



Journal of Advanced Research in Applied Sciences and Engineering Technology

Journal homepage:
https://semarakilmu.com.my/journals/index.php/applied_sciences_eng_tech/index
ISSN: 2462-1943



Investigating the Corrosion Inhibition Performance of a Novel Coconut Oil-Based Poly(urethane-urea) Hybrid Coating on Carbon Steel in 3.5% NaCl Solution

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ARTICLE INFO

Article history:

Received 2 February 2024

Received in revised form 9 May 2024

Accepted 21 August 2024

Available online 18 September 2024

Keywords:

Polyurethane-polyurea; hybrid coating; triethanolamine; coconut oil-based polyol; anticorrosion coating

ABSTRACT

Polyurethane has been used for years as an anti-corrosion coating due to its intrinsic hydrophobic properties. However, its hydrophobicity is not enough to inhibit the permeation of corrosive agents; thus, incorporating it with polyurea would further enhance its hydrophobic properties. In this study, coconut oil, a saturated, low molecular weight vegetable oil, was employed as an eco-friendly precursor for synthesizing a novel poly(urethane-urea)- based hybrid coating. The synthesis process involved the utilization of a coconut oil-based polyol blend, triethanolamine (TEA) as an amine source, and hexamethylene diisocyanate (HDI). The resulting hybrid coating on carbon steel demonstrated remarkable anticorrosion performance in a 3.5 wt. % NaCl solution, owing to the intrinsic hydrophobic characteristics of coconut oil and polyurea. Significant corrosion rate reduction was observed with increasing amine content, accompanied by an enhancement in mechanical properties. Notably, an amine loading of 4% consistently exhibited superior corrosion resistance and mechanical performance in the hybrid coating. Chemical structural analysis revealed a hydrogen-bonding network in polyurea coatings, reducing porosity, enhancing barrier properties, and improving mechanical characteristics, highlighting its potential for sustainable corrosion protection.

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<https://doi.org/10.37934/araset.51.2.7185>

1. Introduction

Metal corrosion is a global issue due to its potential to inflict extensive harm on metal structures, resulting in significant economic losses and posing a direct threat to human safety [1]. Metal substrate corrosion can be effectively mitigated through the application of protective layers, such as organic or polymeric coatings. These coatings serve as highly efficient barriers, shielding the underlying substrate from deterioration. The ideal anticorrosion coating system must be environmentally friendly, worker-safe, durable, and able to expose little or no metal/substrate surface to the environment while being resistant to environmental, mechanical, and chemical damage, and comes at a reasonable cost.

Polyurethanes (PUs) are extensively utilized in the formulation of protective coatings owing to the diverse chemical properties inherent in their structure. This intrinsic versatility facilitates the fine-tuning and optimization of coating properties, making them a preferred choice in coating applications. Polyurethanes (PUs) were originally synthesized through the polyaddition of isocyanates and petroleum-derived polyols [2]. Polyurethane coatings are widely used due to their excellent adhesion to diverse surfaces, abrasion resistance, electrical insulation and durability, and chemical and corrosion resistance [3]. Yet, the escalating costs and rapid depletion of these raw materials, alongside the necessity for advanced processing systems, have prompted concerns regarding their sustainability and feasibility [4]. Moreover, growing environmental concerns and the rising demand for polyurethanes (PU) have underscored the need for sustainable, eco-friendly alternatives.

Vegetable oil (VO) stands out among renewable resources for several reasons, including their abundance and versatility in accommodating a diverse array of chemical modifications [5]. Polyols derived from vegetable oils have shown promise in partially substituting petroleum-based polyols, especially when cross-linked with different isocyanates for PU production [6]. When considering price, toxicity, and environmental impact, VOs offer compelling advantages over petroleum. Commonly utilized VOs in polyol production include soybean, safflower, corn, sunflower seed, coconut, and palm oil [7].

In the previous study of Estrada *et al.*, where they utilized coconut oil-based polyol synthesized through 2-step process (glycerolysis and polycondensation) for anticorrosion polyurethane coating have been successfully made. However, there is a need of incorporating it with expensive nanomaterial such as silane to enhance further its hydrophobicity [8]. This has led the researchers to find low-cost alternative material that is both effective and does not compromise its property.

Aside from polyurethane, considerable attention has been paid to polyurea protective coatings due to their resistance to chemical attack, waterproofing properties, and strength [9]. Polyurea coatings are produced from the reaction of an isocyanate group with a polyamine. It is chemically related to polyurethanes, except that the curing agent does not include a hydroxyl-containing group; thus, it cures faster than polyurethanes due to the presence of amine as a reactant [10].

Several studies have been documented on using polyurea coatings to suppress corrosion in various media. The advantage of polyurea coating is its hydrophobic properties, which are attributed to its rapid curing property due to the fast reaction of amine and isocyanate [11]. However, due to the high-speed kinetics of the isocyanate-amine reaction, effective polyurea processing mandates the utilization of a reactive spray coating technology. The cost of spray technology is relatively high, and operation is strict, making it unsuitable for various commercial and civilian applications. Furthermore, due to polyurea's rapid curing and rigid segments, films become very hard and brittle, resulting in low adhesion to the metal surface [12]. Moreover, the synthesis of pure polyurea is costly,

leading to serious impacts on mass production [13]. Thus, incorporating it with polyurethane at lower amount would help lessen the production cost.

To address the observed limitations within the existing polyurethane and polyurea coating systems and to achieve specific desirable characteristics such as enhanced tensile strength and thermal stability, and increased adhesion and corrosion resistance, this study proposes the incorporation of amines into the current polyurethane coating system, thereby creating a polyurethane-polyurea hybrid. This hybrid coating is synthesized through the reaction of isocyanate with both amine and hydroxyl-terminated compounds. Consequently, the integration of polyurea is anticipated to yield additional advantages for optimizing coating performance. In this study, a poly(urethane-urea) hybrid coating was synthesized using a coconut oil-derived polyester polyol, hexamethylene diisocyanate, and triethanolamine for anticorrosion application.

2. Methodology

2.1 Materials

The coconut oil-based polyester polyol (Cocopol, OH Number =214) was supplied by the Bio Products Research Laboratory, Mindanao State University (MSU)-Iligan Institute of Technology, Philippines. 1,6-Hexamethylene diisocyanate (HDI, NCO content 49.9%; Mw = 168.19 g/mole) (Sigma Aldrich), Triethanolamine (TEA, Mw = 149.19 g/mole), BYK®-022 (defoamer) were supplied by Chemrez Technologies, Inc., Stainless steel (with 2 in. x 3 in. dimension, polished) was purchased from local hardware.

2.2 Methods

Pre-polymerization of polyurethane was performed in a 100 ml beaker and placed above a hot plate. COCOPOL and HDI were prepared, mixed into the beaker using a magnetic stirrer, and heated at 40°C for 10 minutes. The mixture was then allowed to cool for 5 minutes in a water bath. Subsequently, the defoamer (BYK-022) was introduced into the mixture. The polyurethane-polyurea hybrid films were then prepared by adding triethanolamine to the pre-polymerized PU at 0% to 10% loading and were mixed using a magnetic stirrer for 5 minutes. The amine to polyol loading via percent replacement were 0:1.0, 0.02:0.98, 0.04:0.96, 0.06:0.94, 0.08:0.92, and 0.10:0.90. Thereafter, the coating was applied to the metal substrate.

2.3 Application of Poly(urethane-urea) Hybrid Coating

The Polyurethane/Polyurea hybrid coating was applied manually to the metal and glass substrates, measuring 2 inches x 3 inches and having a thickness of 0.25 inches. The application was repeated until the coating was uniformly distributed on the metal substrates. Curing time was done at an average of 48 hours under ambient condition.

2.4 Characterizations and Specifications

The chemical composition analysis of the hybrid coating was performed using Fourier Transform Infrared Spectrometer (IRTRACER-100, SHIMADZU) with the following conditions: ATR method, resolution: 20, and wavenumber range: 4000-400 cm^{-1} . The anticorrosion properties were investigated through Linear Polarization Resistance and Electrochemical Impedance Spectroscopy (EIS) (Biologic SP-150). Before being subjected to testing, the sample was soaked in a 3.5% NaCl

solution for 30 days. The Tafel plot and Nyquist plot were fitted using EC-Lab software. Contact angle measurements were used to measure the hydrophobicity of the coating surface. The contact angles were measured by the sessile drop method using optical tensiometers (Theta Lite) from Biolin Scientific. A 5-10 μL of distilled water was suspended at the end of a syringe onto the surface of the hybrid films. The mechanical properties of the samples were investigated by subjecting dumbbell-shaped specimens to tensile tests. The tests were performed using a universal testing machine (Model AGS-X, Shimadzu) following ASTM Standard D-882. A cross-section tape test (11 parallel cuts spaced 1 mm apart) was performed following ASTM D3359-02 to determine the coating's adhesion to the substrate. The thermal behaviour of the hybrid coating was observed using Differential Scanning Calorimetry (DSC) (Model DSC4000, PerkinElmer) in a nitrogen atmosphere. 5 mg of each coating sample was prepared and placed in aluminium pans. T_g values were determined by heating the samples from $-70\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$ at a $10\text{ }^\circ\text{C}/\text{min}$ heating rate. Glass Transition Temperature (T_g) and the melting temperature (T_m) of both soft and hard segments values were determined using the midpoint temperature in the heat capacity change of the DSC scans.

3. Results

3.1 Chemical Composition Analysis

Figure 1 shows the FTIR spectra of polyurethane coating and its composites. Results confirmed the occurrence of structural characteristics of Poly(urea)urethane Hybrid and its composites.

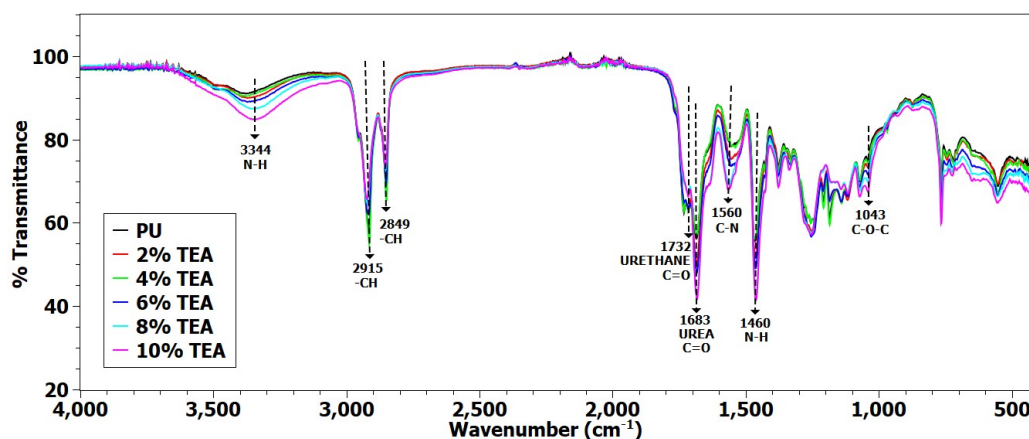


Fig. 1. FTIR spectra of Polyurethane/Polyurea Hybrid coating

The FTIR spectrum of Poly(urea)urethane Hybrid shows signals in the peak of 3344 cm^{-1} , resulting from symmetric and asymmetric stretching vibrations of the N-H groups present in urethane derivatives (Figure 2(a)). The peak at 1732 cm^{-1} indicates the presence of C=O (ester) bond stretching vibrations of the urethane carbonyl groups (Figure 2(b)). Based on the graph, the intensity of the bands originating from the vibrations of urethane carbonyl bonds C=O increases with the increasing Coconut Polyester Polyol (CPP) content. The peak at 1460 cm^{-1} (Figure 2(c)) is attributed to urea N-H bending vibration (amide II). Another urea constituent, C-N , peaks at 1560 cm^{-1} . The urea C=O carbonyl group is visible at peak 1683 cm^{-1} (Figure 2(b)) [8]. It can be observed that the most intense bands in this region occur for the film with the highest amine loading.

The carbonyl group is considered hydrophilic due to its partially negatively charged oxygen atom that may form hydrogen bonds with water molecules, again making the molecule more hydrophilic. Adding amine would introduce -NH groups in the system, forming hydrogen bonding with the carbonyl groups. The presence of -NH and the carbonyl groups C=O permits the formation of

hydrogen bonds in the PU (Figure 2(c)). The elastomer properties depend primarily on the secondary or hydrogen bonding of polar groups in the polymer chains [14]. Hydrogen bonding occurs readily between the NH-groups and the carbonyl groups of the polyurethane-polyurea linkages. The Urea bonds have more -NH bonds in their group than the urethane group. Hydrogen bonding in polyurethane is enough to have good properties. However, hydrogen bonding in polyurea's is more robust and provides a more desirable property [15]. Thus, the addition of amine to create urea linkage contributes even more to the performance of the film [16]. Hydrogen bonding between urea linkages is also responsible for the improved hydrophobicity of the coating, which slows down the corrosion of the substrate [17]. The hydrogen-bonding network of polyurea coatings would reduce the porosity and enhance the barrier properties of the coating. This bonding is also responsible for improving the mechanical properties of the coating [18]. The band at 10% amine loading leads toward hydrophobicity, while the most intense bands, which are the 0-2% amine loading, are considered hydrophilic.

The peaks at 2915 cm^{-1} and 2849 cm^{-1} (Figure 2(d)) corresponded to the -CH stretching vibrations (asymmetric and symmetric vibrations) of the alkyl chain present in coconut oil. With the increasing amount of polyol, the absorbance of bands originating from symmetric and asymmetric stretching of C-H bonds increases [19].

The polyether group that is present in the backbone of polyurea is present at the peak from 1043 cm^{-1} (Figure 1(d)). The polyurethane, polyurea and poly(urethane-urea) hybrid systems all have the polyether backbone in the elastomer [18]. The polyether group (C-O-C) is responsible for the chemical resistance property of the coating. It was observed that the most intense band occurs for the highest amine loading. This indicates that this band has the highest chemical resistance property. The urea linkage found in the polyurea and the hybrid system is more resistant to hydrolysis than the urethane linkage. It was observed that the peak intended for the -NCO group was not visible, signifying that all isocyanates fully reacted with the bio-based polyol and amine, which indicates the successful integration of amine into the Polyurethane prepolymer.

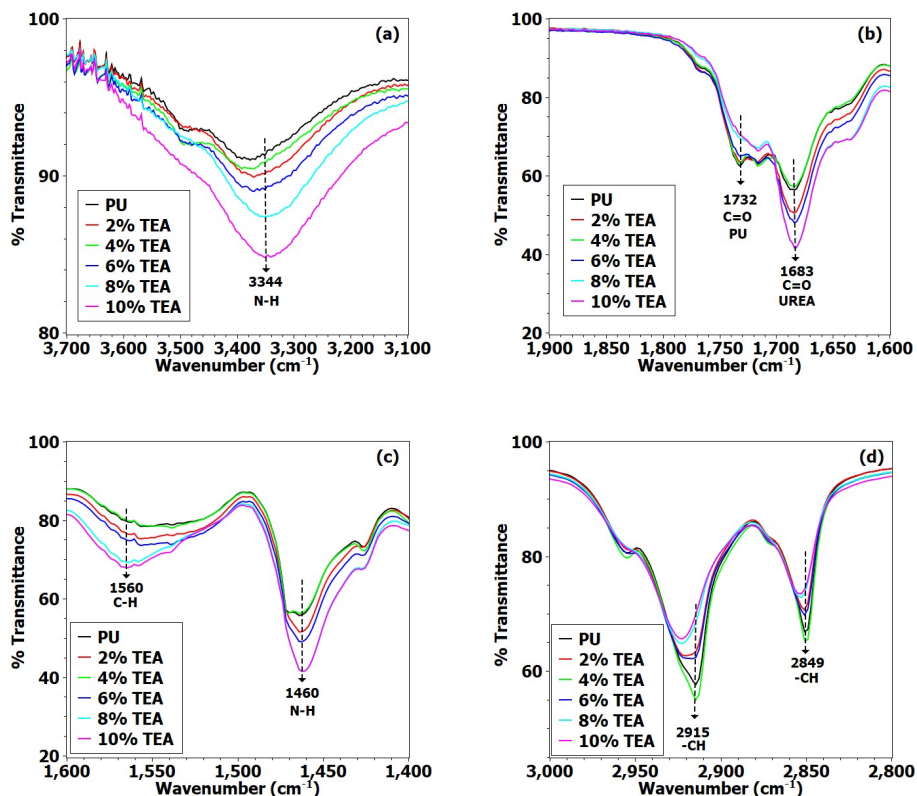


Fig. 2. FTIR spectra for PU, 2%, 4%, 6%, 8%, and 10% TEA loadings (a) N-H bonding, (b) C=O bonding for PU and Urea, (c) C-H and N-H bonding, and (d) -CH bonding

3.2 Corrosion Inhibition Test

3.2.1 Linear Polarization Resistance (LPR) test

LPR measurements were conducted to assess the effects of varying amine loading on the polyurethane/polyurea coating's corrosion resistance. The Tafel plot shows the relationship between the current generated in an electrochemical cell and the electrode potential of a specific metal. Based on Figure 3, the addition of amine caused a shift in corrosion potential (E_{corr}) and reduced the corrosion current (I_{corr}).

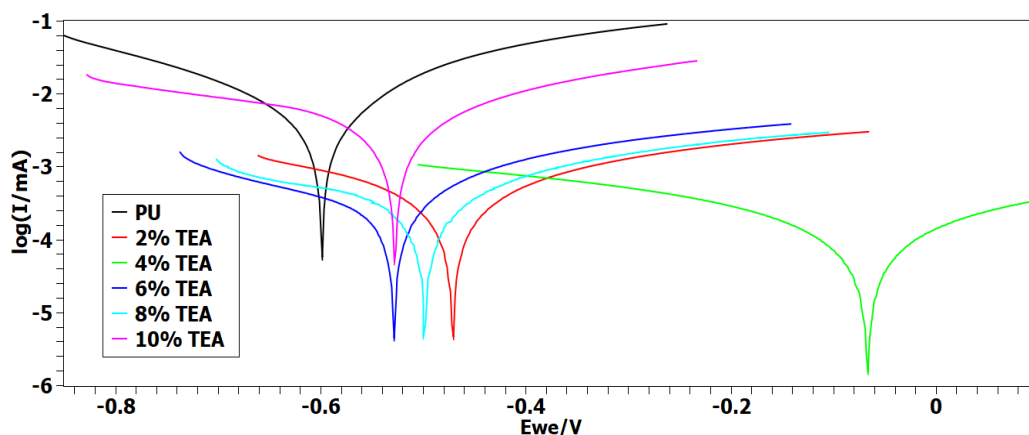


Fig. 3. Potentiodynamic polarization curves of carbon steel soaked in 3.5% NaCl solution for 30 days coated with PU, 2%, 4%, 6%, 8%, and 10% TEA loadings

This observation can also be seen in Table 1, that there was a significant drop in the corrosion potential (E_{corr}) as its value becomes less negative, implying that as the amine concentration increases, the metals' susceptibility to corrode decreases. This downward trend can also be observed in the corrosion current. There was a decline in the electric current generated as the amine loading increased; thus, oxidation reactions in the metals were reduced. The decrease in corrosion potential and corrosion current is accompanied by a sharp decrease in the corrosion rate which only suggests that better corrosion performance is attained with the addition of amine.

Table 1

The potential of corrosion (E_{corr}), corrosion current (I_{corr}), and corrosion rate at different Amine loading of Polyurethane/Polyurea Hybrid Coating

Samples	E_{corr} (mV)	I_{corr} (μ A)	Corrosion Rate
PU	-529.2	0.085	0.315 e^{-3}
2%	-601.7	1.230	4.570 e^{-3}
4%	-65.48	0.015	55.70 e^{-3}
6%	-468.7	0.077	0.286 e^{-3}
8%	-498.6	0.062	0.229 e^{-3}
10%	-527.7	1.057	2.306 e^{-3}

3.2.2 Corrosion mechanism

The samples were soaked in a 3.5% NaCl solution, which introduced aqueous corrosive ions from the surface of the coating, while the coating film created a barrier against the diffusion of ionic electrolytes. This film provides remarkable corrosion protective ability to the underlying metal substrate. The introduction of amine in the polyurethane matrix provides a strong barrier effect against the corrosive ions through the following mechanism (Figure 4). The formation of urea and urethane linkages leads to the formation of hydrogen bonding that highly influences the hydrophobic properties of the coating with strong adhesion to the metal interface. This enhanced hydrophobicity helped in decreasing the soaking capacity of the corroding medium.

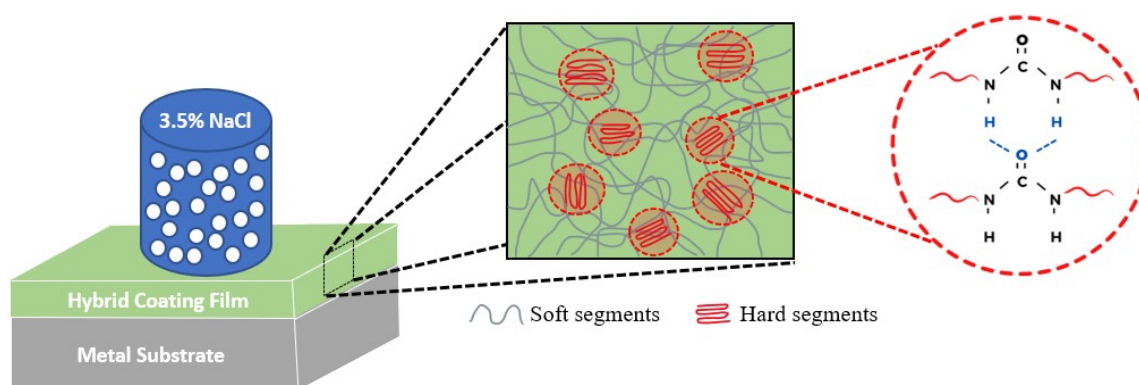


Fig. 4. Corrosion inhibition mechanism of the polyurethane-polyurea hybrid coating

3.2.3 Electrochemical Impedance Spectroscopy (EIS) test

The electrochemical responses of all prepared coating systems were recorded in the form of Nyquist plots, and the coated carbon steel panels were exposed to the 3.5% NaCl solution. The numerical fitting of all the resistance components of the equivalent circuit was carried out by utilizing models A and B of the equivalent circuit, and the resistance values were tabulated in Table 2. The

obtained results were expressed graphically using the Nyquist plot (see Figure 5) after 30 days of immersion.

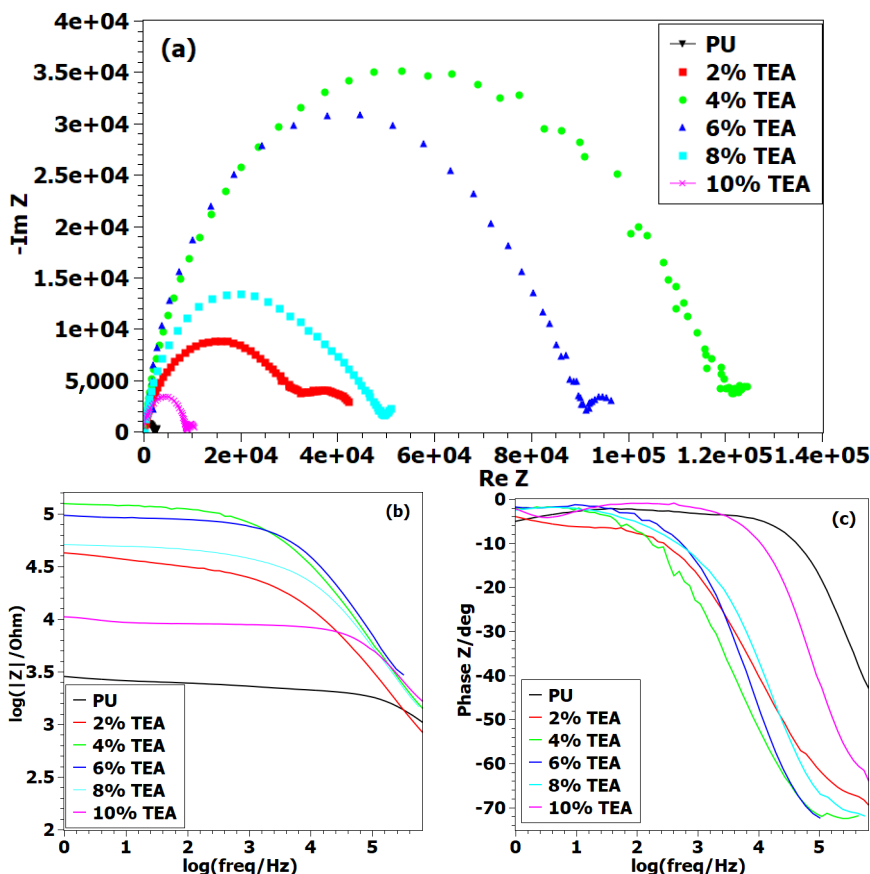


Fig. 5. EIS spectra for samples PU, 2%, 4%, 6%, 8%, and 10% TEA loadings: (a) Nyquist Plots, (b) Impedance, and (c) Phase angles, after 30 days immersion

The EIS results are further fitted by EC-Lab software using the equivalent electric circuits shown in Figure 6. R_s is the solution resistance, and R_c and CPE_c denote coating resistance and constant phase element capacitance, respectively. CPE_{dl} represents a constant phase element double-layer capacitance, and R_{ct} represents a charge transfer resistance. CPE_{diff} pertains to diffused constant phase element capacitance, while the R_{diff} pertains to diffused resistance.

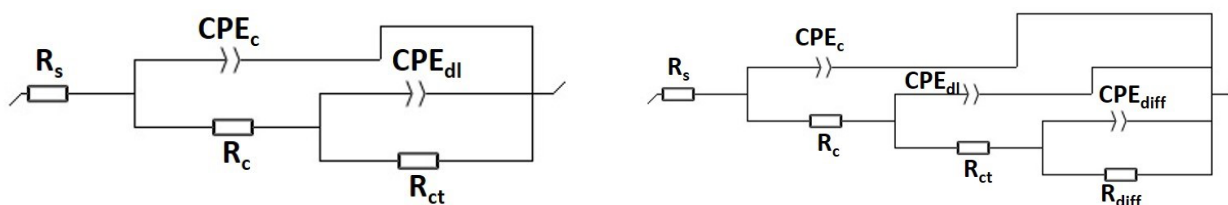


Fig. 6. Example of Nyquist plots for different circuit networks

It can be seen in Table 2 that the polyurethane coating (PU) demonstrated a low coating resistance (R_c) value at $11.3 \Omega \text{ cm}^2$ and falls under the model B circuit; this could be due to the hydrophilic property of polyurethane. The addition of 2% TEA loading shows lower R_c , signifying that the urea formed in the urethane matrix is insufficient to inhibit the corrosive agent's permeation.

The 4% TEA loading exhibited outstanding corrosion resistance with an R_c of $29.9 \text{ e}^{09} \Omega \text{ cm}^2$ and falls under the model A circuit, indicating no corrosion formed even after 30 days of soaking. However, as the TEA loading further increases from 6%, 8%, and 10%, the corrosion resistance starts to drop with a R_c of $22.3 \text{ e}^{03} \Omega \text{ cm}^2$, $7.89 \text{ e}^{03} \Omega \text{ cm}^2$, and $1.92 \text{ e}^{03} \Omega \text{ cm}^2$, respectively.

Table 2

Fitted parameter values of the equivalent circuit elements along with the utilized model after 30 days of immersion

Samples	CPE_c (C)	R_c (Ω)	CPE_{dl} (C)	R_{ct} (Ω)	CPE_{diff} (C)	R_{diff} (Ω)	Circuit Model
PU	5.25e^{-10}	11.3e^{03}	2.17e^{-09}	3474.3	8.43e^{-06}	40732	B
2%	1.68e^{-10}	4.73	1.66e^{-08}	1249.8	0.0005	40731	B
4%	2.05e^{-09}	29.9e^{03}	1.50e^{-07}	96250	-	-	A
6%	2.82e^{-10}	22.3e^{03}	1.47e^{-05}	6988.9	4.21e^{-08}	1700	B
8%	2.34e^{-10}	7.89e^{03}	1.07e^{-07}	78421	5.99e^{-06}	10.3e^{033}	B
10%	1.32e^{-10}	1.92e^{03}	1.47e^{-08}	6988.9	4.21e^{-08}	1700	B

The decreasing corrosion resistance of the poly(urethane-urea) hybrid coating could be due to the following reasons:

- i. The hard segments under these TEA loadings increase, these affect the adhesion strength of the coating material where delamination occurs and allow the permeation of corrosive agents [15]
- ii. The increasing amount of TEA affects the curing of polyurethane and increase the rate of carbon dioxide diffusion that will result to the formation of bubbles, blistering and delamination of coating, leading to a more porous coating material and making it more susceptible to corrosion attacks [22,23].

The presence of carbon dioxide could be due to the interaction between isocyanate and water, which will form carbamic acid [22]. This carbamic acid will eventually decompose into urea and carbon dioxide, as can be seen in Figure 7. The progression of the formation of carbon dioxide in the PU/urea hybrid coating is visible based on the physical appearance of the samples, as can be seen in Figure 8.

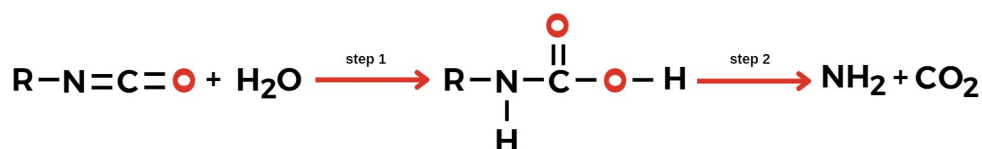


Fig. 7. Reaction between isocyanate and water forming into urea and carbon dioxide

Consequently, 4% TEA loading exhibited outstanding corrosion resistance, which was consistent with the potentiodynamic polarization results showing the lowest corrosion rate.

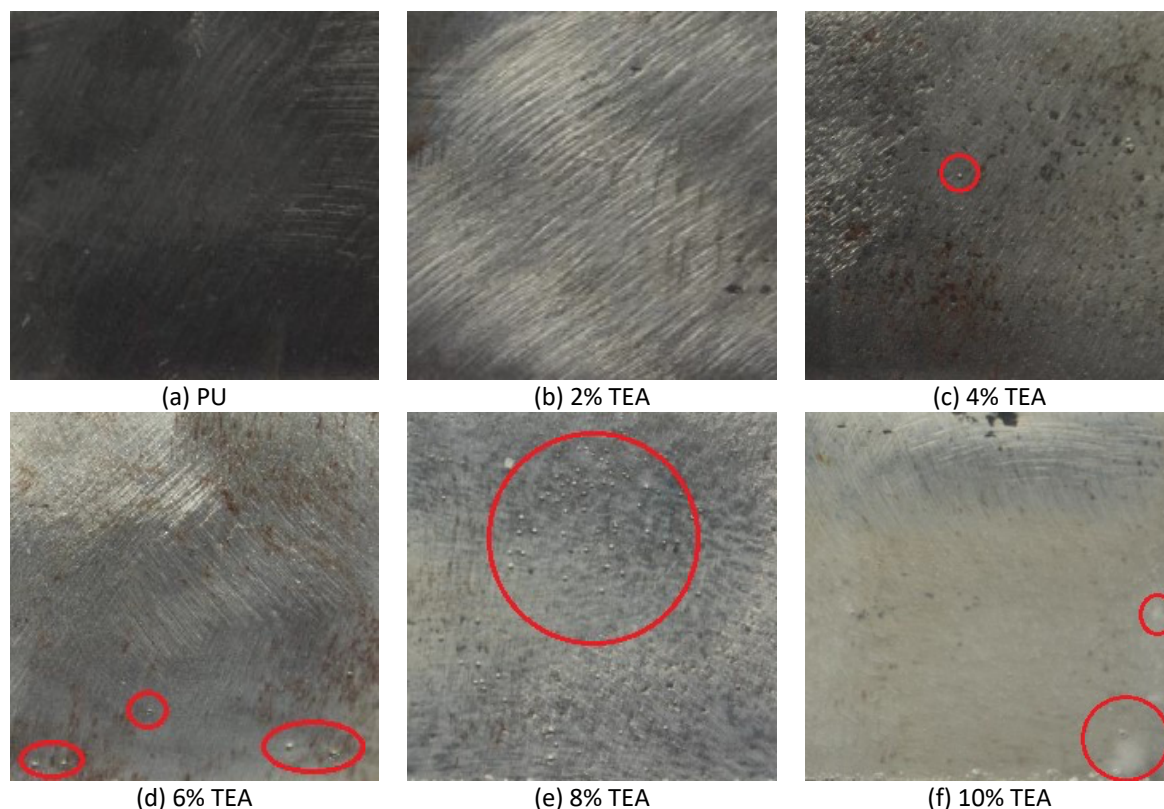


Fig. 8. Progression of formation of carbon dioxide as the concentration of TEA loading increases

3.3 Hydrophobicity Test

The hydrophobicity of the different amounts of amine incorporated in Poly(urethane-urea) coating was investigated with their static contact angles. By forming a droplet on the surface of coatings, the contact angle can be conventionally measured from where a liquid interface meets a solid surface.

The results of the sessile drop measurements, as shown in Figure 9, revealed that the value of contact angle for the hybrid coating at PU, 2%, 4%, 6%, 8%, and 10% TEA loadings are 35.1°, 43.8°, 44.3°, 45.5°, 50.1°, and 53.2° respectively. It can be observed that at 0% amine loading, the contact angle is around 35°.23. This hydrophilic nature of PUs is affected by the presence of hard segments in the PU structure and the hydrophilic urethane group [23]. Although the values fall under the hydrophilic category (below 90°), which could be expected since PU is the majority component of the coating and only a maximum of 10% loading is incorporated, the results showed that with the incorporation of an amine into the coating, the contact angles were found to be increasing leading towards the hydrophobic region.

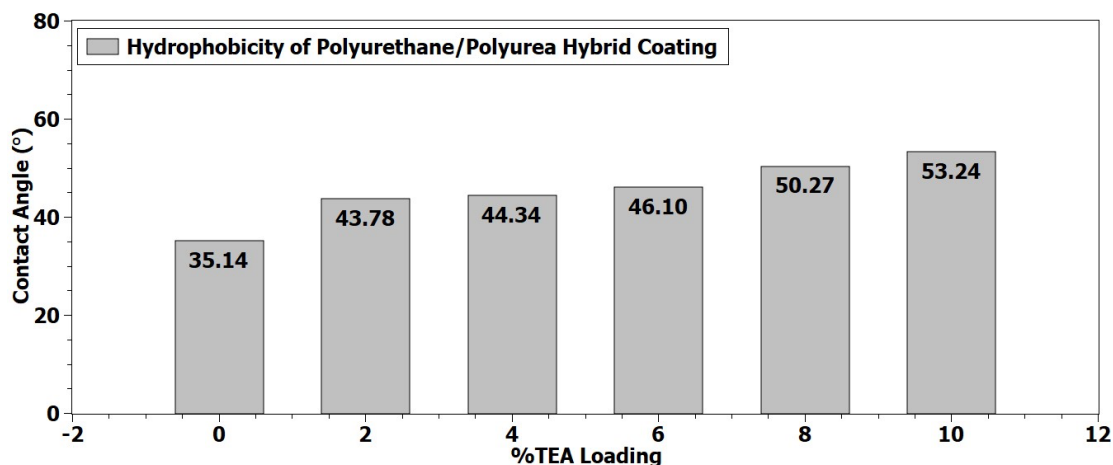


Fig. 9. Hydrophobic trend of poly(urethane-urea) hybrid coating at different amine loading

This increase is due to the hydrophobic properties of polyurea, which can be attributed to its rapid cure speed property due to the fast reaction of amine and isocyanate [11]. The hydrophobic nature of polyurea would enhance the hydrophobicity of the coating surface, which inferiorizes the interaction of the metal surface with electrolytes and improves the barrier property, thus enhancing the corrosion inhibition of the coating [22]. In addition, Feng *et al.*, reported that an increase in polyurea mole fraction up to 50 mol % enhanced the occurrence of H-bonding-induced self-assembly and led to a remarkable improvement in crystallinity and corrosion resistance [24].

The result suggests that the increasing amine concentration up to 4% loading has dramatically improved the coating's hydrophobic properties.

3.4 Mechanical Strength Test

The tensile strength of the poly(urethane-urea) coating was measured according to the ASTM Standard D-882. Tensile strength at break measures the maximum stress a material can withstand while being stretched before breaking. Based on the data in Table 3, the tensile strength of the hybrid coating was significantly affected by the addition of amine. It shows improvement in the tensile strength of the poly(urethane-urea) coating with increased amine concentration. Its effect on the coating's tensile strength was most observable at 8% concentration. However, when the loading of the amine continues to increase, the tensile strength of the poly(urethane-urea) coating is reduced due to the formation of hard segments, which is urea. Thus, the coating becomes more rigid. The formation of blisters on the surface of the coating was also evident. As a result, the coating becomes less elastic and more brittle.

Table 3
 Tensile properties of poly(urethane-urea) hybrid coating with different amine loading

Samples	Maximum Force (N)	Tensile Strength (N/mm ²)
PU	1.15±0.13	1.39±0.15
2%	1.67±0.20	2.29±0.17
4%	1.41±0.42	2.31±0.63
6%	1.93±0.32	3.40±0.06
8%	4.81±0.44	3.66±0.10
10%	4.54±0.57	2.79±0.11

3.5 Thermal Stability Test

Differential Scanning Calorimetry analysis is one of the most convenient methods for analysing the crystallization and melting of semicrystalline polymers. The T_g of the soft segment, T_m of the soft segment, and T_m of the hard segment in the DSC thermograms are shown in Figure 10.

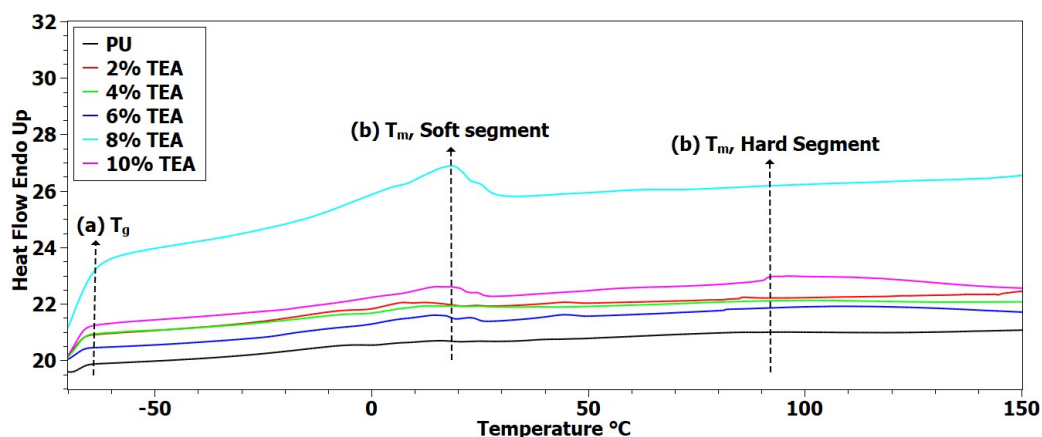


Fig. 10. DSC thermograms of poly(urethane-urea) hybrid: (a) T_g of Soft Segments, (b) T_m of Soft Segments, and (c) T_m of Hard Segments

Table 4 shows that the values obtained for the glass transition temperatures of the hybrid samples and the reference sample (PU) associated with the soft segments (T_g) are in the range of -67 to -68°C. No significant differences were observed in the glass transition of the samples. However, visible changes were observed in the melting points of the soft and hard segments. At 2-10% amine loading, the melting point of the soft segment can be observed in the graph, signifying the presence of flexible segments of our polymer structure. Moreover, there is a visible difference between the melting point values obtained for the reference sample (PU) and the hybrid samples (PU-Hybrid). It can be observed that the melting point (T_m) of the soft segment decreases as the polyol loading increases. The decrease in melting points can be attributed to the fatty acids present in the triglycerides in the polyol. Earlier studies reported that insertion of fatty acids into the polymeric material gives the polymer a low melting point. It was shown that the lowest melting point is the sample that has the highest polyol content, which is the 0% PU [25]. Furthermore, it can also be noted that adding amine increases the melting point of the hybrid coating. The increase in melting point exhibited by polyurea is due to the strong hydrogen bonding within the hard segments [12]. The result confirms that polyurea exhibit superior thermal stability, as stated by Primeaux [17]. The melting point for the hard segment is only visible in the hybrid coating with the highest amine loading, signifying that the hard segment-rich phase was formed at higher amine content. The DSC thermograms of the poly(urethane-urea) hybrid indicated that both the polyol and amine loading influenced the melting points of the hybrid coating. The higher melting point means the greater intermolecular force of attraction and higher stability. Therefore, the polyurethane/polyurea hybrid coating with 10% amine loading exhibits the best thermal properties with a melting point of 18.73 °C and 92.25 °C as compared to the other hybrid samples.

Table 4
 DSC Analysis of Polyurethane/Polyurea Hybrid Coating

Samples	T _g (°C)	T _m (°C) Soft Segments	T _m (°C) Hard Segments
PU	-67.02	6.29	-
2%	-68.31	7.27	-
4%	-68.41	10.74	-
6%	-68.44	16.97	-
8%	-68.47	18.21	-
10%	-68.54	18.73	92.25

3.6 Adhesion Test

A cross-cut tape test was measured on the sample according to ASTM D-3359-02 at room temperature. Three measurements were averaged to determine the thickness of the coatings on a metal substrate with a coated area of 1.25 x 2.5 in2. The cross-cut tape test was performed to evaluate the effect of varying amine loading on the adhesion of the poly(urethane-urea) hybrid coating to the metal substrate, as shown in Table 5. Based on the result, 5.26% of the coating was peeled off from the grid area, falling under the 3B classification, which means that flakes have manifested along the edges of the coating or at the intersections of the cuts. The succeeding coating samples showed 0% percent area removed, which signifies that there was no peeling or chipping around the cut lines, which means that between these increasing amine loading, the coating showed 100% adhesion to the substrate. As the amount of amine incorporated increases, the adhesion is shown to be excellent. The excellent adhesion of coatings could be attributed to urea linkages, which form secondary hydrogen bonding with the substrate [18]. However, the coating sample with a 10% amine concentration showed otherwise. The percent area removed on the coating is about 6.5%, with a 3B rating. This occurrence is due to the fast curing and hard segments of polyurea films become very hard and brittle with low adhesion to the surface of metal [12]. Thus, the result suggests that poly(urethane-urea) hybrid coatings with 2% to 8% amine loading can bind strongly to the surface of the metal substrate.

Table 5
 Adhesion Test Results (According to ASTM D 3359-02)

Samples	Percent Area Removed (%)	Classification
PU	5.26	3B
2%	0	5B
4%	0	5B
6%	3.5	4B
8%	4.8	4B
10%	6.5	3B

4. Conclusion

In summary, the poly(urethane-urea) hybrid coatings with varied amount of amine were successfully synthesized utilizing coconut oil-based polyol blend and TEA which was confirmed by the formation of urea and urethane linkages observed in the chemical structural analysis done by FTIR. Based on the anticorrosion tests performed, there was a decrease in corrosion potential. The corrosion current is accompanied by a sharp reduction in the corrosion rate, which only suggests that better corrosion performance is attained by adding amine. As the TEA loading increases further by 6-10%, the corrosion resistance will be compromised, although the thermal stability, and hydrophobicity are excellent. However, a limitation was observed as the hard segments of the

coating increased, and the film started to become brittle, thus resulting in a decrease in tensile strength and adhesion. This limitation could affect the performance of the coating in the long run. Therefore, with these results, the researchers concluded that the best concentration of amine, which has shown excellent thermal, mechanical, and anticorrosion properties, was 4%.

Acknowledgment

The authors would like to thank the Department of Science and Technology – Science Education Institute (DOST-SEI) for the scholarship grant and the Department of Science and Technology - Philippine Council for Industry, Energy and Emerging Technology Research and Development (DOST-PCIEERD) for the research grant. Moreover, the authors would like to thank the Centre for Sustainable Polymers, Mindanao State University – Iligan Institute of Technology for allowing the researchers to conduct its experiment inside their laboratory.

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