Linseed oil polyol/ZnO bionanocomposite towards mechanically robust, thermally stable, hydrophobic coatings: a novel synergistic approach utilising a sustainable resource

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Linseed oil polyol/ZnO bionanocomposite was prepared to obtain mechanically robust, thermally stable, hydrophobic coatings via a novel synergistic approach utilising a vegetable oil polyol for the first time. The synthesis process obviates the use of reducing agents, surfactants, reaction media, stabilizing agents, solvents, and other chemicals. Linseed polyol serves the purpose of obtaining ZnO nanoparticles. The linseed polyol backbone hosts hydroxyl and carboxylic groups that participate in the generation of ZnO nanoparticles in the polyol matrix (ester elimination, addition–elimination reaction). The progress of the reaction was monitored by recording FTIR spectra at regular intervals of time. The coatings obtained were scratch-resistant, impact-resistant, well-adherent, flexibility-retentive and hydrophobic, showing good chemical resistance under acidic, alkaline, and salt environments. Thermogravimetric analysis revealed that these coatings could be safely used up to 250 °C. The work described is consistent with the principles of ‘Green Chemistry’ (Principles 1, 2, 3, 4, 5, 6, 7, 8, and 12), such as utilising a renewable feedstock, resorting to a solventless approach, and employing safer chemistry. The results showed that these coatings may be well employed as promising candidates towards environmentally friendly corrosion protective coatings.

Introduction

Bionanocomposites [BNCs] are an emerging class of biohybrid materials developed from the combination of biopolymers such as polysaccharides, proteins, nucleic acids, starch, cellulose, oils from plant and animal origin, and others, with inorganic solids (spanning from clays to phosphates or carbonates, and metal oxides) at the nanometric scale. The most significant challenge is to finally obtain BNCs with superior performance, by precise and notable management of the individual properties of their components. The cost-effectiveness, non-toxicity, biocompatibility and biodegradability characteristics of biopolymers, coupled with the mechanical and thermal properties of the inorganic components bridge the gap between functional and structural/reinforcing materials, introducing synergism into the final product. The overall underlying idea is to harness nature’s abundant sustainable resources, by combination of the “green” characteristics of biopolymers and the high performance rendered by nanomaterials for advanced functional applications such as drug delivery, medicine, sensing devices, flame retardancy, food packaging, gas-diffusion barriers, protective coatings and others.1-3,7

Plant oils are nature’s most abundantly available, cost effective, non-toxic and environmentally friendly bioresources. Their derivatives such as alkyls, polyesteramides, polyurethanes [PU] and others find applications as biodiesel, printing inks, lubricants, adhesives, coatings and paints.3-5 BNCs from plant oil derivatives have been obtained with nanosized reinforcements such as nano-clays,6 nano-metal/metal oxides,7 graphene,8,9 carbon nanotubes,10 fumed silica,11 conducting polymers12 and others. The inclusion of such nanoparticles overcomes some drawbacks of plant oil derivatives such as poor load bearing ability, hardness, inadequate rigidity and strength,2,11,12 and improves the antimicrobial behavior,11-16 thermal stability,7,11,16 corrosion protection performance17,18 and other properties, in final BNCs thus broadening their areas of applications. The literature is replete with examples comprising the synthesis, characterization and applications of plant oil...
based BNCs. Heidarian et al. produced castor oil [CO] PU/organically modified montmorillonite [OMMT] clay nanocomposites, via 1–3 wt% loading of OMMT by an in situ polymerization technique through an ultrasonication assisted process, for use as protective coatings that showed superior performance relative to pristine PU. Raju et al. developed hydrophobic CO PU/urea–silica hybrid coatings by introducing hydrolyzable –Si-OCH₃ groups using 3-glycidoxypropyltrimethoxysilane by chemical reaction. Waterborne CO PU–silica nanocomposites with silica nanoparticles chemically bonded to the polymer matrix have been successfully prepared through a sol–gel process by Larock et al. The chemically bonded inorganic silica groups within the oil chains (i) act as reinforcement filler, (ii) increase cross-link density and (iii) improve thermal properties of final PU, rendering better mechanical and viscoelastic properties as compared to plain coatings. Karak et al. reported in situ prepared CO based hyperbranched PU [HPU]/functionalized reduced graphene oxide (f-RGO) nanocomposites obtained through covalent and noncovalent linkages of f-RGO with prepolymer chains of HPU. The use of f-RGO was both as a reactive chain extender as well as a nano-reinforcing agent incorporating improved properties compared to the unmodified counterpart. In another report, Karak et al. prepared CO based hyperbranched BNCs with polyaniline nanofibres as modifier for use as antistatic materials and also as potent antimicrobial materials due to their pronounced antimicrobial activity against a spectrum of bacterial and fungal strains as well as algal species. Kasra and co-workers developed gold nanotube/nanowire–PU composites from CO and polyethylene glycol to develop biodegradable biomaterial scaffold with an optimum initial mechanical integrity for implantation. Recently, Rahman and Ahmad reported the synthesis, characterization and corrosion resistance performance of soy alkyd/Fe₃O₄ nanocomposite coatings. Ferrite nanoparticles played a prominent role in conferring high thermal stability, good hydrophobicity, enhanced physicochemical properties and higher corrosion resistance performance to coatings. In a novel approach, Pramanik et al. opted for green chemistry route for the noncovalent functionalization of multiwall carbon nanotubes [MWCNTs] using fatty amide diol of CO, followed by the preparation of hyperbranched CO polyetheramide/MWCNT nanocomposites by an in situ polymerization technique using CO fatty amide diol functionalized MWCNTs and dibasic acid/anhydride as bifunctional monomers and diethanol amine as trifunctional monomer in appropriate composition. The prepared BNCs showed pronounced antibacterial activity against gram-positive bacterial strains.

Plant oil based polyols are triglycerides of fatty acids bearing number of hydroxyl groups in their backbones. They are obtained chemically by hydroxylation, inserting hydroxyl groups at the double bonds of parent oil. CO is a naturally available polyol. Unlike CO that has one hydroxyl group per fatty triester chain, plant oil polyols (obtained chemically) have the advantage of bearing 4–6 hydroxyl groups per fatty triester chain depending upon the possible extent of hydroxylation. The plurality of hydroxyl groups renders them higher viscosity relative to CO due to inter- and intra-molecular hydrogen bonding. Thus, apart from being nontoxic, inexpensive, and readily available from a renewable resource, such polyols contain multiple hydroxyl groups that provide multifunctional sites to form randomly crosslinked networks and enhance both the degradability and mechanical properties of the resulting polymer.

The increase in the use of environmentally friendly raw materials, environmentally benign syntheses, formulation and processing methods in research and industry has beckoned several researchers to resort to clean and green methods of syntheses. Numerous research papers focus on the synthesis of nanoparticles [NP] by the use of starch, dextrose, arabinose, fruit extracts, plant extracts, biodegradable polymers, bacteria, enzymes, and others as substitute to dangerous chemicals, via little/no solvent process, low temperature heating or by microwave irradiation. The prime advantage herein is that no external capping agent, reducing agent, surfactant or template is required for the synthesis of NP; the green and cost-effective raw material itself performs all these functions. Zinc oxide [ZnO] has wide application in various fields, such as short-wavelength light-emitting diodes, gas sensors, catalysis, solar-energy conversion, and in optoelectronic devices. The in situ synthesis of NP is an important method to prepare nanoscaled particles with good dispersion in polymer matrix obviating the phase segregation phenomenon which is often encountered in the direct melt mixing alcoholysis route. For an in situ approach, whether involving the synthesis of NP such as metal oxides, the intercalation or exfoliation of montmorillonite [MMT] platelets or functionalisation of modifiers like RGO or MWCNTs, advantage is taken of the multitude of functional groups [i.e., hydroxyl, epoxy, urethane, double bonds] present on the plant derivative backbone. The presence of NP in nanocomposite coatings offers significant barrier properties for corrosion protection. They tend to fill cavities and small holes in coatings and cause crack bridging, deflection and crackbowing. They decrease porosity and provide tortuous diffusion path for deleterious species. In plant oil derivatives, NP offer additional advantages of drastically improving mechanical strength relative to the virgin polymer.

The above studies beckoned us to use a plant oil based polyol for the present study. We selected linseed oil [LO] as the parent oil to produce linseed polyol [LP]. Zinc(II) acetate [ZnAc] was used here as the inorganic precursor to generate ZnO NP. We have resorted to an in situ preparation of ZnO NP in LP. This study is the first of its kind utilising plant oil polyol in place of commercial polyols (ethylene glycol, polyethylene glycol). LP derived nanocomposites were tested for their physicochemical performance (scratch hardness, impact resistance, bending ability, and adhesion) by standard methods and also for their corrosion resistance performance in different media, by potentiodynamic polarisation measurements and electrochemical impedance spectroscopy (EIS). LP nanocomposites produced scratch resistant, impact resistant, flexible, glossy, well-adherent, hydrophobic coatings by zero solvent approach, i.e., no solvent was used during the synthesis, formulation and
application of coatings. Such an approach utilizing “green” bioresource based feedstocks via “green” coating technologies such as solventless coatings is a “green + green” solution to the persisting economic and environmental regulations and challenges. 47

Experimental

Materials

ZnAc was obtained from Merck, India. Phthalic anhydride [PAN] was purchased from S.D. Fine Chemicals, India. Petroleum ether, hydrogen peroxide (30%), glacial acetic acid, sodium chloride (99%) and hydrochloric acid (35–36%) were obtained from Fisher Scientific, India, and deionized water was also used.

All the chemicals were of analytical grade and were used as received.

Synthesis of linseed oil polyol [LP]

LP was prepared from LO according to our previously reported method by hydroxylation reaction (peracetic acid procedure). 37, 48 LO and glacial acetic acid (with few drops of sulphuric acid) were placed in a three-necked round-bottomed flask equipped with a thermometer, magnetic stirrer, and cold water condenser. The flask was placed in a cold-water bath and hydrogen peroxide (30%) was added drop wise into the reaction mixture (keeping the ratio of double bonds : acetic acid : hydrogen peroxide as 1 : 0.5 : 1.5). The temperature was then raised to 50 ± 5 °C, and constant stirring was continued. The reaction was monitored by recording epoxide equivalent (EE) at regular intervals of time followed by thin layer chromatography (TLC). When the desired (low) value of EE was achieved, the sample was subjected to spectral analysis to confirm epoxidation. The reaction temperature was further raised to 75 ± 5 °C, and reaction was continued until the desired (high) value of EE was achieved, due to further epoxy ring opening (hydroxylation) producing LP. A small amount of this sample was subjected to spectroscopic analysis to confirm the introduction of hydroxyl groups forming LP. The pure LP was then obtained by first dissolving the reaction product in diethyl ether, followed by washing with sodium chloride aqueous solution in a separatory funnel. It was further dried over anhydrous sodium sulphate. Diethyl ether was removed using a rotary vacuum evaporator at 45 ± 5 °C. While LO is light yellow (Fig. 1a), the obtained LP was golden yellow in color (Fig. 1b). The course of reaction and structure of the final product LP were confirmed by spectral analyses (FTIR and 1H NMR).

Synthesis of linseed oil polyol-polyester [LPP]

LP was placed in a three-necked flat bottomed flask equipped with a thermometer, cold water condenser and nitrogen inlet tube. The assembly was placed over a heating plate with a magnetic stirrer. PAN was gradually added in small portions to the flask containing LP over a period of 15 minutes with constant stirring at 120 ± 5 °C. The flask was then left undisturbed, and stirring was continued until completion of the reaction was achieved, maintaining the reaction temperature. The progress of the reaction was monitored by TLC, acid and hydroxyl value determination, at regular intervals of time. The reaction mixture was observed for clarity and (any) perceptible changes in viscosity throughout the course of the reaction.

Synthesis of the LPP/ZnO composite [LPP/ZnO]

LP was placed in a three-necked flat bottomed flask equipped with a thermometer, cold water condenser and nitrogen inlet tube. The assembly was placed over a heating plate with a magnetic stirrer. PAN was gradually added in small portions to the flask containing LP over a period of 15 minutes with constant stirring at 120 ± 5 °C. The stirring was continued for another 15 minutes; then the temperature was lowered to 80 ± 5 °C followed by the slow and continuous addition of ZnAc in varying amounts (0.04, 0.06, 0.08, 0.1 mol) for a period of another 15 min under constant stirring. The flask was then left undisturbed and stirring was continued until completion of reaction was achieved, maintaining the reaction temperature at 80 ± 5 °C. The progress of the reaction was monitored by recording FTIR spectra of the intermediate species at regular intervals of time. The reaction mixture was closely observed for clarity and (any) perceptible changes in viscosity throughout the course of the reaction. 55, 49

It is worth mentioning that during the synthesis of LPP/ZnO beyond 0.1 mol ZnAc, a highly viscous product was obtained that was not suitable for coating preparation. The obtained LPP/ZnO-0.04, LPP/ZnO-0.06, LPP/ZnO-0.08 and LPP/ZnO-0.1 (0.04,
0.06, 0.08, 0.1 represent the added moles of ZnAc) were golden yellow but of darker hue relative to LP (Fig. 1c.).

Preparation of coatings
The commercially available carbon steel [CS] specimens with composition of (in wt%) 2.87 C and 97.13 Fe, were polished successively with different grades of emery papers (600, 800, 1000, and 1200 grade). The specimens were washed thoroughly with double distilled water, degreased with methanol and acetone, and dried at room temperature. LPP and LPP/ZnO were applied using a brush technique on CS panels of standard size (70 mm x 25 mm x 1 mm) for physico-mechanical tests and (25 mm x 25 mm x 1 mm) for electrochemical corrosion tests as well as morphological studies. The coated CS specimens were placed in a vacuum oven and then stowed at 150 °C for 48 hours to obtain well dried LPP/ZnO coatings.7,50,51

Characterisation
Physicochemical properties of the resins such as iodine value, refractive index, specific gravity and inherent viscosity were determined by standard test methods (Table 1).

FTIR spectra were recorded on an IRAffinity-1 CE (Shimadzu corporation analytical and measuring instrument division, Kyoto, Japan). FTIR spectra of the intermediate species were taken by placing the samples between two zinc selenide windows with a 0.05 mm thick tefflon spacer, every 20 minutes. All the spectra were recorded averaging 40 scans at 4 cm⁻¹ resolution on an IRAffinity-1 spectrometer. All samples were scanned from 4500 to 600 cm⁻¹ with a resolution of 4 cm⁻¹. Data acquisition was carried out through IR solution software.1 H NMR spectra of LO, LP and LPP/ZnO were obtained on a JEOL GSX 300 MHz FX-100 in CDCl₃ using tetramethylsilane (TMS) as the internal standard.

Photographs of the samples were taken with a Nikon camera (COOLPIX8100, 12.1 MP).

Optical images of the samples were recorded using a Lietz Optical Microscope Model (Metallux-3), at 100× and 200× magnifications.

Transmission electron microscopy (TEM) images were captured for the morphological study of individual phases i.e., inorganic ZnO NP and the organic LP, phase, with a TECNAI 200 kV TEM operating at 200 kV (Fei, Electron Optics), equipped with digital imaging and a 35 mm photography system, at the All India Institute of Medical Sciences, New Delhi, India. A well diluted solution of the test sample was prepared in ethanol, transferred to a “click-lock” 1.5 ml microcentrifuge tube, and submerged in water, in an ultrasonic bath for sonication for a 30 minute duration. A drop of this sonicated sample solution was then placed on a carbon Type-B (carbon film supported) 200 mesh copper grid with a micro pipette. The grid was allowed to dry well before being used for TEM analysis.

Table 1: Physico-chemical analyses of LPP and LPP/ZnO

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Iodine value (g I₂/100 g)</th>
<th>Refractive index</th>
<th>Specific gravity</th>
<th>Inherent viscosity (dL/gm)</th>
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</thead>
<tbody>
<tr>
<td>LPP</td>
<td>64</td>
<td>1.48</td>
<td>1.079</td>
<td>0.916</td>
</tr>
<tr>
<td>LPP/ZnO-0.04</td>
<td>60</td>
<td>1.50</td>
<td>1.183</td>
<td>0.930</td>
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<tr>
<td>LPP/ZnO-0.05</td>
<td>57</td>
<td>1.51</td>
<td>1.186</td>
<td>0.953</td>
</tr>
<tr>
<td>LPP/ZnO-0.06</td>
<td>55</td>
<td>1.53</td>
<td>1.199</td>
<td>0.985</td>
</tr>
</tbody>
</table>

Thermal analysis was carried out using a TGA/DSC1 (Mettler Toledo AG, Analytical CH-8603, Schwerzen-bach, Switzerland), in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

Coatings of the nanocomposite were prepared on CS panels (Fig. 1d). Prior to application over the substrate, the material was sonicated with an Ultrasonic wave sonicator (model no. 1.5L 50H) at 30 °C. The coatings of LPP/ZnO were applied on CS panels by brush and were placed in a vacuum oven at 150 °C for 48 hours. The thickness of the well dried coatings was found to be in the range of 80–90 μm as evaluated by an Elcometer (Model 345; Elcometer Instruments, Manchester, UK).

The coatings were tested for physico-mechanical performance by analysing the scratch hardness [SH] [BS 3900], impact resistance (IR) [IS; 101 part 5/sec-3, 1998], specular gloss (at 45°), and performing a bending test (BT) [ASTM-D3281-84] and a cross-hatch adhesion tape test (by cross hatch tester, supplied by CONFORMITY, INDIA; ASTM D-3359-95a). The impact of the aforementioned tests on coating surfaces was also assessed by taking electronically recorded optical micrographs using a Lietz Optical Microscope Model (Metallux-3) Microscope (at 100× and 200× magnifications).

The hydrophobicity of the coatings was evaluated by contact angle measurements using a Drop Shape Analysis System (model DSA10MK2, Kruss GmbH, Germany) with a high speed CCD camera for image capture, at the National Physical Laboratory (NPL) New Delhi, India. Deionized water was used for the evaluation of the hydrophobic properties of the coated substrate. Water was taken up in a syringe, drops (15 mL) were allowed to fall onto the substrate, and the left and right contact angles were measured for 10 s at 1 s intervals. The angle measurements were done in triplicate. By using the three values of the left and right contact angles, the average contact angle was calculated.50–52

The electrochemical corrosion behavior of uncoated CS, LPP and LPP/ZnO nanocomposite coated CS was investigated in 3.5 wt% NaCl and 3.5 wt% HCl solutions, at room temperature. The open circuit potential (OCP), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopic (EIS) studies on the bare CS, LPP and LPP/ZnO nanocomposite coatings were carried out using a EG&G cell with three electrodes, i.e. with the test samples as the working electrode, the Pt gauge as the auxiliary electrode and Ag/AgCl as the reference electrode (Table 3).

Table 1: Physico-chemical analyses of LPP and LPP/ZnO
electrode with a Potentiostat/Galvanostat microAutolab type III (µ3AVT 70762 The Netherlands) controlled by a microprocessor based electrochemical software Nova 1.8. These tests were repeated at least three times to ensure the reproducibility of the results. Tafel parameters were extracted by a curve fitting procedure available in the software. A 1.0 cm² area of the working electrode was exposed to the solution and only the coated surface was exposed to the electrolyte. The working electrode was first maintained in a test environment for 30 min before the impedance run. This step served to put the electrode in a reproducible initial state and to make sure that no blistering occurred during the incubation period of the electrode potential. All experiments were conducted at room temperature. After OCP stabilization, AC (alternating-current) impedance measurements were conducted at the OCP with a 20 mV amplitude of the sinusoidal voltage signal at the applied frequencies in range of 100 kHz to 0.1 Hz using ten points per decade. The impedance spectra obtained for the coated CS can be used to model the behavior of a coated substrate by an equivalent circuit as presented in Fig. 2. The polarization curves were recorded by sweeping the potential from −100 mV to 100 mV (with respect to the OCP) in noble direction at a constant scan rate of 0.001 mV s⁻¹. The corrosion current (Icorr) was determined by superimposing a straight line along the linear portion of the cathodic and anodic curves and extrapolating it through the corrosion potential (Ecorr).

The polarization resistance (Rp) of the tested samples was evaluated by Nova 1.8 software from the slope of potential–current plots (Tafel plots), according to the Stearn–Geary equation:55

\[ R_p = \frac{b_a b_c}{2.303(b_a + b_c)I_{corr}} \]  

(1)

here Icorr is the corrosion current, determined by an intersection of the linear portions of the anodic and cathodic curves, and ba and bc are the anodic and cathodic Tafel slopes (ΔE/Δlog I), respectively. After the PDP and EIS tests, the tested coated panels were observed under an optical microscope and the respective images were recorded.

The salt spray test (ASTM B 117-94) of the coated LPP and LPP/ZnO was carried out for a period of 10 days in a salt mist chamber under a 5 wt% NaCl solution at 90% humidity. Optical micrographs of the corroded as well as the un-corroded coated CS samples were also studied to evaluate the changes in the coatings brought about by exposure to the salt fog environment.

Results and discussion

Synthesis and mechanism

LP was prepared by the hydroxylation (epoxidation followed by hydration) reaction of LO as reported previously. During this reaction, first epoxidation occurred at the double bonds of LO, followed by epoxy ring opening, subsequently producing LP by the addition of hydroxyl groups. The insertion of hydroxyl groups at the double bonds was confirmed by spectral analysis (Fig. 3a, b and 4a). LP has a multitude of hydroxyl groups (Scheme 1). It is highly viscous relative to virgin LO owing to the inter- and intra-molecular hydrogen bonding amongst the constituent hydroxyl groups on the LP backbone. As LP is treated with PAN (acting as crosslinker between LP chains), firstly the anhydride group of PAN and the OH group of LP react with each other (esterification) producing LPP networks (Scheme 2). LPP is also a kind of linseed polyol but with additional ester groups. The LPP matrix has two sites that participate in the generation of ZnO and nanocomposite formation: (i) free hydroxyls, and (ii) free carboxyls (introduced by PAN through a chemical reaction between LP and PAN) in the LPP backbone (as in Scheme 2). The mechanism of the formation of the ZnO nanoparticles proceeds by a nonhydrolytic alcoholysis route based on a well-known ester-elimination reaction that involves the nucleophilic attack of the free hydroxyl groups of LPP on the carbonyl carbon atom of the zinc acetate derivative (Scheme 3 & 4), leading to an in situ “solventless, one pot” preparation of LPP/ZnO. The dimensions of the obtained ZnO range from a few nanometres to micrometers in size. The chemical reactions at the free carboxyl groups of LPP (Scheme 3 & 5) occur between the –COOH group of LPP and ZnAc by an addition–elimination mechanism at the carbonyl double bond of the carboxylic acid end group of the LPP chain (Scheme 5), as is evident from the spectral studies and also from the literature. LPP is used as:

(i) a base matrix,

(ii) a solvent due to its inherent fluidity characteristics,

(iii) a reaction medium providing functional groups for chemical reactions (between the hydroxyls of LPP and Zn–Ac resulting in the formation of nano-sized metal oxide particles in LPP), producing nanocomposites, and also as

(iv) a stabilizer preventing the agglomeration of nanoparticles.

This synthesis process does not require any other chemicals like reducing agents, surfactants, reaction media, stabilizing agents and others. Most importantly, we have also not used any solvents in this work as long aliphatic flexible chains of LP prove advantageous in this context due to their fluidity characteristics. Both LP and LPP act as reactants as well as reaction solvents and capping reagents for particle growth and architectural control. The chemical reaction for the formation of LPP/ZnO was monitored by recording FTIR spectra of the starting materials and the intermediate species formed during the course of the reaction. The mechanism was outlined by studying the FTIR spectra (of the starting materials,
intermediate species and end products), at regular intervals, which is also well supported by the literature.39,49,57–62

Spectral studies (the elucidation of the structure and the reaction mechanism)

FTIR spectra of LO, LP, LPP/ZnO (Fig. 3). LO (cm\(^{-1}\)): the FTIR spectrum of LO reveals the presence of characteristic absorption bands for \(-\text{C}==\text{C}–\text{H}\) (3009), \(-\text{CH}_2–\text{asym}\), \(-\text{CH}_2–\text{sym}\) (2924.6), \(-\text{CH}_2–\text{sym}\) (2854.6), \(-\text{C}==\text{O}\) (ester) (1744), \(-\text{C}==\text{C}–\text{1635}\), \(-\text{C}==\text{O}–\text{O}\) (1250, 1170.5) and \(-\text{O}–\text{C}==\text{C}–\text{1105}\) \(\equiv\text{C}–\text{H}\) (bend) (722) (Fig. 3a).

LP (cm\(^{-1}\)): \(-\text{OH}\) (3442–3381), \(-\text{CH}_2–\text{assym}\), \(-\text{CH}_2–\text{sym}\) (2926), \(-\text{CH}_2–\text{sym}\) (2854), \(-\text{C}==\text{O}\) (ester) (1732, 1714), \(-\text{C}==\text{O}–\text{O}\) (1242, 1176) and \(-\text{O}–\text{C}==\text{C}–\text{1070}\) (Fig. 3b).

LPP/ZnO (cm\(^{-1}\)): \(-\text{OH}\) (alcoholic, carboxylic) (3427–3419), Ar C\(==\text{C}–\text{H}\) (3099), \(-\text{CH}_2–\text{assym}\), \(-\text{CH}_2–\text{assym}\) (2924), \(-\text{CH}_2–\text{sym}\) (2854), \(-\text{C}==\text{O}\) (ester) (1732, 1714, 1680), \(-\text{CH}_3\text{COO}\) (from acetate) (1739), aromatic \(-\text{C}==\text{C}–\text{1615 and 1585}\), \(-\text{Ar}–\text{C}==\text{O}–\text{ZnO}–\text{C}==\text{O}–\text{Ar}–\text{1539 and 1390}\), \(-\text{C}==\text{O}–\text{O}\) (1242, 1178) and \(-\text{O}–\text{C}==\text{C}–\text{1070}\), Ar C\(==\text{C}–\text{H}\) bend (723), Zn–O (603) (str) (Fig. 3g).

The FTIR spectra of LO (Fig. 3a) and LP show characteristic absorption bands as mentioned above. The spectrum of LP (Fig. 3b), shows that the absorption band for double bonds (3009 cm\(^{-1}\)) is absent relative to LO and a broad band occurs at 3442–3400 cm\(^{-1}\) signifying the addition of OH at the double bonds, consuming the double bonds during the course of the hydroxylation reaction. In LPP/ZnO (Fig. 3g), the absorption bands for \(-\text{OH}\) increase in intensity and an additional band appears for Zn–O at 603 cm\(^{-1}\). Actually, we were expecting decreased \(-\text{OH}\) absorption bands in LP/ZnO as compared to LP, because during the chemical reaction (esterification) between the anhydride of PAN and the OH of LP, some OH groups of LP were supposed to be consumed, however, interestingly contrary to this, intense absorption bands were obtained for OH in LPP/ZnO, which can be correlated to OH being present on the surface of ZnO.27,48,65–68

To determine the course of the mechanism of LPP/ZnO formation, we attempted to record FTIR spectra during the course of the reaction as described in the experimental section (synthesis of LPP/ZnO). After the addition of PAN and stirring for 30 min, the FTIR spectrum (Fig. 3c) was recorded. This spectrum showed similarity to the FTIR spectrum of LP with only an increase in the intensity of the absorption band for \(-\text{OH}\) and \(-\text{C}==\text{O}\) (ester). Another FTIR spectrum (not shown here) was then taken soon after the addition of ZnAc. This spectrum was similar to Fig. 3c, and no significant change was observed relative to LP (Fig. 3c). Subsequently, FTIR spectra (d), (e), (f), and (g) were then recorded after intervals of 20 min. In FTIR spectra (d), (e), (f), and (g), on closer observation, we noticed small absorption bands at 1680 cm\(^{-1}\) (C\(==\text{O}\) (ester)) and 3664 cm\(^{-1}\) (Zn–OH). The \(-\text{OH}\) group of LP reacts with carboxylate group of ZnAc producing (I) and (II) (Scheme 3). We correlate the presence of additional absorption bands at 1680 cm\(^{-1}\)
in the spectrum of LPP/ZnO (Fig. 3g), we observed the disappearance of the absorption band of Zn–OH and the appearance of an absorption band at 603 cm\(^{-1}\) characteristic for Zn–O (str) as seen in (III) (Scheme 3). In the FTIR spectrum of LPP/ZnO, a broader –OH absorption band was observed at 3427–3419 cm\(^{-1}\) at a lower value relative to the –OH band of LP (3442–3381 cm\(^{-1}\)) which is attributed to hydrogen bonding between the OH present on surface of ZnO and those in the LPP backbone. The high frequency values are characteristic of hydroxyls (at 3664 cm\(^{-1}\) as in I) with very weak H bonds, while lower frequency bands (3427–3419 cm\(^{-1}\) and 3442–3381 cm\(^{-1}\)) indicate OH– groups with somewhat stronger H bonds.\(^6\)\(^9\)\(^7\) The absorption bands for –OH in LPP/ZnO are more intense relative to LP which is attributed to the –OH groups present at the surface of ZnO.\(^6\)

In the spectrum of LPP/ZnO (Fig. 3f and g), two interesting peaks appear at 1539 cm\(^{-1}\) and 1396 cm\(^{-1}\) which are attributed to the presence of a Zn carboxylate group\(^6\)\(^9\)\(^7\) being formed during the course of the reaction. It is evident that during the course of the reaction, –Ar(–C(=O)O–Zn–O(=C(=O)Ar) (Zn carboxylate) is also formed by a chemical reaction between the free carboxyls of LPP and ZnAc (Scheme 3 and 5) by an addition–elimination mechanism at the carbonyl double bond of the carboxylic acid group of the LPP chain, and acyl substitution involving the same step.\(^6\)

\(^1\)H NMR spectra of LO, LP, LPP/ZnO (Fig. 4). LO (ppm): –CH=HC\(=\)C 5.35, –CH\(_2\)-HC\(=\) (glycerolic) 4.32–4.30, –CH\(_2\) (flanked by –CH\(=\)HC\(=\)) 2.80–2.75, –CH\(_3\) (attached to –C(=O)O–) 2.33–2.28, –CH\(_2\) (attached to –CH=HC\(=\)) 2.10–2.0, –CH\(_2\) (chain) 1.6 and 1.0–1.25, –CH\(_3\) 0.88–0.85 (Fig. 4a).

LP (ppm): –OH 5.5, –CH\(_2\)-HC\(=\) (glycerolic) 4.28–4.11, –CH–OH 3.49, –CH\(_2\) (attached to –C(=O)O–) 2.34–2.29, –CH\(_2\) (attached to –CH=HC\(=\)) 2.10–2.0, –CH\(_2\) (chain) 1.61–1.48 and 1.30–1.25, –CH\(_3\) 0.88–0.85 (Fig. 4b).

LPP/ZnO (ppm): Aromatic ring [Ar] 7.26, –OH 5.8–5.3, –CH\(_2\)-HC\(=\) (glycerolic) 4.30–4.11, –CH (attached to –OC(=O)Ar–) 4.30–4.11, –CH\(_2\)-CH(=O)–CH(=O)(=O)–Ar 3.8, –CH\(_2\)-CH(=OH)-CH(=O)-C(=O)–C–CH\(_3\) 3.59, –CH–OH 3.59–3.39, –CH(OH)–C(=O)–CH\(_3\) 2.47–2.44, –CH\(_2\) (attached to –C(=O)O–) 2.37–2.28, –CH\(_2\)-CH\(_2\)-CH(=O)-C(=O)–CH\(_3\) 2.14, –CH\(_2\) (attached to –CH=HC\(=\)) 2.10–2.0, –CH\(_3\) (chain) 1.61–1.48 and 1.30–1.25, CH\(_2\)COO\(=\) 1.0–0.97, –CH\(_3\) 0.87–0.85 (Fig. 4c).

In the \(^1\)H NMR spectrum of LP (Fig. 4b), a sharp peak at 5.35 ppm for –CH=HC\(=\) as is present in LO (Fig. 4a) is replaced by a broad peak for –OH suggesting that (i) LP was produced from LO, and (ii) the hydroxylation reaction inevitably proceeded at double bonds, consuming the latter and introducing hydroxyl groups at the unsaturated bonds. In the spectrum of LPP/ZnO (Fig. 4c), the appearance of proton resonances at 2.47–2.44 ppm (–CH(=O)=C(=O)–CH\(_3\)), 1.37 ppm (–CH\(_2\)-CH(=O)=C(=O)–CH\(_3\)), and 1.0–0.97 ppm (CH\(_3\)COO\(=\)), and the increased intensity at 4.30–4.11 ppm (–COO-CH\(_3\)) (glycerol backbone) supported the formation of an additional ester (acetate –CH\(_3\)COO\(=\)) bond by the reaction of ZnAc with the OH of LP. Additional bands appear for OH at higher peak values (downfield shift) correlated to the presence of OH on the surface of ZnO.

Thus, we understand that during the formation of the nanocomposite, a chemical reaction takes place at two

(\(\text{CH}_3\)-C\(=\)O (ester)) and 3664 cm\(^{-1}\) to (I) and (II), which also supported the reaction mechanism shown in Scheme 3. Finally in the spectrum of LPP/ZnO (Fig. 3g), we observed the
functional groups in LPP chain, (i) at the free –OH of LPP, between hydroxyls of LPP and the carbonyl carbon atom of ZnAc by an ester elimination reaction (Scheme 4), (ii) at the free –COOH of LPP, between the –COOH of LPP and ZnAc by an addition–elimination mechanism at the carbonyl double bond of the carboxylic acid group of the LPP chain (Scheme 5), as is evident from the spectral studies and also from the literature.

Physico-chemical analysis

The physico-chemical analysis results in Table 1 show that iodine values decrease while refractive index, specific gravity, and inherent viscosity increase with an increase in the ZnAc content in LPP/ZnO. The increase in the amount of ZnAc subsequently leads to an increased content of ZnO nanoparticles in LPP/ZnO, consequently, specific gravity and refractive index also show slight increases. It is important to mention that the iodine values of LO and LP are 184 and 68, respectively. As LO undergoes the hydroxylation reaction (epoxidation followed by hydration), a portion of the unsaturated parts of LO is consumed due to the insertion of hydroxyl groups at the unsaturated bonds of LO, finally forming LP. Thus, the lower iodine value of LP is correlated to the lower content of double bonds in LP compared to LO. It is very important to estimate the iodine value of LP as it informs about (i) the content of unsaturation/double bonds in the final LP, and also (ii) the extent of the consumption of the double bonds of LO during the course of the hydroxylation reaction producing LP.

Morphology

The optical micrographs (Fig. 5) show the presence of large sized ZnO particles. The uniform distribution of color throughout the matrix also implies that the particles are uniformly distributed in the polymer matrix. The TEM micrographs show the presence of ZnO NP of size ranging from >100–200 nm (Fig. 6). The ZnO NP appear as spherical particles with well-defined boundaries. Some particles appear black partially or completely (dark contrast) while some appear as grey (light hue). The particles seem partially or wholly covered with a grey sheath that is the LPP backbone covering the ZnO NP thus rendering their grey appearance. The dark contrast is actually due to the particle itself, as it seems to be peeping through the (grey) sheath. ZnO occurs as unagglomerated NP due to encapsulation by the long flexible aliphatic LPP hydrophobic chains.

Thermogravimetric analysis

Fig. 7 demonstrates the TGA curves for LPP and LPP/ZnO-0.06. The initial weight loss starting at 250 °C, may be correlated to the elimination of trapped moisture. A 10 wt% loss is observed at 310–325 °C and 50 wt% loss occurs at 420–435 °C in LPP and LPP/ZnO-0.06. LPP/ZnO-0.06 shows a relatively higher thermal stability than LPP at higher degradation temperatures. In LPP 90% degradation was completed when the temperature reached 600 °C, while in LPP/ZnO-0.06, 90% thermal degradation was achieved at a comparatively higher temperature as a result of the incorporation of the ZnO NP. We can comprehend that the relatively higher thermal stability of LPP/ZnO-0.06 is attributed to the formation of strong network structures by chemical reactions between the anhydride of PAN and the OH of LP producing LPP and also through hydrogen bonding by the surface hydroxyl groups of ZnO and the OH of the LPP backbone providing thermal insulation and a mass transport barrier to volatile products generated during decomposition and thus increasing the thermal stability of the nanostructured composite material.

The effect of in situ prepared ZnO nanoparticles on the coating properties of LPP/ZnO

Physico-mechanical performance. The chemical reaction for the synthesis of LPP/ZnO proceeded well with 0.04, 0.05 and 0.06 mol loadings of Zn–Ac. At 0.08 mol, an increase in the
viscosity was observed which interfered with the application of the coating over the substrate and at 0.1 mol, a highly viscous product was obtained. LPP/ZnO-0.08 and LPP/ZnO-0.1 produced composites with higher viscosity making them unbrushable and prevented their coating application over the CS substrate. Thus, we studied only three compositions, LPP/ZnO-0.04, LPP/ZnO-0.05 and LPP/ZnO-0.06, along with plain LPP. The best coating performance was obtained with LPP/ZnO-0.06. All of them produced dark brown coatings on the CS substrate. Optical micrographs of the LPP/ZnO coatings (Fig. 8) show the presence of black, spherical ZnO particles in the LPP matrix, which are absent in plain LPP. The best coating performance was obtained with LPP/ZnO-0.06. All of them produced dark brown coatings on the CS substrate. Optical micrographs of the LPP/ZnO coatings (Fig. 8) show the presence of black, spherical ZnO particles in the LPP matrix, which are absent in plain LPP. The ZnO NP occur as distinct spheres engulfed by the LPP chains. The LPP/ZnO coatings showed good scratch hardness, impact resistance, bend test results and (cross hatch) adhesion (Table 2). The performance of these coatings improved with increased content of nano-sized ZnO. The scratch hardness and cross hatch adhesion tape tested coatings were observed under an optical microscope. The images (Fig. 9) distinctly reveal that there are no ridges formed and no peeling off of the coating material occurred after the scratch hardness and cross hatch adhesion tape tests, rather the “scratch” or “cross” is produced in a straight line, without tearing off the coating microstructure. Such good performance can be correlated to the adequate interactions between the organic and inorganic phases, the high surface area (because of the small size) of ZnO as well as the long aliphatic triester chains and polar hydroxyls, collectively, that restricted indentation and consequently enhanced

Scheme 2  The synthesis of LPP.
Scheme 3  The synthesis of LPP/ZnO.

Scheme 4  The mechanism occurring at the –OH end of LPP.
the adhesion and toughness of the coatings. The nanosized particles occupy small hole defects, act as interconnecting bridges, and toughen the crosslinked network in contrast to plain LPP coatings that gave relatively poor responses to the aforementioned tests and were worn out after the tests. Thus, the nano-sized particles not only fill cavities in the coatings but also cause crack bridging.

Hydrophobicity

Hydrophobicity is an important property that augments the corrosion protection performance of coatings. A hydrophobic coating strongly resists the adherence or penetration of water or other corrosive solutions at or within the coating surface. Hydrophobicity thus becomes one of the basic requirements of an anticorrosive coating material. The CCD camera images (Fig. 10) of water droplets on the smooth surface of the LPP and LPP/ZnO-0.06 coatings show that the contact angle values obtained are 78° and 94° suggesting that LPP/ZnO is hydrophobic in nature. As the water contact angle is greater than 90° water cannot penetrate within the coating. The small size of the NP is also advantageous since it enables their penetration into ultra-small holes, indents and capillary areas both in the coating matrix itself and at the surface of the metallic substrate.

Corrosion resistance performance

PDP studies. The PDP curves for the LPP and LPP/ZnO-0.06 coated CS and bare CS recorded in 3.5 wt% NaCl and 3.5 wt% HCl aqueous solutions are shown in Fig. 11. The values of $E_{\text{corr}}$, $I_{\text{corr}}$ as well as $R_p$ which were calculated from the PDP curves for the LPP and LPP/ZnO-0.06 coated CS are summarized in Table 3. It was observed that $I_{\text{corr}}$ decreased from the LPP coating to the LPP/ZnO-0.06 coating. The $E_{\text{corr}}$ value increased from the LPP coating to the LPP/ZnO-0.06 coating. The $R_p$ value for the LPP/ZnO-0.06 coated CS showed a very high (4.46 x 10^5 kΩ, 1.58 x 10^2 kΩ) increase with respect to the LPP coated CS (68.94 kΩ, 18.53 kΩ) in 3.5 wt% NaCl and 3.5 wt% HCl, respectively. Hence, the inclusion of the ZnO NP enhanced the corrosion resistance performance of the plain coating, which was also evident from the low corrosion rate of these coatings (Table 3). These results demonstrate the ability of the nano-composite coatings to inhibit the corrosion process by blocking
the active sites of CS. The enhanced anticorrosive performance of the nanocomposite coated CS can be ascribed to the presence of the ZnO NP, which facilitate adhesion between the coating and the metal substrate. Besides, homogeneously dispersed ZnO in the coatings act as a strong barrier, and provide cathodic protection and a tortuous pathway for corrosive ions to reach the metal surface.

**EIS studies.** Apart from the PDP measurements, EIS was applied to give more detailed information on the electrochemical performance and corrosion protection mechanism of the LPP and LPP/ZnO-0.06 coatings. The coated CS was exposed to 3.5 wt% NaCl and 3.5 wt% HCl solutions for a period of 24 hours. Fig. 12 and 13 show the Nyquist plots (real impedance vs. imaginary impedance) and Bode plots (log frequency vs. log|Z|), respectively. The initial impedance value for the LPP coated CS was found to be below $10^4 \ \Omega$ at the low-frequency end of the semicircle arc with the real axis (Fig. 12c and d), while in case of the LPP/ZnO-0.06 nanocomposite coatings, high impedance values of more than $10^7 \ \Omega$ in a saline environment and $10^6 \ \Omega$ in an acidic environment, were observed. The nanocomposite coatings remarkably show higher impedance in the lowest frequency region as compared to the virgin coatings (Fig. 12a and b), which is a characteristic of intact, well adhered coating systems. The hydrophobic character of the virgin coatings increases with the incorporation of ZnO NP (as discussed in previous section), which do not allow wetting of the surface that inhibits penetration of corrosive ions. The nanocomposite coatings show higher diameters in the Nyquist plots, which confirmed the better corrosion protection performance of the

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**Table 2**  The physico-mechanical performance of LPP and the LPP/ZnO coatings

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Scratch hardness (kgs)</th>
<th>Impact resistance (lb/inch)</th>
<th>Bend test (1/8 inch)</th>
<th>Gloss (45°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPP</td>
<td>1.6</td>
<td>150</td>
<td>Pass</td>
<td>60</td>
</tr>
<tr>
<td>LPP/ZnO-0.04</td>
<td>2.0</td>
<td>200</td>
<td>Pass</td>
<td>68</td>
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<tr>
<td>LPP/ZnO-0.05</td>
<td>2.6</td>
<td>200</td>
<td>Pass</td>
<td>68</td>
</tr>
<tr>
<td>LPP/ZnO-0.06</td>
<td>3.0</td>
<td>200</td>
<td>Pass</td>
<td>69</td>
</tr>
</tbody>
</table>
nanocomposite coatings as is evident from the high impedance values observed from the Bode plot (Fig. 13). In the 3.5 wt% NaCl solution, the LPP as well as LPP/ZnO-0.06 coatings showed better protection as shown in Fig. 12a and c, respectively, while in case of the 3.5 wt% HCl solution both the coatings showed lower protection as shown in Fig. 12b and d respectively, as HCl is more corrosive than NaCl.

In the case of the LPP coating, the diffusion impedance of the coatings with respect to these ions acquires a Warburg impedance shape and the LPP/ZnO-0.06 nanocomposite coating in the 3.5 wt% HCl solution after 12 h also acquires the same pattern, which suggests that the electrolyte penetrates into the polymeric matrix. However, in case of the LPP/ZnO coating only one capacitive time constant was detected in the EIS experiment after 24 h immersion in 3.5 wt% NaCl (Fig. 13a). This indicates that corrosion process has not been initiated on the substrate and the nanocomposite coatings still prevent the underlying metal to come in direct contact with the aqueous corrosive environment. The superior corrosion protective behavior of the nanocomposite coatings can be ascribed to the presence of the ZnO NP, which induce a locking effect and form a strong barrier at the coating metal interface. The presence of ZnO NP impedes the electrolyte at the coating metal interface. The LPP/ZnO nanocomposite coating showed higher impedance values at lower frequency as compared to that of the LPP coated CS.

Optical micrographs of the LPP/ZnO-0.06 coating after EIS measurements in given media

The optical micrographs of the LPP/ZnO-0.06 coating taken after the tests in NaCl (Fig. 14a) show the deposition of salt on the coating surface. However, the coating surface peeping from behind the deposited salt is completely unaffected. There is no peeling, dissolution or even traces of any perceptible deterioration. Similarly, after tests in HCl and water, no detrimental effects could be seen on the coating surface (Fig. 14b and c).

The plausible mechanism of corrosion protection by the LPP/ZnO coating (Fig. 15)

LPP/ZnO-0.06 coatings improve corrosion resistance both by barrier action as well as electrochemical mechanisms. LPP provides polar hydroxy groups and aromatic rings that introduce toughness into the coatings. The ZnO NP tend to occupy the voids and cavities in the coatings and serve as bridges interconnecting the LPP matrix, reducing the total free volume and producing tough well-adhered crosslinked networks, devoid of any disaggregates within the matrix, producing homogenous coatings preventing any delamination. This can also be speculated as one of the reasons for introducing the hydrophobicity in the LPP/ZnO-0.06 coating relative to the LPP coating as is evident from their water contact angle values. Due to their hydrophobic nature, the coatings repel water or any other corrosive species in solution, acting as a strong repelling barrier. The inclusion of ZnO NP as a second phase in LPP, that is also miscible with LPP, further decreases the porosity and zigzags the diffusion path for any corrosive species that can manage (despite the hydrophobic nature of coatings) to penetrate the coating layer. The performance of the LPP/ZnO coatings can be ascribed to the presence of the ZnO NP, which induce a locking effect and form a strong barrier at the coating metal interface. The presence of ZnO NP impedes the electrolyte at the coating metal interface. The LPP/ZnO nanocomposite coating showed higher impedance values at lower frequency as compared to that of the LPP coated CS.

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coating was improved in HCl and NaCl solutions due to better dispersion of ZnO in the LPP matrix, rendering a strong, well-adhered, dense, and continuous network-like coating structure. This retards the penetration of corrosive ions through the coating and metal substrate thus enhancing the protection against corrosion. On the contrary, the poor dispersion or agglomeration of NP in coatings causes microcracks, disturbing the mechanical integrity of the coatings, making them susceptible to attack by corrosive media. Hence, the coating acts as an excellent inhibitor and protects metals from corrosion.

**Significance**

In the present work we resorted to the “zero solvent” approach for the *in situ* preparation of nanocomposite coatings from linseed oil, a sustainable resource, utilizing the fluidity characteristics of linseed oil derivatives, *i.e.*, LP and LPP. The *in situ* approach facilitates the simple preparation and homogenous
dispersion of ZnO NP in LPP. The coatings produced are tough, scratch resistant, glossy, flexibility-retentive, well-adherent hydrophobic surface acts as a “green” barrier to corrosents.

The approach utilises the hydroxyl functional groups present in the linseed oil derived polyol matrix for the in situ preparation of ZnO nanoparticles,

up to 0.06 mole loading of the inorganic precursor, achieved a good coating performance, beyond which LPP/ZnO became unbrushable and could not be applied as coatings over the substrate, thus this is the optimum concentration that can be possibly introduced into the LPP matrix,

the properties of the obtained LPP/ZnO coatings are superior to plain LPP,

synergism is observed as both the matrix and nanoparticles produce a combined effect that results in a simple synthesis strategy, consistent with the principles of “Green Chemistry”, conferring an overall good coating performance,

the overall approach can be considered as environmentally benign,

in future, transition is required from the “in situ zero solvent” approach reported here to other environmentally friendly green solutions utilising the same concept that is nanoparticle incorporated plant oil based waterborne, hyperbranched, high solids and UV curable coatings,

also efforts can be made to augment the in depth knowledge towards further advancements in the utilisation of such “green” “eco-friendly” and “sustainable resource” based “green + green” solutions for applications under aggressive corrosive conditions and as antifouling, antibacterial, antifungal and marine coatings.

**Conclusion and future aspects**

In the present work, we report a green, one-pot, solventless in situ preparation of LPP/ZnO bionanocomposites. We observed that:

1. The coatings produced are tough, scratch resistant, intact resistant, flexibility-retentive, hydrophobic and thermally stable. The simple, easy-to-handle, and less time consuming synthesis, formulation and curing schedule makes the systems more advantageous over their conventional and existing counterparts. Most importantly, we see that synergism predominates the overall approach. While LP and the LPP matrix (as mentioned earlier) provide reaction media and functional groups for the in situ preparation of ZnO nanoparticles, the latter contribute to the enhanced physico-mechanical and corrosion resistance performance of the coatings. The approach can be well applied as a value-added tool to those vegetable oils that are non-edible and non-medicinal. The work described complies with the principles [P] of “Green Chemistry” (P1 Prevention, P2 Atom Economy, P3 Less Hazardous Chemical Syntheses, P4 Designing Safer Chemicals, P5 Safer Solvents and Auxiliaries, P6 Design for Energy Efficiency, P7 Use of Renewable Feedstocks, P8 Reduce Derivatives, P12 Inherently Safer Chemistry for Accident Prevention), utilising a renewable feedstock and less hazardous syntheses conditions, considering atom economy, using a solventless process of coating formulation and application, with reduced derivatives, safer chemistry, and an overall environmentally friendly process.

2. The approach utilises the hydroxyl functional groups present in the linseed oil derived polyol matrix for the in situ preparation of ZnO nanoparticles,

3. up to 0.06 mole loading of the inorganic precursor, achieved a good coating performance, beyond which LPP/ZnO became unbrushable and could not be applied as coatings over the substrate, thus this is the optimum concentration that can be possibly introduced into the LPP matrix,

4. The properties of the obtained LPP/ZnO coatings are superior to plain LPP,

5. Synergism is observed as both the matrix and nanoparticles produce a combined effect that results in a simple synthesis strategy, consistent with the principles of “Green Chemistry”, conferring an overall good coating performance,

6. The overall approach can be considered as environmentally benign,

7. In future, transition is required from the “in situ zero solvent” approach reported here to other environmentally friendly green solutions utilising the same concept that is nanoparticle incorporated plant oil based waterborne, hyperbranched, high solids and UV curable coatings,

8. Also efforts can be made to augment the in depth knowledge towards further advancements in the utilisation of such “green” “eco-friendly” and “sustainable resource” based “green + green” solutions for applications under aggressive corrosive conditions and as antifouling, antibacterial, antifungal and marine coatings.

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**References**


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