Progress in Organic Coatings 74 (2012) 589–595

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Preparation and investigation of anticorrosion properties of the water-based epoxy-clay nanocoating modified by Na^+-MMT and Cloisite 30B

M.R. Bagherzadeh*, T. Mousavinejad

Coating Research Center, Research Institute of Petroleum Industry (RIPI), West Blvd., Near Azadi Sports Complex, Tehran 1485733111, Iran

ARTICLE INFO

Article history:
Received 4 September 2011
Received in revised form 28 January 2012
Accepted 13 February 2012
Available online 14 March 2012

Keywords:
Water-based epoxy coating
Nanocoating
Anticorrosion
RIPI-W.B.H. hardener
Na^+-MMT
Cloisite 30B

ABSTRACT

In this study the effect of using nanoclay particles in two different matrices on anticorrosive performance improvement of a novel water-based epoxy coating was investigated. For this purpose, Na^+-montmorillonite (Na^+-MMT) and organo-montmorillonite (Cloisite 30B) were introduced into water-based hardener (RIPI-W.B.H.) and epoxy resin matrices, separately. Nanoclays were added to polymeric matrices using direct mixing under an ultrasonic homogenizer. The coatings were analyzed to ensure the intercalation and distribution of layered silicates by means of X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses. The structure of products is studied by infrared (IR) spectrometer. The corrosion protection performances of the coatings were investigated using salt spray test and electrochemical impedance spectroscopy (EIS) in 3.5% sodium chloride solution. The results showed that using Cloisite 30B in water-based hardener had the best performance and its application in anticorrosion water-based zinc rich epoxy coating approved of it.

1. Introduction

Organic coatings have been used as one of the best methods for corrosion protection in different situations because they are easy to apply – at a reasonable cost – and are versatile [1]. Epoxy systems are the most common kinds of anticorrosive organic coatings because of their outstanding process ability, excellent chemical properties, good corrosion resistance and strong adhesion performance [2,3]. Research activities for the preparation of epoxy coatings have been gradually shifted to epoxy coatings with low VOC because of environmental and health-related issues [4,5].

One novel way to improve properties of water-based epoxy coatings simultaneously is to use nanoparticles in these coatings. Nanoclay is one of the most promising materials since this material exhibits significant improvement in anticorrosion performance and barrier property of water-based epoxy coatings [6].

Hang et al. [1] focused on using montmorillonite clay (MMT) as filler for solvent-epoxy coatings. It was found that with the addition of 2% nanoclay in an epoxy resin there was significant improvement in the anticorrosive and barrier properties of the coating compared with the neat coating.

Lai et al. [4] investigated anticorrosion performance of water-based polyacrylate latex materials by adding Na^+-montmorillonite (Na^+-MMT). Their results showed anticorrosion efficiency over those of neat polyacrylate. Recently, we have examined anticorrosion and barrier properties of epoxy-clay nanocoatings and have investigated the effect of adding Cloisite 30B of different amounts in solvent-type epoxy resin using direct mixing method. The best anticorrosion performance of coatings was obtained at 3 wt% clay [7]. Yeh et al. [8] studied the effect of adding Na^+-MMT in waterborne polyurethane (WPU) coating. They found that superior anticorrosion had a better efficiency than that of neat WPU.

Kowalczyk and Spychaj [6] focused on the effect of organically modified montmorillonites in epoxy coating on steel substrate. Organophilic montmorillonites were used for waterborne and solvent-type epoxy coating materials. At first modified montmorillonites in the form of dispersions in the epoxy resins were used and then epoxy resins were mixed with hardeners. The results indicated that processing and mechanical properties of coatings were positively affected by nanoclay. Also enhanced water resistance of coats, especially those formed from waterborne coatings, has been found.

In this study two different types of montmorillonites including Na^+-MMT and Cloisite 30B were dispersed into two polymeric matrices of water-based hardener and solvent-based epoxy resin, separately. The nanoclays were added to polymeric matrices using direct mixing under an ultrasonic homogenizer. Anticorrosion properties of the coatings were investigated using salt spray, adhesion tests and electrochemical impedance spectroscopy (EIS)

* Corresponding author at: Coating Research Center, Research Institute of Petroleum Industry (RIPI), West Blvd., Near Azadi Sports Complex, P O Box 14665 137, Tehran 1485733111, Iran. Tel.: +98 21 48253218; fax: +98 21 44739592.
E-mail address: bagherzadehmr@ripi.ir (M.R. Bagherzadeh).

0300-9440/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2012.02.006

Table 1
RIPI-W.B.H. water-based hardener specification.

Properties	Result
Appearance	Clear liquid
Viscosity (cps, at 25 °C)	300–500
Amine value (mg KOH/g)	250–300
Density (g/ml, at 25 °C)	0.943–0.950
pH	9–9.2
Color (Gardner)	7.max
Molecular weight (g/mol)	200–240
Solid content	20–25%

Table 2
Physical characteristics of the zinc powder.

Physical characteristics	Zinc
Form	Solid powder
Color	Dark gray
Shape	Lamellar
Density (g/cm^3)	7.1
Particle size (μm)	Fine (2–4)

method for different immersing times in 3.5% sodium chloride solution.

2. Experimental

2.1. Materials

Two Cloisite montmorillonite clays including Na^+-montmorillonite (Na^+-MMT) and organo-montmorillonite (Cloisite 30B) were used. They were purchased from Southern Clay Products. The epoxy resin is diglicidyl ether of bisphenol A (DGEBA) with EEW = 480, Epon1001 from Shell Company® (in a form of solution in organic solvent). The water-based hardener (RIPI-W.B.H., amine value is 270 mg KOH/g) is the pilot scale product of the RIPI, Iran [9,10] that its specification is given in Table 1. All additives were provided from Efka Company®. Bentonite was kindly supplied by Zhejiang Huate New Material Company. Zinc Powder was purchased from Pars Zinc Company®. The physical characteristics of Zinc Powder are shown in Table 2.

2.2. Preparation

2.2.1. Preparation of water-based epoxy-clay nanocoatings

In order to fabricate water-based epoxy-clay nanocoating containing 5 wt% clay, at first Cloisite 30B and Na^+-MMT were separately dispersed in epoxy resin and water-based hardener part, respectively. The nanoclays were added to polymeric matrices using direct mixing method under an ultrasonic homogenizer at a room temperature for 15 min. Then prepared mixtures were separately added to the epoxy resin and water-based hardener in stoichiometric amount (epoxy resin/hardener = 2.7/1).

2.2.2. Preparation of zinc rich epoxy primer

The epoxy resin and bentonite were mixed into a beaker and thoroughly dispersed in high-speed agitation equipment supplied. The bentonite was added with stirring over a period of 15 min at 1000 rpm. The dispersing agent was introduced in it after 30 min. Then zinc powder was added to mixture gradually for another 15 min. After the mixture's particle size achieved ≤15 μm, coalescing agent and mar resistance were added and the mixture was maintained for 30 min at the room temperature. Eventually the leveling agent was added to mixture and the zinc rich epoxy primer was produced. The formulation of zinc rich epoxy primer is shown in Table 3.

Table 3
Formulation of zinc rich epoxy primer.

Material	Wt%
Epoxy resin (1001)	12
Thickener (Bentonite 34)	1.2
Dispersing agent (Efka 4580)	0.2
Zinc powder	84.45
Coalescing agent (butyl glycol)	1.75
Mar resistance (Efka 3030)	0.15
Leveling agent (Efka 3580)	0.25

Table 4
The preparation methods and abbreviation names of made of coatings.

Preparation methods	Abbreviation
Epoxy resin + hardener	R-H (Ref sample)
Cloisite Na^+ + epoxy resin	Na^+-R
Cloisite Na^+ + hardener	Na^+-H
Cloisite 30B + epoxy resin	30B-R
Cloisite 30B + hardener	30B-H
(Cloisite Na^+ + epoxy resin) + hardener	Na^+R-H
(Cloisite 30B + epoxy resin) + hardener	30BR-H
(Cloisite Na^+ + hardener) + epoxy resin	Na^+H-R
(Cloisite 30B + hardener) + epoxy resin	30BH-R
Zinc rich epoxy + (Cloisite 30B + hardener)	Zinc-30B
Zinc rich epoxy + hardener	Ref Zinc sample

2.2.3. Preparation of nano water-based zinc rich epoxy-clay primer

For preparation of Nano water-based zinc rich epoxy-clay primer, the stoichiometric amount of the 30B-H was mixed with the zinc rich epoxy primer. Table 4 illustrates the name and abbreviation of prepared coatings.

2.3. Surface preparation and the application of the coatings

The prepared coatings were applied by air spray on blasted (Sa 2.5) carbon steel plates according to ASTM D7055. The samples were dried in the room temperature for one week. The thickness of coatings was in the range of 70 ± 5 μm uniformly.

2.4. Characterization

X-ray diffraction (XRD) patterns of clay-polymer mixtures and the resulted coatings were studied using Analytical (model Philips PW 1840) X-ray diffractometer. Transmission electron microscopy (TEM) was used for distinguishing the dispersion of platelets of Cloisite 30B in coating using Philips E108. IR spectroscopy was used to characterize structure of Cloisite 30B, water-based hardener and 30B-H performed using IFS-88 Spectrometer in the range 4000–400 cm^{-1}.

2.5. Corrosion studies

2.5.1. Adhesion test

The adhesion of the coatings to the substrate was carried out according to ASTM D3359 standard. The results are described in the standard and the best result is reported as 5B.

2.5.2. Salt spray test

Salt spray test method was used to evaluate corrosion resistance properties of the coatings using ASTM B117 and then their anticorrosion performance was investigated according to ASTM D714.

2.5.3. Electrochemical impedance spectroscopy

The electrochemical impedance measurements were performed on mild carbon steel panels coated with water-based epoxy coating (Ref sample) and water-based epoxy-clay nanocoating (30BR-H).