SUPPORTING INFORMATION

Vanadium Pentoxide Enwrapped Polydiphenylamine/Polyurethane nanocomposite: High Performance Anticorrosive Coating

Halima Khatoon[1], Sharif Ahmad[1*]

*corresponding author

Halima Khatoon

Materials Research Laboratory

Department of chemistry

Jamia Millia Islamia (A Central University)

New Delhi-110025, India

E-mail address: hkn.nasir02@gmail.com

Orcid Id: 0000-0003-1819-7537

Sharif Ahmad*

Materials Research Laboratory

Department of Chemistry,

Jamia Millia Islamia (A Central University)

New Delhi-110025, India

Tel no. +91 11 26827508 Fax: +91 11 26840229

E-mail address: sharifahmad_jmi@yahoo.co.in

Orcid Id: 0000-0001-5799-7348

*Corresponding Author

Materials

Safflower oil (SFO) (iodine value: 140-150, refractive index: 1.476) was supplied by deve herbs, New Delhi, India. Sodium chloride (99%), Sodium bicarbonate (99%), Hydrogen peroxide (50 %), Glacial acetic acid (99%), conc. Sulphuric acid (99%), Diethyl ether, Diphenyl amine monomer, Ammonium peroxydisulphate, Toluene diisocyanate (TDI), dibutyltin dilaurete (DBTDL) and xylene were purchased from Merk Germany. Vanadium Pentaoxide was obtained from Thomas Baker Chemicals pvt. Limited, Mumbai, India.

Material Characterizations

FTIR spectroscopic analysis was conducted with the help of IR-Affinity-1 Shimadzu spectrophotometer using ZnSe cell. The recording of FTIR spectra was based on 30 scans. ^{1}H and ^{13}C NMR were recorded on a 500 MHz Bruker (Avance 500, Germany), Ultrashield NMR instrument at room temperature using CDCl$_3$ containing 0.03% (v/v) TMS (tetramethylsilane) as the internal standard. Thermal stability and degradation behavior were measured by EXSTAR TG/DTA 6000 under nitrogen atmosphere in the temperature range 0−800 °C at a heating rate of 10 °C min^{-1}. The advance X-ray diffractometer (Rigaku Rodaflex 200B) was used to record the X-Ray diffraction (XRD) patterns at the 2θ in the range of 10º to 70º using Cu Kα radiation.

Adhesion of the coatings with the CS surface was measured by cross hatch method in accordance with the ASTM D3359B-02. The cutting tool was fitted with a blade containing 11 teeth spaced 1.0 mm apart. The cutting tool was used to make the cross-cut pattern at ca. 90 º angles through the surface of coatings. LA-26 tape was applied to the cut surface and rubbed with hands to ensure good contact with the film and then removed after 90 s. Impact resistance, scratch

hardness and bend test were determined by ASTM D2794-93, ASTM D1474-98 and ASTM-D522-93a respectively. The coating thickness was measured by Elcometer (ASTM B 499 Model 345 Elcometer instrument, Menchester, UK).

Water contact angle (CA) values were obtained using a Shape Analysis System (model DSA10MK2 Kruss GmbH, Germany) at ambient temperature with 5 μL of deionized water (Millipore, >1.82 MΩcm) on the surface of coatings. Percent water uptake of all the coated specimens was calculated, using the initial dry weight and the weight after immersion in water followed by drying under vacuum and blotted dry. The coated specimens were weighed after every 24h.

In order to evaluate the effect of oxidising acid on the surface of coatings, the CS, SFPU and V_2O_5-PDPA/SFPU coatings were immersed in an acidic medium (1 M H_2SO_4) for a period of 24h. A highly precise AFM (AFM, WITec, alpha 300 RA, Japan) technique was used to scan the corroded and uncorroded surfaces in a contact mode. The scan was performed on silicon cantilever with a radius of curvature ~8nm, spring constant 42N/m and a resonance frequency 76 KHz. WITec Project Data analysis software was used for data acquisition and image processing.

The salt spray test, ASTM B117-03, for coated substrates were carried out for a period of 10 days in a salt mist chamber under 5% NaCl solution at 90% humidity at 35 °C. The effects on the coated substrates were observed using SEM (Zeiss, EVO 18) under thin gold film at Electron Microscopy Centre.

The electrochemical corrosion measurement was conducted in 5 wt.% NaCl solution by the electrochemical workstation (PGSTAT302, Autolab) using EG&G flat glass cell (400 ml

capacity cell) containing three electrode cell system i.e. Pt wire as a counter electrode and silver electrodes as a reference electrode, while the test specimens as working electrode. The test specimen, with 1.0 cm² surface area was exposed to 5% NaCl solution. Before the potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) measurements, the working electrode (in order to stabilize it) was allowed to stand for 30 min, then the open circuit potential (OCP), for 10 hrs, was measured as a function of time. After the stabilization of OCP, the impedance measurements were performed over a frequency range of 100 kHz-10m Hz, with a signal amplitude perturbation of 10 mV. The potentiodynamic polarization tests were carried out in the potential range ±100 mV (with respect to OCP) at 0.01 mV/s scan rate. Nova 1.10 software was used for data fitting and calculation of results. All the data were run in triplicate for the reproducibility of data.

Surface characterization of the coated and uncoated CS samples after 30 days of exposure to 5wt% NaCl was examined using Lietz Optical Microscope (Model Metallux-3) at 100X. For this, the exposed area of the coated and uncoated CS samples was degreased in acetone and thoroughly washed with distilled water followed by air dry at room temperature.
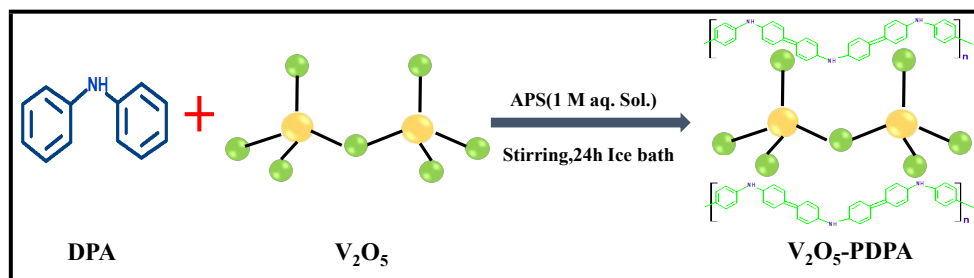
Scheme S1a. Schematic representation for the formation of V$_2$O$_5$-PDPA
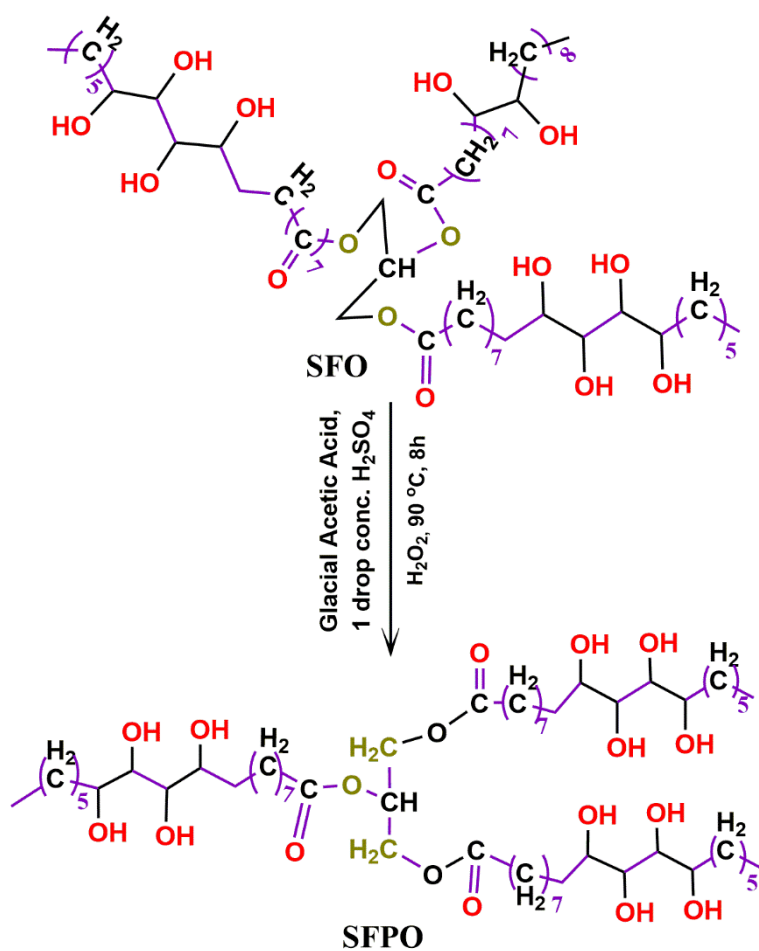
Scheme S1b. Schematic representation for the synthesis of SFPO
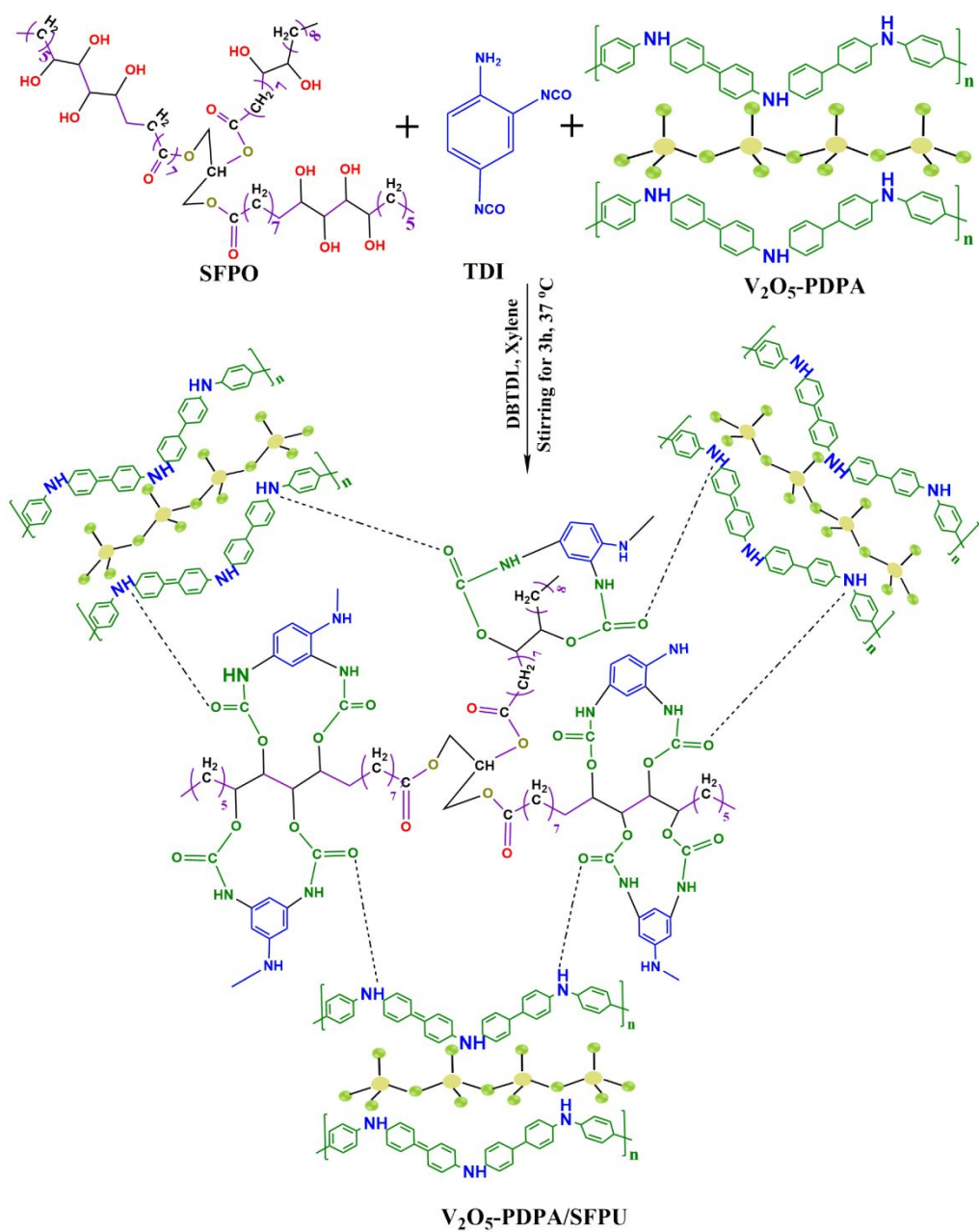
Scheme S1c. Schematic representation for the synthesis of V$_2$O$_5$-PDPA/SFPU
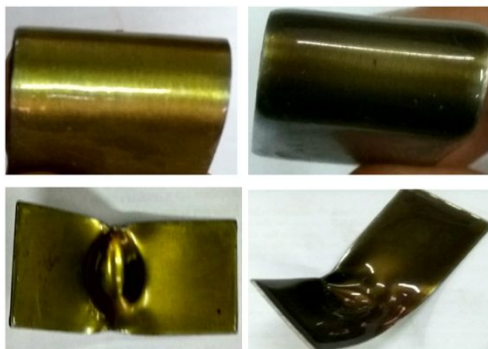
Figure S1. Digital images of SFPU and V_2O_5-PDPA/SFPU nanocomposite after (a) Bend and (b) Impact test

Table S1 Physicochemical properties of SFPU and V_2O_5-PDPA/SFPU nanocomposite coatings

Resin Code	Inherent Viscosity	Referactive Index	Specific Gravity
SFPU	0.956	1.453	1.38
0.5V_2O_5-PDPA/SFPU	1.009	1.485	1.42
1V_2O_5-PDPA/SFPU	1.013	1.489	1.43
2V_2O_5-PDPA/SFPU	1.112	1.493	1.46

Table S2 Physicomechanical properties of SFPU and V_2O_5-PDPA/SFPU nanocomposite coatings

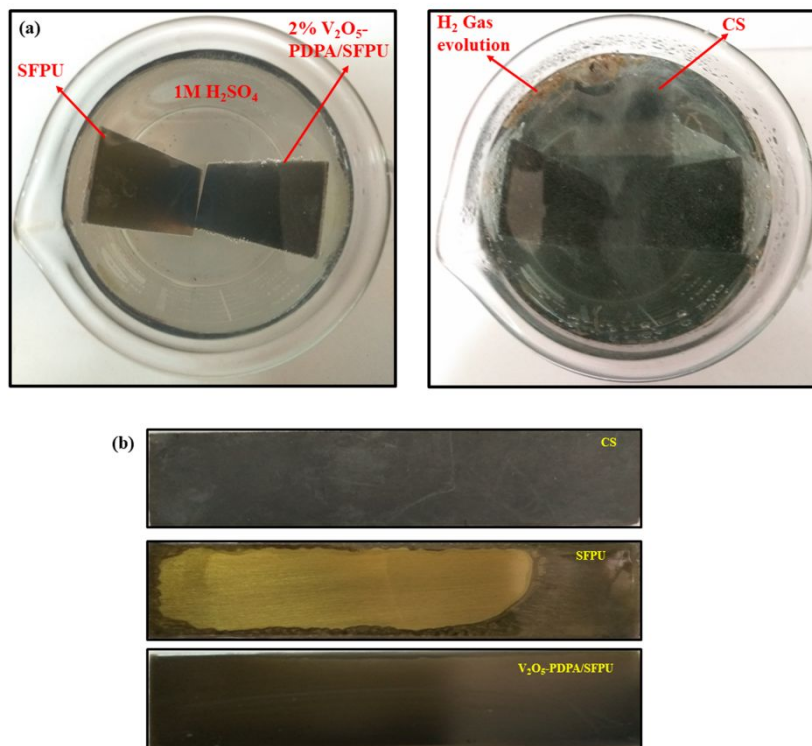| Resin code	Impact Resistance (lb/inch^2)	Scratch Resistance (Kg)	Bend Test (1/8")	Thickness (μm)
SFPU	250	5.17	Pass	89
0.5V$_2$O$_5$-PDPA/SFPU	250	6.17	Pass	92
1V$_2$O$_5$-PDPA/SFPU	250	7.36	Pass	94
2V$_2$O$_5$-PDPA/SFPU	250	8.19	Pass	94

Figure S2. Digital images of the (a) CS, SFPU, V_2O_5-PDPA/SFPU at the time of immersion in 1M H_2SO_4 (b) after the immersion test

Description of equivalent circuit and method of EIS and their calculation

EIS, a non-destructive technique, was used to explore the electrochemical reaction mechanism occurring at the metal-electrolyte and metal-coating interface. It was used to collect the information about the resistance capacity of coatings, charge transfer resistance (corrosion reaction resistance) and electrical double layer capacity at the coating-metal interface.[1] EIS measurements were performed to analyze the electrochemical corrosion behaviour of CS, SFPU and nanocomposite coatings using an electrochemical equivalent circuit based on software NOVA 1.10, represented in Figure S3 a, b and c, respectively. Figure S3a includes solution resistance, R_s (3.23 Ω), pore resistance, R_{pore}, (5631 Ωcm^2) and electrical double-layer

capacitance, CPE_1 (3.785×10^{-5} F) occurred at the metal (CS)/solution (NaCl) interface. Additional elements such as R_{ct} (charge transfer resistance) and CPE2 (constant phase element) for nanocomposite and Warburg resistance (Z_w) for SFPU were obtained. To compensate for the deviation from ideal capacitive behaviour constant phase element (CPE2) is used, and its related exponent (n) symbolizes the degree of deviation from an ideal behaviour. For instance, ideal capacitance has n value equal to 1, whereas, ideal resistor it is absolute 0.[2,3]

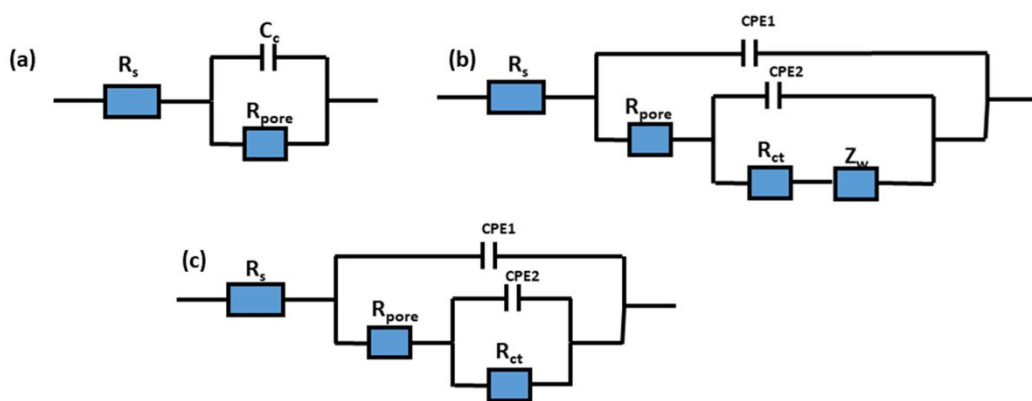

Figure S3. Electrochemical equivalent Circuit for (a) CS (b) SFPU and (c) V_2O_5-PDPA/SFPU
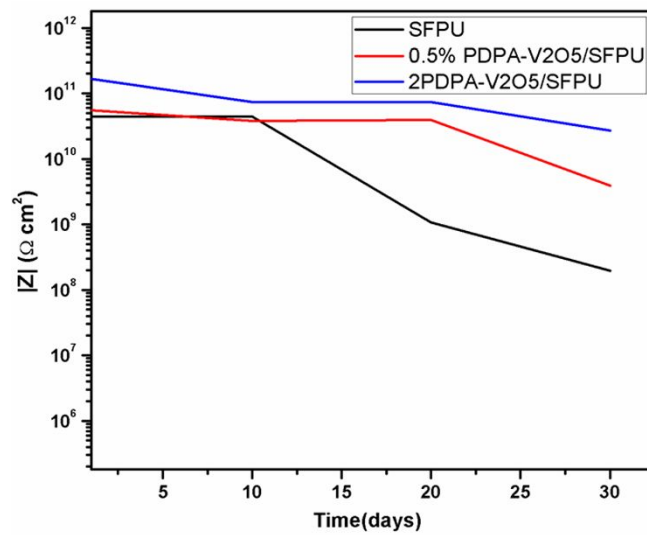
Figure S4. Impedance at low frequency ($|Z|_{0.01}$Hz) for SFPU and V_2O_5-PDPA/SFPU

nanocomposite coatings for 30 days of immersion

Table S3. Comparison for the corrosion resistance properties of SFPU and V_2O_5-PDPA/SFPU nanocomposite coatings with other such reported systems

S. No.	Coating system	Medium/Immersion time	I_{corr} (Acm^{-2})	Polarization resistance (R_p, Ω)	Corrosion rate (mpy)	PE (%)	Ref
1.	SFPU	5 wt % NaCl /30 days	1.41×10^{-9}	1.00×10^8	1.64×10^{-5}	99.991	Present work
2.	PDPA-V_2O_5/SFPU	5wt % NaCl /30 days	7.45×10^{-11}	1.58×10^8	8.66×10^{-7}	99.999	-do-
3.	ETFE-PANI/fCNTs-6	3.5 wt % NaCl/90 days	3.5×10^{-10}	-------	3.93×10^{-5}	99.997	[4]
4.	Epoxy/PSS-PANI/rGO	5 wt% NaCl/7 days	6.52×10^{-8}	4.78	1.52×10^{-3}	-------------	[5]
5.	PANI@BN/PVA	3.5 wt% NaCl/50 days	0.2×10^{-6}	170×10^3	0.007	98.25	[6]
7.	PANI/RGO/WPU	3.5 wt% NaCl/---	3.69×10^{-4}	3057.52	4.30×10^{-6}	249.61	[7]

8.	GP-TiO2/Epoxy	3.5 wt% NaCl/----	105×10^{-9}	-------	55×10^{-3}	99.94	8
9.	PANI/Zeolite	3.5 wt% NaCl/----	0.34×10^{-6}	31.28×10^{3}	0.004	99.2	9
10.	PBMA-ZnO-PANI	3.5 wt% NaCl/----	30×10^{-6}	-----	0.00076	83.03	10
11.	PANI/Ce	3.5 wt% NaCl	5.9×10^{-9}	5.57×10^{7}	--------	99.9	11
12.	1.0POT/COPU	3.5 wt % HCl/ 20 days	7.19×10^{-8}	4.6×10^{7}	$3.7x10^{-3}$	99.76	12
13.	rGO/PVDF/PU	3.5wt% NaCl/1h	0.1×10^{-6}	-------	--------	99	13
14.	ZnO-PANI-PVAc	3.5 wt. % NaCl/15 day	7.37×10^{-9}	--------	-----------	-------	14

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