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Cardanol based anhydride curing agent for epoxy coatings

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ABSTRACT

In the present research work, cardanol based di-anhydride curing agent was synthesized and used in the preparation of anticorrosive epoxy coatings. For this purpose, cardanol and glycidyl methacrylate were first reacted and subsequently malenized using maleic anhydride to yield di-anhydride compound which was used as a curing agent for commercial epoxy resin. Structure of the curing agent was confirmed by evaluating its acid and iodine value as well as Fourier transform infrared spectroscopy, proton and carbon nuclear magnetic resonance spectroscopy and gel permeation chromatography techniques. Coatings were formulated by varying the ratio of epoxy adduct to anhydride on equivalent basis such as 1:0.6, 1:0.8, 1:1. Further, the prepared coatings were characterized for mechanical, chemical, optical, thermal, insulating, anticorrosive properties etc. and compared with commercial methyltetrahydrophthalic anhydride cured epoxy coatings. It was observed that curing agent based on cardanol performed well in all aspects as compared to commercial curing agent.

1. Introduction

Anhydride curing agents are one of the most important classes of curing agents for commercial epoxies as they offer number of attractive properties including low shrinkage, high glass transition temperature, low internal stress, less water absorbent and provide excellent electrical insulation properties [1–5]. The curing reaction of epoxy with an anhydride to form an ester is characterized by low exotherm and longer periods required for obtaining fully cured systems [6,7]. Curing mechanism involves ring opening of epoxy by an anhydride. However, the reaction requires high temperature to initiate the cure ($> 150\,^{\circ}C$). Hence, small amounts of proton containing compounds such as acids, phenols, alcohols or Lewis bases are added to accelerate the curing process. Tertiary amines such as dimethylbenzyl amine and tris(dimethylaminomethyl)phenol are the most commonly used accelerators for curing [8–11]. Curing mechanism of anhydride epoxy is much more complicated than epoxy/amine system. It was proposed that the reaction of epoxy with anhydride initially yields monoester compound with carboxyl group which further opens up the epoxy ring resulting in hydroxyl group and diester compound [12–14]. Recently, Wirasaputra et al. synthesized a flame retardant trianhydride curing agent for epoxies and added in various ratios along with methylhexahydropthalic anhydride. Authors observed that utilization of trianhydride compound significantly improved the flame retardancy and only 2 wt% of phosphorus content was sufficient to obtain LOI values of 35.4 and V-0 rating on UL-94 [15].

Commercial anhydride curing agents are based on petroleum resources, expensive and hazardous to the environment. Therefore, an anhydride compound based on renewable resources would always be preferable, of course without compromising on the final properties of the system [16,17]. In this regards, Wang et al. synthesized flexible anhydride curing agents derived from rosin and concluded that broad range of mechanical and thermal properties could be achieved. Later same group of authors synthesized two acid anhydride curing agents from rosin and studied kinetics of epoxy-anhydride curing reaction. In a similar manner, we have made an attempt to synthesize anhydride curing agent based on cardanol which is renewable, low cost and existing as a component of cashew nut shell liquid (CNSL) [18]. The presence of long C15 aliphatic chain and aromatic ring in the cardanol provide excellent balance of flexibility and hardness which makes it a suitable candidate for various applications [19,20]. Cardanol can be easily modified using number of chemistries including thiol-ene, malenization, sol-gel, epoxidation etc. [21] to introduce newer functionalities for number of applications including synthesis of adhesives, plasticizers, curing agents [22], resins, UV reactive diluents, UV oligomers, lacquers and varnishes [23,24]. Till date, various reports revealed the preparation of bisphenol-A free "green" epoxy from cardanol [25,26]. Studies confirmed that cardanol based epoxy coatings performed at par as against commercial epoxy resin [27] and used as primer coatings for petroleum and gas steel marine environment [22] as well as food contact coatings for glass toughening [28]. In a similar manner, various curing agents were also synthesized from cardanol to cure epoxy or cardanol epoxy adducts. Kathalewar et al. synthesized phenalkamine curing agents for epoxies. These phenalkamines are

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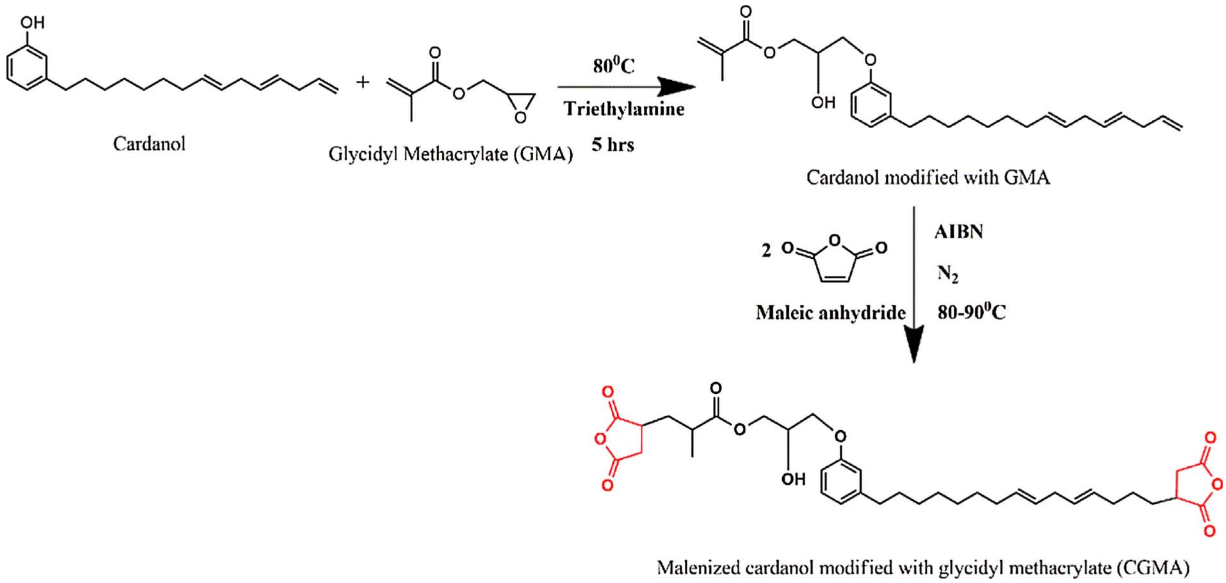

Fig. 1. Synthesis of CGM and CGMA.

Table 1
Formulation of Epoxy anhydride coatings.

Coatings	Quantity of CGMA per 100 g of resin	Quantity of MTHPA per 100 g of resin
CGMA-0 (1:0.6)	106.86	–
CGMA-1 (1:0.8)	142.48	–
CGMA-2 (1:1)	178.09	–
MTHPA-0 (1:0.6)	–	55.33
MTHPA-1 (1:0.8)	–	73.78
MTHPA-2 (1:1)	–	92.22

considered to be excellent due to their fast and low temperature curing at wet or humid conditions and provide balance of hardness and flexibility due to the unique structure of cardanol [29]. In another work, Kugler et al. studied the effect of synthetic and biobased amine crosslinkers on to the performance properties of epoxy coatings containing carbon nanofillers. It was concluded that coatings containing 0.35 wt% of CNT and cured with phenalkamine exhibited outstanding optical properties and excellent cupping resistance as compared to the synthetic amine curing agents [30]. In a more recent work, cardanol based reactive polyamides were developed by varying the mole ratio of acid and amine components. A series of polyamide curing agents having different amine values were synthesized and used as a cross linker for epoxy zinc rich primer. It was observed that with increase in the amine value of polyamides, the mechanical, chemical and anticorrosive properties of the coatings improved [31].

In our previous work we have synthesized silicon containing anhydride curing agent for epoxy resin and it was observed that coatings cured with cardanol based curing agent exhibited excellent mechanical, chemical, insulating and anticorrosive properties [32]. In the present research, another cardanol based anhydride curing agent (CGMA) for epoxy resin was synthesized. The structure of the curing agent was confirmed by FTIR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy as well as determination of acid value, iodine value and hydroxyl number of the product. Further, cardanol based anhydride curing agent was mixed with commercial epoxy resin in varying ratios of 1:0.6, 1:0.8 and 1:1 on equivalent basis and coatings were applied. The effect of concentration of curing agent on various performance properties of coatings was investigated and compared with the coatings based on commercial curing agent viz., methyl tetrahydrophthalic anhydride (MTHPA).

2. Materials

Cardanol (NC-700) was provided by Cardolite Specialty Chemicals Ltd., Mangalore, India. All the reagent grade chemicals including glycidyl methacrylate (GMA), maleic anhydride (MA), ethyl acetate, sodium hydroxide were purchased from SD Fine Chemicals, Mumbai, India. Azoisobutyronitrile (AIBN) was kindly supplied by Veekay Chemicals, Mumbai, India. Commercial epoxy resin (GY-250) is a diglycidyl ether of bisphenol-A having epoxy equivalent weight of 180 g/eq with % NVM of 70 Huntsman International LLC., Mumbai. Commercial anhydride curing agent methyltetrahydrophthalic anhydride and *N, N*-Dimethylbenzylamine (BDMA, tertiary amine catalyst) were procured from Aditya Birla Science and Technology Company Ltd. Mumbai. India.

3. Experimental

3.1. Synthesis of malenized cardanol modified with glycidyl methacrylate (CGMA)

In the first step, cardanol and glycidyl methacrylate in a molar ratio 1:1 were taken into a single necked round bottom flask fixed with a

Table 2
Chemical analysis of products.

Compound	Acid value (mg of KOH/g)		Hydroxyl Value (mg of KOH/g)		Iodine Value (g of I_2/100 g)	
	Theoretical	Practical	Theoretical	Practical	Theoretical	Practical
Cardanol	0	8.74	180–200	189.34	251.28	237.41
CGM	–	–	126.06	128.61	211.02	196.47
CGMA	178.37	171.18	89.19	70.17	100.39	92.11