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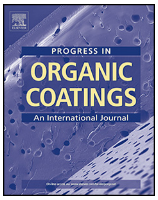

Air-drying bio-based polyurethane dispersion from cardanol: Synthesis and characterization of coatings

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ABSTRACT

Exploring bio-renewable materials to replace petroleum-based building blocks for advanced coatings has been a major thrust area for researchers for the development of eco-friendly and sustainable products. For the last few decades, there has been significant interest among coating researchers around the world to design water-based polyurethane dispersions (PUDs) that can be cured at ambient conditions. In the present work we synthesized auto-oxidizable PUDs based on cardanol as sustainable material that also provides self-crosslinking attribute to the PUDs. Such types of PUDs are expected to be suitable for water-based industrial protective primers. The cardanol-based intermediates and final products are characterized by FTIR spectroscopy for conformation of synthesis reaction and their structures. The dried films of the coatings, formulated using a suitable drier catalyst, exhibited improvement in mechanical properties and solvent resistance. The oxidative curing has also been investigated by FTIR and differential scanning calorimetry (DSC). The corrosion resistance properties of the coatings on steel substrate, as studied by using electrochemical impedance spectroscopy (EIS) technique also showed better performance for cross-linked films.

1. Introduction

Polyurethanes (PUs) are a very important class of polymers that exhibit many desirable characteristics for their diverse applications in coatings, adhesives, sealants, elastomers and plastics. Coating engineers have successfully exploited PUs to design coatings for such end-use applications as coatings for metals, automotive coatings, wood coatings, glass coatings and many more. While solvent-based and high-solid conventional PU coatings have successfully been used, the regulatory push for reduction of VOC has resulted in demand for water-borne systems [1]. Thus waterborne polyurethane dispersions (PUDs) have gained commercial importance over the past few decades. Most of the conventional PUDs are predominantly thermoplastic, high molecular weight, linear ionic polymers which dry by physical drying (coalescence of polymer particles) [2]. Despite their generally good properties for many end-use applications, lack of cross-linking ability in thermoplastic PUDs makes them unsuitable for applications requiring good solvent or chemical resistance as well as higher mechanical properties. To meet these demanding requirements cross-linkable PUDs have been introduced wherein cross-linking is achieved either by external cross-linking agents or through internal self-cross linking. The use of external cross linking agents such as polyisocyanates, aziridine, carbodiimide, or melamine formaldehyde resins is having demerits of mixing of cross-linker at user's end just before application, limited pot life, or toxicity of cross-linkers [3–7]. The oldest but even currently most popular self-crosslinking technology is via auto-oxidation of an unsaturated functionality introduced through vegetable oil derived fatty acids to the polyol component of PUDs [8–16]. The autoxidation curing chemistry is well known in commercial resins such as alkyds, polyurethane-alkyds and epoxy-esters. Besides conferring oxidative drying potential, these fatty acid derivatives also make such PUDs more sustainable.

From the early years of coating technology to till date, vegetable oils have been widely explored as sustainable materials in polymers for coatings, especially in autoxidizable binders. Besides vegetable oils, cashew nut shell liquid (CNSL), an agricultural by-product of the cashew industry, has also been used in binders for coatings for several years. CNSL is a reddish brown viscous phenolic lipid, which is found in the soft honeycomb structure of the shell of cashew nut. The chemistry and composition of CNSL have been extensively studied [17–19]. CNSL comprised primarily of cardanol, anacardic acid, cardol and 2-methyl cardol which are phenolic compounds substituted at the – meta position with unsaturated alkyl chain ($C_{15}H_{31-2n}$, $n = 0–3$) which may be used as autoxidizable sites for curing of polymers. The chemical structures of these constituents

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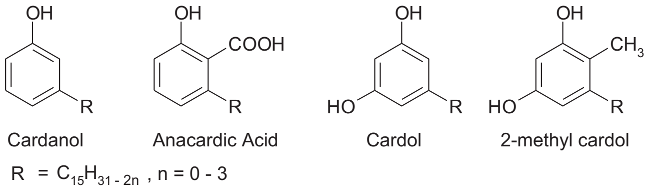

Fig. 1. Primary components of CNSL.

are shown in Fig. 1. High vacuum distillation of CNSL yields cardanol which has been very important precursor for various oligomers and polymers. Over the years, different derivatives of cardanol such as phenolic resin, epoxy resins, vinyl esters, phenalkamines and surfactants have been developed by researchers for their industrial applications in coatings, composites, laminates and adhesives [19–25].

Though CNSL and cardanol have been explored in polyurethanes for different applications [26–30]; to the best of our knowledge, cardanol has not been reported for its application in polyurethane dispersions. In this paper we report synthesis of cardanol-based autoxidizable polyurethane dispersion and its applications in coatings. A unique polyol has been designed and synthesized by condensation of cardanol with epoxy resin and subsequently been used as polyol component (soft segment) in synthesis of polyurethane dispersion. The clear coating compositions prepared from these PUDs, with and without drier (catalyst) additive, have been applied on metal substrate and cured under ambient conditions. The cured films have been evaluated for various mechanical and thermal properties, and also for their corrosion resistance on steel substrate to investigate oxidative curing of the films.

2. Experimental

2.1. Materials

Cardanol was procured from Palmer International Inc., USA. Diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (EPON® 828 RS) and polytetra methylene ether glycol (PTMEG, Terathane® 250) was supplied by Momentive Specialty Chemical Inc., USA and Invista, USA respectively. Isophorone diisocyanate (IPDI, Desmodur® I) was received from Bayer Material Science, USA. Dimethylolpropionic acid (DMPA) was procured from Geo Specialty Chemicals, USA. Borchi® OXY – Coat, used as drier to catalyze oxidative curing of the PUDs developed, was supplied by OMG Americas Inc., USA. All the above materials were used as received. All other chemicals such as ethyltriphenylphosphonium bromide (ETPPB), triethylamine (TEA) as neutralizing agent, ethylene diamine (EDA) as chain extender, N-methylpyrrolidone (NMP), acetone, dibutyltin dilaurate (DBTDL), were purchased from Sigma–Aldrich, USA, and used as received. Low carbon cold-rolled steel panels (type R) were purchased from Q-panel Lab products, USA.

2.2. Preparation of cardanol epoxy condensation polyol (CE)

Reaction of epoxy resin with phenolic compound is well known. In this work cardanol based polyol was prepared by reacting it with diglycidyl ether of bisphenol A type epoxy resin using ethyltriphenylphosphonium bromide catalyst [31]. In a typical process; 185 g (1.0 epoxide equiv.) DGEBA having epoxy equivalent weight (EEW) of 185 g/equiv. (as determined experimentally according to ASTM D 1652-04), and 300 g (1.0 equiv. of phenolic hydroxyl) of cardanol were placed in a 3-neck flask equipped with mechanical stirrer, water condenser, nitrogen inlet, thermo couple and heating mantle connected with temperature controller. The reaction mass was heated to 80 °C with continuous purge of dry nitrogen gas. At this temperature, 278.4 mg (0.75 mmol) ETPPB catalyst, dissolved in minimum quantity of methanol, was then added to the reaction mass and temperature was gradually increased to 190 °C in 30 min. The reaction was then continued at 190 °C until weight percent of oxirane oxygen (%OOC) (ASTM D 1652-04) reduced below 0.3%. The reaction scheme is shown in Fig. 2.

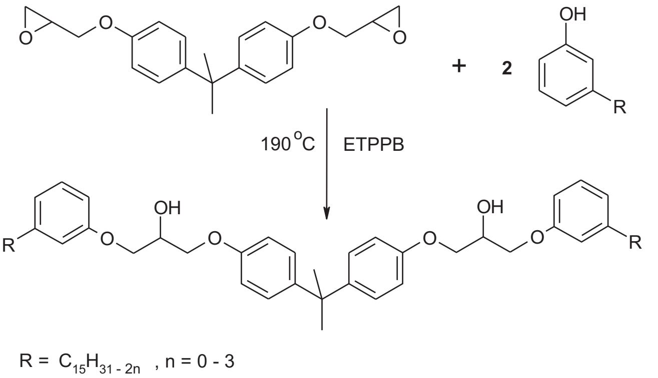

Fig. 2. Reaction scheme of cardanol epoxy condensation polyol (CE).

2.3. Characterization of CE

The initial reaction mass and final product of CE were analyzed by FTIR spectroscopy in the mid operating range of 4000–400 cm^{-1} using Bruker Tensor 27 FTIR analyzer. The representative spectra of %T (transmission) versus wave number are shown in Fig. 3.The prepared polyol (CE) was also characterized for molecular weight using gel-permeation chromatography (GPC). A GPC system consisting of three Phenogel columns from Phenomenex (USA), Phenogel™ 5μ 50A, Phenogel™ 5μ 100A and Phenogel™ 5μ 500A, covering molecular weight range from 100 to 15,000 g/mol; Viscotek VE 3580 RI detector and Malvern 270 Dual detector was used. Sample was dissolved in HPLC grade tetrahydrofuran (THF) (6.16 mg/ml). Sample injection volume was 100 μL, flow rate of carrier solvent (THF) was 1.00 ml min^{-1} and operating temperature was 45 °C. The average molecular masses, M_n, M_w and polydispersity index were determined by software OmniSEC 4.7. Monodispersed polystyrene standards were used to make calibration curve. The polyol (CE) was also evaluated for hydroxyl value (ASTM D 4274-05) and viscosity (ASTM D 4287-00) by using cone and plate viscometer (Brookfield CAP 2000+). The results are shown in Table 2.

2.4. Preparation and characterization of polyurethane dispersion based on CE (CEPUD)

CEPUD was synthesized using prepolymer process described in literature [32–34]. An isocyanate terminated prepolymer was prepared in three neck flask equipped with mechanical stirrer, water condenser, nitrogen inlet, thermo couple and heating mantle connected with temperature controller. Calculated amounts of CE, DMPA, PTMEG, and NMP were placed in the flask and heated to 100 °C to dissolve DMPA. The reaction mass was then cooled to 65 °C and DBTDL catalyst was added followed by controlled addition of IPDI at a rate that does not increase temperature of the reaction more than 70 °C. The reaction was continued at 65 °C until desired percent isocyanate content (% NCO) (ASTM D 2572-97) was reached. Then reaction mixture was cooled to 50 °C and TEA was added to neutralize the prepolymer and stirred for 15 min. The neutralized prepolymer was then dispersed in deionized water using high-speed disperser followed by chain extension by EDA. Table 1 shows the composition of CEPUD. A simplified reaction scheme for synthesis of CEPUD is shown in Fig. 4. CEPUD was characterized