characteristics

2.4.1 Clump strength

Clump strength of the cat litters was determined by Standard Drop Method Test [27] with slight modification. Two grams of cat litters were placed in a plastic cup (diameter of 47 mm and a height of 29 mm) and then 15 mL of distilled water were added onto the samples, the clumped cat litters were then dried in a hot air oven at 45 °C for 24 hours. The clump strength test of the clumped samples was carried out at a height of 12 inches by dropping the samples onto the tray, followed by examination for the breakage by assigning a rating on a scale from 1 to 3, where 1: clump intact (no breakage), 2: clump was slightly broken and there were small fragments, and 3: clump was broken into more than two pieces with scattered small fragments, as shown in Fig. 4.



Fig. 4. Rating for the clump breakage: (a) clump intact (no breakage), (b) slightly broken and (c) moderately broken.

2.4.2 Bulk densities and hydration capacities

Ten grams of the sample (M) were placed in a dry 250 mL graduated cylinder. The apparent volume (V) was measured to the nearest graduated unit. The bulk densities $(g \cdot cm^{-3})$ of each sample were determined from the samples weight divided by the apparent volume.

To determine hydration capacity, 0.5 g of the samples were placed in 27 mL test tubes, then 15 mL of deionized distilled water were added and suspended by a shaking incubator (Daihan Labtech Co., Ltd.) at 150 rpm for 15 min and leave it for 15 min to precipitate the cat litter. The supernatants were carefully removed from the

test tubes using a pipette dropper and the sample tubes were weighed. The hydration capacity $(g_{water} \cdot g_{litter}^{-1})$ were determined from the hydrated samples weight divided by 0.5 g.

2.4.3 Clumping percentage

Clumping activity was determined by adding 2.0 g of each formulation into a plastic cup with the same dimension as described above. Pipette 15 mL of distilled water onto the cat litters, then placed the clumps of cat litter in a hot air oven at 45 °C for 24 hours. The clumps were then put onto a 4 mesh (4.75 mm) sieve and placed on a shaking incubator (Daihan Labtech Co., Ltd.) at 250 rpm for 1 min. Clumping percentage [28] was finally calculated as followed (1)

Clumping $\% = (Weight of clumps on sieve/2.0) \times 100$ (1)

2.5 Statistical design and analyses

Analyses of Variance (one-way ANOVA) were used to analyze differences among the treatments and Duncan test for hydration capacities, bulk densities and clumping percentages. Comparison between different treatments was made using differences of least squares means, when significant F-test values from the ANOVA were obtained at $p \le 0.05$. All statistical analyses were performed using IBM SPSS Statistics Version 19.

Table 1. Chemical composition of cassava trunk pith.

Chemical component	% wet weight basis
Cellulose	47.12
Lignin	30.18
Hemicelluloses	14.07
Extractives	5.69
Ash	2.94



Fig. 5. Cassava trunk pith cross-section.

3 Results and discussion

3.1 Chemical composition of cassava trunk pith

The chemical composition of the cassava trunk piths is showed in Table 1. The cassava trunk piths consisted of cellulose 47.12%, lignin 30.18%, hemicellulose 14.07%, extractives 5.69% and ash 2.94%. The lignocellulose contents of the cassava trunk piths shown here are rather similar to the cassava stem [29], which contain 4.45% starch, 37.61% cellulose, 29.84% hemicelluloses, 19.11% lignin and 3.34% ash. In addition, lignocellulosic profile of cassava pulp residues contains 32% starch, 26% cellulose, 17% hemicelluloses and 16% lignin [30].

The spongy core of the cassava trunk pith tissue (Fig. 5) is formed by the parenchyma cell (pith), xylem and phloem [31]. These plant cell walls are majorly composed of lignocellulose, a natural polymer with many hydrophobic functional groups that are able to absorb moisture and exchange ions in the solution [32]. For instance, the functional groups are the acetyl and ester group of uronic ester in the hemicellulose structure, the carboxyl group and the aryl group in the lignin structure, the hydroxyl groups (-OH) in the cellulose structure, thus lignocellulose or cellulose is used as absorbent because of their capacity for water absorption [20].

The analysis of cassava trunk pith by FT-IR spectroscopy is presented in Figure 6. For cellulose structure, the wavelength between 3,350-3,500 cm⁻¹ represents vibration of -OH group, 2,900-2,890 cm⁻¹ indicating the C-H group [33] and 890-900 cm⁻¹ representing peaks of β -1,4 glycosidic bond between glucose of cellulose. For hemicellulose spectra, the wavelength 1,160-1,110 cm⁻¹ were derived from C-O-C of glycosidic bonds, 1,045 cm⁻¹ assigned to C-O and C-O-C stretching and 1,414-1,467 cm⁻¹ attributed to the CH₂, and 1,600-1,638 cm⁻¹ showing as OH bending [34].

The wavelength of 1,250 cm⁻¹ indicates the C-O-C groups representing for the Arty-alkyl ether of lignin, while that of 1,450-1,520 cm⁻¹ showing as C-H in the aromatic band of phenylpropane [35], which is the main chain of lignin.

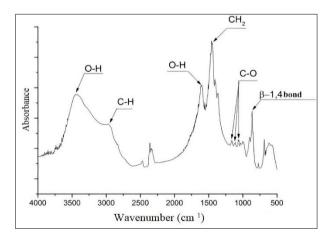


Fig. 6. FTIR spectra for lignocellulose from cassava trunk pith.

3.2 Physical characteristic of litter formulations

3.2.1 Effect of binder on clump strength

The clump strengths the cat litters with different binder by average rating, are presented in Table 2. the clump strength of the samples using glycerol, palm oil, and nonbinder was rated as 1 (clump intact), 2 (slightly broken), and 3 (moderately broken into many small pieces) respectively. Apparently, the types of binder significantly affected to the strength of the clumped cat litters.

There are several types of binders such as oil, water, modified starch, etc. The cat litter without the binder addition contained dust particles from the mixture (Fig. 7 (b)). The binder could help the mixture to blend well and result in higher strength of the clump. However, the use of the binder depends on the composition of the cat litter and the manufacturing process [36, 37].

In this research, glycerol exhibited the highest potential clumping agent. However, it was found the litter grains absorbed more moisture and swollen with the increasing storage time (Fig. 7 (d)) due to a hydrophilic function group in glycerol causing the moisture absorption from the environment. This occurrence would affect the shelf life and ability to absorb water of the cat litters during the long storages. At room temperature, the cat litters immediately absorbed the moisture, clumped and scooped out. The cat litters prepared with glycerol were cracked more easily than the samples with palm oil. Therefore, palm oil is selected to be used as the binder for the preparation of biodegradable cat litters from cassava trunk pith.

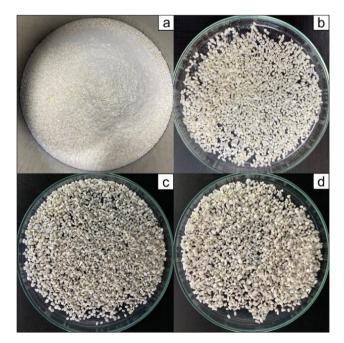


Fig. 7. (a) Ground cassava trunk pith, (b) the cat litter prepared without binder, (c) with palm oil, and (d) glycerol as a binder, respectively.

Table 2. Bulk densities and hydration capacities of cat litter prepared from each formulation.

Guar gum (%w/w)	Xanthan gum (%w/w)	Bulk densities (g·cm ⁻³)	Hydration capacities (g _{water} ·g _{litter} -1)
-	-	0.067	21.90
5.0	-	0.076	21.00
7.5	-	0.078	21.55
10.0	-	0.065	23.35
12.5	-	0.064	25.80
15.0	-	0.067	26.98
-	5.0	0.065	27.15
-	7.5	0.061	30.00
-	10.0	0.069	29.50
-	12.5	0.064	28.60
-	15.0	0.068	28.25

3.2.2 Bulk densities & hydration capacities

Cat litters prepared with guar gum, and xanthan gum revealed their bulk densities ranged 0.064-0.078 and 0.061-0.069 g·cm⁻³ and hydration capacities between 21.00-26.98, and 27.15-30.00 g_{water}·g_{litter}⁻¹, respectively as presented in Table 2.

The hydration capacities of the cat litters with xanthan gum were higher than cat litters with guar gum. While the bulk density of cat litters with xanthan gum was significantly a lower, the addition of clumping agent could increase the hydration capacities. These results indicate that the types and quantity of clumping agent had significantly affected to the density and water absorption capacity of the cat litter.

The density of the cat litters is related to their porosity and the rate of moisture absorption [37]. Thus, the samples with higher density could absorb less moisture than lower density due to the smaller surface area and lower porosity [37]. While the product with low density has a larger surface area and high porosity, thus it can absorb more moisture with faster rate. Additionally, the additives, adsorption carriers and absorbents could also increase the water absorption capacity in cat litter [38]. The comparison with other studies was shown in Table 3, which different raw materials such as eastern red cedar [28], flour pellet [36], corn dried distiller grains [39], and bentonite [40] were used. Different raw materials led to the cat litters with different ranges of bulk density and hydration capacity since each material composted of different compositions and characteristics.

The cat litters prepared from the cassava trunk pith in this study with 10.0-15.0% of xanthan gum and palm oil (as binder) had presented in extremely high hydration capacities as 28.25-29.50 $g_{water} \cdot g_{litter}^{-1}$, which were more preferable than the cat litters that prepared from other raw materials.

Cat litter	Bulk densities (g·cm ⁻³)	Hydration capacities (g _{water} ·g _{litter} -1)	
Cassava trunk pith	0.065-0.068	21.00-30.00	
Eastern red cedar [28]	0.163	8.42	
Corn dried distiller grains [39]	0.430	2.17	
Flour pellet [36]	0.50-0.90	0.53-0.78	
Bentonite [40]	0.52-0.74	0.52-1.17	

 Table 3. Bulk densities and hydration capacities of cat litter made from different materials.

Table 4. Clumping percentage of cat litter	r
from each formulation.	

Guar gum (%w/w)	Xanthan gum (%w/w)	Clumping percentage
-	-	27.17
5.0	-	27.98
7.5	-	26.89
10.0	-	36.42
12.5	-	34.17
15.0	-	32.49
-	5.0	43.70
-	7.5	59.39
-	10.0	67.79
-	12.5	77.87

3.2.3 Clumping percentage

The clumping percentage of the cat litters is shown in Table 4. the increased content of guar gum and xanthan gum led to an increase of clumping percentage of the samples. Using xanthan gum resulted to a significantly higher clumping percentage than the use of guar gum. Clumping percentage is the ability of agglomeration with litter particles that contact with liquid and resulted to the adhesion force of clumping agents and other additives that stick on the particle surface. Thus, cat litter with a high percentage of coagulation can be easily scooped out of uncontaminated cat litter. Additionally, the minimum clumping of cat litters required by consumers is at least 60 percent [28]. In this study, it was found that 10.0-15.0% of xanthan gum can provide a sufficient clumping

4 Conclusion

capacity for the cat litters.

In this study, the development of the biodegradable cat litter has been successfully derived using cassava trunk pith as main material. The cassava trunk is majorly composed with lignocellulose, which demonstrated as a good adsorbent for cat litter. Moreover, the sample with 10.0-15.0% of xanthan gum and palm oil (as binder) has the hydration capacities as 28.25-29.50 $g_{water} g_{litter}^{-1}$, which are higher than other cat litter products. Additionally, the cat litters also provided a sufficient clumping capacity much as 88.80% and suitable to be used for the preparation of biodegradable cat litters as commercial products. Some characteristics have been still in process such as analysis of odor absorption and dustiness.

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