SYNTHESIS AND CHARACTERIZATION OF SOME AMINE, ETHER AND ESTER MODIFIED VEGETABLE OIL FATTY AMIDE DIOL ANTICORROSIVE POLYMER COATINGS

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Metals and their alloys are highly susceptible to corrosion. Corrosion causes enormous loss in economy of developing countries which spend 5-7% of their GDP on corrosion and its protection annually. India spends about 38,000/- crore per annum to combat corrosion related problem. Corrosion can be checked by a number of ways e.g. by alloying, by the use of corrosion inhibitors, by cleaning the surroundings by suitable designing of plants and machines as well as by the use of coatings. Among these methods, use of organic / polymeric coatings is the most successful and preferred mode for the protection of metals and alloys because of their ease of availability and simple application methods. Coatings are generally organic, inorganic or organic/ inorganic in nature and petroleum based in their origin.

The use of petroleum based monomers, in manufacture of polymer coatings, is however, expected to decline in coming years because of spiraling prices and high rate of depletion of their stocks. Besides, they cost hazardous impact on environment. Thus there is an urgency to replace petro-based chemicals by an easily available, nontoxic, non-polluting and environmentally benign substitute. Vegetable oils play an important role to this end They are employed as raw material in the synthesis of different kinds of monomeric / polymeric resins of low molecular weight, viz., fatty amides, alkyds, epoxies, polyurethanes, polyesteramides and other resins. These resins find considerable applications in paints and coatings industries. Common seed oils used in paints and coatings industries include safflower, soybean, castor, linseed and others.

Fatty amide diol monomers consist of terminal hydroxyl groups with long saturated and unsaturated fatty amide moieties. Vegetable oil fatty amide diols have been exhaustively used as monomer in the synthesis of polyesteramide resins. Polyesteramide resins show better performance than alkyd. coatings; However, they fail to provide service under alkaline environment due to the presence of ester groups in their backbone. It is therefore proposed to develop some new types of polymers from vegetable oil fatty amide diol by the incorporation of ether, ester and amine linkages, by using curing agents viz., toluylene-2,4-diisocynate(TDI), butylated melamine formaldehyde (BMF) and styrene co-maleic anhydride (SMA)co-polymer and to develop their corrosion protective coatings. The problem holds academic and commercial importances. In an agricultural country, utilization of indigenously available sustainable resource such as seeds oils to develop value added polymeric resins holds several advantages from socio-economic viewpoints. If successful results are obtained on commercial scale, it is expected that this approach will help to cut off the cost of corrosion and strengthen the economy of the country providing path towards self reliance.

The thesis has been divided into five chapters

Chapter 1 General introduction and literature review

The chapter 1, embodies general introduction and literature review of oil based polymers utilized for coating applications. It provides information regarding vegetable oils, their production, scope, classification, chemical composition and importance. A brief overview of various resins derived from oils for coating purposes such as alkyds, polyesteramides, polyurethanes epoxies has been presented.

Chapter 2 Characterization techniques of oil, synthetic oleoresins and their coatings

Characterization techniques of oils, oleoresins and their coatings have been discussed in this chapter. These include physico-chemical characterization (acid value, hydroxyl value, iodine value, saponification value, specific gravity, viscosity, colour, refractive index), spectral analysis (FT-IR, ^{1}H-NMR, ^{13}C-NMR), thermal analysis (TGA & DSC) of aforementioned resins as well as physico-mechanical (scratch hardness, impact resistance, bend test) and corrosion / chemical resistance of their coatings in various corrosive media such as water, alkali, acids and organic solvents by standard methods and techniques. Various modes of coating application have been discussed.

Chapter 3 Synthesis, characterization and evaluation of amine modified oil fatty amide coatings

This chapter deals with amine modification of fatty amides using piperazine, melamine and o-phenylene diamine to obtain amine modified fatty amide resins viz. PMF, MPEA, PAA. Aforementioned resins were treated with BMF and SMA curing agents and were further characterized by spectral analysis(FT-IR,^{1}H-NMR,^{13}C-NMR), physico-chemical characterization(iodine value, saponification value, refractive index, inherent viscosity) as well as thermal analyses (TGA and DSC). Coatings of these resins were applied on mild steel strips of standard sizes to study their physico-mechanical and chemical resistance behaviour in various corrosive media. Among PMF-BMF resins (Section:1), PMF-80 resins showed the best physico-mechanical performance: scratch hardness 2.5 kg, impact resistance 200 lb/inch, conical mandrel test- passes1/4 inch bend, gloss 75 at 45°. It also showed good corrosion resistance performance in NaOH (2wt%, 4 h), HCl (5wt%, 3 days), NaCl (3.5 wt%, 10 days), H_2O(4 days) and xylene(5 days). Among PAA-SMA resins (Section:2), PAA-35 resin was found to show the best physico-mechanical performance: scratch hardness-3.0 kg, impact resistance 250 lb/inch, conical mandrel test 1/8 inch, gloss-90 at 45°. It also exhibits good corrosion resistance performance in NaOH (5wt%, 2 h), HCl (5wt%, 5days), NaCl (3.5 wt%,8 days), H_2O (7 days) and xylene (5 days). Among MPEA resins (Section 3), MPEA-60 resin was found to show the best physico-mechanical performance: scratch hardness-4.0 kg, impact resistance-250 lb/inch, conical mandrel passes 1/8 inch bend test and gloss 82 at 45°. It also showed good corrosion resistance performance in NaOH (4wt%,4 h), HCl (5wt%, 5days), NaCl (3.5 wt%, 8days), H_2O(7 days) and xylene (7days). Thermal stability and curing behavior of these resins were studied by Thermo gravimetric analyses (TGA) and differential scanning calorimetry (DSC), respectively. These resins can be safely used up to 305 °C.

Chapter 4 Synthesis, characterization and evaluation of ether modified oil fatty amide coatings

Chapter 4 describes the preparation of polyetheramide resins from N, N-bis (2-hydroxy ethyl) oil fattyamide diol, bisphenol-A and resorcinol. They were further treated with toluylene-2, 4-diisocyanate (TDI) and BMF in different weight percentages to obtain urethane modified polyetheramide resins (UPEtA). The structural elucidation of UPEtA, R-UPEtA and PEtA-BMF resins were carried out by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Physico-chemical, thermal and physico-mechanical analyses were performed by standard methods. The solubility of resins was determined in various organic solvents at room temperature. Coatings of UPEtA, R-UPEtA, PEtA-BMF were prepared on mild steel strips. The anticorrosive behaviour of coatings of aforementioned resins in acid, alkali, water and xylene was investigated. Among all the resins PEtA-40 cured at 170°C, UPEtA-25 and R-UPEtA-24 show the best performance. UPEtA-25 passes scratch hardness 1.2 kg impact resistance 150 lb/inch, 1/8 inch bend on conical mandrel and shows slight loss in gloss in H_2O(10 days) and HCl(5wt%, 10 days) loss in gloss is observed in NaCl (3.5wt%, 5 days) and NaOH (5wt%, 2 hours); coatings of these resins are unaffected in xylene(10 days). PEtA-40(170°C) shows scratch hardness 1.5 Kg, impact resistance 150 lb/inch, 1/4 inch bend on conical mandrel. Coated panels remain unaffected in HCl (5wt%, 10 days), NaCl (3.5 wt%, 10 days) H_2O(10 days) and xylene (10 days); in NaOH (5wt%, 1 hour), slight loss in gloss is observed. R-UPEtA-24 passes scratch hardness 2 kgs, impact resistance 150 lb/inch and 1/8 inch bend on conical mandrel. Coatings remain unaffected in NaOH (2wt%,8hours), HCl (5wt%, 6 days), NaCl (3.5 wt%, 7 days); loss weight occurs in H_2O (7 days). The systems can be safely used upto 210°C.

Chapter 5 Synthesis, characterization and evaluation of ester modified oil fatty amide coatings

Chapter 5 presents a novel modification of fatty amide diol by condensation reaction of

N,N-bis(2-hydroxy ethyl) oil fatty amide and tartaric acid (TA), pyridine dicarboxylic acid, ethylene diamine tetra acetic acid to obtain polyesteramide resins viz., tartaric acid modified fatty amide (TAFA), pyridine polyesteramide (Py-PEA) and ethylene diamine polyesteramide(Ed-PEA). Futher, curing of these resins was accomplished with butylated melamine formaldehyde(BMF) and toluylene 2-4 diisocynate(TDI) to obtain TAFA-BMF, Py-UPEA and Ed-UPEA resins. The structural elucidation of the these resins were carried out by FT-IR,^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The physico-chemical characterization of these resins were performed by standard methods. The thermal studies of these resins were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was found that among TAFA-BMF, Ed-UPEA and Py-UPEA resins, TAFA-30, Ed-UPEA-18 and Py-UPEA-14 show the best performance. TAFA-30 shows scratch hardness 1.9 kg, impact resistance 150 lb/inch, passes 1/8 inch bend on conical mandrel; it is unaffected in water (7 days), HCl (5wt%, 7 days), xylene (7 days) and shows loss in gloss and weight in NaOH (5wt%, 3hours). Ed-UPEA-18 shows scratch hardness 4.5 kgs, impact resistance 150lb/inch, passes 1/8 inch bend on conical mandrel. It exhibits loss in gloss in water (7 days) and remains unaffected in HCl (5wt%, 7 days), NaOH (5wt%, 3 hours), xylene (7 days). Py-UPEA-14 exhibits scratch hardness 2.5 kgs, impact resistance 150 lb/inch, passes 1/8 inch bend on conical mandrel. It remains unaffected in water (4 days) and xylene (10 days); it shows loss in gloss in HCl (5wt%, 2 days) and NaOH (5wt%, 1 hour). These systems can be safely used 200^{o}C.