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Jatropha seed oil derived poly(esteramide-urethane)/ fumed silica nanocomposite coatings for corrosion protection

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Abstract: Jatropha oil (JO) based poly (esteramide-urethane) coatings embedded with fumed silica nanoparticles were prepared. JO was converted to N,N-bis(2-hydroxy ethyl) JO fatty amide (HEJA) and was further modified by a tetrafunctional carboxylic acid (trans 1,2 diaminocyclo-hexane-N,N,N',N'-tetraacetic acid) to form poly (diamino cyclohexane esteramide) (PDCEA). PDCEA was then treated with toluene 2,4-diisocynate and fumed silica to prepare poly(diamino cyclohexane urethane esteramide) (PUDCEA) nanocomposite. The formation of PDCEA and PUDCEA nanocomposites was confirmed by FTIR, 1H & 13C NMR spectroscopic techniques. The thermal behavior and morphology of PUDCEA nanocomposite coatings were investigated by TGA/DTG, DSC, SEM, EDX spectroscopy. PUDCEA nanocomposites were applied on carbon steel and their coatings were produced at room temperature. The properties of these nanocomposite coatings were investigated by standard analytical methods. The PUDCEA-3 nanocomposite showed good anticorrosion and physico-mechanical performance. These nanocomposite coatings can be employed safely upto 200°C.

Keywords: Jatropha oil; trans 1,2diaminocyclo-hexane-N,N,N',N'-tetraacetic acid; polyurethane esteramide; coatings.

1 Introduction

Industrial chemicals are mainly being obtained from fossil-based materials. The latter are not only costly and hazardous for human health and environment, but are also becoming less available, with time. Vegetable oils bear great potential attributes to provide alternative sustainable and eco-friendly equivalent substitutes to fossil-based materials [1-4]. Vegetable oils have as their main components triglycerides, which may be modified by different moieties such as diethanolamine, carboxylic acid, alcohol, styrene, and others. They may be utilized in the production of various polymeric materials such as polysteramide, polyepoxy, polyurethane, polyetherimide, and their composites with other polymers [5-9]. Vegetable seed oils from linseed, castor, pongamia glabra, rapeseed, jatropha, soybean, and others are used for the synthesis of various polymers [10-13]. JO contains mostly oleic, linoleic, palmitic, and stearic acid. JO is also used for the preparation of polysteramide, polyetheramide and other polymeric materials [14,15].

trans 1,2diaminocyclo-hexane-N,N,N',N'-tetraacetic acid (CDTA) is a tetrafunctional carboxylic acid. It is mainly applied as a ligand for transition metals, including zirconium, copper, nickel, and others, to form coordination complexes/compounds in field of coordination chemistry and as an anion exchanger for separation of rare earth element complexes [16-18]. CDTA is also used for the electrochemical study of chromium complexes [19].

There are a large number of nanofillers like carbon nanotubes (CNT), multiwalled carbon nanotubes (MWNT), nanoclay, and nanoparticles, being used to reinforce polymer matrices, drastically improving polymer properties for many commercial applications [20,21]. Recently, polymeric resins modified with different nano metal oxides such as ferrite, Al2O3, CaO, SiO2, TiO2, CeO2, and ZnO, with improved physico-mechanical properties have been reported in the literature [22-25,29-31]. Nanoparticle inclusion in polymer resins have improved scratch hardness, tensile strength, thermal stability,
toughness, stiffness and can shift the glass transition temperature of polymeric resins [26]. Silica nanoparticles are widely used as inorganic fillers due to their controlled size, large surface area, uniform structure, and remarkable moisture-barrier properties. The preparation of silica-reinforced polymeric films for coating applications is of great interest. The silica nanoparticle reinforced polymeric films find variety of applications as coating materials [24]. In composite (hybrid) materials, due to physical and chemical interactions between molecules, the properties of composites are significantly affected in the vicinity of individual materials. The properties of nanocomposites are related to degree of thermosets, crystallinity, mobility chain confirmation, and interface with the matrix [27, 28].

Polyurethanes (PUs) are elastic polymers used as elastomers and composites. PUs possess unique properties and is used in various applications including foams, insulations, adhesives, sealants, coatings, and elastomers. For the preparation of urethane linkages through hydroxyl and isocyanate functions, various molecules are used, such as toluene diisocyanate (TDI), isophorone diisocyanate (3-isocyanatomethyl 3,5,5 tri methyl cyclohexylisocyanate) (IPDI), methylene bis(cyclohexyl isocyanate) (HMDI), and others. However, it was found that: (i) IPDI was found to be less reactive than TDI, (ii) a greater amount of HMDI must be used compared to TDI, and (iii) HMDI resins enhance pot life and minimize defects [3, 34, 35].

The manuscript aims to present the synthesis of poly(diamino cyclohexane urethane esteramide) (PUDCEA) and investigate the effect of fumed silica on coating properties. The results of physico-mechanical and corrosion resistance performance show that PUDCEA nanocomposite coatings have desirable properties on mild steel substrate. Furthermore, this study of using JO for poly(diamino cyclohexane urethane esteramide) synthesis illustrates utilization of a sustainable resource that has not been reported earlier.

2 Experimental

2.1 Materials

Jatropha oil [14,15]; trans1,2 diamino cyclo-hexane-N,N,N’,N’-tetraacetic acid (CDTA) (Sigma Chemicals, USA); toluene 2,4-diisocynate (TDI) (Acros Organic, USA); sodium metal, methanol, xylene, diethanolamine, diethyl ether, and sodium chloride (BDH Chemicals, Ltd. Poole, England); and fumed silica(surface area 395±25m2/gm, size 0.007 µm, refractive index 1.46.) (Sigma Aldrich, USA).

2.2 Instruments and methods

FTIR spectra of PDCEA and PUDCEA nanocomposites were collected on an FTIR spectrophotometer (Spectrum 100,Perkin Elmer Cetus Instrument, Norwalk, CT, USA) using a KBr cell. NMR spectra (1H and 13C) were taken on a Jeol DPX400MHz (Japan), where deuterated chloroform and tetramethylsilane were used as solvent and internal standard, respectively. Thermal stability of PUDCEA nanocomposites was measured by TGA and DSC (Mettler Toledo AG, Analytical CH-8603, Schwerzenbach, Switzerland). Here nitrogen atmosphere was maintained and 10°C/min was the heating rate. The molecular weight of PUDCEA was investigated by gel permeation chromatography (GPC) (HT-GPC Module 350A, Viscotek, Houston, TX, USA) using tetrahydrofuran (THF) as eluent at a flow rate of 1.0mL/min. The morphology of PUDCEA coatings was studied by scanning electron microscopy (SEM) (JEOL,JED-2200 Series, Japan). The topography of PUDCEA-coated panel was studied by atomic force microscopy (AFM)(A.P.E. Research, Basovizza 34149, Trieste, Italy). Physico-chemical studies of PDCEA and PUDCEA were evaluated by acid and hydroxyl value determination (ASTM D555-61 and ASTM D1957 -86, respectively).Coating properties of PUDCEA were evaluated by refractive index (ASTM D1218), scratch hardness (BS 3900), adhesion crosshatch (ASTM D3359-02), impact test (IS 101 part 5 s1,1988), pencil hardness test (ASTM D3363-05), flexibility/bending test (ASTM D3281-84), gloss (by Glossmeter, Model: KJG MG6-F1, KJG Photoelectrical Instruments Co., Ltd. Quanzhou, China), and thickness (ASTM D 1186-B). The potentiodynamic studies of PUDCEA nanocomposite coatings were conducted with a Gill AC (ACM Instruments, Cumbria, UK). The potentiodynamic measurements of PUDCEA coatings were performed in a three-electrode system at ambient temperature in various corrosive environments (tap water, 3.5wt% NaCl, and 3.5wt% HCl), with a platinum electrode as the counter electrode and a saturated calomel electrode as the reference electrode. PUDCEA-coated mild steel specimen was used as the working electrode; the exposed surface area of 1.0 cm² was fixed by a PortHoles electrochemical sample mask. Potentiodynamic polarization (PDP) was obtained using a sweep rate of 1.0 mV/s in the potential range ±250 mV with respect to the open circuit potential. PDP was used to evaluate the corrosion protective
performance of PUDCEA coatings. Each coating system was evaluated in triplicate for corrosion protection.

2.3 Preparation of N,N-bis(2-hydroxy ethyl) JO fatty amide (HEJA)

The synthesis of HEJA was carried out as per a previously published paper [14, 15].

2.4 Synthesis of poly(diamino cyclohexane esteramide) (PDCEA)

Initially, 4.0 mol of HEJA were heated to 80°C, and 2.0 mol of CDTA were added in a four-neck round-bottomed flask, placed on a magnetic stirrer with a hot plate. This flask was fitted with a Dean Stark Trap, thermometer and nitrogen inlet tube. The reactants were heated to 200°C, and a small amount of xylene was added for azeotropic distillation. The acid value was determined at regular intervals of time to monitor the progress of the reaction.

After the desired acid value was achieved, the xylene solution of PDCEA was poured in a separating funnel and distilled water was added. The contents were swirled and were allowed to stand till the xylene and water layer separated. The water layer was removed and tested for unreacted acid. The washing process was repeated until the solution was free from any unreacted acid. The xylene solution was then passed through anhydrous sodium sulphate to remove traces of moisture followed by the removal of xylene in rotary evaporator. The pure PDCEA thus obtained was tested by FTIR and NMR.

2.5 Synthesis of poly(diamino cyclohexane urethane esteramide) (PUDCEA)

For urethane modification, 10 g PDCEA, dissolved in xylene (20mL), and TDI (10wt%, 12wt%,14wt%) were added in a four-neck round-bottomed flask, placed on a magnetic stirrer with a hot plate. This flask was fitted with a cold water condenser, Dean Stark Trap, thermometer and nitrogen inlet tube. The contents were heated to a temperature of 120°C. The progress of the reaction was monitored by hydroxyl value determination at regular intervals of time. The solvent was evaporated by vacuum during the physico-mechanical testing; it was found that the 3wt% fumed silica in PUDCEA nanocomposite showed the best coating properties. PUDCEA-3 resin was dissolved in a 40% solution of xylene and applied by brush technique to mild steel panels. The coated panels are left to dry at room temperature After 10 days, coating became dry – to- hard; at this stage they were subjected to physico-mechanical and corrosion tests.

2.6 Synthesis of fumed silica modified poly(diamino cyclohexane urethane esteramide) (PUDCEA)

For nanocomposite preparation, PUDCEA, prepared from 12% TDI, was loaded with 1wt%, 2wt%, and 3wt% fumed silica before the urethane reaction. 10 g PDCEA was dissolved in xylene (20mL), and fumed silica was added in different percentages (1wt%, 2wt%, and 3wt%) at 30°C (to obtain PUDCEA1, PUDCEA2, PUDCEA-3, respectively. The contents of the flask were stirred for 30 minutes and then TDI (12 wt%) was added drop-wise to the reaction flask containing PDCA and fumed silica. This flask was fitted with a cold water condenser, Dean Stark Trap, thermometer and nitrogen inlet tube. The contents were heated to a temperature of 120°C. The progress of the reaction was monitored by hydroxyl value determination at regular intervals of time. The solvent was evaporated by vacuum during the physico-mechanical testing; it was found that the 3wt% fumed silica in PUDCEA nanocomposite showed the best coating properties. PUDCEA-3 resin was dissolved in a 40% solution of xylene and applied by brush technique to mild steel panels. The coated panels are left to dry at room temperature After 10 days, coating became dry – to- hard; at this stage they were subjected to physico-mechanical and corrosion tests.

3 Results and discussion

Scheme 1 and Scheme 2 show the synthesis of PDCEA and PUDCEA. PDCEA, synthesized by chemical reaction (condensation) between HEJA and CDTA, was reacted with TDI through an addition reaction to form PUDCEA, which had added fumed silica (1wt%,2 wt%, and 3wt%). Beyond the 3wt% loading of fumed silica, the coating properties deteriorated. Acid values (20,15,13,12,10), hydroxyl values (261,60,58,57,55) and number of OH group per 100gm (7.923,1.821,1.760,1.730,1.669) decreased from PDCEA to PUDCEA-3, with the descending order PDCEA>PUDCEA>PUDCEA-1>PUDCEA-2>PUDCEA-3. Refractive index values (1.4987,1.5020,1.5119,1.5205,1.5212) increased from PDCEA to PUDCEA-3. These values show noticeable increase, with an increased amount of fumed silica. The molecular weight of PUDCEA was found to be 6285(Mw) and 3928(Mw), with a polymer polydispersity index of 1.60 (Figure 1). The preparation of PDCEA and PUDCEA was confirmed by spectral analyses (FTIR and NMR). PUDCEA resins are soluble in xylene, toluene,
Scheme 1: Synthesis of PDCEA.

Scheme 2: Synthesis of PUDCEA.
dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), chloroform and tetrahydrofuran (THF) and in soluble in aqueous solvent. The coated panels are left to dry at room temperature and the curing occurs in following steps: (i) the evaporation of solvent occurs, (ii) the free –NCO groups undergo curing at room temperature by reacting with atmospheric moisture, and (iii) the double bonds of fatty acid chain of oil also undergo auto-oxidation and the coating is finally cured over the substrate.

3.1 Spectral analysis

PDCEA, FTIR (cm\(^{-1}\)): 3327(OH); 2925 (CH\(_2\), asymmetrical); 2854 (CH\(_2\), symmetrical); 1745 (C=O, ester); 1636(C=O, amide); 1454 (C-N, stretching); 3006 (-CH=CH-);
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1180,1090 (-C(O)O-C- stretching) (Figure 2).

**PUDCEA:** 3300 (N-H, stretching); 3027 (-CH=CH-); 2937 (CH\textsubscript{2}, asymmetrical); 2846 (CH\textsubscript{2}, symmetrical); 2719 (C-H, stretching); 2337 (free NCO); 1736 (C=O, urethane, ester); 1646 (CO, amide); 1446 (C-N, stretching); 1227, 1118, 1046 (-C(O)O-C- stretching); 1500, 864, 773 (aromatic); 700 (NH, bending) (Figure 2).

**PUDCEA-2** and **PUDCEA-3** showed additional bands at 1054 and 1064 (O-Si-O) [31].

**PDCEA**\textsubscript{13}C NMR (CDCl\textsubscript{3}, \textdelta ppm): 13.995 (terminal chain CH\textsubscript{3}); 22.064-26.690 (CH\textsubscript{3} of TDI); 28.684 (–CH\textsubscript{2}– attached CO–); 30.092 (chain–CH\textsubscript{2}–); 31.512 (–CH\textsubscript{2}– attached double bond); 45.564 (CH\textsubscript{2} attached N); 50.051 (–CH\textsubscript{2}–OH); 57.800 (CO–CH\textsubscript{2}–N–); 60.021-66.231 (CH\textsubscript{2}OH, –CH\textsubscript{2}–O–, cyclic CH–N–); 127.520-130.321 (–CH\textsubscript{2}–CH); 172.406-174.685 (CO, amide, ester) (Figure 5). Additional peaks for **PUDCEA:** 19.021 (CH\textsubscript{3} of TDI); 120.231-137.106 (aromatic C); 144.213 (free NCO); 165.021 (CO, urethane) (Figure 6).

### 3.2 SEM and EDX analysis

SEM micrograph (Figure 7) of PUDCEA/fumed silica nanocomposite coating suggests that the coated film has uniform surface. There were no noticeable cracks; silica nanoparticles were not well-defined in shape, however, they showed an even dispersion in PUDCEA matrix. EDX spectrum supported the finding that SiO\textsubscript{2} nanoparticles were present in PUDCEA matrix.

### 3.3 Topography

Figure 7 show the topography of PUDCEA-2 nanocomposite coating before and after it was exposed to salt spray test. The initial topography of PUDCEA-2 (Figure 8A) reveals a smooth and uniform surface with nanoscale roughness (16 nm); the image distinctly reveals the even dispersion of silica nanoparticles in PUDCEA matrix. The AFM topography (Figure 8B) image after exposure in salt spray test indicates that coating surface has nanoscale roughness.
Figure 4: $^1$H NMR spectra of PUDCEA.

Figure 5: $^{13}$C NMR spectra of PDCEA.
Figure 6: $^{13}$C NMR spectra of PUDCEA.

Figure 7: SEM-EDX of PUDCEA-2 nanocomposite.
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roughness (45 nm) and shows some defects in coating like pinholes, pores and increased surface roughness because solvent penetrated the coating surface.

3.4 Thermal analysis

Figure 9 shows TGA thermograms for PDCEA, PUDCEA, and PUDCEA-2 nanocomposite coatings. 5% weight loss of each sample at 257°C, 230°C and 245°C, respectively, can be correlated to the trapped solvent being evaporated. 50% weight losses of PDCEA, PUDCEA and PUDCEA-2 at 418°C, 424°C and 429°C are due to thermal degradation. DTG thermograms of PDCEA, PUDCEA and PUDCEA-2 clearly show each decomposition step in Figure 10. One peak in PDCEA runs between 288°C and 546°C, centered (T\text{max}) at 420°C. The peak in this particular temperature range corresponds to 50% weight loss in the TGA thermogram. In case of PUDCEA, three decomposition peaks are seen: one between 180°C and 305°C, centered (T\text{max}_1) at 262°C; the second decomposition from 305°C to 440°C, centered (T\text{max}_2) at 408°C; and the third decomposition from 440°C to 546°C, centered (T\text{max}_3) at 480°C. In PUDCEA-2, the first decomposition begins at 176°C and ends at

Figure 8: (A) AFM topographic image of PUDCEA coating, (B) AFM topographic image of PUDCEA-3 coating surface after exposed in salt spray.
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210°C, centered ($T_{\text{max}_1}$) at 253°C; the second starts from 210°C to 360°C, centered ($T_{\text{max}_2}$) at 336°C; the third goes from 360°C to 446°C, centered ($T_{\text{max}_3}$) at 427°C; and a fourth decomposition starts at 446°C and ends at 546°C, centered ($T_{\text{max}_4}$) at 475°C. The first, second, and third decomposition peaks of PUDCEA and PUDCEA-2 are due to the decomposition of urethane, ester and amide linkages, and hydrocarbon chains, respectively; slightly shifting of the peaks is due to the inclusion of nanoparticles and the formation of strong polymeric-inorganic interactions.

DSC thermograms (Figure 11) of PDCEA, PUDCEA and PUDCEA-2 show an endotherm peak observed to start at 125°C and end at 275°C, centered at 191°C; second starts from 100°C to 313°C, centered at 215°C; and the third starts from 188°C and goes to 225°C, centered at 202°C, respectively. These peaks can be attributed to the onset of melting of PDCEA, PUDCEA, and PUDCEA-2, followed by the decomposition process. An exotherm is seen beyond this temperature due to decomposition of resin as is also observed in TGA thermogram. Other small peaks are relevant to some configurational changes in the polymer chain backbone.

3.5 Physico-mechanical properties

PUDCEA coatings are produced by drying at ambient temperature. The coating thickness was obtained to be 125 ± 5 µm. The scratch hardness values of PUDCEA coatings increased from PUDCEA (1.8 kg) to PUDCEA-1 (2.5 kg), PUDCEA-2 (3.0 kg) and PUDCEA-3 (2.8 kg), beyond which the scratch hardness value deteriorated. The pencil hardness values were found to be 1B (PUDCEA), 2H (PUDCEA-1), 3H (PUDCEA-2), and HB (PUDCEA-3), deteriorating beyond PUDCEA-2. The coating properties deteriorate...
beyond 2 wt% loading of fumed silica in PUDCEA resin. The coatings showed good impact resistance (150 lb/inch), bending ability (1/8 inch) and the cross-hatch test results were 100%. The thickness of PUDCEA coating was approximately 68±5 µm.

Beyond 3 wt% loading, the performance of the coatings deteriorates. Silica particles increase the adhesion, flexibility and impact resistance of coatings due to good interactions between organic and inorganic phases. Beyond 3 wt% loading, there may be inadequate interactions between organic PU and inorganic Si phases, due to overloading of silica. The fumed silica particles occur as aggregates, these allow for particle-particle interactions and compactness in aggregates. We understand that 3 wt% is the optimum loading of fumed silica for PU nanocomposites, and beyond 3 wt% of fumed silica inclusion, the compactness between particles increases so much that it leads to rigidity, stiffness and brittleness in coatings deteriorating the overall performance [36].

3.6 Corrosion studies

The Tafel plots (Figure 12) of bare carbon steel CS and PUDCEA, PUDCEA-1, PUDCEA-2, and PUDCEA-3 nanocomposite-coated CS permitted the determination of electrochemical parameters after immersion for 300 h in an acidic medium. Table 1 summarizes the values of corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), corrosion rates (CR) and linear polarization resistance (RP) of bare CS and PUDCEA, PUDCEA-1, PUDCEA-2, and PUDCEA-3 nanocomposite-coated CS. The polarization curve indicates positive displacement in $E_{corr}$ relative the value of bare CS. The corrosion parameters for bare CS and PUDCEA coated CS clearly indicate that $E_{corr}$, $I_{corr}$ increases from bare CS to PUDCEA, PUDCEA-1, PUDCEA-2 and PUDCEA-3, and $I_{corr}$ values decreases. These observations indicate that PUDCEA provided a barrier method of corrosion protection for CS, thus enhancing the resistance towards corrosion. The corrosion potential shift indicates improved protection of CS by the barrier provided by PUDCEA coated on CS surface. PDP measurements clearly reveal reduction in CR for PUDCEA-3 coated surface (3.33E-06mpy) with respect to the bare CS (25.049mpy).

Figure 13 shows the Tafel plots after immersion for 240 h in a saline corrosive media. $E_{corr}$ values of CS and PUDCEA, PUDCEA-1, PUDCEA-2, and PUDCEA-3 are given in Table 1. These values shifted to more positive values with increasing amounts of fumed silica in PUDCEA compared to bare CS. $I_{corr}$ values decreased gradually and RP values increased. The $E_{corr}$, $I_{corr}$, and $I_{corr}$ values trends indicate the corrosion resistant nature of nanocomposite coating. PUDCEA coated CS with fumed silica nanoparticles show remarkable improvement in corrosion resistance properties. It is therefore likely that the presence of SiO$_2$ particles in PUDCEA matrix provide protective barrier and reduce the interaction between Cl ions and the CS surface [37-38].

Figure 14 shows the Tafel plots of CS and PUDCEA, PUDCEA-1, PUDCEA-2 and PUDCEA-3 after an immersion period of 240 h in tap water. As indicated in Table 1, $E_{corr}$ values of PUDCEA coated panels showed an increase as the amount of fumed silica inclusion increased in coatings, and also higher values of Rp and smaller values of $I_{corr}$ were observed relative to PUDCEA coated CS strips. The anticorrosive property of PUDCEA-3 film has been enhanced due to the dispersion of SiO$_2$ in PUDCEA.
The corrosion protection effect of PUDCEA-3 is attributed to an increase in amount of SiO$_2$ revealing a reduced permeability of coated surface to corrosive ions and diffusion pathways of water and oxygen, as compared to PUDCEA coating, due to presence of dispersed silica nanoparticles. It was found that lowest corrosion rates were exhibited under PUDCEA-3 nanocomposite film.

### Conclusions

Poly(urethane esteramide) nanocomposites containing fumed silica were prepared from Jatropha oil, a sustainable resource. From this study, it can be concluded that sustainable Jatropha oil can be used successfully for the synthesis of PUDCEA-SiO$_2$ nanocomposite. PUDCEA-SiO$_2$ resins have good adhesion, hardness, gloss, and anticorrosive properties in various corrosive environments (tap water, 3.5wt% NaCl, and 3.5wt% HCl). PUDCEA-SiO$_2$ coating serves as a barrier to protect substrate, such as carbon steel surface. PUDCEA-fumed silica coatings can be used safely at temperatures up to 200°C.

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### Conflict of interest

Authors declare no conflict of interest.
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