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Synthesis and characterization of cardanol based reactive polyamide for epoxy coating application

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ABSTRACT

Cardanol based reactive polyamides having different molecular weights were successfully developed by conventional polycondensation mechanism. The synthesis involved 2-step processes of functionalization of cardanol by maleic anhydride followed by its condensation with diethylenetriamine (DETA) in the 2nd step. The polyamides with different molecular weights were prepared by varying the mole ratios of acid and amine components in the formulation. The developed polyamides were characterized for structural confirmation by FT-IR and NMR spectroscopy. These polyamides were then used as curing agents for thermally curable epoxy coatings. The effect of molecular weights of these polyamides on mechanical, chemical, thermal and solvent resistance properties of conventional epoxy resin was studied and compared with that of commercial polyamide. The anticorrosive properties of the coatings were evaluated by salt spray test and electrochemical impedance spectroscopy. The study revealed that the performance properties of cured material improved with increase in amine value of polyamides due to increased cross-link density. The anticorrosive performance also improved as indicated by higher impedance and electrochemical potential values.

1. Introduction

Considering the environmental and health related concerns regarding use of petroleum based stocks for polymer/resin synthesis, maximum utilization of renewable resources has become an attractive topic as far as academia and industries are concerned. Due to abundant availability, sustainability, ease of handling and lower cost compared to petroleum based materials, the use of renewable materials have attracted worldwide interest nowadays [1].

The exploration of renewable resources for wide variety of applications such as resin synthesis, adhesives, paints, coatings, composites etc. through various chemical modifications has been reported by number of researchers till date [2–8]. Among the variety of resins used in coating industry, epoxy are considered as one of the most versatile classes of polymers due to their excellent overall properties over other chemistries. Being highly useful polymeric materials, epoxy resins have carved their niche in a wide range of applications, including metal coatings, use in electronics/electrical components, high tension electrical insulators, fiber-reinforced plastic materials, structural and engineering adhesives etc. [9]. Commercially epoxy resins are cured with a wide range of co-reactants including polyfunctional amines, polyamides, acids (and acid anhydrides), phenols, alcohols and thiols which forms thermosetting polymer, often with high mechanical properties, temperature and chemical resistance [9,10]. Since 1970s, amongst all curing agents of epoxy resins, polyamides have become the most popular ones for two pack epoxy coatings due to relatively non-toxicity and virtually non-volatility, as opposed toxicity and volatility of amine hardeners, longer pot lives, high degree of internal plasticization, and excellent adhesion on numerous surfaces due to polar nature of polyamides [10]. These polyamides are usually produced by reacting polybasic acids with polyamine compounds and are mainly characterized by presence of amide linkage (HN-CO-). Till date polyamides based on renewable resource viz rosin, dimer fatty acids, oils, isosorbide etc have been well reported [11–13]. However, there exists compound like Cashew Nut Shell Liquid (CNSL), which can be used as a possible substitute for petroleum based feed stocks due to its availability, sustainability, cost effectiveness, and reactive functionalities.

CNSL, an agricultural waste of cashew nut tree contains mixture of cardanol, cardol, anacardic acid and 2-methyl cardol which has

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meta-substituted saturated/unsaturated hydrocarbon long chain along with the reactive phenolic ring. These reactive functionalities make them suitable for number of polymerization reactions through addition as well as condensation mechanisms. Cardanol, one of the key components of CNSL constituents has also been reported as a potential raw material for polymer/oligomer synthesis involving various chemistries such as epoxy, alkyd, phenolic, polyurethane, polyol etc and has proved to be an excellent coating materials when formulated for different types of coatings like modified alkyd based coatings, epoxy coatings, water borne coatings, UV-curable coatings, modified polyurethane coatings and phenolic coatings [14,15]. Besides conventional resin synthesis, synthesis of miscellaneous coating materials has been reported, such as vinyl ester polymers, cyanate ester resins, benzoxazine resin, anti-bio film coatings, fire retardant materials, crosslinked polymers, water soluble mannich bases, molecularly imprinted polymer, adhesives, laminating resins, modifying agents for plastics and various coating additives such as surfactant, doping agent, antioxidant, colorant, corrosion inhibitors, coupling agents, dispersant etc. [16,17]. The modified cardanols with single or multiple functionalities are also available commercially, some of the modified products being Diglycidyl ether of cardanol (Cardolite NC-514), Mono-glycidyl ether of cardanol (Cardolite NC-513), phenalkamines (NC-540, NC-557, NC-566 and So On) and phenalkamide (LITE 3060) which are being for various industrial applications.

The aim of the present work was to develop and characterize cardanol based polyamides with different amine values for epoxy coating applications. The synthesis of polyamides involved 2-steps process of carboxyl functionalization of cardanol followed by its polycondensation with polyamine. Further, the developed resins were characterized for their physical & chemical properties such as color, specific gravity, viscosity, % non-volatile matter, iodine value, acid value and amine value. In addition, some of the instrumental techniques such as FT-IR and NMR were also used to characterize the developed resins. The developed resins were then used as curing agents for epoxy resin and the coatings obtained were evaluated for their properties such as tensile strength, flexural strength, elongation, adhesion, flexibility, impact resistance, cupping resistance, hardness, solvent resistance, chemical resistance, gel content etc. The coatings were also analyzed for their thermal and anti-corrosive properties.

2. Experimental

2.1. Materials

The pure cardanol (NC-700) was procured from Cardolite Speciality Chemicals Ltd., Mangalore, India. The reagents used like maleic anhydride ($C_4H_2O_3$), anhydrous sodium sulphate (Na_2SO_4), glacial acetic acid (GAA), n-methyl-2-pyrollidone (NMP), xylene, butanol, diethyl ether, potassium hydroxide pellets, methanol, phenolphthalein indicator and diethylene triamine (DETA) were purchased from SD Fine chem. Ltd., Mumbai and were used as received. Cobalt octoate (6%) was received from Notional Specialities Product, Vapi and catalyst Fascat 4100 was obtained from Brenntag Specialties, Mumbai. Polyamide resin (Synpol-140) having amine value 340–400 mg of KOH/g and curing catalyst (Tris-(dimethyl amino methyl) phenol widely known in the market as DMP-30) were received from Shalimar Paints ltd., Nashik, India.

2.2. Synthesis of cardanol based polyamides (CPAs)

2.2.1. Functionalization of cardanol

Functionalization of cardanol involved formations of maleic anhydride adduct of cardanol via Ene-mechanism or by formation of chroman ring via Diels-Alder mechanism [18] as shown in Fig. 1. The reaction was carried out in a 4-necked round bottom flask assembled with a thermometer, water condenser, and mechanical stirrer at 180–190 °C for 5 h under nitrogen atmosphere. The required quantity of cardanol (1 mol) and MA (1.1 mol) along with cobalt octoate (6% solids solution) as a catalyst (0.5% w/w) were charged in the reactor. The reaction mixture was charged with nitrogen containing solvent such as *n*-methyl-2-pyrolidone (2 wt%) to avoid undesired currying reaction which may occur resulting in unavoidably gelation of the reaction mixture [19]. After completion of reaction, the mixture was cooled down to 90 °C and hydration was carried out by adding distilled water in it and refluxing the mixture for about 1 h. Further, the product was purified by separating from aqueous phase and was then dried over anhydrous sodium sulphate. The dark brown viscous liquid thus obtained was characterized by FTIR and NMR and evaluated for its acid value & iodine number.

Table 1
Reaction Stochiometry used for synthesis.

	CPA-270	CPA-370	CPA-470
Acid equivalent of Malenized Cardanol	1	1	1
Mole of DETA	0.66	0.78	0.90
Fascat-4100 (Reaction catalyst)	0.5 wt%	0.5 wt%	0.5 wt%
Xylene (Reflux solvent)	20 wt%	20 wt%	20 wt%

2.2.2. Synthesis of reactive polyamide

The free carboxyl groups of functionalized cardanol obtained after hydration were further modified with excess monomeric amine (DETA) (10% excess) to synthesize reactive polyamide via polycondensation mechanism. The reaction assembly involved four necked round bottom flask fitted with stirrer, Dean & Stark apparatus, thermometer and nitrogen inlet. The quantity of DETA was decided on the basis of acid equivalent of malenized cardanol. The molar ratio of DETA to cardanol was varied in order to obtain CPAs with varying amine value. The reaction composition is reported in Table 1. After charging the requisite quantities of malenized cardanol and DETA along with xylene as a refluxing solvent in the reactor, the reaction mixture was heated to 140–150 °C and maintained for 3 h. The temperature was then raised to 160–170 °C and maintained for 3–4 h. The reaction was monitored by measuring acid value of the reaction mixture at regular interval. After removal of water of condensation the reaction was stopped and the reaction mixture was cooled. The products were further evaluated for their physico-chemical properties and characterized by instrumental techniques. Fig. 2 shows a schematic representation of synthesis of polyamide.

The synthesized cardanol based polyamides (CPAs) were denoted as CPA-270, CPA-370 and CPA-470, where CPA stands for cardanol based polyamide and the numbers 270, 370 and 470 stands for their respective amine values.

2.3. Surface preparation

Mild steel panels (6 × 4 square inches) were manually cleaned before application. Cleaning involved degreasing & hand scrubbing using emery paper (120 no.) followed by cleaning with xylene.

2.4. Application and curing of coatings

The cardanol based polyamides were then used as a curing agents for diglycidylether of bisphenol-A on equivalent basis as per following formula;

$$\text{Weightofpolyamide} = (\text{amineequivalentweight}/\text{epoxyequivalentweight}) \times 1$$

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