Soybean extracts as green corrosion inhibiting additives to fluoropolymer coatings

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Research Overview

Fluoropolymers, endowed with hydrophobicity, thermal stability, and chemical inertness, face limitations in surface adhesion due to their low surface energy and nonstick properties. Despite research movement, commercial use remains challenged by the complexity and cost of surface treatment to improve fluoropolymer adhesion to various substrates. Eco-friendly plant extracts, with abundant heteroatoms and pi-electrons, offer a sustainable and promising solution. The goal of this research project is to incorporate soybean extracts (SE) into poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) fluoropolymer coatings and investigate their surface adhesion and corrosion protection toward mild steel substrates. These low-cost, sustainable SE-infused fluoropolymer coatings are expected to present a compelling solution for diverse surface protection applications.

Objectives of the Study

Our research aims to explore the inclusion of SE as reinforcement additives in PVDF-HFP coatings and improve their adhesion to metal substrates and corrosion protection. Specific objectives include (1) obtaining high-concentration SE using eco-friendly solvents via a simple extraction-distillation process, (2) examining the effect of varying SE concentrations on the corrosion resistance of the PVDF-HFP coatings through electrochemical measurements, and (3) evaluating and assessing the influence of SE on the surface adhesion strength of PVDF-HFP coatings on mild steel.

Completed Work

In this project, we have successfully obtained SE using two environmentally friendly solvents, water and hexane. The process is schematically illustrated in **Figure 1a**. The pre-extraction steps include soybean grinding and moisture removal by heating the ground soybeans in an oil bath. The SE was obtained using a Soxhlet extraction procedure, a highly sensitive technique dependent upon the nature of the solvent used. Water (polar) and hexane (nonpolar) were chosen as extracting solvents due to their versatility and low toxicity. Polar components of SE were obtained using water alone, while nonpolar components were extracted using only hexane. The obtained nonpolar SE exhibited an oily liquid state, while the polar SE was solid after drying, as shown in **Figure 1b**. We found no significant difference in the yield amount of SE between Soxhlet extraction times of 8, 12, and 24 h, regardless of the solvent used. We chose the most optimal and least amount of time, that is 8 h as the standard extraction process.

To differentiate the chemical composition of the two extracts, Fourier-transform infrared (FTIR) spectra were collected, as shown in **Figure 1c**. One distinctive feature of the polar SE is the broad band between 3500 and 3000 cm^{-1} (-OH stretching), indicating the presence of hydroxyl-containing extracts. In addition, a peak near ~1150 cm^{-1}, attributed to C-O-C stretch, was observed for the polar SE. For both SEs, a peak at 1750 cm^{-1}, attributed to C=O stretching, indicates the presence of carbonyl-containing components. The presence of these oxygen-containing moieties in the extracts can facilitate adhesion at the coating-metal substrate interface.

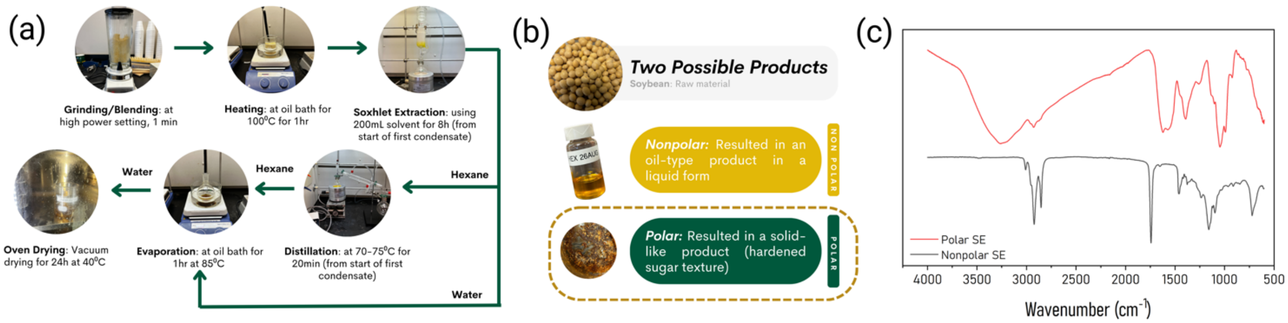

Figure 1. (a) Scheme for obtaining the polar and nonpolar SE using water and hexane, respectively. (b) Physical states of the obtained SEs after Soxhlet extraction. (c) FTIR spectra of polar and nonpolar SEs.

Prior to coating, the mild steel substrates were polished and degreased with acetone in a sonicated bath. The coating solution was prepared by first dissolving the SE in varying concentrations in dimethylsulfoxide (DMSO). After dissolution, PVDF-HFP pellets (at 25 wt.% concentration) were dissolved in the solution. The prepared coating solutions were dip-coated onto the metal substrates, after which the resulting SE/PVDF-HFP coated substrates were dried in an oven. Immediate delamination post-drying was observed for the 3 wt.% nonpolar SE/PVDF-HFP coating as shown in **Figure 2a**. This result may be attributed to the incompatibility between the hydrophobic nonpolar SE and non-oil soluble hydrophobic PVDF-HFP, and the lack of sufficient functional groups needed for effective interaction at the polymer-substrate interface. In addition, the ability of nonpolar SE to act as a lubricant for the fluoropolymer matrix results in a slippery layer at the coating-substrate interface. In addition, the absence of hydrophilic functionalities in nonpolar SE significantly reduces the coating adhesion strength. Although this issue can be resolved by epoxidizing the nonpolar SE, such a task is outside the scope of our current work. With this, we merely focused on the use of polar SE (hereon referred to as simply SE). Three PVDF-HFP coating formulations containing SE have been investigated: 0.25, 0.50, and 1.0 wt.% SE (visual photos of the coated samples are shown in **Figure 2b)**. Pristine PVDF-HFP coating (i.e. 0 wt% SE) was used as the control sample. Note that as the SE concentration was further increased to 3 wt.%, the coating solution processability became severely distressed, as evidenced in **Figure 2c**. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry was conducted to identify the isoflavones present in the obtained SE. **Figure 2d** displays the mass spectra of the six identified isoflavones present in the SE – genistein, daidzein, and glycitein, alongside their corresponding glycoside forms genestin, daidzin, and glycitin, respectively. The functional groups present in their chemical structures are in strong agreement with the identified functional groups (i.e. C=O, -OH, and C-O-C) in the polar SE FTIR spectrum (**Figure 1c**).

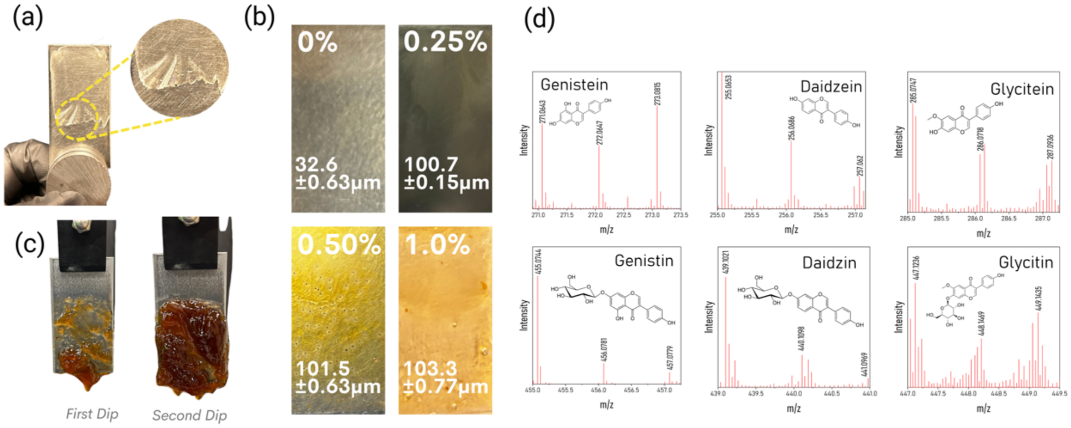

Figure 2. (a) 3 wt.% nonpolar SE-PVDF HFP coating on a mild steel substrate. (b) Optical images of polar SE–PVDF HFP coatings with their respective thickness and %SE. (c) Dip coating with 3 wt.% polar SE-PVDF HFP. (d) High-resolution mass spectra of polar SE showing the presence of isoflavones.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were conducted to evaluate the corrosion protection performance of the coated samples in 3.5 wt.% NaCl solution, analogous to seawater conditions. The Nyquist plots in **Figure 3a** show the wider semicircle size of the 0.5% SE/PVDF-HFP sample (even after 7 d of immersion), which is caused by the faradaic impedance of the coating, resulting in higher corrosion protection compared to other coating samples. The Bode magnitude plots shown in **Figure 3b** quantitatively provide the corrosion resistance of the coatings. It is a common consensus in corrosion studies that when the impedance modulus at low-frequency region, $|Z|_{0.1\text{ Hz}}$, is above 10^6 Ω, the coating is said to provide adequate corrosion protection. In this work, the 0.5% SE/PVDF-HFP coating exhibited the highest $|Z|_{0.1\text{ Hz}}$ with a magnitude of 10^8 Ω after 1 d of immersion. Interestingly, this coating sample demonstrated corrosion protection durability as it maintained a $|Z|_{0.1\text{ Hz}}$ magnitude of 10^8 Ω even after 7 d of continuous immersion. On the other hand, the impedance value for the pristine PVDF-HFP coating decreased by an order of magnitude after 7 d. Although both 0.25 and 1.0% SE/PVDF-HFP coatings had an impedance of 10^5 Ω after 1 d of immersion, the impedance value of the former dropped by 1 magnitude order after 7 d, compared to the latter, which almost retained its impedance value after 7 d of immersion. The stable corrosion protective properties of both 0.50 and 1.0% SE/PVDF-HFP coatings may be attributed to the SE's inherent ability to passivate the defects in the coating system. This phenomenon also suggests that the minimal impedance increase for the 1.0% SE/PVDF-HFP coating after 7 d can be associated with its capability to reduce the presence of the coating pores. An analogous trend can be seen in the Tafel plots in **Figure 3c**, such that after extrapolating the anodic and cathodic regions of the curves, the 0.5% SE/PVDF-HFP coating demonstrated the lowest corrosion current density and a more positive corrosion potential. Among all the coating samples tested, the 0.5% SE/PVDF-HFP coating exhibited the highest corrosion protection even after prolonged immersion in NaCl solution.

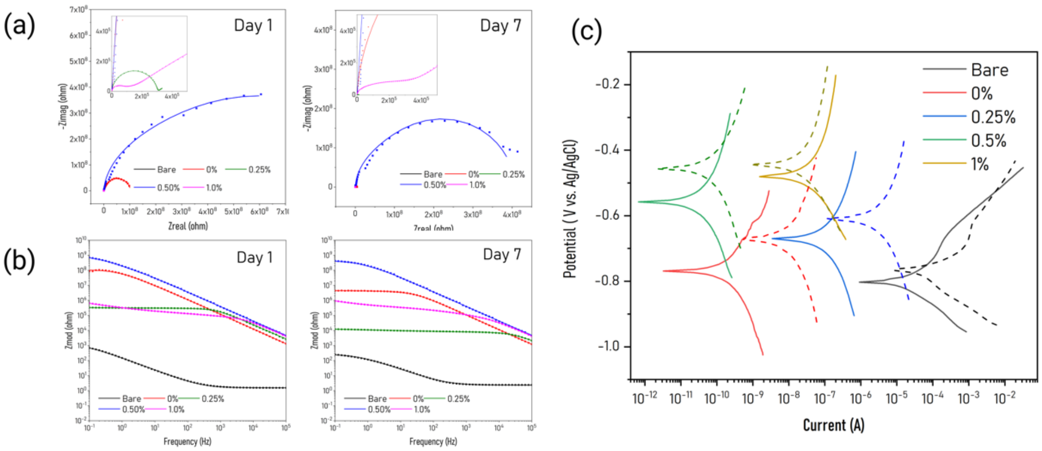

Figure 3. (a) Nyquist and (b) Bode plots of SE/PVDF-HFP coatings at varying immersion times in 3.5 wt.% NaCl solution. Solid lines represent the fitting results. (c) Tafel curves after 1 d (solid lines) and 7 d (dashed lines) of immersion.

Progress of Work and Results to Date

Table 1 summarizes the project's status, where 4 out of 6 of the tasks were completed, with one being completed ahead of the proposed schedule. We were also able to submit a review paper on fluoropolymer adhesion for consideration in a journal and is now currently undergoing a peer-review process.

Table 1. Gantt chart and timeline of activities. Green blocks indicate completed work.

Objective	Task	Milestone	Remarks	Q1	Q2	Q3	Q4
1	Perform soybean extraction	Solvent (hexane or water) giving the highest yield of soybean extracts	%Yield does not depend on the solvent nature and extraction time	🟩	🟩		
	Soybean extract characterization	Spectrum peaks confirming presence of phytochemicals in the extracts	FTIR spectroscopy and mass spectrometry were conducted to confirm the presence of isoflavones		🟩		

	PVDF-HFP/ soybean extract coating preparation	Achieving dry film thickness of 100 µm	Successful coating of polar SE (with varying concentration)/PVDF-HFP with thickness above 100 µm		🟩		
2	Perform electrochemical measurements	Extract concentration in PVDF-HFP coatings providing the highest protection efficiency	Completed ahead of schedule - EIS and potentiodynamic polarization were conducted. Equivalent circuit modeling is still ongoing.		🟩	▨	
	Perform spectroscopy and microscopy experiments	Spectrum peaks confirming the presence of extracts in the PVDF-HFP coatings	Currently on-going			▨	▨
3	Perform cross-cut adhesion tape test and hardness test	Extract concentration in PVDF-HFP coatings providing the highest adhesion strength, as supported by XPS, SFE, and simulation results	To be accomplished			▨	▨

Work to be Completed

Further investigation is crucial toward understanding the coatings' adhesion and corrosion protection capabilities. To determine the impact of the SE on the PVDF-HFP matrix, the FTIR spectra of the coating can provide insights into the functional groups present and effect of varying SE concentrations. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) before and after immersion can also provide information on the structural morphology and elemental composition of the coatings, both of which are helpful in supporting the electrochemical results obtained. In addition, thermogravimetric analysis (TGA) can provide insights into the thermal stability of our coating samples. These characterization experiments are currently ongoing and will be completed in the coming months.

One of the most crucial objectives of our study is enhancing the fluoropolymer adhesion on mild steel. Although this adhesion enhancement has been qualitatively proven by the improved corrosion protection as evidence by the electrochemical results, a comprehensive adhesion investigation still needs to be completed. To avoid redundancy, only ASTM D3359 tape adhesion test (and not pull-off adhesion test) will be performed. ASTM D3363 pencil test will also be conducted to evaluate the coating hardness. Although the two ASTM tests have become the standard in assessing coating mechanical strength, the qualitative nature of the tests can be further supplemented with quantitative findings. Hence, the surface free energy (SFE) of the top and bottom (facing the substrate) sides of the coating will be measured to provide information on the coating's hydrophobicity. We expect the top side of the coating to have a low

SFE and the bottom side to have a slightly higher SFE owing to the migration of SE components at the interface, facilitating the coating adhesion. Supplementing the data gathered from the SFE tests, X-ray photoelectron spectroscopy (XPS), in place of the initially intended X-ray diffraction, will be conducted to compare the surface chemical composition of both the top and bottom sides of the coatings. Higher heteroatom concentrations are expected for the SE/PVDF-HFP samples. By performing all these tests, we would be able to provide a more holistic understanding of the interaction at the coating-metal interface. Furthermore, computational studies using finite element analysis will be done to simulate the coatings' stress, strain, and displacement changes based on experimental swelling rate and tensile test results.

Other Relevant Information:

Potential barriers to achieving objectives. As previously discussed, the nonpolar SE exhibited poor compatibility with the fluoropolymer, leading to premature coating delamination/failure. This issue can be resolved by functionalizing the nonpolar SE components (e.g. by performing epoxidation or using epoxidized SE). Although this is outside the scope of our proposed work, this can be considered as a future work as it requires further investigation and a series of experimental trials.

Summary

This project capitalizes on the utility of soybean extracts (SE) as low-cost and sustainable additives to PVDF-HFP coatings for improving corrosion resistance and surface adhesion. To the date of submission of this report, we have successfully gathered the following findings:

1. Polar and nonpolar SEs were obtained using water and hexane solvents via Soxhlet extraction and were chemically distinguished via spectroscopic techniques.
2. Polar SEs were more compatible with PVDF-HFP compared to nonpolar SEs.
3. Polar SE/PVDF-HFP coatings with varying SE concentrations were coated on mild steel by dip coating and coating thickness above 100 μm was achieved.
4. Several isoflavones were identified in the polar SE as evidenced by MALDI mass spectrometry, the chemical structures of which have been complemented by FTIR spectroscopy.
5. Electrochemical results showed that the 0.50% SE/PVDF-HFP coating had superior corrosion protection even after 7 d of continuous immersion in 3.5 wt. % NaCl solution.

Morphological and structural properties of the coatings before and after immersion will be conducted alongside investigating the coatings' adhesion strength and hardness, supplemented by computational/simulation studies.