

Effect of incorporation of surface treated zinc oxide on non-isocyanate polyurethane based nano-composite coatings

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ARTICLE INFO

Article history:

Received 22 August 2012

Received in revised form 26 March 2013

Accepted 27 March 2013

Available online 28 April 2013

Keywords:

Non-isocyanate
Cyclic carbonate
Polyurethane
Surface treatment
Zinc oxide

ABSTRACT

Non-isocyanate polyurethanes (NIPUs) based on cyclic carbonate-amine chemistry are an emerging area for polymer synthesis and is being extensively studied for various applications. A successful utilization of this technology can eliminate many of the issues associated with conventional polyurethane chemistry. While these polymers have not yet achieved commercial significance, research is being devoted to methods for synthesizing polymers or oligomers containing cyclic carbonate groups as well as studying their applications in thermoplastic and thermosetting systems.

Nevertheless, NIPU based coating systems are still unexplored for corrosion protection of metals. In the current study, zinc oxide (ZnO) particles prepared via in situ method were treated with cyclic carbonate functional alkoxy silane. The surface treatment of ZnO particles was confirmed by particle size analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDAX) and X-Ray Diffraction Spectroscopy (XRD). NIPU formulations with variable proportion of treated and untreated ZnO particles were prepared using cyclic carbonate modified epoxy resin and coated on mild steel substrates. The nano-composite coatings prepared thereof were evaluated for their mechanical and chemical performance. The anticorrosive performance was evaluated by salt spray test and electrochemical impedance spectroscopy (EIS). The study conducted showed significant enhancement in scratch hardness and abrasion resistance along with improvement in other performance properties after addition of treated ZnO particles in nano-composite coating formulations.

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1. Introduction

Non-isocyanate polyurethane (NIPU) is an emerging technology in the field of polymer synthesis for range of applications. The cyclic carbonate-amine reaction leading to hydroxyurethanes has been extensively studied since last few years and is now attracting research interest due to its potential application in the preparations of “green,” non-porous, moisture-insensitive isocyanate free polyurethanes [1,2]. Five- and six-membered cyclic carbonates react with amines generating urethane linkage and a secondary hydroxyl group. The secondary hydroxyl group generated in this process readily forms hydrogen bonding with the urethane group [3–6]. This would result in very good mechanical and chemical performance. Till date, many researchers have reported synthesis of non-isocyanate polyurethanes from various oil sources [7–10], terpenes [11], epoxy resins [12,13], polyesters [14] etc. Though the NIPUs are expected to show very good resistance to chemical

environment, the NIPU based coatings are still unexplored for corrosion protection of metals.

The nano sized zinc oxide (ZnO) with the features of large surface area to volume ratio [15], high ultraviolet absorption (UV) and long life span with respect to its slow photo-degradation [16,17], has been widely used as UV stabilizer in rubber and plastic industry. It also finds application in cathodic anticorrosive coatings but the utilization is limited as the excessive use may lead to increased hardness [18,19]. ZnO particles are also prone to aggregate due to large surface area and high surface energy. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles. The chemical surface modification, which can be classified as surface grafting, is the most promising method because of the strong covalent bond between the surface modified particles and polymer chains. The surface modification reduces its surface energy and hence the aggregate formation can be controlled with improved compatibility and dispersability in polymer matrix [20].

For this purpose, reactive silane coupling agents have often been used as they can form stable chemical bonds with both inorganic and organic materials. To date, literature related to surface functionalization of oxide has largely been focussed on silica particles. Some molecular treatments of ZnO particles have been investigated

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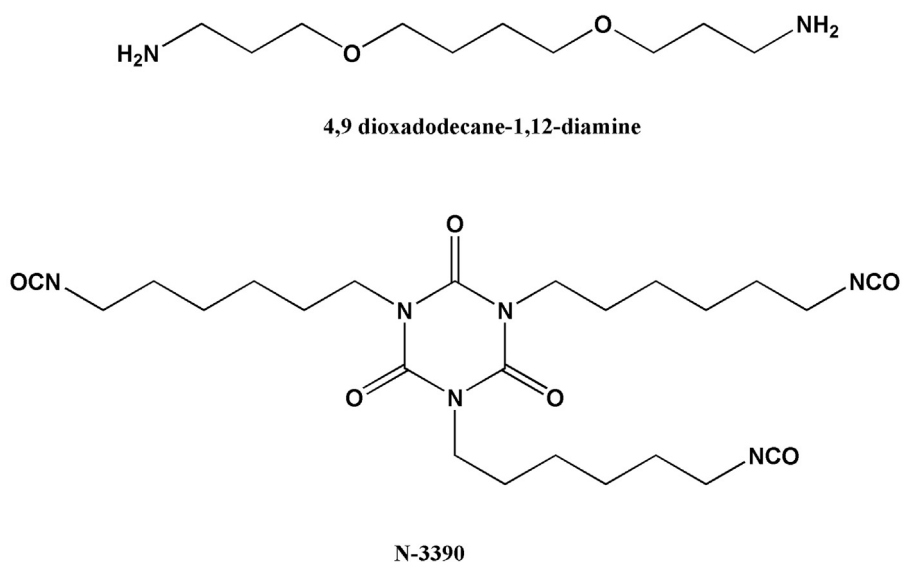


Fig. 1. Typical structures of N-3390 and 4,9 dioxadodecane-1,12-diamine.

using chlorosilanes [21], trialkoxysilanes [22], aminotriethoxysilanes [23,24] and 3-glycidoxypropyltrimethoxysilane [25]. The results obtained in these investigations lead to significant developments in the final characteristic performance of the material [26,27]. Surface treatment of silica particles using cyclic carbonate functional alkoxy silane has also been investigated. This silane coupling agent synthesized from 3-glycidoxypropyltrimethoxy silane contains five membered cyclic carbonate group which can be utilized for preparation of novel nanocomposite materials via non-isocyanate route. Moreover, these nanocomposites are reported to result in better mechanical, chemical and thermal performance [28,29].

The main aim of the current investigation was to study the effect of surface modified and unmodified ZnO particles on overall properties of NIPU based coatings. To accomplish these goals, ZnO particles were surface treated with cyclic carbonate functional trimethoxy silane synthesized from 3-glycidoxypropyl trimethoxy silane via CO₂ addition reaction. These functionalized ZnO particles (TZnO) and untreated ZnO particles were used in different weight proportions on non-isocyanate polyurethane coating formulations. The coating formulation was made with cyclic carbonate derivative of epoxy resin and a polyetheramine cross-linking agent. Further these NIPU based nano-composite coatings were evaluated for their mechanical, chemical and anticorrosive performance characteristics and were compared with the acrylic polyurethane coating based on NCO–OH chemistry.

2. Experimental

2.1. Materials

Laboratory grade oxalic acid dihydrate, zinc acetate dihydrate, diethanolamine (DEA), ethylene glycol (EG), triethylamine (TEA), dichloromethane (DCM), tetrabutyl ammonium bromide (TBAB) were purchased from S.D. Fine Chemicals, Mumbai and were used as received. 3-Glycidoxy propyl trimethoxy silane (GPTMS) was obtained from Wacker Silicones India Ltd., Mumbai. Polyether amine cross-linker, 4,9 dioxadodecane-1,12-diamine was received from BASF India Ltd., Mumbai. The bisphenol-A based epoxy resin (GY-250) with epoxy equivalent weight of 170–180 g/eq (molecular weight = 340–360 g/mol; solids = 70%) was received from Atul Ltd., Mumbai. Acrylic polyol (Synocure

855 S-70; solids = 67–69%; solvents: xylene/butyl acetate) having hydroxyl value 150–160 mgKOH/g and polyisocyanate curing agent (N-3390) (hexamethylene di-isocyanate trimer) were obtained from Asian PPG Ltd., Mumbai. The isocyanate content and non-volatile matter for N-3390 were 19.6% and 90% respectively. Wetting and dispersing agent, BYK-9076, was received from BYK Additives, Mumbai. The typical structures of 4,9 dioxadodecane-1,12-diamine and N-3390 hardeners are as shown in Fig. 1. Mild steel was purchased from a local distributor and were cut in the dimensions of 150 mm × 100 mm × 0.5 mm.

2.2. Synthesis of cyclic carbonate functional alkoxy silane (C-GPTMS)

The cyclic carbonate derivative of 3-glycidoxypropyl trimethoxy silane (GPTMS) was prepared in a 300 mL high pressure autoclave reactor. 50 g of GPTMS was poured into the reactor along with 5% (w/w) tetrabutyl ammonium bromide (TBAB) catalyst (2.5 g) and were mixed with continuous stirring. The reactor was closed and pressurized with CO₂ gas to 200 psi. The reactor was then heated to 120 °C causing the pressure to rise. Once the reaction temperature was reached, the CO₂ pressure was further increased to 600 psi and maintained throughout with necessary addition of CO₂ by the pressure controlling pump. After 6 h of the reaction, the reactor was de-pressurized slowly to allow dissolved CO₂ to leave the carbonated product [30,31]. Further, the collected product was purified with dichloromethane to remove the catalyst and was analyzed by FTIR spectroscopy to confirm functional group conversion. The schematic representation of the conversion of GPTMS to C-GPTMS is as a shown in Fig. 2.

2.3. Preparation of zinc oxide (ZnO) particles

ZnO particles were prepared by aqueous precipitation method as reported by Pillai et al. [32]. The reaction was carried out in a 500 mL beaker. 0.05 mol of zinc acetate dihydrate was first dissolved in 200 mL de-ionized water using magnetic stirrer and heated up to 60 °C until clear solution was obtained. 0.1 mol oxalic acid dihydrate dissolved in 100 mL water was then added dropwise in the zinc acetate solution. Meanwhile, 0.005 mol diethanolamine and 0.005 mol of ethylene glycol were also added to the reaction mixture in first 10 min of addition of zinc acetate solution. The

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