The effect of *Theobroma Cacao* peels extracts inhibitors on mild steel fatigue behaviour

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Abstract. This research relates with polar extract of *Theobroma cacao* peels as an inhibitor for corrosion to improve the fatigue properties of steel. The polar extract of cacao added varies from 5 percent to 2.5 percent, with 1.5M HCl corrosive media, and 32 days immersion time. To see the effect of corrosion, the steel is immersed in solution of HCl which has been added corrosion inhibitors. The results obtained were characterized by AFM, SEM, Energy Dispersive X-Ray, and fatigue strength testing using the ASTM E4662002 procedure. The results of adsorption during immersion showed that inhibitors were able to reduce the corrosion rate and increase inhibitory efficiency, thereby increasing the fatigue properties of mild steel. Surface analysis shows that surface topography looks smoother, because of adsorption on the surface in the form of a film layer that can decrease the corrosion attack. This smooth surface seems effective to avoid initiation of cracks on the surface of steel. Immersion of steel for 32 days in solution HCl 1.5M with 2.5 percent addition of cacao peels polar extract of are very effective to minimize corrosion attacks on surface of steel, then is able to recovery the fatigue properties of mild steel.

1. Introduction
Corrosion is attack or degradation of metals due to reactions of redox between a metal and several substances in its environment which produce unwelcome compounds. Metals corrosion is a conflict matter that must be confronted for safety, environment, and economic reasons. It can be reduced by many strategies which in turn stifle, retard or completely stop the cathodic or anodic reactions or both [1]. Corrosion of steel, will refuse the quality due to the electrochemical or chemical reaction between the environment and its steel.

Quantity methods are done to delay the rate of corrosion such as galvanizing, inhibitor, and electroplating [2]. Inhibitor is one strategy to reduce the impact of the degradation of material that is often used. Inhibitor serves to slow the rate of corrosion that works by forming a film layer on the metal surface [3]. Corrosion Inhibitor usually added slightly in environments of acidic, water of cooling, steam, or other environments.

This time, the inhibitor is the excellent solution to safeguard the corrosion of the metal. Corrosion inhibitor is a protection method that is flexible, can provide protection of the environment is less aggressive to the environment the level of corrosion is very high, simple to apply and the potency of the cost is highest because the barrier is formed very thin, so small amounts are able to prepare broad
protection[4]. Until now, many promoted various types of corrosion inhibitors of both inorganic and organic. The new inhibitor is hoped to minimize the rate of corrosion of materials, especially material of carbon steel. The use of inhibitors of corrosion will prepare protection against the material failure due to the diminishing quality carbon steel is corroded.

Previously, many combinations inorganic inhibitors are used such as Gluconate of Calcium, PEGME (Polyethylene Glycol Methyl Ether) and others. But in use, the inhibitor of inorganic has a weakness, among others: not biodegradable, poisonous and hazardous to the environment [5]. Based on these situations, today many people are switching to using inhibitors of organic are derived from natural materials. Organic corrosion inhibitors are non-poisonous, environmentally friendly, and biodegradable [6]. Attempts to get environmentally friendly inhibitors, which have been done such as the benefit of natural compound from plants such as extracts of bark, seeds, and leaves [7]. Results of prior studies show that some extracts of natural plants can be used for the inhibitor of corrosion. Such as plant of Oxandra Asbeckii [8], peel of Musa Paradica [9], leaves of Asteriscus Graveolens [10], leaves of Spirulina Pantesis [11], peel of Molasses [1], leaves of Zizyphus Spina Christi [12], leaves of Sebasnian Sesban [13], plant of Chlomolaena Odorata L [14], seed of Pongamia Piñata[15], plant of Mymecodia Pendans [16], and Theobroma Cacao peel [17]. These natural ingredients have proven its ability to act as an inhibitor of corrosion for some metals and alloys in several different aggressive medium. Extract of cacao peels is an inhibitor which is capable of improving the efficiency of inhibition of steel up to 96% [3]. A number of inhibitors of corrosion safeguard corrosion by adsorption to form a barrier layer that is not seen with a thickness of some molecules of course, some are due to environmental influences form a precipitate which is seen and protects the metal from attacks that metal of corrodes and products of produce that form a barrier film, and some are eliminating active constituents.

With the increasing the number production of cacao in Indonesia reaches one million tons/ year, resulting in the production of cacao peels will also rise. These production rises, holds tremendous promise to make the extract of cacao peels as an environmentally friendly of inhibitors, which can recovery the mechanical properties of steel after corrosion

2. Experimental procedure

2.1. Preparation materials

Materials used apparatus to set up the study include: the preparation of the cacao peels extarct, steel, and hydrochloric acid (HCl) as media corrosive has been described in prior articles [3]. Just to remind, the extract of cacao peels as corrosion inhibitor obtained by the process of maceration. The Concentration of inhibitor that is used with combination 0.0; 0.5; 1.0; 1.5; 2.0 and 2.5%. The steel sample used in this study was commercial plain carbon steel plate with carbon content around 0.3% using for general construction. This is confirmed by micrograph of optical, where the microstructure of the steel contains Pearlite (P) 1/3 fraction of volume and Ferrite (a) around 2/3 fraction of volume. The steel used form of bars, cut with 12 mm diameter and 2-3 mm thickness for the rate of corrosion specimen determination. Preparation specimen for checking the properties of mechanical using ASTM standards. All of the test piece sanded until smooth and finally rinsed with acetone. Hydrochloric acid as media corrosive was used brand products with 1.5M concentration. The rate of corrosion checking methods are used by three methods has been described by detail in a prior article [3, 17].

2.2. The surface morphology of steel

In a prior article described that corrosion morphology of surface analysis using Stereo Carton Trinocular Photo Optic and S-3400N Scanning Electron microscopy. Analysis of the morphology surface aims to know the steel surfaces, absence and present extract of cacao peels in HCl 1.5 M as medium corrosive. To establish the composition the contained of elements in the steel surface absence and present the inhibitor used Electron Dispersion X-Ray (EDX) with EMAX software. To know the type of absorption elements and view the topography on the are of surface used AFM type nanosurf.
2.3. Testing of mechanical properties
Tensile test using a Universal Testing Machine type RAT-30p CAP 30tf. The test sample was set up in accordance with ASTM E-8. To assign surface hardness of steel used Rockwell Hardness Tester TH 550 with load 980.7N has finished in prior article [3]. Preparation of its to be checked include cutting and polishing. Load and pressure of time are set in agreement with the desired [18]. Specimen of fatigue testing using the procedure of ASTM E466-2002.

2.4. Microstructure and morphology surface
Microstructure of the test piece and morphology of surface of the samples were analysed by optical micrograph. Some test piece surface was also checked by a Hitachi S3400N Scanning Electron Microscopy with a magnification of 1k, 5k and 10k. The purpose of SEM observation is to know in detail the transformation of surface condition previous to and after corrosion process.

3. Results and discussion

3.1. The rate of corrosion analysis
To connect that further discussions later continuous with the prior article [3]. From the result of corrosion test by the three methods, it rise up that the addition of corrosion inhibitors, reduce weight loss and slow the rate of corrosion before given inhibitor. Conversely increase in concentration of inhibitor rise up efficiency of corrosion inhibition on surface of steel. This is because, the larger the surface of steel in relationship with the solution, the more the steel surface coated by a cacao peels of polar extract. The tendency is in accordance with mechanisms of inhibition that occur, that polyphenol compounds contained in peels extract of cacao has a lone pair of electrons [3] that can serve as electron donors, so it will arrange a complex compound with iron. Complex compounds that happen to be stable, not simply oxidized and envelops the steel surfaces, so that rate of corrosion can be prevent.

3.2. Chemical composition
The composition of chemical of the steel used in this research are presented in Table 1. It can be seen that the sample is plain carbon steel with carbon content around 0.3%, and, thus, it can be classified as medium carbon steel.

| No. | Element       | Composition (%) weight |
|-----|---------------|------------------------|
| 1   | Carbon (C)    | 0.32                   |
| 2   | Ferrum (Fe)   | 97.80                  |
| 3   | Silicon (Si)  | 0.22                   |
| 4   | Chrom Cr      | 0.10                   |
| 5   | Molibdenum (Mo)| 0.20                  |
| 6   | Mangan (Mn)  | 0.90                   |
| 7   | Sulphur (S)   | 0.06                   |
| 8   | Copper (Cu)   | 0.30                   |
| 9   | Phosphorus(P) | 0.07                   |
This is analysed by optical micrograph in Figure 1 where the microstructure of the material instead of Pearlite (black area) around 1/3 part of and 2/3 part of Ferrite (white area).

### 3.3. Fatigue Properties Analysis

The result checking of fatigue properties for steel as seen in Table 2. Fatigue properties represented an upgrades with increasing the concentration of extract. The results of this fatigue are the same as the other two mechanical properties, namely strength and hardness which show an increase with the increase in the cacao peels extract concentration added [3]. Its mean the increase of the extract concentration also upgrades the resistance of steel towards corrosive ions in the corrosive media, so that the rate of corrosion can be prevented. This means that the higher the concentration of extract, the amount of extract adsorbed on the surface, so the surface are of mild steel coated by cacao peels extract [18]. The cacao peels extract adsorbed on the surface of it chemically and formed a barrier coating which is difficult to be destructed [19].

**Table 2.** The fatigue properties of mild steel in 1.5 M HCl with various cacao peels extract concentrations

| Extract concentration (%) | Mean fatigue strength stress (MPa) |
|----------------------------|-----------------------------------|
| Mild steel (as received)    | 700                               |
| 0.0                        | 550                               |
| 0.5                        | 600                               |
| 1.0                        | 650                               |
| 1.5                        | 700                               |
| 2.0                        | 700                               |
| 2.5                        | 700                               |

The number of cacao peels extract is adsorbed on the surface illuminated by EDX analysis results in Table 3. Upgrade carbon content in the steel surface not only upgrade the hardness but will also upgrade the surface of coverage [20] the rise the surface of hardness will lower rate of corrosion [18].

The detail analysis of fatigue instead of samples used for testing fatigue is 26 pieces, which were treated the same with combination the concentration of extract in 1.5M HCl the previous research. Fatigue checking was performed according to ISO 12107, with a statistical estimate of the fatigue strength given in fatigue life. The condition of test is as follows: \( f = 10 \text{ Hz}, R = 0.1 \), Fatigue limit given: \( 1 \times 10^5 \) cycles. The fatigue strength of mild steel after being immersion in HCl solution of dropped from 700 MPa to 550 MPa. After using of corrosion inhibitor, fatigue strength back previous the original force as can be shown in Table 2. That is, the fatigue strength increases with increasing inhibitor concentration added. This phenomena due to the adsorption of the extract of cacao peels on the surface.
of steel. From the results of the analysis of the mechanical properties obtained, it turns out the cocoa peel extract can improve the mechanical properties of steel after experiencing corrosion.

3.4 Topography analysis

Micrograph of SEM of some sample surfaces are shown in Figure 2. A relatively smooth surface of polished sample previous to dyeing can be seen in Figure 2a. The surface of the test piece after immersion in the corrosion inhibitor only shows a thin surface film covering the entire mild steel surface (Figure 2b). The surface morphology of the steel after 32 days dyeing in hydrochloric acid 1.5 M as corrosive solution present and absent the addition the extract of cocoa peels is shown in Figure 2c and 2d. Heavy destroyed is found in the surface of mild steel due to heavy corrosion attack of the acid (Figure 2c). It can be showed clearly that there is surface crack in the rust layer, and it becomes initial crack and stress concentration sites. This surface condition is not only strongly related to the loss of elongation (embrittlement), but also responsible to diminish of the strength and hardness of the steel. The presence of *Theobroma cacao* skins extract inhibitor is able to reduce corrosion attack so that the rust is disappeared from the surface (Figure 2d). It means the addition of 2.5% cacao peels extract inhibitor within the acid is able to resist rate of corrosion, by forming a full coating on the surface of steel.

![Figure 2. SEM images of mild steel in 1.5M HCl after 32 days dyeing at room temperature (a) initial surface (polished) (b) dyeing in inhibitor only, (c) dyeing into HCl absence inhibitor, (d) dyeing in HCl presence inhibitor 2.5 %.

Table 3: The elements content identified in EDX analysing.

| Treatment                  | C  | Fe | O   |
|----------------------------|----|----|-----|
| Mild steel                 | 0.32 | 98.79 | -   |
| Mild steel + Extract       | 6.19 | 92.66 | 4.33|
| Mild steel + 1.5M HCl      | 1.50 | 29.39 | 63.54|
| Mild steel + 1.5M HCl + Extract | 16.90 | 37.43 | 44.89|

Analysis results of topography of surface using AFM ParkNX10 obviously shows that there has been an adsorption on the steel surface. Figure 3a shows the surface of mild steel as it is after sanding with sandpaper, but it looks uneven surface smoothness. Figure 3b shows the surface of steel after dyeing in extracts of cacao peels. Its Figure is seen adsorption occurs on the surface of steel, where the surface is covered by its extracts in the form of a barrier layer of smooth and flat. Figure 3c shows the steel surface after dyeing into 1.5M HCl solution.
3.5 Surface analysis of fatigue fracture

The molecule of inhibitor meet on the surface of steel occurs because of the adsorption. Adsorption occurs because the adhesion force among the inhibitor with steel face. Adsorption molecules of inhibitor on the face of steel to produce a barrier layer (film), which can prevent the rate of corrosion. In this situation, the inhibitor of cacao peels extract act as forming a barrier layer on the face that can serve as a control of the rate of corrosion to make a disconnection between the steel with media of corrosion [21]. The adsorption processes the extract of cacao skins on the face of steel occurs in functional groups [19].

The results of surface fracture in varying inhibitor concentrations can be seen in Image 4. The fracture face in Image 4a shows ductile fractures before being treated. While in Image 4b shows that steel in 1.5M HCl media, has a fracture pattern such as a beach mark. 1.5M HCl environmental factor can reduce the strength of fatigue of steel to reduce the endurance limit [22]. Changes in the fracture surface towards recovery due to the addition of various inhibitors of cacao skins extract are shown in Figures 4c, 4d, 4e, and 4f. From the picture it can be shown that the benchmark is lost and begin to form dimple which leads to ductile fracture. The final area of fracture in the specimens with 2.5% the addition of inhibitors, as seen in Figure 4f has a relatively small zone which shows a higher level of material ductility or a low level of brittle. This is associated with ongoing crack growth and instability, resulting in finally fracturing because the reduced cross section is no longer able to withstand the load [23].

From the form of fatigue fractures that occur, there are two zones of fracture fatigue scheme with its characteristic. The first zone is an area that is fairly flat as indicated by a straight arrow, where there is slow propagation of fatigue cracks. The second zone is the rest of the surface of fracture as indicated by the curved arrows that display typical trans crystalline fractures that are rough or static broken, and here a sudden failure occurs. The difference in orientation of the fault field is also seen in standard specimens (without inhibitors) and specimens with the addition of inhibitors. From the results of the analysed fracture, it was seen that the consequent of the presence of inhibitors of cocoa skins extract on fatigue strength was highest at 2.5% the addition of inhibitors and gradually decreased with decreasing inhibitor concentrations.
Figure 4. Fracture surface of fatigue test without and the presence of cacao skins extract after immersed 32 days in HCl 1.5M. a. Steel as received, b. Steel in HCl 1.5 M, c. Steel in 1.5M HCl + 0.5% extract, d. Steel in 1.5M HCl + 1% extract, e. Steel in 1.5M HCl + 1.5% extract, and f. Steel in HCl 1.5M + 2.5% extract.

4. Conclusion
The higher of the extract concentration of cocoa peels will raise the efficiency of inhibition and the coverage of surface that take place on the mild steel face. The extent of the coverage of surface is strongly affect by surface adsorption occurs on the face. Adsorption is establish due to the interaction among the donor atoms of the extract with a face of mild steel. These adsorptions raising the content of carbon in the face, renewal the properties of mechanical of hardness and strength of steel. Polar extract of cocoa skins capable to recovery the fatigue strength of steel that is after damaged by corrosion.

5. References
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**Acknowledgments**
The first author thanks to DRPM-DIKTI for supporting part of this work for research under Fundamental Research Grant II contract No. DIPA 041/PL.1.4/LT/2016