

# Effect of nano-ZnO in lowering yellowing of aliphatic amine-cured DGEBA-based epoxy coatings on UV exposure

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**Abstract-** Epoxy resins as binders are best known in protective coating field for their excellent corrosion resistance. However, the exterior durability of these resins is severely affected by their poor weathering resistance. The exposure of epoxies to outdoor environment causes chemical reactions within them, which leads to deterioration of their useful properties. A few hours of UV-exposure leads to chalking and discoloration of epoxies, caused as a result of photo-degradation. The present work aims to study the extent to which the color change and yellowing of epoxy caused due to weathering of an aliphatic amine namely, Diethylenetriamine (DETA) cured diglycidyl-ether of bisphenol-A (DGEBA) based epoxy system, when exposed to accelerated weathering conditions, could be lowered by means of a UV-blocking additive, namely nano Zinc oxide (ZnO). A titanium dioxide (TiO<sub>2</sub>) based white coating with DGEBA epoxy and DETA was formulated and applied on mild steel (MS) panels for the weathering study. The coated panels were exposed in an UVB-weatherometer. Nano zinc oxide particles were synthesized by chemical route and characterized for size, shape and structure. At 2% (by weight) of total coating formulation, nano-ZnO was found to be an effective UV-stabilizer and lowered the degradation in the epoxy-hardener cured system on UVB exposure. The enhanced resistance to color change and yellowing was indicated by lowered color change (dE) and yellowness index values (YI) for the coatings on UVB exposure.

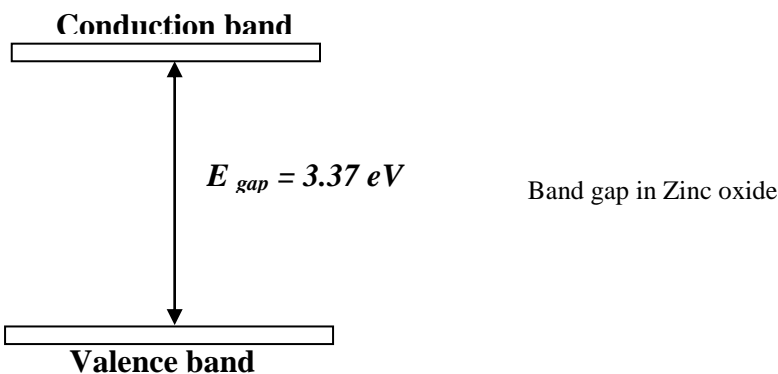
**Index Terms-** Epoxy, nano ZnO, yellowing, UV exposure

## I. INTRODUCTION

Among the different classes of polymers, epoxy resins are known for their high range of attainable properties and versatility. Depending on the chemical structure of curing agents, and curing conditions, it is possible to attain: toughness, chemical resistance, flexibility, high strength and hardness, good heat and electrical resistance. However, inherently epoxies have poor weathering resistance owing to the presence of an aromatic moiety in their polymeric backbone structure. It is this aromatic moiety which absorbs at 300 nm and degrades in the presence of UV light and humidity. This consequently results in discoloration, yellowing and chalking [1, 2].

The best approach to stabilization with respect to weathering degradation in polymers would be to not allow radiation to be absorbed by vulnerable groups and these preventive techniques comprises of screening and absorption. The effectiveness of the stabilizers against weathering depends on solubility, ability to stabilize in different polymer matrix, the distribution in matrix, evaporation loss during processing and use. There are both organic and inorganic UV blockers. The emerging awareness of toxicity of organic UV-stabilizers like HALS and other organic-based UV-scavengers have initiated the need for, making the best use of alternate inorganic metallic oxides like zinc oxide and titania as UV-stabilizers. These oxides basically protect the polymer matrix from degradation by acting as effective UV-blockers.

Zinc oxide (ZnO) ultrafine particles are well known as UV blocking materials, making them feasible to be widely used in polymers, fabrics, woods and cosmetic materials [3]. With the accelerated development of nano-particle technology, nano ZnO has the ability to offer UV protection to coatings and underlying substrates while also being transparent in the visible spectrum. Also, dispersing nano-particles, instead of larger particles, allows a coating formulator to increase the interfacial content in the coating matrix significantly which in turn imparts highly specialized functionality to surface coatings [4, 5]. Nano ZnO particles thus have become an option as formulating materials for UV protection. Also, since they are inorganic and particulate, they have added advantages of being stable and non-migratory within an applied coating, offering better effectiveness and a longer service life. A distinguishing feature of the nano ZnO containing composite coating is a drop in transmission around 370 nm, which corresponds to the absorption of UV radiation by nano ZnO particles ( $E_{\text{gap}} = 368 \text{ nm}$ ) and is indicative of the UV protecting ability of the coating [6, 7].



The present work studies the effect of nano-sized zinc oxide particles on lowering the color change and yellowing of an aliphatic amine cured epoxy system on UVB exposure at different loading concentrations. As epoxy coatings deteriorate rapidly and lose their aesthetic properties with no time under UV exposure, the only aim of this study was to observe, to what extent, a simple  $TiO_2$  based, white DGEBA epoxy cured with an aliphatic amine (DETA) can withstand yellowing or color change with and without nano ZnO under UV (B) light.

## II. EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol A (DGEBA) epoxy with EEW of 185, DER 331 was obtained from DOW Chemicals. An amine-based hardener namely; Diethylenetriamine (DETA) was used for curing of epoxy. Zinc sulfate heptahydrate ( $ZnSO_4 \cdot 7H_2O$ ), aqueous ammonia solution ( $NH_4OH$ ), ammonium bicarbonate ( $NH_4HCO_3$ ) and anhydrous alcohol were obtained from Sigma-Aldrich for the synthesis of nano ZnO particles. BYK additives were used for the formulation of the  $TiO_2$  based epoxy coating.

### Synthesis of nano-zinc oxide

The first stage involved synthesis of the precursor, zinc carbonate hydroxide (ZCH) using 1:10:1 ratio (volume ratio) of aqueous ammonia (7 mol/L):  $ZnSO_4 \cdot 7H_2O$  solution (0.5 mol/L):  $NH_4HCO_3$  (3 mol/L). Aqueous ammonia followed by  $NH_4HCO_3$  solution, both, were drop-wise added to a continuously stirred solution of  $ZnSO_4 \cdot 7H_2O$  at room temperature. The reaction mixture was then heated up to  $60^\circ C$  and stirred for 30 min. The ZCH precipitate was then filtered and washed with deionized water to ensure complete removal of sulphate ions ( $SO_4^{2-}$ ). The ZCH precursor was dried and calcined at  $400^\circ C$  for two hours to obtain nano sized zinc oxide particles.

The synthesized nano-powders were investigated by Transmission Electron Microscopy [TEM, Philips CM200 electron microscope], Scanning Electron Microscopy (SEM, Model no.S3400, Hitachi) and X-ray diffraction [XRD, X'Pert Pro Philips] for its shape, size and crystallinity. FTIR [JASCO FTIR 6100] studies of nano-powders were carried out to study the structure of the oxides.

### Preparation of epoxy coated samples

The mild steel (MS) samples to be coated were de-greased, cleaned and then roughened mechanically with abrasive paper (emery paper grade no.: 100). A  $TiO_2$  based white coating was formulated with 35% pigment concentration, 50% epoxy resin concentration and rest with the appropriate concentrations of additives and xylene as solvent. The nano ZnO modified epoxy coatings were prepared by addition of firstly the micron sized  $TiO_2$  pigment along with the required amount of nano ZnO at different loading levels, maintaining the 35% pigment concentration in the coating followed by the additives. Nano zinc oxide was added to the epoxy resin using ultra-sonication at 1%, 2% and 5% (by weight) of the total coating formulation. The only purpose to take  $TiO_2$  as the pigment was to formulate a white coating and hence evaluate discoloration/ yellowness of the coating on weathering. The pigment concentration was always maintained at 35% with and without nano ZnO while formulating the coatings. The coating formulation for different loading of nano ZnO in the coating is as tabulated as follows

Component	Neat Epoxy (%)	1% nano ZnO + Epoxy (%)	2% nano ZnO + Epoxy (%)	5% nano ZnO + Epoxy (%)
TiO <sub>2</sub> pigment	35.0	34	33	30
Nano ZnO	0	1	2	5
Resin	50.0	50.0	50.0	50.0
BYK 530	2.0	2.0	2.0	2.0
BYK 333	1.0	1.0	1.0	1.0
BYK 9076	1.5	1.5	1.5	1.5
BYK 320	0.5	0.5	0.5	0.5
Xylene	10	10	10	10

As mentioned in the table above, the resin content was kept constant throughout in the coatings, with different nano ZnO concentrations. The resulting blend was ultrasonicated for 20 minutes and the shear time via ultrasonication was kept constant for all loadings of nano ZnO. After mixing TiO<sub>2</sub> pigment, nano ZnO and additives, at the end, hardener and solvent were mixed to obtain the nano ZnO modified epoxy coatings. The formulated coating was applied using brush on the surface treated MS panels so as to achieve uniformly coated panels with good finish and then allowed to hard cure.

### Weathering Test

The coated MS panels were subjected to accelerated weathering in a UV weatherometer [QUV Weatherometer, Q-Lab Products & Services] equipped with UVB-313 nm lamps. The test cycle in UVB-weatherometer comprised of 4 hours UVB simulation at 60°C followed by 4 h of condensation (UVB-lights off during condensation) at 50°C as per accordance of ASTM G-154. The epoxy coated MS panels were exposed to two test cycles, i.e, 16 hours in the weatherometer.

The coatings exposed in UVB weatherometer were characterized for color change (dE) and yellowness index (YI) using a spectrometer (BYK-Gardener Spectrometer) equipped with Color-Lab Quality Control software. The data were reported on L, a, b scales and overall color difference was given in the following equation [1]:

$$dE = [\Delta L^2 + \Delta a^2 + \Delta b^2]^{1/2}$$

where;  $\Delta L = L_2 - L_1$ ,  $\Delta a = a_2 - a_1$ , and  $\Delta b = b_2 - b_1$

Respective numbers 1 and 2 are denoted to samples before and after the exposure test.

The yellowness index was measured as per ASTM D 1925, formulated as:

$$YI = 100 (1.28 X_{CIE} - 1.06 Z_{CIE}) / Y_{CIE}$$

As per ASTM D 1925, the conditions for measurement are as follows: Illuminant: C, Standard Observer function: 2°, denoted as C/2°. X, Y and Z are the tristimulus values and 1.28 and 1.06 are the coefficients as per C/2° conditions.

The surface morphology of the coatings was studied using SEM microscopy [SEM, Model no.S3400, Hitachi] to look for the distribution of nano zinc oxide at different loading levels in the coatings.

## III. RESULTS

### Characterization of nano-ZnO

#### FTIR analysis

The FTIR spectrum for synthesized zinc oxide is shown in figure.1. The characteristic Zn – O peaks were observed at around 468 and 480 cm<sup>-1</sup>, confirming the zinc oxide structure [6, 8]

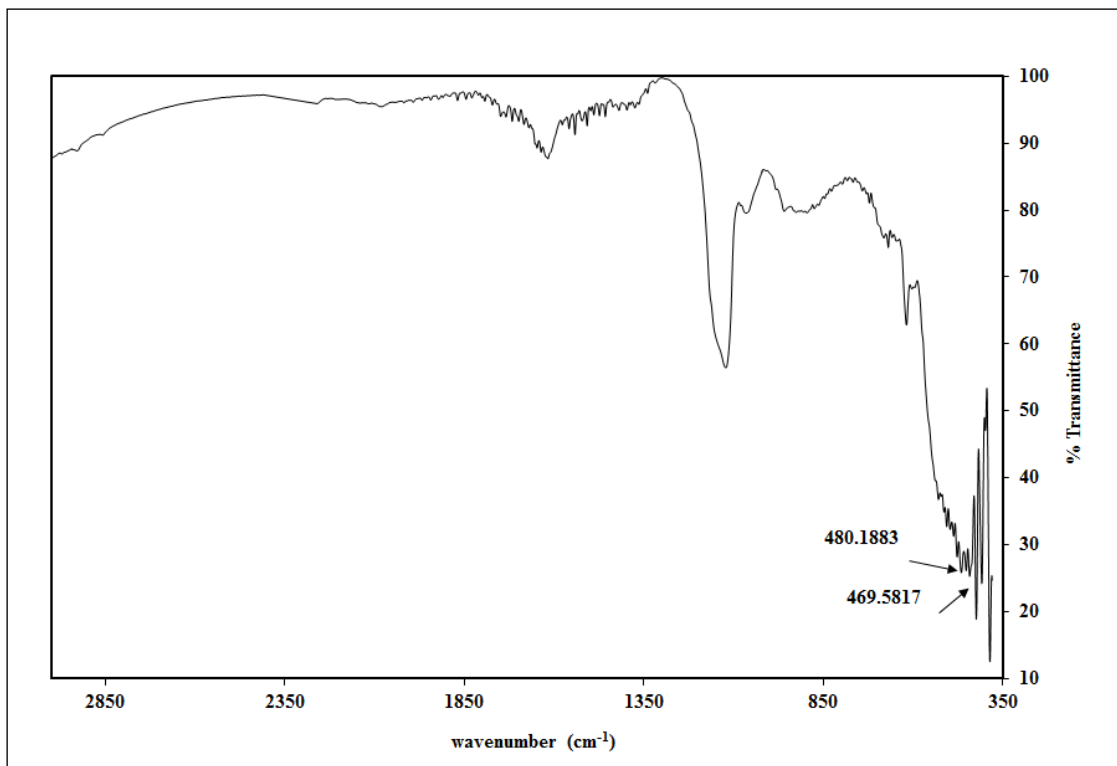


Figure.1. FTIR spectrum of nano zinc oxide

### XRD analysis

The XRD spectrum for the synthesized zinc oxide particles is shown in figure.2. The XRD analysis identified well indexed diffraction peaks in good agreement with those of a wurtzite hexagonal structure of ZnO (ICSD Reference code 01-075-0576)<sup>[9-11]</sup>.

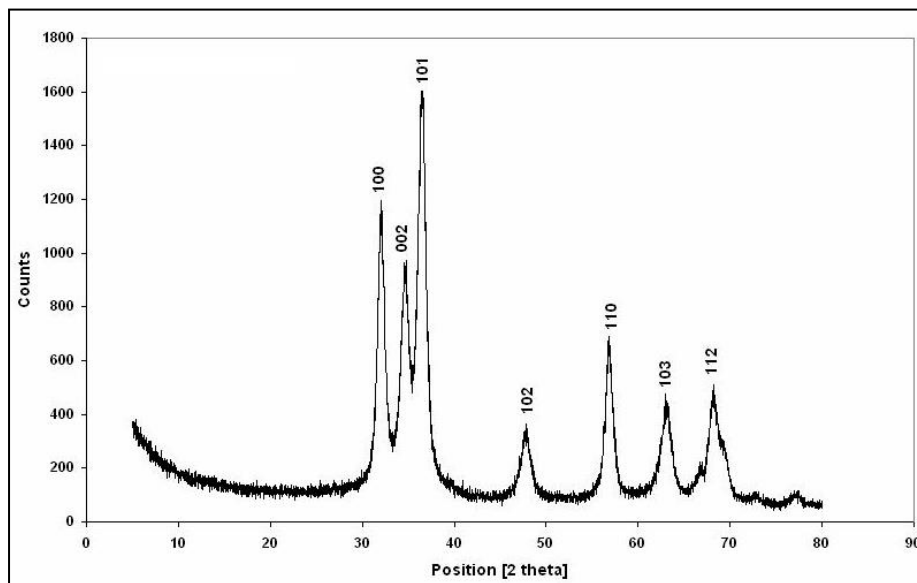


Figure.2. XRD spectrum of nano ZnO

### SEM & TEM analysis

The SEM micrographs showed the zinc oxide particles having flake-like morphology (figure.3). TEM results confirmed that the flake-like particles were composed of small spherical particles with diameter ranging from 7 to 20 nm (figure.4.a). The nano size of synthesized zinc oxide particles was thereby confirmed from TEM analysis. The lattice fringes of synthesized zinc oxide were clearly

identified in the HR-TEM image as shown in figure.4.b. The inter-planar spacing i.e. d-spacing was obtained as 0.29 nm which closely matches to the d-spacing of 100 plane (0.281nm) of zinc oxide [12-14].

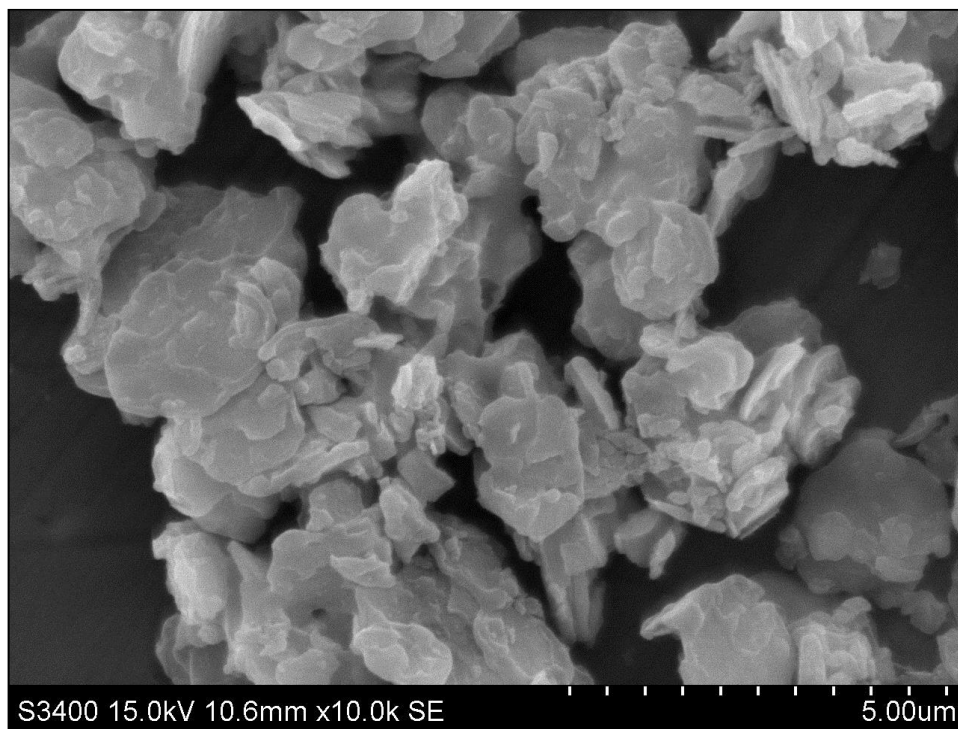


Figure.3. SEM micrograph of nano ZnO

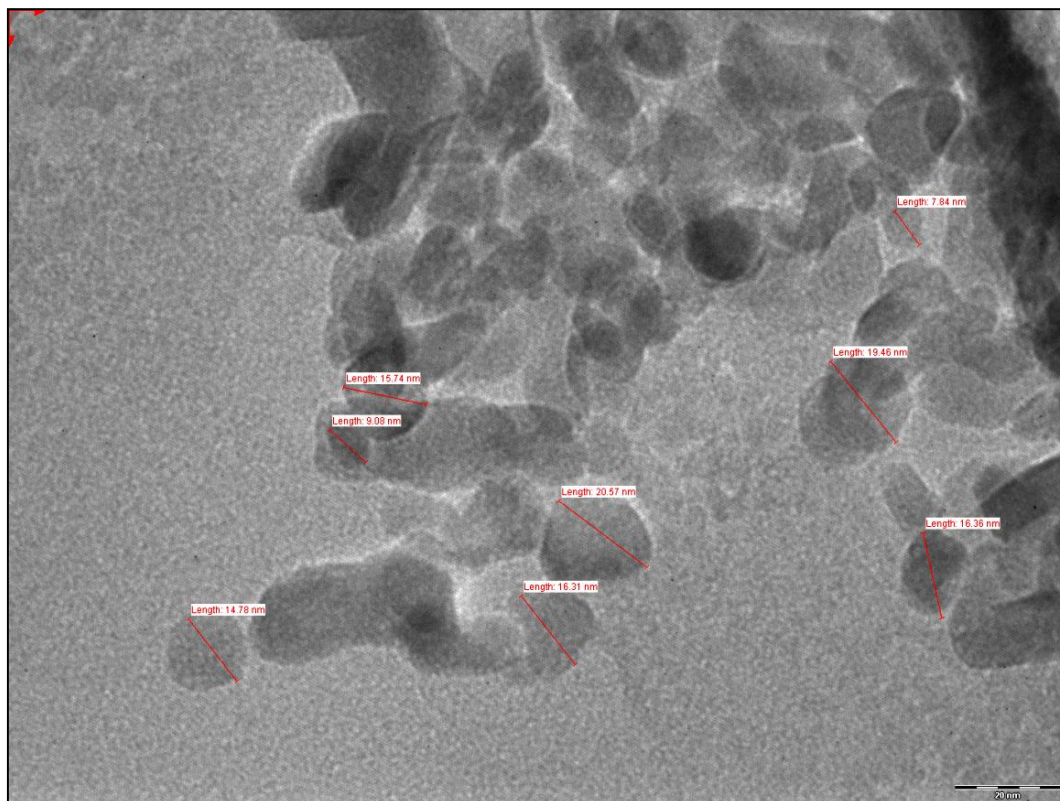


Figure.4. (a) TEM image of nano ZnO

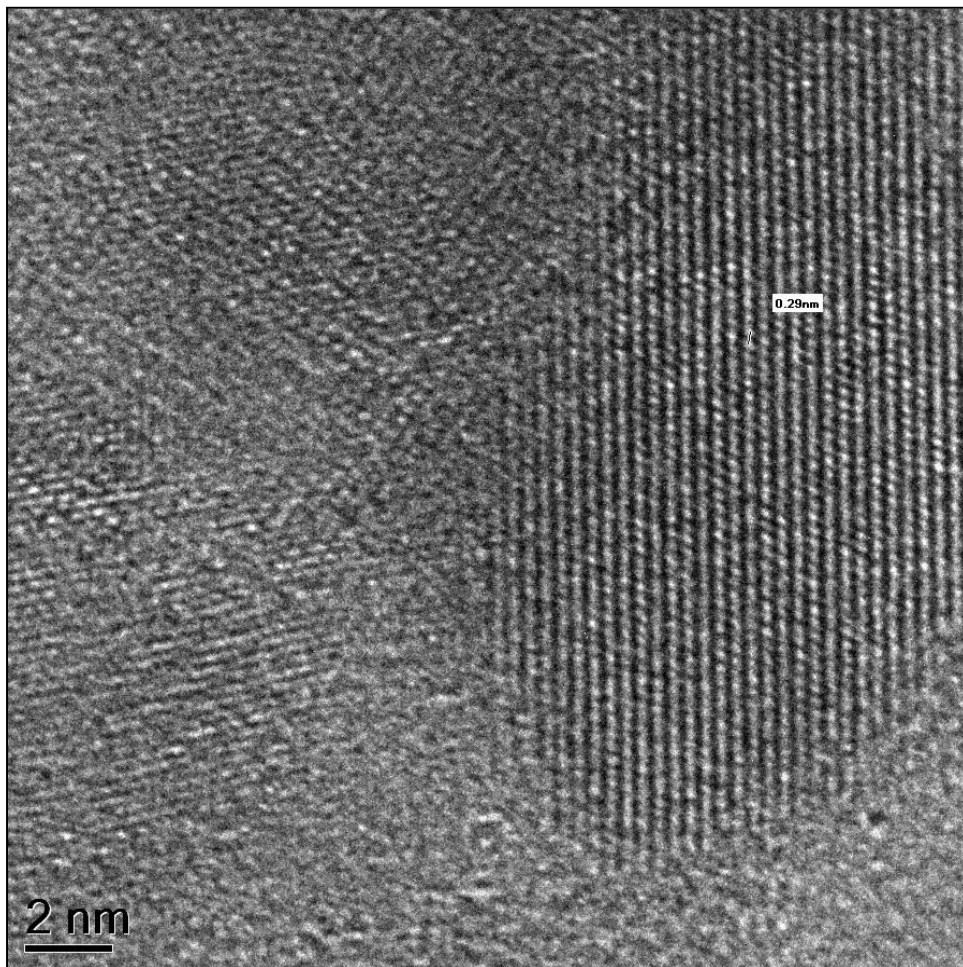


Figure.4. (b) HR-TEM image of nano ZnO

### Characterization of epoxy coated panels

#### Color change (dE) and Yellowness Index (YI) measurements of UVB-weathered epoxy coated panels

The epoxy coating formulated with and without nano-ZnO, was applied on 0.7 mm thick MS panels by brush. The coating thickness was determined using a thickness measuring gauge [Elcometer DFT Gauge] and the coating thickness for the coating systems were found to be in the range of 85-100 microns. The dE and YI results were evaluated after a mere 16 hours of UV (B) exposure. i.e, two cycles of UV (B) weathering were each cycle of 8 hours comprises of 4 hour UV (B) light followed by 4 hour condensation. The dE and d [YI] values for the DETA cured epoxy coatings for the neat and nano ZnO modified systems are as shown in figure.5.a-5.b. The discoloration observed in epoxies on weathering is attributed to the formation of a quinone- methide structure and has been confirmed in many cited studies by both infrared and UV-Vis analysis<sup>[15]</sup>. The nano ZnO incorporated coatings show lowered color change and yellowing than the neat epoxy system, however, the minimal color change and yellowing on UVB exposure was exhibited by the system incorporated with 2% nano-ZnO comparative to 1% and 5% loading levels. The color change lowered by 10 units and yellowing lowered by eight units at 2% loading level of nano ZnO in the coating.

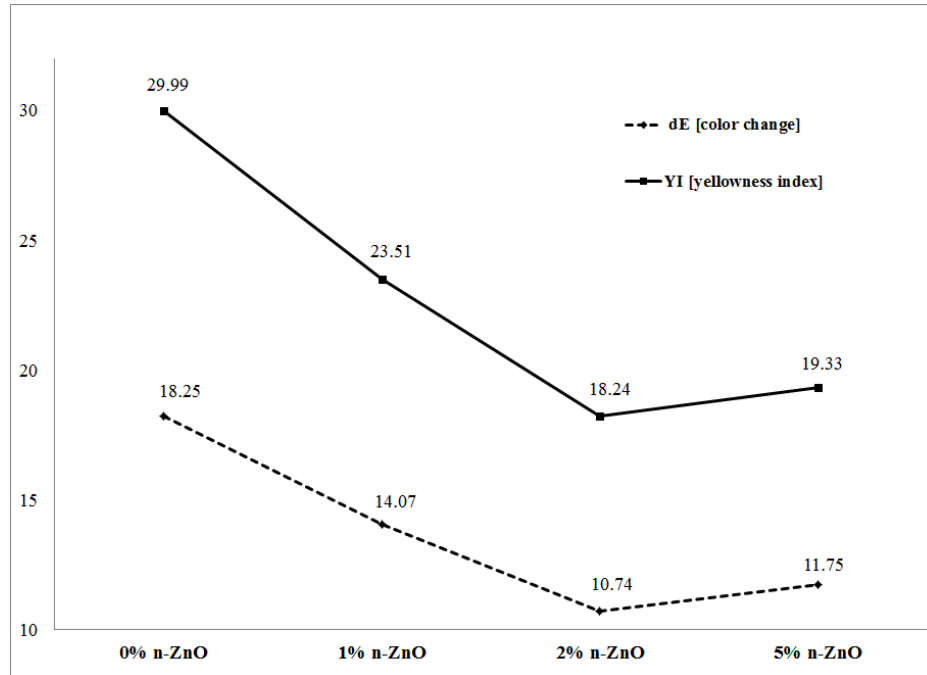


Figure.5.a. Color change (dE) and Yellowness index (YI) plot after 2 UVB test cycles (16 hours)

The extent of weathering resistance, offered by the nano ZnO modified epoxy coating systems were determined by evaluating the percentage reductions in color change (dE) and yellowing (YI) during the exposure. The percentage reduction values were calculated as follows: Suppose after 2 UVB cycles in weatherometer,

Neat Epoxy = A

Modified Epoxy = B

Where A and B are dE (or YI value) after the weathering cycle, then;

$$\% \text{ Reduction in dE (or YI)} = [(A-B) / A] \times 100$$

The percentage reduction values in figure. 5.b are relative to the dE and YI value for the neat epoxy coating without nano ZnO i.e, 0% nano ZnO and hence don't have the column bar for 0%.

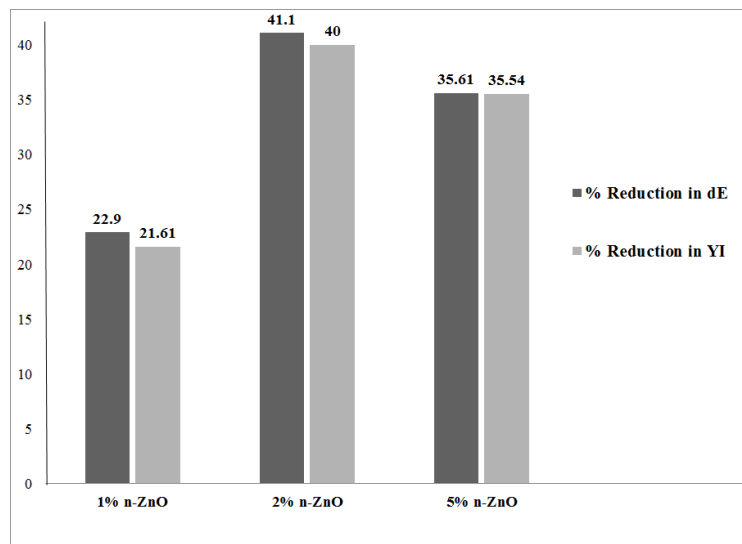


Figure.5.b. Color change [dE] and Yellowness index [YI] percentage reduction plot after 2 UVB test cycles (16 hours)

Table.1 Color change [dE] and Yellowness index [YI] results after 2 UVB test cycles (16 hours)

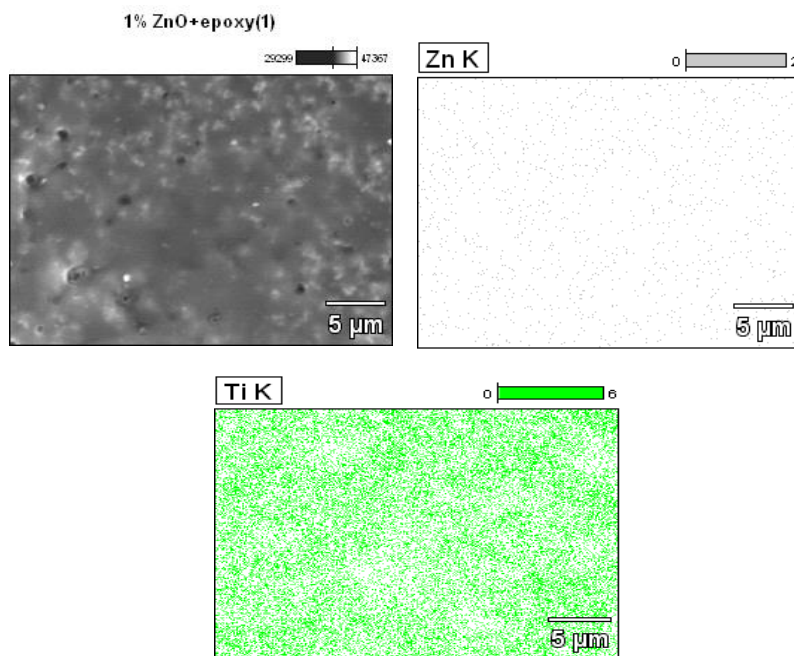
System	dE	YI	% Reduction in dE	% Reduction in YI
Neat Epoxy	18.25	29.99		
1% nano ZnO + epoxy	14.07	23.51	22.9%	21.61%
2% nano ZnO + epoxy	10.74	18.24	41.1%	40%
5% nano ZnO + epoxy	11.75	19.33	35.61%	35.54%

Both the lower (1%) and higher concentration (5%) concentration of nano zinc oxide does not provide efficient weathering resistance compared to the 2% loading level. As observed from the spectrophotometric results, the dE and YI values for 2% and 5% loading of nano ZnO in the epoxy coating showed a difference of only a single unit. The undesired performance at higher concentration of nano ZnO is attributed to the agglomeration of nano ZnO particles in the coating matrix, while at 1% loading level; the concentration is just not enough to impart appreciable weathering resistance to the coating. At 2% loading level of nano-ZnO, color change and yellowing was lowered by 40% compared to the neat epoxy system and thus proved to be the optimized loading level in the coating for effective weathering resistance.

The enhanced weathering resistance for the nano-ZnO incorporated coating is due to UV-absorption property of nano ZnO owing to its large band gap energy. Zinc oxide has a band-gap at around 3.37 eV corresponding to 376 nm and thus it absorbs light that matches or exceeds this band gap energy. UV-range of solar spectrum lies within this range and thus UV light gets absorbed by zinc oxide particles. The large band gap energy inherent of ZnO and the size of particles in nano-dimensions together, effectively imparts resistance to yellowing to the epoxy system under study at the optimized loading level of 2% (by weight of epoxy resin).

**SEM and EDX analysis**

The SEM micrographs and EDX mapping images of the epoxy coating at 1%, 2% and 5% loading levels is as shown in figure.6.a -6.c



(a)



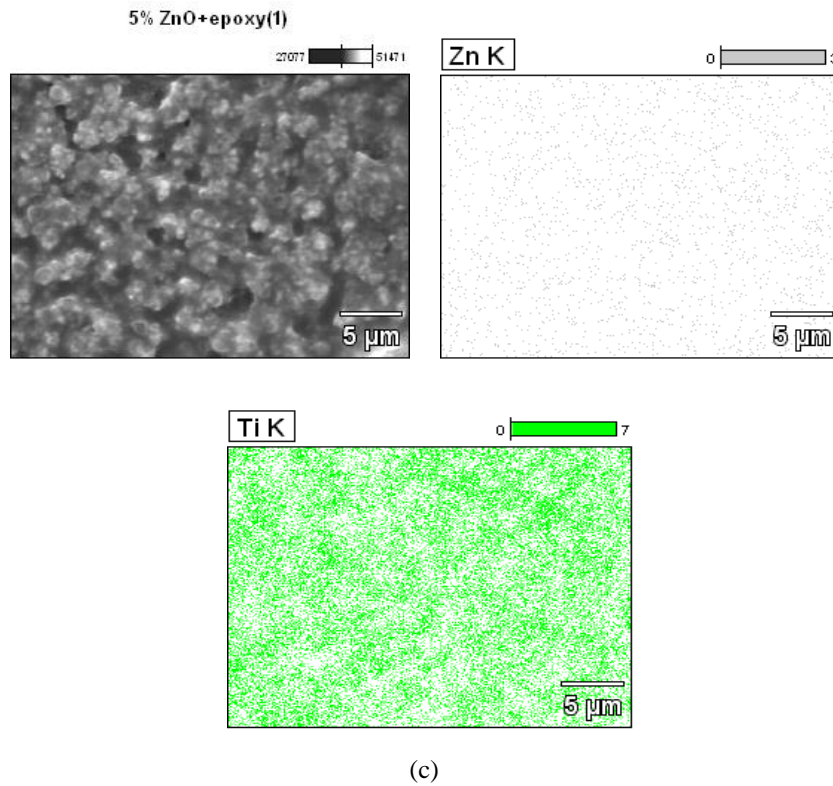
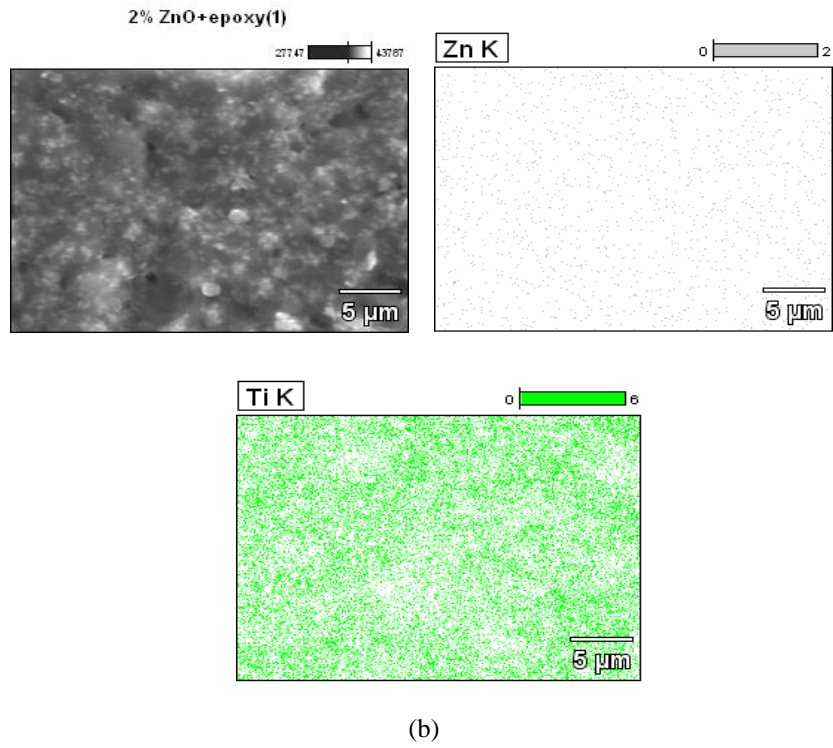


Figure.6. SEM micrographs and EDX mapping images of epoxy coating incorporated with (a) 1% nano ZnO (b) 2% nano ZnO (c) 5% nano ZnO

The elemental analysis of Zn (due to ZnO) and Ti (due to TiO<sub>2</sub>) was carried by EDAX technique and results are shown in table.2.

Table.2. EDX elemental analysis

System	Elements (Weight %)	
	Ti	Zn
1% n-ZnO + Epoxy	58.89	1.98
2% n-ZnO + Epoxy	54.86	3.87
5% n-ZnO + Epoxy	52.88	7.46

At 1% and 2% (by weight) loading levels of nano-ZnO the distribution is fairly uniform with no presence of agglomerates. However at 5% loading level, the nano particles get agglomerated leading to a very non-uniform inhomogeneous distribution in the epoxy matrix. The agglomeration sites are more pre-dominant in 5% nano ZnO coating followed by the epoxy coating with 2% nano ZnO and least in 1% nano ZnO incorporated epoxy coating. And as mentioned in the coating formulation table, TiO<sub>2</sub> content is lesser in 5% nano ZnO incorporated coating than in 2% and 1% nano ZnO incorporated coating. So, the agglomeration phenomenon as observed in the SEM micrographs is being asserted to be associated with nano ZnO content in the coating matrix and not the TiO<sub>2</sub> pigment. The agglomerates at 5% loading, in the SEM image can be seen almost projected out from binder matrix. Agglomeration of nano-particles is un-desirable as it makes nano-particles lose their high surface area and thus the desired functional properties [5]. The agglomerated nano ZnO would also protect the material underneath the agglomerate. However, the result of agglomeration is that the nano ZnO would not be evenly distributed and so there will be regions in the coating that would be starved of zinc oxide and not protected, by zinc oxide in the coating.

With increase in nano ZnO concentration in the coating, the distribution of nano ZnO varied and SEM study was carried out to observe the same. The SEM images showed that the agglomerates formed at 5% loading of nano ZnO, were not binded or wetted by the resin effectively resulting in inhomogeneous distribution. We inferred from the SEM images that with the same resin content available in the coatings with 1%, 2% and 5% nano ZnO, as the agglomeration tendency of the nano ZnO increased from 1% to 5% loading, the binding or wetting of nano ZnO by resin was poor. It can be visibly observed that at 5% loading, the agglomerates projecting out of the coating matrix due to insufficient binding with the resin. Consequently, the epoxy coating with 5% nano ZnO showed higher dE and YI value by a unit compared to the epoxy coting with optimum loading of 2% nano ZnO.

#### IV. CONCLUSION

1. NANO ZNO SYNTHESIZED WITH FLAKE-LIKE MORPHOLOGY, LOWERED DISCOLORATION AND YELLOWING BY 40 % AT AN OPTIMIZED LOADING LEVEL OF 2% (BY WEIGHT OF EPOXY RESIN) IN THE EPOXY COATING SYSTEM UNDER STUDY.
2. LOWER CONCENTRATION OR A HIGHER CONCENTRATION THAN THE OPTIMUM LOADING OF 2% RESULTED IN LOWERING THE RESISTANCE TO DISCOLORATION AND YELLOWING.
3. THE FLAKE-LIKE MORPHOLOGY AND NANO-SIZE DIMENSIONS, ALONG WITH THE OPTIMUM LOADING CONCENTRATION OF ZNO, HELPED IN EFFECTIVE LOWERING OF DISCOLORATION AND YELLOWING OF THE EPOXY COATING ON ACCELERATED UVB EXPOSURE.

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