



Epoxy/nanopigment coatings: Preparation and evaluation of physical-mechanical properties



A. Mahmoodi, M. Ebrahimi*, A. Khosravi

Polymer Eng. and Color Tech. Department, Amirkabir University of Technology, P.O. Box 15875-4413, 424 Hafez Ave., Tehran, Iran

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ABSTRACT

In this research, new hybrid epoxy/nanopigment coatings were prepared and their physical and mechanical properties were studied. For this purpose, blue hybrid dye-clay nano-pigments (DCNPs) were synthesized by using the cationic exchange reaction between methylene blue (MB) and an organically modified clay (Cloisite 15A, C15A). Thereafter, blue color epoxy formulations were prepared by the incorporation of DCNPs into an epoxy system. In addition, two common organic and inorganic pigments (namely, C.I. pigment blue 15:2 and C.I. pigment blue 28) were used to prepare two common blue color epoxy resins as reference samples. Finally, the physical and mechanical performances of these coatings were evaluated and compared with each other. Different techniques including CHNS, XRD, TEM, DMTA, QUV accelerated weathering tester and spectrophotometry were used in this study. The results showed that the dispersion and interaction/exfoliation of DCNPs in epoxy matrix were better than those of C15A. Moreover, it was found that the color characteristics and mechanical properties of the epoxy/nanopigment coatings were superior compared to those of reference coatings.

1. Introduction

Organic coatings based on epoxy resin, due to their strong adhesion and excellent durability, are widely used for a variety of industrial purposes. Epoxy coatings are usually used in the form of paints and they include pigments and fillers [1]. A wide range of macro- and nano-sized particles have been incorporated in epoxy coatings in order to achieve functional and/or aesthetic characteristics. For example, organic pigments such as phthalocyanine-based pigments used for coloration and inorganic pigments like metallic zinc powders are utilized for improving corrosion-protection performance of epoxy coatings [2,3]. Moreover, the mechanical and barrier properties of epoxy coatings can be improved by the incorporation of nano particles such as fumed silica and clay nano particles [4–7].

Hybrid dye-clay nanopigments have been recently introduced in polymer and textile industries. It seems that these pigments enjoy the good features of organic and inorganic pigments. For instance, they present good colorimetric properties and good thermal stability of organic and inorganic pigments, respectively. On the other hand, they provide very good barrier properties because of their layered nature [8–10]. In recent years, several researchers have worked on the preparation and application of dye-clay nanopigments. Validi et al. [11] prepared different clay-based nanopigments using natural clay and methylene blue. They studied the effect of reaction time and

concentration of dye on the extent of methylene blue intercalation into clay layers. They reported that the higher extent of intercalation was achieved when a higher concentration of methylene blue and longer reaction time were employed. Few other reports have been published on the synthesis and characterization of DCNPs. They found that the cationic exchange reaction of cationic dyes with clay could improve UV and the thermal stability of corresponding cationic dyes [12–14].

Marchante et al. [15,16] studied the physical and mechanical properties of LLDPE colored with a blue nanopigment and conventional blue pigments. They found that samples containing blue nanopigments presented better color characteristics and mechanical properties compared to samples colored with conventional pigments. In addition, they claimed that all samples showed the same thermal stability. Other researchers prepared different clay-based nanopigments using different cationic dye/quaternary ammonium salt ratios and used them in ethylene vinyl acetate (EVA) polymer. They reported that the presence of quaternary ammonium as a clay modifier improved the dispersion state of nanopigments in EVA matrices which led to the production of nanocomposites with better mechanical and colorimetric properties [17,18].

In our previous paper [19], a dye-clay nanopigment was incorporated into an epoxy coating formulation and its corrosion resistance behavior was studied. It was found that the corrosion protection performance of epoxy coating was significantly improved by

* Corresponding author.

E-mail address: ebrahimi@aut.ac.ir (M. Ebrahimi).

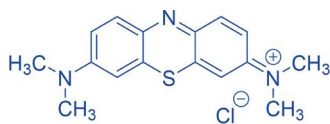


Fig. 1. Chemical structure of methylene blue (MB).

adding only 3 wt.% of DCNP into the formulation.

In fact, this work is an extension to our previous work. The major objective of this study was to evaluate the colorimetric and physical-mechanical properties of blue colored epoxy/nanopigments and two other commercial blue epoxy coatings.

2. Experimental

2.1. Materials

Diglycidyl ether bisphenol-A (EP) with an epoxy equivalent weight of 185–192 g/eq (Epikote 828) and an amine hardener with a hydrogen equivalent weight of 102–106 g/eq (Epikure F205) were supplied by HEXION Inc., USA. An organoclay with a modifier concentration of 125 meq/100 g (Cloisite 15A) was purchased from BYK additives, Germany. Methylene blue (see Fig. 1) as a cationic colorant was obtained from Aldrich Chemical Company Inc., USA. Ethanol was procured from Merck GmbH, Germany. Two conventional blue organic pigment (OP) and inorganic pigment (IP) with color indexes of C.I. pigment blue 15:2 and C.I. pigment blue 28, respectively, were obtained from Clariant Company, Germany. All chemicals were used as received.

2.2. Synthesis of DCNPs

500 mL of water/ethanol mixture (25:75 v/v) was poured into a container and then 10 g of C15A was added into the mixture. Subsequently, various amounts of MB (i.e. 15–75% based on clay CEC) were dissolved in 200 mL water in weak acidic condition (for protonation). Afterwards, dye solution was added to clay suspension while they were stirred vigorously and final mixtures were maintained at ambient temperature and under a stirring speed of 600 rpm for 24 h. The stirrer was switched off to allow DCNP particles settled down during a period of 12 h. The DCNP sediments were filtered and washed with de-ionized water for three times and were put into a vacuum oven to be dried at 60 °C for 12 h. Dried filtrate was ground and sieved to a specific particle size. The blue DCNP particles were named as DCNP-X where X resembled the percentage of initial dye concentration based on clay CEC. Samples names and specifications are presented in Table 1.

2.3. Sample preparation

Specific amounts of C15A, DCNPs, MB, organic pigment (OP) and inorganic pigment (IP) were incorporated into epoxy resin (see Table 2) and were mixed vigorously at ambient temperature for 2 h. Then, they were sonicated (Hielscher UP400S ultrasonic sonicator, Germany) at a power of 100 W for 30 min and degassed under a vacuum condition. Subsequently, a stoichiometric amount of curing agent was added and gently mixed. The resulting mixtures were coated onto standard black and white papers and glass substrates (film thickness = 200 μm).

Table 1
Samples names and specifications.

Sample	C15A (g)	MB (% based on CEC)
DCNP-15	10	15
DCNP-30	10	30
DCNP-50	10	50
DCNP-75	10	75

Samples containing DCNPs were specified by EP-XY codes where X resembled the percentage of initial dye concentration based on clay CEC and Y resembled the percentage of DCNP in formulation. For example, EP-153 means a sample of epoxy coating contained 3 wt.% of DCNP-15. Finally, it should be noted that the amount of colorants in EP-503, EP-OP, EP-IP and EP-MB were adjusted to be the same. It means that the amount of colorant (i.e. 0.395 g of MB) in EP-503 was the same as that in EP-MB, EP-OP, and EP-IP. It should be noted that 3 wt.% of DCNP-50 was used for the preparation of EP-503. The cation exchange reaction between MB and C15A and intercalation of epoxy resin into DCNP layers are schematically shown in Fig. 2.

2.4. Characterization

2.4.1. Synthesis and morphology of DCNPs

The extent of cation exchange reaction between MB and C15A was calculated using CHNS data. An elemental analyzer (i.e. Costec ECS 4010 CHNS analyzer) was employed to determine the mass percentage of carbon, nitrogen and sulfur of samples. Afterwards, the following instruction was utilized in order to determine the amount of MB and quaternary ammonium modifier. Each molecule of MB included one sulfur atom. Therefore, the amount of MB in DCNPs was calculated by measuring the mass of sulfur in DCNPs. Additionally, remained quaternary ammonium modifiers in DCNPs were determined from the nitrogen content of DCNPs after subtracting of nitrogen attributed to MB.

The extent of organoclay dispersion in epoxy matrix was determined using X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. XRD measurements were carried out on a Philips X'Pert MPD X-ray generator (tube Cu Kα, λ = 1.54 Å) at room temperature. The diffraction patterns were recorded at scattering angles from 0.5° to 10° at a scanning rate of 0.02°/s. The d-spacing of samples (d) was calculated using Bragg equation.

The TEM micrograph of one of samples was taken by using EM 900 TEM of Carl Zeiss with an acceleration voltage of 80 kV. Worth noting that the cross section of specimen was cut from a cured resin using an ultra-microtome equipped with a diamond knife.

2.4.2. Dynamic mechanical properties of coatings

The physical-mechanical properties of coatings were studied using a dynamic mechanical analyzer (Triton TTDMA model). Samples dimensions were chosen to be 30 × 10 × 0.2 mm³ and the experiments were carried out under tension mode. A frequency of 1 Hz with a temperature ramp of 5 °C/min and a scanning temperature range from room temperature to 180 °C were employed. The glass transition temperature (T_g) of samples was determined from the peak of tan δ curve.

2.4.3. Color stability of coatings

The color stability of samples was evaluated using a QUV-Spray accelerated weatherometer (Q-Panel Co.) based on ASTM G 154. In this test, samples were exposed to UV irradiation with wave lengths in the range of 295–365 nm. Specimens were experienced cycles composed of 8 h of UV irradiation at 60 °C, followed by 4 h of water vapor condensation at 50 °C in cyclic manner for 110 h. The color differences ΔE* (CIE 1976) of samples before and after weathering test were measured and considered as a criterion to determine the color stability of samples using following Eq.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

2.4.4. Color characteristics

Color characteristics of samples were determined according to CIELAB color scale relative to standard illuminant D65 over a white tile (CIE L* = 82.3, a* = -0.1 and b* = -0.6) and a black tile (CIE L* = 3.4, a* = -0.2 and b* = -1.2) using a Gretag Macbeth Color Eye 7000A spectrophotometer, an instrument with 8/d geometry in a

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