Phase Transformation of Rust in the Presence of Various Tannins

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Abstract: *Rust converters are chemical formulations that can be applied to corroded surfaces causing the passivation and elimination of possible further attack after the application of a coating. Tannins extracted from mangrove, chestnut, quebracho and mimosa as rust converters were evaluated. Two different types of pre-rusted sample preparations were adopted. The pre-rusted samples were immersed in 5 g/l of the various tannin solutions and the phase transformations were analyzed via Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The rust components were mainly lepidocrocite (γ-FeOOH) and magnetite (Fe_3O_4) and were found to be dependent on sample preparations. Transformation of rust components to ferric-tannates, particularly lepidocrocite, in the presence of various tannins could be observed. The relation between the partial transformation of pre-rusted samples and sample preparation is correlated.*

Keywords: tannins, phase transformations, rust converters, lepidocrocite, magnetite

Abstrak: *Penukar karat merupakan formulasi kimia yang boleh diaplikasi ke atas permukaan berkarat yang mengakibatkan pempasifan dan mengelakkan kemungkinan serangan lanjutan selepas aplikasi penglitup. Tanin diekstrak daripada bakau, buah berangan,* quebracho *dan* mimosa *yang bertindak sebagai penukar karat telah dikaji. Dua jenis kaedah penyediaan sampel permukaan berkarat yang berbeza telah digunakan. Sampel berkarat telah direndam di dalam pelbagai jenis tanin yang berkepekatan 5 g/l dan perubahan fasa karat telah dianalisis menggunakan Spektroskopi Inframerah (FTIR), Spektrometer Belauan Sinar-X (XRD) dan Mikroskop Elektron Imbasan (SEM). Pembentukan utama komponen karat yang terdiri daripada lepidokrosit (γ-FeOOH) dan magnetit (Fe_3O_4) didapati bergantung kepada kaedah penyediaan sampel. Perubahan komponen karat kepada ferik-tanat khususnya lepidokrosit dengan kehadiran pelbagai jenis tanin dapat dilihat. Perhubungan di antara perubahan separa sampel terkarat dan penyediaan sampel adalah berkait.*

Kata kunci: tanin, perubahan fasa, penukar karat, lepidokrosit, magnetit

1.   INTRODUCTION

The atmospheric corrosion of steel structures often results in the formation of iron oxyhydroxides such as geothites (α-FeOOH), lepidocrocite (γ-FeOOH), and akagonite (β-FeOOH) as well as iron oxides such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). Nowadays, applications of corrosion inhibitors, rust converters and chemical cleaning agents for removing iron-based deposits or as oxygen scavengers for boiler water treatment are the most popular ways of protecting rust. Recently, tannins have been reported to have an influence upon the anticorrosive properties of steel.[1] Tannins exist primarily in condensed and hydrolysable forms. Condensed tannins such as mangrove, quebracho and mimosa consist of oligimers and polymers of flavanoids while hydrolysable tannins such as chestnut are made up of sugars (primarily glucose) and gallic acid.

Tannins are able to form chelates with iron and other metallic cations due to the vicinity of hydroxyl groups on the aromatic rings. Tannins also have been referred as rust converters since their presence converts active rust into non-reactive protecting oxides. Protection properties result from the reactions of polyphenolic parts of the tannin molecule with ferric ions thereby forming a highly cross-linked network of ferric-tannates.[2] Gust has reported that via Mossbauer spectroscopy, a mixture of mono and bis complexes were formed as a result of a reaction between rust-phase components and oak tannins in aqueous solution.[3] Similar mixtures were also observed when reacting several plants extracts of Panama with ferrous and ferric salts.[4] A rust modifying or stabilizing action, resulting in the formation of more dense and pore free corrosion or rusted layers, may affect the protective property of tannins used.[5] In addition, the composition of the rust layer and its time of formation at the corroded steel surface are other factors influencing the converter protection efficiency. Infrared spectroscopy has shown that lepidocrocite reacted most rapidly with phosphoric acid followed by magnetite and finally goethite.[1,3,6] Due to the diversity of the material used in different studies, different explanations on the inhibitory mechanisms have been suggested. In this work, several tannins as rust converters are used to study the relation between the transformation of pre-rusted samples and two methods of sample preparations.

2.   METHOD

Two different types of pre-rusted sample preparations were adopted in this study. Total immersion of steel in 3.5% (w/v) NaCl was carried out for 55 days. The rusted samples (powder and plates) were then immersed in 10 ml of 5 g/l mangrove and quebracho tannin solutions, and allowed to react for the

duration of 1, 7, 14 and 30 days. Meanwhile, alternative immersion of steel in 3.5% (w/v) NaCl was conducted for 49 days. The rusted samples (powder and plates) were immersed in 10 ml of 5 g/l chestnut, mimosa and mixed (chestnut: mimosa = 1:1) tannin solutions, and allowed to react for the duration of 1, 2, 3 and 4 weeks. Precipitated samples from both procedures were collected, filtered with fine filter paper and dried in an oven at 40°C for 24 h before being analyzed. The transformation of rusted samples was analyzed with FTIR spectroscopy, SEM and XRD. Mangrove tannins from bark extracts were obtained from Larut Matang, Taping, Malaysia while commercial mimosa, quebracho and chestnut tannins were obtained from SILVACHIMICA, Italy.

3.   RESULTS AND DISCUSSION

3.1   Total Immersion

For the untreated pre-rusted sample, the peaks at 1021, 886, and 744 cm^{-1} designate the presence of lepidocrocite while the peak at 472 cm^{-1} designates the presence of magnetite (Fig. 1). Among these bands, 1021 cm^{-1} was the strongest and could be considered as lepidocrocite's major band[6] and will be used as the reference band. The mangrove tannin treated samples appeared to initially dissolved the lepidocrocite, followed by the formation of a new phase. The formation of ferric-tannates were evident with the presence of peaks at around 1443, 1354 and 1250 cm^{-1}. The lepidocrocite peaks seems to reduce after one week immersion but remained unchanged after two weeks onwards although several tannate peaks were evident. The same trend was observed for quebracho treated samples.

Figure 2 shows the XRD patterns of rust powder. Lepidocrocite and magnetite were the main components present with lepidocrocite as the dominating phase. Ferric-tannates are amorphous as confirmed by XRD analysis. Upon immersion in the mangrove and quebracho tannin solutions, several lepidocrocite peaks diminished as well as reduced in favor of the formation of ferric-tannates. For example, the lepidocrocite peak at $2\theta = 32.0$ diminished upon the addition of quebracho tannins (Fig. 3). The magnetite peaks, however, remained unchanged. It has been reported that in the presence of ferrous ions and reducing agents, lepidocrocite is transformed into magnetite. Magnetite is a stable oxide and is strongly adhered to the metal and will consequently result in a fairly impermeable layer against further corrosion.[7,8] However, one of the reaction mechanisms of tannins with rust is suggested by Deslauriers[9] which involves three general steps: (i) adsorption of the tannins to the rusty surface, (ii) complexation of ferrous/ferric ions or complexation of surface iron
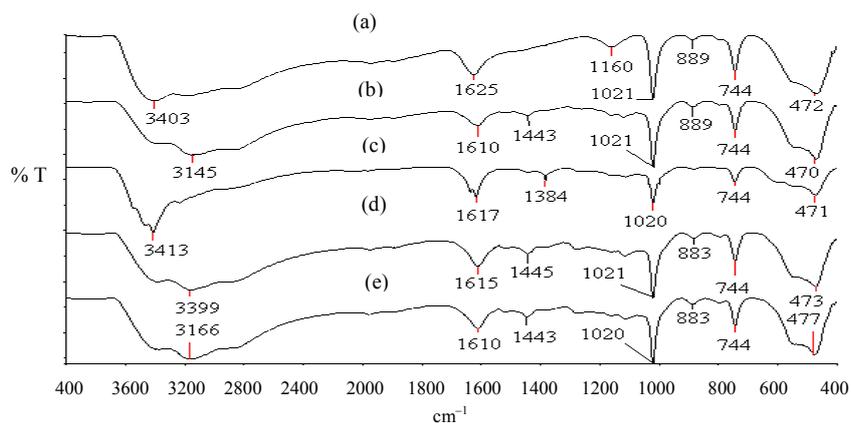
Figure 1: FTIR spectra of (a) untreated rust powder and treated samples in 5 g/l mangrove tannin solution after (b) 1 day, (c) 7 days, (d) 14 days and (e) 30 days.

hydroxides/oxides followed by dissolution, and (iii) partial or complete re-adsorption of the iron-tannate complexes to the substrate. In addition, tannate formation acidified the reaction environment, making its reaction with clean or oxidized metallic substrate self-catalyzed.[10] According to previous work on mangrove tannins[11], they act on the iron ions available in three ways. First the tannins can complex with Fe^{2+} ions to form ferrous-tannates which can be easily oxidized into ferric-tannates, a blue-black deposit when in contact with oxygen. Secondly, the tannins can act directly on the Fe^{3+} ions available to form ferric-tannates and thirdly, tannins can reduce Fe (III) oxides into Fe^{2+} ions due to their high reducing power. These Fe^{2+} ions can then be easily complexed by tannins, and into ferric-tannates in the presence of oxygen. Interestingly, the chloride compound peak also diminished.

The SEM micrographs in Figure 4 represent the rusted surfaces before and after immersion in the mangrove and quebracho tannins. For the untreated pre-rusted plate, coral-like structures seem to cover the entire surface as shown in Figure 4(a). Both tannins produced the same morphology of a coarse layer of irregular shaped cracks typical of ferric-tannates.[12] A closer inspection of the surface revealed coral-like and finger-like structures of rust components underneath the transformed tannins. Thus all the analyses conducted indicated that partial transformation of rust into ferric-tannates had occurred. However the degree of transformation of mangrove and quebracho tannins could not be distinguished.
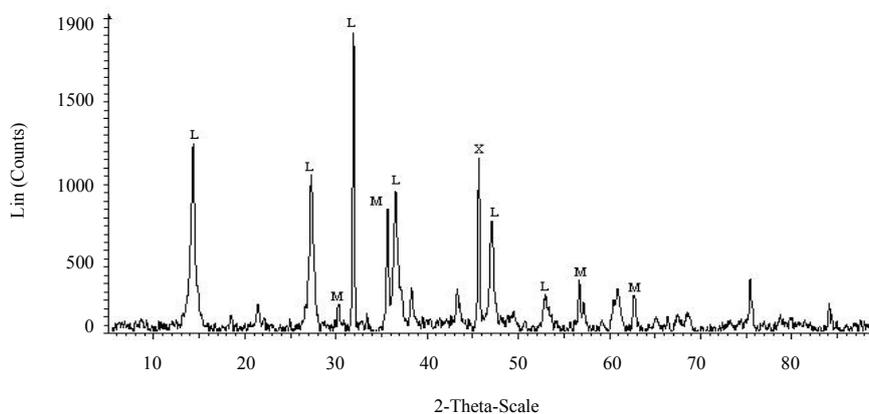
Figure 2: XRD patterns of rust powder. L – lepidocrocite; M – magnetite; and X – chloride compound.
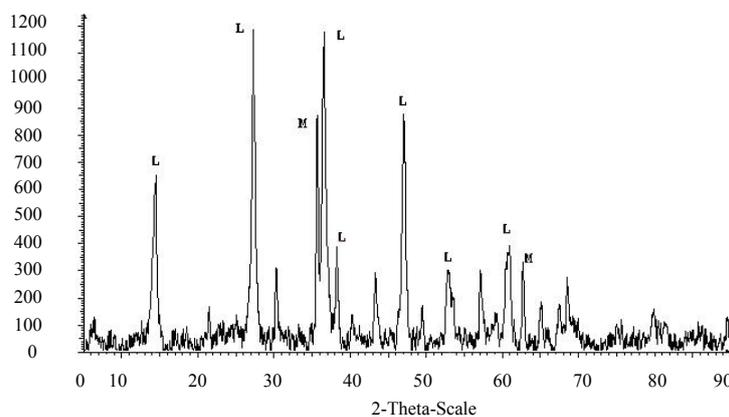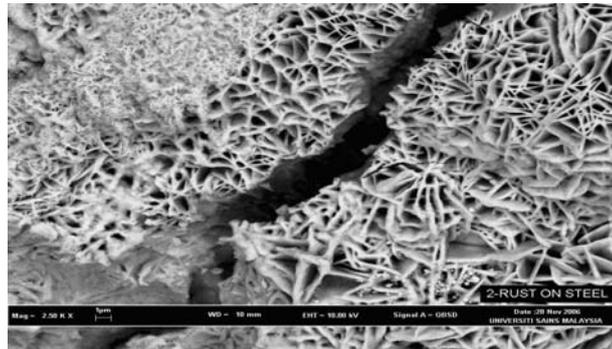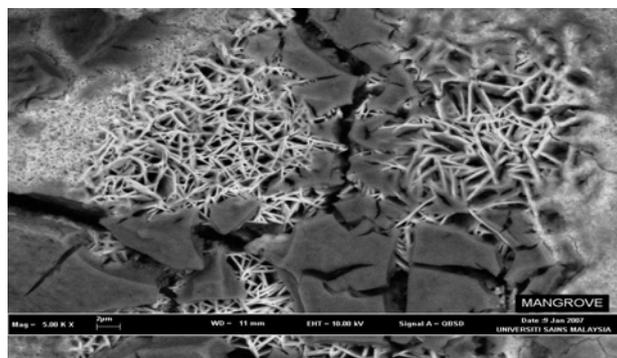

Figure 3: XRD patterns of rust powder when treated with 5 g/l quebracho tannins. L– lepidocrocite; M– magnetite.

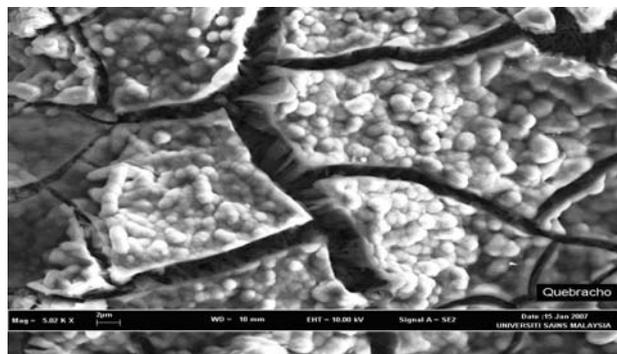## 3.2   Alternative Immersion

The FTIR analysis of untreated pre-rusted samples showed that the lepidocrocite and magnetite were the main rust components. Upon immersion of 2 mg rust powder into mimosa, chestnut and mixed (chestnut and mimosa) tannin solutions, formation of ferric-tannates were evident. For example, several peaks for chestnut tannins shifted to lower wave numbers (from 1736 to 1698 cm^{-1} and 1342 to 1333 cm^{-1} after two weeks) as shown in Figure 5. The lepidocrocite peak

(a)

(b)

(c)

Figure 4: SEM micrographs of (a) pre-rusted plate before treated and rusted plates treated with (b) 5 g/l mangrove tannins and (c) 5 g/l quebracho tannins.
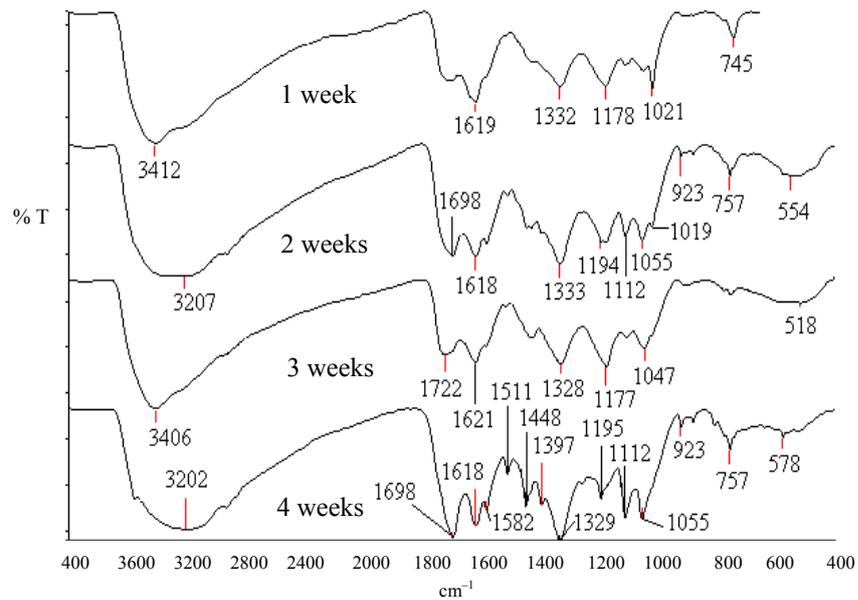
Figure 5: FTIR spectra of chestnut tannins with respect to time of immersion.

initially began to reduce after two weeks of immersion and almost disappeared after three and four weeks. The degree of transformation of the various tannins was as follows:

chestnut tannins ≈ mixed (chestnut and mimosa) tannins > mimosa tannins

XRD patterns of the rusted plates differ from that of the rust powder whereby the magnetite component seems to dominate the surface (Fig. 6). It was also observed that the intensities of the magnetite peaks of the plates from the alternative immersion technique were higher than that of the total immersion technique. This is not surprising since in the alternative immersion technique, more rust powders rich in lepidocrocite were produced leaving an inner compact layer of magnetite on the plate. FTIR analysis has also demonstrated that the transformation rate of the individual rust component was in the following order:[3,6]

lepidocrocite > magnetite > maghemite > goethite

Thus the XRD analysis did not show any reduction in the magnetite peaks when immersed in all tannin solutions.
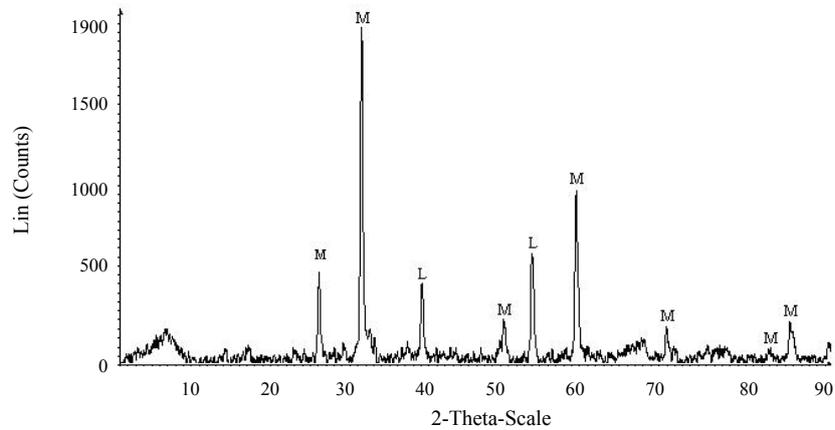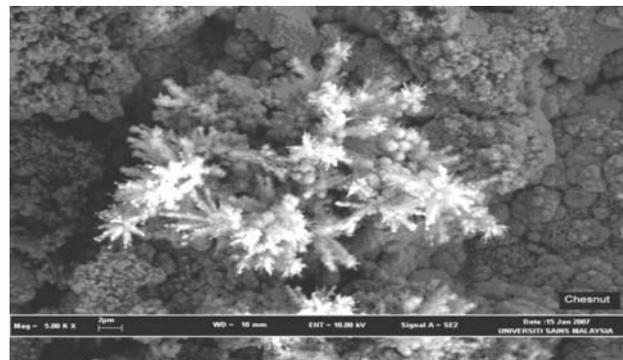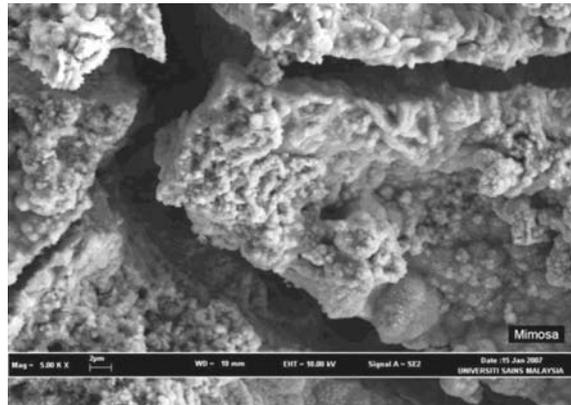
Figure 6: XRD patterns of a rusted plate. L – lepidocrocite; M – magnetite.

Figure 7 shows the SEM micrographs of the rusted surfaces after immersion in the chestnut, mimosa and mixed (chestnut and mimosa) tannins. Upon treatment with chestnut tannins, the micrograph exhibited brocoli-like structures while mimosa treated plates exhibited similar morphology to that of mangrove and quebracho tannins. The cracks observed for the mimosa treated samples are indeed larger than the chestnut treated samples. The transformed rust plate treated with the mixed (chestnut and mimosa) tannins seem to be dominated by brocoli-like structures similar to that of chestnut tannins and again unconverted rust are evident.
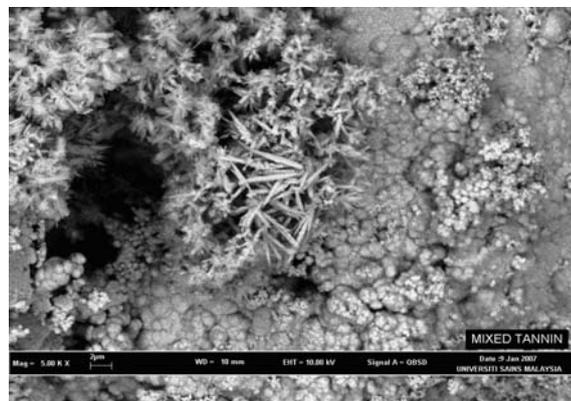

(a)

Figure 7: SEM micrographs of rusted plates immersed in (a) 5 g/l chestnut tannins, (b) 5 g/l mimosa tannins and (c) 5 g/l mixed tannins.

(b)

(c)

Figure 7: *(continued)*

4.   CONCLUSION

Both types of sample preparations produced lepidocrocite and magnetite as the main rust components. These rust components were transformed into ferric-tannates when reacted with both condensed tannins (mangrove, mimosa and quebracho) and hydrolysable tannins (chestnut). However, only partial and temporary transformations were observed from the FTIR, XRD and SEM analyses. It is suggested that the rust transformation in different techniques of sample preparation by all types of tannins in this study is mainly superficial.

5.   ACKNOWLEDGEMENTS

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