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Research paper

Coating of Tin Octoate on Ceramic Support: Effect of Polyvinyl Alcohol and Polyethylene Glycol as Binders

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Abstract

It has been an 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 ease of recycling and separating the catalyst. The objectives of this study are to produce ceramic support coating using polyethylene glycol (PEG) and polyvinyl alcohol (PVA) binders and to characterize the tin (II) octoate coating using EDX and standard adhesion test. Ceramic powder was obtained from ceramic waste and used to make the support by mixing with diluted PVA in a ratio of 3:1 before compressing and sintering in furnace at 1100^{o}C. Then, a 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 sintering 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 only 0.46 % of that containing PVA binder. In addition, result from adhesion test showed that the thin layer sample containing PEG did not peel off from the ceramic surface, while the thin layer containing PVA stuck to the tape and peeled off from the surface of ceramic at 37.5 %. In conclusion, PEG binder was recommended for the immobilization of high composition of tin (II) octoate on the ceramic surface.

Keywords: *Tin (II) Octoate, binders, ceramic coating, polyethylene glycol (PEG), polyvinyl alcohol (PVA)*

1. Introduction

Nowadays, there is a growing interest on the production of biodegradable polymers due to several disadvantages of petrochemical based polymers including increasing 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 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 addition, 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. The most common catalyst used was stannous octoate (tin (II) octoate) [4]. Among various types of catalyst, tin (II) octoate is the most preferable due to its 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 causes a major drawback since the catalyst is miscible in the reaction medium and made it difficult and costly process to remove the catalyst from the reaction medium. Besides, it dissolved into the solution and defect the final product. In addition, the difficulty to remove the catalyst leads to several problems 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 is introduced using solid porous support [8]. This method is done for easier separation and reuses the immobilized catalyst. The recovered 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 toxic metal catalysts [9].

The potential support that can be used to immobilize the catalyst is ceramic. 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 long chain polymer that provides strength to the ceramic body by forming 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).

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^{o}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 in 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 tin (II) octoate coating 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. Energy Dispersive X – Ray (EDX) and Adhesion Test (AT) were used to characterize the effect of the ceramic support coating.

2. Methodology

2.1. Materials and Chemicals

The raw material of ceramic was collected from 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.

2.2. Preparation of Ceramic Powder from Ceramic Waste

The ceramic waste was ground using a grinder Model DFY – 200 to reduce the particle size to smaller size. Then, the ground 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.

2.3. Preparation of Fabrication of Ceramic Support

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

The ceramic powder and the PVA was then mixed with a ratio of 3:1 before being compressed to remove the excess water and to make it like coin shape with a diameter of 32 mm approximately. The sample was dried for 24 hours in an oven before sintered. Front Loading Furnace (Carbolite) was used in the sintering process for 2.5 hours with temperature of 1100^{o}C. The same process was repeated using PEG.

2.4. 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 or 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^{o}C for 30 minutes. Then, 10 mL of PVA (binder) was added to the solution and stirred for 6 hours to get 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 before being sintered in an oven. This method was followed from Zaiton et.al [15].

2.5. 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. In addition, adhesion test was performed in order to evaluate the durability of the tin (II) octoate coating layer on the surface of the ceramic support. For this purpose, standard method D3359 was followed. An ‘X’ cut is made on the surface of the ceramic, pressure – sensitive tape was applied over the cut and removed with a steady motion by pulling at 180^{o} angle within 60 seconds. The ‘X’ – cut area was inspected for removal of coating from previous coating and rates the adhesion using provided scale.

3. Result and discussion

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

Fig. 1 and 2 show the EDX image of the elemental composition of the coating layer on ceramic surface by 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, tin, is present in the EDX image in both graphs. It can be concluded that tin (II) octoate is present in the coating layer of the ceramic surface.

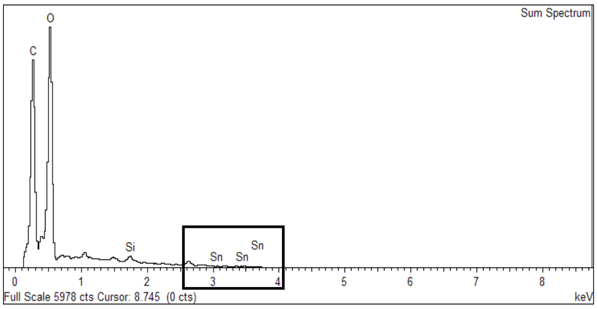


Fig. 1: EDX image for PVA binder

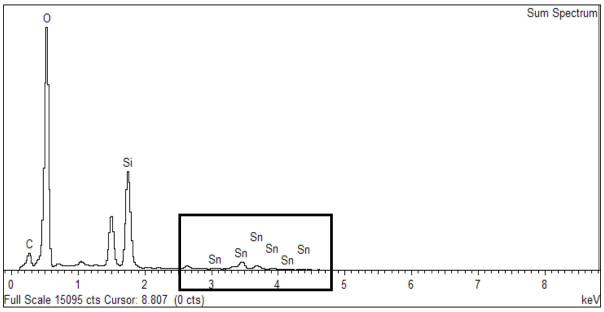


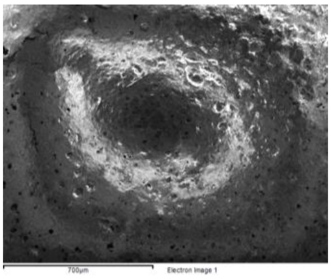
Fig. 2: EDX image for PEG binder

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

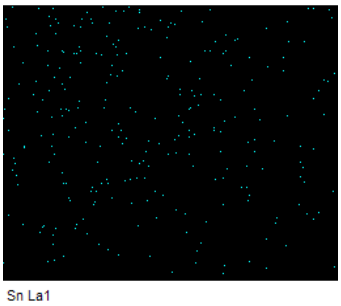
Table 1: Weight percent of elements exist in the coating layer

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

Based on Fig. 1 and 2, it is clearly observed that the graph containing PEG has more tin composition compared to PVA. Graph on Fig. 1 does not show any significant peak value for the composition of tin while graph on Fig. 2 shows two significant peaks that indicates the element of tin on the coating surface. In addition, Table 1 shows the exact composition of all elements analyzed by the EDX. The sample containing PEG shows high value of tin composition which is 5.50 % while the sample containing PVA shows low value of tin composition which is only 0.46 %. Based on the image in Fig. 3 and 4, the composition of tin is more in the PEG binders compared to PVA binders. The composition of the tin can be determined by the numbers and compaction of the blue dots. Fig. 4(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 Fig. 3(b).



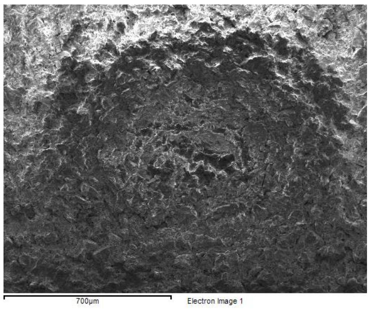
(a)



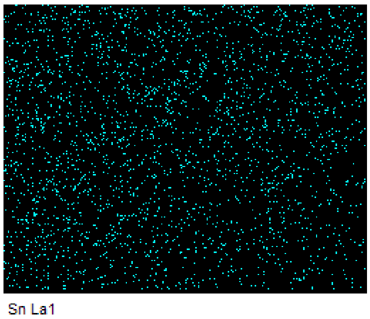
(b)

Fig. 3: (a) SEM image for coating of ceramic surface using PVA (b) Composition of tin by mapping technique using EDX

Meanwhile, Fig. 3(a) and 4(a) show the SEM image of the coating layer using PVA and PEG respectively. It can be seen from the figure that, the morphology of the coating layer is differ between each other with the result of using different binder. Layer with PVA binder seems to be more shinning compared to the one using PEG. The shining surface caused the layer to be weak in adhesion test (discussed later). While for PEG, the surface is quite rough where the particle structure can be seen clearly in the image. This rough morphology helps in producing a strong coating layer.
Based on the result analyzed from 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 [16] proving that immobilized TiO_2 – PEG as binder was very stable and showed excellent sustainable photocatalytic activity. In additional, Lidija et.al. [17] proved that addition of PEG on glass by using sol – gel dip coating method showed 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].



(a)

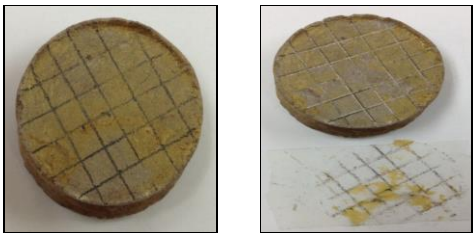


(b)

Fig. 4: (a) SEM image for coating of ceramic surface using PEG (b) Composition of tin by mapping technique using EDX

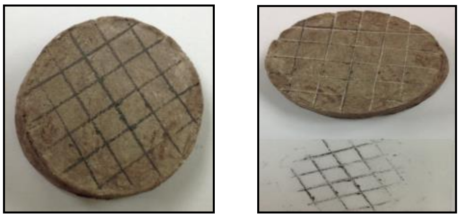
3.2. Effect of Binders on the Mechanical Strength of Thin Layer of Coating

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 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.
Fig. 5(a) shows the surface area before performing the adhesion test for PVA binders while Fig. 5(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 that 6/16 of the 'X' cut is peeled off from the surface of ceramic which are equivalent to 37.5 % damaged.
Based on Fig. 6, the surface of the ceramic does not undergo any physical changes and the pressure – sensitive tape is 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 is no coating that peeled off from the ceramic. It can be concluded that sample containing PEG as binder have more binding forces between the coating and ceramic surface. This result is about to be similar with the one reported by Amirjan and Khorsand [18], except for different material used for the study. They applied aluminium powder with different types of binder system. Out of the six binder system used, 3 wt% PEG/CMC binders revealed the best final film quality.



(a) (b)

Fig. 5: Surface area for PVA (a) before adhesion test and (b) after adhesion test



(a) (b)

Fig. 6: Surface area for PEG (a) before adhesion test and (b) after adhesion test

4. 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 using EDX. The composition of tin present in the thin layer containing PEG is 5.50 % compared to only 0.46 % for 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 % of damaged.

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References

[1] Jamshidian, M., Tehrany, E. A., Imran, M., & Jacquot, M. (2010). Poly-Lactic Acid : Production, Applications, Nanocomposites, and Release Studies, 9, 552–571.

[2] Taylor, P., Mehta, R., Kumar, V., & Bhunia, H. (2012). Journal of Macromolecular Science, Part C : Polymer Reviews Synthesis of Poly (Lactic Acid): A Review Synthesis of Poly (Lactic Acid): A Review, 37–41.

[3] Kozlovskiy, R., Shvets, V., & Kuznetsov, A. (2017). Technological aspects of the production of biodegradable polymers and other chemicals from renewable sources using lactic acid. Journal of Cleaner Production, 155, 157–163.

[4] Bakibaev, A. A., Gazaliev, A. M., Kabieva, S. K., Fedorchenko, V. I., & Guba, G. Y. (2015). Polymerization of Lacti c Acid Using Microwave and Conventional Heating. Procedia Chemistry, 15, 97–102.

[5] Schwach, G., Coudane, J., Engel, R., & Vert, M. (1997). Polymerization of Lactides in the Presence of Stannous Octoate, 3431–3440.

[6] Govan, J., & Gun, Y. K. (2014). Recent Advances in the Application of Magnetic Nanoparticles as a Support for Homogenous Catalysts, 222–241.

[7] Lebeau, J. M., & Boonyongmaneerat, Y. (2007). Comparison study of aqueous binder systems for slurry-based processing, 458, 17–24.

[8] Carneiro, L., Silva, A. R., Shuttleworth, P. S., Budarin, V., & Clark, J. H. (2014). Synthesis, Immobilization and Catalytic Activity of a Copper (II) Complex with a Chiral Bis(oxazoline), (Ii), 11988–11998.

[9] Wei, L. (2012). Designing Immobilized Catalysts For Chemical Transformations : New Platforms To Tune The Accessibility Of Active Sites Designing Immobilized Catalysts For Chemical Transformations, (August).

[10] Sáenz, A., Rivera-muñoz, E., Brostow, W., Castaño, V. M., Física, E. De, Rica. (1999). Ceramic Biomaterials : An Introductory Overview, 21, 297–306.

[11] Taktak, R., Baklouti, S., & Bouaziz, J. (2011). Effect of binders on microstructural and mechanical properties of sintered alumina. Materials Characterization, 62(9), 912–916.

[12] Chen, Q., Cabanas-polo, S., Goudouri, O., & Boccaccini, A. R. (2014). Electrophoretic co-deposition of polyvinyl alcohol (PVA) reinforced alginate – Bioglass ® composite coating on stainless steel : Mechanical properties and in-vitro bioactivity assessment. Materials Science & Engineering C, 40, 55–64.

[13] Hassan, C. M., & Peppas, N. A. (2000). Structure and Applications of Poly (vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing / Thawing Methods, 153.

[14] Tasi, N., Brankovi, Z., Marinkovi, Z., & Brankovi, G. (2012). Effect of Binder Molecular Weight on Morphology of TiO 2 Films Prepared by Tape Casting and Their Photovoltaic Performance, 44, 365–372.

[15] Zaiton, R., Omar, N. A., & Ibrahim, N. (2018). Morphology and Chemical Structure of Sn (2) Oct Thin Layer Added Binder Via Sol Gel Method, 22(2), 311–317.

[16] Nawawi, W. I., Zaharudi, R., Azlan, M., Ishak, M., & Ismail, K. (2017). Applied Science: The Preparation and Charactherization of Immobimized TiO2/PEG by using DSAT as support binder.

[17] Lidija, C., Fiamengo, I., & Tomas, N. (2011). Synthesis, Charactherization, and Photocatalytic Properties of Sol – Gel TiO2 film, 37, 1153 – 1160.

[18] Amirjan, M. & Khorsand, H. (2014). Processing and properties of Al-based powder suspension/slurry: A comparison study of aqueous binder systems, stability and film uniformity. Powder Technology, 254, 12-21.