



Role of a hybrid dye-clay nano-pigment (DCNP) on corrosion resistance of epoxy coatings

A. Mahmoodi, M. Ebrahimi*

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 work, we combined the desirable color characteristics of cationic dyes and the good barrier properties of organoclays by synthesizing hybrid dye-clay nano-pigments (DCNPs) via cationic exchange of two cationic dyes (i.e. basic blue 9 and basic yellow 87) and different commercial organoclays (Cloisite 15A, 20A and 30B). Then, different amounts of synthesized DCNPs were incorporated in an epoxy coating and their corrosion resistance behaviors were investigated by using electrochemical impedance spectroscopy (EIS) and salt spray test. The dry and wet adhesions of samples were measured employing pull-off adhesion test. In addition, the morphology of dispersed DCNPs in epoxy matrix was evaluated by using different techniques including XRD and TEM. Results showed that the extent of intercalation/exfoliation of DCNPs was greater than that of organoclays. Moreover, it was found that DCNPs based on Cloisite 20A had the best dispersion properties among different organoclays. It was revealed that the corrosion resistance of coatings containing DCNPs (based on Cloisite 20A) was superior in comparison to coatings containing only Cloisite 20A. Finally, results demonstrated the technical feasibility of preparation of colored epoxy coatings with superior corrosion resistance by the incorporation of DCNPs (in the range of 1–5 wt.%) into epoxy matrix.

1. Introduction

Pigmentation of organic coatings is among the most widespread approaches employing to provide a specific color, enhance mechanical properties and/or improve corrosion protection performance of coatings [1]. In this regard, organic and inorganic pigments are usually used in these coatings. Inorganic pigments can provide good mechanical, thermal and corrosion resistances, however, they suffer from relatively poor color characteristics. In fact, they cover just a limited range of hues and their shades are not relatively desirable in comparison with organic pigments. Organic pigments and dyes represent more diverse, brighter and purer in color than those of inorganic pigments, however, they do not exhibit good anti-corrosive properties in coatings [2–6]. To modify the corrosion resistance of coatings, clay nano-particles were incorporated into organic coatings [7–13]. In fact, planar structure and high aspect ratio of clay nano-particles improve barrier properties of coatings and this modification results in improving corrosion protection properties of final coatings [14–16]. In the last decade, several researchers attempted to utilize the good color characteristics of dyes and the good stabilities and barrier properties of nanoclays by combining (physically and/or chemically) these two components [17–19]. For example, Sanchez-Ochoa et al. and Zhang et al. developed a blue hybrid

pigment (namely, Maya Pigment) by trapping of a blue dye inside of a specific clay (i.e. palygorskite). They could synthesize a hybrid pigment with good color characteristics and excellent chemical and heat stabilities [20–22]. Recently, a new class of hybrid pigments named as dye-clay nanopigments (DCNPs) are synthesized via cationic exchange reaction between cationic dyes and nano-clay particles [23]. Raha et al. synthesized a red DCNP through cationic exchange reaction of a cationic dye (i.e. rhodamine-B) with a montmorillonite. They compared the thermal and photo stability of rhodamine-B before and after its cationic exchange with montmorillonite and found that the exchanged dye showed better stabilities than those of pure dye [24]. Smith et al. investigated the ultraviolet and chemical stability of a rhodamine-6G intercalated montmorillonite nano-pigment and demonstrated the good stability of nano-pigments against ultraviolet and normal mineral acids and bases [25]. Beltrán et al. and Marchante et al. modified a montmorillonite with a cationic dye (i.e. methylene blue) and an ammonium salt at different dye/salt ratios to obtain a series of DCNPs. They incorporated these DCNPs and conventional organic and inorganic pigments in linear low-density polyethylene and ethylene vinyl acetate composites. They reported that the polymeric composites prepared using DCNPs presented better color characteristics and mechanical properties comparison to those prepared by using conventional

* Corresponding author.

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

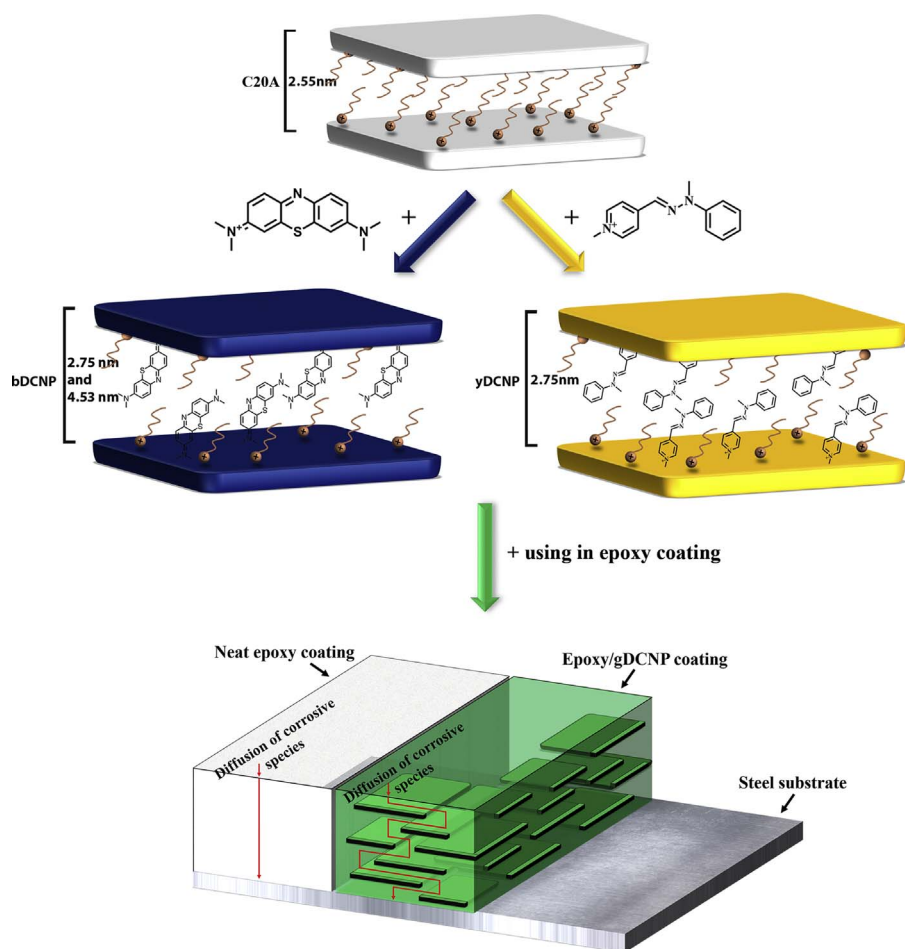


Fig. 1. Schematic procedure for the preparation of DCNPs and green epoxy coating.

Table 1
Sample codes and their specifications.

Substances	C15A	C20A	C30B	bDCNP (15A)	bDCNP (20A)	bDCNP (30B)	yDCNP (15A)	yDCNP (20A)	yDCNP (30B)	gDCNP (20A)	EP
Neat EP	–	–	–	–	–	–	–	–	–	–	100 wt.%
EP-15A3	3 wt.%	–	–	–	–	–	–	–	–	–	97 wt.%
EP-20A3	–	3 wt.%	–	–	–	–	–	–	–	–	97 wt.%
EP-30B3	–	–	3 wt.%	–	–	–	–	–	–	–	97 wt.%
EP-bDCNP3(15A)	–	–	–	3 wt.%	–	–	–	–	–	–	97 wt.%
EP-bDCNP3(20A)	–	–	–	–	3 wt.%	–	–	–	–	–	97 wt.%
EP-bDCNP3(30B)	–	–	–	–	–	3 wt.%	–	–	–	–	97 wt.%
EP-yDCNP3(15A)	–	–	–	–	–	–	3 wt.%	–	–	–	97 wt.%
EP-yDCNP3(20A)	–	–	–	–	–	–	–	3 wt.%	–	–	97 wt.%
EP-yDCNP3(30B)	–	–	–	–	–	–	–	–	3 wt.%	–	97 wt.%
EP-gDCNP1(20A)	–	–	–	–	–	–	–	–	–	1 wt.%	99 wt.%
EP-gDCNP3(20A)	–	–	–	–	–	–	–	–	–	3 wt.%	97 wt.%
EP-gDCNP5(20A)	–	–	–	–	–	–	–	–	–	5 wt.%	95 wt.%

pigments. They also claimed that the presence of surfactant in the intergallery spacing of DCNPs improved dispersion of DCNPs in polymeric matrices [26,27].

In our previous paper, we synthesized a DCNP using MB and C15A for the first time. Then we incorporated the prepared DCNP in an epoxy matrix and we studied its corrosion resistance behavior and color characteristics. We found that coating containing DCNP showed a superior corrosion protection performance and colorimetric properties compared to other coatings [28].

The aim of this work was to synthesize different blue and yellow DCNPs through cationic exchange between two cationic dyes (namely, basic blue 9 and basic yellow 87) and different commercial organoclays (i.e. Cloisite 15A, Cloisite 20A and Cloisite 30B) and investigate the

effect of prepared DCNPs and organoclays on the corrosion resistance of an epoxy coating.

2. Experimental

2.1. Materials

To prepare coating samples, a di-glycidyl ether bisphenol-A with an epoxy equivalent weight of 434–555 g/eq (Epiran-01X75) was supplied by Khuzestan petrochemical company, Iran. In addition, a poly-amidoamine hardener with a hydrogen equivalent weight of 130 g/eq (Aradur 125) was supplied by Huntsman, USA. Different commercial organoclays namely, Cloisite 30 B (C30B), Cloisite 20A (C20A) and

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