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IJIE

Journal homepage: http://penerbit.uthm.edu.my/ojs/index.php/ijie
ISSN : 2229-838X e-ISSN : 2600-7916

The International Journal of Integrated Engineering

The Effect of Electrophoretic Deposition Current to Tinplate Coating with Chitosan

Femiana Gapsari[1*], Putu H Setyarini[1], Erfinda F Fajrin[1]

[1]Mechanical Engineering Department, Brawijaya University,
Jl. MT. Haryono 167, Malang, 65145, INDONESIA

*Corresponding Author

DOI: https://doi.org/10.30880/ijie.2019.11.05.003
Received 8 January 2019; Accepted 17 April 2019; Available online 10 August 2019

Abstract: This study was a preliminary study in applying chitosan as coating for tinplate. Tinplate was used as the material for packaging because it was cheap, attractive, shiny, and easy to shape. Chitosan coating on tinplate with electrophoretic deposition (EPD) method and variation of EPD current was performed in this study. The variation of the current was 2, 4, 6,and 8A. Coating thickness was measured using NOVOTEST TP-1M. The surface roughness was tested using Mitutoyo Surface Roughness Tester SJ-210. The corrosion test applied the polarization method of PotentiodynamicAutolab PGSTAT 128N with Control software NOVA 1.11. The corrosion test of the specimen was run in 3.5% NaCl solution. The specimens without treatment had higher corrosion rate compared to the specimen with EPD current of 8A which was 0.00061927 mpy. At the current variation of 8A, the coating thickness was 78.9 ± 1.58 %.The higher the current used in the EPD, the lower the corrosion rate was. It was indicated by coating that protected the tinplate and produced homogeneous coating. This was in line with the result of surface roughness which decreased along with the increase of EPD current. The lowest surface roughness was at variation of 8A which was 0.152 µm.

Keywords: Chitosan, coating, corrosion, electrodeposition, tinplate

1. Introduction

Rapid development has been happening in the coating technology, which is not only in biomaterial but also in food industry. We know that in this era, where everything is practical, people demand for practical and long shelf-life-food. This triggers many industries to innovate and adjust the packaging of their food production in order to meet the consumers' standard. Cans for food and drink are usually made from tinplate.Tinplate is used for packaging material because it is cheap, attractive, shiny, and easy to shape.Tin plate is one of the materials which has been used 80 % as a new altenative packaging material. It consists of carbon steel compound coated with pure tin on the both sides.Even though tinplate has been widely applied as food packaging material, there are some serious problems found during the application. One of them is the possibility to corrode which is triggered by the interaction between the packaging and the product [1, 2]. This promotes other problems such as broken seal and the colour change of the product [3]. This usually happens to the food cans which have been opened. This is caused by the reaction between the can and the environment. This reaction is defined as a corrosion reaction. Corrosion is a process of material and quality degradation caused by the influence of chemical and electrochemical reaction with the environment. In order to make the cans to not easily corrode, there should be some preventive solutions such as the coating process on the can surface [4,5], cathodic protection [6,7], or adding corrosion inhibitor [8-12].

Many studies on the application of chitosan as coating material [13-15] and inhibitor [16-18] have been conducted. This kind of material is a natural polymer which is extracted from shells, bones, or skin in seafood waste [19]. Applying chitosan as biopolymer coating for metal was conducted [14]. Chitosan structure modification with mixture of epoxy and vanadate was applied on Aluminium 2024 T3 compound, where chitosan contained a very reactive hydroxil and amina group which was able to form complex with metal ion on aluminum surface. EIS measurement

*Corresponding author: femianagapsari@gmail.com

result showed that thecoatedsample using modified chitosan had better corrosion resistance with high impedancy result compared with the uncoated sample [13].The result was the decrease in corrosion rate of the coated metal. Chitosan derived from the sea wasteusually has food grade quality. Thus, it can be used as coating for the tinplate of the food can. Chitosan is also used as organic coating material for tinplate which is environmental friendly, unpoisonous and economical. Chitosan is natural polysacaride which can be found on *crustacea* shell/skin like shrimps, crabs, insects' epidermis, and cell walls of fungi. Chitosan is classified into N-deacetylated chitin product. It possesses high ability to form film coating, antimicrobial activity, biogdegradability, and biocompatibility which makes it favorable in industry. Chitosan and cellulose are alike and Chitosan is classsified as linear polyamine.

The coating method which is usually performed is electrophoretic deposition (EPD). EPD method is influenced by some factors such as time, substrate conductivity, potential giving, and suspension concentration [20, 21]. The influence of EPD time is related with the amount of chitosan molecule that will sediment. The potential variation influences the speed of chitosan molecule movement. Chitosan coating on tinplate with EPD method and current variations was conducted in this study.

2. Method

The chitosan used in this study was chitosan C3646. This kind of chitosan was derived from shrimp shells. The EPD tool was made for coating with carbon as an anode, tinplate as acathode, and chitosan as a coater that had been dissolved using 0.026 M acetic acid.The carbon used in the study had diameter of 3mm and length of 40 mm. Tinplate with section width of 4 cm x 1 cm was washed cleanly with aquades and then dried. Next, anode and cathode were immersed in a tub with 0.3% chitosan solution and charged with electric current through power supply.The current in the EPD process was varied in 2, 4, 6, and 8A. The coating thickness was measured with NOVOTEST TP-1M. Coating thickness used the type of probe NF-2 with thickness of coating range between 0 to 500 µm with probe diameter 12 x 35 mm.The surface roughness was tested using Mitutoyo Surface Roughness Tester SJ-210with standard of ISO 1997. The corrosion test was performed with polarization method of PotentiodynamicAutolab PGSTAT 128N with control software NOVA 1.11.The tinplate specimen was used as working electrode. The reference electrode was Ag/AgCl and the auxiliary electrode was platen. The polarization measurement was run at scan rate with range -1 V to +1 V at Open Circuit Potential (OCP).The corrosion rate test on the specimen was performed in 3.5% NaCl solution. Fourier-Transform Infrared Spectroscopy (FTIR) measurement was conducted to know the change of chitosan function group and chitosan on the surface of the tinplate.

3. Results and Discussions

The data of the coating thickness measurement

Table 1- The Coating thickness.

Current (A)	Coating Thickness (µm)
2	29.5 ± 4.62 %
4	45.7 ± 3.80 %
6	67.7 ± 2.31%
8	78.9± 1.58 %

Table 1 displays data of coating thickness (measurement ranging from 2 A to 8 A). Therefore, the thickness homogeneity willincrease. Decreasing deviation standard will produce high thickness homogeneity which is indicated by the even coating on the tinplate surface.If there is high coating homogeneity, the pore diameter will be smaller which will make the surface of the oxide coating smoother and more solid. Thus, the width of contact zone and the corrosive compound will be smaller and the corrosion rate will decrease too. The coating on the tinplate is influenced by the kinetics. This is prompted by the particle accumulation rate which coats the specimen. At the current range of 0 to 8A, chitosan particles are able to coat specimen perfectly and form close-packed structure [20, 21] This also can be proved by roughness testing on Table 2. The increase of coating thickness will make the surface roughness smaller.

Table 2- The result of surface roughness test

Current	Ra

(A)	(μm)
Uncoated	0.297
2	0.250
4	0.192
6	0.170
8	0.152

In Table 2. the results show that untreated specimen has the highest roughness value which is 0.297 μm. The current variation of 2A produces roughness value 0.250 μm, 4A produces 0.192 μm, and 6A produces 0.170 μm. The lowest value is obtained at 8A current with roughness value 0.152 μm.

The quality of the surface can be seen based on the surface roughness value of specimen, both the result of coating and machinary[22-24]. The higher the current used in EPD process, the lower the corrosion rate is. It is indicated by the coating which protects tinplate and produces homogeneous coating. This is shown by the surface roughness which is getting low [25] with the increase of current in EPD process of tinplate with chitosan

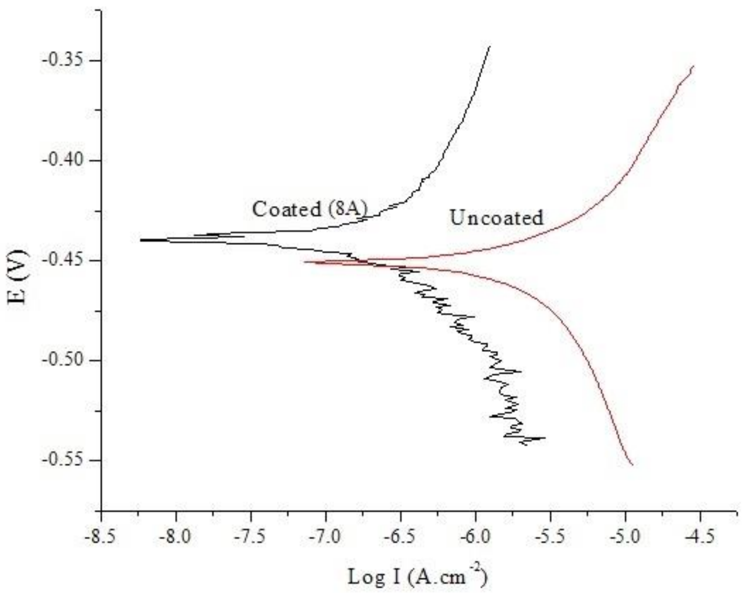

Fig. 3 - The Tafel Plot of the corrosion rate on the coated and uncoated metal

Table 3-The Potentiodynamic polarization parameters for the coated and uncoated tinplate

Variation	Ba (V/dec)	Bc (V/dec)	Ecorr (V)	Icorr (A/cm^2)	Corrosion Rate (mm/year)
Uncoated	3.9319	0.11573	-0.4507	$8.1x10^{-6}$	0.10798
8 A	0.02216	0.01841	-0.4542	$4.6\ x10^{-8}$	0.00061927

From Figure 1 and Table 3, it can be summed up that the untreated specimenshave higher corrosion rate compared to the specimens with EPD current of 8A with value of 0.00061927 mm/year. This is because the coating formed is getting thicker with the increase of current in the process of EPD. If the current used becomes higher, the solution temperature will increase and it causes the cation and anion on the condition move aggressively.Temperature also influences the quality of EDP coating. Optimum temperature will produce good coating quality.However, it does not influence the coating texture.The high current also causes the electrolyte solution ability increase and it will increase the coating speed which will make the tinplate well protected. The coating is getting much formed which can protect the tinplate from the solution/environment. The data of corrosion rate are in line with the coating thickness measurement. The coating efficiency produced at 8A is 99.4%.

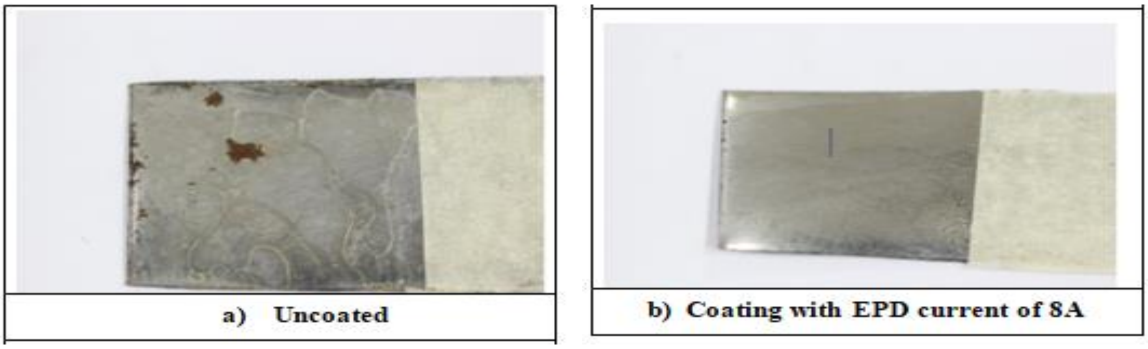

Fig. 2-The Macro photo of the specimen a) uncoated; b) coating with EPD current of 8A

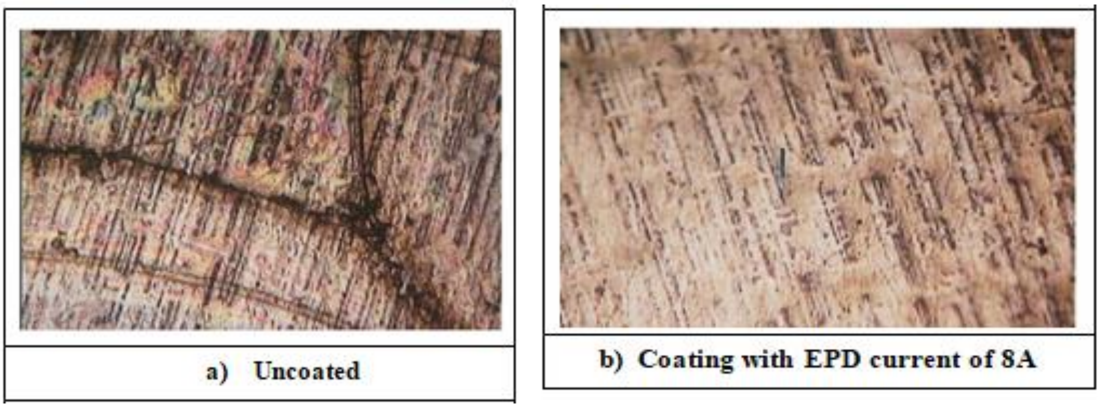

Fig. 3- Micro photo with magnification of 200X of the specimen a) uncoated; b) coating with EPD current of 8A

Figure 2 and 3 shows that micro photo indicatesthe formation of smooth ,uniform, and crack-free coating on the tinplate. The type of corrosion that occurs on the tinplate is in the form of pitting corrosion. In EPD process, there are three main components which are cathode, anode, and electrolyte solution. The reaction among the three components may cause chitosan coat the workpiece.

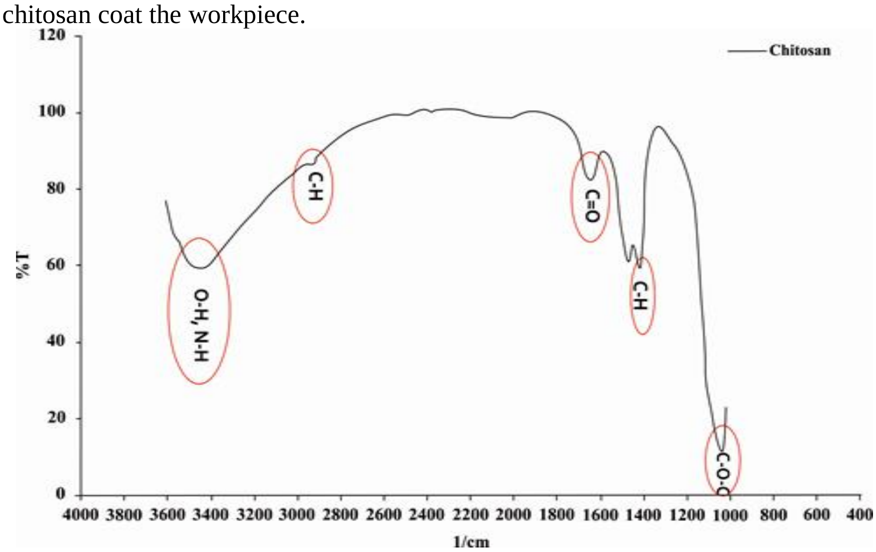

Fig. 4-FTIR spectra of chitosan

FTIR test was performed to prove the chitosan adsorption with EPD. The results are presented on Fig. 4. It can be seen the bound of O-H, N-H, C-H, C=O, C=H, C-O-C. These groups are the standard functional groups of chitosan.

Fig. 5 - FTIR spectra of the EDP specimen coating with chitosan

The results of metal FTIR after EDP with chitosan and the formed functional groups are presented in Fig. 5. At the wave number of 1600 - 1700 cm -1, there is N-H bound. There is CH_3-Sn-N at the wave number of 800-900 cm-1. This proves that there is adsorption of chitosan on the tinplate with the formation of protecting layer. It can be concluded that EDP tinplate with chitosan has ability to form protective layers on the surface.

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