International Journal of Engineering & Technology, 7 (4.18) (2018) 301-305

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Coating of Tin Octoate on Ceramic Support as A Function of Concentration and Sintering Temperature

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Abstract

Tin octoate was used as condensation polymerization catalyst in the production of polylactic acid (PLA). As the phase of catalyst was similar to PLA as product and lactide as reactant, this caused difficulty in recycling the catalyst and contaminant of PLA product if the catalyst remained in the product solution. Therefore, this study aimed to prepare heterogeneous catalyst by depositing tin octoate onto ceramic support using sol-gel method. Effects of concentration of tin octoate and sintering temperature of the coated layer were studied. The concentrations of catalyst used in preparing the coating solution were 250 ppm, 500 ppm and 750 ppm, while the temperatures were ranged from 150°C to 250°C. The coated layer was characterized by adhesion and Energy Dispersive X- ray (EDX) test. The result showed that ceramic support coated with 500 ppm of tin octoate solution had the highest distribution of tin and the strongest adhesion compared to the other two. While for the temperature, it had been shown that sintering temperature at 150°C produced high quality of coating as the percentage area removed was only 5%. However, temperature at 200 ^{o}C presented the highest amount of tin which was 11.97%. In conclusion, good heterogeneous catalyst in terms of catalyst distribution and its attachment on ceramic support was able to be produced using 500 ppm of tin octoate at sintering temperature of 200 ^{o}C.

Keywords: *Tin (II) Octoate, sol gel coating, ceramic support, deposition, polylactic acid*

1. Introduction

Tin octoate or stannous octoate, $Sn(Oct)_2$ is widely used in paints and coatings applications. It is also commonly used as metal catalyst in the production of polylactic acid (PLA) [1]. It is reported that this catalyst can act as an initiator which can provide high reaction velocity and high transformation [2]. Polylactic acid is used in the production of food packaging due to its low toxicity level which makes it suitable and safe to be used by consumer [3]. Currently, biocompatible thermoplastic of PLA is the most promising and popular material with the highest development prospect and is considered as -'green' eco-friendly material. This is because PLA biomaterial product can reduce the reliable on petroleum and therefore replacing oil-based traditional plastics.

Although the reaction can achieve high yield of PLA, this process has some disadvantage which comes from the catalyst itself. In previous invention of industrial process, this catalyst is mixed homogeneously together with raw material and both exist in liquid form. This results in difficulty to remove the catalyst at the end of the process and therefore hard to be recycled. The products need to be purified through purification process in order to separate the catalyst and product which made the process complicated and expensive [4].

It is reported that immobilizing homogenous catalyst on support, which is known as heterogenization process, can help in isolation of surface active species to prevent agglomerization of catalyst. Hence, the catalyst can be used for a longer period. However, in order to prepare heterogenous catalyst, several parameters need to be considered, among others are the catalyst concentration and sintering temperature of the sample. In order to get a homogenous solution, a specified concentration of tin octoate on ceramic support coating is needed. On the other hand, based on [5], the issue regarding sintering temperature is about the sintering technique itself. This is because it affects the microstructure of particle and grain density. For conventional sintering method which is direct sintering, it produces uneven pore size distribution and non-uniform grain size distribution.

In this study, the effect of tin octoate concentration in preparing the coating solution and sintering temperature of the coated layer was investigated. The ceramic support was fabricated and used in the coating step. The characterization of the coated layer was carried out using adhesion test and Energy Dispersive X-ray (EDX) spectroscopy.

2. Methodology

2.1. Preparation of ceramic support

The ceramic waste was grinded using a grinder Model DFY – 200 to reduce the particle size to smaller size. The grinded ceramic was sieved for 20 minutes using Endecotts Octagon 2000 Digital Sieve Shaker with two different trays which were 150 µm and 125 µm to get particle size of approximately 125 µm. The method to prepare the ceramic support was followed from Norliza et al. [6].

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2.2. Preparation of coating solution

In order to prepare 250 ppm of coating solution, about 100 ml of ethylene glycol was added with 5 ml tin octoate and stirred for 30 min at room temperature. Next, 1 ml of 0.1 M nitric acid was added to peptize the sol. Then 10 mL of PVA was added into the solution and stirred for 6 hours at 90°C using magnetic hot plate and left for 24 hours for aging process. All steps were repeated using 10 and 15 mL of tin octoate for preparing 500 ppm and 750 ppm of tin octoate solution respectively.

2.3. Coating of thin layer on ceramic support

Ceramic support was dipped into the prepared coating solution for about 5 minutes before being sintered in an oven. The sintering temperature was varied from 150°C, 200°C and 250°C for 2 hours.

2.4. Characterization of ceramic support coating

The characterization technique was focused on the composition of the tin octoate on the surface of the ceramic support. Energy Dispersive x – ray (EDX) spectroscopy was used to identify the elemental composition of the materials. In addition, adhesion test was performed according to Standard D3359. This test was done in order to evaluate the durability of coated layer on the surface of the ceramic support.

3. Result and discussion

3.1. Mechanical strength of the coating layer

Fig. 1 shows the coated layer attached to the pressure-sensitive tape after adhesion test. It can be seen clearly that the coated layer sintered at 150 ^{o}C shown in Fig 1(a) presents the strongest mechanical strength compared to the other two as no yellowish color of the coated layer can be seen attached to the tape (0/16). While in Fig 1 (b) and (c) which representing sintering temperature of 200 ^{o}C and 250 ^{o}C, the attachment of yellowish color is 8/16 and 16/16 respectively. It seems that increasing the temperature caused the strength to reduce accordingly.

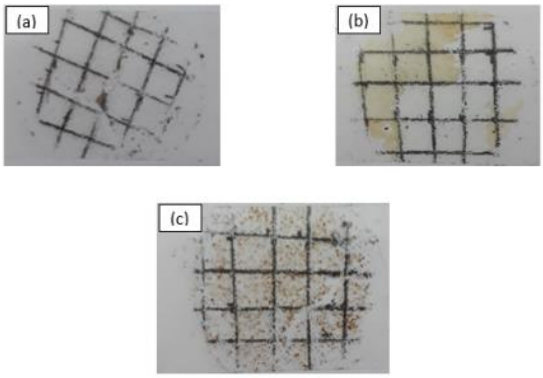


Fig. 1: Surface of pressure-sensitive tape after the adhesion test at sintering temperature of (a) 150°C (b) 200°C and (c) 250°C

The percentage of area removed at different sintering temperature is summarized in Table 1. It can be seen that the area removed using 150 ^{o}C of sintering temperature is the lowest which is 5%. It is classified under 4B which indicate only small flakes of the coating are detached at the intersections. As the temperature increase, the area removed is also increased. Meanwhile, for sample at 200 ^{o}C, it is under 2B and the area removed is 35% where the coating flakes along the edges and whole of the square are detached at some of the parts. Next, for 250 ^{o}C, it is under 0B classification because the affected detachment area is large (more than 65%).

Table 1: Percentage of area removed at different sintering temperature

Sintering temperature (^{o}C)	Percent area removed (%)	Classification
150	5	4B
200	35	2B
250	90	0B

It was reported by Xiao et al. [7] that increasing the sintering temperature of ceramic aggregates, the abrasion resistance of the coating initially increased until achieving certain temperature. For their study, the abrasion resistance of the coating reached the highest value at 400°C, compared to other temperature of study which was 200°C, 600°C and 800°C. When the sintering temperature exceeded 600 °C, the abrasion resistance began to decrease, and after the coating was sintered at 800°C, the wear resistance of the coating was reduced. The reason of that observation was because after the ceramic coating was sintered at 200°C, 400°C, 600°C and 800°C, the gel in the coating forms a continuous sintered body, and the moisture migrates and evaporates to produce systolic compressive stress. Meanwhile, the main reason for the decrease in the abrasion resistance of the coating after sintering at 800°C was the full expansion of the crack. In this study, sintering temperature at 150°C is the best condition with the same reason. This observation was also supported by Rubi et al. [8] in their study of wear properties of sol–gel alumina coatings on surface pre-treated mild steel. The best condition was also at 400°C. The occurrence of a superior bonding between the sol–gel alumina coatings and the substrate at a sintering temperature of 400°C could be the reason for the exhibition of its higher wear resistance. Fig. 2 shows the surface of the coated layer using different tin concentration. Tin concentration of 500 ppm gives the best adhesion resistance where only 7/16 of the square being detached from the surface compared to 10/16 and 13/16 for 250 and 750 ppm respectively. This is supported by the area removed using this concentration, which is 30%, as can been in Table 2.

Study by Huang et al. [9] on the effect of titanium concentration on wear resistance indicated that, with the increasing of Ti concentration, the film structure changes and cause an increament in graphitization. This condition cause the wear rate to increase and this observation was also presented in the current study except for that of 250 ppm. Besides, the friction debris which was originated from soft Ti6Al4V counterpart, used in their study, created the adhesive wear on the worn surface which caused high wear rate. In the current study, the debris was originated from the ceramic support itself. This was also supported by Yazdani et al. [10] which revealed that another logical explanation for this behavior could be the crystallization of the amorphous coated sample during the wear test, due to the heat generation.

Table 2: Percentage area removed at different concentration

Concentration	Percent area removed (%)	Classification
250 ppm	48	1B
500 ppm	30	2B
750 ppm	67	0B

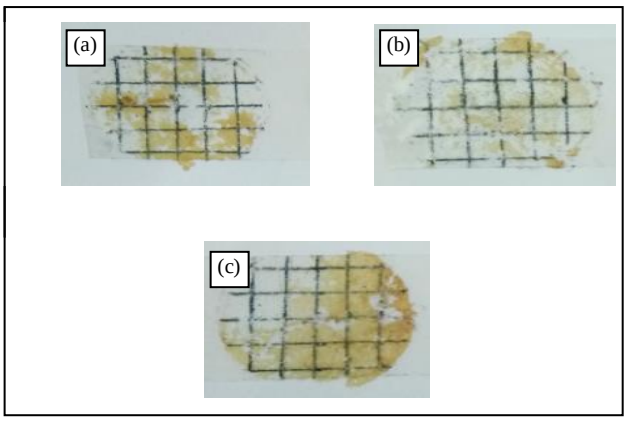


Fig. 2: Surface of pressure-sensitive tape after the adhesion test at tin octoate concentration of (a) 250 ppm (b) 500 ppm and (c) 750 ppm

3.2. Elemental compositions on coating layer

In EDX analysis, the composition of the elemental component in the sample can be determined. The elemental compositions of main component in the coated layer are summarized in Table 3. For the coated sample sintered at 150 ^{o}C, the amount of the carbon (C), oxygen (O) and tin (Sn) components in the sample are 45.47%, 51.59% and 2.67% respectively. It can be seen clearly that the amount of tin component is the lowest compared to the other two components. This can be seen clearly in Fig. 3(a) and 4(a) which shows the distribution of the tin is less compared to C and O. This is because C and O elements presence in all raw material used in the experiment such as nitric acid (HNO_3), polyvinyl alcohol or PVA ($(C_2H_4O)n$), ethylene glycol ($C_2H_6O_2$) and distilled water. Meanwhile, tin component only presents in tin octoate, $Sn(Oct)_2$ compound.

Table 3: The elemental compositions of coated layer using different sintering temperature

Sintering temperature	Weight of the element component (%)		
	Carbon, C	Oxygen, O	Tin, Sn
150	45.74	51.59	2.67
200	33.25	54.78	11.97
250	40.54	57.61	0

For the coated sample sintered at 200 ^{0}C, the amount of the carbon (C), oxygen (O) and tin (Sn) components in the sample were 33.25%, 54.78% and 11.97% respectively. While for coated layer sintered at 250 ^{o}C, the compositions of the element were 40.54%, 57.61% and 0% respectively. This pattern of results is supported by Fig. 3 and 4, which show the distribution of the three elements at different sintering temperature. From Fig. 3(b), which is at 200 ^{o}C, the tin spectrum is the largest compared to temperature of 150 ^{o}C and 250 ^{o}C. The same goes to Fig. 4, where at sintering temperature of 200 ^{o}C, the tin distribution is the most.

The coated layer shows the highest content of tin at 200 ^{0}C. This result was supported by Xiao et al. [7] which indicated that the highest amount of elemental component was obtained from dense layer with no coarse pores and cracks. Increasing the temperature caused the coated layer to gradually increasing the cracks. This shows that sample at 200 ^{0}C has better structure and the porosity of the sample was reduced because of no coarse pore in the sample compared to others. Due to these factors, the amount of tin increased [11].

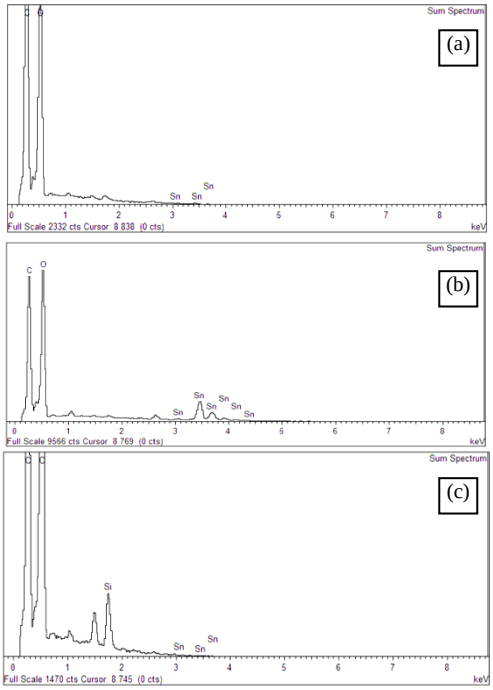


Fig. 3: The EDX spectrum of the elemental component at (a) 150^{0}C (b) 200 ^{o}C and (c) 250 ^{o}C

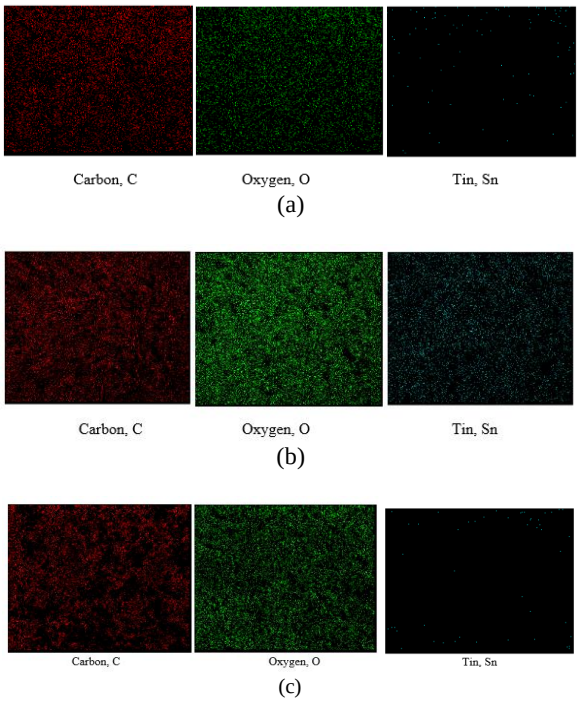


Fig. 4: The EDX analysis for C, O and Sn distribution on the coated layer at (a) 150^{0}C (b) 200 ^{o}C and (c) 250 ^{o}C

The boiling temperature of tin octoate is at 228 ^{o}C. It can be understood from the results obtained that tin decomposed when sintered at 250 ^{0}C. Meanwhile, sintering temperature of 150 ^{0}C shows unsuitability that leads to the poor quality of coating. In addition, the result was agreed with the study done by Gültekin [12] who state that sintering temperature gave a huge impact to the porosity properties. Moreover, according to the Liu et al. [11], sintering temperature was influencing the composition and the microstructure of the coatings. As the sintering temperature increasing, the porosity of the sample becomes decreasing. When the porosity is reduced in a sample, the void space in the solid sample (ceramic support) is also reduced. Hence, it can increase the amount of tin in the coating layer. This can be said that sinter-

ing temperature affects the properties, composition and the microstructure of the coating layer.

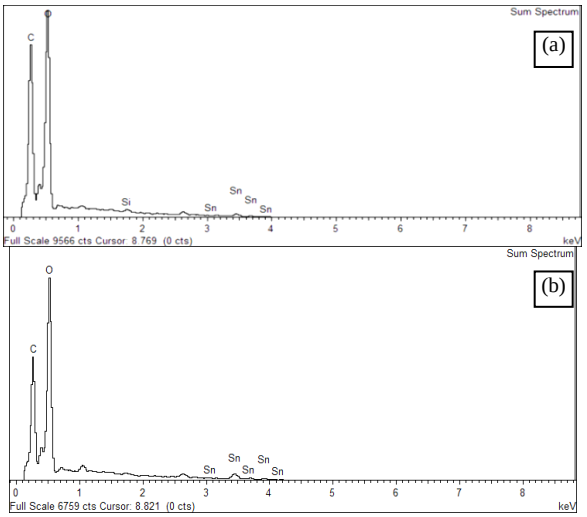
Effect of tin concentration towards the elemental compositions of the coated layer is given in Table 4. The weight percentages of C, O and tin components for tin concentration of 250 ppm were 38.49 %, 60.10 % and 1.14 % respectively. At 500 ppm, the tin element increases to 3.19% which later drops to 0.21% when the concentration increases to 700 ppm. On the other hand, Fig. 5 and 6 represents the distribution of the element discussed in the study. It is clearly shown a dense concentration of tin at 500 ppm compared to the other two concentrations.

Low weight percent of tin at 250 ppm was because of low concentration of tin octoate in the coating layer. Hence, low distribution of tin was observed in the sample. Meanwhile, sample at 750 ppm tin octoate concentration shows the lowest distribution of tin. This was resulted from the high concentration of tin octoate that produced dense layer of coating. This dense layer caused cracking after sintering and destroyed the coating structure. Tin concentration at 250 ppm was the best for the study, where at this concentration, the coating produced had smooth appearance and formed more compact and higher aggregates.

It was found that the high adhesion and very good exploitative properties of coating are undoubtedly connected with the existence of intermediate zones between the substrate and the coating [13]. Other than that, Burnat et al. [14] reported that coatings doped with lower concentrations of calcium ions had a fine crystalline structure. Whereas in case of the highest concentration of calcium ions, such fine crystalline structure was not observed, but the pores were visible. In the current study, the visibility of the pores gave defect to the coating layer and caused the reduction in elemental distribution and strength of the coating layer. Moreover, the concentration of doped calcium ions affects the surfaces roughness of the coating in microscale.

Table 4: The elemental compositions of coated layer using different tin concentration

Tin concentration (ppm)	Weight of the element component (%)		
	Carbon, C	Oxygen, O	Tin, Sn
250	38.49	60.1	1.14
500	32.1	64.71	3.19
750	49.39	49.84	0.21



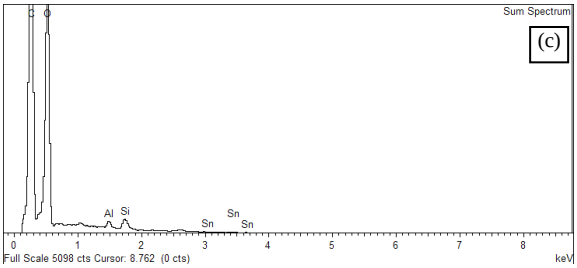


Fig. 5: The EDX spectrum of the elemental component at (a) 250 (b) 500 and (c) 750 ppm

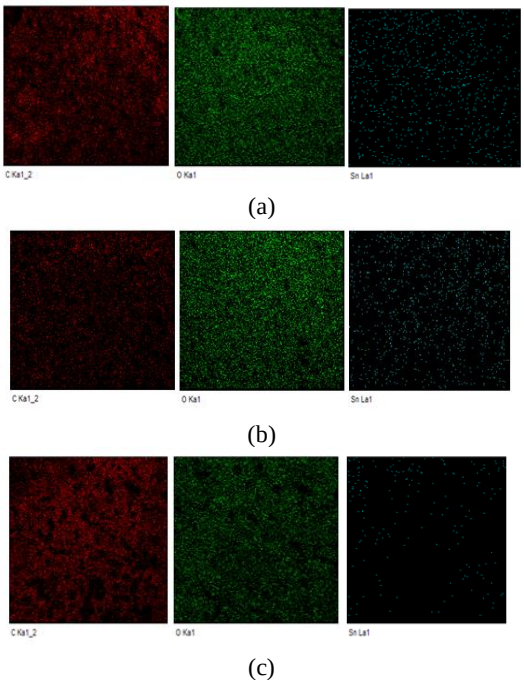


Fig. 6: The EDX analysis for element C, O and Sn distribution on the coated layer at (a) 250 (b) 500 and (c) 750 ppm.

4. Conclusion

In the present study, the usability of sol-gel technique to produce tin octoate coatings was demonstrated. It was proved that sintering temperature and tin concentration influences the final properties of produced coatings. The obtained results showed that sintering temperature at 150°C produced the highest strength layer of the coating on ceramic support where only 5% of area was detached after the adhesion test. It was found that at tin concentration of 500 ppm leads to the highest percentage of tin element in the coating layer up to 3.19%. For sintering temperature, the highest percentage of tin element was at 200 ^{o}C with a value of 11.97%.

Acknowledgement

The authors would like to thank the Ministry of Education Malaysia for financial support via Fundamental Research Grant Scheme (600-IRMI/FRGS 5/3 (93/2016)). The authors gratefully acknowledge Universiti Teknologi Mara especially Faculty of Chemical Engineering and Dentistry for use of research facilities available.

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