

PREPARATION OF CERAMIC SUPPORT COATING USING TIN (II) OCTOATE: EFFECT OF POLYVINYL ALCOHOL AND POLYETHYLENE GLYCOL AS BINDERS

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Abstract— Nowadays, it have been interest to produce immobilized tin (II) octoate catalyst on the surface of the ceramic support for the production of polylactic acid (PLA) from lactic acid (LA) due to easily recycle and separate the catalyst. The objectives of this study is to produce ceramic support coating by using PEG and PVA binders and to characterize the effect of ceramic support coating by using EDX and standard adhesion test. Ceramic powder was obtained from the ceramic waste and used to make the support by mixing with diluted PVA in ratio of 3:1 before compressed and sintered in furnace at 1100 °C. Then, thin layer of tin (II) octoate was prepared using nitric acid, ethylene glycol (EG) and different types of binders. Dip coating technique was used to coat the thin layer on the ceramic surface before sintered in an oven. Based on the EDX result, the composition of tin present in the thin layer containing PEG binder is 5.50 % compared to 0.46 % composition of tin present in the thin layer containing PVA binder. In additional, result from adhesion test shows thin layer sample containing PEG does not peel off from the ceramic surface while the thin layer containing PVA stick to the tape and peel off from the surface of ceramic at 37.5 %. In conclusion, PEG binder was recommended for the immobilization of high composition of the tin (II) octoate on the ceramic surface.

Keywords— Binders, ceramic coating, polyethylene glycol (PEG), polyvinyl alcohol (PVA), tin (II) octoate

I. INTRODUCTION

Nowadays, it has been interest on the production of biodegradable polymers due to several disadvantages of petrochemical based polymers including increasing of petroleum price, depletion of fossil fuels resources, environmental concern as well as global warming [1]. Polylactic acid (PLA) and lactic acid based polymers is derived from lactic acid (LA) produced from renewable sources. It has great performance to be a new generation polymer due to its versatility and degradability as well as expected price [2]. In additional, the performance of PLA – based polymer is better than petrochemical polymers in term of environmental issues such as global warming, dependency of fossil fuels, and toxicity [3].

In the production of polylactic acid, homogenous catalyst was introduced into the reactor in order to increase the rate of reaction and product yield in order to reduce the waste. The most common catalyst used was stannous octoate (tin (II) octoate) [4]. Among various types of catalyst, tin (II) octoate was most preferable due to high conversion and reaction rate, low toxicity as well as high

molecular weight under mild condition during polymerization [5]. Previously, the catalyst was fed homogenously into the reactor either through dissolving of catalyst into the solution or injection method. This cause a major drawback since the catalyst is miscible in the reaction medium as it will be difficult and costly process to remove the catalyst from the reaction medium and it will dissolve into the solution and defect the final product. In additional, the difficulty to remove the catalyst will lead to problem such as retaining the catalyst for reuse and difficult for separation and recycling the catalyst since they are very expensive [6]. Moreover, homogenous catalyst used in the batch process required large amount of solvent during reaction and separation process [7].

In order to overcome this problem, the homogenize catalyst is coated on the surface of the ceramic support by using immobilization technique. In order to combine the advantages of both homogenous and heterogeneous catalysts, technique of heterogenization of homogenous catalyst was introduced using solid porous support [8]. This method was done for easier separation and reuses the immobilized catalyst. The recover catalyst can be further used in catalytic recycle which can optimize the costs. On the other hand, it is more efficient for the product purification as well as catalyst residues removal, especially when involving with toxic metal catalysts [9].

The potential support that can be used to immobilize the catalyst is ceramic. Nowadays, ceramic become popular materials due to their biocompatibility, resistance to corrosion, low electrical and thermal conductivity. Some examples of ceramics are aluminum oxides, calcium aluminates, titanium oxides, calcium phosphate, bioglass and carbon [10].

In order to use the immobilization technique on the ceramic support, binder is used as binding agents. Binders can be defined as the long chain polymer that provides strength to the ceramic body by formed bridges between the particles [11]. Besides, binders also will provide plasticity to the feed materials and help the forming process. Generally, most of the organic substance can be used as binders where some of the binders are soluble in water while others are soluble in organic liquids. Examples of organic binders are polyvinyl alcohol (PVA) and polyethylene glycol (PEG) [11].

PVA can be defined as simple chemical structure with a suspended hydroxyl group. PVA is widely used because it is low cost and toxicity, biocompatibility as well as good mechanical properties [12]. Chemical properties such as crystallizability and solubility of PVA are highly depending on the degree of hydrolysis where PVA with high degree of hydrolysis has low solubility in water. In order for the PVA to dissolve, the water temperature must be above 70 °C. In addition, the properties of PVA are depending on the molecular weight such as diffusivity, crystallizability, adhesion, and mechanical strength [13]. On the other hand, PEG is a suitable substance for coating because of the hydrophilic polymer

properties and reduces the formation of cracked surface of the immobilized system. In additional, PEG can be categorized as nonionic surfactant commonly used in thin film fabrication as structure directing agent, low glass transition temperature as well as good solubility in organic solvents and water [14].

In this paper, the experiment was conducted to study the effect of PVA and PEG binders on the behavior of coating of tin (II) octoate on the ceramic support made from ceramic waste. The ceramic was prepared and coated with a thin layer of tin (II) octoate catalyst by using different binders. Then, two set of tests which are Energy Dispersive X – Ray (EDX) and Adhesion Test (AT) were used to characterize the effect of the ceramic support coating.

II. METHODOLOGY

A. Materials and Chemicals

The raw material which is ceramic was collected from the ceramic waste from the Top Glove located in Klang, Selangor. The chemicals which are PVA, PEG, ethylene glycol (EG), nitric acid and tin (II) octoate were supplied from Chemistry Laboratory in Faculty of Chemical Engineering, UiTM Shah Alam.

B. Preparation of Ceramic Powder from Ceramic Waste

The ceramic waste was grinded using a grinder Model DFY – 200 to reduce the particle size to smaller size. Then, the grinded ceramic was sieve for 20 minutes using Endecotts Octagon 2000 Digital Sieve Shaker with two different trays which are 150 μm and 125 μm to get the particle size approximately 125 μm .

C. Preparation of Fabrication of Ceramic Support

5 g of PVA in solid form was diluted into 100 mL of the distilled water. The distilled water was heated in a Protech Shaker Incubator unit (Model SI – 50D) until the temperature 60 $^{\circ}\text{C}$ before PVA was added. The mixture is shaken for an hour at constant temperature of 90 $^{\circ}\text{C}$ until it become homogenous.

The ceramic powder and the PVA is then mixed with a ratio of 3:1 before being compressed to remove the excess water and to make it like coin shape. The sample was dried for 24 hours in an oven before being sintered. Front Loading Furnace (Carbolite) was used in the sintering process for 2.5 hours with temperature of 1100 $^{\circ}\text{C}$.

D. Preparation of Thin Layer of Tin (II) Octoate on Ceramic Support

The thin layer solution was prepared by using EG, tin (II) octoate, nitric acid, PVA, and PEG. Tin (II) octoate and ethylene glycol (solvent) was mixed and stirred with ratio of 1:10 before 1 mL of nitric acid was added to the solution at temperature of 90 $^{\circ}\text{C}$ for 30 minutes. Then, 10 mL of PVA (binder) was added to the solution and stirred for 6 hours to get the homogenous solution. The solution was kept rest for 24 hours for aging process. This process was repeated by using PEG as binders. Then, the ceramic support was dipped into the solution for about 5 minutes before being sintered in an oven. Then, the sample was analyzed to study the effect of binders on the ceramic support [15].

E. Characterization of Ceramic Support Coating

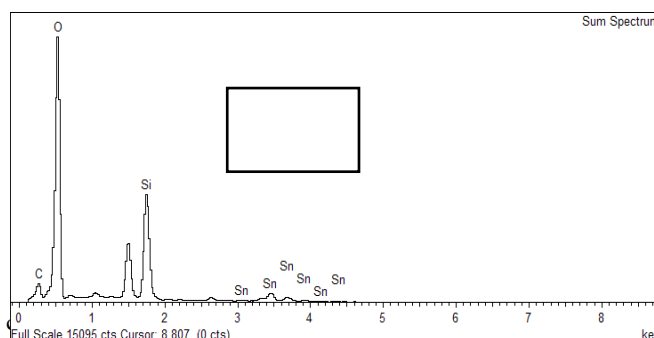
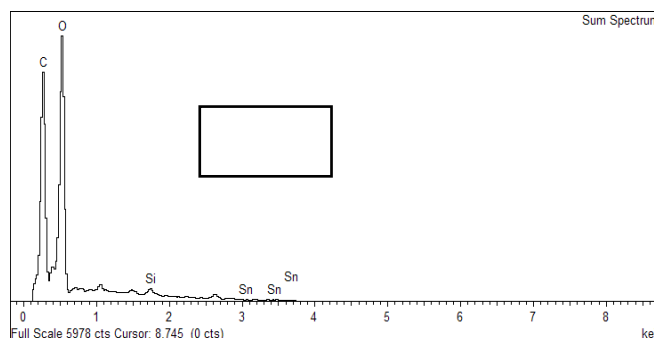
The characterization technique was focused on the composition of the tin (II) octoate on the surface of the ceramic sample. Energy

Dispersive x – ray spectroscopy (EDX) was used to identify the element composition of the materials. It is an analytical technique to identify the elemental composition and distribution as well as mapping across the studied area. The elemental composition shown by the EDX can be expressed quantitatively as atomic percentages or weight percentages and can be used to study the surface area down to few nanometer diameters [16]. This technique was used to identify the element composition of tin (II) octoate on the surface of the ceramic support. In additional, adhesion test was performed in order to evaluate the durability of layer of tin (II) octoate coating on the surface of the ceramic support. An 'X' cut is made on the surface of the ceramic, pressure – sensitive tape is applied over the cut and removed with a steady motion by pulling at 180 $^{\circ}$ angle within 60 seconds. The 'X' – cut area was inspected for removal of coating from previous coating and rates the adhesion using provided scale [17].

III. RESULTS AND DISCUSSION

A. Effect of Binders on the Composition of Tin on the Surface of Ceramic

Two different types of binders were used in this experiment which is polyethylene glycol (PEG) and polyvinyl alcohol (PVA). These binders were used for ceramic dry – pressing due to high green density and high green strength for ceramic [18]. Energy Dispersive X – Ray (EDX) was used to determine the elemental composition of tin on the ceramic surface by mapping technique across the ceramic surface. The elemental composition from the EDX can be expressed using quantitative method as atomic percent and weight percent and can be used to study particular area as small as a few nanometer diameters.



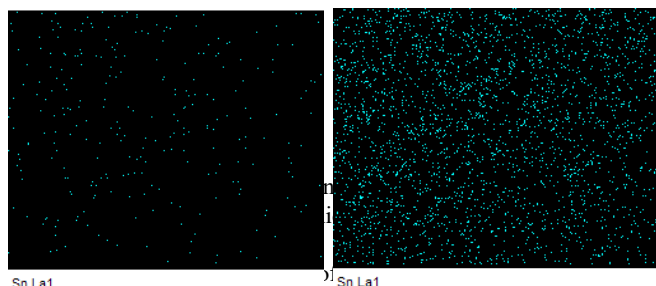
using PVA and PEG as binders, respectively. The thin layer solutions consist of nitric acid, ethylene glycol, PVA, PEG, and tin (II) octoate. Based on the EDX image, the elements presented in

the thin layer of coating are carbon (C), oxygen (O), silica (Si), and tin (Sn). The target element which is tin was present in the EDX image in both graphs. It can be concluded that the tin (II) octoate was present on the thin layer of the ceramic surface.

Table 1: Percent weight of the elements

Element	PVA	PEG
	Weight (%)	Weight (%)
Carbon(C)	39.46	8.65
Oxygen(O)	59.65	71.11
Silica(Si)	0.44	14.74
Tin(Sn)	0.46	5.50
Totals	100.00	100.00

The data obtained from the EDX was summarized in Table 1. Based on the EDX results, it shows that the composition of tin on the ceramic surface for PVA binder was 0.46 %. Element of carbon and oxygen dominated the composition by 39.46 % and 59.65 %, respectively. On the other hands, for the PEG, it is clearly observed that oxygen dominated the composition of the elements on the surface of ceramic by 71.11 %, followed by silica by 14.74 %, carbon by 8.65 % and tin by 5.50 %. The highest composition of oxygen was contributed from the preparation of solution which contains more number of oxygen element compared to other elements.



mapping technique by using EDX. The distribution or composition of the tin element was represented by the blue dots. The more the blue dots appear in the image, the higher the composition of the tin element on the thin layer of coating on the ceramic surface. Figure 3(a) shows 0.46 % composition of tin while Figure 3(b) shows the 5.50 % composition of tin that represent in the thin layer on the ceramic surface.

Based on the Figure 1 and Figure 2, it is clearly observed that the graph containing PEG has more tin composition compared to PVA. Graph on Figure 1 does not show any significant peak value for the composition of tin while graph on Figure 2 shows two significant peaks that indicates the element of tin on the coating surface. In additional, Table 1 shows the exact composition of all the elements analyzed by the EDX. The sample containing PEG shows high value of tin composition which is 5.50 % while the sample containing PVA show the low value of tin composition which is 0.46 % in composition. Based on the image on Figure 3, the composition of tin is more on the PEG binders compared to PVA binders. The composition of the tin can be determined by the numbers and compaction of the blue dots. Figure 3(b) shows more blue dots that indicate the element of tin and the distance of the dots are very closely to each other compared to Figure 3(a).

Based on the result analyzed from the EDX, it can be concluded that PEG binder have a great potential to immobilize the catalyst which is tin (II) octoate on the surface of the ceramic. Tasi et. al. [14] stated that PEG is hydrophilic polymer properties and can reduce the formation of cracked surface of the immobilized system.

Moreover, PEG is nonionic surfactant used in the thin film fabrication as well as good solubility in water and organic solvent. This result was supported by Nawawi et. al. [19] proving that immobilized TiO_2 – PEG as binder was very stable and shows excellent sustainable photocatalytic activity. In additional, Lidija et.al. [20] proved that addition of PEG on glass by using sol – gel dip coating method shows smooth appearance and produces stabilization and formation of more compact and higher aggregates. On the other hand, the composition of tin on the ceramic surface when using PVA as binder was lower compared to PEG because of low molecular weight. Molecular weight is important due to it effect towards mechanical strength, adhesion, and diffusivity [5].

B. Effect of Binders on the Mechanical Strength of Thin Layer of Coating

Standard adhesion test was performed to analyze the durability of the tin (II) octoate coating on the surface of the ceramic support. This test was crucial in thin film preparation because the thin layers are fragile and must be withstand to certain standard of adhesion test. This test was conducted in order to evaluate the mechanical strength of different binders on the binding forces between two materials in contact with each other.

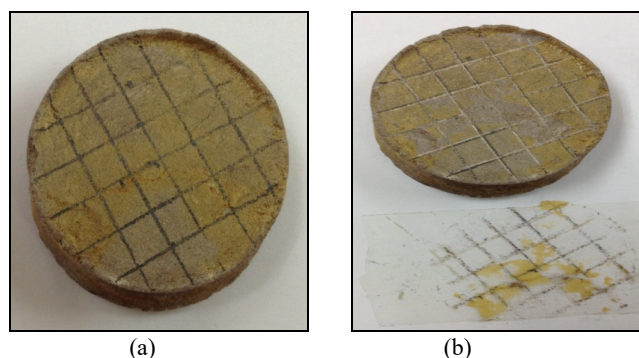


Figure 4: Surface area for PVA (a) before adhesion test and (b) after adhesion test

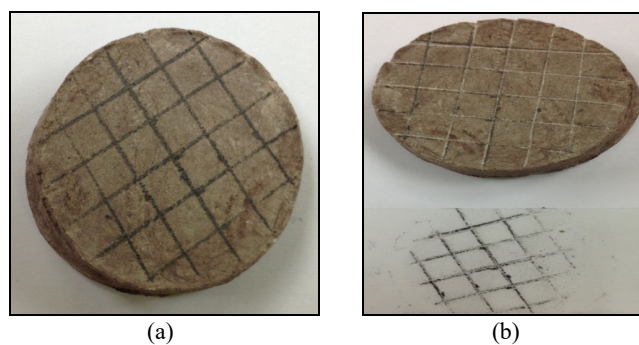


Figure 5: Surface area for PEG (a) before adhesion test and (b) after adhesion test

Figure 4(a) shows the surface area before performing the adhesion test for PVA binders while Figure 4(b) shows the surface area after adhesion test with pressure – sensitive tape. The 'X' cut made on the surface of the support have the width of 5 mm and the area covered for the adhesion test was 20 mm X 20 mm. The layer of the coating containing PVA and tin (II) octoate that sticks on the pressure – sensitive tape was observed. The results shows 6/16 of the 'X' cut was peeled off from the surface of ceramic which are equivalent to 37.5 % damaged.

The test was repeated for the sample of ceramic that containing PEG binders in order to evaluate the binding forces between the coating and the ceramic. Based on Figure 5(b), the surface of the ceramic does not undergo any physical changes and the pressure –

sensitive tape was clear without any coating sticks on it. The tape only has several dots of the coating that sticks and it can be concluded that there was no coating that peeled off from the ceramic. According to Chen et. al. [12], low amount of PVA binder will increase the mechanical strength and relative density. Thus, 3 % of PVA have relatively high cohesion and become harder and said to have better sample properties compared to high amount of PVA binders.

Based on the adhesion test that have been performed on the sample containing PVA and PEG as binders, it can be concluded that sample containing PEG as binder have more binding forces between the coating and ceramic surface. Ceramic sample containing PEG have no defect compared to sample containing PVA which is 37.5 % defects. This result can be clearly observed on the pressure – sensitive tape where the tape on the PVA sample shows the coating stick on the tape while the tape on the PEG sample shows no coating that stick and the tape is clear.

IV. CONCLUSION

In conclusion, PEG binders is recommended in order to immobilize high composition of tin on the ceramic surface due to high composition of tin element presents on the surface of the ceramic when analyzed with EDX. The composition of tin present in the thin layer containing PEG is 5.50 % compared to 0.46 % composition of tin present in the thin layer containing PVA binder. Adhesion test result shows that thin layer containing PEG does not peel off from the ceramic surface while the thin layer containing PVA stick to the tape and peel off from the surface of ceramic at 37.5 %.damaged.

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