1 **Biorenewable Vegetable Oil Derived Nonisocyanate Polyurethanes and Nanocomposites;**

2 **Formulation, Characterisation, Biodegradation, Anticorrosion and Antifouling Coatings**

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Materials

51   Glycerol 1,2-carbonate (GC), 1,12-diaminododecane (DDA) were procured from Carbanio

52   chemicals, Hyderabad, India. Succinic anhydride (SA), triethylamine (Et$_3$N), 4-

53   dimethylaminopyridine (DMAP), N, N′-dicyclohexylcarbodiimide (DCC), ferric trichloride

54   hexahydrate (FeCl$_3$.6H$_2$O), aqueous ammonia (25% solution), sodium acetate (CH$_3$COONa),

55   ethylene glycol, tetraethyl orthosilicate (TEOS), (3-aminopropyl) trimethoxysilane (APTMS),

56   acetonitrile (CH$_3$CN), methanol, dichloromethane (DCM), chloroform, 1,4-dioxane and toluene

57   were supplied by Siscon Research Laboraties Pvt. Ltd., Chennai, India. All the organic solvents

58   were dried and distilled prior to use. Castor oil (CO, ~ mol. wt. 927 g/mol.) was purchased from

59   the domestic commercial store and heated in oil bath at 100°C under reduced pressure to eliminate

60   the trace quantity of moisture. The mild carbon steel for coating studies were purchased from

61   hardware suppliers.

Methods

63   ^{1}H and ^{13}C NMR data was acquired from Bruker Avance III NMR instrument operating

64   at 500 MHz by dissolving in deuterated solvents, CDCl$_3$ or DMSO-d^6 with the internal standard,

65   tetramethylsilane. Mestrenova software was used to process the NMR data as well as to find the

66   chemical shift values. FT IR data was collected from IR Tracr 100 Shimadzu instrument by ATR-

67   FTIR mode. The morphology of film sample and respective elemental mapping was recorded using

68   Thermoscientific Apreo S Scanning electron microscopy (SEM). Thermogravimetric analysis

69   (TGA) was performed in the instrument of Netzsch-STA 2500 Regulus, while the sample of 5mg

70   placed on platinum pan and heated from ambient temperature to 600°C at the heating rate of

71 10°C/min. Differential Scanning calorimetry (DSC) analyses were carried out by the instrument

72 Netzsch-DSC 214 Polyma, between ambient temperature to 500°C at the heating rate of 10°C/min.

73 powder XRD analysis was conducted in Bruker Xray Diffractometer USA D8 Advance, Davinci

74 with aid of Copper-ray tube (CuKa), wavelength (k=1.5148A°) by the scanning range of 2θ

75 diffraction from 10 to 80°.Water contact angle for the hydrophilicity samples was measured at

76 ambient condition by use of 2μL volume of Milli Q water through sessile drop method from DMs-

77 401, Japan. The magnetism data of pristine and functionalized nanomaterials was measured by

78 Agilent technologies LakeShore Vibrating Sample Magnetometer (VSM) of model number 7407

79 at ambient temperature. Optical microscope images were collected from GOKO MIAMB, India.

80 **Statistical analysis**

81 The statistical information was analysed utilizing Origin pro 8.5 software. These results are

82 expressed in the form of means ± standard deviation. The error bars tend to be represented by

83 means for standard deviation for n =3 and the statistical significance (minor error) $p \leq (0.05)$.[11]

84 **Experimental**

85 **Synthesis of acid groups functionalised castor oil [CO-(COOH)]**

86   This synthesis was performed upon modification of previously reported procedure.[5] In a

87 clean and dry Schlenk tube, castor oil (5 g, 0.0054 mol) was weighed after the elimination of

88 moisture and dissolved in 1,4-dioxane (20 mL) and allowed to stirred for 5 min. at ambient

89 condition. To the above solution, triethylamine (1.619 g, 0.016 mol) was added and stirred for 2 h

90 at ambient temperature under N_2 atm. In another RB flask (100 mL), succinic anhydride (1.601 g,

91 0.016 mol) and 4-dimethylaminopyridine (1.95 g, 0.016 mol) were taken and stirred for 2 h after

92 added 1,4-dioxane (20 mL) under N_2 atm. The solution of succinic anhydride and 4-

93 dimethylaminopyridine in 1,4-dioxane was added over 30 min. into the Schlenk tube containing

94 the reaction mixture and continued to stir for 24 h under N_2 atm.

95 The reaction mixture was filtered and the filtrate was washed three times using dil. HCl (2N,

96 15 mL) to eliminate the excess 4-dimethylaminopyridine and triethylamine. The reaction product

97 was concentrated under vacuum and recrystallized using methanol to obtain pale yellow colour

98 semisolid. Yield: 3.1 g (48 %)

99 ^{1}H NMR [CDCl$_3$, 500 MHz, δ (ppm)]: 0.86 (-CH$_3$),1.29 (-CH$_2$), 1.5-1.6 (-CH=CH-CH$_2$-CH (OH)-

100 CH$_2$), 2.2 (CH=CH-CH$_2$-CH (OH)-CH$_2$), 2.61(CH-(OCO)-CH$_2$-CH$_2$-COOH), 2.7 (CH-(OCO)-

101 CH$_2$-COOH), 4.13-4.2 (CH-(OCO)-CH$_2$-CH$_2$ -COOH), 4.87 (-OH),5.3-5.4 (-CH=CH-).0.86(-

102 CH$_3$, H$_{12}$), 1.29(-CH$_2$, H$_9$, H$_{13}$), 1.51-1.6(-CH$_2$, H$_8$, H$_{13}$), 2.29 (-CH$_2$), 2.61(-CH$_2$), 3.6 (-CH, H$_2$),

103 4.1-4.2 (-CH$_2$, H$_5$), 4.8 (-CH, H$_6$), 5.2-5.5 (CH-O, CH=CH, H$_{12}$, H$_3$, H$_4$)

104 ^{13}C NMR [CDCl$_3$, 100.6 MHz, δ(ppm)] CO-COOH 14 (C$_1$), 20-35 (C$_{13,7,8}$, b, c),26-35 (C$_{3,7,9,10,11}$),

105 61 (C$_5$), 67 (C$_1$), 75 (C$_2$),124 (C$_3$),133 (C$_4$),75 (C $_6$), 124 (C$_3$), 133(C$_4$). [6]

106 **Synthesis of castor oil cyclic carbonate (CO-CC)**

107 This synthesis was performed upon modification of previously reported procedure.[5] In a

108 clean and dry RB flask (100 mL), acid groups functionalised castor oil [CO-(COOH), 3g, 0.0025

109 mol] and N,N′-dicyclohexylcarbodiimide (DCC, 1.522g, 0.00738 mol) were charged and

110 dissolved in DCM (20 mL) and the reaction mixture was stirred at ambient temperature for 1h

111 under N_2 atm. In another RB flask, glycerol 1,2-carbonate (GC, 0.871g, 0.00738 mol) and 4-

112 dimethylaminopyridine (DMAP, 0.901g, 0.00738 mol) were added into DCM (10 mL) and stirred

113 at ambient temperature under nitrogen atmosphere for 1h. The solution of glycerol 1,2-carbonate

114 and 4-diemthylaminopyridine in DCM was added slowly into the RB flask containing CO-

115 (COOH) and DCC in DCM. The reaction mixture was continued to stir at ambient temperature for

116 24h under N_2 atm. After the completion of the reaction, the reaction mixture was filtered and the

117 filtrate concentrated in rotavapor and the viscous product was recrystallized using methanol and

118 kept in the refrigerator to obtain yellow semi solid product. Yield: 2.4 g (63%)

119 ^{1}H NMR (CDCl$_3$, 500 MHz): 0.86 (-CH$_3$, H$_{12}$), 1.30(-CH$_2$, H$_9$, H$_{13}$), 1.53-1.60 (-CH$_2$, H$_8$, H$_{13}$),

120 2.31(-CH$_2$), 2.61 (-CH$_2$), 3.68 (-CH, H$_2$), 4.1-4.2 (-CH$_2$, H$_5$, e), 4.4-4.5 (-CH$_2$, d), 4.7(-CH, f), 4.8

121 (-CH, H$_6$), 5.2-5.5 (CH-O, CH=CH, H$_{12}$, H$_3$, H$_4$).

122 ^{13}C NMR (δ, 100.6 MHz, ppm) of CO-CC as represented in Fig. S3 14 (C$_1$), 20-35 (C$_{5, 7, 8, b, c}$),

123 51 (C$_e$), 55(C$_d$) ,69(C$_f$), 75 (C$_6$), 124(C$_3$), 133 (C$_4$) ,154 (C$_h$),173-174 (C $_{a, g}$) [7,8]

124 **Formulation of nonisocyanate polyurethanes (NIPU)**

125   The synthesis of NIPU was executed upon loading all components in a high pressure tube.

126 Herein, the ratio (1:1.5) was chosen among the castor oil cyclic carbonate (CO-CC) and 1,12-

127 diaminododecane (DDA). Castor oil cyclic carbonate (CO-CC, 3g, 0.001955 mol) and acetonitrile

128 (3 mL) were charged in high pressure tube and stirred at ambient condition for 15 min.

129 Subsequently, 1,12-diaminododecane (DDA, 0.587g, 0.00293 mol) was added to the pressure tube

130 and continued to stir for 30 min prior to the addition of dry triethylamine (TEA, 0.36 mL) as a

131 catalyst. The pressure tube was closed firmly and stirred for 8 h while heated in hot oil bath at

132 110°C. The yellow colour was intensified at the end of reaction and the resulting viscous product

133 was poured on surface of glass plates and allowed for curing at ambient temperature for 3 days.

134 Further curing was carried out in vacuum oven at 70°C for 32 h to recover as NIPU film.

135 **Formulation of nonisocyanate polyurethanes nanocomposites (NIPU-F)**

136   The same procedure for NIPU was adopted for the synthesis of NIPU-F for the covalent

137 incorporation of amine functionalized silica coated on iron oxide nanoparticles (0.5wt.%). Castor

138 oil cyclic carbonate (CO-CC, 3g, 0.001955 mol) and acetonitrile (3 mL) were charged in high

139 pressure tube and stirred at ambient condition for 15 min. Subsequently, 1,12-diaminododecane

140 (DDA, 0.587g, 0.00293 mol) and amine functionalised silica coated iron oxide nanoparticles

141 ($Fe_3O_4@SiO_2$-NH_2, 18 mg, 0.5 wt.%) were added to the pressure tube and continued to stir for 30

142 min prior to the addition of dry triethylamine (TEA, 0.36 mL) as a catalyst. The pressure tube was

143 closed firmly and stirred for 8 h while heated in hot oil bath at 110°C. The mild brown colour was

144 intensified at the end of reaction and the resulting viscous product was poured on the surface of

145 glass plates and allowed for curing at ambient temperature for 3 days. Further curing was carried

146 out in a vacuum oven at 70°C for 32 h to recover as NIPU-F film.

147 Synthesis of magnetic iron oxide (Fe_3O_4) nanoparticles

148   Fe_3O_4 nanoparticles was synthesised via hydrothermal method by modification of

149 previously reported procedure.[9] In a clean RB flask, $FeCl_3.6H_2O$ (1.352 g, 0.005 mol) was

150 dissolved in ethylene glycol (40 mL) and allowed to stir at ambient condition for 10 min. To the

151 above solution, sodium acetate (CH_3COONa, 0.596 g, 0.00438 mol) was added and continued to

152 stir at ambient condition for 1 h prior to transferring the reaction mixture into Teflon coated

153 autoclave (100 mL) and placed inside a muffle furnace maintained at 200°C for the duration of 10

154 h. After this hydrothermal treatment, the autoclave was allowed to attain the ambient temperature

155 and the resulting product was further washed repeatedly with distilled water and ethanol. Finally,

156 the magnetic spherical nanoparticles dried under high vacuum at ambient temperature.

157 Synthesis of silica coated magnetic iron oxide nanoparticles ($Fe_3O_4@SiO_2$)

158   To execute the silica coating on the spherical surface of iron oxide nanoparticles, adopted

159 the Stobber's method by modification of previous report.[10] The above synthesised iron oxide

160 nanoparticles (0.4 g) was added into a mixture (10:1) of ethanol (40mL) and deionized water (4

161 mL) and the uniform dispersion was achieved by subjecting to ultrasonication for 20 min.

162 Subsequently, tetraethyl orthosilicate (TEOS, 0.8 mL) was added and aqueous ammonia (1.2 mL,

163 25% solution) added slowly under nitrogen atmosphere. The above reaction mixture was refluxed

164 at 60°C and stirred vigorously under inert condition for the period of 12 h. After cooling down to

165 ambient temperature, the brown precipitate was separated with the aid of a magnet and washed

166 with ethanol and the nanoparticles dried under high vacuum at ambient temperature.

167 **Synthesis of amine functionalized silica coated iron oxide nanoparticles. ($Fe_3O_4@SiO_2$-NH_2)**

168　　　　To functionalise the amine groups on the surface of silica coated magnetic iron oxide

169 nanoparticles ($Fe_3O_4@SiO_2$), the reaction performed by modification of previously reported

170 procedure.[10] Silica coated magnetic iron oxide nanoparticles ($Fe_3O_4@SiO_2$, 0.8 g) was dispersed

171 in toluene (20 mL) under nitrogen atmosphere. To the above suspension, 3-aminopropyl

172 trimethoxysilane (APTMS, 0.96 mL) was added and the suspension was subjected to

173 ultrasonication. Further, the resulting mixture was refluxed in a hot oil bath at 120°C for 10 h.

174 After the reaction, the product, $Fe_3O_4@SiO_2$-NH_2 was isolated with the aid of magnet and washed

175 thrice using anhydrous ethanol, the product was dried high under vacuum at ambient condition.

176 **Coatings**

177　　　　In the context of coating application, mild carbon steel serves as a foundational panel or

178 substrate for evaluating the efficacy of corrosion resistance, antibacterial properties, whereas glass

179 slide was used for assessing antifouling studies. To execute the steel panel for coating, a series of

180 pre-preparatory steps were adopted in these studies. These steps include the use of abrasive

181 materials for cleaning the surface followed by thorough rinsing by distilled water followed by

182 acetone. In each coating, the thickness of NIPU as well as NIPU-F coatings was approximately

183 100 μm.

184 **Method of biodegradation studies**

185   The degradation study was conducted in a phosphate buffer saline solution of pH value 7.4.

186 The dry form of film samples occurred to cut into dimensions (~10 × 10 mm) with initial weight

187 of 100 mg. These samples were soaked in glass vials containing PBS (15ml) and then incubated

188 at 37°C. In a periodic interval of every 5 days the samples were removed from the buffer solution,

189 rinsed using distilled water and subsequently dried in a vacuum oven before measuring its reduced

190 weight to determine the percentage of weight loss. The degradation medium, PBS was refreshed

191 at every 5 days and the weight loss percentage, indicative of hydrolytic degradation was

192 determined by the following equation.[1]

193 Remaining mass % = $W_2/W_1 *100$

194 where, W_1 and W_2 denote the initial mass and final mass of sample before and after degradation

195 study.

196 **Studies on corrosion resistance**

197   Electrochemical impedance spectroscopy (EIS) was employed to assess the corrosion

198 resistance of the coated panels. These evaluations were conducted using a biologic VST 300

199 instrument equipped with EC lab software. All electrochemical measurements were performed at

200 room temperature using a 3.5% sodium chloride (NaCl) solution. The experimental setup consisted

201 of a three-electrode cell configuration, comprising a calomel electrode, a platinum electrode and a

202 coated panel functioning as the reference electrode, counter electrode and working electrode

203 respectively. The exposed surface area of the coated panels in contact with the NaCl solution was

204 consistent at 1cm^2 for all test cases.[2]

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207 **Evaluation of antibacterial properties**

208 Escherichia coli (E. coli) was chosen as the model bacterium to assess the antibacterial properties

209 of the coatings using the shaking flask technique. The experimental procedure for this method was

210 as follows: coating samples were immersed in a sterile 0.9wt% saline solution (40ml). the mixture

211 was then agitated at a temperature of 37 for a duration of 4h. Afterward, a 0.1ml portion was

212 extracted from the test tube and subjected to a ten-fold dilution. The resulting diluted solution was

213 subsequently plated onto nutrient -agar plates in triplicate and incubated at 37 °C for 72 hours. The

214 count of bacterial colonies on each plate was documented.

215 To calculate the rate of bacterial elimination (R) concerning viable bacteria, the following formula

216 was employed=(Nc-Ns)/Nc,

217 Where, Nc represents the number of microbial colonies observed in the control tube (absent any

218 coating), and Ns corresponds to the number of microbial colonies observes in the tube containing

219 the coatings.[3]

220 **Evaluation of antifouling properties**

221 Spirulina platensis (S. platensis) was selected as the marine algae for the studies of anti-fouling

222 characteristics of coatings.[4] The culture was placed in a light incubator at a temperature of 30°C

223 for a duration of 7 days. To prepare for the algae biofouling test,20ml suspension of S. platensis

224 in the log-phase was diluted tenfold using the same medium and incubated. After 7 days at 30°C,

225 each sample was gently rinsed with deionized water to remove non-adherent cells from the surface.

226 The attachment of cells and growth of the biofilm were evaluated using a fluorescence microscope

227 (Neubauer's improved chamber type). The algae biofouling was quantified as the coverage of the

228 biofilm by cells. The number of algae cells/ml was calculated using the formula given below,

229 Algae cells per smallest square = X/Y*specific factor

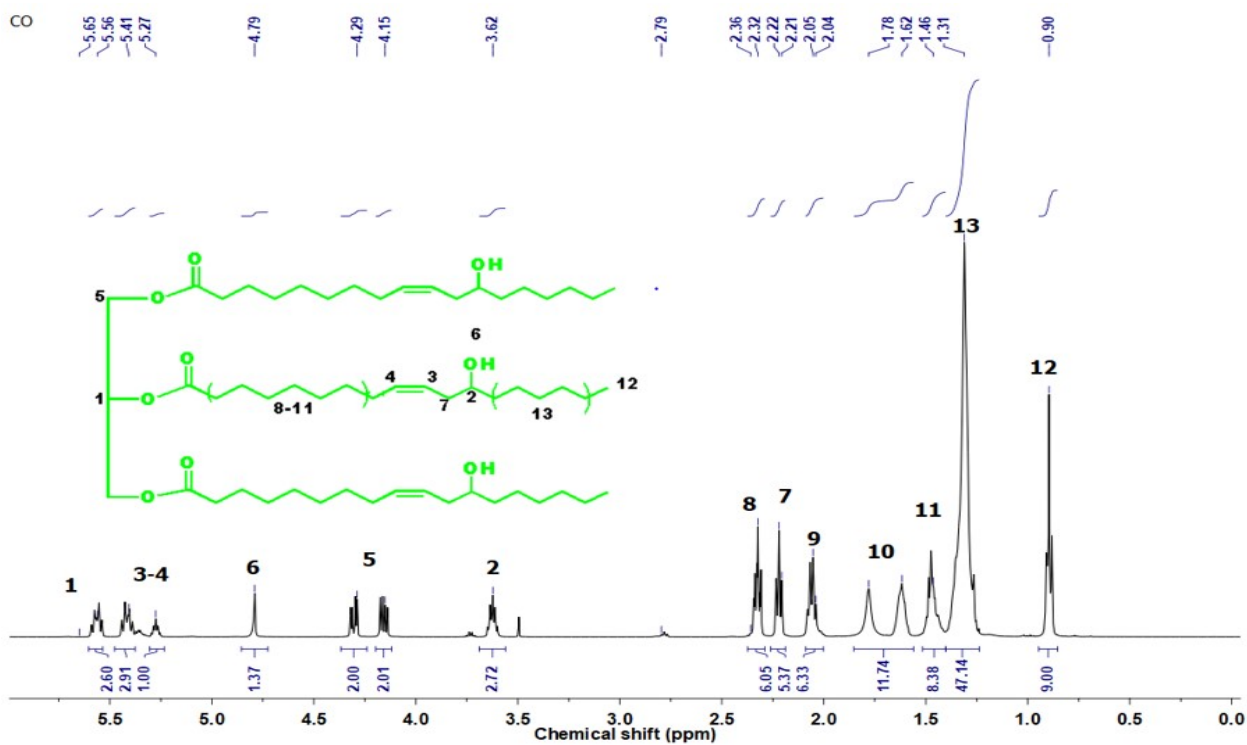230 Where, X =Total sum of counted cells Y =Total smallest squares Specific factor =4
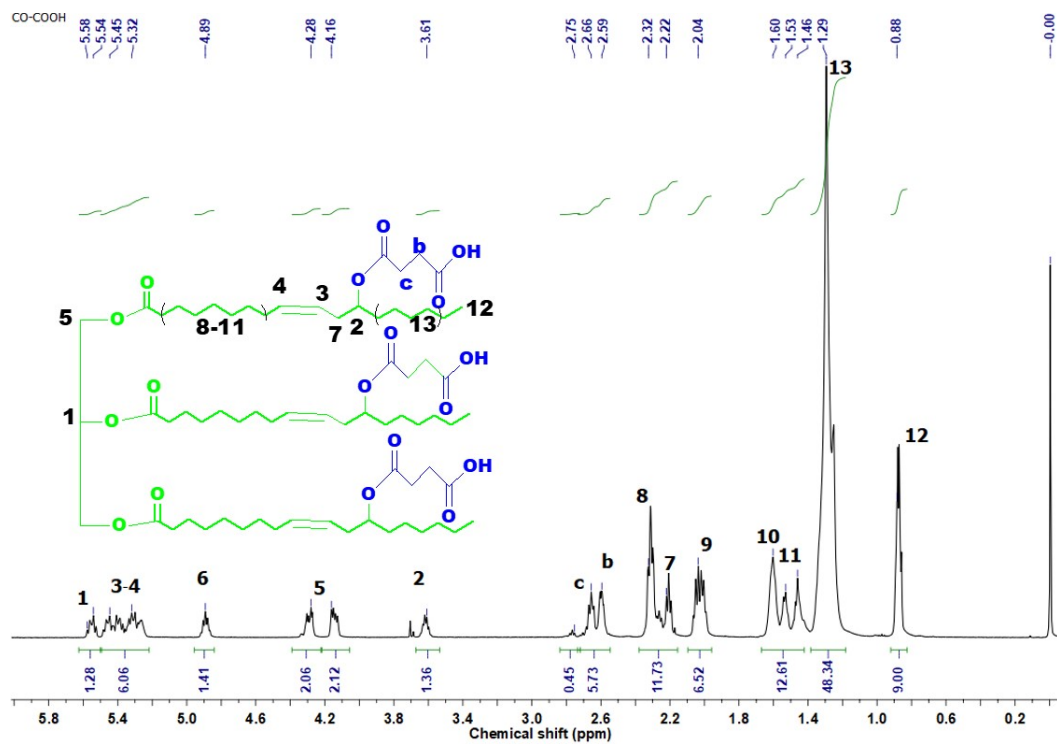
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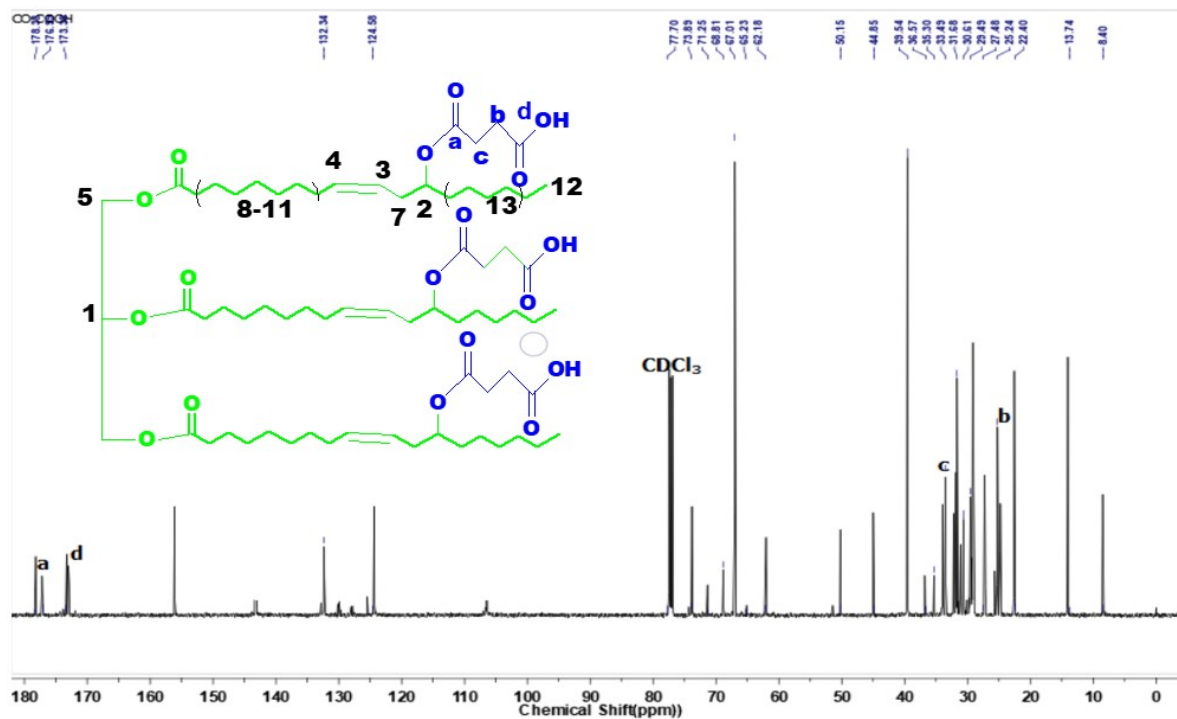232
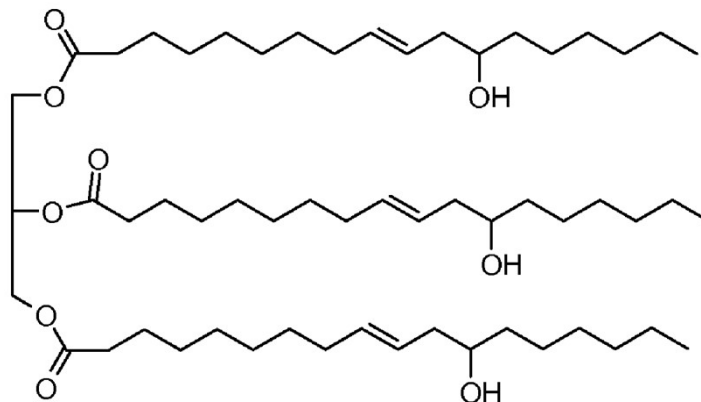
Fig.S1 Structure of castor oil (CO).

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Fig. S2 ^{1}H NMR spectrum of commercial castor oil (CO).
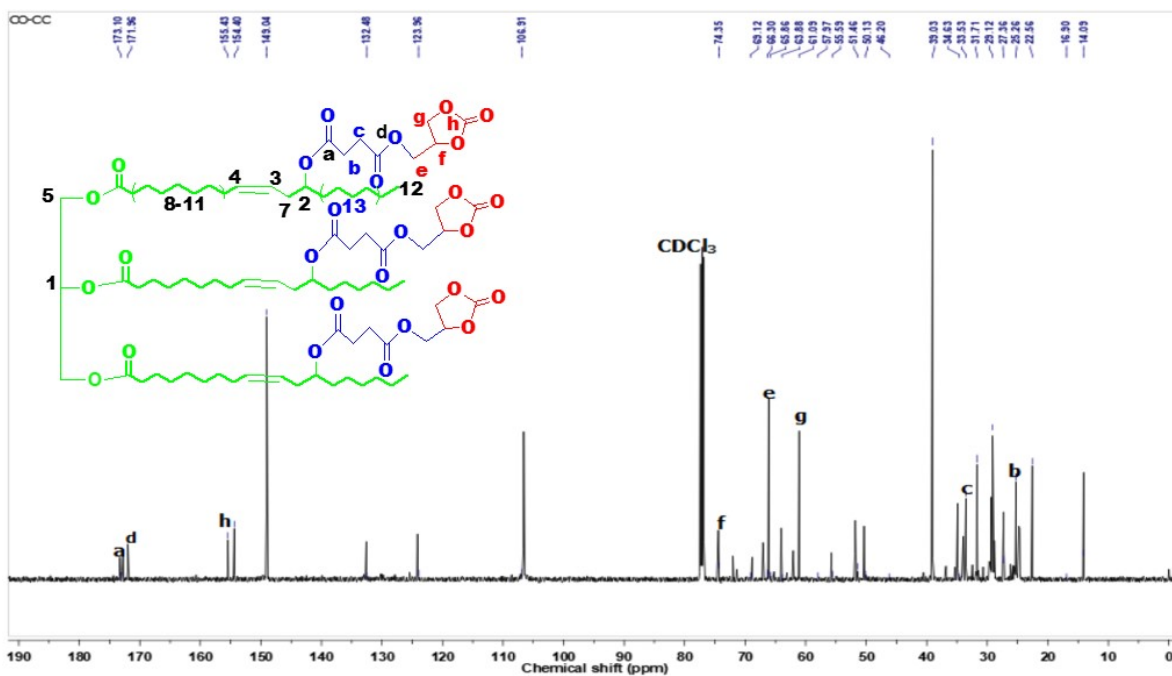
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Fig. S3 ^{1}H NMR spectrum of acid groups functionalised castor oil (CO-COOH).
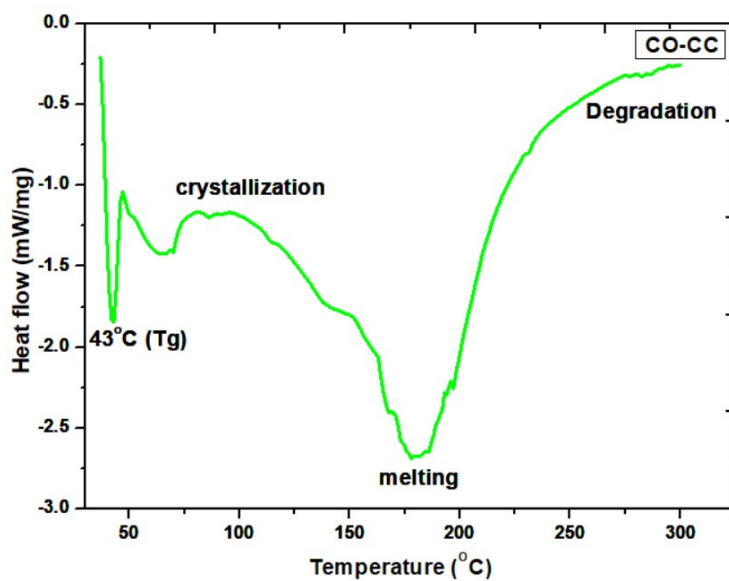
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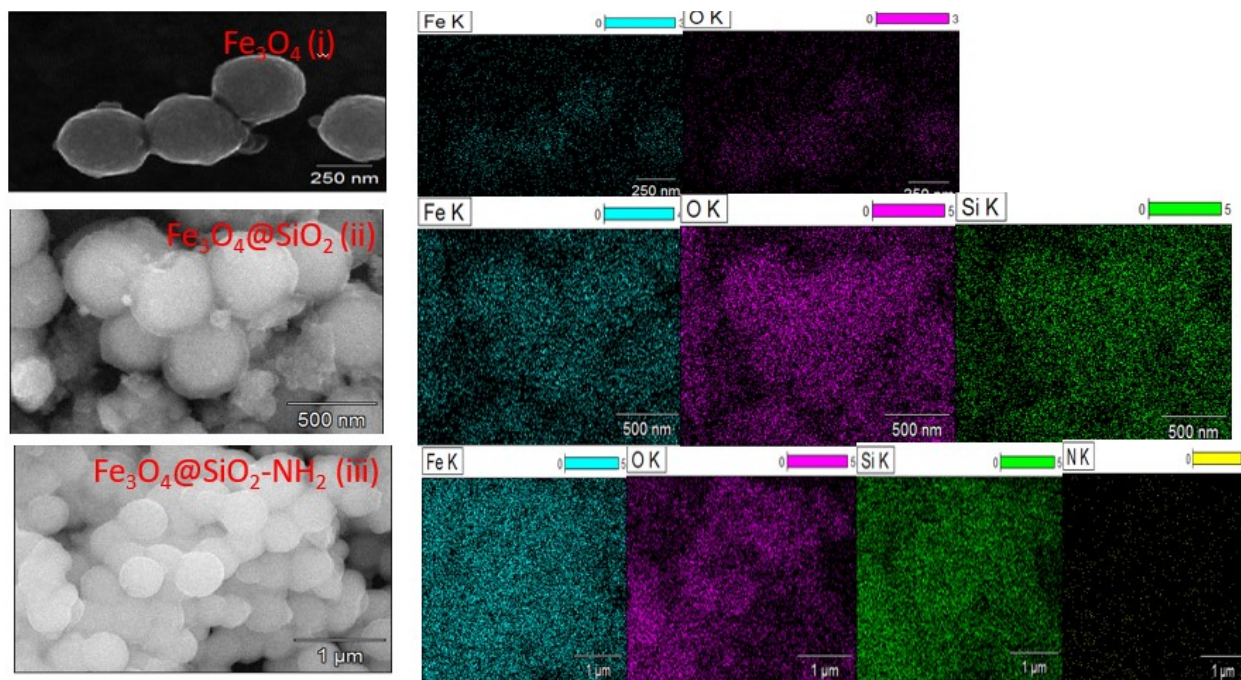**Fig. S4** ^{13}C NMR spectrum of acid groups functionalized castor oil (CO-COOH).

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242   **Fig. S5** ^{13}C NMR spectrum of castor oil cyclic carbonate (CO-CC).
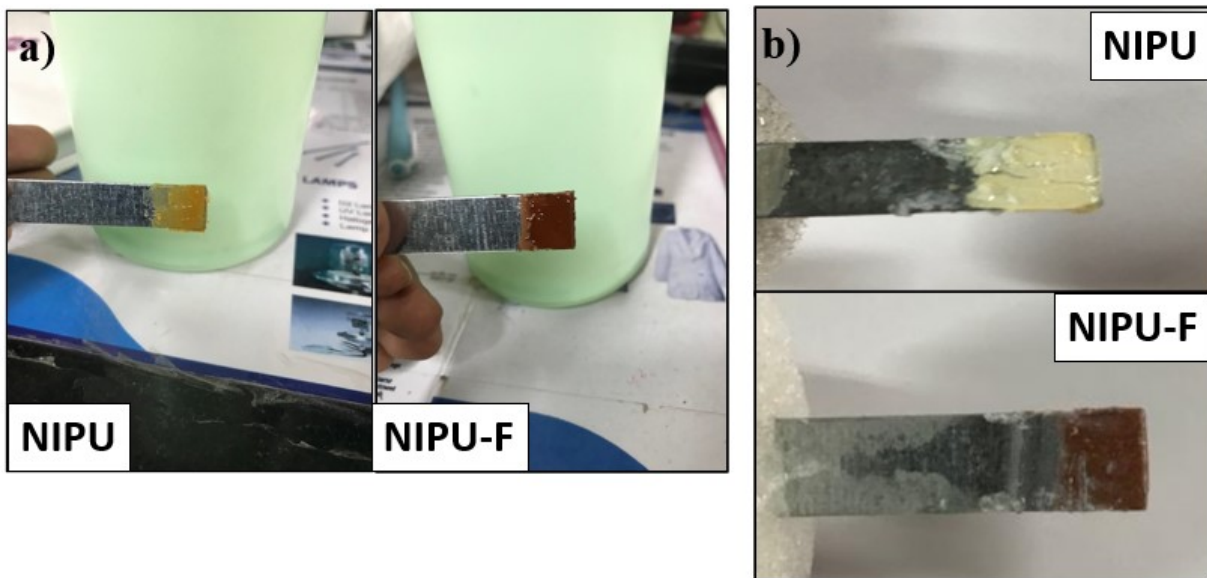

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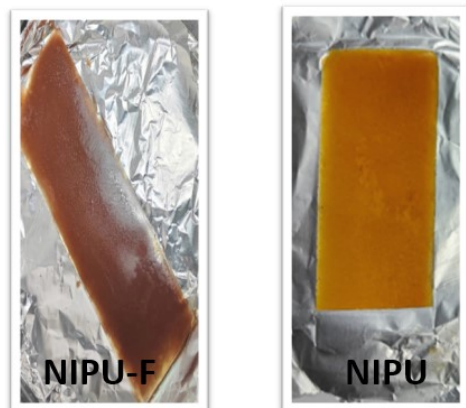244   **Fig. S6** DSC profile of castor oil cyclic carbonate (CO-CC).

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Fig. S7 Elemental mapping images of synthesized i) Fe_3O_4 ii) Fe_3O_4@SiO_2

and iii) Fe_3O_4@SiO_2-NH_2.
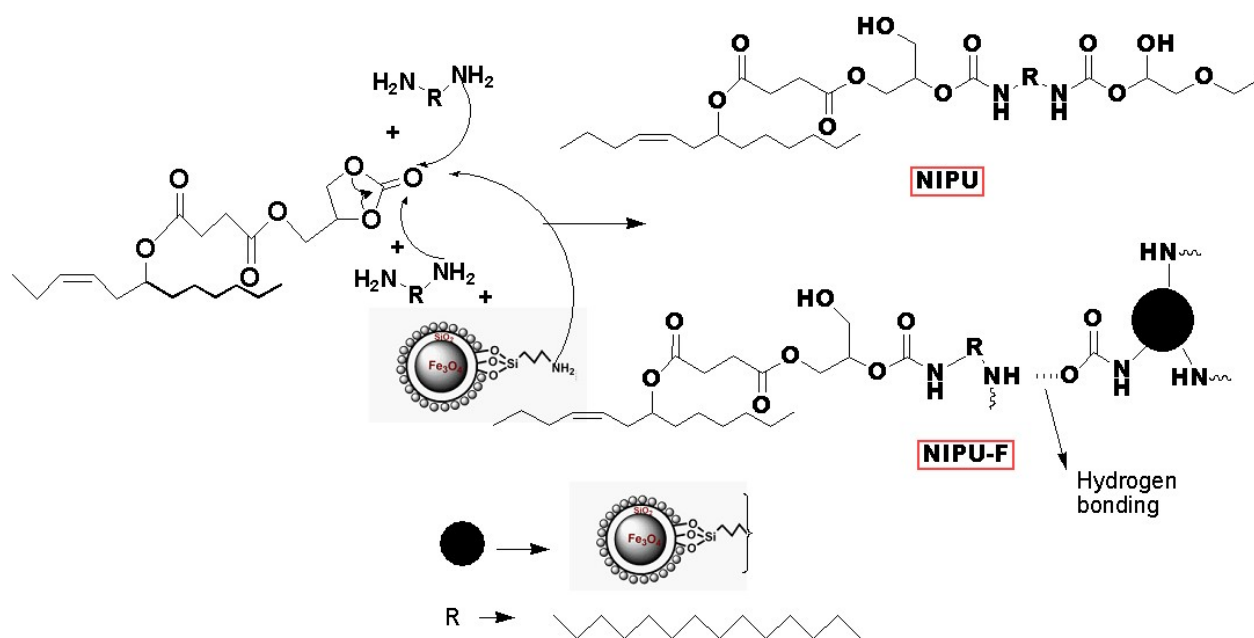

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Fig. S8 Physical images of coatings on mild carbon steel a) before and b) after immersion in

electrolyte solution.
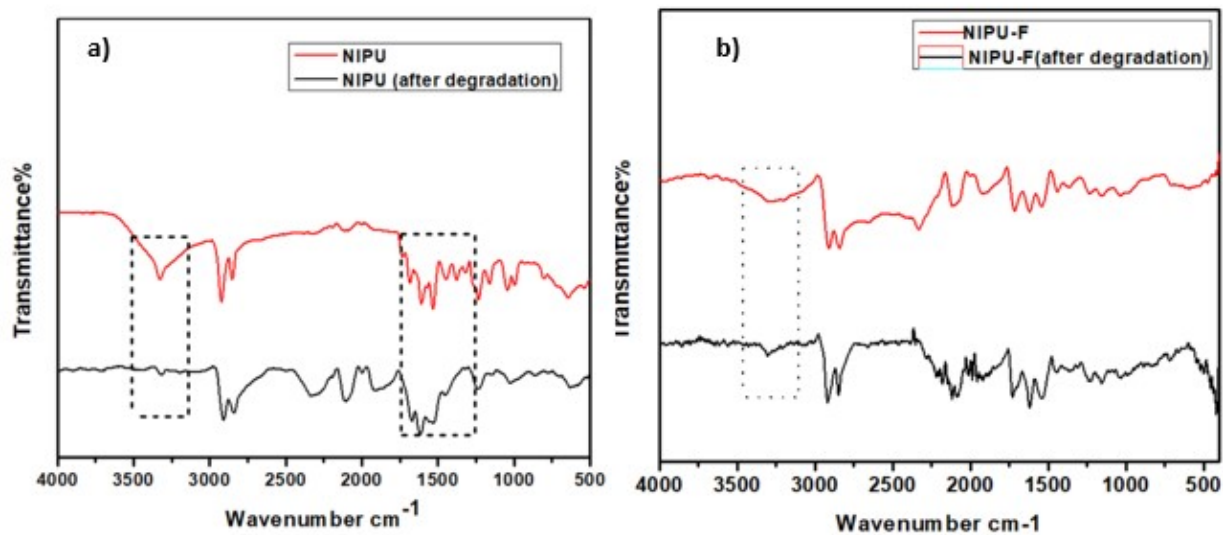
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253   **Fig. S9** Photograph images of NIPU and NIPU-F films.
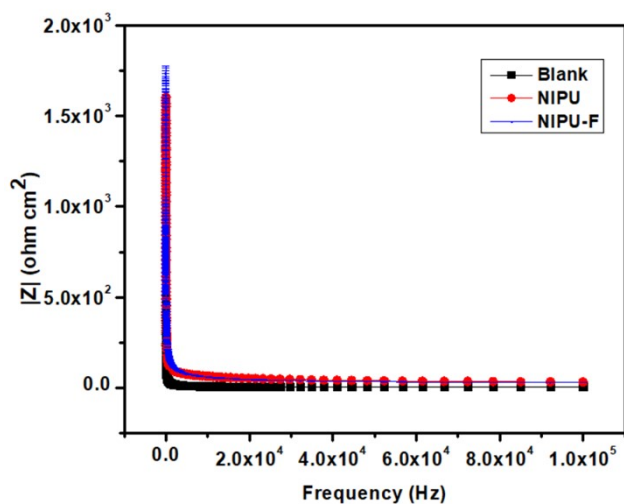

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256   **Fig. S10** Chemical mechanism for the formulation of NIPU and NIPU-F (only one amine

257   functional group is shown in amine functionalised Fe_3O_4 nanoparticles for clarity).

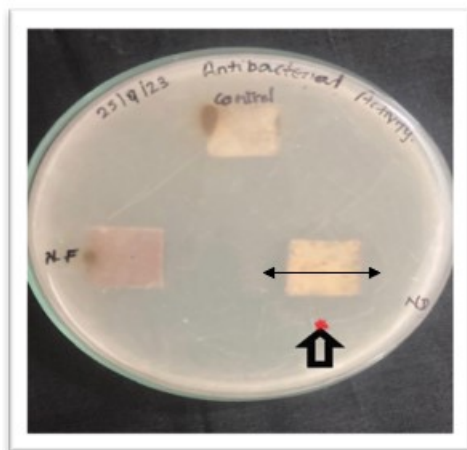**Fig.S11** FT IR data of biodegradation studies in PBS saline medium a) NIPU and b) NIPU-F.

Fig.S12 Bode diagrams for blank, NIPU and NIPU-F after immersed in electrolyte for 24h.

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265 **Fig.S13** Zone of inhibition test for qualitative analysis of antibacterial efficacy in NIPU, NIPU-F

266 and blank substrate.

267 **Table.S1 Equivalent circuit-based impedance data for coatings immersed in 3.5 wt.% of**
268 **NaCl for 1h and 24 h**

Coatings	Immersion time(1h)		Immersion time (24h)				
	R_s (Ω cm²)	R_{ct} (KΩ cm²)	R_s (Ω cm²)	R_c (KΩ cm²)	R_{ct} (Ω cm²)	CPE_c (F cm⁻²)	CPE_{dl} (F cm⁻²)
Blank	4.20	0.187	4.51	0.135	0.308	$6.05*10^{-3}$	$0.19*10^{-3}$
NIPU	4.61	1.113	14.64	0.104	0.716	$26.6*10^{-3}$	$62.5*10^{-6}$
NIPU-F	4.99	2.544	16.82	0.936	1.115	$25.3*10^{-6}$	$54.3*10^{-6}$

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277 **Table.S2 Statistical analysis data for the sample NIPU and NIPU-F undergoes degradation**

278 **for 45 days in PBS saline medium**

degradation time (days)	0	5	10	15	20	25	30	35	40	45
Mean (NIPU)	100.1	77.3	74.3	73.3	70.3	68.1	68.1	68.1	68.1	68.1
SD (NIPU)	0.1	0.264	0.264	0.264	0.057	0.152	0.23	0.057	0.173	0.2
Mean (NIPU-F)	100.1	81.2	80.2	80.3	80.1	78.2	76.2	76.2	76.2	76.2
SD (NIPU-F)	0.1	0.208	0.2	0.321	0.23	0.2	0.113	0.2	0.173	0.2

279 SD-standard deviation;

280 **Table.S3 Statistical analysis data for antibacterial and anti-algae studies**

Test type	antibacterial (E.Coli)		anti-algae (S.Platensis)	
samples	Mean	SD	Mean	SD
Blank	45000	89.938	8.5	0.08736
NIPU-F	5080	13.719	4.143	0.00832
NIPU	120	6.649	2.526	0.00152

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