

Lignin nanoparticles: Synthesis, characterization and their corrosion protection performance

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Characterization

Different analytical techniques were used to characterize the SERSL and LNP. Fourier transform infrared (FTIR), spectra were recorded on a Thermo Nicolet Nexus 6700 FTIR spectrometer using a KBr pellet technique 32 scans per samples were acquired at a resolution of 4 cm⁻¹ in the range of 4000 to 400 cm⁻¹. The proton and carbon nuclear magnetic resonance (¹H NMR, and ¹³C NMR) spectra were recorded on a Bruker 400 MHz AVANCE III NMR spectrometer. For ¹H NMR, 20 mg samples were dissolved in 1 mL of D₂O and for ¹³C NMR, 40 mg of samples were dissolved in D₂O. All chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and elemental analysis were carried out using, JEM-1011 and FEI Quanta FEG 250, respectively. Thermal stabilities of lignin were studied by TGA using PerkinElmer Pyris Diamond instrument under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 25-800 °C. Tg of SERSL and LNP were determined by differential scanning calorimetry (DSC) using Polyma, Netisch, the heating and cooling of the samples were performed at the rates of 10 °C min⁻¹ under nitrogen

atmosphere in the temperature range of 30 °C to 200 °C for first run and 0 °C to 250 °C for second run. The contact angles of composites were tested by a contact angle meter (OCA20, Data physics, Germany) and the values were averages of taking at three readings at different place of coated sample surfaces. Electrochemical and potentiodynamic polarization test were performed according to ASTM G 59-97 methods as reported earlier.¹ The corrosion resistance of coated and uncoated samples was investigated in 3.5 wt. % NaCl solution, at room temperature using CHI660D electrochemical workstation. A conventional three-electrode electrochemical cell i.e. test samples as working electrode, Pt gauge as auxiliary electrode and Ag/AgCl as a reference electrode were used for EIS and potentiodynamic polarization studies. The system was supported by electrochemical Zview software which was used to study the electrochemical corrosion behavior, of coated and uncoated substrate. The impedance and Tafel parameters were extracted by Tafel extrapolation method. EIS analysis were carried out in the frequency range of $10^5 \sim 10^{-1}$ Hz and the sinusoidal voltage signal amplitude was 20 mV. Water absorption (θ) was calculated by coating capacitance obtained from EIS and calculated by the Brasher-Kingsbury equation.² Salt spray test (SST) was carried out in a Q-FOG CCT-1100 salt spray cabinet according to the international standard (ASTM B117-09).

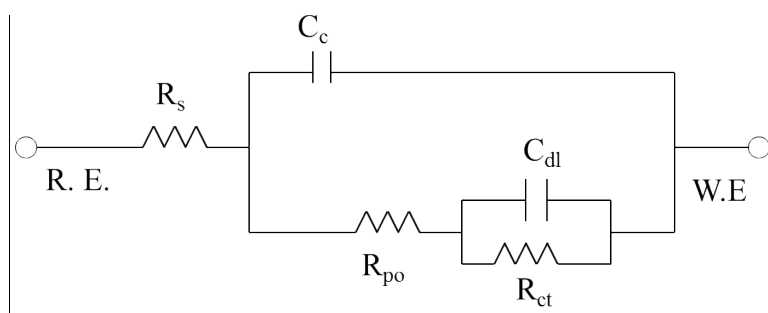
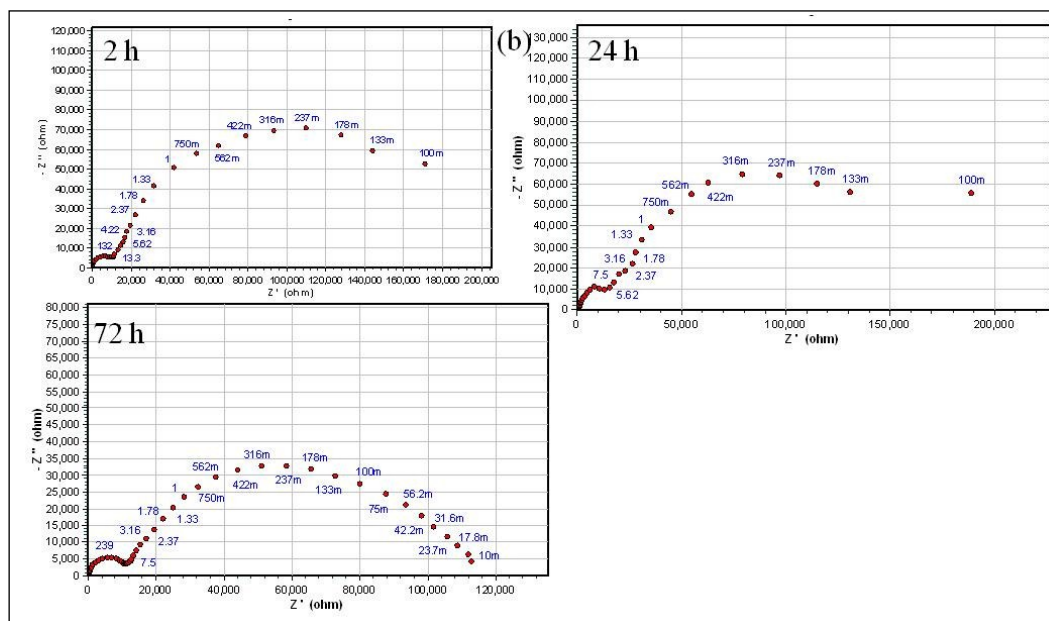
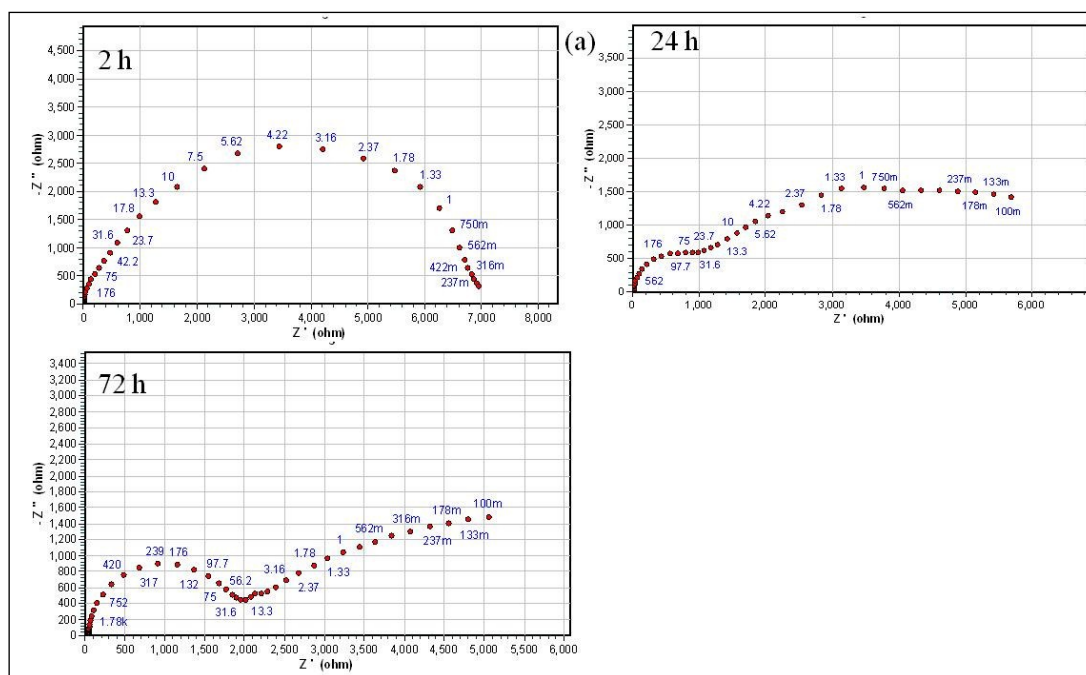


Figure S1 Equivalent circuit used in EIS



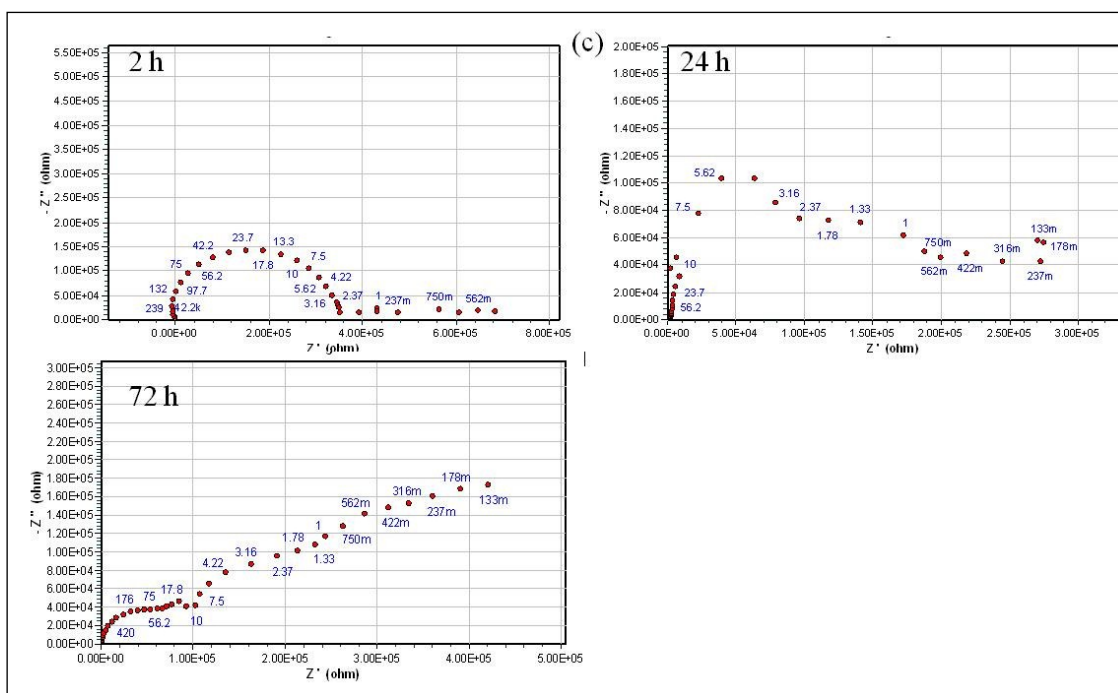


Figure S2 c Nyquist plot of the E-LNP-1.0 coatings

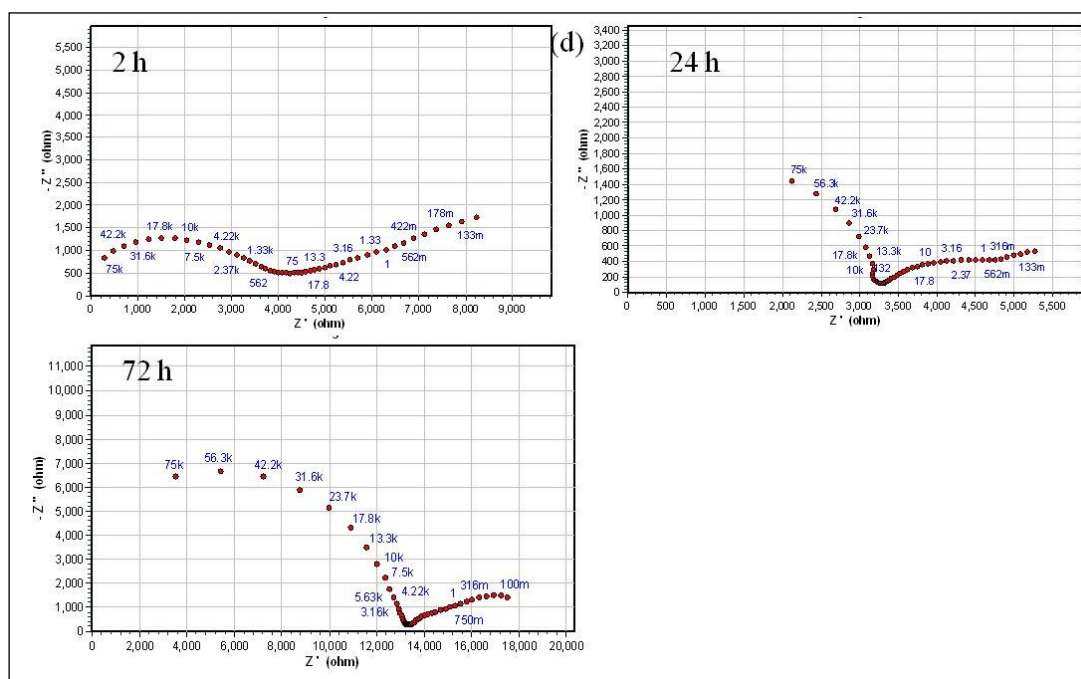


Figure S2 d Nyquist plot of the E-LNP-1.5 coatings

Table S1 Physico-mechanical studies

Sample	Impact test	Pencil Scratch Hardness Test	Cross hatch adhesion test
Epoxy	pass	4h	pass
E-LNP-0.5	pass	4h	pass
E-LNP-1.0	pass	6h	pass
E-LNP-1.5	pass	6h	pass

Table S2. EIS parameters after equivalent circuit fitting

Sample	Time(h)	R_s (ohm)	R_p (ohm)	C_c (F)	R_{ct} (ohm)	C_{dl} (F)
Epoxy	2	1.000E-02	6.314E+001	7.827E-009	1.420E+01	2.155E-07
Epoxy	12	3.292E+02	1.378E+04	7.392E-08	2.452E+05	2.161E-06
Epoxy	24	9.105E+02	2.242E+04	3.847E-007	1.375E+05	3.210E-06
Epoxy	48	3.456E+02	1.196E+04	7.662E-08	6.972E+04	3.752E-06
Epoxy	72	3.626E+02	1.264E+04	5.542E-08	8.342E+05	4.700E-06
E-LNP-0.5	2	1.352E+01	1.640E+05	2.396E-06	5.062E+03	5.180E-06
E-LNP-0.5	12	2.587E+01	1.686E+03	9.825E-07	5.618E+03	1.732E-05
E-LNP-0.5	24	2.739E+01	1.455E+03	1.020E-06	4.719E+04	2.940E-05
E-LNP-0.5	48	2.583E+01	1.168E+03	1.104E-06	3.631E+03	9.693E-05
E-LNP-0.5	72	5.404E+01	2.046E+03	3.698E-07	2.806E+01	7.189E-05
E-LNP-1.0	2	1.000E-02	7.898E+02	4.881E-09	4.488E+05	2.135E-08
E-LNP-1.0	12	2.116E+02	1.604E+05	6.067E-09	6.933E+05	1.255E-08
E-LNP-1.0	24	6.605E+01	1.882E+03	5.541E-09	2.329E+05	2.507E-07
E-LNP-1.0	48	8.222E+02	8.775E+04	1.045E-08	3.031E+05	3.710E-07
E-LNP-1.0	72	1.235E+02	1.944E+03	4.878E-09	2.084E+05	5.140E-07
E-LNP-1.5	2	2.606E+02	3.723E+03	3.143E-09	3.134E+03	1.222E-05
E-LNP-1.5	12	1.857E+02	4.231E+05	3.223E-07	4.028E+03	1.312E-06
E-LNP-1.5	24	7.866E+02	2.651E+03	8.390E-010	1.932E+03	3.538E-05
E-LNP-1.5	48	5.258E+03	7.103E+03	3.847E-010	1.885E+03	3.883E-05
E-LNP-1.5	72	1.000E-02	1.350E+04	4.878E-09	4.618E+03	6.036E-05

1. ur Rahman, O.; Ahmad, S., Physico-mechanical and electrochemical corrosion behavior of soy alkyd/Fe₃O₄ nanocomposite coatings. *RSC Advances* **2014**, 4 (29), 14936-14947.
2. Brasher, D.; Kingsbury, A., Electrical measurements in the study of immersed paint coatings on metal. I. Comparison between capacitance and gravimetric methods of estimating water-uptake. *Journal of Chemical Technology and Biotechnology* **1954**, 4 (2), 62-72.