

Review on Feasibility Study on Co-pyrolyzation of Microplastic in Conventional Sewage Sludge for the Cementitious Application

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Abstract

Microplastics (MPs) have recently been classified as one of the emerging pollutants that need to be removed. MPs will only continue to be problematic to human and ecosystem health due to continues usage of plastics grow worldwide. Usually, MPs will be end up in the sewage sludge from the wastewater treatment plant and it will become waste if not turning into something valuable such as biochar since it is not easily degraded. Although there were several studies on the use of biochar as a construction material but deposition of MPs in sludge to biochar was never done before. Thus, turning MPs in sewage sludge to biochar for brick application by co-pyrolysis process is one of the possible useful methods. However, certain characteristic of biochar needs to be achieved so that it can be used as brick or other cementitious application. This can be done through investigation on its chemical composition, thermal properties, and surface morphology to meet its suitable construction material. Thus, the purpose of this study is to evaluate the feasibility of MPs in sewage sludge as a cementitious material by evaluating its characteristics. Hence, the best process condition (temperature) during co-pyrolysis need to be measured. The study was done through collecting the MPs sewage sludge from wastewater treatment plant and their physical properties will be determined. Then, it will be dry before transferred into muffle furnace for co-pyrolysis at different temperature condition which is 400°C, 500°C and 600°C. Characteristics of biochar produced will then analyzed using TGA, DSC and BET. The properties of MPs biochar produce from co-pyrolysis is expected to be classifies in its suitable construction application.

Keywords: microplastic; cementitious; co-pyrolysis; sewage sludge; biochar

1.0 INTRODUCTION

Microplastics (MPs) is a tiny plastic debris with size limits below 50mm and have recently been classified as emerging dangerous contaminants [1]. They usually present in the environment including air, soil and freshwater which can causes threat to the aquatic ecosystem and human health [2]. The toxic impact of MPs is getting more attention among researchers due to its potential in absorbing and desorbing toxicants like PAHs, PCBs and metal ions. Although MPs is hard to degrade, they still present abundantly due to the increasing usage of plastic. Leakages and transportation accident of plastic industries, wear and tear plastic items or personal care product and synthetic textile washing are among sources of MPs contamination in the environment [3]. MPs can be identified visually or using analytical equipment such as Fourier transforms infrared spectroscopy (FTIR) [4].

Even though MPs was found abundantly in the marine environment, the route of MPs in the wastewater treatment plant should not be ignored and some study shows that soils store more MPs than the ocean [5]. There are a few researches was discovered the contamination of MPs in the wastewater and sewage sludge [6]. Even though MPs does not affect the process treatment efficiency, it can provide surfaces for microbial attachment and growth [7]. Due to the long-term exposure to high level of MPs, it is estimated the amount of waste sludge will increase by 9.1% [9]. Usually, most of MPs are removed during the primary treatment but some were end up to recipient water [8]. If most of MPs was transferred to wastewater treatment plant (WWTP) sludge, it can be further used in green construction which is more significant route in the environment. Among the MPs found in the WWTP are polypropylene (PP), polyethylenes (PE), polystyrene, propylene/ethylene copolymer(PS) and polyethylene terephthalate (PET) where it can exist as fragments, fibre and pellet. However, the polyethylene was found the highest mixture contain comparing to others [9]. The purpose of the present study is to review on the application of plastic in brick, classification of cementitious material.

2.0 REVIEW ON THE APPLICATION OF PLASTIC IN BRICK

The strong stream of growing literature on the application of plastic as a construction material shows the current researcher's interest towards

utilization this waste into bricks. Table 1 summarized example of application of plastic in construction material.

Table 1. Application of plastic in brick

Application	Concentration (%)	Reference
PET binder	10	[10]
PET mould	9/block	[11]
PE/PET mould	40.1	[12]
PET aggregate	42.2	[13]
PET/PC aggregate	38	[14]
Plastic aggregates	14.06	[15]
PE aggregates	24	[16]
PE aggregates	8.16	[17]
PE Aggregate, Binder	8.91	[18]

3.0 REVIEW ON THE APPLICATION OF SEWAGE SLUDGE IN BRICK

Chemical and agricultural waste usually present in the sludge and when they are mixed with MPs, it becomes good adsorbent. Thus, a significant number of inorganic components such as Ca, Mg, Si, Mn, Ti, Al, Fe, Pb can be absorb which can enhance levels of cementitious materials in the ashes. Besides, SiO₂, CaO, Al₂O₃, Fe₂O₃, TiO₂, SO₃, MgO, MnO are among important elements presence in the ash to be used as cementitious material [19]. To best of our knowledge, no specific study was done on the effect of MPs in the sludge for the application of cementitious material.

Several studies had shown sludge waste as biochar can be utilized as a secondary resource or partial replacement in concrete, brick or lightweight aggregates [1][19][20]. Introduction of biochar in construction material provides many benefits including reducing the greenhouse gas emission through carbon capture and sequester in construction. Sewage sludge can be a good binder because of its high organic content. Biochar in the cementitious application has been investigated by several authors where the findings show that it can improve crack resistance in cement; enhance thermal insulations and acoustics properties of concrete; improve compressive strength, flexure strength (toughness) and tensile properties; and use as self-healing agent in mortar. However, biochar produced is depending on the pyrolysis

condition such as temperature. As the temperature increase, the Sulphur content were reduced to near zero, but the energy value is increased because of increasing carbon content [21].

Previous studies had listed three most suitable properties for a construction which are low thermal conductivity, high chemical stability and low flammability. The porosity of biochar surface will determine its thermal conductivity which can be set during pyrolysis process. Chemical stability of biochar also important to prevent harmful products formed from the reaction of biochar with other components in the concrete mix. The chemical stability can be determined by composition of carbon and oxygen in the mixture which was measured by CHNOS Elemental Analyzer and then analyzed by Thermogravimetric analysis (TGA). Figure 1 shows the example of TGA analysis of biomass with polyurethane co-pyrolysis products, As seen from the TG curves in Figure 1, the ratio of residual ash depends on the pyrolysis temperature for plastic waste and straw. At 180 °C most of plastics already began to melt and entered the thermoplastic transition. The residual ash ratio of plastic waste increases with the increment of the pyrolysis temperature since the faster melting of plastic samples inhibits the volatile release at higher temperatures. The pyrolysis temperature for wood and straw, is increases by a certain degree when the pyrolysis temperature increase from 700 °C to 900 °C. The minimum temperatures for the complete re-lease of volatiles for wood and straw respectively require 700 °C and 900 °C under condition of 0 °C to 1000 °C and heating rate of 20 °C min⁻¹ in a 20 vol% O₂ atmosphere (N₂ as the balance gas) with a flow rate of 100 ml min⁻¹ [23]. From the DTG curves of straw char in Figure 5b, a small shoulder peak for the straw char prepared at 700 °C occurred, this indicate the uncompleted decomposition.

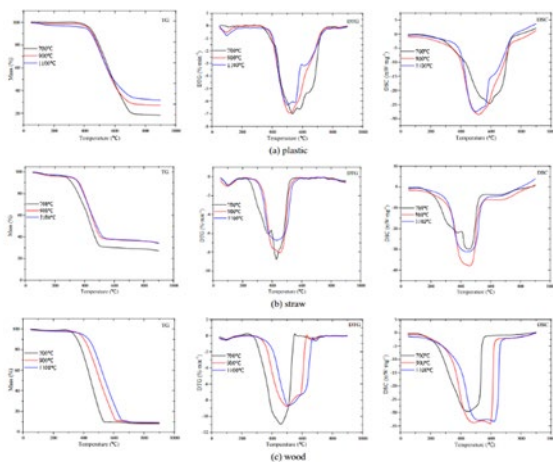


Figure 1. TG-DTG-DSC curves of char oxidation for different fuel types and pyrolysis temperatures.

Figure 2 shows the example of TGA analysis for polyethylene terephthalate (PET). Based on figure 1, one significant mass loss event occurs stretching to approximately 520 °C. The maximum rate of mass loss for PET is observed at 441 °C. The thermal degradation of the polymer backbone i.e. chain scission of the ester bonds caused the maximum loss to occur [26]. From the past research, the TGA and DSC analysis on biochar containing PET not yet been covered.

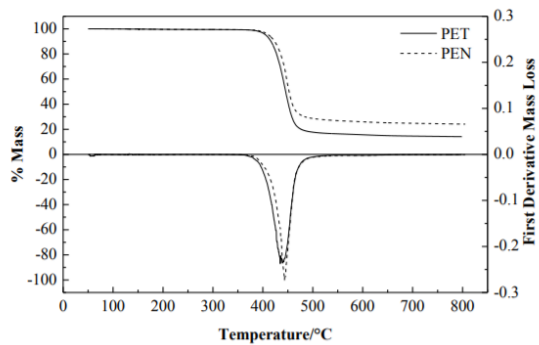


Figure 2. TG and DTG curves of PET and PEN in helium, 30-800 °C, 10 °C min⁻¹.

In the case of flammability of biochar, it is depending on how slow or fast the pyrolysis process. Hence, the volatility of component needs to be evaluated by determining the content of alcohol and carboxylic acid groups in the biochar which is measured by FTIR analysis. Slow pyrolysis of biochar offers reduced surface area compared to fast pyrolysis and is more effective in reducing the carbon-free radicals that result in lower flammability of char [21].

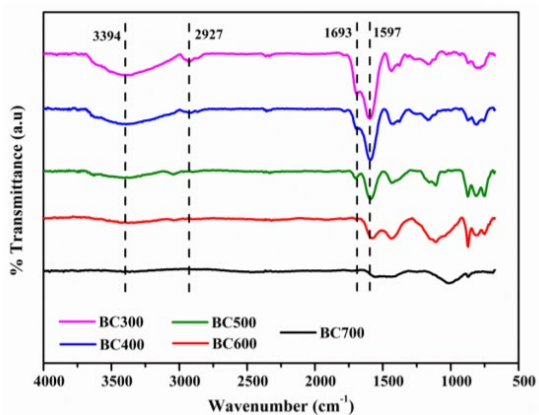


Figure 2. FTIR spectrum for biochar sample at different temperature

The FTIR spectra of biochar samples show a deep

peak at 3394 cm^{-1} which correlated to the O–H bond stretching of the alcoholic and phenolic hydroxyl groups. At lower pyrolysis temperature the intensity of this peak was found to be extraordinarily strong and negligible at higher temperature. At 2927 cm^{-1} the characteristic C–H stretching vibration of alkyl structure of aliphatic group were seen. The peak at 1693 cm^{-1} indicates the stretching of carbonyl bonds (C=O) of the carboxylic groups or conjugated ketone. At 1597 cm^{-1} the stretching vibrations of the aliphatic –C=C– appeared. When the pyrolysis temperature increased, the intensity of all these peaks decreases. The deterioration of hydroxyl groups of aliphatic chain of biomass takes place between $120\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$. The cracking of aliphatic methyl, methylene, methoxyl groups, and reformation of other functional groups such as carbonyl and carboxyl occurs at approximate $400\text{ }^{\circ}\text{C}$. Almost no aliphatic functional groups will be present in the biochar at more than $600\text{ }^{\circ}\text{C}$. These aliphatic structures are known to reform into aromatic structures, resulting in the increased presence of phenolic and ether groups. Moreover, at high temperatures many C=C bond deterioration take place due to availability of adequate energy. Therefore, at higher temperature, due to extensive carbonization, formation of graphite-like structures of the biochar occurs which shows less intense peaks [21].

to recycled PET, whereas blue colour plotting referring to virgin PET. Recycled PET resin is use for recycling bottle production. From figure 4, every peak position shows the fundamental to molecular bonding structure or functional group existing in the material or resin. Meanwhile, variation in intensity of peak in a spectrum correlates to the proportion of that functional group present in the material. O–H bond stretching of the alcoholic and phenolic hydroxyl groups exist in the infrared absorption spectra in the region $3650\text{--}2500\text{ cm}^{-1}$ which are remarkably similar in both spectra. Two prominent similarity are observed within the spectra of recycle and virgin PET, corresponding 2931.6 cm^{-1} and 2860.2 cm^{-1} to 2935.5 cm^{-1} and 2862.2 cm^{-1} . This shows the characteristic C–H stretching vibration of alkyl structure of aliphatic group. Characteristic infrared spectra in the range $1850\text{--}1730\text{ cm}^{-1}$ corresponds to (C=O) stretching, doublet in the carbonyl group is also comparable within these spectra. In the range $1700\text{--}1680\text{ cm}^{-1}$, the C=O stretching mode of vibration in aliphatic ketone or alkanal, aromatic ketone, alkanolic acid alkanoyl chloride and alkanooate ester appears. There are multiple similar peaks between two spectra in the range $1400\text{--}1000\text{ cm}^{-1}$, from Figure 4 shows that the C-O stretching, strong modes in alkanooate ester and alkoxy ether have at that characteristic peaks [27]. The FTIR spectra not even shows the details character of the mixture but can make comparison between difference alike material.

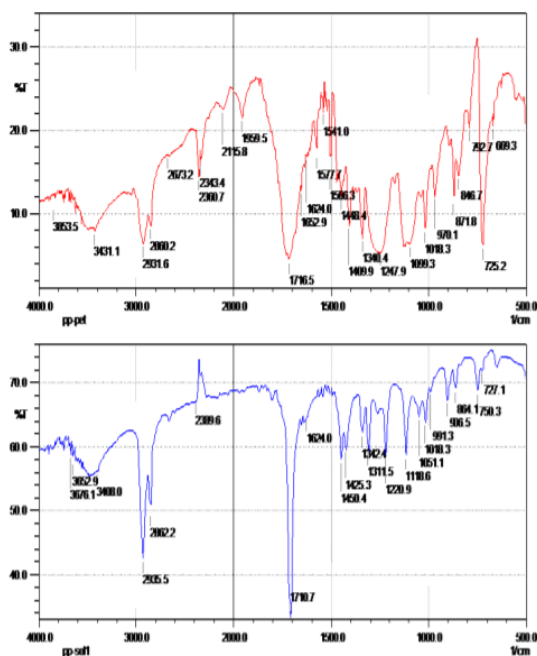


Figure 4. FTIR spectrum for recycled PET and virgin PET

From figure 4, the red colour plotting referring

The biochar containing sewage sludge with microplastics should be analyzed in detail using FTIR but until know there is no recent research covers on the topics. The data given in Figure 3 and Figure 4 can be the basis of comparison for biochar containing sewage sludge with microplastics for future experimental study.

Table 2. Characterization test

Investigation	Function	Equipment
Quantitative chemical analysis	Determination of the amount or percentage of metal element in the sample for brick.	Energy Dispersive X-Ray Fluorescence (XRF)
CHNOS Analysis	To measure percentage of carbon, hydrogen, oxygen and sulfur in the biochar.	CHNOS analyzer
Thermogravime	Mass change as	Thermogravimetric

tric	a function of pyrolysis temperature.	analysis (TGA) Perkin Elmer 8000
Differential Scanning Calorimetry	Investigation of inorganic and organic construction materials.	Differential Scanning Calorimetry (DSC)
Morphological Analysis	Surface morphology, porosity of biochar	Scanning Electron Microscope (SEM) JEOL JSM-IT200
Transmittance spectra	Identify the developed surface functional groups	Fourier Transform Infrared (FTIR) Spectrometer – Brucker Vertex 70
Particle size distribution	Measure size of particle to determine the application as highly active pozzolanic material and normal pozzolanic material	Particle size analyzer
Specific surface area	Determine surface area of the elements	Brunauer, Emmett and Teller (BET)

Most of organic wastes including municipal sewage sludge can be used as feedstock for producing biochar typically through a co-pyrolysis process. The co-pyrolysis process is combusted under low oxygen condition. It was proving that the co-pyrolysis of combine sludge will improve the porosity and provide low density carbon rich material. Moreover, co-pyrolysis provides better adsorbent which increase components value present in the sewage sludge. Previous study had done on co-pyrolysis of rice straw (RS) with polypropylene (PP), polyethylene (PE), or polystyrene (PS). Result shows that the co-pyrolysis of these compositions increased the carbon content, cation exchange capacity (CEC), surface area, and pH of the biochar [22]. Some study found that co-pyrolysis of polymer (plastic) with biomass at 550°C yield more char than individual biomass pyrolysis. Moreover, the char produced has higher heating value [23].

Also, to develop cementitious material, the study of the sludge composition for biochar of is important to meet criteria for the green

construction. Gabriel et al. confirms the presence of silica and alumina as major components in the sewage sludge and contains essentially quartz and kaolinite. The composition and calcined temperature of sludge also will affect compressive strength of cement production [24].

The potential application of the calcined sludge as raw material in the production of supplementary cementitious material will be investigated through compliance with the chemical and physical requirements of standards applicable to highly active and normal pozzolanic material according to classification in the Table 3.

Table 3. Classification of cementitious material[24]

Chemical /Physical requirements	Highly active pozzolanic material	Normal pozzolonic material
CaO + MgO	≤1.5%	-
SiO ₂	≥44% and ≤65%	-
Al ₂ O ₃	≤32% and ≤46%	-
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	-	≥ 70%
SO ₃	≤1%	≤ 4%
NO ₂ O	≤0.5%	-
NO ₂ O equivalent	≤1.5%	≤ 1.5%
Moisture content	≤2%	≤ 3%
Loss on ignition	≤4%	≤ 10%
Percentage retained on 45 sieves	≤10%	≤ 20%
BET specific surface area	≥15 m ² g	-
Performance Index with cement at 7days	≥1.5%	-
Performance Index with cement at 28 days	-	90%

As far as authors concern, no research has been performed on the study of MPs in sewage sludge which turn into biochar for the cementitious applications. Therefore, characteristic study should be done on biochar which produced from MPs in sewage sludge to meet the application type of brick. A suitable process had been chosen, co-

pyrolysis to turn MPs in sewage sludge into brick as shown in Figure 5.

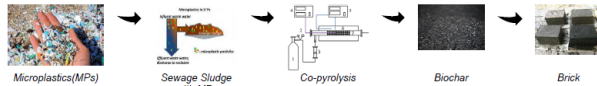


Figure 5: Image of the picture (a) on the left and (b) on the right.

4.0 CONCLUSION

As a conclusion based on the review study on the application of MPs in the cementitious material:

- a) MPs in sewage sludge is something new in the cementitious material but the plastic wastes have been used in many ways in the brick production and brick's properties produced comply the standard outlined.
- b) However, a certain proportion of MPs in sewage sludge and other material used should be optimized to meet the manufacturing for cementitious material standard. Further research and development are needed to improve their quality.
- c) Emerging pollutant like microplastics should be utilized into something valuable to reduce its adverse effect to the environment and human health.

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