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# Solvent-Free Coating Using MACO Bio-Based Reactive Diluent

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# Solvent-Free Coating Using MACO Bio-Based Reactive Diluent

Honors Project
4250 497

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# Table of Contents

# Abstract

The project performed utilizes methacrylated cardanol (MACO) and a linseed oil resin to test how different weight percentages of MACO affect coating performance. MACO is synthesized from a phenolic lipid extracted from cashew nut shells, which are a cashew industry waste product. Not only does it utilize a waste product, but being a bio-based reactive diluent means it can replace the use of volatile organic solvents that are harmful to both humans and the environment. Weight percentage samples of 0%, 10%, 20%, 30%, and 40% were used. Coatings were applied using a 6-mil drawn down bar, with samples being prepared for two different tests. Electrochemical impedance spectroscopy (EIS) and salt spray testing were utilized to determine which percentages performed the best. Based on the test results and ease of application, the 20 wt% samples performed the best out of all the samples.

# Executive Summary

*Purpose of the Work*

The purpose of this work was to determine how different weight percentages of Methacrylated Cardanol (MACO) has on a linseed oil resin coating. This project is important as the MACO is used in place of a volatile organic solvent, which can cause harm to human health and the environment. Being something harmful, a bio-based reactive diluent such as MACO to act in place of the solvent is very desirable. The MACO is synthesized from cardanol, which is a phenolic lipid extracted from cashew nut shells which are normally waste products to the cashew industry.

*Results*

Samples for the weight percentages of 0, 10, 20, 30, and 40 were used for both EIS testing and salt spray testing. EIS testing found that the 20 wt% and 40 wt% performed the best. The 30 wt% performed middle of the road, with the 0 and 10 wt% performed poorly. Looking at the salt spray testing, the 20, 30, and 40 wt% performed well, only having corrosion issue at the scribing. The 0 and 10 wt% performed poorly, resulting in rather severe corrosion.

*Conclusions*

Based on the results obtained, the 20 wt% and 40 wt% MACO were the best performers and would be recommended. However, looking at the ease of application and coating thickness, the 20 wt% is recommended over the 40 wt% for purposes of use.

*Broader Work Implications*

While working on this project, I gained further lab experience that built off what I learned in the corrosion curriculum. Instead of spending one or two weeks on a lab working with others and learning the basics of various methods, I was able to spend a couple months making samples myself, and further honed my skills at certain tests. I believe that the results from this experiment are beneficial as it not only helps improve health and safety issues, but also utilizes something that normally is just a waste product.

*Recommendations*

For future work, it is recommended to obtain more samples for each weight percentage. The 30 wt% EIS sample performed out of expected, being below the 20 and 40 wt%. It would be expected to be somewhere near the two, but seeing as it underperformed, it is believed that there was some sort of issue with either the application or the coating itself. More samples would also allow for an average polarization resistance value to be obtained and consistent coating thickness for samples.

# Introduction

The purpose of this project is to find out the effect different weight percentages of Methacrylated Cardanol (MACO) has on the properties of a linseed oil based alkyd coating as opposed to a volatile solvent. Alkyd resins are the most widely used bio-based polymer resin and are expected to be used more and more to satisfy the increasing desire for bio-based coatings. In order to reduce viscosity of the resin for application, volatile organic solvents are usually used in the range of 30-60 wt%. These volatile organic compounds (VOC) are harmful for human health and for the environment, so demand for something that will reduce this need to use VOC is growing. MACO is made from Cardanol (CO), which is a phenolic lipid extracted from cashew nut shells, which are normally a waste product in the cashew industry but have use through the CO it contains. What this project will determine is which weight percentage provides the best results as a bio-based diluent based on salt spray testing and electrochemical impedance spectroscopy (EIS) testing.

# Background

This project builds off of the experiment conducted by Wang et al. where the tested the properties of alkyd coatings using no solvent, CO at 30 wt%, MACO at 30 wt%, and Triethoxysilane-Functionalized Cardanol (TSCO) 30 wt%.[1] While the TSCO provided improvements in several aspects, the MACO showed to have properties closest to the resin by itself. The MACO is the main focus since the properties of the original coating will want to be maintained without too much. As previously stated, what will be tested in this project will be different weight percentages of MACO to see which will have the best performance.

# Experimental Methods

The MACO was prepared as described in section 2.2 of the article by Wang et al.[1] Preparation of the linseed oil alkyd resin was done by following section 2.3 of the article Işeri-Çağlar et al. wrote.[2] The other materials used for the coating included methyl ethyl ketone (MEK) and a solvent borne wetting agent. Preparation of the coatings were done in small glass vials, separated by weight percent of MACO. The weight percentages used for this experiment were 0%, 10%, 20%, 30%, and 40% MACO. The balance weight was filled with the linseed oil resin. In the case of the 0% MACO, 10 wt% MEK was used to act as a solvent to make the coating able to be worked with. Once the resin and MACO had been added, 3-5 drops of the solvent borne wetting agent were added. With all components in the vial, a stir rod was used to mix thoroughly until combined. The vial was then placed in a sonic water bath for 15 minutes to remove any bubbles that resulted from the mixing process. While the bubbles were being removed, stainless steel Q panels were prepared by wiping with acetone and drying with air. They were then labelled appropriately for the weight percentage MACO applied. The coating was applied to the panels using a 6-mil draw down bar. A minimum of four samples were made for each weight percentage, with additional samples being made if enough coating remained. Once the samples were coated, they were placed in a laboratory oven at 120°C for 2 hours, and then 160°C for 3 hours. Once the samples had baked, the thickness of the coatings were measured before being used for testing. At each weight percentage, two samples were used for EIS testing, and two were used for salt spray testing. The samples for EIS were exposed to 3.5 wt% NaCl solution in the cell for the testing. The EIS testing was performed using Gamry Framework™ and the preset EIS test settings. While two samples were used for each weight percentage, only one was chosen for each based on which one gave consistent data. The salt spray samples were taped up as to only expose a section of the coating. Once taped, an X with

2 cm long lines was scribed into the coating. With these samples ready, they were then placed into a Q-FOG machine and followed ASTM B117 procedure for salt spray testing. Once all data was collected, it was compiled together and analyzed to review performance.

## Data and Results

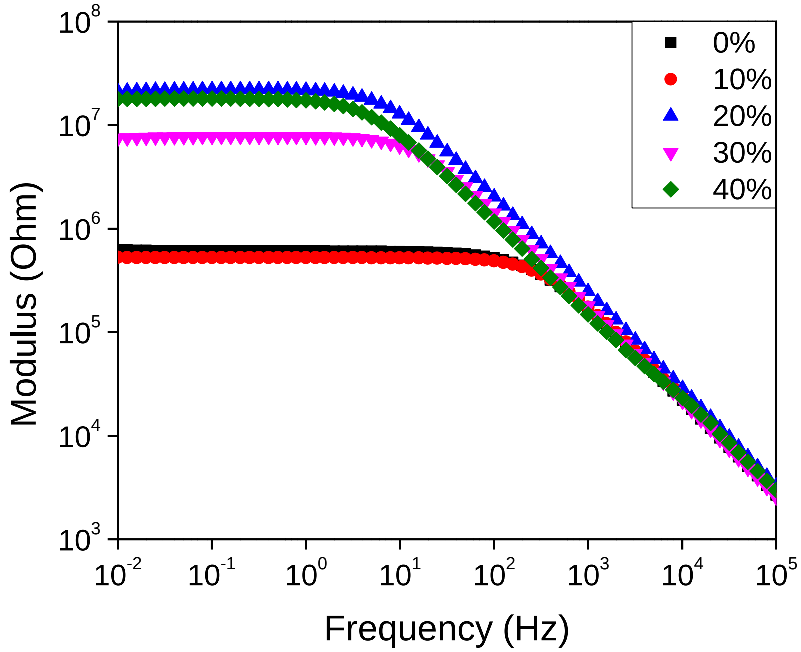



**Figure 1** Bode plot for 1-day EIS testing of samples

**Figure 1** shows the EIS data obtained for all the different weight percentage samples after 1 day of testing. The pattern seen for the samples on the first day stay relatively the same throughout the remainder of the EIS testing.

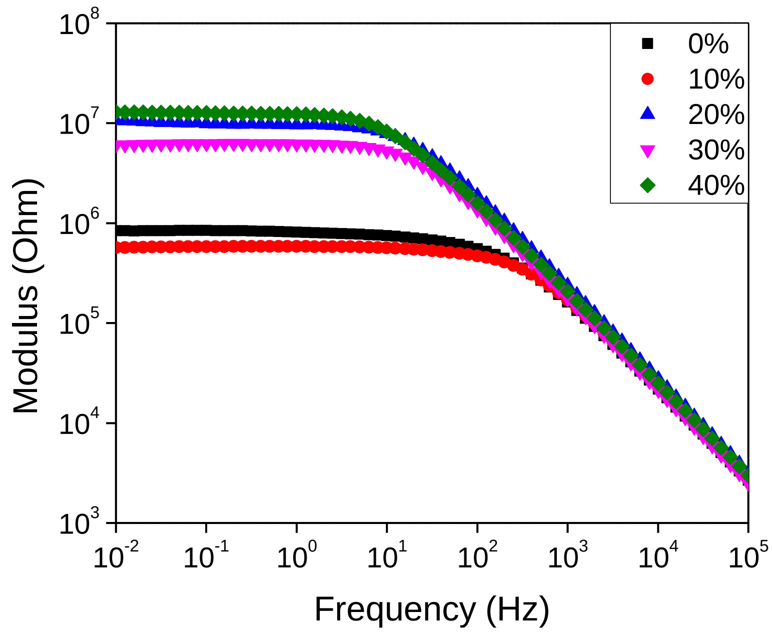



**Figure 2** Bode plot for 7-day EIS testing of samples

**Figure 2&3** show the 7-day and 14-day testing results, respectively, and follow the trend that **Figure 1** shown initially. As is expected, the modulus is decreasing as time goes on.

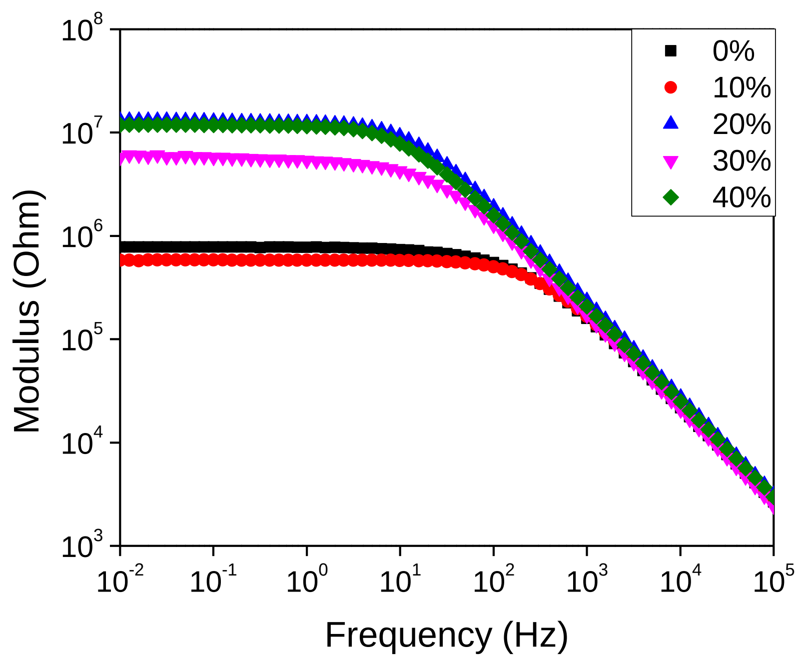



**Figure 3** Bode plot for 14-day EIS testing of samples

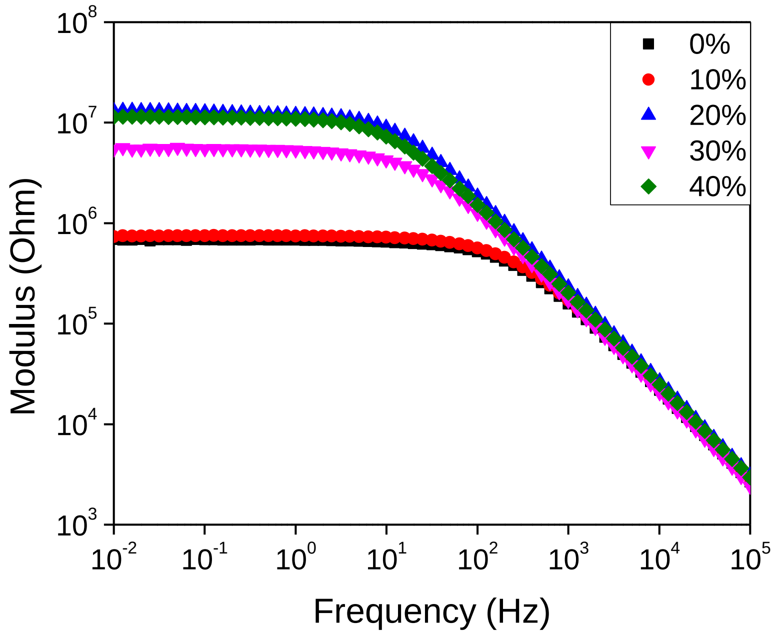



**Figure 4** Bode plot for 21-day EIS testing of samples

**Figure 4&5** show the data obtained from the 21-day and 28-day testing, respectively. The trend shown in previous figures continues to be shown in these graphs.

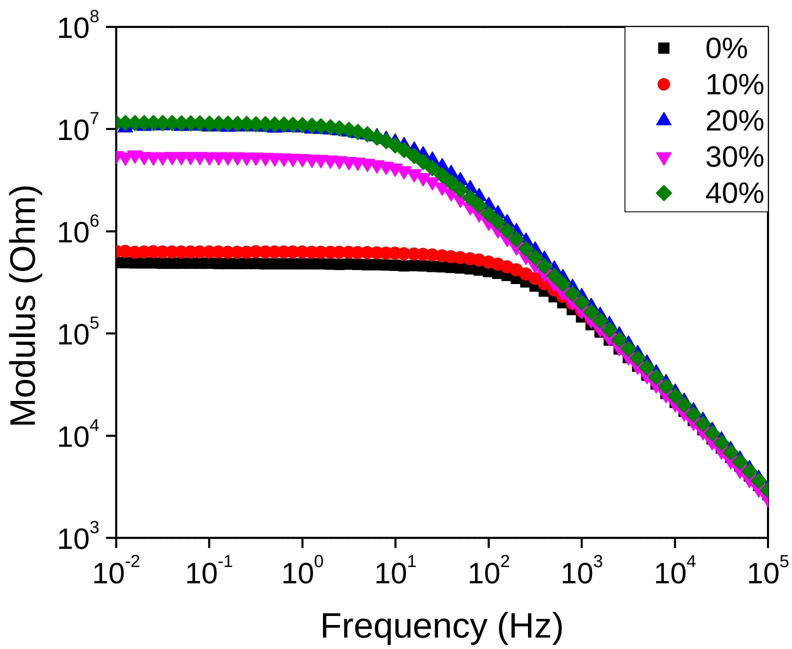



**Figure 5** Bode plot for 28-day EIS testing of samples

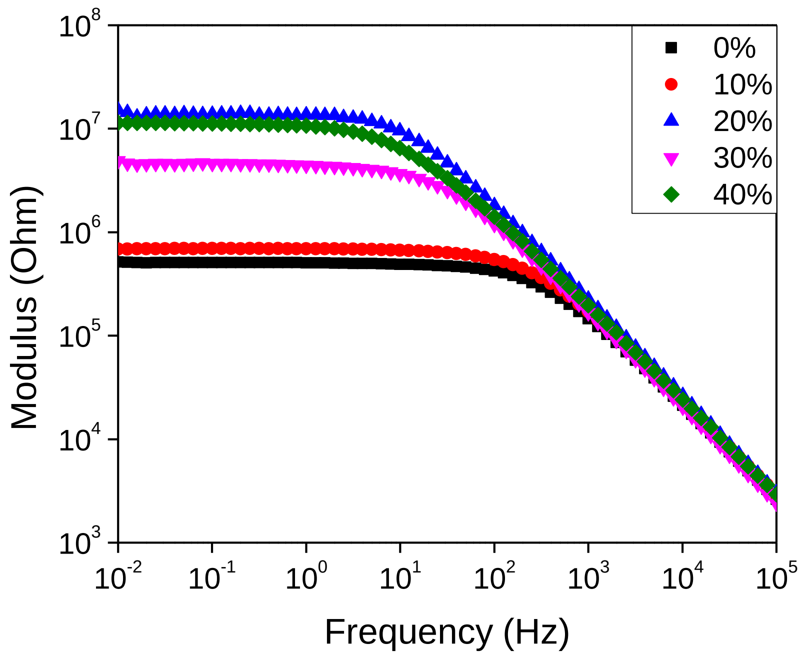



**Figure 6** Bode plot for 35-day EIS testing of samples

**Figure 6** is the final day that EIS testing was performed at 35 days. As with the other days of testing, the trend remained. For the samples that were used for graphing purposes, the coating thickness for the 0%, 10%, 20%, 30%, and 40% were averaged 89 µm, 84.5 µm, 83.1 µm, 67.0 µm, and 69.7 µm respectively. The same samples were used to create the following Nyquist plots.

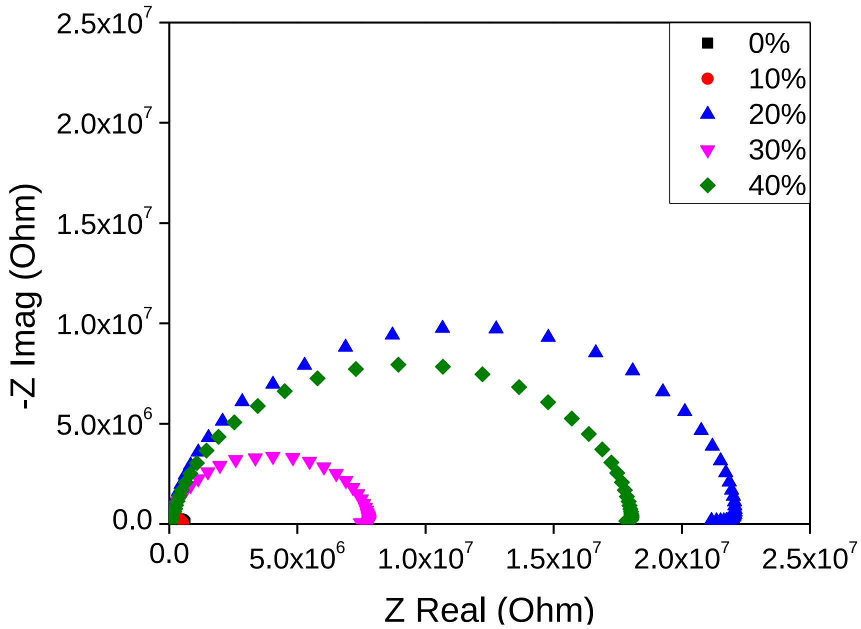



**Figure 7** Nyquist plot for 1-day EIS testing of samples

**Figure 7** and **Figure 8** show the Nyquist plots for the 1 and 7-day EIS testing of the samples. As can be seen, the 20 wt% and 40 wt% have the largest semi-circles, with the 30 wt% being average, and the 0 and 10 wt% being below average.

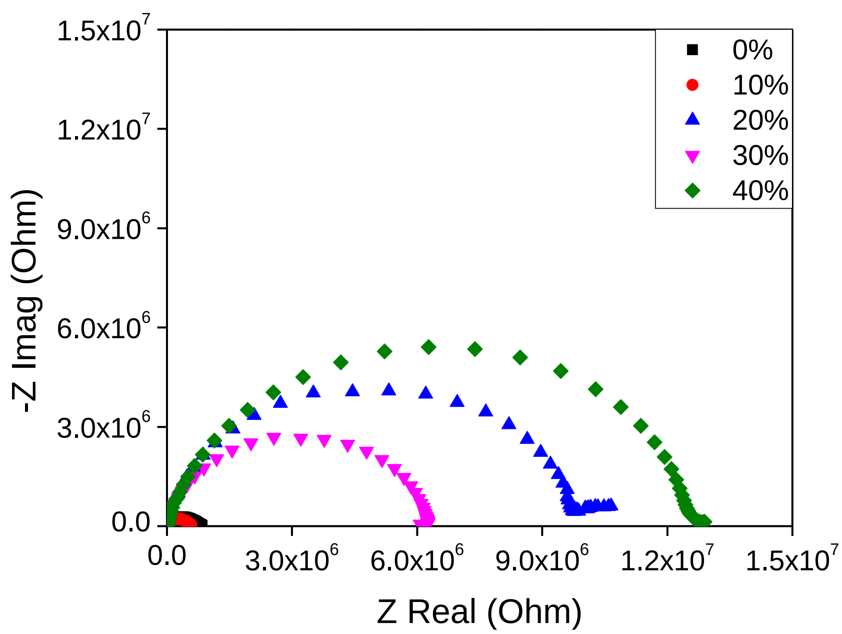



**Figure 8** Nyquist plot for 7-day EIS testing of samples

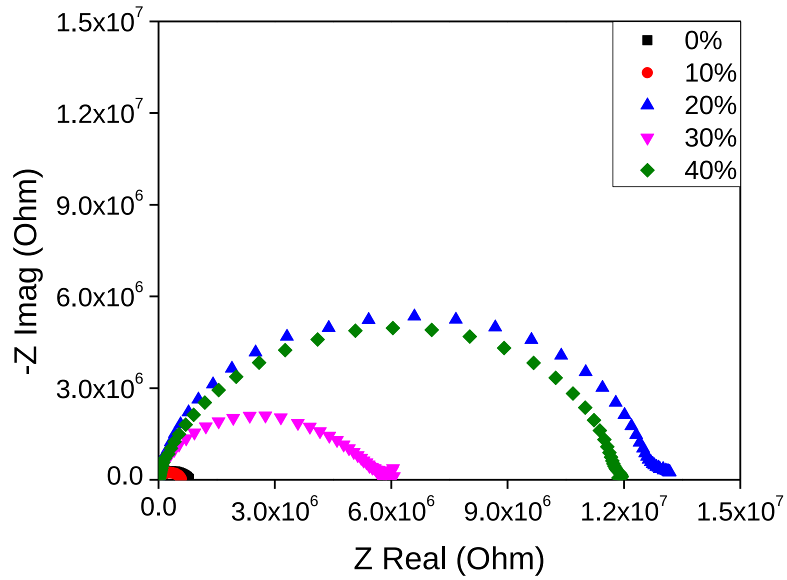



**Figure 9** Nyquist plot for 14-day EIS testing of samples

**Figures 9&10** show the Nyquist plots obtained from the 14 and 21-day testing of the samples. The trend of performance for the samples follows the trend seen with the 1 and 7-day tests.

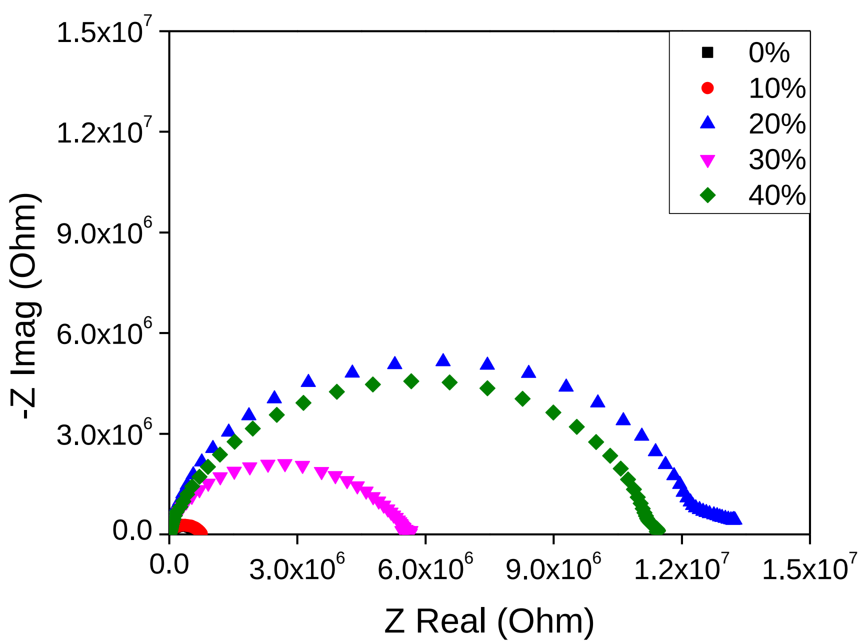



**Figure 10** Nyquist plot for 21-day EIS testing of samples

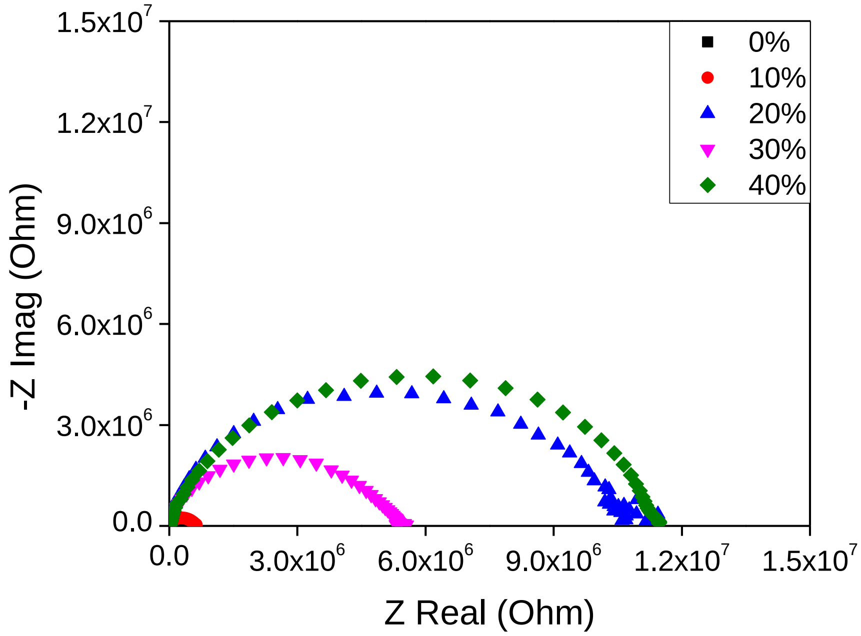



**Figure 11** Nyquist plot for 28-day EIS testing of samples

**Figures 11&12** show the Nyquist plots obtained from the 28 and 35-day testing of the samples. As with the previous days of testing, the performance trend continued.

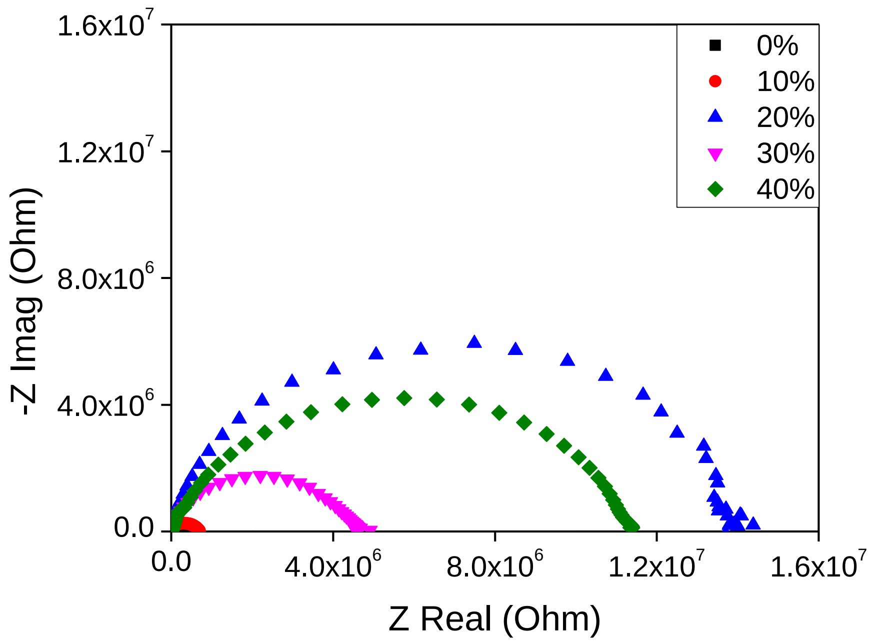



**Figure 12** Nyquist plot for 35-day EIS testing of samples

The following tables consist of salt spray images for the samples at each percentage.

**Table 1** Salt Spray images for 0% MACO

| | 0 Day | 1 Day | 2 Day | 4 Day | 7 Day |
|---|---|---|---|---|---|
| A |  |  |  |  |  |
| B |  |  |  |  |  |

**Table 1** shows the results for the 0 wt% MACO samples for salt spray testing. The coating thickness for the two samples averaged were 75.88 µm for sample A, and 79.62 µm for sample B.

**Table 2** Salt Spray images for 10% MACO

| | 0 Day | 1 Day | 2 Day | 4 Day | 7 Day |
|---|---|---|---|---|---|
| A |  |  |  |  |  |
| B |  |  |  |  |  |

**Table 2** shows the results of the salt spray testing for the 10 wt% MACO samples. The thickness of the coatings averaged were 60.06 µm for sample A, and 60.74 µm for sample B.

**Table 3** Salt spray images for 20% MACO

| | 0 Day | 1 Day | 2 Day | 4 Day | 7 Day |
|---|---|---|---|---|---|
| A |  |  |  |  |  |
| B |  |  |  |  |  |

**Table 3** shows the salt spray results for the 20 wt% MACO samples. The coating thickness for the samples averaged were 67.66 µm for sample A, and 72.58 µm for sample B.

**Table 4** Salt spray images for 30% MACO

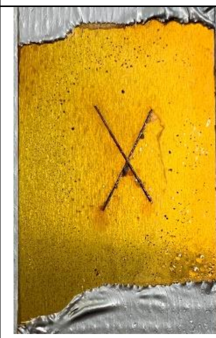
| | 0 Day | 1 Day | 2 Day | 4 Day | 7 Day |
|---|---|---|---|---|---|
| A |  |  |  |  |  |
| B |  |  |  |  |  |

**Table 4** shows the results of the salt spray testing for the 30 wt% MACO samples. The average coating thickness for the samples were 71.56 μm for sample A, and 79.38 μm for sample B.

**Table 5** Salt spray images for 40% MACO

| | 0 Day | 1 Day | 2 Day | 4 Day | 7 Day |
|---|---|---|---|---|---|
| A |  |  |  |  |  |
| B |  |  |  |  |  |

**Table 5** shows the results of the salt spray testing for the 40 wt% MACO samples. The average coating thickness for the samples were 58.00 μm for sample A, and 64.16 μm for sample B.

## Analysis

In terms of EIS testing, what is being looked for is whichever has the highest polarization resistance ($R_p$) value. To determine this the graphs must be observed at the high frequency and low frequency points of the Bode plots, and the diameter of the semi-circles for the Nyquist plots. The low frequency points of the Bode plots represent the impedance modulus for the polarization resistance plus the solution resistance ($R_s$), while the high frequency points represent just the solution resistance. Since they all have about the same $R_s$ value, the main focus can be towards the low frequency values to determine which samples had higher $R_p$ values. The $R_p$ value is of interest because of its relation to the corrosion rate. A higher $R_p$ means a lower corrosion rate based on the following relations:

$$i_{corr} = \frac{1}{R_p} \frac{b_a b_c}{2.303(b_a + b_c)}$$

$$CR = \frac{i_{corr} K \cdot EW}{\rho A}$$

Where $b_a$ is the anodic Tafel constant, $b_c$ is the cathodic tafel constant, and $i_{corr}$ is the corrosion current for the first equation. For the second, CR is the corrosion rate, K is a constant to define the units for the corrosion rate, EQ is the equivalent weight, ρ is the density, and A is the sample area.

The Nyquist plots are similar in how to obtain the $R_p$ values. The leftmost end of the semi-circle represents the $R_s$ value, with the rightmost point being the $R_s$ plus the $R_p$ value. Therefore, the diameter of the semi-circle represents the polarization resistance value.

Based on the results obtained in the EIS testing, the best performing samples were the 20 wt% and 40 wt% MACO. The 30 wt% did middle of the road in terms of performance, which was unexpected considering both the 20% and 40% performed well. The 0% and 10% performed as expected, doing not terribly well.

Looking at the salt spray results, the 20%, 30%, and 40% all did similarly well with minimal failures. The 0% and 10% both performed poorly, which matches the results seen in the EIS testing. The other three's performance also matched with what was observed from the EIS testing. Based on the results seen, the recommendation would be to use either the 20 wt% or the 40 wt%. However, looking at the other factors, 20 wt% would be the better choice. While the 40%

performed just as well, the coating thickness was lower than the 20%, and also was more difficult to work with for application due to the lower viscosity of the mixture.

*Future Work*

Further work should be done to test the consistency of results. The results for the EIS testing of the 30 wt% were inconsistent with what was to be expected, so some sort of issue must have occurred to result in that outcome. More samples to obtain data from would allow a better look at what the average $R_p$ values for the differing percentages would be. Another improvement upon the experiment would be to have a consistent coating thickness for all the samples. The samples used in this experiment had varying coating thickness, and while mostly similar, the variance could cause issues.

*Design Constraints*

Design constraints that can be considered for this project include safety, regulations, and marketing. In terms of safety, MACO replaces more common solvents that give of gases harmful to human health and the environment. These solvents are usually very effective, but are composed of VOCs. These can cause many issues such as irritation, damage to organs, and even forms of cancer. MACO is bio-based, being synthesized from an extract from cashew shells. Using a bio-based reactive diluent means that the negative effects of using the VOC solvents are not to be worried about. In terms of the actual experiment, proper safety measures were followed the entire duration. Proper PPE, such as gloves, goggles, and a lab coat, were worn at all times to ensure safety was a top priority.

Playing into the safety aspect, the MACO will help meet any regulations that are in place. The EPA has requirements about VOC release depending on the use. If issues were being had where there was difficulty in reducing VOC release, something such as MACO to replace the organic solvents would erase the need to worry about VOC emissions.

Playing off both of these is the marketing aspect. As the years have been going on, the desire to be more environmentally friendly has been on the rise. Should a company opt to utilize MACO as their solvent of choice, not only would they easily meet regulation requirements, but they can market that their company is environmentally friendly. Not only will it help the environment, but it will also help the company image.

## Works Cited

[1] Wang, H., Zhang, C., Zeng, W., & Zhou, Q. (2019). Making alkyd greener: Modified cardanol as bio-based reactive diluents for alkyd coating. *Progress in Organic Coatings*, *135*, 281–290. doi: 10.1016/j.porgcoat.2019.06.018

[2] Işeri-Çağlar, D., Baştürk, E., Oktay, B., & Kahraman, M. V. (2014). Preparation and evaluation of linseed oil based alkyd paints. *Progress in Organic Coatings*, *77*(1), 81–86. doi: 10.1016/j.porgcoat.2013.08.005