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ARTICLE TYPE

Development of anticorrosive two pack polyurethane coatings based on modified fatty amide of *Azadirachta indica juss* oil cured at room temperature – A sustainable resource

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We report the modification of *Azadirachta indica juss* oil (renewable source) fatty amide by piperazine molecule to develop new polyol. Two pack polyurethane (PU) coatings on mild steel plates were prepared by reacting newly developed polyol with toluene diisocyanate (TDI) at room temperature. Spectral study of *Azadirachta indica juss* oil based fatty amide and piperazine modified fatty amide were carried out using spectroscopic techniques to confirm the modification. The prepared resins were also characterized by end group analysis such as amine and hydroxyl values. Anticorrosive properties of the prepared PU coatings were examined by immersion test in an aqueous salt solution. Thermal stability of coatings was studied by TGA. Other coating properties such as gloss, scratch hardness, adhesion, flexibility, impact resistance and chemical resistance were evaluated using standard methods. It was observed that presence of nitrogen containing piperazine moiety in a back bone of PU chain shown better anticorrosive properties compared to the *Azadirachta indica juss* oil fatty amide based PU coatings.

Introduction

The growing charges of raw materials based on petroleum feed stock and decreasing their availability in nature forced scientists to focus their attention towards the use of renewable resources in the preparation of polymeric resins. [1-4] Renewable resources such as cellulose, carbohydrates, polysaccharides, starch, fatty acids and vegetable oils are natural and agricultural products which have been preferred as raw materials in preparation of polymers.[5-8] Considering the sustainability and easy availability, vegetable oils and their derivatives has given more wattage as renewable source based feed stocks for polymer sector. [9-10] Plant oils such as soybean (*Glycine max)*, linseed (*Linum usitatissimum*), tall (liquid rosin), palm (*Elaeis)*, nahar (*Mesua ferrea)*, canola (*Brassica)*, cotton (*Gossypium)*, jatropha (*Pongamia pinnata*), tung (*Vernicia fordii)*, castor (*Ricinus communis)* and neem (*Azadirachta indica)* oils were used to prepare the polymeric resins by appealing the characteristic properties of individual oils. [11-18] Vegetable oils have their own fatty acid compositions, the diversity in fatty acid compositions and variation in the degree of unsaturations depend on growing conditions, season and environment present to the particular plant or crop for example colder climate increases the level of unsaturated fatty acids in oil.[19] Oils such as castor oil and lesquerella oil are having naturally occurring hydroxyl groups on their triglyceride molecules. The structures of ricinoleic and lesquerolic acids of these oils contain hydroxyl groups at C12 and C14 positions respectively.[20] Therefore, these oils are referred as hydroxyl polyols which have ability to react with diisocyanates to develop PU or highly cross-linked polymers. Most of the vegetable oils do not show hydroxyl groups in their structure, due to this reason production of hydroxyl terminated derivatives of vegetable oils is now ongoing task for current polymeric researchers. Number of reports for conversion of vegetable oils into polyols by chemical modification such as ozonolysis, [19] epoxidation, [21] hydroformylation, [22] esterification [23] and amidation [24-27] are appeared in the literature. During chemical modifications hydroxyl groups are introduced in the structure of vegetable oils to form the bio-based polyols.[28] In last ten years, extensive work has been done to develop diethanol amides of fatty acids by amidation of various vegetable oils. The prepared diethanol amides are popularly used as non-ionic surfactants and foam boosters for shampoos, detergent and cosmetic industries. [29] The coating formulation scientists are now set the focal point for the use of such fatty amides in the preparation of polyesteramides, [30, 31] polyetheramides [17] and useful hydroxyl terminated polyols for applications in PU coatings. In the case of vegetable oil based polymers, polyurethanes are having tremendous importance and versatile applications in adhesives, elastomers, foams and surface coatings.

The *Azadirachta indica juss* oil is present in plentiful amount in an Indian continent and other parts of the word. It has lot of attraction for its use in agrochemicals [32] and pharmaceuticals [33] applications. Peter et al [34] investigated use of *Azadirachta indica* extract as corrosion inhibitor and found that it has high inhibition efficiency to the metallic corrosion comparing with root and leaf extracts of the plant. *Azadirachta indica* seed contains 33-38 % oil which possesses five major fatty acids viz. palmitic, stearic, arachidic, oleic and linoleic acids. Considering the fatty acid composition and unsaturations present in *Azadirachta indica juss* oil, it has potential in making of polymeric resins such as poly(urethane-fatty amide),[18] poly(urethane-esteramide) [30] and poly(urethane-ether amide) [35] as directed in earlier reports.

Utilization of this oil in the development of different polyols will definitely show environmental compensation like reduction in the requirement of fossil or petroleum resources and formation of very low greenhouse gas emission. Use of *Azadirachta indica juss* oil in the synthesis of polyurethane resin by piperazine modified fatty amides was not reported or focused earlier. Piperazine is a cyclic compound containing N atom in its cyclic ring, which has widely been used as a condensing agent in the preparation of polyamides.[36-37] Corrosion to the metal surface is now the major issue in all over the globe and it is one of the challenge how to eliminate or reduce the corrosion of metals. Nitrogen atom present in the piperazine molecule contains a lone pair of electrons, which introduces hydrophilicity in the coatings that can enhance adhesion of coating against the hydrophilic substrates (metals) and also used as corrosion inhibitor for metal iron and steel.[38] One more objective behind this modification was to develop high molecular weight resin in order to get more flexible and soft PU coatings.

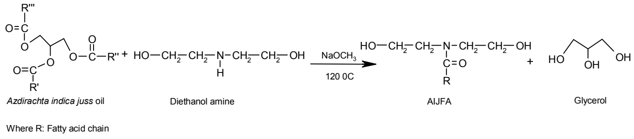
The present work attempted to develop renewable source *Azadirachta indica juss* oil based fatty amide and its further modification by piperazine to develop anticorrosive two pack PU coatings. The prepared coatings were cured at room temperature conditions. Coating properties including anticorrosive, thermal, chemical resistance, gloss, impact resistance, adhesion, flexibility were also studied.

Experimental

Azadirachta indica juss oil was collected from local supplier and characterized for its physical properties such as specific gravity, refractive index, saponification value, hydroxyl value, peroxide value and iodine value. These characterizations were matched with the standards and avoided any further chemical modification. Piperazine (diazacyclohexane) and dibutyltin dilaurate (DBTDL) were of Aldrich Chemicals. Toluene diisocyanate (TDI) was of commercial grade and characterized by determining isocyanate content by ASTM D-2572-97 before use. Cylcohexanone, tetrahydrofuran (THF) and diethanol amine of analytical grade were obtained from SDFCL, India. Remaining chemicals and solvents used for synthesis or analysis were of either synthesis or of analytical grades and purchased from Aldrich Chemicals.

Synthesis of AIJFA

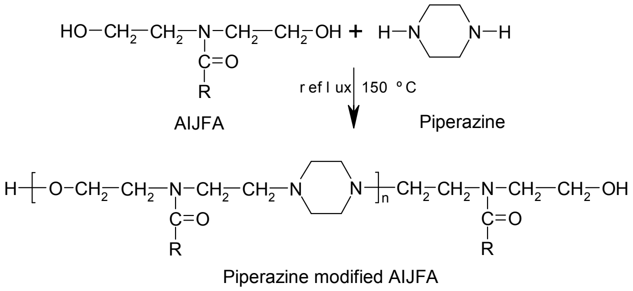
Synthesis of *Azadirachta indica juss* oil based fatty amide (AIJFA) was carried out by the reacting oil with diethanol amine as per our previous report.[17] General reaction for synthesis of AIJFA is as given in the **Scheme 1**.



Scheme -1 Synthesis of AIJFA

Synthesis of piperazine modified fatty amides (PAIJFA)

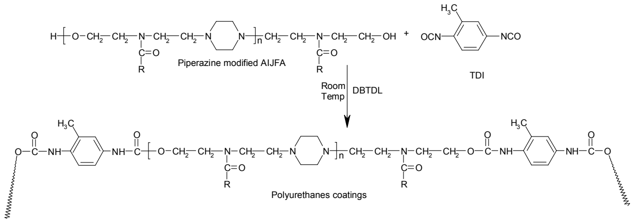
The synthesized AIJFA (1.3 mol) was dissolved in 50 mL xylene and transferred to three necked round-bottom flask that was equipped with a Dean-Stark trap, nitrogen inlet tube, thermometer and magnetic stirrer. Piperazine (1.0 mol) was added in a solution of AIJFA and the reaction mixture was refluxed at 150 ºC until the calculated amount of water was not collected in the Dean-Stark trap. The modification reaction was also confirmed by determining amine value of the mixture at regular intervals. The amine value of sample (dissolved in a mixture of isopropanol and water) taken at regular interval was estimated by titrating it against a 0.5N HCl solution until solution became yellow colour in the presence of bromophenol blue as an indicator. As the amine value went below 10 mg of KOH/g of sample, the reaction was stopped. After the completion of the reaction, the product was cooled to room temperature. The trace amount of xylene was evaporated in a rotary vacuum evaporator under reduced pressure to obtain the pure PAIJFA. The general reaction for modification of AIJFA by piperazine is given in the **Scheme 2**.



Scheme - 2 Synthesis of PAIJFA

Preparation of PU coatings

Synthesis of PU was done by reacting the prepared PAIJFA resin at room temperature with TDI in the NCO/OH ratio of 1.1:1. The presence of excess NCO group hydrolyzes gradually by reacting with moisture present in the air and giving urea groups and lift up the crosslink density, improve physical properties and chemical resistance of PU. This also rules out possibility of poor durability to coatings due to the presence of unreacted OH groups. In actual process 50 % solid content solution of PAIJFA was prepared in a cyclohexanone and THF (80:20) mixture with catalyst DBTDL (0.05 %) for controlling the rate of reaction. The PAIJFA solution containing catalyst was mixed with TDI and stirred manually for next 5 min to attain pourable viscosity. Then reaction mixture was used to coat using a bar applicator on MS steel panels of 4 x 6 inch dimensions and the prepared coating panels were subjected to cure at room temperature under visual examination. Same procedure was used for preparation of the PU coatings using the previously synthesized AIJFA. Before application of the coatings, all the steel panels used in the study were pretreated by sandpaper, washed with acetone and dried in an air. The PU samples prepared from AIJFA and PAIJFA were coded as PU-AIJFA and PU-PAIJFA. The general reaction scheme for the preparation of PU coatings obtained from PAIJFA is given in the **Scheme 3**.



Scheme - 3 Preparation of polyurethane coatings

Characterizations

Analysis of raw materials used in PU coatings

Physical properties such as iodine value, specific gravity and refractive index of AIJFA and PAIJFA were determined by standard experimental methods. Viscosities of AIJFA and PAIJFA were determined on a Brookfield Rheometer (RHEO 2000 version 2.5, Brookfield Engineering Laboratories Inc., USA) in triplicate at 25 ^{0}C temperature and 20 rpm speed for 120 second. The FTIR spectra of AIJFA and PAIJFA were obtained by a Perkin-Elemer 2000 FTIR spectrometer in the range of 4000 to 500 cm^{-1} in KBr pellets. ^{1}H-NMR measurements of AIJFA and PAIJFA were also performed on a Varian Mercury 300 MHz spectrometer using TMS as an internal standard in the presence of $CDCl_3$ as a solvent.

Hydroxyl and amine value determination

The hydroxyl and amine values of *Azadirachta indica juss* oil, AIJFA and PAIJFA were estimated by acetylating reagent (ASTM D 4274 – 99) and isopropanol methods (ASTM D 2017 – 04) respectively.

Polyurethane coatings characterization

Gloss

The importance of gloss measurement is associated with the capacity of a surface to reflect more light. The digital gloss meter (Model BYK Additive & Instruments) was kept on the coated sample with auto calibration mode at an angle 60 ^{0}. The precautions were taken during the measurement in such a way that the coated panel sample should not come in contact with oil and geometry of the gloss meter should remain at 60 ^{0}.

Flexibility

The film or coatings attached to the metal substrates are elongated when the substrates are bent that tests ability of coatings to resist cracking when elongated. Flexibility of the coated samples was performed on a conical mandrel. While performing the test, mandrel was free to rotate on its axis and then coated samples were kept in between the rotating axis. The handle of a conical mandrel was lowered in a vertical direction to obtain specific angles.

Pencil hardness

The pencil hardness of the coating was measured by using a pencil hardness tester (Model BYK Additive & Instruments, Germany). In this test pencils having different (soft and hard) grades were used to move over the surface of the coated panels from the distance of 6 mm at fixed 45^0 by using a standard holder. The force were applied on the pencil and moved over the surface of the test samples at a fixed angle. The coated panels were checked for the removal of the film. The same procedure was repeated with pencil of higher grades of hardness until the film was not scratched or penetrated. The pencil which does not remove the coating denotes pencil hardness of that coating.

Cross cut adhesion

In this test a cross cut adhesion tester consisting of a die with 11 number of closed set of parallel blades was passed and pressed on the PU coated panels in two directions at right angle to each other so that the lattice of 100 squares of 1 mm area each was formed. Then adhesion tape was placed at the centre over the lattice present on panels and within 5 minutes, the tape was removed by pulling it steadily in 2 seconds at an angle which is close as possible to 60º. Then the samples were examined carefully with the help of magnifier to determine the percentage of cubes remained on the coating panels.

Impact and mar resistances

Impact resistance test was carried out to evaluate the load carrying capacity of the coated samples. During this test the PU coated panels were placed on hock properly and movable weighted indenter (1.818 lb) was lifted from the certain height starting from 5-40 inch until the film cracked. After falling weighted indenter peeling, cracking and film detachment from substrate was examined. If there is presence of any cracks on coatings, test was considered as failed otherwise it was considered as passed. The mar resistance of the prepared PU coating samples was evaluated in the laboratory by a mar resistance tester of BYK Instruments. This resistance is expressed in ‘g’ the term of load that failed to spoil the coated film.

Water and chemical resistances

The chemical resistance tests of PU coated panels were performed in water, solvent (xylene), acid (5 % HCl) and alkali (5 % NaOH) in beakers. Periodic visual inspection was taken for 7 days to find any evidence of softening, deterioration or development of cracks.

Corrosion resistance by immersion test

The corrosion to the metal generally depends upon the type of metal and presence of electrolytes such as hard water, salt water, battery fluids, etc. with time of exposure. The anticorrosion properties of prepared PU coatings were evaluated in our laboratory through immersion test in an aqueous salt solution. Three sample panels viz. uncoated (steel panel), PU-AIJFA coated and PU-PAIJFA coated panels were immersed in a 3.5 % NaCl solution. The test was continued until the deterioration of coatings due to the corrosion to the surface of panels was not observed. As blistering was found at one of the sample panels of PU coatings, panels were removed from salt solution and examined visually. The visual inspection of corrosion to surface of MS panels was recorded using digital camera (Sony, 16 mega pixels) in the form of images.

Thermal analysis of PU coatings

Thermal analysis of the prepared PU coatings was performed on a thermogravimetric analyzer (TGA 4000, Perkin Elmer, USA) in the range of room to 700 ^{o}C temperature at heating rate of 20 ^{o}C/min in an inert (N_2) atmosphere. Around 3 mg of the samples were taken for the thermal study and interpretation of results were done by the Pyris software program provided by the manufacturer.

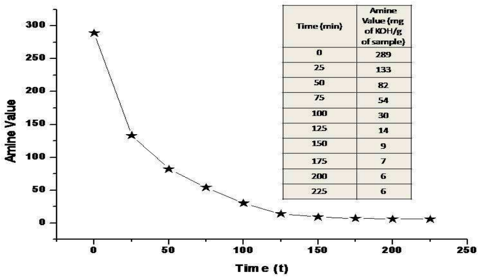
Results and Discussion

Characteristic properties of *Azadirachta indica juss* oil, AIJFA and PAIJFA

The prepared AIJFA and PAIJFA resins showed solubility in xylene, toluene, chloroform, carbon tetrachloride, ether, acetone, cyclohexanone and THF. The presence of long fatty acid hydrocarbon chain in resins may associate the solubility behaviour of resins. Specific gravity, viscosity, refractive index, saponification value, acid value and iodine value of oil, AIJFA and PAIJFA were determined by standard methods and results are given in the Supporting information **(SI)Table S1**.

Change in amine value during reaction

The formation of PAIJFA was monitored by determining the amine value of the sample taken from the reaction mixture at various time intervals. The decreasing the amine value with reaction time for the preparation of PAIJFA samples is shown in the **Figure 1**. It showed that at the initial stage of reaction, the rate of decreasing of amine value was higher later on rate decreased slowly. This may be due to more availability of functional groups at initial stage of condensation reaction and presence of equilibrium more towards product's direction at the early stage. In addition to this, from the visual inspection the increment in viscosity of the reaction mixture was noted due to the increase in length of product formed. The reaction was stopped after 225 min where final amine value obtained was 6.75 mg of KOH per gram of sample. From the ratio of difference between initial and final amine values to the initial amine value, extent of reaction P_{av} was calculated. It was observed that from the value of P_{av}, almost 97.64 % reaction was completed. The degree of polymerization and molecular weight of prepared PAIJFA were found to be 6.576 and 2937 respectively.



Time (min)	Amine Value (mg of KOH/g of sample)
0	289
25	133
50	82
75	54
100	30
125	14
150	9
175	7
200	6
225	6

Fig. 1: Plot of change in amine value versus reaction time

FTIR and NMR spectrum of PAIJFA

The FTIR spectrum of piperazine modified AIJFA is shown in the **Figure S1 (SI)**. The characteristic band of OH groups was occurred at 3291 cm^{-1}. At 2855 and 2926 cm^{-1} symmetrical and asymmetrical stretching vibrations respectively of $-CH_2$ and $-CH_3$ were attributed. The peak at 1615 cm^{-1} was obtained for amide carbonyl, while the absorption band for C-N of amide was observed at 1465 cm^{-1} and the band at 1358 cm^{-1} was attributed to C–N of piperazine. The formation of PAIJFA was supported by the presence of characteristic peaks in the FTIR spectrum of it.

The ^1H- NMR spectrum [**Figure S2 (SI)**] of piperazine modified AIJFA showed the peak of terminal $-CH_3$ at 0.88 ppm. A chemical shift for $-CH_2$ of long fatty amide chain was seen at 1.25 ppm. Appearance of peaks at 3.57 and 3.59 ppm corresponded to $-CH_2-$ linked with nitrogen of piperazine molecule. Methylene adjacent to olefin $=CH-CH_2-$ and -OH found at 1.61 and 3.84 ppm respectively, while $-CH_2-$ attached to amide nitrogen appeared at 3.51 ppm. The peak at 3.89 ppm was attributed to proton of hydroxyl group and the protons near to olefinic unsaturation given the peak at 5.37 ppm. The above observations and structural features confirmed the formation PAIJFA.

Coating properties

The prepared PU coatings on MS panels were cured at room temperature. The outcome of tested coating properties for the prepared coatings included surface dry test, gloss, mar resistance, pencil hardness, impact resistance, flexibility and cross cut adhesion which are furnished in the **Table S2 (SI)**. Surface dry or dry to touch of PU-AIJFA and PU-PAIJFA coatings were found 80 and 65 min respectively. This indicated that presence of the piperazine moiety in PU-PAIJFA coating decreased the drying time of the coatings because presence of piperazine introduces tertiary amine and it is well known fact that tertiary amine is acting as catalysts for the isocyanate-hydroxyl reactions.[39] Adhesion of both the PU samples with metal substrate was within the range of 95-98 %. The gloss of the PU samples was observed 68 for PU-AIJFA and 82 for PU-PAIJFA coatings. The increased gloss at PU-PAIJFA coating may be associated with increase in oil based component i.e. amount of fatty acid in final coatings that increases the capacity of a surface to reflect more light. Impact and mar resistances of the PU-PAIJFA coatings were found higher than that of the PU-AIJFA. The increment in impact and mar resistances of the PU-PAIJFA might have arise due to more amount of soft segment in the PU-PAIJFA coatings than PU-AIJFA coatings. In the case of pencil hardness test, up to the level of 1H grade pencil, the film of both PU coatings samples were not cut, indicating that both types of coatings were with good pencil hardness. Both the prepared PU coatings passed the mandrel flexibility test and no any sort of failure was found.

Water and chemical resistances

The result obtained by chemical resistance tests of the prepared PU coated panels is furnished in the **Table S3 (SI)**. It was found that both PU coating samples were shown notable water resistance. In the case of acid and solvent resistance tests the PU-AIJFA sample showed some swelling and blistering to the film while only slight loss in gloss was found to PU-PAIJFA sample. Swelling, blistering and slight cracks of the PU-AIJFA coatings might be associated with shorter length of soft segment in the case of PU-AIJFA than PU-PAIJFA which resulted into the brittleness and poor adhesion as discussed in the previous section. No significant change in the physical appearance of the PU-PAIJFA coating sample was found after exposing it to water while minor loss in gloss was found when it was immersed in acid, alkali and solvent. Thus from above observations, it was cleared that the PU-PAIJFA coating exhibited the good resistance towards water, acid, alkali and solvent than the PU-AIJFA coating.

Thermo gravimetric analysis (TGA)

TGA curves of the PU-AIJFA and PU-PAIJFA coating samples shown three steps degradation as given in the **Figure S3 (SI)**. First and second step degradations for both the samples showed the same temperature range while the third step was slight different. The first step degradation was seen in the temperature range of 187 – 224 ºC and degradation resulted into 9 % weight loss which may be attributed to loss of solvent and moisture present in the coatings during the curing process. Second step degradation occurred in between 223 – 301 ºC temperature due to the decomposition of urethane group of the prepared PU coatings and it was found up to 16 % weight loss. At the last, third step degradation was obtained in the temperature range of 305 – 517 ºC with decomposition of around 55 % for both the samples. While in the case of PU-PAIJFA coatings it showed slightly higher degradation temperature than PU-AIJFA. Third step degradation may be due to the decomposition of hydrocarbon chains of fatty acids contributed by oil. Therefore, from the result of thermal analysis, we concluded that the piperazine modified fatty amide based PU coatings showed the comparable and slightly better thermal stability in the third step than unmodified fatty amide based PU coatings.

Weight gain and weight loss study of coatings in water and NaCl solution

The prepared PU coated samples (2 x 2 cm dimension) were subjected for dip study in water and NaCl solutions for evaluating coating stability with the substrate. From the **Figure S4 (SI)**, it was observed that PU-PAIJFA coatings showed better anticorrosive nature than PU-AIJFA coatings. The weight gain and weight loss has been studied by measuring the sample's weight every day and results are given in the **Table S4 (SI)**. From the data we found that, panels dipped in water showed initially weight gain upto 5 days for the PU-AIJFA sample while 7 days for the PU-PAIJFA sample. Increment in weight gain for PU-PAIJFA sample may be due to the higher molar mass of PU-AIJFA compared with the same of PU-AIJFA sample. Higher weight loss was found for the PU-AIJFA compared with the PU-PAIJFA in water.

When both prepared sample panels were subjected for dip study in corrosive media (3.5 % NaCl), initially weight gain was observed upto 4 days for the PU-AIJFA sample while 7 days for the PU-PAIJFA sample. Weight losses due to the corrosion were started at PU-AIJFA and PU-PAIJFA samples after 4 and 7 days respectively. From the figure it was cleared that higher anticorrosive nature was found to the PU-PAIJFA compared with PU-AIJFA in water and NaCl solution.

Anticorrosive study by immersion in salt solution

Uncoated steel panels, PU-AIJFA coated and PU-PAIJFA coated steel panels were exposed in the salt solution for 240 h for the study of their anticorrosive performance. The results in the form of images of anticorrosive test are shown in the **Figure 2**. It was found that uncoated steel panels showed highest corrosion than PU-AIJFA coated and PU-PAIJFA coated panels during the period of testing. In the case of coated panels the PU-PAIJFA coatings were with the better anticorrosive resistance than PU-AIJFA coatings. No severe corrosion was found for the PU-PAIJFA coatings on steel panels and adhesion of film to the substrate was not affected much more even after 240 h. The enhanced anticorrosive properties of the PU-PAIJFA coatings may be due to the existence of nitrogen atom containing cyclic ring of piperazine moiety in PU-PAIJFA coatings [38]. Better adhesion of the PU-PAIJFA coating to the metal surface may also be the supplementary reason behind the improved anticorrosive performance. The results visibly revealed the corrosion was decreased due to the incorporation of piperazine moiety in PU coatings network. Therefore, from immersion in salt solution test, it can be concluded that the prepared coatings protected the metal surface and the piperazine modified fatty amides offered better anticorrosion property than fatty amides based PU coatings.

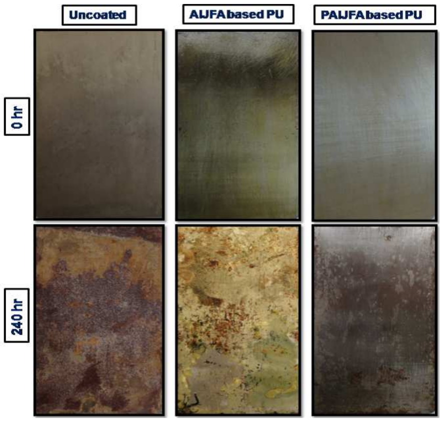


Fig. 2: Images of anticorrosive resistance test of prepared PU coatings

Corrosion Protection Mechanism

Corrosion processes on metallic surface involve conversion of metal (iron) atoms into the ionic state by having oxidation reaction at anode [40, 41]

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

The further reaction can only occur if there is a suitable electron acceptor to combine with the electron released by iron atom. Water contains dissolved atmospheric oxygen which readily serves the purpose of electron acceptor and electrochemically reduced to hydroxyl ions in the cathodic reaction.

$$O_2 + 2\,H_2O + 4\,e^{-} \rightarrow 4OH^{-}$$

The ferrous ions and hydroxyl ions combine together to produce ferrous hydroxide which further reacts with more oxygen to form hydrated ferric oxide, the familiar reddish brown rust (corrosion)

$$Fe^{2+} + 4OH^{-} \rightarrow Fe\,(OH)_2$$

$$Fe\,(OH)_2 + O_2 \rightarrow Fe_2O_3.H_2O$$

Reaction of corrosion process can simply represented as:

$$\underset{\text{Iron}}{4Fe} + \underset{\text{Oxygen}}{3O_2} + \underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Rust}}{2Fe_2O_3.H_2O}$$

In the case of PAIJFA based PU formed uniform and well adhered coating over the metal substrate which prohibits the permeation of corrosive media. The protection mechanism shown in the **Figure 3** is purely through barrier action attributed to the hydrophobic oil based resin. [42] Due to the electro-neutrality principle of electrons released from the iron atom need to be taken up by the oxidizing agent.

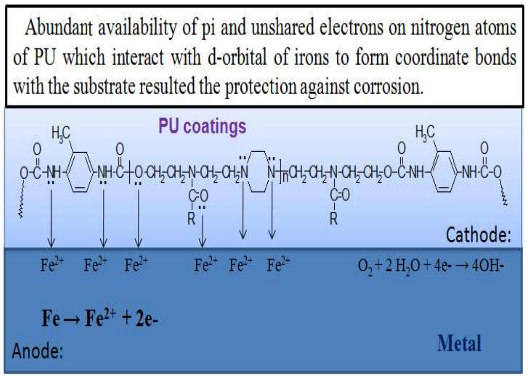


Fig. 3: Corrosion Protection Mechanism

The amide and carbonyl (polar) groups have a strong affinity with iron surface which may be due to the abundance of lone pairs of electrons on the nitrogen/oxygen atom that can interact with vacant d-orbital of mild steel to form coordination bonds.[43, 44] In this way improvement in adhesion between the piperazine modified resin and the mild steel substrate can result in a well adhered coating system which does not allow the corrosive media such as O_2 and water to penetrate easily through the coating network and inhibits panels from the attack of the corrosive species as mentioned in earlier reactions.

Conclusions

In conclusion, the piperazine modified fatty amide of *Azadirachta indica juss* oil was successfully characterized by the determination of physical properties and spectroscopic studies. The PU coatings obtained from piperazine modified AIJFA with TDI showed excellent improvement in the drying property over AIJFA based PU coatings. The physico-chemical and anticorrosive performance has also been studied and found satisfactory results. In immersion test for anticorrosive study, significant role played by piperazine moiety in improving the PU coating properties. This modified resin have good potential for making formulation of surface coating as a binder for paints considering the equivalence ratio 1.1:1 of NCO/OH. The renewable neem oil after modifications was utilized successfully for the synthesis of the industrial PU coatings and can be used to substitute petroleum based materials.

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Notes and references

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1. A. Gandini, *Macromolecules*, 2008, **41** 9491.
2. M.A.R. Meier, J.O. Metzger, U.S. Schubert, *Chem. Soc. Rev.*, 2007, **36** 1788–1802
3. L.M. Espinosa, M.A.R. Meier, *Eur. Polym. J.*, 2011, **47** 837.
4. J.V. Haveren, E.A. Oostveen, E. Micciche, BAJ. Noordover, C.E. Koning, RATM. Benthem, A.E. Frissen, J.G.J Weijnen, *J. Coat. Technol. Res.*, 2007, **41**, 77.
5. D.N.S. Hon, Adhesives from Renewable Resources, ACS Symposium Series 385 (R.W. Hemingway and A.H. Conner, eds.), American Chemical Society, Washington, DC, 291-310 (1989).
6. L.C. Wadworth, Daponte D., Cellulose Chemistry and Its Applications (T.P. Nevell, and S.H. Zeronian, eds.), Ellis Horwood, Chichester, UK, England, 349-365 (1985).
7. A. Anand, R.D. Kulkarni, V.V.Gite, *Prog. Org. Coat.*, 2011, **74**, 764.
8. J.C. Ronda, G. Lligadas, M. Galia, V. Cadiz, *Eur. J. Lipid Sci. Technol.*, 2011, **113**, 46.
9. V.V. Gite, A.B. Chaudhari, D.G. Hundiwale, R.D. Kulkarni, *Pigm. Res. Technol.*, 2013, **42**, 353.
10. F.S. Guner, Y. Yagci, A.T. Erciyes, *Prog. Polym. Sci.*, 2006, **31**, 633.
11. M. Ionescu, Z. Petrovic, X. Wan, *J. Polym. Environ.*, 2007, **15**, 237.
12. M. Alam, S.M. Ashraf, A.K. Roy, S. Ahamad, *J. Polym. Environ.*, 2010, **18**, 208.
13. R.V. Nimbalkar, V.D. Athawale, *J. Am. Oil Chem. Soc.*, 2010, **87,** 947.
14. Z. Chen, B. Chisholm, R. Patani, J. Wu, S. Fernando, K. Jogodzinski, D. Webster, *J. Coat. Technol. Res.*, 2010, **7**, 603.
15. S. Oprea, *J. Mater. Sci.*, 2010, **45**, 1315.
16. S. Narine, J. Yue, X. Kong, *J. Am. Oil Chem. Soc.*, 2007, **84**, 173.
17. P.D. Meshram, R.G. Puri, A.L. Patil, V.V. Gite, *J. Coat. Technol. Res.*, 2013, **10**, 331.
18. A.B. Chaudhari, A. Anand, S.D. Rajput, R.D. Kulkarni, V.V. Gite, *Prog. Org. Coat.*, 2013, **76**, 1779.
19. L.H. Sperling, J.A. Manson, *J. Am. Oil. Chem. Soc*, 1983, **60** 1887.
20. D.L. Compton, J.A. Laszlo, T.A. Isbell, *J. Am. Oil. Chem. Soc.*, 2004, **81**, 945.
21. Z.S. Petrovic, W. Zhang, I. Javni, *Biomarcomolecules*, 2005, **6**, 713.
22. B. Roy, N. Karak, *Polym. Bull.*, 2012, 68, 2299.
23. A. Guo, D. Demydov, W. Zhang, Z.S. Petrovic, *J. Polym. Environ.*, 2002, **10**, 49.
24. S. Pramanik, R. Konwarh, K. Sagar, B.K. Konwar, N. Karak, *Prog. Org. Coat.*, 2013, **76**, 689.
25. M. Kashif, F. Zafar, S. Ahmad, *J. Appl. Poly. Sci.*, 2010, **117**, 1245.
26. O. Saravari, P. Phapant, V. Pimpan, *J. Appl. Polym. Sci.*, 2005, **96**, 1170.
27. S.D. Rajput, P.P. Mahulikar, V.V.Gite, *Prog. Org. Coat.*, 2014, **77**, 38.
28. M.A. Mosiewicki, U. Casado, N.E. Marcovich, M.I. Aranguren, *Polym. Eng. Sci.*, 2009, **49**, 685.
29. C.S. Lee, T.L. Ooi, C.H. Chuah, *Am. J. Appl. Sci.*, 2009, **6**, 72.
30. A.B. Chaudhari, P.D. Tatita, R.K. Hedaoo, R.D. Kulkarni, V.V. Gite, *Ind. Eng. Chem. Res.*, 2013, 52, 10189.
31. A. Zlantanic, C. Lava, W. Zhang, Z.S. Petrovic, *J. Polym. Sci. Part B: Polym. Phys.*, 2004, **42**, 809.

32. A.V. Bagle, R.S. Jadhav, V.V.Gite, D.G. Hundiwale, P.P. Mahulikar, *Int. J. Polymer. Mater. Polymer. Biomater.,* 2013, **62**, 421.
33. K. Biswas, I. Chattopadhyay, R.K. Banerjee, U Bandyopadhyay, *Curr. Sci.,* 2002, **82**, 1336.
34. O.C. Peter, E.E. Ebenso, J.E. Udofot, *Int. J. Electrochem. Sci.*, 2010, **5,** 978.
35. A.B. Chaudhari, V.V. Gite, S.D. Rajput, P.P. Mahulikar, R.D. Kulkarni, *Ind. Crops Prod.* 2013, **50**, 550.
36. J.A. Mikroyannidis, *J. Appl. Polym. Sci.,* 1992, **46**, 1001.
37. P. Nylen, E.Sunderland, Modern Surface Coatings. John Wiley, London (1965).
38. N.K. Patel, J. Franco, *Mater. Corros.,* 1975, **26**, 124.
39. M. Barrere, K. Landfester, *Macromolecules,* 2003, ***36,*** 5119.
40. H. Ma, S. Chen, Z. Liu, Y. Sun, *J. Mol. Str. (Theochem),* 1999, **488**, 223.
41. T. Yang, C. W. Peng, Y.L. Lin, C.J. Weng, G. Edgington, A. Mylonakis, T.C. Huang, C.H. Hsu, J.M. Yeh, Y. Wei, *J. Mater. Chem.,* 2012, **22**, 15845.
42. S. Pathan, S. Ahmad, *J. Mater. Chem. A,* 2013, **1**, 14227
43. M. Alam, A.R. Ray, S.M. Ashraf, S. Ahmad, *J. Am. Oil Chem. Soc.,* 2009, **86**, 573.
44. M. Alam, S.M. Ashraf, S. Ahmad, *J. Polym. Res.,* 2008, **15**, 343.