

Development of poly(urethane-ester)amide from corn oil and their anticorrosive studies

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ABSTRACT

Corn oil-based poly(urethane-ester)amide was synthesized from corn oil-based fatty amide diol, camphoric acid, and tolylene 2,4-diisocyanate. The structure of corn polyesteramide and corn poly(urethane-ester)amide (CPEA) was confirmed by Fourier transform infrared, ¹H NMR, and ¹³C NMR spectroscopic techniques. CPUEA coatings were made on mild steel strips and their physicomechanical analysis (scratch hardness, impact test, conical mandrel test, and pencil hardness tests) was performed by standard methods. The surface morphology of coatings was observed by scanning electron microscopy and thermal stability was assessed by thermogravimetric analysis/differential scanning calorimetry. Anticorrosion properties of CPUEA were observed in acidic, saline, and tap water medium at room temperature using potentiodynamic polarization technique. The results of CPUEA coatings exhibit good physicomechanical and anticorrosive properties and can find application up to 175°C.

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Introduction

Vegetable oils (VOs) are easily available, biodegradable, low cost, easy to modify, environmentally benign, and eco-friendly resources.^[1–5] VOs are used for various applications like in the preparation of polymers, pharmaceuticals, agrochemicals, soaps, cosmetics, biodiesel, lubricants, and others.^[6–8] VOs such as linseed, corn, neem seed, soybean, *Pongamia glabra*, jatropha, and others have been transformed into polymers, namely, alkyd, polyesters, polyesteramide, polyetheramide, polyurethane by numerous chemical pathways, for various applications.^[9–14] These thermoplastic materials are used as protective coatings for mild steel (MS) in various corrosive media.

Polyurethanes (PUs) are one of the most important class of polymers. PUs are used as flexible and rigid foams, in automotive insulation, coatings, adhesives, sealants, and elastomers. PUs bear flexibility, elasticity, strength, and abrasion resistance.^[15–21]

Camphoric acid (1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid) is a penta-carbon cyclic compound. It is used in the field of coordination chemistry as ligand^[22] and in the formation of metal complexes such as ruthenium, iridium complexes,^[23] for coordination polymer synthesis,^[24] and also used in liquid crystal polyesters.^[25]

Polymer coating on metal substrate showed good adhesion in presence of polar and nonpolar moieties in polymeric resin and also barrier between corrosive ions and conducting metal substrate.^[26,27] Polymer organic coatings consist filler, pigments such as nanoparticle of metals to improve the adhesion and anticorrosion performance.^[28] In corrosion electrochemical reactions, electrochemical methods play an important role for evaluation of corrosion performance. Polarization

studies have been widely used in the area of metallic corrosion which includes, namely, adhesion to substrate, water and oxygen uptake of coatings, dielectric properties, ion penetration, surface characteristic of metal substrates, and environmental condition.^[29]

For the first time, we used camphoric acid in the preparation of urethane-modified corn oil-based polyesteramide (CPEA). Based on the evaluation of physicomechanical and corrosion resistance performance, we found that corn poly(urethane-ester)amide (CPUEA) shows good coating properties on mild steel substrate. The corrosion protective properties of CPUEA polymer coating are studied by a potentiodynamic (Tafel) polarization technique.

Experimental section

Materials

Corn oil (Afia International Company, Jeddah, KSA),^[12] camphoric acid (E Merck, Darmstadt, Germany), diethanolamine (Riedel-deHaen, Germany), sodium metal, methanol, xylene, (BDH Chemicals, Ltd. Poole, England), Toluene 2,4-diisocyanate (Acros Organic, USA) are used as received.

Instruments and methods

Fourier transform infrared (FTIR) spectra of CPEA and CPUEA were taken on FTIR spectrophotometer (Spectrum 100, PerkinElmer, USA). ¹H and ¹³C NMR spectra were recorded on Jeol DPX400 MHz using deuterated chloroform as solvents and tetramethylsilane as an internal standard. Thermal analysis of CPUEA resin was performed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Model TGA/DSC1, Mettler Toledo AG, Analytical CH-8603, Schwerzenbach, Switzerland) in nitrogen atmosphere at a heating rate of 10°C min⁻¹. Molecular weight of CPUEA resin was investigated by Gel permeation chromatography (GPC) (HT-GPC Module 350A, Viscotek, Houston, TX, USA). Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 ml min⁻¹. Morphology was studied by scanning electron microscope (SEM) (JEOL, JED-2200 Series, Japan). Coating properties were evaluated by impact resistance (IS: 101 part 5 sec 3, 1988), scratch hardness (BS 3900), crosshatch adhesion (ASTM D3359-02), conical mandrel bend test (ASTM D3281-84), pencil hardness test (ASTM)(Wolff- Wilborn tester, Sheen Instruments, England), Gill AC (ACM Instruments, Cumbria, UK) by standard methods. The thickness (Elcometer Coating Thickness Gauge, Model 456; Elcometer Instruments, Manchester, UK), and gloss (by Glossmeter, Model: KSJ MG6-F1, KSJ Photoelectrical Instruments Co., Ltd. Quanzhou, China) of coatings were also evaluated. Potentiodynamic measurements were performed in three-electrode system at ambient temperature, platinum electrode as counter electrode and saturated calomel electrode as reference electrode. The mild steel specimen served as working electrode; exposed surface area 1.0 cm² was fixed by PortHoles electrochemical sample mask. The corrosive media selected were 3.5 wt% HCl, 5 wt% NaCl, and tap water (Cl⁻ ion 163.303 ppm). Potentiodynamic polarization (PDP) was obtained using a sweep rate of 1.0 mV s⁻¹ in the potential range ±250 mV with respect to open circuit potential. PDP was used for the evaluation of protective properties of CPUEA coatings. Each coating system was evaluated in triplicate for corrosion protection.

Synthesis of *N,N*-bis(2-hydroxy ethyl) corn oil fatty amide

N,N-bis(2-hydroxy ethyl) corn oil fatty amide (HECFA) was synthesized according to previously published paper.^[12]

Synthesis of corn oil polyesteramide

N,N-bis(2-hydroxy ethyl) corn oil fatty amide (0.02 mol) and camphoric acid (0.018 mol) were dissolved in 50 ml blend of xylene and DMF (80:20) in three-necked round-bottom flask equipped

with Dean-Stark trap, thermometer, nitrogen inlet tube, and magnetic stirrer. The reaction temperature was maintained at 120°C and refluxed until the reaction completed. The progress of the reaction was monitored by acid value determination at regular interval of time. After completion of reaction, the blend (xylene and DMF) was evaporated in rotary vacuum evaporator at reduced pressure to obtain CPEA resin.

Synthesis of poly(urethane-ester)amide

The synthesis was performed by CPEA and TDI (25, 30, 35 wt%,) in xylene at 120°C according to the procedure described in our published paper, resulting in the formation of CPUEA25, CPUEA30, and CPUEA35.^[30]

Results and discussion

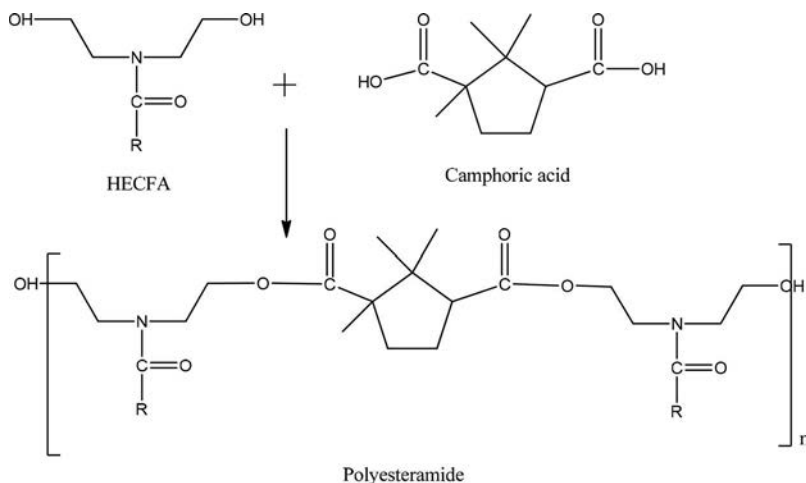
Schemes 1 and 2 show the synthesis of CPEA and CPUEA. HECFA was synthesized by the aminolysis reaction between corn oil and diethanolamine.^[12] HECFA condensation reaction with camphoric acid and produced CPEA, which further reacted with TDI through addition reaction forming CPUEA. The chemical reactions were confirmed by FTIR, ¹H NMR, and ¹³C NMR. The molecular weight of CPUEA30 was observed to be 5,975 g mol⁻¹ (Mw) and 3,678 g mol⁻¹ (Mn) with polydispersity index as 1.62.

Spectral analysis

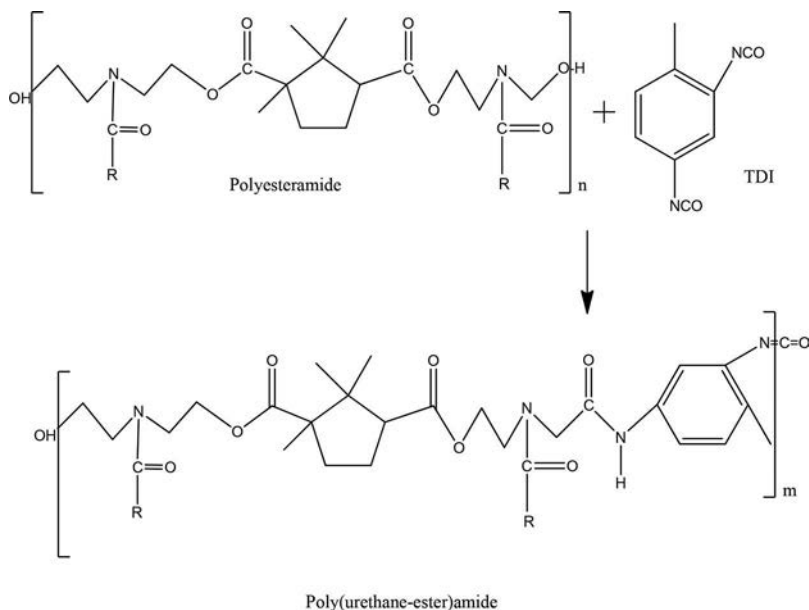
CPEA, FTIR (cm⁻¹): 3355 (OH); 2926.79 (CH₂, asymmetrical); 2854.89 (CH₂, symmetrical); 1726.67 (C=O, ester); 1632.88 (C=O, amide); 1460.53 (C–N, stretching); 3009.01 (–CH=CH–); 1251.31, 1168.50, 1115.57, 1073.83 (–C(CO)O–C–stretching) (Figure 1).

¹H-NMR (CDCl₃, δ ppm): 0.839–0.857 (–CH₃), 1.202–1.220 (–CH₂–), 1.585 (–CO–CH₂–CH₂), 1.801 (cyclic –CH₂–), 2.007–2.050 (–CH₂–, attached double bond), 2.243 (CH₂ attached CO), 2.32 (cyclic CH attached to CO), 2.721–2.753 (CH₂ between double bond), 3.571–3.706 (–CH₂–N<), 4.181 (–CH₂–O–(CO)–), 5.306–5.320 (OH), 5.503 (–CH=CH–) (Figure 2).

¹³C-NMR (CDCl₃, δ ppm): 14.013 (–CH₃); 18.226–25.559 (–CH₂–CH₃, cyclic –CH₂– and –CH₃); 27.127 (–CH₂ attached to CO, amide); 29.253 (chain –CH₂–); 31.447 (–CH₂ attached –CH–); 34.231 (cyclic –CH₂–); 46.320 (–CH₂– attached N); 48.234 (cyclic >C<); 50.302



Scheme 1. Synthesis of corn oil polyesteramide.



Scheme 2. Synthesis of corn oil poly(urethane-ester)amide.

($-\text{CH}_2-\text{CH}_2-\text{OH}$); 54.001 (cyclic, $>\text{CH}-$); 56.105 (cyclic $>\text{C}<$ attached two CH_3); 60.204 ($-\text{CH}_2-\text{OH}$); 62.121 ($-\text{CH}_2$ attached OCO); 128.012–130.162 ($-\text{CH}=\text{CH}-$); 174.231 (CO , amide); 175.802 (CO , ester) (Figure 3).

CPUEA, FTIR (cm^{-1}): 3114.54 ($-\text{CH}=\text{CH}-$); 2927.01 (CH_2 , asymmetrical); 2855.06 (CH_2 , symmetrical); 2275.72 (free NCO); 1726.57 (CO , ester); 1710.45 (CO , urethane); 1658.73 (CO , amide); 1456.18 ($\text{C}-\text{N}$ stretching); 1226.40 ($\text{NCOO}-$); 1070.16 ($-\text{C}(\text{CO})\text{O}-\text{C}-$ stretching); 1536.76, 767.82 (aromatic); 700.12 (NH , bending) (Figure 1).

$^1\text{H-NMR}$ (CDCl_3 , δ ppm): 0.857–0.895 ($-\text{CH}_3$), 1.153–1.252 ($-\text{CH}_2-$), 1.602 ($-\text{CO}-\text{CH}_2-\text{CH}_2$), 1.781 (cyclic $-\text{CH}_2-$), 2.000–2.080 ($-\text{CH}_2-$, attached double bond), 2.233–2.451 (CH_2 attached CO ,

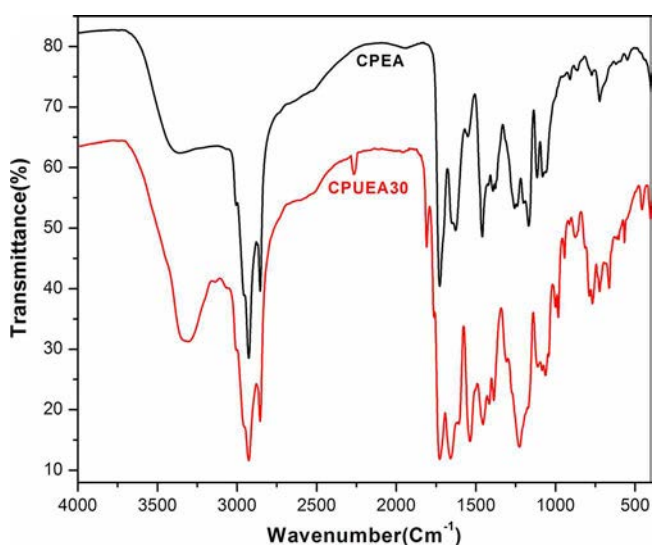


Figure 1. FTIR spectra of CPEA and CPUEA30.

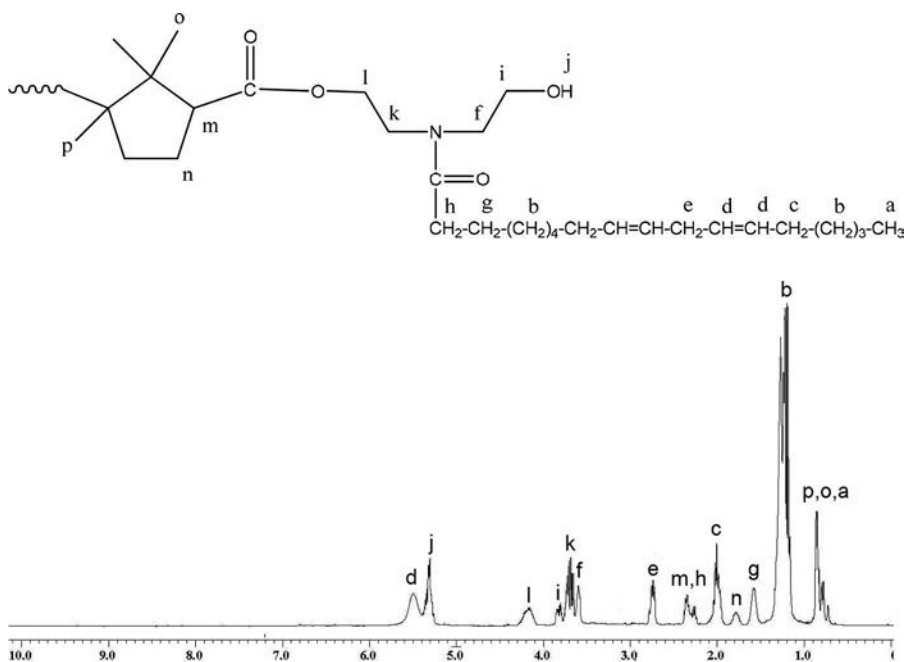


Figure 2. ^1H NMR spectra of CPEA.

cyclic CH attached to CO, CH_3 of TDI), 2.711–2.902 (CH_2 between double bond), 3.556–3.686 ($-\text{CH}_2-\text{N}<$), 4.121–4.252 ($-\text{CH}_2-\text{O}-(\text{CO})-$) 5.290 (OH), 5.452 ($-\text{CH}=\text{CH}-$), 7.197–7.401 (aromatic ring of TDI), 7.951 ($-\text{NH}$, urethane) (Figure 4).

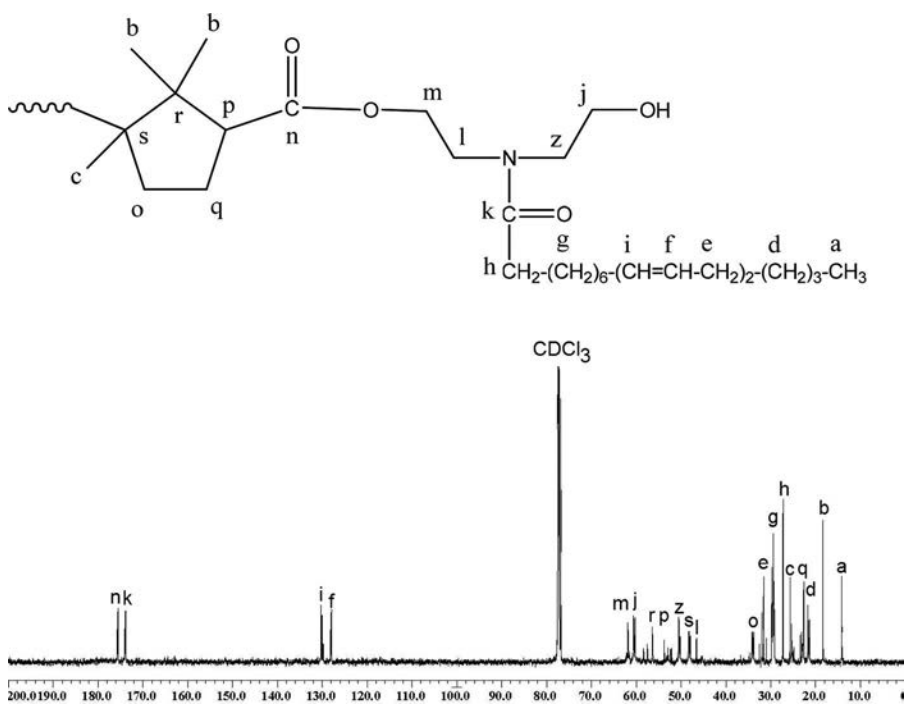


Figure 3. ^{13}C NMR spectra of CPEA.

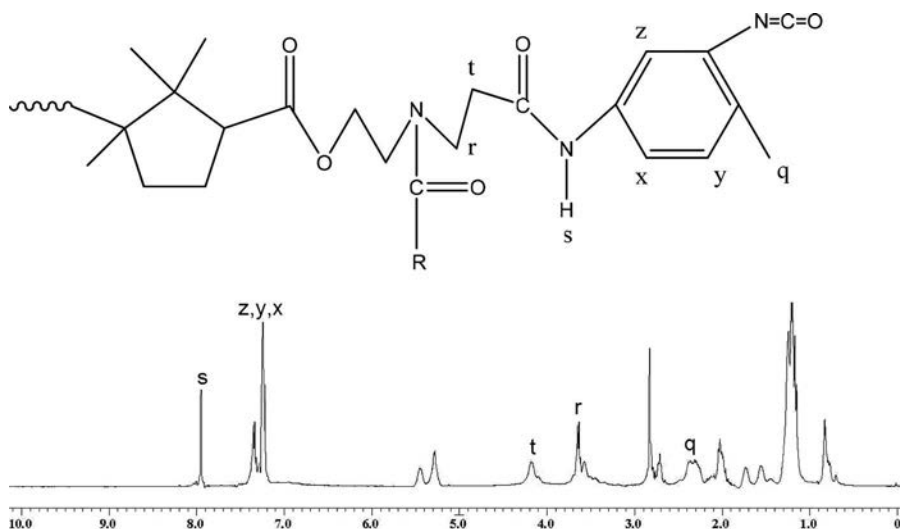


Figure 4. ^1H NMR spectra of CPUEA30.

^{13}C -NMR (CDCl_3 , δ ppm): 14.180 ($-\text{CH}_3$); 18.407–25.672 ($-\text{CH}_2-\text{CH}_3$, cyclic $-\text{CH}_2-$ and $-\text{CH}_3$, $-\text{CH}_3$ of TDI); 27.240 ($-\text{CH}_2$ attached to CO, amide); 29.381–29.702 (chain $-\text{CH}_2-$); 31.522 ($-\text{CH}_2$ attached $-\text{CH}-$); 36.607 (cyclic $-\text{CH}_2-$); 46.757 ($-\text{CH}_2-$ attached N); 54.384 (cyclic $>\text{CH}-$); 56.213 (cyclic $>\text{C}<$ attached two CH_3); 58.240 ($-\text{CH}_2$ attached $-\text{CONH}$); 62.053 ($-\text{CH}_2$ attached OCO); 126.957–130.258 (aromatic C and $-\text{CH}=\text{CH}-$); 156.742 (free $-\text{NCO}-$); 162.327 (CO, urethane); 174.321 (CO, amide); 176.105 (CO, ester) (Figure 5).

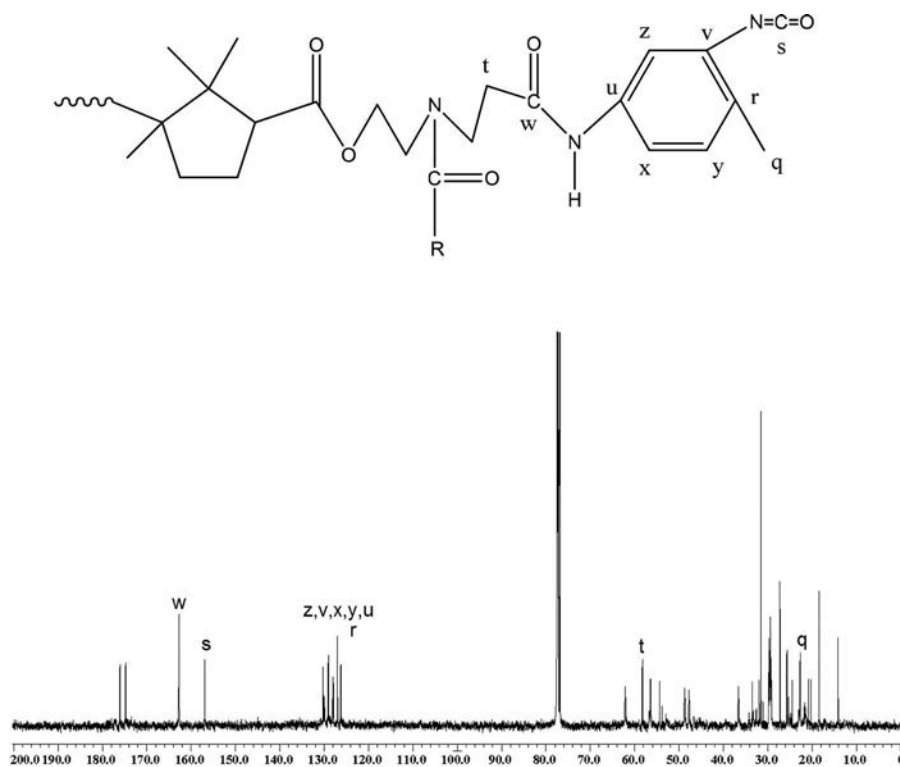


Figure 5. ^{13}C NMR spectra of CPUEA30.

Table 1. Corrosion parameters for bare mild steel and CPUEA coated mild steel in various corrosive medium.

Code	Medium	E_{corr} (mV)	β_a (mV)	β_c (mV)	I_{corr} (mA/cm ²)	Corrosion rate (mm/year)	LPR ($\Omega \cdot \text{cm}^2$)
MS	3.5 wt% HCl	-470.09	71.36	66.955	1.01	10.623	16.385
CPUEA25	3.5 wt% HCl	-464.15	75.81	188.10	4.10×10^{-5}	0.476	571.960
CPUEA30	3.5 wt% HCl	-446.33	67.64	76.56	1.86×10^{-5}	2.158×10^{-1}	838.310
CPUEA35	3.5 wt% HCl	-443.36	70.46	92.60	8.59×10^{-5}	9.965×10^{-2}	20.232×10^2
MS	Tap water	-650.71	143.26	394.84	2.69×10^{-2}	3.123×10^{-1}	169.490
CPUEA25	Tap water	-504.59	55.06	129.52	1.20×10^{-3}	1.395×10^{-2}	13.956×10^2
CPUEA30	Tap water	-65.94	392.35	275.34	1.97×10^{-7}	2.284×10^{-5}	3.570×10^7
CPUEA35	Tap water	-18.94	352.96	273.25	3.63×10^{-7}	4.217×10^{-6}	1.841×10^7
MS	5 wt% NaCl	-476.30	77.762	198.59	2.092×10^{-1}	1.242	116.120
CPUEA25	5 wt% NaCl	-489.73	164.60	138.07	1.888×10^{-4}	2.188×10^{-3}	17.292×10^2
CPUEA30	5 wt% NaCl	-395.76	51.11	136.57	1.37×10^{-4}	1.5883×10^{-3}	15.010×10^2
CPUEA35	5 wt% NaCl	-132.32	119.83	189.92	8.314×10^{-5}	9.636×10^{-4}	38.423×10^2

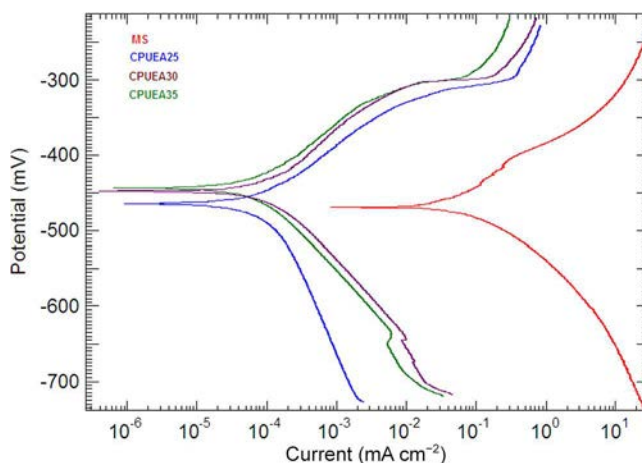
Mild steel → MS.

Physicomechanical properties

The CPUEA coatings were cured at ambient temperature and subjected to physicomechanical tests and corrosion studies. The thickness of these coatings was found as $120 \pm 5 \mu\text{m}$. The curing process of CPUEA coating followed solvent evaporation, moisture curing by reaction of free isocyanates of CPUEA with moisture, and auto-oxidation. The best coating performance was exhibited by CPUEA30. The CPUEA30 coating showed good scratch hardness (2.5 Kg), cross hatch (100%), impact resistance (150 lb inch^{-1}), flexibility retention (1/8 inch conical mandrel), gloss (52), and pencil hardness (5H). The CPUEA30 coating indicates good adhesion to the mild steel substrate contributed by polar hydroxyls, isocyanate, urethane, and amide linkages.

Corrosion studies

Potentiodynamic polarization scans were performed to investigate the barrier properties of corrosive ions in CPUEA coatings. Different concentrations of TDI were used to optimize the concentration and evaluate its effect on CPUEA coatings. Table 1 represents the E_{corr} (corrosion potential) and I_{corr} (corrosion current) values obtained by Tafel analysis of PDP data for CPUEA coatings with different amounts of TDI. Figure 6 shows PDP curve of bare MS, CPUEA25, CPUEA30, and CPUEA35 after 240 h immersion in 3.5 wt% HCl solution. The E_{corr} values of bare MS shifted to more noble values

**Figure 6.** Tafel plots of MS, CPUEA25, CPUEA30, and CPUEA35 in HCl solution.

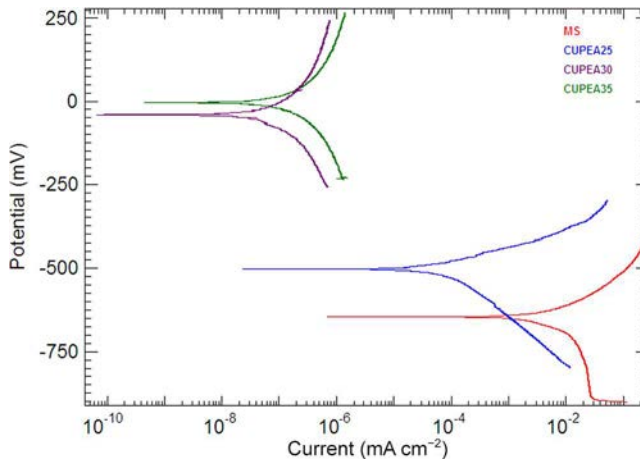


Figure 7. Tafel plots of MS, CPUEA25, CPUEA30, and CPUEA35 in Tap water.

−470.09 to −464.15, −446.33, and −443.36 mV vs with reference electrode. As is seen in Table 1, the linear polarization resistance (LPR) values of CPUEA coatings are greater than bare MS. In Figure 7, for PDP curve in tap water after 250 h immersion, E_{corr} as well as LPR increases and current density decreases from bare MS to CPUEA35 (Table 1). Figure 8 represents PDP curve in 5 wt% NaCl after 240 h immersion. E_{corr} and LPR of bare MS as compared to CPUEA25, CPUEA30, and CPUEA35 have greater values (Table 1) and corrosion current density values are smaller that indicate the formation of resilient film with tenacious adhesion and good barrier properties. The corrosion current densities of coated samples are significantly changed to that bare mild steel (MS to CPUEA35). These results showed that CPUEA coatings act as a protective film on MS to improve the corrosion protection performance. The uniform CPUEA coatings form hydrophobic and impermeable barrier at the interface of MS and corrosive ions.^[31,32]

Morphology studies

Scanning electron micrographs of CPUEA30 coatings were taken after immersion in different corrosive media. Figure 9 shows micrograph of CPUEA30 coating tested in NaCl solution which

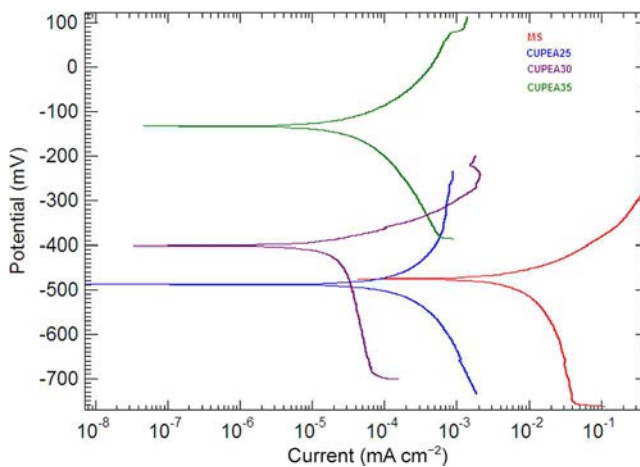


Figure 8. Tafel plots of MS, CPUEA25, CPUEA30, and CPUEA35 in NaCl solution.

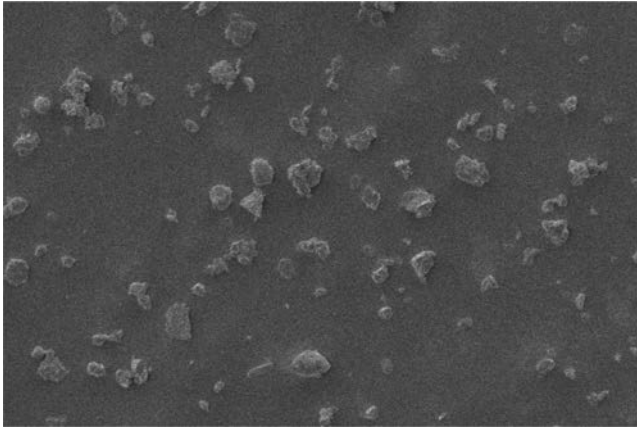


Figure 9. SEM micrograph of CPUEA30 after immersion in tap water.

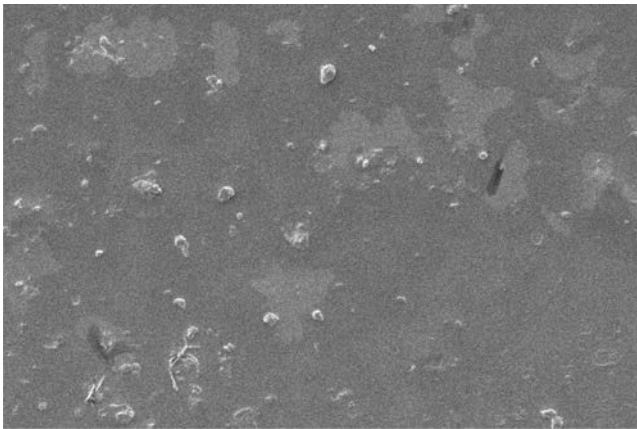


Figure 10. SEM micrograph of CPUEA30 after immersion in NaCl solution.

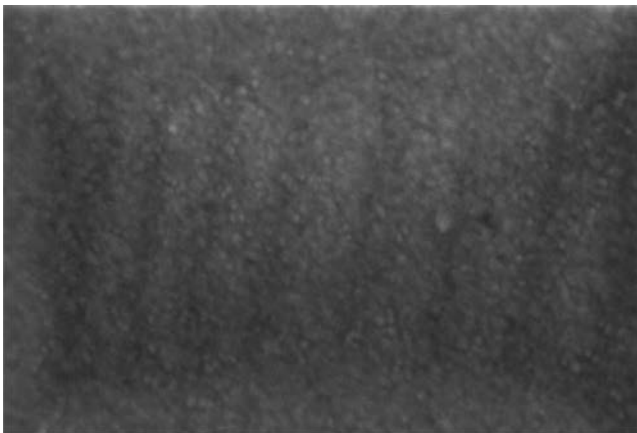


Figure 11. SEM micrograph of CPUEA30 after immersion in HCl solution.

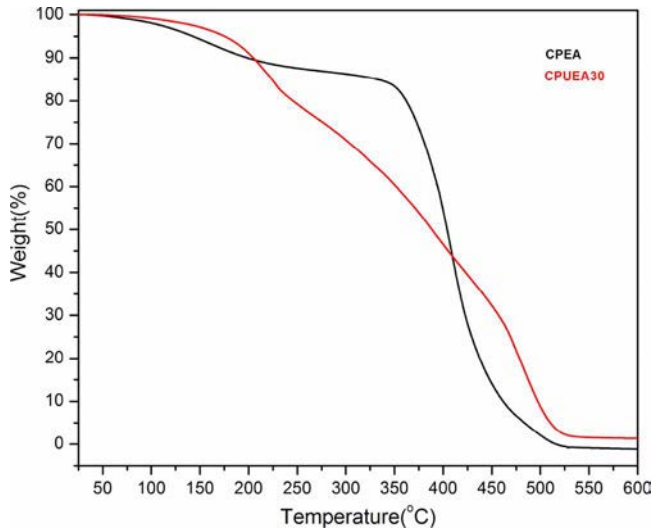


Figure 12. TGA thermogram of CPEA and CPUEA30.

shows that the coating is unaffected with salt deposition on the surface. After being subjected to tap water, the micrograph (Figure 10) shows that coating is unaffected, some white spots show salt deposition. The micrograph (Figure 11) of the coating in acidic environment shows that coating is unaffected and only slight loss in gloss was observed. The CPUEA30 does not show any crack on the coating surface after immersion in different corrosive media, however the electrolyte ions are unable to penetrate the CPUEA30 coating and reach the substrate and the coating does not show any dissolution or deterioration.

Thermal analysis

Figure 12 shows the TGA thermograms of CPEA and CPUEA30. The initial 5% weight loss was observed at 140°C for CPEA and 175°C for CPUEA30, it can be correlated with the evaporation of

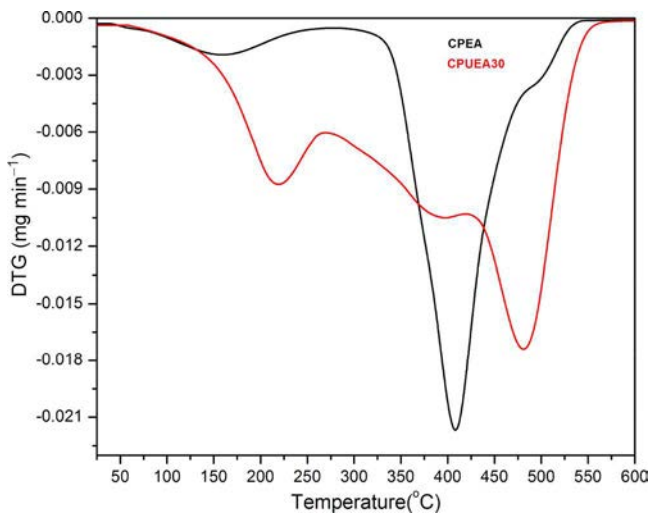


Figure 13. DTG thermogram of CPEA and CPUEA30.

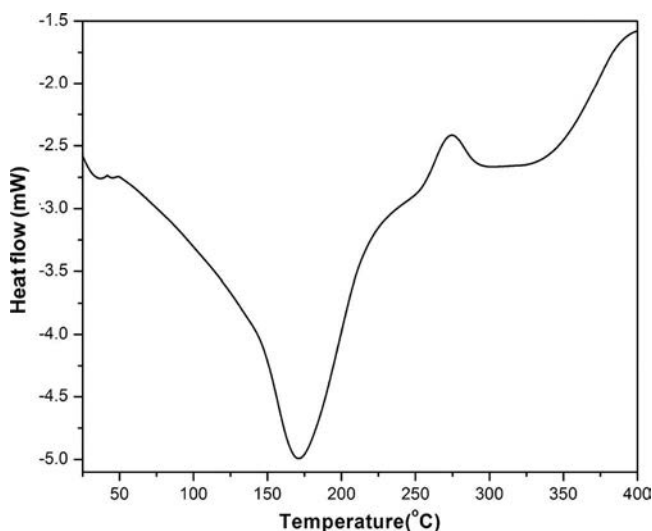


Figure 14. DSC thermogram of CPUEA30.

the entrapped solvent. 20% weight loss of CPUEA30 occurs at 225°C due to degradation of urethane linkages^[13] while CPEA does not show this decomposition. 50% weight loss at 403 and 365°C occurs for CPEA and CPUEA30, respectively, due to the presence of amide linkage.

Differential Thermo Gravimetric (DTG) thermogram (Figure 13) of CPEA and CPUEA30 clearly indicates decomposition events. CPEA shows two decompositions while CPUEA30 shows three events. First event of CPUEA occurs from 75 to 250°C and centered at 156°C while from second 313 to 540°C centered at 408°C. In CPUEA30, first event occurs from 75 to 268°C centered at 218°C, and second event from 274 to 420°C centered at 395, while the third occurs from 425 to 564°C centered at 481°C. These decomposition events are relevant to urethane, amide moiety, and hydrocarbon chains, respectively.

Differential scanning calorimetry (DSC) thermogram (Figure 14) of CPEAU30 showed that the endothermic peak is observed in the temperature span of 143–225°C and centered at 171°C. This peak can be attributed to the onset of melting of CPEAU30 resin followed by decomposition process. An exotherm ensues beyond 253°C in DSC thermogram due to the decomposition of resin as is also observed in TGA thermogram.

Conclusion

Corn oil-based poly(urethane-ester-amide) coatings were prepared by condensation and addition chemical reaction and were cured at ambient temperature. This approach highlights an alternative route for utilization of corn oil in surface coatings. CPUEA30 coating showed good scratch hardness, flexibility, gloss, and corrosion resistance and can be safely used up to 175°C as an eco-friendly coating material.

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