



## Anticorrosive and insulating properties of cardanol based anhydride curing agent for epoxy coatings



Kunal Wazarkar, Mukesh Kathalewar, Anagha Sabnis\*

Dept. of Polymer and Surface Engineering, Institute of Chemical Technology, Matunga, Mumbai 400019, India

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### ABSTRACT

Present research reveals the synthesis of anhydride curing agent for preparation of anticorrosive epoxy coatings. A novel dianhydride compound was synthesized from cardanol and used as a curing agent for commercial epoxy resin. The structure of the curing agent was confirmed by chemical and spectroscopic analysis. Coatings were formulated with varying ratio of epoxy resin to anhydride on equivalent basis such as 1:0.6, 1:0.8, 1:1. The effect of varying concentration of curing agent on mechanical, chemical, optical, thermal, electrical and anticorrosive properties of coatings was investigated and compared to coatings cured with commercial methyltetrahydrophthalic anhydride (MTHPA). It was observed that, curing agent based on cardanol performed extraordinarily in all aspects as compared to the commercial curing agent.

### 1. Introduction

Epoxy resins are versatile class of polymers and one of the most commercially used thermosetting materials. They possess excellent adhesion to the substrate, superior chemical resistance, good mechanical properties, excellent anticorrosive and thermal stability [1–3] which make them good candidates for a variety of applications including adhesives, coatings, moulding compounds, composites, construction materials, electronic insulation components etc. [4–7]. The epoxy resins are often mixed with other component to improve the properties of resin further. These are called curing agents or hardener, depending on application variety of curing agents are available for epoxies. Most commonly used hardeners include amines, polyamides, anhydride, carboxyl, phenolic compounds etc. Amongst these, amine curing agents are the most popular as they provide room temperature curing with good performance properties. However, they possess certain disadvantages such as the formation of polar groups which increase water absorption thereby reducing mechanical and electrical properties of the system. This formation of polar groups does not occur when carboxyl or anhydride curing agents are used. Consequently, after amines anhydrides constitute the next most important class of curing agents. The less exothermic reaction of epoxies with anhydride results in low shrinkage, low internal stresses, reduced water absorption, high glass transition temperature and excellent electrical insulation [8,9]. However, most anhydride-epoxy systems are less reactive and require high temperature (> 120 °C) to initiate and propagate curing reaction [10–14]. To increase the rate of curing reaction and lower the curing

temperature sometimes accelerators are added to the formulation [14]. These accelerators are mainly lewis bases such as tertiary amines [15,16], imidazoles or quaternary ammonium salts etc. [17,18]

These curing agents are generally derived from petroleum based resources and require complicated chemical processes in end product syntheses. Rapid depletion of petroleum resources and their rising cost has forced researchers to develop materials that are sustainable and economical. For this reason, various biobased materials have been explored in the past, including vegetable oils, lignin and its derivatives, sugar derivatives, amino acids, vanillin, eugenol, citric, tartaric and itaconic acid, cashew nut shell liquid (CNSL) and its derivatives etc. Recently, CNSL and its derivatives have received much attention of the scientists as they are easily and abundantly available throughout the world. CNSL mainly contains four components; cardol, 2-methyl cardol, cardanol and anacardic acid. Amongst all these cardanol is mostly preferred as it contains one phenolic ring and C15 unsaturated aliphatic chain which give the perfect balance of hardness and flexibility [19]. In recent years, lots of chemical modifications of cardanol are have been studied to make it suitable for a wide variety of applications in polymer and coatings such as plasticizers, UV diluents, isocyanate free polyurethanes, epoxies etc. [20–24]

Here we have made an attempt to synthesize novel silicon containing anhydride curing agent for epoxies. The structure of the curing agent was confirmed by FTIR spectroscopy, <sup>1</sup>H NMR spectroscopy, acid value and iodine value. The curing agent was further used for curing commercial epoxy resin in varying ratio 1:0.6, 1:0.8 and 1:1 on an equivalent basis. Further, the effect of concentration of curing agent on

\* Corresponding author.

E-mail address: [as.sabnis@ictmumbai.edu.in](mailto:as.sabnis@ictmumbai.edu.in) (A. Sabnis).

various performance properties was investigated. In addition, commercial Methyl tetrahydrophthalic anhydride (MTHPA) was used for comparative study.

## 2. Materials and methods

### 2.1. Raw materials and chemicals

Cardanol (NC-700) was provided by Cardolite Specialty Chemicals Ltd., Mangalore, India. All the reagent grade chemicals including maleic anhydride (MA), dichlorodimethylsilane (DCDMS), ethyl acetate, sodium hydroxide, triethylamine, sodium hydride, cobalt octoate was purchased from SD Fine Chemicals, Mumbai, India. Commercial anhydride curing agent methyltetrahydrophthalic anhydride (MTHPA) and *N,N*-Dimethylbenzylamine (BDMA, tertiary amine catalyst) was a courtesy from Aditya Birla Science and Technology Company Ltd. Mumbai, India. All reagent grade chemicals were used as received without further purification.

### 2.2. Synthesis of malenized silicon containing cardanol (MSIL)

In the first step, 100 ml of ethyl acetate was poured into the four necked flask fitted with water condenser, thermometer pocket, nitrogen inlet and dropping funnel. The entire assembly was put into an ice bath and stoichiometric amount of sodium hydride was added into the flask slowly. After that, cardanol was added to the above mixture in a drop wise manner for a period of 20–25 min by maintaining the temperature maximum to 10 °C. After complete addition of cardanol, the temperature of the mixture was gradually increased to 60–70 °C and the mixture was allowed to stir for an hour. Further, the reaction mixture was again cooled to 5–10 °C and dichlorodimethyl silane was added drop wise for a period of 1–1.5 h. The stoichiometric ratio of cardanol:DCDMS:sodium hydride was 2:1:2. After complete addition of DCDMS, the temperature of the mixture was gradually raised to 70 °C and allowed to stir for 8 h. The product abbreviated as “SIL” was then washed several times with lukewarm water to ensure complete removal of sodium chloride salt. In the second step, SIL and maleic anhydride in the molar ratio 1:2.2 was taken in four necked flask fitted with water condenser, thermometer pocket, nitrogen inlet and mechanical stirrer. Cobalt octoate was added as a catalyst (1 wt% of total reaction mass) and the temperature was increased to 140–150 °C. The reaction mixture was vigorously stirred for 4–5 h. After completion of the reaction, the mixture was diluted in ethyl acetate and washed several times with 1% NaCl solution followed by lukewarm water to ensure complete removal of maleic anhydride. The viscous product abbreviated as “MSIL” was confirmed by chemical as well as spectroscopic analysis. Reaction scheme is shown in Fig. 1.

### 2.3. Coating preparation

Mild steel panels (5 in. × 3 in.) were first degreased with cleaner solution for 15 min and further washed under tap water and dried. The substrates were then polished with emery paper 800 and finally wiped with acetone.

To prepare coating formulations, the ratio of MSIL to the epoxy resin was varied on an equivalent basis as 0.6:1, 0.8:1 and 1:1. Similarly, commercial MTHPA was also used to prepare coatings for comparison. The calculated amount of anhydride curing agent and epoxy resin were mixed with xylene/butanol (70/30 on v/v) solvent mixture to attain application viscosity. BDMA (1 wt% of total formulation) was added as a catalyst. The mixture was applied on mild steel substrates and after a flash off for 10–15 min the coated substrates were kept in an air circulating oven. The substrates were then thermally cured at 150 °C for 30 min to get completely dried coating. After 24 h of conditioning period, the coated substrates were evaluated for physical, mechanical, chemical, thermal and anticorrosive properties. Coatings

cured with 0.6, 0.8 and 1 equivalent of MSIL and MTHPA were represented by the name of curing agent followed by numbers 0, 1 and 2 respectively. The amount of curing agent required for curing epoxy resin is given by Eq. (1).

$$\frac{\text{Weight of epoxy}}{\text{epoxy equivalent weight}} = \frac{\text{Weight of curing agent}}{\text{No. of equivalents} \times \text{equivalent weight of curing agent}} \quad (1)$$

### 2.4. Characterization

The acid value and iodine value were calculated as per ASTM D 1980 and ASTM D 1959 respectively. The gel content (GC) was determined by standard gravimetric analysis. The known weight of sample (W<sub>0</sub>) was put into 20 ml THF for 24 h. These samples were then dried in oven at 50 °C and weighed again (W<sub>2</sub>). GC was then calculated using Eq. (2).

$$\text{Gel content (\%)} = \frac{W_2 \times 100}{W_0} \quad (2)$$

To measure water absorption of cross-linked sample, sample with known weight was kept in water at room temperature for 24 h. After completion of the test period, any drops of water left on polymer samples were soaked with cotton and weighed. The water absorption was then calculated according to Eq. (3) from the difference in the weights of the sample before and after soaking in water.

$$\text{Water absorption (\%)} = \frac{(\text{Wafter} - \text{Wbefore}) \times 100}{\text{Wbefore}} \quad (3)$$

where, Wafter is the weight of the sample after dipping in water and Wbefore is the weight of the sample before dipping in water.

The coatings were tested for adhesion properties by Cross Cut Adhesion according to ASTM D-3359. A lattice pattern of cuts with equal spacing was made on the coating surface with the cross hatch cutter and commercial cellophane tape was applied over the lattice. The substrate was then examined for any loss of the squares from the lattice pattern. Pull off adhesion strength of coatings was evaluated by the portable adhesion tester as per ASTM D-4591. Pencil & scratch hardness of the coatings were measured on hardness tester according to ASTM D-3363 & IS-104 respectively. Flexibility and load distribution property of the coating were determined by conical mandrel and Impact tester as per ASTM D-522 and ASTM D-2794 respectively. Impact resistance was measured on the impact tester with maximum height of 23.6 in. and a load of 3 lbs. The chemical resistance of the coated panels was evaluated by acid & alkali as well as a water immersion method according to ASTM D-1308 and ASTM D-870 respectively. The degree of adhesion and visual inspection of blister and cracks was evaluated for coated panels after immersion for 24 h. The solvent resistance was measured by a rub test using methyl ethyl ketone and xylene as per ASTM D-4752. Hydrolytic stability was evaluated according to ASTM B-1308, coated panel was immersed in boiling water for 4 h and evaluated for loss of adhesion and blister formation, if any.

### 2.5. Instrumentation

The FTIR spectra were recorded on Bruker Instruments in the wavelength range 4000–400 cm<sup>-1</sup> at 24 scans and 2 cm<sup>-1</sup> of resolution. NMR spectra were recorded on Mercury Plus NMR spectrometer (400 MHz, Varian, USA). CDCl<sub>3</sub> was used as a solvent for all the samples evaluated. The chemical shifts in the discussion are reported in parts per million. The number average molecular weight (M<sub>n</sub>) and molecular weight distribution was determined by gel permeation chromatography (GPC) (Agilent 1100 series). The sample was dissolved in tetrahydrofuran and placed in Agilent 1100 series instrument, consisting of a refractive index (RI) detector and Agilent PL gel 10 μm column.

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