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High performance polyurea coatings based on cardanol

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ABSTRACT

Present research work deals with synthesis of phenalkamines and their use as curing agents for blocked polyisocyanates to yield high performance polyurea coatings. In this work, several phenalkamines were synthesized by conventional Mannich reaction; selecting various structural amines such as hexamethylene diamine (HMDA), isophorone diamine (IPDA), diaminodiphenyl methane (DDM), Jeffamine D-400 and Jeffamine T-403. Structures of these phenalkamines were confirmed by FTIR, ^{1}H NMR spectroscopy and evaluation of amine value. These curing agents were mixed with HDI and IPDI based blocked polyisocyanates to obtain polyurea coatings which were subsequently characterized for mechanical, chemical, optical, thermal and anticorrosive properties. In addition, structure property relationship of all the systems was studied and compared with commercial phenalkamine (AG-141). Anticorrosive properties evaluated by salt spray test and electrochemical impedance spectroscopy (EIS) revealed significant improvement in anticorrosive performance when compared with commercial phenalkamine. All polyurea coatings exhibited excellent performance properties irrespective of the isocyanates used.

1. Introduction

Phenalkamines are majorly used as epoxy curing agents due to their advantages such as fast and low temperature curing even at wet or humid conditions. These are mainly synthesized from renewable material, cashew nut shell liquid (CNSL). CNSL is a low cost, renewable material. CNSL mainly contains cardanol, cardol, 2-methyl cardol and anacardic acid. With little modification, these derivatives can be efficiently used in applications such as coatings, adhesives, additives, plastic materials etc. [1]. Amongst four cardanol, having unsaturated C15 aliphatic chain attached to phenol gives perfect balance of overall properties and have a great potential to be considered as a raw material in coating industry [2–4].

Phenalkamines are the Mannich reaction products of cardanol, formaldehyde and polyamines reacted in equimolar quantities. Cardanol is responsible for giving chemical resistance due to the presence of aromatic ring and excellent flexibility contributed by C15 aliphatic chain. Further enhancement in performance properties can be achieved by choosing different polyamines. Faster curing rates of phenalkamines are due to the phenolic —OH group that acts as a catalyst and facilitates opening of epoxy ring even at low temperature. These phenalkamines impart excellent adhesion to the substrate, water resistance, good flexibility, and good chemical resistance [5–8].

Other than epoxy resins, phenalkamines can be used to react with polyisocyanates to produce polyurea coatings. However, the reaction between the primary amines and isocyanate [9] is almost instantaneous and results in a gel or hardening of material [10,11]. Therefore, certain measures need to be taken in order to avoid gelation. This can be achieved by using two nozzle spray gun wherein isocyanate and amine components are allowed to react at the time of application directly. However, there are so many parameters one has to take care of to have uniform layer of coating without any defects. Another solution could be the use of blocked polyisocyanates, wherein amine and polyisocyanate reaction takes place above the deblocking temperature of polyisocyanates. Blocking of polyisocyanates enables to form one pack system that is stable under normal storage conditions. Fig. 1 represents the blocking and deblocking reaction of polyisocyanates.

Blocking agents are mainly compounds containing active hydrogen such as phenol, alcohol, caprolactum etc. Depending on the nature of blocking agent, deblocking temperature varies from 100 °C to as high as 200 °C. Polyurea coatings exhibit high tensile strength, high elongation, excellent chemical and corrosion resistance, abrasion resistant and weather resistant [12,13]. Polyureas are widely used for high performance applications such as marine coatings, industrial protective coatings, elastomeric coatings, automotive and transportation applications, composite materials for aircrafts etc [14–17].

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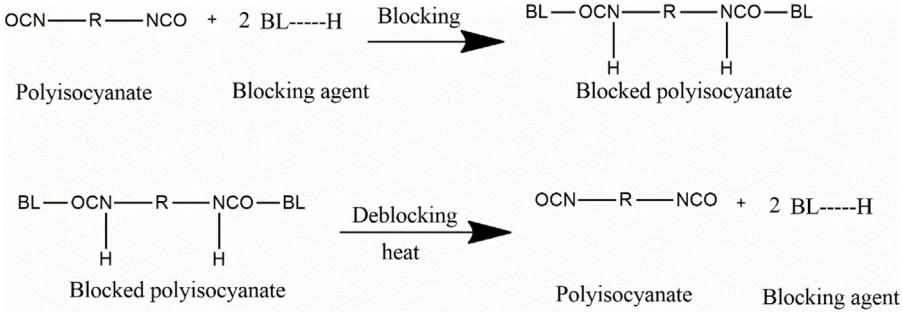

Fig. 1. Schematic representation of blocking reaction of isocyanate.

In the present work, various phenalkamines were synthesized by choosing different polyamines including HMDA, IPDA, DDM, Jeffamine D-400 and Jeffamine T-403. All these phenalkamines were reacted with HDI and IPDI based blocked polyisocyanate to produce corresponding polyurea coatings. Resultant coatings were evaluated for their mechanical, chemical, thermal, optical and anticorrosive properties. To study the comparative performance of the PU coatings a commercial phenalkamine AG-141 was used.

2. Materials

Cardanol (NC-700) was provided by Cardolite Specialty Chemicals Ltd., Mangalore, India. All the reagent grade chemicals including formaldehyde (37 wt%), hexamethylene diamine (HMDA), diaminodiphenyl methane (DDM), diethyl ether were purchased from SD Fine Chemicals Ltd. Mumbai, India. Isophorone diamine (IPDA), Jeffamine D-400 and T-403 were received from BASF India Ltd., Mumbai, India. HDI Blocked isocyanate (Desmodur BL 3175 SN) (solids: 75%, isocyanate equivalent weight: 378) was provided by Bayer Material Science Pvt. Ltd. Mumbai, India. Blocking of IPDI with caprolactam was carried out in lab (solids: 70%; isocyanate equivalent weight: 224). Commercial phenalkamine, AG 141 (amine value = 290–325 mg KOH/g; solids = 100%) manufactured by ARK Golden India Pvt. Ltd., Vadodara, Gujarat was kindly provided by Grauer & Weil (India) Ltd., Mumbai, India.

3. Experimental

3.1. Synthesis of phenalkamines

Cardanol based phenalkamine was prepared as reported in our previous study [5]. Cardanol, formaldehyde and polyamines in a molar ratio 1:1:1 were charged in a four necked flask provided with stirrer, Dean Stark apparatus and thermometer assembly. Reaction mixture was stirred at 80–90 °C for first 3 h and then temperature was increased to 100–110 °C for an hour to remove the water of reaction. After completion of the reaction, the product was diluted in ethyl acetate and washed several times with lukewarm water till neutral pH which indicated complete removal of unreacted amine and formaldehyde. More than 88% yield of phenalkamine was obtained in all the cases. % NVM of all phenalkamines were adjusted to 85 using ethyl acetate solvent. Synthesis reaction of phenalkamines is given in Fig. 2. Table 1 provides the physical and chemical properties of phenalkamines.

3.2. Panel 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.

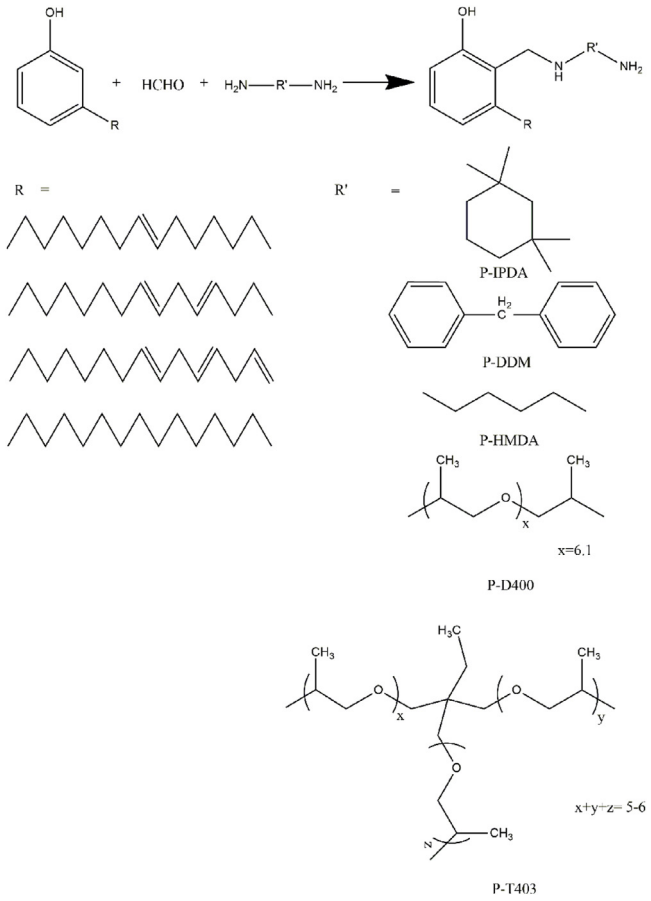

Fig. 2. Schematic representation of preparation of phenalkamines.

3.3. Preparation of polyurea coatings

Phenalkamines and blocked isocyanates were mixed in a proportion calculated by Eq. (1), to which butyl acetate:butanol (80:20 v/v) mixture was added to achieve required viscosity. The panels were then coated with the mixture by flow method. After 15 min of flash off, the panels were kept in air circulating oven at 160–165 °C for 15–20 min. Polyurea coatings cured with HDI were denoted by prefix "P" and IPDI cured coatings were denoted by prefix "IP".

$$\text{Amount of Phenalkamine required} = \frac{\text{Weight of isocyanate x amine equivalent weight of phenalkamines}}{\text{isocyante equivalent weight}} \quad (1)$$