Carbon black-ZnO Hybrid Coatings for Corrosion Protection

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Abstract— **Carbon black supported ZnO (ZnO@CB) nanoparticles are prepared and dispersed in a waterborne Epoxy (WEp) matrix by a solution blending method with different ZnO@CB loading levels(0.1,0.2& 0.3 %). The as-prepared ZnO@CB nanoparticles have been characterized by using FT-IR, SEM and XRD. The ZnO@CB incorporated WEp nanocomposites (WEpN) are coated on mild steel and their corrosion protection behaviour has been studied by using potentiodynamic polarization. The studies reveal that WPU incorporated with 0.3% ZnO@CB shows improved resistance to corrosion behaviour.**

Keywords: Carbon black; Nanocomposites; Waterborne epoxy; Corrosion resistance; Dispersion.

I. INTRODUCTION

Nanoparticles are being incorporated into waterborne polymer matrices as filler to improve the mechanical, rheological, anticorrosive, and light-resistance properties. Especially nano metal oxides such as TiO_2, Fe_2O_3, ZnO, SiO_2, Al_2O_3, $CaCO_3$ and zirconia have been used as nano filler for corrosion protection on mild steel were under study for more than a decade [1-4]. The anticorrosive property of these coatings provides a barrier protection against the penetration of aggressive environmental constituents and prevents the cathodic reaction ($2H_2O + O_2 + 4e^- \rightarrow 4\ OH^-$) occurring on the substrate/coating interface. Dispersing nanoparticles into a polymer matrix is still a tedious process as they tend to aggregate and settle down.

Carbon black is a hydrophobic pigment which consists of 97–99% elemental carbon. Carbon black finds application in paint industry, super capacitors, chemical sensors, and fuel cells etc., due to its excellent chemical stability, weatherability and colorability [5-9]. The dispersion of CB is also a difficult factor to attain a uniform dispersion in polymer matrix by mechanical mixing method. To overcome this, modification methods have been developed such as oxidation, grafting by polymer and surfactant and dispersant addition etc., for improving the dispersion of CB [10-17]. Grafting onto or from the surface of carbon black particles has improved the dispersity of the carbon black in organic solvents and polymers. Meanwhile dispersion in water-borne media also has attracted more attention for their lower pollution, lower price and better quality than traditional organic solvents. The surface of carbon black is required to modify to disperse it in an aqueous medium and also be a requisite to improve its properties once dispersed in polymer matrix. One of the modifications is to oxidize the surface of CB by acid treatment to get its hydrophilic nature. Self-aggregation of CB particles in aqueous media, however, greatly limits their utility. Therefore, it is of great significance, but is still a challenge to prepare stable CB dispersion in water.

In this study, we attempted to get the benefits of carbon black and zinc oxide nanoparticles together in a single system to get uniform dispersion as well as corrosion resistance in waterborne coatings. We prepared nano ZnO coated with acid functionalized carbon black to get CB @ZnO hybrid filler which was dispersed in a waterborne epoxy medium by a solution blending method. The corresponding epoxy nanocomposite was coated on mild steel by a dipping method and its resistance to corrosion has been studied.

II. EXPERIMENTAL

A. Materials and methods

Waterborne epoxy dispersion (Epotec THW4504 & YD 127) was procured from Adithya Birla Ltd. Analar grades of zinc acetate, sodium hydroxide, cetyl trimethylammonium bromide (CTAB), nitric acid (HNO_3) and methanol were purchased from S.D. Fine chemicals (Mumbai, India) and used without further purification. Carbon black was received from Alfa-aesar.

B. Synthesis of carbon black supported nano ZnO

Carbon black supported ZnO nanofiller were prepared using a reported procedure with minor modifications [7, 18].

Step 1: Hydrophobic carbon black was oxidized by 5 M HNO_3 at 90°C. After 4 hours, the residue was filtered washed with water several times to get neutral pH. Then water was evaporated to get the functionalized carbon black (FCB) powder.

*Step 2: F*unctionalized carbon black (0.5 g) was dispersed in 100 ml of water using ultrasonication for 30 mins. Then 6.57 g of zinc acetate dihydrate and 0.5 g CTAB were added to the solution followed by dropwise addition of 3 M sodium hydroxide (100ml) and stirred at room temperature. A milky white precipitate was obtained at ~pH 13. The solution was then transferred in a three-neck round bottom flask and heated at 90°C. After 30 min, the grey powder was filtered and washed with methanol, dried.

C. Preparation of nanocomposite coatings

ZnO@CB nano filler were incorporated into the WEp dispersion (THW 4504 - waterborne epoxy curing agent) by solution blending method with different ratios 0.1, 0.2, and 0.3% (w/w), followed by ultrasonication.Then the epoxy resin (EPOTEC YD 127) and its curing agent (THW 4504) and water were mixed with ratio of 1:1.3:1. The resulting dispersion was coated on mild steel (1 cm×1 cm×0.05 cm) by dipping method and cured at 75 °C for 30 min. After 72 hrs of air drying, the panels were used for electrochemical studies. Mild steel was subjected to mechanical polishing using Emery #100 and Emery #400, followed by rinsing with distilled water and acetone, prior to coating.

D. Characterization

FT–IR spectra were recorded using Model Y 40 of Perkin-Elmer in the range of 400 to 4000 cm^{-1}. XRD patterns were recorded using Brucker D8 advance diffractometer with monochromatic Cu-Kα1 radiation (λ = 1.5418 Å) while the voltage and current were held at 40 kV and 20 mA (2θ = 20–80°) respectively. The morphology of the composite was analyzed through FE–SEM instrument (Hitachi Ltd., SU6600).

E. Electrochemical Studies

Potentiodynamic polarisation measurements were recorded in electrochemical analyzer (BAS-IM6) employing three electrode cell assembly connected to Thales 4.15 USB Software system. A platinum strip of 1 cm^2 area served as a counter electrode. A saturated calomel electrode was used as the reference electrode and the coated MS substrate (area 1 cm^2) was served as a working electrode. Studies related to resistance to corrosion were performed at room temperature using 3.5% aqueous solution of NaCl. 1sq.cm of the test panel was immersed in the corrosion medium whereby an open circuit potential was obtained prior to the start of evaluation. After reaching a stable open-circuit potential, the upper and lower potential limits of linear sweep voltammetry were set at ± 200 mV with respect to the E_{OCP}.The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were deduced from the Tafel plot (log I Vs E). The corrosion current was obtained using the Stern–Geary equation.

$$I_{corr} = [b_a\, b_c / \{2.303(b_a + b_c)\}]\, [1/R_p] \qquad (1)$$

where b_a and b_c are the Tafel slopes or the Tafel constants, expressed in V/decade (V/dec) and R_p is the polarization resistance expressed in KΩ cm^2.The coatings inhibit the corrosion that can be understood through its inhibition efficiency (IE) is calculated using the formula given below.

$$\%IE = \{(I_{corr\,(0)} - I_{corr\,(i)}) / I_{corr\,(0)}\} * 100 \qquad (2)$$

III. RESULTS AND DISCUSSION

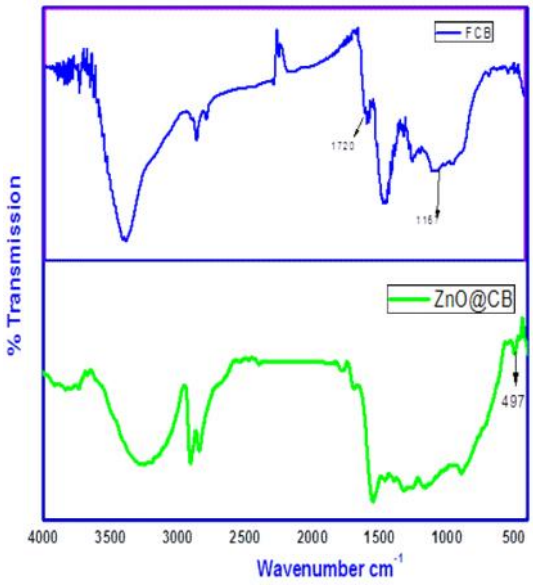
Fig. 1 shows the FTIR spectrum of FCB and ZnO@CB. The intensive peak at 3450 and 1630 cm^{-1} are mainly attributed to stretching and bending modes of water molecule absorbed on the sample or KBr. The peak at 497 cm^{-1} in the spectrum of ZnO@CB can be attributed to Zn-O vibrational modes. The peak at 1720 cm^{-1} attributed to C=O group in the spectrum of FCB was weakened in the spectrum of ZnO@CB. This indicates that carbonyl group is in coordination with the surface of ZnO nanoparticles [19].

Fig. 2 shows the XRD patterns of FCB and ZnO@CB. The peak centered at 25° corresponds to the (002) reflections of carbon black. The results demonstrate that the incorporation of ZnO on carbon black surface the peak at 25° diminishes thereby confirming amorphous carbon black anchored the crystalline zinc oxide. The zinc oxide pattern in ZnO@CB gave the peaks assigned to the (100), (002), (101), (102) and (110) hexagonal wurtzite phase crystal structure (JCPDS 36-1451) [13].

In Fig. 3 FE-SEM image for ZnO@CB is presented. The shape of the primary aggregates is quasi spherical, ranging from 50 - 75 nm. EDAX spectrum (Fig. 4) of ZnO@CB depicts that the presence of ZnO in carbon black. The Al and Au peaks are due to the aluminium substrate and gold coating used for analysis. The

stability of the prepared ZnO@CB hybrid filler incorporated in WEp dispersion was stable up to one hour was observed.

The anti-corrosion performances of the WEpN coatings were evaluated by potentiodynamic polarization technique conducted in 3.5 wt. % NaCl aqueous solution at room temperature. Figure 5 shows the polarization



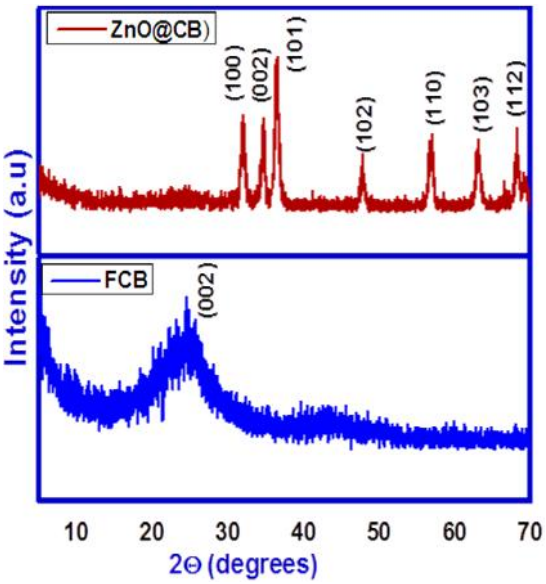


Figure 1 FT-IR spectra of FCB and ZnO@CB

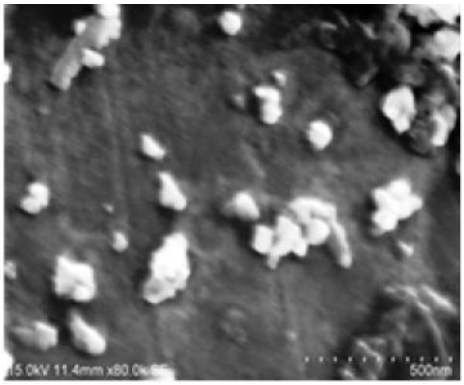


Figure 3 SEM images of ZnO@CB

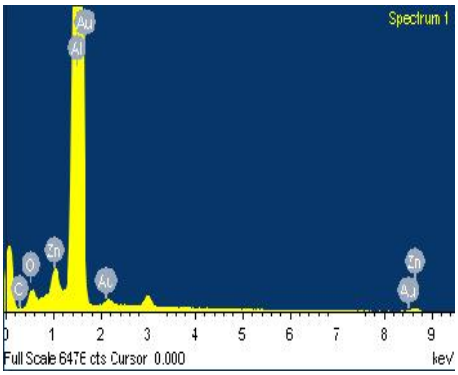


Figure 4 EDAX image of ZnO@CB

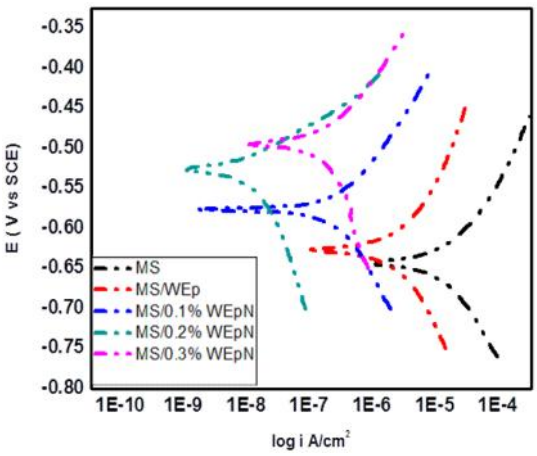


Figure 5 Potentiodynamic polarization curves of MS, WEp coated MS and WEpN composites coated MS

curves of the WEpN coatings of various percentages. The corrosion potential of the MS is -0.643V which shifted to positive side in case of WEpN [6]. The maximum shift (to -0.494 V) was obtained in case of WEpN with 0.3 % ZnO indicating the efficient protection by the WEpN coatings. Moreover, the corrosion current density of the WEpN coatings (0.0125 $\mu A/cm^2$) is much lower than that of the MS (11.83 $\mu A/cm^2$). It is well known that a lower corrosion current density or a higher corrosion potential represents lower corrosion rate and better corrosion resistance. Corrosion resistance of WEp coatings usually suffer from their relatively porous structure during long-term service. The ZnO@CB in WEp layer effectively inhibits migration and penetration of chloride ions (corrosive ions) into the WEp coating, thus enhancing the anti-corrosion performances of the coatings.

In summary, ZnO@CB incorporated with Waterborne Epoxy dispersion coated on mild steel substrate was investigated. It was found that addition of carbon black supported ZnO enhance the resistance to corrosion. The potentiodynamic polarization measurements reveals that WEp with 0.3% ZnO@CB nanocomposite coated on MS exhibited improved corrosion resistance as compared to that of WEp coated on MS. This environmental friendly cost-effective nanocomposites coating could be potentially used for a variety of anti-corrosion applications.

TABLE -1

POTENTIODYNAMIC POLARIZATION CURVES OF MS AND WEp AND WEpN COATED MILD STEEL IN 3.5% NaCl SOLUTION.

COMPOSITION	I_{corr}	E_{corr}	b_a	b_c	R_p	IE%
	($\mu A/cm^2$)	(V)	(V/dec)	(V/dec)	$K\Omega\ cm^2$	I_{corr}
MS	11.83	-0.643	0.103	0.124	0.469	-
MS/WEp*	2.41	-0.621	0.123	0.127	3.321	79.6
MS/0.1% WEpN**	0.238	-0.576	0.1	0.127	23.0	97.9
MS/0.2%WEpN	0.129	-0.525	0.083	0.143	39.6	98.9
MS/ 0.3% WEpN	0.0125	-0.494	0.049	0.199	340	99.8

*WEp – Waterborne Epoxy Dispersion
**WEpN – ZnO@CB incorporated Waterborne Epoxy dispersion

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REFERENCES

[1] Shailesh K. Dhoke, A.S. Khanna, T. Jai Mangal Sinha, Effect of nano-ZnO particles on the Corrosion behavior of alkyd-based waterborne coatings, Progress in Organic Coatings 64 (2009) 371–382.
[2] H. Li, K. Liang, L. Mei, S. Gu, S. Wang, Corrosion protection of mild steel by Zirconia sol–gel coatings, J. Mater. Sci. Lett. 20 (2001) 1081–1083.
[3] Xianming Shi ,Tuan Anh Nguyen, Zhiyong Suo, Yajun Liu, Recep Avci, Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating, Surface & Coatings Technology 204 (2009) 237–245.
[4] Sarita Kango, Susheel Kalia, Annamaria Celli , James Njuguna, Youssef Habibi, Rajesh Kumar, Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—A review, Progress in Polymer Science 38 (2013) 1232– 1261.

[5] Hui Qin, Qingliang Liao, Guangjie Zhang, Yunhua Huang, Yue Zhang, Microwave absorption properties of carbon black and tetrapod-like ZnO whiskers composites , Applied Surface Science 286 (2013) 7– 11.
[6] Wei Long, Zhanhong Yang, Xinming Fan, Bin Yang, Zhiyuan Zhao, Jing Jing, The effects of carbon coating on the electrochemical performances of ZnO in Ni–Zn secondary batteries, Electrochimica Acta 105 (2013) 40– 46.
[7] M. Atif, R. Bongiovanni, M. Giorcelli, E. Celasco, A. Tagliaferro, Modification and characterization of carbon black withmercaptopropyltrimethoxysilane , Applied Surface Science 286 (2013) 142– 148.
[8] Jiali Zhai, Lingling Wang, Dejun Wang, Yanhong Lin, Dongqing He, Tengfeng Xie, UV-illumination room-temperature gas sensing activity of carbon-doped ZnO Microspheres, Sensors and Actuators B 161 (2012) 292– 297.
[9] Kai Jiang, Teng Fei, Fan Jiang, Guan Wang, Tong Zhang, A dew sensor based on modified carbon black and polyvinyl alcohol composites, Sensors and Actuators B 192 (2014) 658– 663.
[10] Shaohai fu, Changsen Du, Chunxia Wang, Anli Tian, Changhai Xu, Properties of lyocell spinning solution with the addition of carbon black/latex composite, Colloids and Surfaces A: Physicochemical. Eng. Aspects 428 (2013) 1– 8.
[11] Peng-Wei Shi, Qiu-Ying Li, You-Chen Li, Chi-Fei Wu, Preparation and characterization of poly (sodium4-styrenesulfonate)-decorated hydrophilic carbon black by one-step in situ ball milling, Colloids and Surfaces A: Physicochem. Eng. Aspects 443 (2014) 135– 140.
[12] Erasto Armando Zaragoza-Contreras, Claudia Alejandra Hernández-Escobar, Alfredo Navarrete-Fontes, Sergio Gabriel Flores-Gallardo, Synthesis of carbon black/polystyrene conductive nanocomposite. Pickering emulsion effect characterized by TEM, Micron 42 (2011) 263–270.
[13] Reza Darvishi, Cheshmeh Soltani, Abbas Rezaee, and Alireza Khataee, Combination of Carbon Black−ZnO/UV Process with an Electrochemical Process Equipped with a Carbon Black−PTFE-Coated Gas-Diffusion Cathode for Removal of a Textile Dye, Ind. Eng. Chem. Res. 2013, 52, 14133−14142.
[14] Tianqi Liu, Shijun Ji, Tomasz Kowalewski, and Krzyszt of Matyjaszewski, Water-Dispersible Carbon Black Nanocomposites Prepared by Surface-Initiated Atom Transfer Radical Polymerization in Protic Media, Macromolecules 2006, 39, 548-556.
[15] Rosa M. Casado, Peter A. Lovell, Parnia Navabpour, John L. Stanford, Polymer encapsulation of surface-modified carbon blacks using surfactant-free emulsion polymerization, Polymer 48 (2007) 2554-2563.
[16] Han-Ying Li, Hong-Zheng Chen, Wen-Jun Xu, Fang Yuan, Jie-Ru Wang, Mang Wang Polymer-encapsulated hydrophilic carbon black nanoparticles free from aggregation, Colloids and Surfaces A: Physicochem. Eng. Aspects 254 (2005) 173–178.
[17] Wenjun Xu, Hongzheng Chen, Hanying Li, Mang Wang, Fabrication of carbon black/crosslinked poly(vinyl pyrrolidone) core-shell nanoparticles stable in water, Colloids and Surfaces A: Physicochem. Eng. Aspects 266 (2005) 68–72.
[18] Jun Wang, ZanGao, Zhanshuang Li, BinWang, YanxiaYan, QiLiu, TomMann, Milin Zhang, Zhaohu Jiang, Green synthesis of graphene Nano sheets/ZnO composites and electrochemical properties, Journal of SolidState Chemistry184(2011)1421–1427.
[19] Xiuying Wang, Baiying Xi, Xingfu Zhu, Jiesheng Chen, Shilun Qiu, Jixue Li, Controlled modification of multiwalled carbon nanotubes with ZnO nanostructures, Journal of Solid State Chemistry 181 (2008) 822–827.